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Characterization of Wettability in Porous Media Using the Lattice Boltzmann Method

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May 2020

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Submitted in part fulfilment of the requirements for the degree of
Doctor of Philosophy in Department of Earth Science and Engineering of
Imperial College London
and the Diploma of Imperial College London

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Abstract

This thesis is concerned with multiphase flow in porous media, focusing primarily on applications to oil recovery from subsurface rocks. The wettability of crude oil-brine-rock systems in petroleum reservoirs often exhibits mixed-wet states where effective contact angle varies locally, because surface active components such as asphaltenes in the crude oil can alter the wettability from its original water-wet to more oil-wet states. Furthermore, when a lower salinity brine than that of formation brine is injected to displace oil, which is known as low salinity water flooding, wettability alteration from a mixed-wet state to more water-wet condition can occur, resulting in an improvement of oil recovery.

We use direct numerical simulation to study the impact of wettability and its alteration on multiphase flow in porous media at the pore-scale. A numerical model is constructed based on the lattice Boltzmann method with two newly developed numerical methods: a wetting boundary condition which precisely models contact angle, and a model to capture wettability alteration which changes contact angle depending on the computed local salinity. The numerical model is validated using several test cases where analytical solutions are available. In particular, the new wetting boundary condition is extensively validated using the static test cases of a flat, curved and staircase solid surfaces, and a dynamic test case of capillary rise.

Water flooding in mixed-wet media is studied using the numerical model. Water flooding experiments imaged with a micro-CT by Alhammadi et al. [13] are used in which hundreds of thousands of geometrically measured in situ contact angles are available using the method of AlRatrout et al. [15]. We show that a good agreement in both the fluid configurations and effective water permeability is obtained when we model the spatial distribution of contact angle on a pore-by-pore basis, but using higher contact angles than those measured in oil-wet regions of the pore space. This physically makes sense because the contact angle to use in simulations is the locally largest value that determines the threshold capillary pressure, whereas the geometrically measured angle may represent a hinging value on pores where displacement has not occurred.

Using the matched simulation model to the water flooding experiments of Alhammadi et al. [13], we study three enhanced oil recovery (EOR) methods – low salinity water flooding, surfactant flooding, and polymer flooding – through a parametric study changing fluid and/or rock properties of the simulation. This illustrates the use of a simulation model, namely to predict the behavior outside the range studied experimentally. We show the impact of these enhanced oil recovery methods on the microscopic displacement efficiency of the rock. Although this study does not consider the mixing between brine originally in the pore space and injected
EOR fluids, this mixing is modeled for low salinity water flooding in the next study, using the two-phase lattice Boltzmann model coupled with mass transport of ions in water.

We study wettability alteration caused by exposure to low salinity water using the new wettability alteration model. The numerical model is validated using two experiments performed at the pore-scale: detachment of oil droplets exposed to low salinity water by Mahani et al. [83], and low salinity water flooding on a sinusoidal micro-model by Bartels et al. [23]. The phenomena observed in the experiments, including wettability alteration, detachment of oil droplets and recovery of trapped oil, are successfully simulated using a progressive wettability alteration driven by the slow development of thin water films implemented in the numerical model. The numerical model is, then, applied to micro-CT images of a Bentheimer sandstone. Higher oil recovery is observed in secondary mode injection compared to that of tertiary mode, whose mechanism is explained based on the simulation results, where a more stable displacement front is seen for secondary flooding.

Lastly, we use the numerical model to validate recently developed pore-scale image analysis methods. A method to measure the interfacial curvature to obtain capillary pressure is studied. Through a comparison between measured curvature and curvature obtained from the simulated capillary pressure, the validation of the method and the assessment of its uncertainty is presented. We, then, validate a method to measure a thermodynamic contact angle by Blunt et al. [27], through a comparison between the input contact angle of the simulations and the thermodynamic contact angle found from the simulated fluid configurations. Furthermore, we demonstrate how to use this method on a pore-by-pore basis to obtain the spatial distribution of wettability. We show that in mixed-wet media we can accurately capture the variation in local contact angle. Significant discrepancies are only seen in less consolidated media where the invading meniscus straddles several pores.

Overall the thesis provides an improved method for direct simulation of flow in porous media which have undergone a wettability alteration. The work has been used to interpret experimental work and make predictions for local displacement efficiency for enhanced oil recovery processes. It has also been used to suggest methodologies to measure curvature and wettability from pore-scale imaging experiments.
Declaration

I declare that this thesis, titled “Characterization of Wettability in Porous Media using the Lattice Boltzmann Method”, is entirely my own work under the supervision of Prof. Martin J Blunt and Dr Branko Bijeljic. All published and unpublished materials used in the thesis have been given full acknowledgement. This work has not been previously submitted, in whole or in part, to any other academic institution for a degree, diploma, or any other qualification.

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Acknowledgements

I would like to thank my supervisors, Prof. Martin J Blunt and Dr Branko Bijeljic, for their support and encouraging and insightful guidance during my PhD study.

I would like to extend my appreciation to my PhD examiners, Dr Nicolas Agenet from TOTAL E&P and Prof. Stephen Neethling from Imperial College London for their time and consideration.

I would like to thank my colleagues at Imperial College London for their helpful and stimulating discussions during my PhD study.

I also thank Japan Oil, Gas and Metals National Corporation (JOGMEC) for their financial support to my PhD study.

Last but not least, I would like to express my deepest gratitude to my family, and particularly to Sae and Kiko, for their unconditional love and support.

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6.14. Sequence of oil displacement for the mixed-wet cases computed for (a) the bead pack and (b) Bentheimer sandstone. All the pore regions were classified into five groups based on their input contact angle, which ranged from 45° to 165°. The number of oil filled voxels on the y-axis was normalized by its value at the beginning of water injection.

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1. Introduction
1.1. Background

Multiphase flow in porous media has a wide range of applications including oil recovery, carbon capture and storage, designing efficient membrane fuel cells, and water flow in unsaturated zones [26, 102, 55, 46, 42]. In these applications, at the pore scale, the flow is generally slow and dominated by capillary forces arising from the interfacial tension between fluid phases. Under this condition, the displacement of a phase by another phase is strongly influenced by the wettability of the solid surface.

Based on the Young equation, the wettability is defined using contact angle: the angle that the two-fluid interface forms at the solid surface. In experiments, the contact angle is traditionally measured from the shape of a droplet placed on a solid surface, which is typically performed using a flat, smooth solid surface composed of a pure mineral — an ideal surface [2]. A contact angle measured on an ideal surface is referred to as an intrinsic contact angle. However, the surface of porous media in the natural systems of our interest is not smooth at any scale. Hence, for applications to porous media, we typically use an effective contact angle, which is an apparent contact angle as measured from an equivalent smooth surface aligned with a larger scale geometry of pore spaces [26].

This effective contact angle can be significantly different from its intrinsic one because of contact angle hysteresis. There are four reasons for contact angle hysteresis: (1) wettability alteration, (2) surface roughness, (3) chemical heterogeneity, and (4) flow rate. The first three items are of particular importance for crude oil-brine-rock systems in petroleum reservoirs [26]. The surface of rocks can be altered from its original water-wet to more oil-wet states through the contact with surface active components in the crude oil [89, 114]. Furthermore, as we already discussed, the surface of rocks is not ideally smooth at any scale, and the rocks can be composed of different minerals. As a result, these systems often exhibit a mixed-wet state where effective contact angle varies spatially. In spite of the common occurrence of mixed-wet states in natural systems, multiphase flow in mixed-wet media has not been fully understood, partly because it is far more complex than that in uniformly wet media, but mainly because the characterization of locally varying wettability in porous media has been difficult.

Advances in high-resolution three-dimensional X-ray micro-computed tomography (micro-CT) imaging has provided a tool to analyze multiphase flow in porous media. It is now possible to image the configuration of fluids and solid phases in porous media during flow experiments. Furthermore, several image analysis methods have recently been developed to experimentally study multiphase flow in porous media; for instance, the measurement of interfacial curvature to obtain capillary pressure [18, 19], and the measurement of contact angle from the images [15, 27].

Considering these recent advances in pore-scale imaging and its analysis, there is a need to develop a numerical model which can reproduce, interpret and predict the considerable detail obtained experimentally from micro-CT images. If such a numerical model is used with experimental pore-scale imaging approaches, it can be a valuable tool as the numerical model
provides additional information that is difficult to obtain from experiments, such as the spatial distribution of fluid pressure and velocity in the pore space. Furthermore, this combined approach between pore-scale imaging and modeling could lead to a comprehensive workflow through experiments to predictive modeling.

This work is concerned with modeling of multiphase flow in porous media. The numerical modeling approach discussed in this work can be used for many engineering applications including carbon capture and storage, designing efficient membrane fuel cells, and water flow in unsaturated zones [26, 102, 55, 46, 42], but we primarily focus on applications to oil recovery from subsurface rocks. The objectives of the work are to improve our understanding of the role of wettability and its alteration in displacement processes, which will be specifically described in section 1.3. Although our approach is mainly based on a numerical model, the numerical model is closely linked to experimental approaches throughout the work.

We will now review the state of the art experimental efforts in improving our understanding on the role of wettability in multiphase flow in porous media. An emphasis will be placed on pore-scale imaging and analysis methods.

1.2. Literature review on multiphase flow in porous media

1.2.1. Experimental work

First, we review water flooding experiments combined with micro-CT imaging performed on mixed-wet media; in section 4.2 we will compare simulated predictions with experimental data to assess and interpret wettability in reservoir samples. In these experiments, the wettability of rocks were altered to mixed-wet states applying aging with crude oil, to simulate oil reservoir conditions. Next, we review experimental work on low salinity water flooding in which the wettablility of rocks was altered from an initial oil-wet state in a high salinity brine environment to a more water-wet state after exposure to lower salinity brine; in chapter 5 we will simulate low salinity flooding and reproduce the behavior observed experimentally. Lastly, two recently developed experimental pore-scale image analysis methods are reviewed: curvature measurement and contact angle measurement; this will be discussed in the light of our simulation results in chapter 6.

Water flooding experiments on mixed-wet media with micro-CT imaging

Alhammadi et al. [13] performed unsteady-state water flooding experiments on three carbonate rock samples drilled from a larger core from a producing oil reservoir. These samples were conditioned to three wettability states applying different aging protocols with crude oil from the reservoir. Before and after water flooding, fluid configurations in pore spaces were imaged with a micro-CT. On the images, in situ contact angle was measured using an automated method by AlRatrout et al. [15], which will be described later.
The measured contact angles showed a wide range with different mean contact angles for the three samples. We refer to these samples as water-wet, mixed-wet and oil-wet based on their mean and standard deviation of the measured values of $\theta = 77^\circ \pm 21^\circ$, $\theta = 94^\circ \pm 24^\circ$, and $\theta = 104^\circ \pm 26^\circ$, respectively. These samples displayed a distinct difference in the morphology of remaining oil clusters: the remaining oil of the water-wet sample formed a spherical shape, while that of the mixed-wet and oil-wet samples formed sheet-like structures with better connectivity than that in the water-wet sample as shown in Fig. 1.1. They observed the highest oil recovery of 84% for the mixed-wet sample having a mean angle close to 90°, while the lowest recovery of 59% was observed for the oil-wet sample. They therefore showed that oil recovery from porous media was strongly influenced by wettability. It is of interest to determine how to incorporate this in situ measured contact angle in numerical modeling of two-phase flow. We will analyze and simulate this dataset in section 4.2.

![Figure 1.1](image-url) Remaining oil imaged with a micro-CT for the three wettability states. (a) The remaining oil clusters for the water-wet, (b) the oil-wet, and (c) the mixed-wet states. (d,e,f) show the enlarged views for the above figures. The colors represent different oil clusters. These figures are adapted from Alhammadi et al. [13].

Lin et al. [73] also observed the significant impact of wettability on multiphase flow in porous media in their steady-state water flooding experiments. Two Bentheimer sandstone samples conditioned to different wettability states were used for steady-state experiments in which oil and water were simultaneously injected at a specified ratio of flow rate (fractional flow rate). At the steady-state achieved for each fractional flow, fluid configurations were imaged with a micro-CT. They also obtained relative permeability from the measured pressure drop during the flow experiments. On the images, they measured in situ contact angle using the method of AlRatrout et al. [15]. Furthermore, they measured interfacial curvature on the oil/water interface extracted from the images, to obtain capillary pressure, which will be further described.
later and presented in detail in section 6.2.

The measured contact angle of these two samples was $\theta = 66^\circ \pm 22^\circ$ and $\theta = 80^\circ \pm 17^\circ$, which are referred to as water-wet and mixed-wet, respectively. Similar to the experiments of Alhammadi et al. [13], the mixed-wet sample whose mean angle was close to $90^\circ$ showed better oil recovery with lower residual oil. In this sample, the capillary pressure estimated from the measurement of interfacial curvature had a small negative value of $\sim -0.2$ kPa, while that in the water-wet sample was $\sim 2.5$ kPa. They showed that the oil/water interface observed for the mixed-wet case formed not a flat but approximately a minimal surface having an equal magnitude of two principal curvatures but opposite sign in orthogonal directions: $\kappa_1 \sim -\kappa_2 \Rightarrow \kappa_m = (\kappa_1 + \kappa_2)/2 \sim 0$ and $\kappa_G = \kappa_1 \cdot \kappa_2 < 0$, where $\kappa_1$ and $\kappa_2$ are the two principal curvatures and $\kappa_m$ and $\kappa_G$ are the mean and Gaussian curvature, respectively. This topology of the interface explained the better oil recovery in the mixed-wet sample — almost zero mean curvature interfaces that were locally saddle-shaped and that moved through the rock displacing the vast majority of the oil with little change in capillary pressure, while maintaining a good connectivity in both oil and water with little trapping [73].

**Wettability alteration due to exposure to low salinity water**

The wettability of crude oil-brine-rock systems can be altered when the system is exposed to a brine with lower salinity. This is the most commonly accepted mechanism for low salinity water injection, which is an emerging enhanced oil recovery methods [86, 90, 83, 23, 125].

Mahani et al. [83] used a model system consisting of a quartz substrate coated by clay minerals. Oil droplets were deposited on the clay surface and initially exposed to high salinity brine. Then, low salinity brine was introduced to the system by diffusion. After exposure to the low salinity brine, the contact angle changed toward a more water-wet state and the oil droplets eventually detached from the solid surface. Figs. 1.2a and b show an oil droplet in high and low salinity water. Considering a slower wettability alteration process than that expected by diffusion only, they concluded that the kinetics is consistent with a slow electrokinetics ion-diffusion mechanism in a thin water film affected by the surface charge of the interfaces.

Bartels et al. [23] used sinusoidal micro-models through which a series of flooding experiments were performed for different aging conditions and presence/absence of clay minerals. The micro-models were initially saturated with crude oil and aging was performed with the crude oil. Water flooding was performed with high salinity brine followed by low salinity brine. For experiments performed with aging, after water flooding with high salinity water, the wettability state showed an oil-wet condition with a contact angle of approximately $120^\circ$, indicated by the negative curvature of the oil/water interface. After water flooding with low salinity brine, an experiment performed with the absence of clay minerals showed a significant change in the fluid configuration, resulting in the remobilization of trapped oil which was caused by the progressive water invasions through the corners of the void spaces as shown in Fig. 1.2c and d. These observations can be understood as the consequence of wettability alteration. We will
reproduce the behavior of these two experiments in chapter 5. Meanwhile, the cause of wettability alternation has also been studied. The wettability is influenced by the electrical surface charge in thin water films which coat the rock surface with a thickness of typically less than 10 nm [50]. An increase in electrical repulsion forces in the films makes the films more stable, resulting in more water-wet states. This mechanism and associated chemical interactions have been studied based on both experimental [56, 11, 40, 1] and modeling approaches [80, 61, 124]. While these provide an atomic-scale explanation for the wettability changes, it is still not clear how this results in improved oil recovery from the complicated three-dimensional pore spaces of rocks.

Figure 1.2. Experimentally observed wettability alteration caused by low salinity water. An oil droplet placed on a flat surface composed of clay minerals (a) in a high salinity water environment and (b) in a low salinity water environment. These are adapted from Mahani et al. [83]. Low salinity water flooding on a micro-model. (c) After high salinity water flooding. (d) After low salinity water flooding. These are adapted from Bartels [22]

Experimental image analysis methods: curvature and contact angle

Recently, it has been shown that capillary pressure can be obtained from the measurement of interfacial curvature extracted from micro-CT images during flow experiments, based on the Young-Laplace equation: $P_c = 2\sigma \kappa_m$, where $\sigma$ is the interfacial tension between fluids, and $\kappa_m$ is the mean curvature which is the mean of the two principal curvatures. Armstrong, Porter and Wildenschild [19] used synchrotron-based tomographic datasets of oil/water drainage and imbibition experiments on a bead pack [97] in which the curvature measurement was performed on the oil/water interface extracted from segmented CT images through the fitting of a quadratic form equation to find two principal curvatures. Since the segmented CT images had a staircase shape, the surface smoothing was performed prior to the fitting of a quadratic form surface. The capillary pressure obtained from curvature measurements showed a fairly good agreement with that obtained from pressure transducers for imbibition cycles, whereas a systematically lower capillary pressure was estimated for drainage. Li et al. [71] applied their improved curvature computation method to the same dataset and provided a better agreement between the pressure measurements and values derived from curvature computation. An example of the curvature measurement used in experiments of Lin et al. [74], in which water flooding was performed on a water-wet Bentheimer sample, is shown in Fig. 1.3. Although this image-based curvature measurement provides useful information which characterizes multiphase flow in porous media,
there is an potential difficulty in this measurement: the use of voxelized image data may introduce significant error, which has not – to date – been quantified. This will be done using simulation results in section 6.1.

![Image](image-url)

Figure 1.3. An example of curvature measurement adapted from Lin et al. [74]. (a) Gray-scale CT images for a Bentheimer sandstone. (b) Segmented images. Oil, water and solid are shown in yellow, blue and red, respectively. (c) The extracted oil/water interface. (d) Computed curvature on the oil/water interface.

Fluid configurations obtained with micro-CT images have also been used to measure in situ contact angle during multiphase flow experiments. The first work to do this was presented by Andrew et al. [16] for a super critical CO$_2$-brine-carbonate system. Later, AlRatrout et al. [15] developed an automated method to geometrically measure contact angle from micro-CT images. The method provides typically a million measurement points along the three-phase contact lines from a billion-voxel image and it has been successfully applied to reservoir rocks to characterize different wettability states [13]. Although the method gives useful information on the spatial distribution of contact angle, there are some limitations. Since it uses a snap-shot of the images during displacement, the measured angle may represent a hinging value on pores where displacement has not occurred. The other problem is that the accuracy of the measurement is highly dependent on the quality of images because the measurement is performed at the three-phase contact line where uncertainty in image segmentation can be high.

Blunt et al. [27] has recently proposed a method to measure a thermodynamically consistent contact angle – thermodynamic contact angle – from micro-CT images based on the energy balance of displacement. The method determines the thermodynamic contact angle from two images datasets in capillary equilibrium. It provides a contact angle at the onset of displacement. Hence, this is the angle to use in the modeling of multiphase flow, specifically, in Mayer-Stowe-Princen calculations of threshold capillary pressure [84, 98, 99, 100]. The method has demonstrated that the thermodynamic contact angle provides a more sensitive characterization of wettability of two experiments performed on sandstones with different wettability states [74, 73], compared to the geometrical measurement of contact angle [15]. However, in their derivation of the method, viscous dissipation was ignored. Hence, it is necessary to validate the method with the consideration of viscous dissipation. Furthermore, the method only provides
a single representative angle for an entire rock sample and it is not clear if the method can provide the spatial information of wettability states which is of great importance for the accurate characterization of mixed-wet media [85, 92, 128, 5, 27]. These two topics – viscous dissipation and pore-by-pore assessment – are addressed in section 6.2.

1.2.2. Numerical modeling

This section reviews advances in pore-scale modeling, which is the main tool that has been developed throughout this thesis. There are mainly two approaches to model multiphase flow in porous media at the pore-scale: pore network modeling and direct numerical simulation. This section presents a review of these approaches.

Pore network modeling

In a pore network modeling approach, the void spaces of porous media are represented by a network of pore bodies defined as a wide region in the pore spaces connected by pore throats [92]. These pore bodies and throats are idealized by a simpler geometry than that of an actual rock structure: normally pore bodies are represented by a sphere, while pore throats are by a cylinder with a triangular cross section. The pore network can be constructed either from the 3D statistical reconstruction of pore spaces, or a 3D pore structure directly obtained with a micro-CT. From a 3D pore structure, the topological skeleton is extracted, for instance, using a maximum ball algorithm which finds the largest sphere that just touches solid boundaries [119]. Then, a clustering algorithm to define pore bodies and throats is applied based on the defined maximum balls [37]. We will use this network characterization in our simulation work, even though it is not network modeling, to identify wettability and pore occupancy in chapters 4-6.

Multiphase flow is solved on the network, assuming that the flow is capillary dominated with viscous pressure drop being insignificant (quasi-static). The flow is modeled by semi-analytical relations based on predefined displacement processes under this assumption [128].

The pore network modeling has been successfully applied to study multiphase flow in porous media [85, 92, 128]. One of the main advantages of pore network modeling over direct numerical simulation is its computational efficiency. According to Raeini et al. [105], their direct numerical simulations based on the volume of fluid method took 13 days for drainage and 8 days for imbibition with 24 processors, while pore network flow simulations performed on the same pore structure took less than 2 seconds on a single processor. This implies that pore network models are faster than the direct simulations by roughly 6 orders of magnitude. Owing to its computational efficiency, pore network models can easily handle a cm-scale pore network extracted from micro-CT images with a size of $1800 \times 1800 \times 3400$ voxel$^3$ at a voxel size of $3.56 \ \mu$m [31].

However, the computational efficiency comes at the cost of the simplifications of pore geometry and displacement processes. The uncertainty of pore network extraction would have an impact on the results of computations. Furthermore, to be predictive, all the necessary physics has
to be explicitly implemented as semi-analytical relations in the model, before the use of the model. As a result pore networks can be viewed as an upscaled representation of the flow; this upscaling, to be accurate, relies on direct numerical simulation at the sub-pore and pore scales, described next.

**Direct numerical simulation**

Direct numerical simulation is a numerical scheme which solves the mass conservation and momentum conservation, the Navier-Stokes equation, equations with a boundary condition given at the structural boundaries of a numerical domain. Immiscible two-phase flow can be modeled by solving these equations separately for each phase with coupling the two phases across the interface through a pressure jump condition based on the Young-Laplace equation. For porous media applications, several numerical schemes to solve these equations have been proposed in the literature, for instance the volume-of-fluid method [107, 108, 105], the level set method [101, 58] and the lattice Boltzmann (LB) method [127, 110, 109, 29, 67].

When we chose a numerical model for our applications, there are three key points to consider: low spurious velocity, good mass conservation, and high computational efficiency. First, spurious velocity refers to unphysical small currents which are commonly observed at the interface of two fluids in direct numerical simulations. These unphysical micro currents have to be kept as low as possible, because the flow of our interest is in general quite slow — for instance, typical capillary numbers in petroleum reservoirs are in the range of $Ca = \mu \sigma / u_D = 10^{-10} \sim 10^{-5}$ [63]; where $u_D$ is the Darcy velocity, $\mu$ is viscosity and $\sigma$ is the interfacial tension. Second, to capture the complex motion of the oil/water interface, the time step size, $\Delta t$, of direct numerical simulations tends to small, e.g., $\Delta t = 10^{-7} \sim 10^{-6}$ second. More than a million iterations are necessary to simulate a few seconds of displacement. Hence, good mass conservation is required for each iteration. Lastly, since many time steps are required, high computational efficiency is also required.

Among the numerical schemes described above, the applicability of LB method to the pore-space images obtained with micro-CT imaging has been demonstrated by several previous studies [3, 110, 109, 29, 67]. This suggests that the LB method satisfies the above mentioned three requirements for practical applications on micro-CT images. Liu et al. [78] gave a comprehensive review of five classes of multiphase LB models: the color gradient model, the inter-particle potential model, the free-energy model, the mean-field theory model and the stabilized diffuse-interface model as summarized in Table 1.1.
Table 1.1. Summary of the five classes of representative multiphase lattice Boltzmann models, reformatted from Liu, Wu, Ba, Xi and Zhang [79].

<table>
<thead>
<tr>
<th>Model</th>
<th>Color gradient</th>
<th>Inter-particle potential</th>
<th>Free-energy</th>
<th>Mean-field theory</th>
<th>Stabilized diffuse-interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interfacial tension</td>
<td>can be given directly</td>
<td>Static bubble test is required</td>
<td>can be given directly</td>
<td>Static bubble test is required</td>
<td>can be given directly</td>
</tr>
<tr>
<td>Spurious currents</td>
<td>medium</td>
<td>large</td>
<td>small</td>
<td>medium</td>
<td>very small</td>
</tr>
<tr>
<td>Dissolution for tiny bubbles</td>
<td>very small</td>
<td>small</td>
<td>large</td>
<td>very large</td>
<td>medium</td>
</tr>
<tr>
<td>Density ratio</td>
<td>1000*</td>
<td>1000†</td>
<td>1</td>
<td>up to around 15</td>
<td>1000</td>
</tr>
<tr>
<td>Kinetic viscosity ratio</td>
<td>1000</td>
<td>1000‡</td>
<td>up to 8</td>
<td>unknown</td>
<td>unknown</td>
</tr>
<tr>
<td>Computing cost</td>
<td>average</td>
<td>average</td>
<td>average</td>
<td>greater</td>
<td>large</td>
</tr>
</tbody>
</table>

* Achieved in static bubble test using the color gradient model presented in [77].
† Achieved in static bubble test using equations of state different from the original Shan-Chen model.
‡ Achieved in static bubble test and two-phase co-current flow using the model presented in [96].

We present an example which provides an idea of the practical application of the LB model to problems similar to our interests. Leclaire et al. [67] used the color gradient LB model to simulate drainage and imbibition on a Berea sandstone with a size of $440 \times 400 \times 400$ voxel$^3$ with a voxel size of 5.3 $\mu$m obtained with a micro-CT. They discussed the residual fluid saturation of the drainage and imbibition processes for different flow regimes i.e., the viscous fingering, stable displacement and capillary fingering regime. Their work suggests the feasibility of the color gradient LB model to simulate multiphase flow in reasonably large pore structures. However, as pointed out by the authors, there is a problem in the modeling of wettability in the color gradient LB model. A fictitious density wetting boundary condition proposed by Latva-Kokko and Rothman [65] is the most widely used wetting boundary condition in the color gradient LB model [110, 109, 39, 53, 78]. This wetting boundary condition can be inaccurate because of unphysical mass transfer of the wetting phase along the solid. Therefore, it is necessary to develop an accurate wetting boundary condition to study details of wetting phenomena in porous media; this will be presented in section 2.2.1.

1.2.3. Wettability and contact angle

In this section, through the review of previous work in the literature, we define terms to refer to wettability and contact angle used in this thesis.

*Intrinsic contact angle* is the angle which the interface of two fluids forms at a perfectly smooth, flat surface composed of a single material — an ideal surface [88]. This angle is purely determined from the force balance acting on the three-phase contact line where the interface of the two fluid meets the solid surface — the Young equation:

$$\sigma_{nws} = \sigma_{ws} + \sigma \cos \theta,$$

(1.1)
where $\sigma_{nws}$ is the interfacial tension between the non-wetting phase and the solid, while $\sigma_{ws}$ is the interfacial tension between the wetting phase and the solid. $\theta$ is the intrinsic contact angle. It shows unique angle regardless of an advancing or receding interface [103].

*Effective contact angle* is defined for a surface with roughness (a non-ideal surface). This angle is measured from an equivalent smooth surface aligned to a geometry of the surface at a certain resolution [26]. Because of the roughness, it shows a higher angle than its intrinsic angle for an advancing interface, whereas a lower angle is observed for a receding interface. These angles are called receding contact angle, $\theta_R$, and advancing contact angle, $\theta_A$, respectively [88].

*Geometrical contact angle* is a geometrically measured angle from the configurations of fluids and solid. As described in section 1.2.1, it is normally obtained from the dot product of vectors describing the fluid/fluid interface and the solid surface, where they meet at the three-phase contact line [15]. The geometrical contact angle is same as the effective contact angle. If the interface does not involve displacement, the geometrical angle measured on the interface shows a hinging angle, $\theta_H$, of any value between $\theta_R$ and $\theta_A$ [27]:

$$\theta_R \leq \theta_H \leq \theta_A.$$  \hfill (1.2)

*Thermodynamic contact angle* is found from energy balance during displacement as described in section 1.2.1. It provides a contact angle at the onset of displacement [27]. Hence, it is the angle to use in Mayer-Stowe-Princen calculations of threshold capillary pressure [84, 98, 99, 100]. When the displacement has occurred by an advancing interface, it is equivalent to the advancing angle, whereas when the displacement has occurred by a receding interface, it is the receding angle. We will compare this thermodynamic contact angle obtained from the fluid configurations with the input angle used in our simulations in section 6.2.

At the molecular level, the wettability of the surface can no longer be described by the simple force balance of the interfacial tensions. The wettability is influenced by thin water films which coat the rock surface with a thickness of typically less than 10 nm [50, 126]. The stability of the film is determined by disjoining pressure, $\Pi(h)$, which is a function of film thickness, $h$, determined by three main forces, electric double layer, $\Pi_{DL}$, van der Waals, $\Pi_{LV,A}$ and structural forces, $\Pi_s$: $\Pi(h) = \Pi_{DL} + \Pi_{LV,A} + \Pi_s$ [113, 125]. These forces contribute to the wettability through capillary pressure as described by the augmented Young-Laplace equation [34, 28]:

$$P_c = \kappa \sigma + \Pi(h),$$  \hfill (1.3)

where $\kappa$ is the total curvature. This is particularly important when the alteration of wettability is considered. The collapse of the films leads to the direct contact of oil to the solid surface, resulting in more oil-wet states, whereas the thickening of the films leads to more water-wet states as seen in low salinity water flooding, which will be discussed in sections 2.2.2 and 3.2.4.
1.3. Knowledge gaps and objectives of this work

Knowledge gaps

As we have seen in the literature review, pore-scale imaging is now able to provide considerable detail of multiphase flow in porous media including complex three-dimensional pore structures, fluid configurations, and in situ contact angle, with the measurements of Darcy-scale macroscopic properties of multiphase flow (capillary pressure and relative permeability). Hence, it is of great interest to determine how to incorporate this information into numerical modeling of two-phase flow.

Furthermore, it is evident from experiments that wettability and its alteration have a significant impact on the efficiency of oil recovery. In particular, for low salinity water flooding, although the cause of wettability alteration has been studied in terms of electro-chemistry at an atomic level, it is still not clear how this results in improved oil recovery from the complicated three-dimensional pore spaces of rocks, because this phenomenon involves multiple length scales from nanometers upwards.

It is also important to validate pore-scale experimental image analysis methods, and assess the uncertainty of the methods. This could be performed with a help of additional information which is available in simulations, but not in experiments.

We use direct numerical simulation because it more rigorously characterizes wettability considering the complex geometry of porous media than pore network model. Furthermore, direct numerical simulation can be used to directly compare the simulated fluid configurations with those obtained from experiments.

Among the numerical methods in the literature, the color-gradient lattice Boltzmann (LB) method was chosen in this work, considering the three requirements for practical applications on micro-CT images discussed in section 1.2.2: low spurious velocity, good mass conservation, and high computational efficiency.

However, an existing wetting boundary condition for the color gradient LB method does not precisely capture contact angle in porous media. Furthermore, there is no direct numerical simulation model in the literature which can handle wettability alteration caused by low salinity water injection. These numerical models have to be developed.

Objectives of this work

Considering the above mentioned knowledge gaps, the objectives of this work are as follows:

(1) to develop a direct numerical simulation model which can accurately characterize wettability in porous media,

(2) to determine how to incorporate the information of wettability obtained with experiments into numerical modeling of two-phase flow, using the numerical model developed,
(3) to develop a direct numerical simulation model which handles wettability alteration caused by the injection of low salinity water,

(4) to study how the wettability alteration caused by an atomic level chemical interaction results in improved oil recovery from the complicated three-dimensional pore spaces of rocks,

(5) to validate experimental analysis methods of measuring curvature and contact angle from micro-CT images of displacement and access their uncertainty, using the new numerical model.

1.4. Outline of this thesis

Chapter 2 describes the numerical models developed in this work. Existing models in the literature are briefly described, while newly developed methods in this work are detailed. In Chapter 3, the new numerical models are validated using several test cases where analytical solutions are available.

In Chapters 4 and 5, these numerical models are used to study multiphase flow in porous media with particular focus on wettability and its alteration. In Chapter 4, the two-phase lattice Boltzmann method with our improved wetting boundary condition is used. First, dynamic contact angle is studied using capillary rise experiments. Then, we study water flooding on mixed-wet rocks where contact angle varies locally, using experimentally obtained fluid configurations and in situ contact angle measured on the images. Using the matched simulation model to the experiments, we study the application of enhanced oil recovery methods through a parametric study changing fluid and/or rock properties of the simulation. This illustrates the use of a simulation model, namely to predict the behavior outside the range studied experimentally.

In Chapter 5, we use the two-phase lattice Boltzmann model coupled with mass transport for ions in water to study wettability alteration caused by injection of low salinity water, leading to improved oil recovery.

Chapter 6 is conceptually distinct from the previous two chapters — pore-scale oil/water fluid configurations obtained from numerical simulations are used to test experimental analysis methods. With a help of additional information which is available from numerical simulations, but difficult to obtain from experiments, we study two recently developed pore-scale image analysis method: a method to measure the curvature of the oil/water interface to derive capillary pressure, and a method to determine contact angle from pore-scale images.

Lastly, Chapter 7 provides a summary of conclusions and potential areas for future work.
2. Development of numerical models
This chapter describes the numerical models developed in this work. Existing models in the literature are introduced in section 2.1. The key part of this chapter is section 2.2, which describes the new numerical models.

All the numerical models described here are used in Chapter 5, while the two-phase LB model combined with the wetting boundary condition is used in Chapters 4 and 6.

2.1. Existing lattice Boltzmann model

In this section, two existing numerical models are described: (1) the immiscible two-phase lattice Boltzmann (LB) model to solve the two-phase Navier-Stokes equation in section 2.1.1; (2) the LB model based on a passive scaler approach to solve the advection-diffusion equation for the mass transport of solute components in water in section 2.1.2.

2.1.1. The immiscible two-phase flow

We use the lattice Boltzmann (LB) method to solve the Navier-Stokes equation for immiscible two-phase flow. Among a few types of multiphase LB methods in the literature, the color-gradient lattice Boltzmann method based on Halliday et al. [44] is chosen for this work, because it has good mass conservation with small spurious velocity [76]. The model is constructed for the D3Q19 lattice velocity model.

The solution of the two-phase Navier-Stokes equation

The mass conservation and momentum conservation, the Navier-Stokes equation, for isothermal incompressible Newtonian flow, are described by:

\[
\nabla \cdot \mathbf{u} = 0, \tag{2.1}
\]

\[
\rho \frac{D\mathbf{u}}{Dt} = -\nabla p + \mu \nabla^2 \mathbf{u} + \mathbf{f}, \tag{2.2}
\]

where \(D/Dt\) is the material derivative, \(\rho\) and \(\mu\) are the fluid density and viscosity, respectively; \(p\) is the fluid pressure; \(\mathbf{f}\) denotes any body force. Immiscible two-phase flow can be modeled by solving these equations separately for each phase with coupling the two phases across the the interface through the Young-Laplace equation given by:

\[
P_c = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2}\right), \tag{2.3}
\]

where \(P_c\) is the pressure difference across the interface and \(\sigma\) is the interfacial tension between the phases, \(r_1\) and \(r_2\) are the principal radii of curvature of the interface.

The two-phase Navier-Stokes (NS) equation is solved using the Multiple-Relaxation-Time (MRT) color gradient lattice Boltzmann (LB) method constructed for the D3Q19 lattice model.
in which the lattice velocity \( \mathbf{e}_i^f \) is given as:

\[
\mathbf{e}_i^f = \begin{cases} 
(0, 0, 0), & \text{for } i=0, \\
(\pm 1, 0, 1)c, (0, \pm 1, 0)c, (0, 0, \pm 1)c, & \text{for } i=1,...,6, \\
(\pm 1, \pm 1, 0)c, (\pm 1, 0, \pm 1)c, (0, \pm 1, \pm 1)c, & \text{for } i=7,...,18,
\end{cases}
\] (2.4)

where \( c = \Delta x/\Delta t \) is the lattice speed with \( \Delta x \) and \( \Delta t \) being the lattice unit length and the time step size, respectively; the subscript \( i \) is the index of the lattice velocity taking values from 0 to 18 for the D3Q19 model. We set \( \Delta x = \Delta t = 1 \) in this study. The particle distributions of two immiscible fluids labeled red and blue are defined as \( f^r_i(x, t) \) and \( f^b_i(x, t) \) for position \( x \) and time \( t \).

The total particle distribution defined by \( f_i = f^r_i + f^b_i \) undergoes the following collision processes:

\[
f_i^*(x, t) = f_i(x, t) + \Omega_i(x, t) + \bar{F}_i,
\] (2.5)

where \( f_i^*(x, t) \) is the post-collision total particle distribution; \( \Omega_i(x, t) \) is the collision operator; \( \bar{F}_i \) is the source term which introduces a body force in the fluid. We use the Multiple-Relaxation-Time collision operator \([35]\) expressed as:

\[
\Omega_i = -(\mathbf{M}^{-1}\mathbf{S})_{ij}[f_j - f_{ij}^{eq}],
\] (2.6)

where \( \mathbf{M} \) and \( \mathbf{S} \) are the transformation matrix and the diagonal relaxation matrix, respectively. The specific form of these matrices are given in Appendix A.1. \( f_{ij}^{eq} \) is the equilibrium distribution function which is obtained by a second-order Taylor expansion of the Maxwell-Boltzmann distribution with respect to the local fluid velocity as:

\[
f_{ij}^{eq} = \rho \omega_i \left[ 1 + \frac{\mathbf{e}_i^f \cdot \mathbf{u}}{c_s^2} + \frac{\left( \mathbf{e}_i^f \cdot \mathbf{u} \right)^2}{2c_s^4} - \frac{\mathbf{u}^2}{2c_s^2} \right],
\] (2.7)

where \( \rho \) is the total density given by \( \rho = \rho_r + \rho_b \), in which \( \rho_r \) and \( \rho_b \) are the density of red and blue phase, respectively; \( \mathbf{u} \) is the local fluid velocity; \( c_s \) is the speed of sound and \( \omega_i \) is the weight coefficient which is given by

\[
\omega_i = \begin{cases} 
\frac{1}{3}, & \text{for } i=0, \\
\frac{1}{15}, & \text{for } i=1,...,6, \\
\frac{1}{36}, & \text{for } i=7,...,18.
\end{cases}
\] (2.8)

The location of the interface was tracked using a color function \( \rho^N \) defined by:

\[
\rho^N(x, t) = \frac{\rho_r(x, t) - \rho_b(x, t)}{\rho_r(x, t) + \rho_b(x, t)} \quad -1 \leq \rho^N \leq 1.
\] (2.9)
Using the color function, the interfacial tension between two fluids is computed as a spatially varying body force, \( \mathbf{F} \), based on the continuum surface force (CSF) model \([30]\) given by:

\[
\mathbf{F} = -\frac{1}{2} \sigma \kappa \nabla \rho \mathbf{N},
\]

(2.10)

where \( \sigma \) is the interfacial tension and \( \kappa_m \) is the mean curvature of the interface which can be calculated by

\[
\kappa = -[(\mathbf{I} - \mathbf{n} \otimes \mathbf{n}) \cdot \nabla \cdot \mathbf{n},
\]

(2.11)

where \( \mathbf{n} \) is the unit normal vector defined by

\[
\mathbf{n} = -\frac{\nabla \rho \mathbf{N}}{|\nabla \rho \mathbf{N}|}.
\]

(2.12)

In Eq. 2.10 and Eq. 2.11, the partial derivatives are calculated using an isotropic finite difference scheme:

\[
\frac{\partial \psi(\mathbf{x})}{\partial x_\alpha} = \frac{3}{c_s^2} \sum_i \omega_i \psi(\mathbf{x} + e_{fi}) e_{i\alpha},
\]

(2.13)

where \( \psi \) is any function. The spatially varying body force \( \mathbf{F} \) is incorporated into the lattice Boltzmann equation through the body force term \( \bar{\mathbf{F}}_i \). For the MRT model, this is performed by transforming the forcing term proposed by Guo et al. \([41]\) using the scheme presented in Yu and Fan \([133]\):

\[
\bar{\mathbf{F}} = \mathbf{M}^{-1} (\mathbf{I} - \frac{1}{2} \mathbf{S}) \mathbf{M} \tilde{\mathbf{F}},
\]

(2.14)

where \( \mathbf{I} \) is a 19 \( \times \) 19 unit matrix; \( \bar{\mathbf{F}} = [\bar{F}_0, \bar{F}_1, \bar{F}_2, ..., \bar{F}_{18}]^T \); \( \tilde{\mathbf{F}} = [\tilde{F}_0, \tilde{F}_1, \tilde{F}_2, ..., \tilde{F}_{18}]^T \) given by

\[
\tilde{F}_i = \omega_i \left[ \frac{\mathbf{e}_f^i - \mathbf{u}}{c_s^2} + \frac{\mathbf{e}_f^i \cdot \mathbf{u}}{c_s^4} \right] \cdot \mathbf{F} \Delta t.
\]

(2.15)

Then, the recoloring algorithm proposed by Latva-Kokko and Rothman \([64]\) is applied to these distributions to ensure phase segregation and maintain the interface, which is given as:

\[
\begin{align*}
    f^r_i &= \frac{\rho_r}{\rho} f^* + \beta_f \frac{\rho_r \rho_b}{\rho} \omega_i \cos(\varphi) |\mathbf{e}_f^i|, \\
    f^b_i &= \frac{\rho_b}{\rho} f^* - \beta_f \frac{\rho_r \rho_b}{\rho} \omega_i \cos(\varphi) |\mathbf{e}_f^i|,
\end{align*}
\]

(2.16)

where \( \beta_f \) is the segregation parameter which can take a value in \((0, 1)\) and \( \varphi \) is the angle between the color gradient and the lattice vector, which can be obtained by

\[
\cos(\varphi) = \frac{\mathbf{e}_f^i \cdot \nabla \rho \mathbf{N}}{|\mathbf{e}_f^i||\nabla \rho \mathbf{N}|}.
\]

(2.17)

This results in a slightly diffusive interface whose thickness is about 2 to 3 lattice units.
After the recoloring step, the particle distribution functions stream to the neighboring lattice by

\[ f_i^k(x + e_i^f \Delta t, t + \Delta t) = f_i^k(x, t), \quad k = r \text{ or } b. \]  

(2.18)

Through the Chapman-Enskog expansion analysis of the above scheme, the continuity equation and Navier-Stokes equation are recovered with the following relations:

\[ \rho_k = \sum_i f_i^k(x, t), \quad k = r \text{ or } b, \]  

(2.19)

\[ \rho u = \sum_i f_i(x, t)e_i^f + \frac{1}{2} F \Delta t, \]  

(2.20)

\[ \nu_k = \frac{1}{3}(\tau_k - \frac{1}{2}), \quad k = r \text{ or } b, \]  

(2.21)

\[ c_s = \frac{1}{\sqrt{3}} c, \]  

(2.22)

\[ p = \rho(c_s)^2 = \frac{\rho}{3}, \]  

(2.23)

where \( \nu_k \) is the kinetic viscosity of fluid \( k \); \( \tau_k \) is the relaxation time parameter for fluid \( k \); \( p \) is the hydrodynamic pressure in the fluid. In the interface region, the relaxation time is determined by the harmonic average of the viscosity of the fluids:

\[ \frac{1}{\bar{\nu}} = \frac{\rho_r}{\rho_r + \rho_b \nu_r} + \frac{\rho_b}{\rho_r + \rho_b \nu_b}, \]  

(2.24)

\[ \tau = 3\bar{\nu} + \frac{1}{2}, \]  

(2.25)

where \( \tau \) is related to elements of the diagonal relaxation matrix \( S \) as shown in Appendix A.1.

**Boundary conditions**

To specify the boundary conditions, we divide lattice nodes into four categories:

- \( C_{FB} \): a list of lattice nodes that belong to the fluid domain and are in contact with at least one lattice node in the solid domain.
- \( C_{Fl} \): a list of lattice nodes that belong to the fluid domain but are not in contact with any lattice nodes in the solid domain.
- \( C_{SB} \): a list of lattice nodes that belong to the solid domain and are in contact with at least one lattice node in the fluid domain.
- \( C_{Sl} \): a list of lattice nodes that belong to the solid domain but are not in contact with any lattice nodes in the fluid domain.

At the lattice sites of \( C_{SB} \), the non-slip boundary condition is imposed using the full-way
bounce back scheme expressed as:

\[ f^k_i(x, t) = f^k_i(x, t), \quad k=r \text{ or } b. \]  

(2.26)

where \( f^k_i \) is the distribution function in the opposite direction to \( e_i \).

The wettabillity of the solid surface is modeled by imposing the wetting boundary condition at the lattice nodes of \( C_{FB} \) described in section 2.2.1 of this thesis. In this boundary condition, the estimated direction of the unit normal vector of the interface \( (\mathbf{n}) \) at \( C_{FB} \) is modified to make an angle \( \theta \) with \( \mathbf{n}_s \), where \( \theta \) is the specified contact angle and \( \mathbf{n}_s \) is the wall normal vector. This wetting boundary condition accurately assigns contact angles for 3D arbitrary geometries with smaller spurious currents compared to the widely used fictitious density boundary condition. Further details of this wetting boundary condition can be found in section 2.2.1.

For the inlet and outlet boundaries, a constant velocity and constant pressure boundary condition are used based on the method proposed by Zou and He [134].

This LB model was coded by Fortran and parallelized with Message Passing Interface (MPI). Since the most operations in the LB algorithm are a local operation, a good parallel efficiency has been achieved in our LB code. Furthermore, the collision term given by Eq. 2.30 requires the matrix multiplication operations of the \( 19 \times 19 \) matrix. These operations have been explicitly coded to avoid multiplications by zero elements.

2.1.2. The mass transport of solute components

We consider the transport of solute components in fluid. The mass transport of the solute components in a bulk phase region described by the advection-diffusion (AD) equation is solved by a passive scalar approach in a LB framework in which the fluid velocity, \( \mathbf{u} \), is obtained from the solver for the flow field. In a fluid/fluid interface region, the scheme proposed by Riaud et al. [111] is used to satisfy a correct equation of state.

The solution of the advection-diffusion equation in a bulk phase region

The transport of solutes in bulk fluid is modeled by the advection-diffusion (AD) equation:

\[ \frac{\partial C_s}{\partial t} = \nabla \cdot (D_s \nabla C_s) - \nabla \cdot (\mathbf{u}C_s) + R_s, \]  

(2.27)

where \( C_s \) is the concentration of components; \( D_s \) is the diffusion coefficient; \( R_s \) is the source or sink of the quantity \( C_s \) to account for the chemical reaction of the solutes components. In our study, this advection-diffusion equation is solved based on the passive scalar approach in a lattice Boltzmann framework [120]. To recover the advection-diffusion equation, a lower isotropy model than that to recover the Navier-Stokes equation has been proven to be sufficient.
[62], hence we use the D3Q7 lattice model, in which the lattice velocity \( \mathbf{e}_i \) is given as:

\[
\mathbf{e}_i^s = \begin{cases} 
(0, 0, 0), & \text{for } i = 0, \\
(\pm 1, 0, 0)c, (0, \pm 1, 0)c, (0, 0, \pm 1)c, & \text{for } i = 1, \ldots, 6,
\end{cases}
\]

(2.28)

where \( c = \Delta x / \Delta t \) is the lattice speed with \( \Delta x \) and \( \Delta t \) being the lattice unit length and the time step size, respectively; the subscript \( i \) is the index of the lattice velocity taking values from 0 to 6 for the D3Q7 model. The particle distribution of solute components is defined as \( g_i^n(x, t) \), where the superscript \( n \) is the number of components considered.

The particle distributions of solute components undergo the following collision and streaming processes:

\[
g_i^n(x + \mathbf{e}_i \Delta t, t + \Delta t) = g_i^n(x, t) + \Omega_i^n + S_i
\]

(2.29)

where \( \Omega_i^n \) is the collision term and \( S_i \) is the body force term which may be used for chemical reaction. In this study, we consider a single component (hence, we simply write \( g_1^n \) as \( g_i \)) and do not consider chemical reaction among components, i.e., \( S_i = 0 \).

We use the Multiple-Relaxation-Time collision operator developed for the D3Q7 lattice model [131], which is expressed as:

\[
\Omega_i = -(\mathbf{M}_S^{-1} \mathbf{S}_S \mathbf{M}_S)_{i,j} [g_j - g_j^{eq}]
\]

(2.30)

where \( \mathbf{M}_S \) and \( \mathbf{S}_S \) are the transformation matrix and the diagonal relaxation matrix for solute transport, respectively. The specific form of these matrices are given in Appendix A.2. \( g_i^{eq} \) is the equilibrium distribution given by:

\[
g_i^{eq} = \omega_i^s C_s \left( 1 + \frac{7}{6 - a_T} \frac{\mathbf{e}_i \cdot \mathbf{u}}{c_s^2} \right)
\]

(2.31)

where \( a_T \) is the constant; \( c_s \) is the speed of sound which satisfies \( c_s^2 = 1/3 \); \( \omega_i^s \) is the weight coefficient given by:

\[
\omega_i^s = \begin{cases} 
1 + \frac{a_T}{7}, & \text{for } i = 0, \\
\frac{6 - a_T}{42}, & \text{for } i = 1, \ldots, 6.
\end{cases}
\]

(2.32)

In the passive scalar approach, the fluid velocity \( \mathbf{u} \) in the equilibrium function is determined from the solution of the Navier-Stokes solver.

The concentration of the component \( C_s \) and the diffusion coefficient \( D_s \) are obtained by:

\[
C_s = \sum_i g_i(x, t), \quad (2.33)
\]

\[
D_s = \frac{6 - a_T}{7} c_s^2 \left( \frac{1}{2} - \frac{\tau_s}{2} \right) = \frac{6 - a_T}{21} \left( \frac{\tau_s}{2} - \frac{1}{2} \right), \quad (2.34)
\]
where $\tau_s$ is related to elements of the diagonal relaxation matrix $S_s$ as shown in Appendix A.2.

### The mass transport of solute components in an interface region

In addition to the mass transfer in a bulk fluid region, multiphase mass transfer has to satisfy a correct equation of state at the fluid interface. This is achieved based on the scheme proposed by Riaud et al. [111]. In this method, the following additional operation similar to Eq. 2.16 is performed on the particle distribution:

$$g_i(x,t) = g_i^*(x,t) + \beta_s W_s(x_b) g_i^{eq,0} \frac{e_i^s \cdot n}{|e_i^s|},$$  

(2.35)

$$x_b = \frac{\rho_b}{\rho_r + \rho_b},$$  

(2.36)

where $g_i^*$ is the post-collision and before recoloring distribution function; $g_i^{eq,0}$ is the equilibrium distribution for $u = 0$ as defined in Eq. 2.31; $W_s(x_b)$ is an arbitrary function to make the components sensitive to the solvent phase. Through a perturbation analysis of Eq. 2.35, Riaud et al. [111] derived the following equation of state of the solute:

$$0 = \frac{dC_s}{dx_b} + \lambda_s \frac{W_s(x_b)}{x_b(1 - x_b)} C_s,$$  

(2.37)

$$\lambda_s = \frac{\tau_s \beta_s k_s}{6D_s \beta_f k_f},$$  

(2.38)

where $\lambda_s$ is the parameter which controls the resulting equation of state; $k$ is the geometric factor unique to the lattice velocity model given by:

$$2k_p I = \sum_i \omega_i^p \frac{e_i^p \otimes e_i^p}{|e_i^p|}, \quad p=f \text{ or } s.$$  

(2.39)

In the original work by Riaud et al. [111], a D2Q9 lattice velocity was used to compute both two-phase flow field and solute transport. Hence, Eq. 2.38 simplifies into $\lambda_s = \tau_s \beta_s / (6 \beta_f D_s)$. However, when different lattice velocity models are used to compute flow field and solute transport, Eq. 2.39 has to be taken into account. In this study, to make a component soluble only in water, we chose the following function for $W_s(x_b)$:

$$W_s(x_b) = x_b - 1.$$  

(2.40)

Integrating Eq. 2.37 with Eq. 2.40, we obtain the equation of state as follows:

$$\frac{C_s(x_b)}{C_s^{max}} = (x_b)^{\lambda_s},$$  

(2.41)

$$x_b(C_s^{max}) = 1.$$  

(2.42)
Lastly, we set $\lambda_s = 1$ to attain the best numerical stability by backcalculating $\beta_s$ based on Eq. 2.38.

In addition, other types of the equation of state are also possible by defining the dependence of the solute concentration on the phase distribution through the function of $W_s(x_b)$ in Eq. 2.40. Table 2.1 summarizes the $W_s(x_b)$ functions for single soluble, surface adsorbed, and amphiphilic soluble components [111]. For all types of solutes, the corresponding equation of state, $C_s(x_b)/C^\text{max}_s$, can be obtained by solving Eq. 2.38 with the $W_s(x_b)$ functions.

Table 2.1. Summary of the concentration profile near the interface. Here, $x_b$ is defined by Eq. 2.36 and $\lambda_s$ is the segregation parameter of the concentration. Modified after [111].

<table>
<thead>
<tr>
<th>Type</th>
<th>Abbreviation</th>
<th>$W_s(x_b)$</th>
<th>$C_s(x_b)/C^\text{max}_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-phase Soluble</td>
<td>SS</td>
<td>$x_b - 1$</td>
<td>$(x_b)^{\lambda_s}$</td>
</tr>
<tr>
<td>Surface Adsorbed</td>
<td>SA</td>
<td>$x_b - 0.5$</td>
<td>$e^{\lambda_s(x_b - 1)}$</td>
</tr>
<tr>
<td>Amphiphilic Soluble</td>
<td>AS</td>
<td>$x_b(x_b - 1)$</td>
<td>$[4x_b(1 - x_b)]^{\lambda_s/2}$</td>
</tr>
</tbody>
</table>

**Boundary conditions**

At solid and fluid boundary lattice nodes, an impermeable boundary condition is imposed using the full-way bounce back scheme expressed as [62]:

$$g_i(x, t) = g_i(x, t),$$ (2.43)

where $g_i$ is the distribution function in the opposite direction to $e_s^i$.

A constant concentration boundary condition of $C_s = C_0$ used for inlet lattice nodes is imposed using the anti-bounce-back scheme expressed as [131]:

$$g_i(x, t + \Delta t) = -g_i(x, t) + \frac{6 - a_f}{21} C_0,$$ (2.44)

where $C_0$ is the known concentration value and set to 1 in this paper.

A zero-gradient concentration boundary condition of $\partial C_s/\partial x = 0$ used for outlet lattice nodes is imposed using the extrapolation scheme [62].

$$g_i(x_l, y, z, t) = g_i(x_l - 1, y, z, t),$$ (2.45)

where we consider the boundary perpendicular to $x$-direction and $x_l$ is the last fluid lattice node in $x$-direction of a simulation domain.

The solver for the mass transport of solute components was also coded by Fortran and parallelized with MPI, and coupled with the Navier-Stokes solver described in section 2.1.1. We note that the use the D3Q7 lattice velocity model significantly saves computational time and memory consumption, compared to D3Q19 lattice velocity model. Hence, the model can handle...
multiple chemical species if necessary.

2.1.3. Unit conversion in the lattice Boltzmann method

The LB computations are performed in a non-dimensional domain. To relate parameters to the physical space, an appropriate unit conversion must be required. In this section, the unit conversion from the non-dimensional space in the lattice Boltzmann computation to the physical space is explained.

We consider the conversion factor for length \( L_c \), mass \( M_c \) and time \( T_c \). An unit length in the simulation of \( l_{sim} \) has the following relationship with the physical length scale of \( l_{phy} \):

\[
L_c = \frac{l_{phy}}{l_{sim}}
\]  
(2.46)

Typically, the unit length of the LBM simulation equals to the resolution of image data to be calculated. Second, since the dimension of density is \([M][L]^{-3}\), the conversion factor for mass \( (M_c) \) can be calculated as:

\[
\frac{\rho_{phy}}{\rho_{sim}} = \frac{M_c}{L_c^3} \Leftrightarrow M_c = \frac{\rho_{phy}}{\rho_{sim}} L_c^3
\]  
(2.47)

In the LBM, the kinetic viscosity is obtained from the relaxation time \( \tau \) with the following equation:

\[
\nu = \frac{(\tau - 0.5)}{3}
\]  
(2.48)

Finally, the conversion factor for the time \( (T_c) \) is obtained from the relationship of kinetic viscosities in the non-dimensional space and the physical space.

\[
\frac{\nu_{phy}}{\nu_{sim}} = \frac{L_c^2}{T_c} \Leftrightarrow T_c = \frac{\nu_{sim}}{\nu_{phy}} L_c^2
\]  
(2.49)

With these conversion factors, other parameters can be converted to the physical domain based on their dimension. For example,

\[
\sigma_{phy} = M_c T_c^{-2} \sigma_{sim}
\]  
(2.50)

\[
p_{phy} = M_c L_c^{-1} T_c^{-2} p_{sim}
\]  
(2.51)

where \( \sigma \) is the interfacial tension and \( p \) is the hydrodynamic pressure.

For a practical application of the lattice Boltzmann computation, we choose a time step size of simulations, \( T_c \), by tuning \( \tau \) in Eq. 2.48 so as to satisfy the following empirical criteria for numerical stability:

- \( U_{max} \leq 10^{-2} \), where \( U_{max} \) is the maximum velocity in a computational domain.
- \( \sigma \leq 0.1 \), where \( \sigma \) is the interfacial tension in simulations
- \( \tau \geq 1/2 \), where \( \tau \) is the relaxation time in simulations which is related to the kinetic viscosity by Eq. 2.48.
As a result, we use typical time step sizes of $10^{-7} \sim 10^{-6}$ second per time step for a grid sizes of a few $\mu$m.

2.2. New model developments

This section describes the two new models developed in this thesis: a wetting boundary condition to impose accurate contact angle at the three-phase contact line in section 2.2.1; and a wettability alteration model for the modeling of low salinity water flooding in section 2.2.2.

2.2.1. Wetting boundary condition

We describe a new wetting boundary condition which directly imposes the correct direction of the interface normal vector at solid/fluid boundary lattice nodes based on the wall normal vector and input contact angle of the solid surface. The fictitious-density boundary condition which is a widely used wetting boundary condition in the color gradient LB method is also described to provide reference cases which will be compared with our wetting boundary condition in section 3.1.3.

The fictitious-density wetting boundary condition

The fictitious-density boundary condition was originally proposed by Latva-Kokko and Rothman [65]. In this method, a fictitious density is assigned at solid nodes $x_s$ to compute the color function at the solid nodes. The color function at the solid nodes $\rho^N(x_s)$ takes effect when the color gradient $\nabla \rho^N$ of the flow domain next to the solid node is calculated. Based on the force balance at the contact line, the contact angle $\theta$ is expressed as

$$\theta = \arccos \rho^N(x_s). \quad (2.52)$$

Since this boundary condition is easy to implement, several studies using the color gradient LB model have adopted this approach [110, 109, 39, 53, 78]. However, Leclaire et al. [66] showed that this approach can be inaccurate because of unphysical mass transfer of the wetting phase along the solid.

Imposing a contact angle directly

The basic idea of our wetting boundary condition is to modify the direction of the color gradient, $\nabla \rho^N$, at the boundary according to a prescribed input contact angle. Liu et al. [75] showed an implementation of this wetting boundary condition in the 2D color gradient LB method. Their approach is based on the geometrical formulation proposed by Ding and Spelt [36]. This method accurately simulates wetting phenomena on a flat surface [53, 75, 72] and can be extended to a flat surface in 3D [132]; but the implementation for arbitrary surfaces is not obvious.
Leclaire et al. [67] proposed a way to find the proper direction of the color gradient, $\nabla \rho^N$, based on the recurrence relation for the secant method. However, the recurrence relation would in principle require many iterations, which could increase computational costs.

Our wetting boundary condition is similar to a method by Xu et al. [130]. They proposed a wetting boundary condition for 2D problems. In their work the direction of the color gradient, $\nabla \rho^N$, is enforced so as to match the prescribed contact angle at the boundary. The direction is obtained by rotating the normal vector to the boundary by the contact angle $\theta$ using the vector transformation equation in 2D. However, this algorithm is only applicable to 2D problems. We propose a wetting boundary condition which is applicable to 3D geometries based on the extension of the method of Xu et al. [130].

Following the work by Leclaire et al. [66] and Xu et al. [130], lattice nodes are divided into four categories:

- $C_{FB}$: a list of lattice nodes that belong to the fluid domain and are in contact with at least one lattice node in the solid domain.
- $C_{Fl}$: a list of lattice nodes that belong to the fluid domain but are not in contact with any lattice nodes in the solid domain.
- $C_{SB}$: a list of lattice nodes that belong to the solid domain and are in contact with at least one lattice node in the fluid domain.
- $C_{Sl}$: a list of lattice nodes that belong to the solid domain but are not in contact with any lattice nodes in the fluid domain.

A schematic image of the wetting boundary condition is shown in Fig. 2.1. First, to define the direction of the wall boundary, the unit normal vector of the boundary $\mathbf{n}_s$ is calculated for the lattice nodes belonging to $C_{FB}$. For complex geometries, a method presented in [130] can be used to calculate $\mathbf{n}_s$. Because the calculation of the color gradient $\nabla \rho^N$ needs to be performed for all the lattice nodes belonging to $C_{FB}$ and $C_{Fl}$ by the gradient operator defined by Eq. (2.13), the color function $\rho^N$ at the nodes belonging to $C_{SB}$ is required. This is estimated by the extrapolation of the color function at neighboring lattice nodes which belong to $C_{FB}$ by the following lattice-weighted average scheme:

$$\rho^N(x,t) = \frac{\sum_{i:x+e_i\delta t \in C_{FB}} \omega_i \rho^N(x + e_i\delta t,t)}{\sum_{i:x+e_i\delta t \in C_{FB}} \omega_i}, \quad x \in C_{SB}. \quad (2.53)$$

With the values of $\rho^N$ at the nodes belonging to $C_{SB}$, it is possible to estimate the color gradient $\nabla \rho^N$ for the lattice nodes in $C_{Fl}$. This estimated value is denoted as $\nabla \rho^{N*}$. In the next step, the direction of $\nabla \rho^{N*}$ is modified to match the prescribed contact angle against the wall boundary while keeping the norm of $\nabla \rho^{N*}$ unchanged. The direction of $\nabla \rho^{N*}$ is given by

$$\mathbf{n}^* = -\frac{\nabla \rho^{N*}}{|\nabla \rho^{N*}|}. \quad (2.54)$$
The unit vector \( \mathbf{n}^\ast \) is understood as the estimated unit normal vector to the red and blue fluid interface at the wall boundary (\( \mathbf{x} \in C_{FB} \)). In a modification step, the direction of the color gradient is modified in accordance with the prescribed contact angle \( \theta \). In a 2D problem, Xu et al. [130] proposed a vector transformation that rotates \( \mathbf{n}_s \) by the angle \( \theta \). However, in a 3D problem, the normal vector that forms an angle \( \theta \) to \( \mathbf{n}_s \) makes a circle around \( \mathbf{n}_s \). We adopt the method employed in the OpenFOAM finite volume library [91]. In Fig. 2.1, two contact lines (points in 2D) are shown. For each contact line, there are two possible unit vectors making an angle \( \theta \) with \( \mathbf{n}_s \) (i.e., the unit vector, \( \mathbf{n}_+ \), which is rotated by an angle \( \theta \) in a counter clockwise direction from \( \mathbf{n}_s \) and the unit vector, \( \mathbf{n}_- \), which is rotated by an angle \( \theta \) in a clockwise direction from \( \mathbf{n}_s \)). These two unit vectors, \( \mathbf{n}_\pm \), are obtained by the linear combination of \( \mathbf{n}_s \) and \( \mathbf{n}^\ast \) as:

\[
\mathbf{n}_\pm = \left( \cos \pm \theta - \frac{\sin \pm \theta \cos \theta'}{\sin \theta'} \right) \mathbf{n}_s + \frac{\sin \pm \theta}{\sin \theta'} \mathbf{n}^\ast,
\]

\[
\theta' = \arccos(\mathbf{n}_s \cdot \mathbf{n}^\ast).
\]  

(2.55)

The Euclidean distances between \( \mathbf{n}_\pm \) and \( \mathbf{n}^\ast \) are evaluated, then \( \mathbf{n}^\ast \) is replaced with either \( \mathbf{n}_+ \) or \( \mathbf{n}_- \) which has the shorter Euclidean distance to \( \mathbf{n}^\ast \). For instance, at the left contact line in Fig. 2.1, \( \mathbf{n}^\ast \) is replaced with \( \mathbf{n}_+ \), whereas at the right contact line, \( \mathbf{n}^\ast \) is replaced with \( \mathbf{n}_- \). With this, the modified interface normal vector falls into the plane spanned by the unit vectors \( \mathbf{n}^\ast \) and \( \mathbf{n}_s \).

![Figure 2.1. Schematic image of the wetting boundary condition. \( \mathbf{n}_s \) is the unit normal vector of the wall while \( \mathbf{n}_+ \) and \( \mathbf{n}_- \) are the possible two unit vectors which have an angle \( \theta \) from \( \mathbf{n}_s \) in a counter clockwise and clockwise direction, respectively. These unit vectors, \( \mathbf{n}_\pm \), are obtained by the linear combination of \( \mathbf{n}_s \) and the estimated unit normal vector to the fluids interface, \( \mathbf{n}^\ast \), using Eq. (2.55), then \( \mathbf{n}^\ast \) is replaced with either \( \mathbf{n}_+ \) or \( \mathbf{n}_- \) which has the shorter Euclidean distance to \( \mathbf{n}^\ast \). Here, \( \theta' \) is the angle between \( \mathbf{n}_s \) and \( \mathbf{n}^\ast \).](image)

Note that up to this point, the contact angle is defined as the angle measured through the red fluid to be consistent with the previous literature, for instance [65]. However from the next section, we refer to the contact angle as the angle measured through the blue fluid since the blue fluid typically represents the denser water phase.
2.2.2. Wettability alteration model for low salinity water flooding

A wettability alteration model is developed to simulate alteration of the wettability of solid surfaces caused by exposure to low salinity water. First, we describe a wettability alteration mechanism during low salinity water flooding (LSWF) upon which our model is based. Then, its numerical implementation is described.

Wettability alteration mechanism and its modeling

Two-phase flow where water displaces oil with an effective contact angle of $\theta$ at the pore-scale is considered. Wettability is influenced by thin water films which coat the rock surface with a thickness of typically less than 10 nm [50, 126]. The stability of the film is determined by the disjoining pressure, $\Pi(h)$, which is a function of film thickness, $h$. In general, when LS water is injected, adsorption or desorption of certain ions onto/from rock surface occurs in the film. This causes a change in the electrical surface charge of the oil/water and water/solid interfaces in the film, resulting in positive contributions to disjoining pressure. Specific atomic-level chemical interactions which cause the change in the electrical surface charge are described in [90, 56, 12]. The positive contributions to disjoining pressure make the films more stable, resulting in a change of effective contact angle toward more water-wet conditions.

There are some attempts to numerically model this wettability alteration in the literature. Aziz et al. [21] showed that numerical modeling of low salinity water flooding in which the Navier-Stokes equation of flow field and the advection and diffusion equation for mass transport of components in water phase were solved based on the volume of fluid method implemented with OpenFoam. In their approach, the wettability of rock surface was changed as a linear function of salinity of a grid block at the fluid/solid boundaries. Although their numerical model successfully simulated spatially non-uniform wettability alteration based on the distribution of salinity, there was an issue in their wettability alteration model. Because there is no mass transfer of ions in water phase across the oil/water interface, their wettability alteration model can only change the contact angle of the solid surface previously covered with water and it cannot alter the wettability of the solid surface covered with oil. This results in a limited sensitivity of contact angle to salinity, which prevented a significant wettability alteration around the three-phase contact line. This will be further discussed in section 5.2.

Maes and Geiger [82] showed a more rigorous approach to model wettability alteration induced by low salinity water. They also solved the two transport equations based on the volume of fluid method implemented with OpenFoam. Furthermore, they modeled the electrical surface potential of the solid surface based on the Surface Complexation Model (SCM), which was determined by chemical reactions between chemical spices in water phase and solid surface. The contact angle in their model was modeled as a function of electrical surface potential. Their model successfully simulated the detachment of oil droplets observed in the experiments by Mahani et al. [83]. However, as stated in their paper, even though they rigorously modeled the electrical potential of rock surface, they had to use an effective diffusion coefficient accounting...
for slower diffusion in thin water films than that in bulk water, which cannot be determined a-priori and need to be tuned to the experiments. They also mentioned that with their model they cannot simulate the remobilization of oil in the absence of buoyancy as observed in the experiments by Bartels et al. [23], because they did not explicitly model the expansion of thin water films.

In this thesis, we propose a phenomenological approach to model wettability alteration induced by low salinity water. In our model, we consider the adsorption and desorption of chemical components onto the solid surface, and the contact angle of the solid surface is modeled as a function of the amount of adsorption. The slow kinetics of the reaction is modeled by a reaction rate constant in our model, whereas it was modeled by the effective diffusion coefficient in the model by Maes and Geiger [82]. This wettability alteration mechanism, which will be detailed in the following section, is implemented into our lattice Boltzmann code to solve two equations: the Navier-Stokes (NS) equation for immiscible two-phase flow of oil and water, and the advection-diffusion (AD) equation for the transport of the concentration of ions. A schematic description of the model is shown in Fig. 2.2. Furthermore, we will show that our numerical simulations performed in three-dimensional geometries can mimic the progressive development of thin water films as observed in the experiments by Bartels et al. [23] in section 5.3.

![Figure 2.2. Schematic image of the numerical model. The distribution of the color function is shown with the simulation grid. The exact location of the interface ($\rho^N = 0$) is shown by the yellow line, while the iso-contour lines corresponding to $\rho^N = \pm 0.5$ are shown by the red and blue lines, respectively. Ions in water shown by the yellow circles undergo advection-diffusion in the bulk water region and adsorption at the solid/fluid boundary nodes indicated by the black dashed square.](image)

**Modeling wettability alteration**

The effect of a change in wetting states in water films is modeled by considering the following adsorption and desorption reaction of ions at the solid/fluid surface:

$$A + R \rightleftharpoons AR,$$  \hspace{1cm} (2.56)
where $A$ is an ion component in water, $R$ is the rock surface for adsorption, and $AR$ is the adsorbed component on the surface. Assuming the Langmuir adsorption model, the amount of adsorption at equilibrium and the rate of adsorption are given as:

$$\Theta = \frac{K_{eq}C_s}{1 + K_{eq}C_s}, \quad (2.57)$$

$$v = k \left[ C_s(1 - \Theta) - \frac{\Theta}{K_{eq}} \right], \quad (2.58)$$

where $\Theta$ is the fractional occupancy of the adsorption sites. $C_s$ is the concentration of low salinity (LS) water, $K_{eq}$ is the equilibrium constant whose dimension is the reciprocal of concentration. Since the normalized concentration, $C_s$, is used, $K_{eq}$ was also non-dimensional in this work. $k$ is the reaction rate constant whose dimension is the reciprocal of time. Based on Eq. 2.58, the reaction products by $v\Delta t$ is accumulated at every time step at the solid/fluid boundary nodes. Since the maximum concentration $C_s = 1$ is assigned through a constant concentration boundary condition at the inlet, the maximum occupancy, $\Theta_{max}$, is given by:

$$\Theta_{max}|_{C_s=1} = \frac{K_{eq}}{1 + K_{eq}}. \quad (2.59)$$

Then, the normalized equilibrium amount of adsorption, $\bar{\Theta}$, is given by:

$$\bar{\Theta} = \frac{\Theta}{\Theta_{max}} = \frac{(1 + K_{eq})C_s}{1 + K_{eq}C_s}, \quad 0 \leq \bar{\Theta} \leq 1. \quad (2.60)$$

At every time step, contact angles were locally imposed using the wetting boundary condition described in section 2.2.1, based on the following linear equation:

$$\theta = (\theta_{min} - \theta_{init})\bar{\Theta} + \theta_{init}, \quad (2.61)$$

where $\theta_{init}$ and $\theta_{min}$ are the initial contact angle before wettability alteration and the minimum contact angle at the maximum occupancy, $\Theta_{max}$.

We now describe how our wettability alteration model works in the vicinity of the three-phase contact line. Fig. 2.3 shows our model representing wettability alteration which occurs at solid/fluid boundary nodes as shown by the black dashed square in Fig. 2.2. Depending on the LS concentration ($C_s$) at these nodes, adsorption occurs toward the normalized equilibrium amount of adsorption ($\bar{\Theta}$) over time steps based on Eq. 2.60 (Fig. 2.3a). The color function ($\rho^N$) around the oil/water interface located at $x = 0$ changes sharply from -1 in water to 1 in oil within a few lattice nodes of the interface region (Fig. 2.3b). The LS concentration of these nodes is obtained from the equation of state, Eq. 2.41, as shown in the figure. Based on the LS concentration, the altered contact angles for these nodes are then obtained from Eqs. 2.60 and 2.61 for different $K_{eq}$ (Fig. 2.3c). In this figure, we also plot the altered contact angle simply obtained by a linear function of $C_s$ as used in Aziz et al. [21].

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When the contact angle is changed based on the linear function of $C_s$, or on our model with $K_{eq} = 1$, the contact angle at the three-phase contact at $x = 0$ where $\rho^N = 0$ can be altered to around $(\theta_{init} + \theta_{min})/2$: the full wettability change to $\theta_{min}$ cannot be captured. Furthermore, the contact angles of the surface covered with oil remains $\sim \theta_{init}$. As we will show later, this can result in pinning of the three-phase contact (see section 5.2). On the other hand, when a higher value of $K_{eq}$ is used in our model, the contact angle can change to a value close to $\theta_{min}$ wherever there is some water present, including slightly in advance (towards the oil) of the three-phase contact line. This effect is illustrated in Fig. 2.3c using $K_{eq} = 100$ as an example. This mimics the effect of wettability alteration occurring through the thickening of a water film which is below the resolution of the model. As a result, this enables the contact line to advance across a previously oil-covered surface. Moreover, the time to reach the equilibrium amount of adsorption is not instantaneous, but it is controlled by the reaction rate constant. Hence, a slower kinetics of wettability alteration than that estimated from diffusion only can be modeled through the reaction rate constant.

In summary, the equilibrium constant ($K_{eq}$) controls the sensitivity of the wettability alteration to the LS concentration, while the reaction rate constant ($k$) controls how rapidly the alteration occurs. The validation of our wettability alteration model against theoretical solutions is provided in section 3.2.4.
Figure 2.3. Wettability alteration model. (a) Normalized amount of adsorption as a function of the LS concentration for different equilibrium constants ($K_{eq}$) obtained with Eq. 2.60. (b) The profiles of the color function ($\rho^N$) and LS concentration ($C_s$) around the oil/water interface located at $x = 0$. These lattice nodes correspond to the nodes surrounded by the black dashed square in Fig. 2.2. (c) The altered contact angle around the interface corresponding to the LS concentration in the above. The blue line is obtained by a simple linear function of $C_s$, while the others are obtained from our model with $K_{eq} = 1$ and $K_{eq} = 100$ based on Eqs. 2.60 and 2.61.
3. Validation of numerical models
In this chapter, we validate the numerical models developed in chapter 2 using test cases where analytical solutions are available.

In section 3.1, the validations of the two-phase LB model are provided. The viscous force and interfacial tension in the numerical model are verified in sections 3.1.1 and 3.1.2, respectively. Through section 3.1.3 to 3.1.5, our wetting boundary condition is extensively validated using a flat, curved, and staircase solid surfaces.

In section 3.2, validations of the mass transfer model are provided. First, in sections 3.2.1 and 3.2.2, the analytical solution of the one-dimensional advection-diffusion equation is used to validate the numerical model of the mass transfer in the single phase LB model. Then, in section 3.2.3, the distribution of solute components across the interface of two immiscible fluids is verified using the multiphase mass transfer model of Riaud et al. [111] implemented in the two-phase LB model. Lastly, our wettability alteration model (see section 2.2.2) implemented in the two-phase LB model coupled with mass transport is demonstrated using a simple test case.

3.1. Validation of the two-phase lattice Boltzmann model

3.1.1. Two-phase flow between parallel plates

Two-phase flow between parallel walls was simulated to validate the representation of viscous forces in the numerical model. Red fluid flowed the center of the gap between the plates, while blue fluid flowed in the rest of the domain. The simulated fluid velocity distribution perpendicular to the flow direction was compared with its analytical solution [78].

A 2D simulation domain consisting of $42 \times 11$ lattice nodes was used. A periodic boundary condition was applied in the $y$-direction to represent infinite extension in this direction, while wall boundaries were placed on the top ($x = 0$) and bottom ($x = 41$) of the $x$-direction. The flow was driven by the body force applied in the $y$-direction. The red fluid was placed from $x = 11 \sim 31$, blue fluid was placed from $x = 1 \sim 10$ and $x = 32 \sim 41$. The simulations were performed with three cases of viscosity ratio of $M = \mu_r/\mu_b=1, 0.01$ and 100. The interfacial tension was fixed as $\sigma = 0.1$.

Table. 3.1 summarizes the total fluid flux in $y$-direction obtained from the analytical solutions and simulations. Fig. 3.1 shows a comparison of fluid velocity in $y$-direction along the $x$-axis. The simulated fluid velocity agreed well with the analytical solution for a wide range of viscosity ratios.
Table 3.1. Summary of the two-phase flow between parallel plates.

<table>
<thead>
<tr>
<th>Viscosity ratio</th>
<th>Total flux in y-direction</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>analytical</td>
<td>simulation</td>
</tr>
<tr>
<td>1</td>
<td>$3.20 \times 10^{-4}$</td>
<td>$3.20 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.01</td>
<td>$2.14 \times 10^{-3}$</td>
<td>$2.29 \times 10^{-3}$</td>
</tr>
<tr>
<td>100</td>
<td>$1.40 \times 10^{-2}$</td>
<td>$1.39 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

Figure 3.1. Result of two-phase flow between parallel plates for different viscosity ratio $M = \mu_r/\mu_b$. (a) $M=1$. (b) $M=0.01$. (c) $M=100$.

3.1.2. Young-Laplace law: 3D static droplet

A red droplet placed in blue fluid was simulated to validate the interfacial tension between the two fluids. The simulation domain was composed of $65 \times 65 \times 65$ lattice nodes. A periodic boundary condition was applied for all boundaries. Initially, a red droplet with a radius of 16 lattice units was placed at the center of a blue fluid domain. Based on the Young-Laplace equation, at equilibrium, the pressure difference across the interface of the red and blue fluids, $\Delta p$, is related to the interfacial tension, $\sigma$, and the radius of the droplet, $R$, as:

$$\Delta p = \frac{2\sigma}{R}.$$  \hspace{1cm} (3.1)

The pressure difference between the phases, $\Delta p$, and the radius of the droplet, $R$, were obtained from the simulation results in equilibrium. Then, the interfacial tension, $\sigma$, calculated using Eq. 3.1 was compared with the input value. The simulations were performed with three cases of viscosity ratio of $M = \mu_r/\mu_b=1$, 0.01 and 100. The input interfacial tension was fixed.
as \( \sigma = 1.0 \).

Table 3.2 shows the result of the simulations. The \(|U|_{\text{max}}\) shows a maximum spurious velocity observed in the simulations. In the last column of the table, the maximum spurious velocity is normalized by the viscosity of outer fluid, \(\mu_b\), and the interfacial tension, \(\sigma\). Fig. 3.2 shows the fluid configuration and spurious velocity obtained with the viscosity ratio of 1.0 as an example.

Table 3.2. Summary of the 3D static droplet test cases.

| Mobility ratio | \(\sigma_{\text{theory}}\) | \(\sigma_{\text{sim}}\) | error | \(|U|_{\text{max}}\) | \(\mu_b|U|_{\text{max}}/\sigma\) |
|----------------|---------------------|---------------------|-------|---------------------|-------------------------------|
| 1              | 1.000 \(\times\) 10\(^{-1}\) | 1.009 \(\times\) 10\(^{-1}\) | 0.87\% | 2.88 \(\times\) 10\(^{-5}\) | 4.81 \(\times\) 10\(^{-5}\) |
| 0.01           | 1.000 \(\times\) 10\(^{-1}\) | 1.009 \(\times\) 10\(^{-1}\) | 0.89\% | 1.24 \(\times\) 10\(^{-4}\) | 4.15 \(\times\) 10\(^{-4}\) |
| 100            | 1.000 \(\times\) 10\(^{-1}\) | 1.009 \(\times\) 10\(^{-1}\) | 0.88\% | 4.26 \(\times\) 10\(^{-4}\) | 1.42 \(\times\) 10\(^{-5}\) |

Figure 3.2. An example of a 3D static droplet test case. (a) The shape of the red fluid. Here, blue fluid is not shown (b) Spurious velocity shown in the 2D cross-section at the equilibrium condition (after 50,000 time steps). The oil/water interface is shown in black.

Our LB model based on the color-gradient model [44] showed spurious velocities with a maximum magnitude of the order of \(C_\alpha = 10^{-5}\) for the case of identical viscosity. Table 3.3 summarizes the maximum spurious velocity obtained with various types of multiphase lattice Boltzmann model reported in the literature. In the last column, the spurious current is normalized in terms of the capillary number (|\(\tilde{U}\)| = \(\mu|U|/\sigma\)). Our numerical model produced low unphysical spurious velocity which is comparable to that of the free-energy based model.
Table 3.3. Comparison of maximum spurious velocity reported in the literature. In the last row, the maximum spurious velocity $|\bar{U}|$ is normalized by $|\bar{U}| = \mu|U|/\sigma$.

<table>
<thead>
<tr>
<th>Multiphase LBM model</th>
<th>Reference</th>
<th>Interfacial tension</th>
<th>Maximum spurious velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>lattice value</td>
</tr>
<tr>
<td>Color gradient</td>
<td>This work*</td>
<td>1.00×10^{-1}</td>
<td>2.88×10^{-5}</td>
</tr>
<tr>
<td>Color gradient</td>
<td>Liu et al. [77]*</td>
<td>9.60×10^{-2}</td>
<td>1.90×10^{-3}</td>
</tr>
<tr>
<td>Inter-particle potential</td>
<td>Otomo et al. [93]†</td>
<td>1.00×10^{-1}</td>
<td>2.76×10^{-3}</td>
</tr>
<tr>
<td>Free-energy</td>
<td>Shao et al. [116]‡</td>
<td>1.00×10^{-3}</td>
<td>2.43×10^{-7}</td>
</tr>
</tbody>
</table>

* 3D droplet with $R = 16$ placed in a 65×65×65 domain.
† 3D droplet with $R = 24$ placed in a 120×120×120 domain.
‡ 2D droplet with $R = 40$ placed in a 220×220 domain with interface width of 5 lattice nodes.

3.1.3. Static contact angle on a flat solid surface

The new wetting boundary condition (described in section 2.2.1) is validated using the test case of a static contact angle on a flat surface in 2D. Here, the results are shown with a comparison to the fictitious-density boundary condition which is commonly used in the color gradient LB method. The wetting boundary condition is also validated using a test case of a static contact angle on a flat surface in 3D.

Static contact angle on a flat surface in 2D

The simulations were performed in a 2D domain with a domain containing 101×301 lattice nodes. Solid walls were placed on both upper and lower boundaries and periodic boundary conditions were applied for both left and right boundaries. As shown in Fig. 3.3, blue fluid was initially placed in the center of the domain, while red fluid was placed in the rest of the domain. The prescribed contact angle varied from 30° to 150° for both the fictitious-density boundary condition and our boundary condition. The other parameters were fixed as $\sigma = 0.1$, $\rho = \rho_r = \rho_b = 1.0$, $\beta = 0.7$ and $\tau_r = \tau_b = 1.0$. The simulations were conducted for 200,000 time steps to achieve an equilibrium state (Fig. 3.3). Then the simulated contact angle was evaluated using the following geometrical relation:

$$\theta = \frac{\pi}{2} - 2 \arctan \frac{H}{R},$$

where $\theta$ is the contact angle, $R$ is the half width of the capillary slit and $H$ is the height of the non-wetting fluid measured from the contact line (point in 2D) as shown in Fig. 3.3.
The simulated contact angle and capillary pressure were compared with those analytical values for both wetting boundary conditions shown in Fig. 3.4. To quantify the error between an analytical value, $X_0$, and a simulated value, $X_{sim}$, the relative error, $E(X)$, is defined by

$$E(X) = \frac{|X_{sim} - X_0|}{X_0}. \quad (3.3)$$

Our method showed an excellent agreement between the prescribed and simulated contact angle for the entire range of values with a maximum relative error of $E(\theta) = 1.5\%$ for $\theta = 30^\circ$, whereas the fictitious-density boundary condition showed a discrepancy especially for contact angles close to $0^\circ$ and $180^\circ$ with a maximum relative error of $E(\theta) = 34.1\%$ for $\theta = 30^\circ$. The average pressure for each phase was calculated and then the capillary pressure was obtained from the difference. Because of the inaccuracy in the simulated contact angle, the results obtained using the fictitious-density boundary condition showed a discrepancy from the analytically evaluated capillary pressure with the maximum relative error of $E(P_c) = 47.5\%$ for $\theta = 120^\circ$, whereas our method showed an excellent agreement with a maximum relative error of $E(P_c) = 1.1\%$ for $\theta = 30^\circ$. 

Figure 3.3. 2D static contact angle test of a $30^\circ$ prescribed contact angle with our boundary condition is shown as an example. (a) Initial condition (red and blue show fluid phases while the wall is black.) (b) Equilibrium state after 200,000 time steps. (c) Estimation of the simulated contact angle based on Eq. (3.2).
Figure 3.4. Comparison between our wetting boundary condition and the fictitious-density boundary condition. (a) Simulated contact angle against prescribed contact angle. (b) Simulated capillary pressure against analytically obtained capillary pressure. Here, the dashed lines show a unit slope indicating a perfect agreement.

Fig. 3.5 shows an enlarged view of the color function around the three-phase contact line (point in 2D) for a prescribed contact angle of 30°. For the fictitious-density boundary condition, the interface moved along the wall boundary. This unphysical mass transfer of wetting phase made the simulated contact angle inaccurate.

Figure 3.5. Comparison of two wetting boundary conditions for a 30° prescribed contact angle between (a) our proposed boundary condition, and (b) the fictitious-density boundary condition where unphysical mass transfer along the top and bottom walls is observed.

Fig. 3.6 shows the fluid velocity distribution around the three-phase contact line with a prescribed contact angle of 60°. In these figures, the fluid/fluid interface is indicated by the yellow line and velocity vectors are color coded based on their magnitude (vectors whose magnitude is below $10^{-5}$ ln/ts (lattice units per time step) are shown in black, while vectors above $10^{-3}$...
lu/ts are shown in white). In both cases, an unphysical, spurious, current persisted around the three-phase contact line. With the new wetting boundary condition, the spurious current around the three-phase contact line was on the order of $10^{-5}$ to $10^{-3}$ lu/ts and the velocity further away was less than $10^{-5}$ lu/ts. In contrast, with the fictitious-density boundary condition, the magnitude of spurious velocity around the three-phase contact line was greater than $10^{-3}$ lu/ts.

Figure 3.6. Comparison of the spurious current for the case of $\theta = 60^\circ$ (a) with our wetting boundary condition, and (b) with the fictitious-density wetting boundary condition. The fluid interface is shown by the yellow line and velocity vectors are color coded based on their magnitude (black and white show vectors below $10^{-5}$ lu/ts and above $10^{-3}$ lu/ts, respectively.)

Table 3.4 summarizes the comparison of the static contact angle estimation, capillary pressure estimation and the magnitude of the maximum spurious current for both boundary conditions. It can be concluded that our method gives a more accurate estimation for both contact angle and capillary pressure with lower spurious velocity compared to the fictitious-density boundary condition. These features are particularly important when we consider slow flow in porous media where capillary forces are significant – cases presented in the remainder of this thesis.
Table 3.4. Summary of the 2D static contact angle test. In the last row, the maximum spurious velocity $|\hat{U}|$ is normalized by $|\hat{U}| = \mu|U|/\sigma$.

<table>
<thead>
<tr>
<th>Wetting B.C.</th>
<th>Contact angle</th>
<th>Capillary pressure</th>
<th>Maximum spurious velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>prescribed</td>
<td>simulated</td>
<td>analytical</td>
</tr>
<tr>
<td></td>
<td>[deg]</td>
<td>[deg]</td>
<td>[-]</td>
</tr>
<tr>
<td>Fictitious-density B.C.</td>
<td>30.00</td>
<td>19.78</td>
<td>$1.75 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>60.00</td>
<td>40.71</td>
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<td>90.00</td>
<td>90.00</td>
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</tr>
<tr>
<td></td>
<td>120.00</td>
<td>139.30</td>
<td>$-1.01 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>150.00</td>
<td>163.49</td>
<td>$-1.75 \times 10^{-3}$</td>
</tr>
<tr>
<td>This study</td>
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<td>30.44</td>
<td>$1.75 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>60.00</td>
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<td>$1.01 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>90.00</td>
<td>90.00</td>
<td>$0.00 \times 10^{0}$</td>
</tr>
<tr>
<td></td>
<td>120.00</td>
<td>119.58</td>
<td>$-1.01 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>150.00</td>
<td>149.56</td>
<td>$-1.75 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

**Static contact angle on a flat surface in 3D**

A 3D static droplet placed on a flat solid surface was simulated. The simulation domain was composed of $101 \times 101 \times 101$ lattice nodes. Solid walls were placed on the upper and lower boundaries. Periodic boundary conditions are applied for all other boundaries. Initially, a semi-spherical shape with a radius of 20 lattice units of the red phase was placed on the lower wall. The prescribed contact angle varied from $30^\circ$ to $150^\circ$. Simulations were conducted until they reached equilibrium conditions (500,000 time steps).

The shapes of the droplet at equilibrium for simulations for different prescribed contact angles are shown in Fig. 3.7. Based on the shape of the droplet, the simulated contact angle was obtained and compared with the prescribed contact angle (Fig. 3.8). As shown in the figure, an excellent agreement with the maximum relative error of $E(\theta) = 2.3\%$ for $\theta = 60^\circ$ was also observed for this 3D test case.
Figure 3.7. 3D static contact angle test. The blue phase is not shown in these figures. (a) Initial condition and equilibrium conditions for (b) $\theta = 30^\circ$ (c) $\theta = 60^\circ$ (d) $\theta = 90^\circ$ (e) $\theta = 120^\circ$ (f) $\theta = 150^\circ$.

Figure 3.8. Comparison of the prescribed contact angle and simulated contact angle for the 3D droplet test case.

3.1.4. Static contact angle on a curved solid surface

The wetting boundary condition was validated for a droplet placed on a curved solid surface. The simulated shape of the droplet was compared to its analytical shape. The shape of a red
droplet with a radius of curvature $R_1$ placed on a spherical solid object with radius $R_2$ can be obtained analytically, as shown in Fig. 3.9.

The simulation domain was composed of $101 \times 101 \times 101$ lattice nodes. A spherical solid object occupied the following region:

$$(x - 50)^2 + (y - 50)^2 + (z - 30)^2 \leq R_2^2,$$

where $R_2$ is the radius of spherical solid object that was fixed at 40 lattice units. The simulations were conducted for contact angles $\theta = 60^\circ$ and $\theta = 120^\circ$. Initially, a known volume of red fluid was placed around the solid object occupying part of a sphere so that the radius of curvature of the red fluid $R_1$ in equilibrium is 22.5 lattice units. The rest of the domain is filled with blue fluid. Analytical solutions were obtained by calculating $R_3$ from the known values of $\theta$, $R_1$, and $R_2$. The simulations were continued until they reached an equilibrium state (30,000 time steps). Fig. 3.10 shows the results of the simulations, in which the analytical solution is shown by the black dotted lines. The equilibrium droplet shape agreed with the analytical solution for both $\theta = 60^\circ$ and $\theta = 120^\circ$.

![Figure 3.9. Schematic image of the shape of a red fluid droplet placed on a spherical solid object (green). $R_1$ and $R_2$ are the radius of curvature of the red droplet and the radius of the solid object, respectively. The distance between the center of the red droplet and the solid object, $R_3$, is determined so as to satisfy $\theta = \alpha + \beta$, where $\theta$ is the contact angle. $n_p$ is the unit normal vector to the fluids interface and $n_s$ is the unit normal vector of the wall.](image_url)

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Figure 3.10. Validation of the wetting boundary condition for a 3D curved geometry. In the upper row, a 3D view of the red fluid and the solid (green) are shown while blue fluid is not shown. In the lower row, a $xz$ cross-section at $y = 50$ is presented. (a) and (d) show the initial condition, while (b), (c), (e) and (f) show equilibrium conditions. The black dotted lines in (b), (c), (e) and (f) show analytical solutions corresponding to $\theta = 60^\circ$ and $\theta = 120^\circ$, respectively.

3.1.5. Capillary pressure in a triangular pore space

Capillary pressure, $P_c$, in a corner of a triangular pore was studied. This test case was performed with physical units to investigate the accuracy of simulated $P_c$ as a function of grid resolutions. A 2D pore structure with an isosceles triangle shape as shown in Fig. 3.11 was used. Here, the length of $L_x$ and $L_y$ were set to 70 $\mu$m. $R$ is the radius of curvature of the interface; $\theta$ is the contact angle; $\beta$ is the half angle of the corner of the triangle, which is given by: $\tan \beta = L_x/2L_y$. This pore structure was modeled with four grid sizes of $\Delta = 1.0$, 2.0, 3.5 and 5.0 $\mu$m.

The identical density and viscosity of the water and oil phases were set to 1,000 kg/m$^3$ and 1 mPa·s, respectively. The interfacial tension and contact angle were set to 18 mN/m and 45$^\circ$, respectively. Initially, the lower part of the pore structure was filled with oil to a specified oil saturation, while the other part at the top corner was filled with water. Then, simulations were performed for 50,000 time steps until they reached equilibrium. In this pore geometry, the radius of curvature, $R$, can be analytically derived based on the geometrical relationship, which is given by:

$$ R^2 = \frac{S_wL_x^2}{4\tan \beta} \left[ \frac{\cos^2 \alpha \cos \beta}{\sin \beta} + \sin \alpha \cos \alpha - \left( \frac{\pi}{2} - \alpha \right) \right]^{-1}, \quad (3.5) $$

$$ \alpha = \theta + \beta \quad (3.6) $$
where $S_w$ is the water saturation and the other parameters are shown in Fig. 3.11. This analytically derived radius of curvature was used to compare with the simulated radius of curvature. Based on the simulated fluid configurations, the exact location of the interface corresponding to $\rho^N = 0$ was extracted as shown in Fig. 3.12. Then, the radius of the curvature of this interface was obtained by fitting a circle to the interface, since in 2D in equilibrium the analytical shape of the interface is a part of a circle.

Table 3.5 shows a comparison between the radius of curvature obtained from the analytical solution and that obtained with a circle fit to the simulated interface for different grid sizes. The relative error in the radius of curvature is less than 3% for these grid resolutions. This suggests that a good agreement in capillary pressure can also be obtained since the capillary pressure is directly linked to the radius of curvature through the Young-Laplace equation: $P_c = 2\sigma/R$.

![Figure 3.11. Schematic of the isosceles triangular pore used for the simulations.](image)

<table>
<thead>
<tr>
<th>grid size</th>
<th>$S_w$</th>
<th>$R$</th>
<th>$R$</th>
<th>%Diff</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu m$</td>
<td>%</td>
<td>$\mu m$</td>
<td>$\mu m$</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
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<td>70.3</td>
<td>70.9</td>
<td>0.91%</td>
</tr>
<tr>
<td>2.0</td>
<td>35.6%</td>
<td>69.9</td>
<td>68.2</td>
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</tr>
<tr>
<td>3.5</td>
<td>36.0%</td>
<td>70.3</td>
<td>68.3</td>
<td>-2.97%</td>
</tr>
<tr>
<td>5.0</td>
<td>32.7%</td>
<td>67.0</td>
<td>65.9</td>
<td>-1.66%</td>
</tr>
</tbody>
</table>

Table 3.5. Comparison between the radius of curvature obtained from the analytical solution and that obtained with a circle fit to the simulated interface for different grid sizes.
3.2. Validation of the two-phase mass transfer lattice Boltzmann model

3.2.1. Diffusive transport

The one-dimensional diffusive mass transfer of solute components in water was considered with the mass transfer in the single phase LB model. The one-dimensional diffusion equation (Fick’s second law) is given by:

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2},$$

where $C$ is the concentration of a component and $D$ is the diffusive coefficient. When a component with its concentration of $C_0$ is initially placed in a domain $x \leq \pm h$ in an infinite domain, an analytical solution of Eq. 3.7 is given by [33]:

$$C = C_i + \frac{C_0}{2} \left[ \text{erf}\left(\frac{h + x}{\sqrt{4Dt}}\right) + \text{erf}\left(\frac{h - x}{\sqrt{4Dt}}\right) \right],$$

where $C_i$ is the initial concentration for $|x| > h$.

A simulation domain composed of $201 \times 3$ lattice nodes was used. The lattice size and time step size was chosen to $\Delta x = 1 \mu m$ and $\Delta t = 1 \times 10^{-7}$ second. Initially, solute components was placed with an initial concentration $C_0 = 1.0$ for $95 \mu m \leq x \leq 105 \mu m$ and $C_i = 0.1$ for the rest of the domain. The density and viscosity of water were set to $\rho_w = 1000 \text{ kg/m}^3$ and $\mu_w = 1.0 \text{ mPa·s}$. Two cases with different diffusion coefficient were simulated: case 1 with $D = 2 \times 10^{-7}$
m\(^2\)/s and case 2 with \(D = 2 \times 10^{-9} \text{ m}^2/\text{s}\). Fig. 3.13 shows the simulated concentration profile as a function of the \(x\)-coordinate after 10 ms for case 1, and after 100 ms for case 2. The analytical solution obtained from Eq. 3.8 is also shown in the figure by the black line. The simulated concentration profiles show a good agreement with the analytical values in both cases.

![Simulated concentration profile](image)

Figure 3.13. Simulated concentration profile as a function of the \(x\)-coordinate. The initial condition and analytical solution are shown in the dotted and solid lines, respectively, while the simulated results are shown by the open circles for case 1 and crosses for case 2.

### 3.2.2. Adective diffusive transport

The one-dimensional advective and diffusive mass transfer of solute components in water was considered with the mass transfer in the single phase LB model. The one-dimensional advection diffusion equation (ADE) is given by:

\[
\frac{dC}{dt} = -u \frac{dC}{dx} + D \frac{d^2C}{dx^2},
\]

(3.9)

where \(u\) is the velocity of the fluid and \(D\) is the diffusion coefficient of a component. When a concentration of \(C_0\) is placed at \(x = 0\) under a constant velocity of the fluid \((u)\), an analytical solution of Eq. 3.9 for the concentration at position \(x\) can be obtained under the following boundary conditions:

\[
C(0, t) = C_0, \quad \frac{dC}{dx}(\infty, t) = 0,
\]

(3.10)

(3.11)
as [60]:

\[ C(x,t) = C_0 \frac{1}{2} \text{erfc} \frac{x - ut}{\sqrt{4Dt}} + C_0 \frac{1}{2} \exp\left(\frac{x}{D}\right) \text{erfc} \frac{x + ut}{\sqrt{4Dt}} \]  

(3.12)

A simulation domain composed of 201 × 3 lattice nodes was used. The lattice size and time step size was chosen to \( \Delta x = 1 \) \( \mu \text{m} \) and \( \Delta t = 1 \times 10^{-7} \) second. First, the single phase flow simulation was performed with imposing a constant velocity boundary condition at \( x = 0 \) \( \mu \text{m} \) and \( x = 200 \) \( \mu \text{m} \) to establish a uniform fluid velocity field. Then, the concentration of the simulation domain was initialized with \( C(x,0) = 0 \). A constant concentration boundary condition was imposed at \( x = 0 \) \( \mu \text{m} \) with \( C(0,t) = C_0 = 1 \), while a zero-gradient concentration boundary condition of \( \partial C/\partial x = 0 \) was imposed at \( x = 200 \) \( \mu \text{m} \). For the other boundaries in the \( y \)-direction, a periodic boundary condition was applied. The simulated concentration at \( x = 25 \) \( \mu \text{m} \) was monitored as a function of time and it was compared with the analytical solution obtained from Eq. 3.12.

The density and viscosity of water were set to \( \rho_w = 1000 \text{ kg/m}^3 \) and \( \mu_w = 1.0 \text{ mPa} \cdot \text{s} \), respectively. The transport of a component governed by Eq. 3.9 is characterized by the non-dimensional number of Péclet number \( \text{(Pe)} \), which is defined by

\[ Pe = \frac{uL}{D} \]  

(3.13)

where \( L \) is the characteristic length and we used \( L = 25 \) \( \mu \text{m} \). To validate the numerical model for a range of Péclet number, four simulations were designed with different diffusion coefficient and flow velocity as shown in Table 3.6.

| Case 1 | 2.0 × 10^{-9} | 5.0 × 10^{-6} | 2.5 × 10^{-3} |
| Case 2 | 2.0 × 10^{-9} | 5.0 × 10^{-4} | 2.5 × 10^{-1} |
| Case 3 | 2.0 × 10^{-8} | 5.0 × 10^{-4} | 2.5 × 10^{-2} |
| Case 4 | 2.0 × 10^{-8} | 5.0 × 10^{-2} | 2.5 × 10^{0} |

Fig. 3.14 shows a comparison between the simulated concentration and analytically obtained concentration from Eq. 3.12. The simulated concentration profiles show a good agreement with the analytical values for a wide range of Péclet number \( (2.5 \times 10^{-3} \leq Pe \leq 2.5) \).
3.2.3. Mass transfer in two-phase flow

The mass transfer of solute components across the interface of two immiscible fluids was studied with the two-phase mass transfer numerical model. In this case, mass transfer of the components was affected by the solubility of the component to each phase. Here, three solubility characteristics were studied: a single soluble component which is only soluble in a single phase (SS), a surface adsorbed (SA) component, and an amphiphilic soluble component (AS) which is soluble in both phases.

A 2D domain containing $100 \times 3$ lattice nodes with a lattice size $\Delta x = 2 \, \mu m$ was considered. The time step was $\Delta t = 2.67 \times 10^{-7}$ second. Water was placed in the center of the domain ($50 \, \mu m \leq x \leq 150 \, \mu m$), while oil was placed in the rest of the domain. The concentration of a component was initially set to $C_i = 1.0$ for the entire domain. A periodic boundary condition for both concentration and fluid flow was applied for all the boundaries.

The identical density and viscosity of oil and water were used as $\rho_o = \rho_w = 1000 \, kg/m^3$ and $\mu_o = \mu_w = 1 \, mPa\cdot s$, respectively. The interfacial tension between the two fluid was 11 mN/m. We used a diffusion coefficient of $D = 5 \times 10^{-9} \, m^2/s$. Although the diffusion coefficient used was slightly higher than that of a typical value for a solute component in water and oil, we had to use this value since a smaller value than this resulted in numerical instability. With this lattice size and time step size, this diffusion coefficient was attained with a non-dimensional diffusion coefficient of $\bar{D} = 3.3 \times 10^{-4}$. When the non-dimensional diffusion coefficient is below $10^{-4}$, oscillations between negative and positive values of concentration have been reported by Drazer and Koplik [38].

Figure 3.14. Comparison the concentration at $x = 25 \, \mu m$ between analytical solutions and simulations for the four cases described in Table 3.6.
Three solubility characteristics were considered with using different functional shapes of $W_s(x_b)$ which controls the separation of a component in each phase. Table 3.7 shows three solubility characteristics and expected concentration profiles near the interface ($C_s(x_b)/C_s^{\text{max}}$). These simulations were performed for $10^7$ time steps (2.7 seconds).

Table 3.7. Summary of the concentration profile near the interface. Here, $x_b$ is defined by Eq. 2.36 and $\lambda_s$ is the segregation parameter of the concentration. Modified after [111].

<table>
<thead>
<tr>
<th>Type</th>
<th>Abbreviation</th>
<th>$W_s(x_b)$</th>
<th>$C_s(x_b)/C_s^{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-phase Soluble</td>
<td>SS</td>
<td>$x_b - 1$</td>
<td>$(x_b)^{\lambda_s}$</td>
</tr>
<tr>
<td>Surface Adsorbed</td>
<td>SA</td>
<td>$x_b - 0.5$</td>
<td>$e^{\lambda_s(x_b-1)}$</td>
</tr>
<tr>
<td>Amphiphilic Soluble</td>
<td>AS</td>
<td>$x_b(x_b-1)$</td>
<td>$[4x_b(1-x_b)]^{\lambda_s/2}$</td>
</tr>
</tbody>
</table>

Fig. 3.15 shows a comparison of the prescribed and simulated concentration for three solubility characteristics. The concentration profile near the interface is properly controlled through the function of $W_s(x_b)$.

Fig. 3.15. Comparison of the prescribed and simulated concentration for (a) single phase (SS), (b) surface adsorbed (SA), and (c) amphiphilic soluble (AS) components (see Table 3.7).

3.2.4. Wettability alteration model

We validate the numerical model for low salinity water flooding which combines the two-phase LB model coupled with mass transport with the wettability alteration model described in section
2.2.2.

A 2D domain with $201 \times 32$ lattice units (l.u.) was used. A solid wall was placed at the top and bottom of the domain. Water was placed in the center of the domain for $67 \leq x \leq 133$ (a width of 67 l.u.), while the rest of the pore space was filled with oil. In the center of the water-filled part for $84 \leq x \leq 116$ (a width of 33 l.u.), low salinity (LS) water was placed at a concentration of $C_s = 67/33$. In the $x$-direction, a periodic boundary condition was applied for both the flow and concentration.

The simulations were performed in a non-dimensional domain with the following fluid parameters: fluid densities of $\rho_r = \rho_b = 1.0$; relaxation time parameters of $\tau_r = \tau_b = 1.0$ which gave dynamic viscosities of $\mu_r = \mu_b = 1/6$; interfacial tension of $\sigma = 0.1$; diffusion coefficient of $D = 2 \times 10^{-3}$. Table 3.8 shows the parameters used for the wettability alteration model. For all the cases, the initial contact angle ($\theta_{init}$) was set to $60^\circ$. There was no change in the contact angle for cases 1 to 3, whereas the contact angle for cases 4 and 5 was altered from its original value of $60^\circ$ to $0^\circ$. These non-dimensional parameters for the fluid properties and wettability alteration were chosen based on the values to be used to represent typical reservoir conditions, which will be discussed in Chapter 5.

Table 3.8. Summary of the input parameters of the wettability alteration model $K_{eq}$ is the equilibrium constant; $k$ is the reaction rate constant; $\theta_{min}$ is the minimum angle after alteration. See section 2.2.2 for their definitions.

<table>
<thead>
<tr>
<th></th>
<th>$K_{eq}$</th>
<th>$k$</th>
<th>$\theta_{min}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>1</td>
<td>$2 \times 10^{-4}$</td>
<td>60</td>
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<tr>
<td>Case 2</td>
<td>100</td>
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<td>60</td>
</tr>
<tr>
<td>Case 3</td>
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<td>60</td>
</tr>
<tr>
<td>Case 4</td>
<td>$\infty$</td>
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<td>0</td>
</tr>
<tr>
<td>Case 5</td>
<td>$\infty$</td>
<td>$1 \times 10^{-3}$</td>
<td>0</td>
</tr>
</tbody>
</table>

First, we discuss cases 1 to 3 where no contact angle change was considered. These cases resulted in the same fluid configuration and concentration field since there was no change in the contact angle—they only had a difference in the amount of adsorption on the solid surface. The simulated fluid configuration and concentration field for case 1 are shown in Fig. 3.16. After $1 \times 10^5$ time steps (t.s.), the fluid configuration already reached its equilibrium to satisfy the assigned contact angle of $60^\circ$, whereas the concentration had not yet reached a uniform distribution. After $30 \times 10^5$ t.s., the concentration showed a uniform distribution without entering the oil. In Fig. 3.17, we show the LS concentration and normalized amount of adsorption at $y = 1$ where adsorption onto the solid surface occurred. In Fig. 3.17a, the simulated $C_s$ showed a good agreement with the values obtained from the simulated $\rho_r$ and $\rho_b$ based on Eq. 2.41. In Fig. 3.17b, the simulated amount of adsorption ($\Theta$) was compared with the values
obtained using the simulated $C_s$ based on Eq. 2.60. All the cases showed a good agreement with the theoretically derived amount of adsorption. When a larger equilibrium constant ($K_{eq}$) was used, a region of adsorption further advanced into the oil-covered solid surface beyond the three-phase contact where the oil/water interface ($\rho^N = 0$) meets the solid surface.

Next, we discuss cases 4 and 5 where a change in contact angle was considered. Fig. 3.18 shows the simulated phase configuration and normalized amount of adsorption for cases 3 to 5 after $30 \times 10^5$ t.s. Cases 4 and 5 resulted in a smaller contact angle than case 3. Fig. 3.19 shows the color function ($\rho^N$) and normalized amount of adsorption at $y = 1$ for these cases. As shown in Fig. 3.19a, the exact location of the interface moved to achieve a smaller contact angle in cases 4 and 5. The movements of the three-phase contact shown in Fig. 3.19b were faster in case 5 compared to case 4, since this case had a higher reaction rate.

We showed the validation of our numerical model which mimics the effect of wettability alteration driven by the development of water films over the solid surface. In the model, the equilibrium constant ($K_{eq}$) controls the sensitivity of the wettability alteration to the LS concentration, while the reaction rate constant ($k$) controls how quickly the alteration occurs.
Figure 3.16. Simulation results of case 1 at \( t = 0, 1 \times 10^5 \) and \( 30 \times 10^5 \) t.s. (a) The phase configuration. Water and oil are shown in blue and red, respectively. (b) The LS concentration distribution.

Figure 3.17. LS concentration \( (C_s) \) and normalized amount of adsorption \( (\bar{\Theta}) \) at \( y = 1 \) as a function of the \( x \)-coordinate. (a) The simulated LS concentration is compared with the values obtained from the simulated \( \rho_r \) and \( \rho_b \) based on Eq. 2.41. (b) The simulated normalized amount of adsorption is compared with the theoretical values obtained from the simulated \( C_s \) based on Eq. 2.60 in the main text. In (a) and (b), the exact location of the oil/water interface \( (\rho^N = 0) \) is indicated by the vertical dotted black lines.
Figure 3.18. Simulation results of case 3 to 5 after $30 \times 10^5$ t.s. (a) The phase configuration. Water and oil are shown in blue and red, respectively. (b) The LS concentration distribution.

Figure 3.19. Advancement of wettability alteration for case 3 to 5 after $30 \times 10^5$ t.s. (a) The simulated phase distribution at $y = 1$ as a function of the $x$-coordinate. (b) The simulated amount of adsorption at $y = 1$ as a function of the $x$-coordinate.

Now that we have validated our models on simple analytical test cases, we will apply them to study several problems in multiphase flow in geological porous media, with an emphasis on understanding wettability and wettability alteration.
4. Applications of the two-phase lattice Boltzmann model
In this chapter, the two-phase lattice Boltzmann method with the improved wetting boundary condition is used.

In section 4.1, dynamic contact angle is studied using capillary rise experiments of Heshmati and Piri [49]. When the contact line between the two fluids and the solid surface moves, we can observe contact angle which depends on the speed of movement of the contact line. This is modeled with our numerical simulations.

In section 4.2, mixed-wet states where contact angle varies locally are studied using experiments of Alhammadi et al. [13] in which reservoir carbonates were used for water flooding for different wettability states. Experimentally measured in situ contact angle [15] is used as input data for the simulations, then we directly compare the simulated fluid configurations with those observed in the experiments. Furthermore, a simulation model matched to the experiments is used to study the impact of enhanced oil recovery methods on the microscopic displacement efficiency of the rock by changing fluid and/or rock properties in the simulations.

4.1. Capillary rise

4.1.1. Introduction

Capillary rise experiments are used to test the applicability of the wetting boundary condition developed in section 2.2.1 to a dynamic problem. Capillary rise is a phenomenon in which a dense wetting fluid imbibes up a capillary tube until equilibrium between the capillary force and the gravitational force is achieved. Washburn [129] first modeled this behavior and proposed an analytical solution, assuming a constant contact angle. However, the contact angle during capillary rise does change. There have been several experiments that have measured the dynamic contact angles as a function of capillary number, for instance [52, 112, 45]. This phenomenon is simulated with assigning an input contact angle as a function of computed capillary number during capillary rise. This work has been published in Akai, Bijeljic and Blunt [7].

4.1.2. Capillary rise experiments

We studied the experiments of Heshmati and Piri [49]. They observed the change of dynamic contact angle during capillary rise with high speed cameras. Three experiments were performed using an air/water system in a glass tube with internal diameters of 0.75 mm, 1.0 mm and 1.3 mm. We define the Bond number as:

$$Bo = \frac{\Delta \rho g r^2}{\sigma},$$

(4.1)

where $\Delta \rho$ is the difference in density, $g$ is the gravitational acceleration, $\sigma$ is the interfacial tension between two fluids, and $r$ is the characteristic length. This length, $r$, is the tube radius.
in 3D or the slit width in 2D. We also define the capillary number as:

\[ Ca = \frac{\mu_w u}{\sigma}, \]  

(4.2)

where \( \mu_w \) is the dynamic viscosity of water and \( u \) is the velocity of the fluid/fluid interface. The fluid properties and Bond numbers corresponding to each diameter of capillary tube are shown in Table 4.1. Fig. 4.1 shows the measured rise as a function of time and the measured dynamic contact angle as a function of capillary number for the three experiments. Sheng and Zhou [118] showed that the relationship between dynamic contact angle and capillary number is approximated well by:

\[ \cos \theta_d = \cos \theta_s - Ca \log \left( \frac{KL}{l_s} \right), \]  

(4.3)

where \( \theta_s \) and \( \theta_d \) are the static and dynamic contact angle respectively, \( Ca \) is the capillary number, \( K \) is a constant, \( L \) is characteristic length and \( l_s \) is the slip length. Through least squares fitting of Eq. 4.3 to the experimental data, \( \theta_s = 5.59^\circ \) and \( \log(KL/l_s) = 39.37 \) were obtained as shown by the black line in Fig. 4.1.

Table 4.1. Summary of the fluid properties and Bond numbers corresponding to each diameter of capillary tube.

<table>
<thead>
<tr>
<th>Tube diameter</th>
<th>0.75 mm</th>
<th>1.0 mm</th>
<th>1.3 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water density*</td>
<td>[kg/m³]</td>
<td>997</td>
<td></td>
</tr>
<tr>
<td>Air density†</td>
<td>[kg/m³]</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>Water viscosity*</td>
<td>[Pa · s]</td>
<td>1.10 × 10⁻³</td>
<td></td>
</tr>
<tr>
<td>Air viscosity†</td>
<td>[Pa · s]</td>
<td>1.85 × 10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>Interfacial tension*</td>
<td>[N/m]</td>
<td>7.28 × 10⁻²</td>
<td></td>
</tr>
<tr>
<td>Viscosity ratio</td>
<td>[−]</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>Bond number</td>
<td>[−]</td>
<td>1.9 × 10⁻²</td>
<td>3.4 × 10⁻²</td>
</tr>
</tbody>
</table>

* Data taken from [49].
† Data taken from [123].
4.1.3. Capillary rise simulations

Simulations were conducted for capillary rise in a 2D slit, as opposed to a circular cylinder, to save computation time and to avoid errors associated with the discretization of the circular cross-section of a 3D tube. Assuming laminar flow of an incompressible Newtonian fluids and constant contact angle, the capillary rise is analytically described by the Lucas-Washburn equation: [45]:

\[ At = -h(t) - h_e \ln \left( 1 - \frac{h(t)}{h_e} \right), \quad h_e = \frac{2 \sigma \cos \theta}{\rho g r}, \quad A = \frac{\rho g r^2}{k \mu}, \quad (4.4) \]

where \( r \) is a characteristic length for the problem and \( k \) is a dimensionless flow conductance (\( k = 8 \) for the 3D capillary tube and \( k = 12 \) for the 2D capillary slit). Using the following non-dimensional quantities,

\[ t^* = \frac{\rho g r}{k \mu} t, \quad h^* = \frac{1}{r} h, \quad Bo^* = \frac{\rho g r^2}{\sigma}, \quad (4.5) \]

Eq. 4.4 can be rewritten as:

\[ \frac{Bo^*}{2 \cos \theta} t^* = -\frac{Bo^*}{2 \cos \theta} h^* - \ln \left( 1 - \frac{Bo^*}{2 \cos \theta} h^* \right). \quad (4.6) \]

Based on these non-dimensional time, \( t^* \), and height, \( h^* \), our simulation results were compared with the experimental results of Heshmati and Piri [49].

A 2D capillary slit with a size of \( 21 \times 3000 \) lattice nodes was used. The viscosities of air and water were chosen to give a viscosity ratio similar to that in the experiments: \( M = \)
\( \mu_{\text{water}}/\mu_{\text{air}} = 50 \). Although we used an identical density for the two fluids, the body force was only applied to water to simulate the three Bond numbers corresponding to the experiments. Initially, the domain was fully filled with air. Water was placed at the bottom with a constant pressure boundary condition \( (p_{\text{inlet}} = p_{\text{water}} = p_0) \), while the outlet boundary at the top was also controlled by a constant pressure boundary condition \( (p_{\text{outlet}} = p_{\text{air}} = p_0) \).

Two contact angle cases were performed: a constant contact angle and a dynamic contact angle case. For the constant contact angle case, an input contact angle of 5.59° was used based on the experimentally obtained static contact angle. For the dynamic contact angle case, at every time step, an input contact angle was obtained from Eq. 4.3 with \( \theta_s = 5.59^\circ \) and \( \log(KL/l_s) = 39.37 \) using the capillary number computed from the velocity of the moving interface.

Since Heshmati and Piri [49] used a high-speed camera with a large field of view to detect the position of the meniscus and time-stamp the images, there was experimental uncertainty in the determination of the start time corresponding to the frame speed of the camera. Considering this, a time shift was applied to the experimental data points so that the first measured time coincided with the simulated time at the first measured height. This resulted in 7 ms of time shift for the experiment with a 0.75 mm capillary tube, 5.7 ms for the 1.0 mm capillary tube and 13 ms for the 1.3 mm capillary tube.

Fig. 4.2 shows the simulation results, experimental results and analytical predictions based on the Lucas-Washburn equation with a constant contact angle \( \theta_s = 5.59^\circ \). In Fig. 4.2a, our simulations with the constant contact angle show a good agreement with the analytical prediction by the Lucas-Washburn equation, but both of them show a faster rise compared to the experimental data, especially in the early time region \( (t^* < 20) \). In Fig. 4.2b, compared to the constant contact angle case, the simulation results were shifted downward and the match to the experiments was improved, albeit with a slight difference in the early time region for the case of \( Bo = 5.7 \times 10^{-3} \).

Fig. 4.3 shows a comparison between the input contact angle and the resultant simulated contact angle during the capillary rise simulations. The latter was geometrically obtained from the shape of the simulated air/water interface and width of the capillary tubes. For both the constant angle and the dynamic angle cases, the simulated contact angles agree with the prescribed values for a wide range of capillary number \( (10^{-6} < C_a < 10^{-2}) \).
Figure 4.2. Capillary rise simulation with (a) constant contact angle and (b) dynamic contact angle. In the figure, black, red and blue represent the case of $Bo = 1.9 \times 10^{-2}$, $Bo = 3.4 \times 10^{-2}$ and $Bo = 5.7 \times 10^{-2}$. The circles show experimental data, the dotted lines show analytical predictions by the Lucas-Washburn equation and lines show the LBM simulation results.

Figure 4.3. Simulated contact angles during the simulations. In the figure, triangles and circles represent the resultant simulated contact angles with the constant and the dynamic contact angle implementation, respectively. Black, red and blue symbols represent the case of $Bo = 1.9 \times 10^{-2}$, $Bo = 3.4 \times 10^{-2}$ and $Bo = 5.7 \times 10^{-2}$, respectively. The prescribed contact angles for the constant and dynamic contact angle implementations are shown by the black and red dotted lines, respectively.
4.1.4. Summary

- We have shown the implementation of a dynamic contact angle which changes the prescribed contact angle at every time step depending on the capillary number (the velocity of the moving interface) using the wetting boundary condition developed.

- A match between the experiments and simulations has been improved by applying experimentally observed dynamic contact angle.

- We have observed a good agreement between the input contact angle and resultant contact angle which was geometrically measured from the shape of the simulated air/water interface and width of the capillary tubes for a wide range of capillary number ($10^{-6} < C_a < 10^{-2}$). This means that the wetting boundary condition precisely controls contact angle for dynamic problems regardless of the fluid velocity. This is important when we alter wettability during simulations, which will be discussed in Chapter 5 for the modeling of low salinity water flooding.

4.2. Water flooding in mixed-wet rocks

4.2.1. Introduction

Water flooding in mixed-wet rocks where contact angle varies locally is studied in this section. Experimentally obtained oil and water configurations with a micro-CT are used to provide a pore-scale comparison between simulations and experiments. Contact angle in the simulations is determined based on experimentally measured in situ contact angle. We demonstrate how to use measured contact angle data to improve the predictability of direct numerical simulation.

Furthermore, a simulation model matched to the water flooding experiments is used to study the impact of the application of several enhanced oil recovery methods on microscopic displacement efficiency through a parametric study with changing input parameters of rock/fluid properties of the matched simulation model. This work has been published in Akai, Alhammadi, Blunt and Bijeljic [6, 4, 5].

4.2.2. Water flooding experiments and measured contact angle

We used the water flooding experiments of Alhammadi et al. [13] in which three carbonate samples drilled from the same core plug and crude oil (a light crude oil from the same reservoir) were used. The sample was mainly composed of calcite (96.5 ± 1.9 weight %). The helium porosity and permeability measured on the plug were 27.0% and $6.8 \times 10^{-13}$ m$^2$ (686 mD), respectively. Through applying three aging protocols, three distinct wettability states were established after primary drainage.

In simulations, we used the experiment on the most oil-wet rock, presented as sample 2 in Alhammadi et al. [13]. This core, of 4.75 mm diameter and 13.1 mm long, was first flooded...
with 20 pore volumes (PVs) of crude oil at 80 °C and 10 MPa. Micro-CT images were acquired at the center of the sample with a resolution of 2 μm/voxel before and after 20 PVs of water flooding. The images were taken 2 hours after the end of water flooding to avoid the movement of fluids during image acquisition. Three-phase segmentation (oil, brine and rock) was performed on an image volume with a size of 976 × 1014 × 601 voxel³. From this data, a cubic sub-volume consisting of 640 × 640 × 500 voxel³ (1.28 × 1.28 × 1.00 mm³) was extracted for our simulations. The original raw micro-CT images and their three-phase segmented images before and after water flooding are shown in Fig. 4.4.

![Image](image_url)

Figure 4.4. Micro-CT images for the water flooding experiment conducted on the aged sample. Here, the volume used for image analysis are shown. (a) Original raw gray-scale micro-CT images before water flooding. (b) Three-phase segmented images before water flooding. (c) Original raw gray-scale micro-CT images after water flooding. (d) Three-phase segmented images after water flooding. In (a) and (c), oil, brine and rock are shown in black, dark gray and light gray, respectively. In (b) and (d), oil, brine and rock are shown in red, blue and white, respectively. The black squares in (c) and (d) indicate the cubic sub-volume used for our simulation study.

To save computational time, the three-phase segmented data of the sub-volume at 2 μm/voxel resolution was upscaled into a coarse grid system with a grid size of 5 μm/voxel, resulting in a domain of 256 × 256 × 200 voxel³ (1.28 × 1.28 × 1.00 mm³). The segmented label data was also used to compare experimentally measured local fluid occupancy after water flooding to the simulated results. After removing isolated void spaces in the sub-volume, the connected void space had a porosity of 17.8%.

Based on the distance map of the pore structure, the void space was partitioned into 360 individual pore regions as shown in Fig. 4.5. The algorithm is similar to that described by other authors, for instance Dong and Blunt [37] and Raeini et al. [106].
In this experiment, \textit{in situ} contact angles were measured using the automated algorithm of AlRatrout et al. [15]. In total, 485,511 \textit{in situ} measured contact angles thorough the water phase were available within the sub-volume (Fig. 4.6). The measured contact angles showed a wide distribution with an average value of 107°, which is smaller than 141° measured on a flat calcite mineral surface using the same crude oil and brine as in the flooding experiment [13].

These angles would represent effective contact angles on a rough surface in equilibrium once flow has stopped rather than dynamic contact angles to be used to simulate a displacement process, i.e., advancing and receding angles. In addition, when a three-phase contact line is pinned at sharp corners, various angles can be formed. Therefore, instead of using locally different angles for each pore, a mean contact angle for each individual pore region, $\theta_p$, was obtained by taking the average of the measured angles (Fig. 4.6). 322 pores out of 360 pores had more than 100 contact angle measurements, while 13 pores had no measured contact angles since — in the experiments — no three-phase contact line was detected within them: after water flooding they were entirely water or oil filled. If $\theta_p$ of a pore was greater than 110°, which means most measured angles in the pore were greater than 90°, the pore was classified as oil-wet (OW). If $\theta_p$ was smaller than 110° and greater than 70°, the pore was classified as neutrally-wet (NW). If $\theta_p$ was smaller than 70°, the pore was classified as water-wet (WW). As a result, the 360 pores were divided into 5 WW pores, 212 NW pores, 130 WW pores, with 13 undefined pores. The contact angles for these undefined pores were assumed to be 107°, which was the average of all the data points. As summarized in Table 4.2, 63% of the pore volume was in NW pores, 36% in OW pores with only a small contribution from WW and undefined regions.
Table 4.2. Summary of the wettability of each pore region. Here, $\theta_p$ is the mean contact angle of each pore region which is obtained by taking an average of the measured angles within it.

<table>
<thead>
<tr>
<th>Pore type</th>
<th>Criteria</th>
<th>No. pores</th>
<th>Pore volume</th>
<th>Mean $\theta_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-wet (WW)</td>
<td>$0^\circ \leq \theta_p &lt; 70^\circ$</td>
<td>5</td>
<td>0.40%</td>
<td>61$^\circ$</td>
</tr>
<tr>
<td>Neutrally-wet (NW)</td>
<td>$70^\circ \leq \theta_p &lt; 110^\circ$</td>
<td>212</td>
<td>63.30%</td>
<td>101$^\circ$</td>
</tr>
<tr>
<td>Oil-wet (OW)</td>
<td>$110^\circ \leq \theta_p \leq 180^\circ$</td>
<td>130</td>
<td>36.21%</td>
<td>114$^\circ$</td>
</tr>
<tr>
<td>Undefined</td>
<td>-</td>
<td>13</td>
<td>0.09%</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>-</td>
<td>360</td>
<td>100.00%</td>
<td>106$^\circ$</td>
</tr>
</tbody>
</table>

* The average value of the 360 mean contact angles for each pore region.

![Figure 4.6](image.png)

Figure 4.6. Measured contact angle. (a) The histogram of all 485,111 data points. (b) The histogram of mean contact angles for each pore. Here, the pores are classified into three types i.e., water-wet (WW), neutrally-wet (NW) and oil-wet (OW).

4.2.3. Comparison between the water flooding experiment and simulations

Simulation conditions

According to the images taken before water flooding, the initial water saturation was estimated at 6% of which only a saturation of 1% was in the connected pore space. In this work we assigned an initial water saturation of 1% in the locations where water was imaged in the experiments after primary drainage. In reality, more water was present in unresolved micro-porosity and it is likely that the water was connected, but through layers that were not resolved in the images. Higher-resolution imaging and simulations are required to assess the impact of this water and micro-porosity on the displacement behavior.

In the simulations, as in the experiments, the main flow direction was vertical, in the $z$-direction. 10 lattice nodes as a buffer zone (0.05 mm) was attached to the inlet and outlet; therefore the model used for the simulations consisted of $256 \times 256 \times 220$ voxel$^3$ at 5 $\mu$m/voxel ($1.28 \times 1.28 \times 1.10$ mm$^3$). Water was injected from the inlet face at $z = 0$ mm with a constant
Table 4.3. Comparison between experimental and simulation conditions.

<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil/water viscosity</td>
<td>5.64</td>
<td>5.00</td>
</tr>
<tr>
<td>Capillary number</td>
<td>$3.0 \times 10^{-7}$</td>
<td>$3.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>Amount of water injected</td>
<td>20 PV</td>
<td>10 PV</td>
</tr>
</tbody>
</table>

velocity, while the outlet face at $z = 1.10$ mm had a constant pressure.

The capillary number is defined as

$$Ca = \frac{\mu_w q_w}{\sigma},$$

where $\mu_w$ is the viscosity of water, $q_w$ is the Darcy velocity of injected water and $\sigma$ is the interfacial tension between oil and water. Table 4.3 shows a comparison between experimental and simulation conditions. Similar to other studies using direct numerical simulations for water flooding [108, 67, 29, 57], our simulations were performed with $Ca$ of order $10^{-5}$, which is two orders of magnitude higher than the experimental value since computational time significantly increases as the capillary number decreases below $10^{-5}$. Chatzis and Morrow [32] reported that an average capillary number below which mobilization of residual oil occurs was $Ca = 3.8 \times 10^{-5}$ based on core flooding experiments on various sandstone cores. For carbonate rocks, Tanino et al. [121] showed the threshold occurred between $Ca = 1 \times 10^{-4}$ and $8 \times 10^{-4}$ based on altered wettability limestone samples. Hence, we assume that the simulations were comparable to the experiment as they are both in a capillary dominated regime. However, another recent experimental work indicated that in mixed-wet conditions dynamic effects can occur even for a capillary number of order $10^{-6}$ [135], hence this assumption has to be further investigated.

Six simulations with different wettability states were conducted by assigning different contact angles to solid/fluid boundary lattice nodes belonging to each pore region. As summarized in Table 4.4, a single value of the contact angle was assigned for all solid/fluid boundary nodes for cases 1 to 3 (constant contact angle cases). Cases 1 and 3 represent a uniformly water-wet and oil-wet rock, respectively. The contact angle of case 2 was $107^\circ$ based on the average of all 485,111 measured values. On the other hand, different contact angles were assigned for solid/fluid boundary nodes belonging to each pore for cases 4 to 6 (non-uniform contact angle cases). In case 4, the average contact angles for each pore were directly assigned. Since the measured contact angles were obtained from the fluid configuration at equilibrium after water flooding, they can be different from the angles to be assigned for a simulation of a dynamic process. Furthermore, it is not evident that a single average value of contact angle, rather than a maximum, for instance, properly represents the critical value necessary to determine accurately the local capillary pressure for displacement. Therefore, two additional cases informed by the measured contact angles were prepared. In case 5, contact angles of $150^\circ$, $100^\circ$ and $30^\circ$ were assigned to OW, NW and WW pores, respectively. This case was designed to represent the correct threshold capillary pressures in a dynamic displacement process which is limited by
the largest local contact angle in OW pores. In case 6, contact angles 150°, 80° and 30° were assigned to OW, NW and WW pores, respectively. Here it was further assumed that the NW pores are effectively weakly water-wet.

**Fluid saturation during water flooding**

All the simulations were run for 10 PVs of water injection. The oil saturation as a function of pore volumes of water injected is shown in Fig. 4.7. As expected, a significant difference in oil recovery was observed. The oil saturation from the experiment was 36% after 20 PVs of water injection. As shown in Fig. 4.7, case 1 (constant contact angle of $\theta = 30^\circ$) showed a rapid decrease in the oil saturation and reached a steady state after 3 PVs, whereas the other cases showed a slow decrease in the oil saturation. Except for case 1, there are pore regions with contact angles greater than $90^\circ$. In these oil-wet regions, oil flowed as a connected oil layer with low conductance in the corners of the pore spaces; therefore production of oil continued long after water breakthrough. As shown in the figure, the average oil saturation of case 5 reached 36% after 8.4 PVs of water injection, then stabilized. This was consistent with the remaining oil saturation observed in the experiment.
After 10 PVs of water flooding, the simulations were continued while stopping water injection as in the experiment. We continued the simulations until the average fluid velocity became 10 times lower than the water velocity used for water flooding. This equilibrium process was conducted to compare the simulation results with the experimental result which was imaged 2 hours after the end of water injection. In fact, there was no appreciable change in the average fluid saturation between the end of 10 PVs of water flooding and the equilibrium process. However, in oil-wet cases (case 2 to 6), we observed intermittent water pathways in the later part of water flooding. This intermittent change in water phase connectivity could affect the water effective permeability. Thus, the equilibrium simulations were continued to completely disconnect these unstable water pathways which did not exist in the experimentally obtained fluid distribution in equilibrium.

Fluid distributions obtained from the simulations in equilibrium following 10 PVs of water flooding were compared to those obtained from the experiment. Fig. 4.8 shows the average oil saturations in each slice perpendicular to the flow direction as a function of distance from the inlet. Cases 5 and 6 give a similar trend to that obtained from the experiment, especially in the region $0.15 \text{ mm} \leq z \leq 0.65 \text{ mm}$. In all six cases, a considerable change in the oil saturation influenced by the boundary conditions can be seen for $z < 0.15 \text{ mm}$ and $z > 0.95 \text{ mm}$. Therefore, the area of $0.15 \text{ mm} \leq z \leq 0.95 \text{ mm}$ was selected as an area of interest (AoI), which accounts for 80% of the entire simulation domain, for further quantitative comparisons between the experiment and simulations.
Figure 4.8. Oil saturation as a function of distance from the inlet after the equilibrium process following 10 PVs of water flooding. Three cases with constant contact angle are shown in (a) while the other three cases with non-uniform contact angles are shown in (b). Here, the influence of the boundary conditions can be seen in the simulation results near the inlet and outlet. Therefore, an area of interest (AoI) was defined as shown by the black squares for further quantitative analyses.

Local fluid occupancy based on the pore size

The local fluid occupancy in the AoI was studied as a function of pore size. For each pore region, the number of oil-filled voxels at the initial conditions and after water flooding were counted and summarized into histograms (Fig. 4.9) by sampling for every 5 µm increment of equivalent pore diameter, which is the diameter of the largest sphere that just can fit in each pore region. Note that these are pore-volume weighted histograms and not pore-number weighted. As shown in the figure, the fluid occupancy of each pore size is well predicted for cases 2, 3 and 5.
Figure 4.9. Histograms of fluid occupancy of the oil phase as a function of equivalent pore diameter. The simulation results from case 1 to case 6 are shown from (a) to (f). Here, the black dashed line with cross marks shows the histogram of the oil saturation at the initial condition, while the black lines with black and red circles show the histograms of the oil saturation after water flooding for the experimental and simulated results, respectively.

Additionally, recovery factors from each pore region were evaluated as shown in Fig. 4.10. The experiment showed greater recovery from the larger pores. This is expected for an oil-wet system, where water preferentially fills the larger pore spaces first, retaining oil in the narrower regions or as thin layers [26]. This overall trend was captured in the simulations, except for case 1, where water-wet conditions were assumed. Here, recovery was greater from the smaller pores, which were preferentially filled with water, while oil was trapped in the larger pores. In case 6 we made the NW pores weakly water-wet. As a consequence, we see that the smaller pores see a higher recovery — they are preferentially filled with water. This is clearly inconsistent with the experimental trend: case 5 where the NW pores had a contact angle above 90° provides a better match to the experiment.
To quantitatively compare match between the experiment and simulations, the pore volume-weighted difference in recovery factor for each pore was evaluated as shown in Table 4.5. It is defined as:

$$\Delta RF = \sum_{n=1}^{N_b} \phi_n \times |RF_n^{sim} - RF_n^{exp}|,$$

(4.8)

where $N_b$ is the number of bins for the pore radius, $\phi_n$ is the total pore volume of the pore regions belonging to the $n^{th}$ bin and $RF_n^{sim}$ and $RF_n^{exp}$ are the $RF$ of the $n^{th}$ bin obtained from the simulation and experimental results, respectively. As shown in Table 4.5, cases 2 and 5 show the smallest error in recovery factors for each pore region. This means that the right amount of fluid was properly placed in the correct pore sizes in these cases.

Figure 4.10. Recovery factors from each pore as a function of equivalent pore diameter. The simulation results from case 1 to case 6 are shown from (a) to (f). Here, black and red circles show the experimental and simulated results, respectively.
Local fluid occupancy based on the sub-pore scale

We compared the local fluid occupancy between the experiment and simulations on a voxel-by-voxel basis using the following error index:

\[
E_{\text{local}} = \frac{1}{N_p} \sum_{(i,j,k) \in \text{pore}} |l_{i,j,k}^{\text{sim}} - l_{i,j,k}^{\text{exp}}|,
\]

(4.9)

where \(N_p\) is the number of pore voxels within the AoI (1,849,485 voxels) and \(l_{i,j,k}^{\text{sim}}\) and \(l_{i,j,k}^{\text{exp}}\) are the labels defined at fluid voxels that take 1 if the voxel is filled with oil and 0 if the voxel is filled with water, evaluated based on the simulated and experimentally obtained fluid distributions, respectively. The error index \(E_{\text{local}}\) goes to 0 if the experimental and simulated results are perfectly matched, while it becomes 1 if the results are completely different. Table 4.5 summarizes the resultant error index. As expected, case 1 where water-wet conditions are assumed had the worst error index. The other cases showed 30 to 40\% of error in the local fluid occupancy. Fig. 4.11 visually compares the fluid distribution in the slice at \(z=0.45\) mm (the slice perpendicular to the flow direction) between the experiment and simulation for case 2 and 5 in which the best agreement was obtained for the recovery factors for each pore. As shown in Fig. 4.11, most pores are properly filled. However there was still disagreement with the experimental distribution, resulting in 31\% and 35\% of error in the local fluid occupancy, respectively.

Bultreys et al. [31] showed the variation in local fluid occupancy in experiments using five repeated CO\(_2\) drainage-imbibition experiments on a single Bentheimer sandstone sample conducted by Andrew et al. [17]. They observed that some pores are filled with a different fluid in the repeated experiments, although averaged statistical properties, such as the residual saturation, size distribution of trapped clusters and the occupancy as a function of pore size, as shown in Figs. 4.9 and 4.10, remained the same. The discrepancy was largest for pores of intermediate size. We therefore consider the observed error inevitable because of the unavoidable sensitivity of displacement to perturbations in the boundary and initial conditions. Considering this experimental uncertainty, we suggest that pore occupancy as a function of pore size is a more appropriate measure for a comparison between the experiment and simulation, as observed in Figs. 4.9 and 4.10.
Fluid conductance

The 3D distributions of the water phase after the equilibrium process following water flooding are shown in Fig. 4.12. It can be seen that the water phase distribution obtained from case 5 is similar to that obtained from the experiment. The 3D phase distribution and its connectivity controls the conductance of the phase (i.e., the relative permeability). Therefore, the 3D water phase distribution after water flooding was evaluated in terms of fluid conductance. Since a relative permeability measurement was not available in the experiment, its water effective permeability after water flooding was estimated by conducting single-phase LB simulations on the water phase obtained from the micro-CT images. For consistent comparison, single-phase LB simulations were also performed on the water-phase obtained from the two-phase LB
Figure 4.12. Comparison of 3D water phase distributions after water flooding. The experimental result is shown in (a) and the simulation results from cases 1 to 6 are shown from (b) to (g). Here, only the water phase is shown.

The comparison of water effective permeability after water flooding is summarized in Table 4.5. Case 5 showed the best agreement with the computed water effective permeability of the experiment with only 0.7% difference. Note that if a constant contact angle of $\theta = 107^\circ$ (case 2) is used, which also had the best agreement in recovery factors for each pore and is a reasonable assumption when measured contact angles are not available, the water effective permeability was overestimated by 54% although the predicted water saturation was lower than that of the experiment. As discussed in the previous sections, in case 5, even though the voxel-by-voxel prediction of occupancy has an error of 35%, a proper placement of fluid in correct pore sizes as shown in Figs. 4.9 and 4.10 and a proper representation of fluid connectivity results in an accurate prediction of the water effective permeability.
Table 4.5. Summary of the quantitative comparison between the simulations and experiment. ∆RF and $E_{local}$ are the difference in recovery factors from each pore defined by Eq. 4.8 and the difference in local fluid occupancy on a voxel-by-voxel basis defined by Eq. 4.9. Both the water saturation, $S_w$, and the water effective permeability, $k_w$, are evaluated for the AoI.

<table>
<thead>
<tr>
<th></th>
<th>∆RF [%]</th>
<th>$E_{local}$ [%]</th>
<th>$S_w$ [%]</th>
<th>Diff. [%]</th>
<th>$k_w$ [mD]</th>
<th>Diff. [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>-</td>
<td>-</td>
<td>65%</td>
<td>-</td>
<td>537</td>
<td></td>
</tr>
<tr>
<td>Case 1</td>
<td>22%</td>
<td>52%</td>
<td>75%</td>
<td>15.3%</td>
<td>717</td>
<td>33.5%</td>
</tr>
<tr>
<td>Case 2</td>
<td>6%</td>
<td>31%</td>
<td>61%</td>
<td>-6.0%</td>
<td>829</td>
<td>54.4%</td>
</tr>
<tr>
<td>Case 3</td>
<td>9%</td>
<td>37%</td>
<td>62%</td>
<td>-4.7%</td>
<td>484</td>
<td>-9.8%</td>
</tr>
<tr>
<td>Case 4</td>
<td>9%</td>
<td>37%</td>
<td>57%</td>
<td>-11.8%</td>
<td>686</td>
<td>27.7%</td>
</tr>
<tr>
<td>Case 5</td>
<td>6%</td>
<td>35%</td>
<td>64%</td>
<td>-0.3%</td>
<td>533</td>
<td>-0.7%</td>
</tr>
<tr>
<td>Case 6</td>
<td>10%</td>
<td>40%</td>
<td>64%</td>
<td>-1.5%</td>
<td>496</td>
<td>-7.6%</td>
</tr>
</tbody>
</table>

* The relative error against experimental values.

Comparison between the matched simulation and experiment

The best matched simulation of case 5 was further compared with the experiment. Fig. 4.13 shows spatial distributions of the computed fluid velocity. Here, the computed absolute velocity ($U_{abs}$) of each grid block is normalized by the average velocity ($U_{avg}$). Figs. 4.13c and g show histograms of $U_{abs}/U_{avg}$ sampled uniformly in 200 bins of log($U_{abs}/U_{avg}$). For the computed velocity distributions of the water phase, the simulation gives a good agreement in both the spatial distribution of the water pathways and the histogram of the fluid velocity. For the computed velocity of the oil phase, although an exact match for the oil flow pathways was not obtained, it can be seen that in both the experiment and the simulation oil flow is confined to thin layers, as expected after a long period of water flooding in a mixed-wet or oil-wet medium.
Figure 4.13. Comparison of 3D fluid velocity distributions after water flooding. (a) and (b) show the spatial distributions of water velocity obtained from the water phase distribution from the experiment and simulation, respectively. (d) and (e) show the spatial distributions of oil velocity obtained from the oil phase distribution of the experiment and simulation, respectively. (c) and (g) show histograms of the normalized voxel velocity $U_{\text{abs}}/U_{\text{avg}}$ sampled uniformly in 200 bins of $\log (U_{\text{abs}}/U_{\text{avg}})$.

Fig. 4.14 shows the distribution of sizes of remaining oil ganglia. Each individual remaining oil ganglion cluster was labeled and the number of clusters were plotted as a function of their volume. In both the simulation and experiment, a single large cluster was observed, whose volume was of the order of $10^8 \mu m^3$. Although the simulation underestimated the number of clusters for cluster sizes smaller than $10^4 \mu m^3$, the volumetric contribution of these clusters is small. We consider this discrepancy is mainly caused by the insufficient resolution of the grid size used in our simulations since a few voxels are required to form the stable shape of a disconnected droplet.
Figure 4.14. Comparison of 3D fluid distributions. (a) and (c) show the experimentally obtained water and oil distribution after water flooding. (b) and (d) show the simulated water and oil distribution after water flooding. (e) The number of residual oil ganglion clusters are shown as a function of their size. The dotted line in the figure indicates the smallest resolvable ganglion size in our study (5 × 5 × 5 µm³).

To understand the thin oil layers observed in both the experiment and simulation, fluid occupancy was studied as a function of distance from the pore walls. The distance from each pore voxel to the nearest pore wall voxel was calculated for all pore voxels, Fig 4.15. Using this distance map, the number of oil and water filled voxels after water flooding were counted and sampled for every 5 µm increment. The number of oil filled voxels was also normalized by the total number of voxels belonging to each distance increment.

As shown in Fig 4.15b, a good agreement between the experiment and simulation can be seen for the water phase, while the simulation tends to place more oil away from pore walls compared to the experiment. This means that in the experiment, the oil was more confined to thinner layers close to pore walls compared to the simulation. Nevertheless, the trends observed for the experiment and simulation are similar — 40% to 50% of fluid voxels immediately adjacent to the solid are occupied with oil. In addition, we observe that the number of oil-filled voxels decreases as the distance from pore walls increases and for voxels whose distance from pore walls are longer than 30 µm, which is a center of a relatively large pore, most voxels (> 90%) are occupied with water.

In both the experiment and the simulation, these thin oil layers confined to pore walls maintained good connectivity and contributed to the formation of large spanning oil clusters as shown in Fig. 4.14e, resulting in small, but finite oil relative permeability after a long period.
of water flooding.

![Image](image.png)

Figure 4.15. Fluid occupancy as a function of distance from pore walls. (a) Distance map in the slice at $z = 0.45$ mm. (b) Number of oil and water filled voxels as a function of distance from pore walls. (c) Oil filled voxels normalized by the total number of voxels as a function of distance.

### 4.2.4. Simulations for enhanced oil recovery cases

#### Case descriptions

The best matched simulation was used to study the impact of enhanced oil recovery (EOR) methods on the microscopic displacement efficiency of this rock through a parametric study changing fluid and/or rock properties of the simulation. This illustrates the use of a simulation model, namely to predict the behavior outside the range studied experimentally. Three EOR methods were considered: low salinity water flooding (LSWF), surfactant flooding (SF), and polymer flooding (PF).

We note that the simulations discussed in this section were performed in secondary mode by injecting EOR fluids into an initial oil condition. Furthermore, we do not consider the mixing of injected EOR fluids with existing water in the pore space at the initial oil condition. Although the impact of the three EOR processes obtained with tertiary mode flooding could be smaller compared to those obtained for secondary flooding, the results presented in this study help interpret such cases. Enhanced oil recovery in tertiary mode injection with considering the mixing between injected fluid and existing pore water will be discussed in section 5 for low salinity water flooding.

LSWF is an EOR method in which brine with lower salinity than that of formation brine is injected into a formation. Although the underlying mechanisms of additional oil recovery are poorly understood, the change of wettability toward more water-wet states by injection of low salinity water seems to be the most accepted cause of the additional recovery as discussed
in Chapter 1 [86, 117, 83, 23]. This mechanism is further described in Chapter 5. Two cases (LSWF1 and LSWF2) were designed by changing the contact angles of the rock surfaces. In LSWF1, the contact angles of neutrally-wet pores, accounting for 63.4% of pore volume, were changed from 100° to 80°, while in LSWF2, the contact angle of both oil-wet and neutrally-wet pores were changed to 80° (See Table 4.6).

SF is a chemical EOR process in which a surface-active agent (surfactant) is injected to decrease the interfacial tension between oil and water. The impact of interfacial tension on the trapping of oil is best described as a competition between viscous and capillary forces and understood thorough a capillary desaturation curve (CDC) [63]. Considering a typical CDC in which a sudden drop in residual phase saturation is seen at a critical capillary number of around $10^{-4}$, the interfacial tension has to be reduced from typical values of 20 to 30 mN/m to ultralow values in the range of 0.001 to 0.01 mN/m [51]. This corresponds to an increase in the capillary number from a typical field value of $C_a = 10^{-7}$ to $10^{-4} \sim 10^{-3}$. In our simulations, two surfactant flooding cases (SF1 and SF2) were designed by reducing the oil-water interfacial tension by a factor of 10 and 100 to achieve $C_a = 3.3 \times 10^{-4}$ and $C_a = 3.3 \times 10^{-3}$, respectively (See Table 4.6).

Polymer Flooding (PF) consists of adding polymer to the injected water to decrease its mobility. Generally, polymer flooding works well when a reservoir has an unfavorable mobility ratio and high heterogeneity. In this situation, viscous fingering of injected water occurs both at the field-scale and at the pore-scale [63]. A polymer flooding (PF1) case was designed by increasing the viscosity of the injection water to that of oil, to make the viscosity ratio $M = 1$. According to Eq. 4.7, increasing the viscosity of water while keeping the same injection velocity results in an increase in the capillary number. However, in a practical application of polymer flooding, the injectivity of water decreases because of the increase in viscosity. Therefore, an additional case was considered by reducing the oil viscosity, to make the viscosity ratio $M = 1$: this case retains the same capillary number as in the base case. This case will be called PF2 (See Table 4.6).
Table 4.6. Summary of the simulation cases for the application of enhanced oil recovery.

<table>
<thead>
<tr>
<th>Case Name</th>
<th>Description</th>
<th>( Ca \times 10^{-5} )</th>
<th>( M )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>The model was calibrated to the water flooding</td>
<td>( 3.3 \times 10^{-5} )</td>
<td>5.00</td>
</tr>
<tr>
<td>LSWF1</td>
<td>Contact angles of NW pores were changed to 80°.</td>
<td>( 3.3 \times 10^{-5} )</td>
<td>5.00</td>
</tr>
<tr>
<td>LSWF2</td>
<td>Contact angles of NW and OW pores were changed to 80°.</td>
<td>( 3.3 \times 10^{-5} )</td>
<td>5.00</td>
</tr>
<tr>
<td>SF1</td>
<td>Interfacial tension between oil and water was reduced by a factor of 10.</td>
<td>( 3.3 \times 10^{-4} )</td>
<td>5.00</td>
</tr>
<tr>
<td>SF2</td>
<td>Interfacial tension between oil and water was reduced by a factor of 100.</td>
<td>( 3.3 \times 10^{-3} )</td>
<td>5.00</td>
</tr>
<tr>
<td>PF1</td>
<td>Viscosity of water was increased to that of oil.</td>
<td>( 1.7 \times 10^{-4} )</td>
<td>1.00</td>
</tr>
<tr>
<td>PF2</td>
<td>Viscosity of oil was decreased to that of water.</td>
<td>( 3.3 \times 10^{-5} )</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Simulation results for the enhanced oil recovery cases

All the cases were performed in a secondary mode — that is, injection into the initial oil saturation — until 5 PVs of water injection. The evolution of recovery factor as a function of pore volumes of water injected is shown in Fig. 4.16. A summary of the recovery factors at 2 and 5 PVs of water injection is summarized in Table 4.7.

Figure 4.16. Comparison of the recovery factors for EOR cases as a function of pore volumes of water injected. (a) Low salinity water flooding cases (b) Surfactant flooding cases (c) Polymer flooding cases. For a description of each case, see Table 4.6.
Table 4.7. Summary of the recovery factor for each case.

<table>
<thead>
<tr>
<th>Recovery factor</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at 2 PVs</td>
<td>at 5 PVs</td>
</tr>
<tr>
<td>Base</td>
<td>50%</td>
<td>61%</td>
</tr>
<tr>
<td>LSWF1</td>
<td>52%</td>
<td>63%</td>
</tr>
<tr>
<td>LSWF2</td>
<td>64%</td>
<td>69%</td>
</tr>
<tr>
<td>SF1</td>
<td>59%</td>
<td>73%</td>
</tr>
<tr>
<td>SF2</td>
<td>62%</td>
<td>77%</td>
</tr>
<tr>
<td>PF1</td>
<td>68%</td>
<td>76%</td>
</tr>
<tr>
<td>PF2</td>
<td>50%</td>
<td>61%</td>
</tr>
</tbody>
</table>

For the LSWF cases, slightly modifying the wettability of NW pores from a weakly oil-wet to a weakly water-wet state (LSWF1) resulted in a modest increase of recovery factor by 2% after 5 PVs of water injection. Further modifying the wettability of OW pores to a weakly water-wet state (LSWF2) resulted in an increase of recovery factor by 8%. As we can see from Fig. 4.16, the rate of oil recovery in LSWF2 was much faster than in the base case. Fig. 4.17 shows the location of remaining oil as a function of the pore size and the distance from pore walls. In LSWF1, a slight decrease in remaining oil for pore diameters smaller than 40 µm can be seen, while, in LSWF2, a clear decrease in remaining oil can be observed for small to medium sized pores with an increase in remaining oil saturation for large pores. Fig. 4.17b and c show that the amount of filling close to the solid (in layers) decreases and the amount of oil away from pore walls increases as the solid becomes more water-wet. More favorable displacement of oil from the centers of pore spaces without leaving oil layers behind in the low salinity flooding cases leads to better oil recovery, consistent with a water-wet medium.
Figure 4.17. Comparison of the location of remaining oil for low salinity water flooding cases as a function of pore size (a) and as a function of distance from pore walls (b) and (c). For a description of each case, see Table 4.6.

Surfactant flooding showed a significant increase in recovery factor by 12% for SF1 and 16% for SF2. Increasing the capillary number to $10^{-4} \sim 10^{-3}$ removed trapped oil by viscous forces. Fig. 4.18 shows the location of remaining oil. Most pore sizes show lower remaining oil compared to the base case. As shown in Fig. 4.18b and c, the remaining oil for SF still mostly exists in voxels close to pore walls as confined oil layers. Fig. 4.19 shows the number of remaining oil ganglion clusters as a function of their size. The largest oil cluster with a size greater than $10^8 \, \mu m^3$ observed in the base case is not seen in both SF1 and SF2, while these cases show more small clusters. This indicates that as the capillary number increases, the size of remaining oil ganglia becomes smaller. This trend is consistent with experimental results of Pak et al. [94]. They observed break-up of oil ganglia as the capillary number increased in their water flooding experiments conducted on a water-wet carbonate. However, the appearance of remaining oil ganglia in our results was different: they observed approximately spherical fragmented oil droplets for their water-wet experiments, while we observed thin oil layers for mixed-wet state simulations as indicated by the higher oil occupancy close to the pore walls for SF1 and SF2 (Fig. 4.18c).
PF1 showed a significant increase in the recovery factor by 15%. However, PF2 did not show an increase in oil recovery. The remaining oil was located in a similar place to that of SF1 as shown in Fig. 4.20. The increase in recovery in PF1 was mainly caused by the increase in capillary number rather than the improvement in viscosity ratio. From a comparison between
the base case and PF2, this level of viscosity ratio ($M = 5$) does not cause unfavorable viscous fingering at the pore scale at a capillary number of $Ca \sim 10^{-5}$. This is consistent with the fact that the experimental condition of $Ca$ and $M$ falls in the capillary fingering regime in Lenormand’s phase diagram rather than in the viscous fingering regime [68]. Nevertheless, viscosity ratio can have an impact on microscopic displacement efficiency if the capillary number becomes higher. When we compare PF1 and SF1, a higher recovery factor was obtained with PF1 although its capillary number is lower than that in SF1, because viscous forces start to take effect at a capillary number of $10^{-4}$; the more favorable viscosity ratio in PF1 gave better recovery than that in SF1 despite the lower capillary number.

The comparison between the base case and PF2 gives an additional insight into the experiments of Alhammadi et al. [13]. They conducted water flooding experiments using three carbonate core plugs conditioned to different wettability states. The highest recovery factor of 84% was observed for a mixed-wet sample with a mean values of measured contact angles of 94°, while the oil-wet sample with a mean angle of 104°, which is the sample discussed in this study, showed a much lower recovery factor of 55%. These experiments were performed with different sets of oil and brine systems, resulting in oil/brine viscosity ratios of $M = 0.8$ and $M = 5.64$, respectively. The obvious question is whether the higher recovery factor in the mixed-wet sample was caused by the wettability state or the favorable viscosity ratio. From the fact that the simulation performed with $M = 1$ for the oil-wet sample did not show an increase in oil recovery, we conclude that the difference in recovery observed in the experiments of Alhammadi et al. [13] was mainly caused by wettability.

Figure 4.20. Comparison of the location of remaining oil for polymer flooding cases as a function of pore size (a) and as a function of distance from pore walls (b) and (c). For a description of each case, see Table 4.6
4.2.5. Summary

- Direct numerical simulations with locally varying contact angle obtained from experimental measurements have been performed. Then, a direct comparison of fluid occupancy between experiments and simulations has been presented.

- Applying a constant contact angle of $\theta = 107^\circ$, which was the average value of the measured angles, gave a good agreement in the local fluid occupancy. However, this case did not accurately predict the water effective permeability, meaning that the spatial heterogeneity of the wettability observed in the experiment has to be taken into account to predict fluid connectivity. However, directly applying pore-averaged measured values to each pore region did not improve the match.

- Applying a higher contact angle than the pore-averaged measured value for oil-wet pore regions improved the agreement. In a process when non-wetting phase displaces wetting phase, it is locally the largest contact angle that determines the threshold capillary pressure at which one phase can advance and displace another. As a consequence, using contact angle values near the maximum observed within each pore provided the most accurate reproduction of the experimental results.

- Low salinity water flooding has been studied by changing the wettability of the pore walls. The simulated results suggest that an increase in oil recovery is made by favoring displacement of oil from the centers of pores without leaving oil layers behind.

- Surfactant flooding has been studied by reducing the interfacial tension. This showed an increase of 16% in recovery factor. As expected, reducing interfacial tension has a significant impact on microscopic displacement efficiency. In mixed-wet rocks, the size of the remaining oil clusters became smaller for the surfactant flooding cases.

- Polymer flooding has been studied by changing the viscosity ratio. It did not show an increase in oil recovery as long as the capillary number was kept the same as in the base case. This level of viscosity ratio ($M = 5$) does not have a negative impact on microscopic displacement efficiency in this rock sample at a $Ca$ of $10^{-5}$. However, at a $Ca$ of $10^{-4}$, it improved microscopic displacement efficiency because viscous forces start to take effect.

- The comparison between the base case and PF2, in which only the viscosity ratio was changed while retaining the same capillary number as in the base case, suggested that the difference in recovery factor observed in the experiments of Alhammadi et al. [13] was mainly caused by wettability.

- In the EOR simulations discussed here, we have not considered the mixing between brine and injected EOR fluids (low salinity brine, surfactant, polymer). In reality, however, the change of fluid/rock properties occurs according to the local concentration of the EOR fluids. This will be discussed in the next chapter.
5. Applications of the two-phase lattice Boltzmann model coupled with mass transport: low salinity water flooding
5.1. Introduction

We study wettability alteration caused by injection of low salinity water. The wettability of the rock surface in the simulations is altered based on the computed local salinity. The transport of ions in water is modeled based on the two-phase lattice Boltzmann model coupled with mass transport, while the alteration of the rock surface wettability is modeled based on the wettability alteration model described in section 2.2.2.

In sections 5.2 and 5.3, we study two experiments performed with relatively simple systems to validate the numerical model. Lastly, in section 5.4, we demonstrate the applicability of the numerical model to a realistically complex pore structure of rocks using the pore structure of a Bentheimer sandstone. This work has been published in Akai et al. [9].

5.2. Detachment of an oil droplet exposed to low salinity water

We used experiments of Mahani et al. [83], refer to Chapter 1, where the detachment of oil droplets deposited on a solid surface was observed after exposure to low salinity (LS) water. A quartz substrate coated by clay minerals was used to represent surface of reservoir sandstones. Oil droplets were deposited on the clay surface and initially exposed to high salinity (HS) brine. Then, LS brine was introduced to the system by diffusion. After exposure to the LS brine, the contact angle changed toward a more water-wet state and the oil droplets eventually detached from the solid surface.

A simulation domain consisting of $73 \times 73 \times 73$ lattice nodes with a resolution of $1 \ \mu m/l.u.$ was used. The time step (t.s.) in the simulations was $1 \times 10^{-7}$ sec/t.s. In the $z$-direction, the domain was bounded by solid walls placed at the top and bottom boundaries. In the $x$ and $y$-directions, a periodic boundary condition was applied for the flow field. Initially, a semi-spherical oil drop with a radius of $20 \ \mu m$ was placed on the bottom wall and the rest of the space was filled with HS water. The oil droplet was equilibrated by performing two-phase LB simulations with a contact angle of 90° which is the value observed in the experiments for a HS environment. Table 5.1 summarizes the fluid properties and simulation conditions in comparison with those in the experiments.

The Bond number ($Bo$) is defined by:

$$Bo = \frac{\Delta \rho g r^2}{\sigma},$$

where $\Delta \rho$ is the density difference between oil and water; $g$ is the gravitational acceleration; $r$ is the radius of the oil droplet; $\sigma$ is the oil/water interfacial tension. During the simulations, the gravity force was applied by imposing a body force only on oil to achieve the same Bond number as in the experiments.
Table 5.1. Summary of the fluid properties and simulation conditions in comparison with those in the experiments of Mahani et al. [83].

<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil viscosity</td>
<td>6.5 mPa·s</td>
<td>6.5 mPa·s</td>
</tr>
<tr>
<td>Water viscosity</td>
<td>1.0 mPa·s</td>
<td>1.0 mPa·s</td>
</tr>
<tr>
<td>Interfacial tension</td>
<td>10 mN/m</td>
<td>10 mN/m</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>$1 \sim 2 \times 10^{-9}$ m$^2$/s*</td>
<td>$2 \times 10^{-9}$ m$^2$/s</td>
</tr>
<tr>
<td>Droplet radius</td>
<td>1000 µm</td>
<td>20 µm</td>
</tr>
<tr>
<td>Bond number†</td>
<td>0.16</td>
<td>0.16</td>
</tr>
</tbody>
</table>

* Typical diffusion coefficients for inorganic ions in water taken from Parkhurst and Appelo [95].
† Bond number is defined by Eq. 5.1

Since the detachment is controlled by the competition between the buoyancy and adhesion forces which is a function of contact angle, to find a threshold contact angle below which buoyancy force overcomes the adhesion force, we performed the two-phase LB simulations changing contact angle every $10^\circ$. We found that the threshold contact angle for detachment at this Bond number was between $30^\circ$ and $40^\circ$. Hence, we used $\theta_{\text{min}} = 30^\circ$ for our LSWF simulations. We set $K_{eq} = \infty$ with $k = 4 \times 10^{-4}$ t.s.$^{-1}$ to allow the contact angle to reach $\theta_{\text{min}}$ through the solid/fluid surface (see section 3.2.4 for the definition of these parameters). LS water was introduced to the simulation domain in the $x$-direction by imposing a constant concentration boundary condition with $C_s = 1.0$, while in the $y$-direction a periodic boundary condition was applied for the concentration.

The comparison between the simulation results and those of the experiment is shown in Fig. 5.1. Here, the time scale is normalized by the detachment time ($T_{\text{detach}}$) of 71 hours for the experiment and 0.62 seconds for the simulation. The simulation qualitatively captured the experiment. The difference in the detachment time is discussed later in this section.
We compared our simulations with those obtained with the existing approach by Aziz et al. [21] in which the contact angle was changed as a linear function of computed LS concentration. Here, the minimum contact angle for LS water was set to $0^\circ$ to allow the maximum wettability alteration. As a result, the three-phase contact line in our model continued to move owing to the wettability alteration allowed through the adsortion in the diffuse interface that penetrated a few lattice nodes in advance into the oil-coated part of the surface of the three-phase contact, and it eventually detached at 0.62 seconds, whereas the contact line in the other approach no longer moved after 0.15 seconds. This is because the approach by Aziz et al. [21] had a limited sensitivity of contact angle to LS concentration, which prevented a significant wettability alteration around the three-phase contact line. The comparison of the movement of the interface between our wettability alteration model and the existing approach is shown in Fig. 5.2.
An additional three simulations changing the reaction rate by a factor of 1/2, 1/3 and 1/4 were performed. As shown in Fig. 5.3, the detachment time is inversely proportional to the reaction rate. The intercept of 0.15 second corresponds to the time required for the ion to have contact with the oil droplet by diffusion, which is faster than the time scale for the chemical reaction for the detachment of 0.6 to 2.0 seconds for these four cases.

Based on this linear trend, we could reproduce the experimentally observed detachment time of 71 hours with the reaction rate constant of $7.2 \times 10^{-7}$ t.s.$^{-1}$ ($7.2 \times 10^{-3}$ sec$^{-1}$); however, this 3 orders of magnitude smaller reaction rate constant than that used in the current simulations would lead to an excessively long computation time.

Hence, in the following sections, we will use the reaction rate constant of $4 \times 10^{-4}$ t.s.$^{-1}$ as used in this section. Although this reaction rate would be higher than a realistic reaction rate constant, as shown in Fig. 5.3, the time scale of the speed of reaction is slower than that for a diffusion process.
5.3. Low salinity water flooding on a sinusoidal micro-model

The low salinity water flooding experiments by Bartels et al. [23], see Chapter 1, are simulated in this section. Using sinusoidal micro-models, a series of flooding experiments was performed for different aging conditions and presence/absence of clay minerals. We chose two of their experiments for our simulation study. In both the experiments, crude oil was used as an oil phase and aging was performed with this crude oil. In experiment 1 the solid surface had no clay minerals present, while in experiment 2 the surface was coated with clay. Water flooding was performed with HS brine followed by LS brine. For both the experiments, the wettability state for HS brine showed an oil-wet state with a contact angle of around 120°. After LSWF, experiment 1 without clay showed a significant change in the fluid configuration, resulting in the remobilization of trapped oil, whereas experiment 2 with clay showed flattening of the oil/water interface without a significant change in the fluid configuration.

Simulations were performed on a sinusoidal model of the same size. The simulation model was composed of $120 \times 12 \times 82$ lattice nodes at a lattice size of 5 $\mu m$ with four pore regions. A buffer region was attached to the inlet and outlet. As in the experiments, the domain was initially fully saturated with oil, then water flooding was performed with HS water followed by LS water. The geometry of the model and the fluid configuration at the end of HS water flooding for the two experiments are shown in Fig. 5.4.
As before, we define the capillary ($Ca$) and Péclet ($Pe$) numbers as:

$$Ca = \frac{\mu_w q_w}{\sigma},$$  \hspace{1cm} (5.2)

$$Pe = \frac{L q_w}{D},$$  \hspace{1cm} (5.3)

where $\mu_w$ is the viscosity of water; $q_w$ is the Darcy velocity of water; $\sigma$ is the interfacial tension between oil and water; $L$ is the characteristic length taken as the throat (restriction) width of 55 $\mu$m; and $D$ is the molecular diffusion coefficient of the ion in water. Table 5.2 shows a comparison of flooding conditions between the experiment and simulation. To save computation time, we used an approximately 50 times higher capillary number in the simulations. However, we assume that our simulations are comparable to the experiments since they were performed at a capillary number lower than the critical value of approximately $10^{-4}$ below which mobilization of residual oil occurs, as discussed in the previous chapter [32, 68, 104] — viscous forces do not directly contribute to mobilization of oil. The molecular diffusion coefficient in the simulation was chosen to have a similar Péclet number as in the experiment.
Table 5.2. Summary of the simulation conditions in comparison to the experimental conditions in Bartels et al. [23].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experiment</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity ratio ($\mu_o/\mu_w$)</td>
<td>6.6</td>
<td>6.5</td>
</tr>
<tr>
<td>Capillary number</td>
<td>$4.6 \times 10^{-7}$</td>
<td>$2.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>Péclet number*</td>
<td>$1.2 \times 10^{-1}$†</td>
<td>$1.0 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

* Péclet number is defined by Eq. 5.3.
† Péclet number was estimated assuming a molecular diffusion coefficient of $2 \times 10^{-9}$ m$^2$/s [95].

For the simulation of HS water flooding, an initial contact angle of 120° was assigned, with a contact angle of 30° for the buffer regions. We used these water-wet buffer regions to establish a stable phase distribution after HS water flooding by avoiding snap-offs of water droplets at the outlet.

Two LSWF cases were simulated. For experiment 1 without clay, we used $K_{eq} = \infty$ and $\theta_{min} = 15^\circ$ to allow the maximum change in contact angle at the three-phase contact line (case 1). On the other hand, for experiment 2 with clay, we used $K_{eq} = 1$ and $\theta_{min} = 15^\circ$ to make the wettability alteration less sensitive to the LS concentration (case 2).

Although in the experiments LSWF was performed for 14 pore volumes (PVs) and after that the system was kept for 14 days while stopping fluid injection, LS flooding was kept for 20 PVs in the simulations to avoid any disturbance in the flow field potentially caused by changing the flow conditions.

The simulation results for cases 1 and 2 are shown in Figs. 5.5 and 5.6, respectively. In both cases, after 14 PVs of LS flooding, the curvature of the oil/water interface changed to positive in case 1 and almost flat in case 2 from the original negative curvature (see Fig 5.4b). In case 1, since the contact angle of the simulation continued to change toward the minimum angle of 15°, the progressive development of the wettability alteration into oil-covered regions of the solid shown by semi-transparent blue in the figure was observed in the corners and top and bottom walls of the model. In contrast, there was no such change in case 2. The films observed in case 1 continued to develop, resulting in a significant change in the fluid configuration at 17.7 PVs, whereas the fluid configuration in case 2 remained the same until the end of the simulation at 20 PVs.
Figure 5.5. Comparison of LSWF on a sinusoidal micro-model between the experiment and simulation for case 1. (a) Experimentally observed phase configuration. Brown and blue show crude oil and brine, respectively. Here, the left figure shows the fluid configuration at the end of LSWF after 14 PVs, while the right figure shows the fluid configuration after 7 days of a shut-in period which followed the LSWF. (b) Simulated phase configurations after 14, 17.7 and 20 PVs of LSWF. Oil and water are shown in red and semi-transparent blue. (c) Simulated concentration distributions corresponding to the times shown. (a) is adapted from Bartels [22].
Overall, we can reproduce the behavior seen in these experiments. In the next section we will apply our model to more complex three-dimensional geometries.

5.4. Low salinity water flooding in complex 3D porous media

5.4.1. Pore structure and simulation domain

The pore structure of a Bentheimer sandstone obtained with a micro-CT with 3.58 µm/voxel was used for a simulation study of LSWF. A domain composed of $288 \times 288 \times 288$ l.u. ($\sim 1 \text{ mm}^3$) was selected from the images. This porous domain had a porosity of 21%, while the volume-weighted mean pore diameter was $60 \mu m$. A void buffer region with a size of $50 \times 288 \times 288$ l.u.$^3$ was attached to the upstream and downstream of the porous domain in the $x$-direction.
Each buffer region accounted for approximately 0.5 PV. Consequently, the simulation domain consisted of $388 \times 288 \times 288$ lattice nodes, i.e., $(x, y, z) \in [0, 387] \times [0, 287] \times [0, 287]$.

5.4.2. Drainage simulation

To establish an irreducible water saturation, a drainage simulation was performed by injecting oil into the domain initially saturated with HS water with a contact angle of $45^\circ$. Once the oil saturation stabilized, an aging process was simulated by altering the contact angle of the domain to $120^\circ$ and continuing the simulation with the same boundary conditions until the oil saturation stabilized again. As a result, the simulation domain had an initial oil saturation of 74%.

5.4.3. Water flooding simulation

Three water flooding scenarios were considered: HS water flooding, secondary mode and tertiary mode LSWF. HS water flooding was performed for 4 PVs of injection. In secondary mode, LS water was injected directly into the irreducible water saturation, while in tertiary mode, LS water was injected after 2 PVs of HS water injection. In both these flooding modes, the LS water was injected for 2 PVs. A constant concentration ($C_s = 1.0$) boundary condition was applied for the inlet lattice nodes at $x = 0$ (l.u.) and a zero-gradient ($\partial C_s/\partial x = 0$) boundary condition for the outlet lattice nodes at $x = 387$ (l.u.), respectively.

Table 5.3 summarizes the simulation conditions in comparison with the flooding conditions used in the experiments by Bartels et al. [23]. Similar to the simulations in section 5.3, we chose a capillary number of the order of $10^{-5}$, while maintaining a Péclet number of order $10^{-1}$ which is typical of reservoir conditions. For the wettability alteration model, the parameters used to match the experiment by Bartels et al. [23] in which a significant change in fluid configuration was observed were used: $K_{eq} = \infty$ and $\theta_{min} = 15^\circ$, see section 5.3.
Table 5.3. Summary of the simulation conditions in comparison with the experimental conditions in Bartels et al. [23].

<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity ratio ($\mu_o/\mu_w$)</td>
<td>6.6</td>
<td>6.5</td>
</tr>
<tr>
<td>Throat diameter</td>
<td>55 $\mu$m</td>
<td>60 $\mu$m*</td>
</tr>
<tr>
<td>Capillary number</td>
<td>$4.6 \times 10^{-7}$</td>
<td>$2.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>Péclet number†</td>
<td>$1.2 \times 10^{-1}$</td>
<td>$1.0 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

* The throat diameter in the simulation was obtained from the volume-weighted mean throat diameter.
† Péclet number was defined taking the throat diameter as a characteristic length scale.

Figs. 5.7 and 5.8 show the distribution of fluid and concentration during LSWF for the secondary and tertiary floods, respectively. The secondary mode showed a more uniform distribution of LS concentration at the early stage of LS water injection (Fig. 5.7c), while that of the tertiary mode showed a more diffused distribution (Fig. 5.8c). This is because injected LS water in secondary flood did not mix with high salinity water in the pore space which was disconnected by oil, whereas injected LS water in the tertiary flood had connected pathways with pore water from the beginning of LS water injection.

This stabilization of the concentration front is more clearly seen in the average concentration in a slice perpendicular to the flooding direction in Fig. 5.9. At 0.2 PV of LS water injection, the concentration front for the secondary flood propagated to around 300 $\mu$m from the first slice of the porous domain, whereas that of the tertiary flood had already reached the last slice by advection through connected water pathways. At 0.6 PV, the concentration of the secondary mode was slightly higher than that of the tertiary mode for most of the slices owing to better mixing in the secondary flood by the stabilized concentration front. However, after 2.0 PVs, in both the flooding modes, the concentration reached its maximum value of 1 for almost all the slices. Another point to mention is that the average concentration at the first slice of the porous domain which was located 50 lattice units away from the inlet lattice nodes at which the constant concentration boundary condition was applied, already had $C_s \sim 0.8$ at 0.2 PV of injection for both cases. This suggests that at this low Péclet number of the order of $10^{-1}$, the diffusive flux ($-D_s \nabla C_s$) was more predominant than the advective flux ($uC_s$).

Aziz et al. [21] observed stagnant regions during their LSWF simulations. They concluded that the presence of stagnant regions might have a negative impact on oil recovery. Their simulations were performed on a 2D structure at a capillary number of $7 \times 10^{-4}$ with a Péclet number of a few hundreds. This means that diffusion cannot readily allow recovery from stagnant regions where the flow is slow. However, as indicated by $C_s \sim 1$ for all the slices at 2.0
Figure 5.7. Distribution of fluid and concentration during secondary LS water injection. Oil distribution (a) after 0.2 PV and (b) after 2.0 PVs of LS water injection. The LS concentration (a) after 0.2 PV and (b) after 2.0 PVs of LS water injection.

PVs, there was no significant recovery impediment effect of stagnant regions in our simulations performed at a Péclet number of order $10^{-1}$ which is in a diffusion dominated flow regime [25]. Hence, we conclude that the mixing of LS and HS water is predominantly controlled by diffusion under this low Péclet number condition which is typical of LSWF in oil reservoirs.
Figure 5.8. Distribution of fluid and concentration during tertiary LS water injection. Oil distribution (a) after 0.2 PV and (b) after 2.0 PVs of LS water injection. The LS concentration (a) after 0.2 PV and (b) after 2.0 PVs of LS water injection.

Figure 5.9. Computed average concentration during LSWF on a Bentheimer sandstone. The figure shows the average concentration in a slice perpendicular to the flooding direction as a function of the distance from the inlet of the porous domain.
The change of recovery factor as a function of pore volumes of water injected for the three cases is shown in Fig. 5.10. Secondary flooding gave a recovery factor of 67%, which is 2% higher than that of tertiary flooding. The stabilized concentration front contributes to better oil recovery. Nevertheless, since the final displacement efficiency would also be determined by how remobilized oil ganglia get connected with the surrounding oil and how they form connected pathways to the outlet, a further parametric study with the different wettability alteration parameters is required to conclude which flooding mode gives better recovery.

![Graph showing change of recovery factor as a function of pore volumes water injected.](image)

**Figure 5.10.** Change of recovery factor as a function of pore volumes water injected.

### 5.5. Summary

- A new pore-scale numerical simulation model for LSWF has been proposed. The model solves two transport equations with the lattice Boltzmann method: the Navier-Stokes equation for oil and water two-phase flow, and the advection-diffusion equation for ion transport in water. The model has been validated against two LSWF experiments in the literature [83, 23], then applied to micro-CT images of a Bentheimer sandstone.

- In the experiments by Mahani et al. [83], at the same Bond number as in the experiments, our model has correctly captured the balance between buoyancy and adhesion forces, resulting in the detachment of an oil droplet, whereas the existing approach by Aziz et al. [21] did not capture the detachment because of pinning of the three-phase contact line. Moreover, we have shown that the time for the detachment can be controlled by the reaction rate in the model.

- The role of the parameter which controls the sensitivity of wettability alteration has been demonstrated using the experiments by Bartels et al. [23]. When a substantial wettability alteration around the three-phase contact line was allowed in our model, a significant
alteration of fluid configuration observed in the experiment was simulated. In contrast, the experiment in which they observed only the flattening of the oil/water interface was successfully simulated with an alteration that was less sensitive to LS water.

- We have performed LSWF simulations on 3D micro-CT images of a Bentheimer sandstone. In secondary mode LS water injection, the concentration was stabilized by the two-phase displacement front because the injected LS water did not mix with HS pore water disconnected by oil. This contributed to better oil recovery in secondary mode compared to that in tertiary mode. Furthermore, our simulations performed at a Péclet number of order $10^{-1}$ showed no significant impact of stagnant regions on the mixing between HS and LS water.

This concludes our studies of the effect of wettability on multiphase flow. However, one major issue remains outstanding. While we can simulate flow for different contact angles, how do we measure these angles in experiments for input into pore-scale models? Furthermore, how accurately can interfacial curvature be used to estimate capillary pressure from pore-space images? These questions are addressed in the next chapter.
6. Validation of pore-scale analysis methods using numerical modeling
In this chapter, we study recently developed pore-scale image analysis methods. This chapter is conceptually distinct from the previous ones. We use the two-phase lattice Boltzmann model to obtain pore-scale fluid configurations similar to what is obtained with micro-CT imaging during multiphase flow experiments. Using these fluid configurations and additional information which is available in simulations, but difficult to obtain from experiments, we validate experimental analysis methods and investigate their uncertainty.

A method to measure the curvature of the oil/water interface to obtain capillary pressure is studied in section 6.1, while a method to find a thermodynamically-consistent contact angle from pore-scale images is studied in section 6.2.

### 6.1. Measurement of interfacial curvature of the interface

#### 6.1.1. Introduction

The measurement of the interfacial curvature on micro-CT images has recently been employed in many studies to obtain capillary pressure \([18, 19, 16, 47, 71, 74]\), based on the Young-Laplace equation presented previously:

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

where \(\sigma\) is the interfacial tension, \(r_1\) and \(r_2\) are the principal radii of curvature of the interface, and \(\kappa_m\) is the mean curvature. However, there is a potential difficulty in image-based curvature measurements: the use of voxelized image data may introduce significant error, which has not — to date — been quantified. To find the best method to compute curvature from micro-CT images and quantify the likely error, we study this experimental method using pore-scale fluid configurations obtained from a numerical model. This work has been published in Akai, Lin, Alhosani, Bijeljic and Blunt [10] and Akai, Bijeljic and Blunt [8].

#### 6.1.2. A method to measure curvature on voxelized images

We follow a curvature computation method presented in the literature [18, 19, 16, 47, 71, 74]. In this approach, curvature is measured on a smoothed fluid interface extracted from voxelized, segmented image data through the fitting of a quadratic form locally to the interface [18].

We start with three-phase segmented label data (oil, water and solid) obtained from raw gray-scale CT images. Using the marching cubes algorithm [81], the oil/water interface is extracted from the label data. Since this surface has a staircase shape, it has to be smoothed before computing curvature. In this study, we compare three smoothing methods: Constrained Gaussian smoothing (CGS), Laplacian smoothing (LPS) and boundary preserving Gaussian smoothing (BPGS). CGS is applied when the surface is extracted using the marching cubes algorithm. A Gaussian kernel filter with different kernel sizes is applied to label data, then an
isosurface is extracted. In this process, the constraint to preserve the location of an original label is imposed.

LPS [48] and BPGS [122] are applied after the extraction of the surface with the marching cubes algorithm. The extracted surface with a staircase shape is modeled as a triangulated surface. Then, the vertices of the triangle elements are moved with these smoothing methods. In LPS, the position of a vertex is moved to the average position of its neighboring vertices. BPGS also moves the position of a vertex based on the position of its neighboring vertices. The scale factor which determines the degree of the movement in one iteration is defined. Two consecutive smoothing steps with a positive and negative scaling factor are performed in one iteration. This smoothing produces a surface which preserves the original boundary without shrinkage [122]. The degree of the smoothing in LPS and BPGS is controlled by the number of iterations.

After the generation of a smoothed triangulated surface, the elemental triangles are fitted by a quadratic form:

\[ ax^2 + by^2 + cz^2 + 2exy + 2fyz + 2gxz + 2lx + 2my + 2nz + d = 0. \]

Then, the principal curvature values and directions of principal curvature are obtained from the eigenvalues and eigenvectors of the fitted quadratic form in Eq. 6.2 [19].

6.1.3. Curvature of the interface in a simple pore geometry

To investigate the curvature computation algorithm described in section 6.1.2, a simple 3D test case was performed. We used a cylindrical pore structure with the length of 171.5 µm with an isosceles triangular cross-section as shown in Fig. 3.11. This pore structure was modeled with a grid size of 3.5 µm. The identical density and viscosity of the water and oil phases were set to 1,000 kg/m³ and 1 mPa·s, respectively. The interfacial tension and contact angle were set to 18 mN/m and 45°, respectively. Initially, oil was placed in the central region of the pore space as shown in Fig. 6.1a. Then, simulations were performed for 50,000 time steps until they formed a single oil droplet after equilibrium. The initial and equilibrium conditions are shown in Fig. 6.1.
Two types of the oil/water interface were prepared based on the simulation results: a “simulated interface” and a “smoothed interface”. The simulated interface was obtained by extracting the contour line of the color function $\rho^N=0$. This surface originally had a sub-resolution smoothness. The other surface, the smoothed interface, was obtained from synthetic voxelized label data. The simulated distribution of the color function was segmented into label data with the threshold of $\rho^N=0$, then the oil/water interface was extracted using the marching cubes algorithm. This surface had a staircase shape due to the shape of a voxelized grid system. This reproduces the type of interface that would be obtained from a pore-scale imaging experiment. Therefore, it had to be smoothed before computing curvature. The three smoothing methods described previously were applied: Constrained Gaussian smoothing (CGS), Laplacian smoothing (LPS) and boundary preserving Gaussian smoothing (BPGS). The parameters used for the smoothing are summarized in Table 6.1.

Based on the simulated fluid pressure, the capillary pressure was obtained by $P^\text{sim}_c = P^\text{avg}_o - P^\text{avg}_w$, where $P^\text{avg}_o$ and $P^\text{avg}_w$ are the average fluid pressure in the oil and water phases, respectively. Then, $P^\text{sim}_c$ was converted to the simulated mean curvature using Eq. 6.1 with $\sigma = 18$ mN/m. We refer to this mean curvature as the fluid pressure derived mean curvature, $\kappa^P_m$. 

Table 6.1. Parameters used for Constrained Gaussian smoothing (CGS), Laplacian smoothing (LPS) and boundary preserving Gaussian smoothing (BPGS).

<table>
<thead>
<tr>
<th>smoothing method</th>
<th>parameters</th>
<th>smoothing level</th>
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<tbody>
<tr>
<td></td>
<td></td>
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<tr>
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</tr>
<tr>
<td>LPS</td>
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</tr>
<tr>
<td>BPGS</td>
<td>number of iterations</td>
<td>50</td>
</tr>
</tbody>
</table>

Figure 6.1. An oil droplet in a 3D triangular pore space. (a) Initial condition. (b) Equilibrium condition. Here, solid is shown in transparent green and the oil phase is shown in red.
Fig. 6.2 shows the oil/water interface after smoothing, colored by computed mean curvature. For all the smoothed surfaces, we see a variation in the computed mean curvature, although the correct mean curvature should give a uniform value as shown in the curvature computed on the simulated interface (Fig. 6.2j), because the oil droplet was in capillary equilibrium. Furthermore, we see errors around the edge of the interface (close to the three-phase contact lines) for all the smoothed interfaces (Fig. 6.2a to i). Therefore, we decided to discard those data points whose distance from solid surface is fewer than 3 voxels. This 3 voxels long distance cutoff was used for all the following analyses. Table 6.2 summarizes the average and standard deviation of the computed mean curvature and the relative difference to the fluid pressure derived mean curvature, $\kappa_P^m = 0.133$ voxel$^{-1}$ for the smoothing level 2 as shown in Fig. 6.2b, e, and h.

In fact, the optimum smoothing method and its level of smoothing is dependent on the shape and the size of an object. Therefore, here, we only provide the qualitative features of the three smoothing methods. CGS preserves the shape of an object, but significant smoothing cannot be applied even with increasing the kernel size, because the resultant surface is constrained by the original voxel data. As a result, CGS tends to give a wider range of variation. LPS can apply significant smoothing by increasing the number of iterations, however, this could change the shape of the interface as shown in a top part of the interface in Fig. 6.2(f) where we see the bending of the interface towards the opposite direction. This is caused by the propagation of errors in the three-phase contact line through many iterations. However, combining with the distance cutoff, this erroneous part can be effectively removed while preserving a well smoothed surface in the middle of the interface. BPGS gives the similar results to LPS, while better keeping the shape of an object compared to LPS.

For the simulated interface, the computed curvature showed a good agreement with the fluid pressure derived curvature with a smaller standard deviation (Table 6.2). Moreover, since this surface did not show the errors close to the three-phase contact line, the average and standard deviation without the distance cutoff also gave similar values, i.e., an average of 0.132 voxel$^{-1}$ and standard deviation of $3.99 \times 10^{-3}$ voxel$^{-1}$. 

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Figure 6.2. Oil/water interface after the application of the several smoothing methods with different smoothing levels. CGS with a kernel size of (a) 1 voxel, (b) 3 voxels and (c) 9 voxels. LPS with (d) 200 iterations, (e) 600 iterations and (f) 1800 iterations. BPGS with (g) 50 iterations, (h) 150 iterations and (i) 450 iterations. (j) The simulated interface. Here, the surface is colored by the value of mean curvature. The correct surface should present a uniform mean curvature as seen in the simulated interface since the droplet is in a capillary equilibrium for which the capillary pressure is uniform.

Table 6.2. Computed curvature on the simulated interface and smoothed voxel based interfaces with the smoothing level 2 (see Table 6.5) and a distance cutoff of 3 voxels. Here, the relative difference was computed to the fluid pressure derived mean curvature of $\kappa_m^P = 0.133 \text{ voxel}^{-1}$.

<table>
<thead>
<tr>
<th>surface</th>
<th>computed curvature</th>
<th>relative difference</th>
<th>avg.</th>
<th>std.</th>
<th>%</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>avg. [voxel$^{-1}$]</td>
<td>std. [voxel$^{-1}$]</td>
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<tr>
<td>simulated interface</td>
<td>0.134</td>
<td>$3.23 \times 10^{-3}$</td>
<td>0.7%</td>
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<tr>
<td>smoothed with CGS</td>
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<td>$3.23 \times 10^{-2}$</td>
<td>12.1%</td>
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<td></td>
</tr>
<tr>
<td>smoothed with LPS</td>
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<td>$2.40 \times 10^{-2}$</td>
<td>-0.1%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>smoothed with BPGS</td>
<td>0.139</td>
<td>$2.68 \times 10^{-2}$</td>
<td>5.0%</td>
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</tr>
</tbody>
</table>
6.1.4. Curvature of the interface in complex pore spaces

Simulation conditions

We used the pore structures of a synthetic bead pack pore structure and micro-CT images of Bentheimer sandstone. Simulation domains were composed of $256 \times 256 \times 256$ lattice nodes with a lattice size $\Delta x = 3.58 \mu m$ as shown in Fig 6.3. The time step size was $\Delta t = 4.27 \times 10^{-7}$ second. For the analysis of the simulation results, the pore structures were divided into pore regions, resulting in 402 and 272 pore regions for the bead pack and Bentheimer sandstone structure, respectively. The identical density and viscosity of water and oil phase were set to 1,000 kg/m$^3$ and 1 mPa·s, respectively. The interfacial tension and contact angle were set to 25 mN/m and 45$^\circ$, respectively.

![Figure 6.3. Pore structures of (a) the bead pack and (b) Bentheimer sandstone.](image)

All 6 faces of the cubic simulation domain were covered with solid voxels: a no-slip boundary condition was applied. Initially, 50% of oil and 50% of water were randomly placed in pore voxels, then the simulations were performed with no external force for 250,000 time steps (corresponding to 0.1 seconds) until they reached equilibrium conditions. Fig. 6.4 shows the simulated phase distribution at the equilibrium condition. A different size of oil clusters with different radius of curvature corresponding to local pore sizes were obtained for each pore structure.

![Figure 6.4. Simulated phase distribution of (a) the bead pack and (b) Bentheimer sandstone. Here, only oil is shown in red, while water and solid are transparent. The extracted interface based on the simulation results for (c) the bead pack and (d) Bentheimer sandstone, which were obtained from the contour surface of $\rho^N = 0$.](image)
Measurement of interfacial curvature

Similar to the analysis presented in the previous section, the simulated interface and the smoothed interface were prepared from the simulation results. Curvature computation was performed on these surfaces. Figs. 6.5 and 6.6 show the histogram of the computed curvature for the bead pack and Bentheimer sandstone, respectively. The fluid pressure derived mean curvature, $\kappa_m^P$, is also shown by the vertical line. The average and standard deviation of these distributions are summarized in Table 6.3 for the bead pack and Table 6.4 for the Bentheimer sandstone.

Here, we can make two observations. (1) The histograms obtained from the smoothed interface show a wide range of the distribution when the cutoff is not applied, while the histogram obtained with the simulated interface shows a much narrower range. For the histograms without the cutoff, the difference between the distributions obtained with the smoothed interfaces and the simulated interface suggests that there are many erroneous values in curvature computation on the smoothed surfaces. The histograms obtained with CGS appeared to have the most similar distribution to that obtained with the simulated interface. However, as shown in Table 6.3 and 6.4, their average values are much higher than that obtained from the fluid pressure and simulated interface because of the long tails of their distribution toward values higher than 0.3 voxel$^{-1}$, which are not shown in Fig. 6.5 and 6.6. (2) With the distance cutoff, all the histograms obtained with the smoothed interface become similar to that obtained with the simulated interface. However, in both the smoothed and the simulated interface, the data points of high curvature values have been lost. This is because the distance cutoff removes the data points of not only the edges of the interface but also the entire parts of the interface in small pores, which tend to give a high curvature value.

Although a high curvature value is not captured when the distance cutoff is applied, the smoothed interface seems to provide a good estimate of local mean curvature values of the interface. This will be further discussed in the following analysis. Among the three smoothing methods, when the cutoff is applied, LPS as before gave the most close average value of the mean curvature to that obtained from the simulated interface with the smallest standard deviation.
Figure 6.5. Histogram of computed $\kappa_m$ for the bead pack, computed on the smoothed interface without and with the distance cutoff (a and b), and computed on the simulated interface without and with the distance cutoff (c and d).

Table 6.3. Average and standard deviation of the distribution of computed mean curvature for the beads pack shown in Fig. 6.5.

<table>
<thead>
<tr>
<th>curvature</th>
<th>avg. [voxel$^{-1}$]</th>
<th>std. [voxel$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>simulated fluid pressure</td>
<td>$7.40 \times 10^{-2}$</td>
<td>N/A</td>
</tr>
<tr>
<td>without the cutoff</td>
<td></td>
<td></td>
</tr>
<tr>
<td>simulated interface</td>
<td>$7.36 \times 10^{-2}$</td>
<td>$4.25 \times 10^{-2}$</td>
</tr>
<tr>
<td>CSG smoothed surface</td>
<td>$11.5 \times 10^{-2}$</td>
<td>$16.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>LPS smoothed surface</td>
<td>$3.06 \times 10^{-2}$</td>
<td>$5.63 \times 10^{-2}$</td>
</tr>
<tr>
<td>BPGS smoothed surface</td>
<td>$4.54 \times 10^{-2}$</td>
<td>$6.87 \times 10^{-2}$</td>
</tr>
<tr>
<td>with the cutoff</td>
<td></td>
<td></td>
</tr>
<tr>
<td>simulated interface</td>
<td>$7.12 \times 10^{-2}$</td>
<td>$1.22 \times 10^{-2}$</td>
</tr>
<tr>
<td>CSG smoothed surface</td>
<td>$8.02 \times 10^{-2}$</td>
<td>$8.43 \times 10^{-2}$</td>
</tr>
<tr>
<td>LPS smoothed surface</td>
<td>$7.01 \times 10^{-2}$</td>
<td>$2.03 \times 10^{-2}$</td>
</tr>
<tr>
<td>BPGS smoothed surface</td>
<td>$7.62 \times 10^{-2}$</td>
<td>$2.54 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
Figure 6.6. Histogram of computed $\kappa_m$ for the Bentheimer sandstone, computed on the smoothed interface without and with the distance cutoff (a and b), and computed on the simulated interface without and with the distance cutoff (c and d).

Table 6.4. Average and standard deviation of the distribution of computed mean curvature for Bentheimer sandstone shown in Fig. 6.6.

<table>
<thead>
<tr>
<th>curvature</th>
<th>avg. [voxel$^{-1}$]</th>
<th>std. [voxel$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>simulated fluid pressure</td>
<td>$9.73 \times 10^{-2}$</td>
<td>N/A</td>
</tr>
<tr>
<td>without the cutoff</td>
<td></td>
<td></td>
</tr>
<tr>
<td>simulated interface</td>
<td>$11.1 \times 10^{-2}$</td>
<td>$8.20 \times 10^{-2}$</td>
</tr>
<tr>
<td>CSG smoothed surface</td>
<td>$19.3 \times 10^{-2}$</td>
<td>$27.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>LPS smoothed surface</td>
<td>$4.24 \times 10^{-2}$</td>
<td>$7.64 \times 10^{-2}$</td>
</tr>
<tr>
<td>BPGS smoothed surface</td>
<td>$8.51 \times 10^{-2}$</td>
<td>$10.8 \times 10^{-2}$</td>
</tr>
<tr>
<td>with the cutoff</td>
<td></td>
<td></td>
</tr>
<tr>
<td>simulated interface</td>
<td>$7.17 \times 10^{-2}$</td>
<td>$2.51 \times 10^{-2}$</td>
</tr>
<tr>
<td>CSG smoothed surface</td>
<td>$8.16 \times 10^{-2}$</td>
<td>$8.48 \times 10^{-2}$</td>
</tr>
<tr>
<td>LPS smoothed surface</td>
<td>$7.45 \times 10^{-2}$</td>
<td>$3.12 \times 10^{-2}$</td>
</tr>
<tr>
<td>BPGS smoothed surface</td>
<td>$7.81 \times 10^{-2}$</td>
<td>$3.60 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
Measurement of interfacial curvature on a pore-by-pore basis

The curvature computation was made on a pore-by-pore basis. We computed local capillary pressure for each pore region from the simulated fluid pressure. This local capillary pressure was then converted to the mean curvature for each pore region using Eq. 6.1, which is referred to as mean curvature obtained from the fluid pressure. We also obtained the mean curvature for each pore region by taking the average of the computed curvature values on the interfaces in that pore region.

Fig. 6.7 shows a comparison between the dimensionless mean curvature obtained from the simulated fluid pressure and that obtained from the computed curvature on the interface for the bead pack and Bentheimer sandstone, respectively. In both, the curvature computed on the simulated interfaces gave consistent values with those obtained from the fluid pressure. This means that when the interface is reasonably smooth, the computation of curvature gives an accurate estimation of local capillary pressure. For the curvature computed on the smoothed interface, CGS shows highly overestimated curvature values for some pore regions, while LPS and BPGS estimate curvature within a range of about ±20% difference from the curvatures obtained with the fluid pressure for the mean curvature smaller than approximately 0.15 voxel$^{-1}$. Therefore, with LPS or BPGS incorporating the distance cutoff of 3 voxels, local capillary pressure can be measured within the range of ±20% error up to 0.15 voxel$^{-1}$: this means that to have an error of 20% of lower, the radius of curvature has to be at least 7 times the voxel size.

Figure 6.7. Comparison of local $\kappa_m$ on a pore-by-pore basis for (a) the bead pack and (b) Bentheimer sandstone. x-axis shows the dimensionless mean curvature obtained from the simulated fluid pressure, while the y-axis shows that computed on the interface. A unit slope indicating perfect agreement in these values is shown by a black solid line, while ±20% difference is shown by black dotted lines.
6.1.5. Summary

- We have studied the measurement of interfacial curvature using a single oil droplet in a triangular pore space. Computed curvature values on the simulated interface showed a narrow distribution whose average value was consistent with that obtained from the fluid pressure, meaning that when the surface is sufficiently smooth, the fitting of a quadratic form equation to the surface properly computes local curvatures.

- On the other hand, computed curvature values on the smoothed interface showed a wide distribution with erroneous values close to the three-phase contact lines. Therefore, we discarded values whose distance from solid surface was fewer than 3 voxels. With the distance cutoff, the average of computed mean curvature values became closer to that obtained from the fluid pressure.

- The pore structures of a bead pack and Bentheimer sandstone have been used to simulate oil droplets in complex porous media at capillary equilibrium.

- The simulated interface gave an average value of mean curvature consistent with that obtained from the fluid pressure for both porous media, when the distance cutoff was not applied. However, when the cutoff was applied, the average value became lower than that from the fluid pressure. This is because the distance cutoff removes the data points of not only the edges of the interface but also the entire parts of the interface in small pores, which tend to give a high curvature value.

- For the smoothed interfaces obtained from the segmented images, the distributions obtained without the cutoff were quite different from that obtained from the simulated interface. Many negative values of computed mean curvatures suggested significant errors in these cases. After the application of the distance cutoff, the distribution became closer to that obtained with the simulated interface.

- We have evaluated mean curvature on a pore-by-pore basis. Oil droplets with different mean curvature values corresponding to different pore sizes were obtained. A good agreement between mean curvature obtained from the fluid pressure and that computed from the simulated surface for each pore region has been obtained. The variation of local capillary pressure has been properly captured by the range of measured curvature on the simulated interface.

- For the smoothed interfaces, the application of the distance cutoff is necessary to remove the errors close to the three-phase contact line. Among the three tested smoothing methods, LPS appeared to be the best method since it gave the closest average of mean curvature values to that obtained from the simulated interface with the smallest standard deviation. When this method is used, it gave good estimates of the local mean curvature for each pore with a $\pm 20\%$ error up to 0.15 voxel$^{-1}$. This means that in experiments, even with ideal imaging and segmentation, to have an error of $20\%$ of lower, the radius of curvature has to be at least 7 times the voxel size.
6.2. Measurement of thermodynamic contact angle

6.2.1. Introduction

Blunt et al. [27] has recently shown that a thermodynamically consistent contact angle can be determined from micro-CT images based on energy balance during two-phase displacement in porous media. However, in their derivation of the method, viscous dissipation was ignored. Hence, it is necessary to validate the method with the consideration of viscous dissipation. Furthermore, the method only provides a single representative angle for an entire rock sample and it is not clear if the method can provide the spatial information of wettability states.

In this section, using fluid configurations obtained with two-phase direct numerical simulation on pore-scale images of complex 3D porous media, we validate the method to calculate the thermodynamic contact angle considering viscous dissipation. Furthermore, we demonstrate the applicability of the method to inform the spatial distribution of wettability states by applying the method on a pore-by-pore basis through a comparison between the measured thermodynamic contact angle and input contact angle. This work has been submitted for publication [9].

6.2.2. A method to measure thermodynamic contact from pore scale images

We present a derivation of an equation to measure a thermodynamically consistent contact angle, which is extended from the original work by Blunt et al. [27] to account for the impact of viscous dissipation on energy balance.

Following a thermodynamics approach by Morrow [87], we consider energy balance of two capillary equilibrium states for an isothermal irreversible process in an arbitrary control volume [87, 59]:

\[
\Delta W_{\text{ext}} = \Delta E_{\text{surf}} + \Delta E_{\text{vis}},
\]

where \(\Delta W_{\text{ext}}\) is the applied external work to the control volume during displacement between the two states, \(\Delta E_{\text{surf}}\) is the change in surface energy, \(E_{\text{surf}}\), and \(\Delta E_{\text{vis}}\) is the energy dissipated by viscous forces during displacement between the two states. Since \(\Delta E_{\text{vis}}\) scales as the square of the flow rate [26], this term can be negligible under the assumption of macroscopically slow displacement. However, even in such a case, locally rapid pore-filling events called Haines jumps [43] can yield a non-negligible positive value of \(\Delta E_{\text{vis}}\) [24, 59], which is lost as heat [26]. Since Eq. 6.3 is valid for the summation of a series of capillary equilibrium states, and the dissipated energy, \(\Delta E_{\text{vis}}\), is always positive, we obtain:

\[
\sum \Delta E_{\text{surf}} - \sum \Delta W_{\text{ext}} = - \sum \Delta E_{\text{vis}} \leq 0.
\]

The surface energy of the control volume is given by:

\[
E_{\text{surf}} = A_{1s} \sigma_{1s} + A_{2s} \sigma_{2s} + A_{12} \sigma,
\]
where $A$ is an area, while the subscript 1, 2 and $s$ refer to phase 1, phase 2 and the solid, respectively. These subscripts will be used to refer to water, oil, and solid, respectively in the following sections. $\sigma$ is the interfacial tension between these two phases while $\sigma_{1s}$ and $\sigma_{2s}$ represent the interfacial tensions between the solid surface, and phases 1 and 2 respectively. The total solid area $A_s = A_{1s} + A_{2s}$ is fixed. Hence, Eq. 6.5 becomes:

$$E_{\text{surf}} = A_s \sigma_{2s} + A_{1s} (\sigma_{1s} - \sigma_{2s}) + A_{12} \sigma.$$  \hspace{1cm} (6.6)

The Young equation can be written as [26]:

$$\sigma \cos \theta_t = -\Delta e = \sigma_{2s} - \sigma_{1s},$$  \hspace{1cm} (6.7)

where $\Delta e$ is the change in surface energy per unit area and $\theta_t$ is the thermodynamic contact angle. This can be derived from an energy balance at fixed volume, to find the most favorable $\theta_t$ with a constant volume of fluid residing on a solid surface, while the easiest, and standard, way to derive this is from a force balance at the three-phase contact line [87, 26]. Inserting Eq. 6.7 into Eq. 6.6, the surface energy can be written as:

$$E_{\text{surf}} = A_s \sigma_{2s} + (A_{12} - A_{1s} \cos \theta_t) \sigma.$$  \hspace{1cm} (6.8)

Finally, the change in the surface energy, $E_{\text{surf}}$, is given by:

$$\Delta E_{\text{surf}} = (\Delta A_{12} - \Delta A_{1s} \cos \theta_t) \sigma,$$  \hspace{1cm} (6.9)

where $\Delta A$ is the change in the surface area.

The external work, $\Delta W_{\text{ext}}$, is obtained based on pressure-volume work as:

$$\Delta W_{\text{ext}} = P_1 \Delta V_1 + P_2 \Delta V_2 = -P_c \Delta V_1$$  \hspace{1cm} (6.10)

$$= -\sigma \kappa \phi V \Delta S_1,$$  \hspace{1cm} (6.11)

where $P$ and $\Delta V$ are the fluid pressure and the change in the volume, $P_c$ is the capillary pressure defined by $P_c = P_2 - P_1$, $\kappa$ is the total curvature, $\phi$ is the porosity, $V$ is the volume of the control volume, and $\Delta S_1$ is the change in the saturation of phase 1. Here we have used $\Delta V_1 = -\Delta V_2 = \phi V \Delta S_1$ and the Young-Laplace equation:

$$P_c = \sigma \kappa = \sigma \left( \frac{1}{r_1} + \frac{1}{r_2} \right),$$  \hspace{1cm} (6.12)

where $r_1$ and $r_2$ are the principal radii of curvature of the interface. Here we use total curvature $\kappa$ rather than mean curvature $\kappa_m$ as before: $\kappa = 2\kappa_m.$
We represent the viscous dissipation energy as:

\[ \Delta E_{\text{vis}} = R \Delta E_{\text{surf}}, \]  

(6.13)

where \( R \) is the ratio of the viscous dissipation energy to the surface energy. Inserting Eqs. 6.9, 6.11, and 6.13 into Eq. 6.3, the energy balance is described as:

\[ \kappa \phi V \Delta S_1 = (1 + R) (\Delta A_{1s} \cos \theta_t - \Delta A_{12}). \]  

(6.14)

Rearranging Eq. 6.14, the thermodynamic contact angle, \( \theta_t \), is obtained with:

\[ \cos \theta_t = \frac{1}{\Delta A_{1s}} \left( \frac{\kappa \phi V \Delta S_1}{1 + R} + \Delta A_{12} \right). \]  

(6.15)

The derivation is strictly correct for infinitesimal, irreversible, changes in fluid configuration. When \( R = 0 \), this equation reduces to the equation provided in [27].

In experiments, \( \theta_t \) and \( R \) in Eq. 6.15 are undetermined parameters, while the others, the saturation, the interfacial area, and the interfacial curvature, can be measured from fluid configurations obtained from micro-CT images during displacement. To find \( \theta_t \) from experimentally obtained images, we need to assume a value of \( R \), normally that \( R = 0 \). This assumption has to be validated. One of the key objectives of this study is that we validate this assumption using numerical simulations with different wettability states where all the terms in Eq. 6.15 are independently determined.

In simulations, when we use a uniform input contact angle, \( \theta_i \), we can determine \( R \) as we know \( \theta_t = \theta_i \). Specifically, \( R \) is determined from the cross-plot between \( \sum \Delta W_{\text{ext}} \) and \( \sum \Delta E_{\text{surf}} \) obtained from simulation results, using Eqs. 6.9 and 6.10. Assuming \( R \) is constant for a series of capillary equilibrium states, from Eqs. 6.4 and 6.13, we obtain:

\[ \sum \Delta E_{\text{surf}} = \frac{1}{(1 + R)} \sum \Delta W_{\text{ext}}. \]  

(6.16)

Although \( R \) is not necessarily constant during displacement, we use this relationship to find an average of viscous dissipation ratio, \( R \), from the slope of the cross-plot.

6.2.3. Numerical simulations

Simulations were performed on synthetic images of a bead pack and micro-CT images of a Bentheimer sandstone, as in section 6.1.4. However, here, to study contact angle we need to simulate a displacement sequence. These images were composed of a porous domain of 288 × 288 × 288 cubic voxels of size 3.58 \( \mu \text{m} \) (a size of \( \sim 1 \text{ mm}^3 \)). The pore structures are shown in Fig. 6.8. The porosity of these structures were 36% for the bead pack, and 21% for Bentheimer sandstone. The pore spaces of these structures were divided into pore regions, resulting in 630 and 414 pore regions for the bead pack and Bentheimer sandstone, respectively. A pore is
defined as a wide region in the pore space; its center is the center of the largest sphere that can fit in the pore space. A pore region contains all the void voxels associated with a pore [26, 106]. The mean pore diameter (defined as the diameter of the largest sphere) which accounted for 50% of the pore volume was 77 µm and 63 µm for the bead pack and Bentheimer sandstone, respectively.

Drainage and water injection were performed with water- and oil-wet porous plates attached to the $-x$ and $+x$ faces of the porous domain, respectively. These porous plates consisted of a mesh of square 5 voxels in width and 20 voxels in length with contact angles of 30° and 150°, respectively. These porous plate domains were followed by 10 slices of a complete void space as a buffer domain as shown in Fig. 6.8. This simulation condition mimics a laboratory porous plate capillary pressure measurement.

![Figure 6.8](image_url)

Figure 6.8. The simulation models with a dimension of $348 \times 288 \times 288$ lattice nodes used for (a) the bead pack and (b) Bentheimer sandstone. The pore structures of the bead pack and Bentheimer sandstone with a size of $288 \times 288 \times 288$ lattice nodes are followed by 20 slices of porous plate and 10 slices of void buffer regions. (c) The water-wet and oil-wet porous plates consisted of a mesh of square 5 lattice nodes in width and 20 lattice nodes in length with a contact angle of 30° and 150°, respectively. These porous plate domains were followed by 10 slices of a complete void space as a buffer domain.
The grid size and time step used in the simulations were $\Delta x = 3.58 \, \mu m$ and $\Delta t = 4.27 \times 10^{-7}$ second, respectively. The identical density and viscosity of water and oil were used: $\rho = \rho_w = \rho_o = 1000 \, \text{kg/m}^3$ and $\mu = \mu_w = \mu_o = 1 \, \text{mPa} \cdot \text{s}$. The interfacial tension between oil and water was set to $\sigma = 25 \, \text{mN/m}$.

Drainage (DR) was performed with a uniform input contact angle of $\theta_i = 45^\circ$. Oil was introduced into the porous domain initially filled with water by gradually increasing the capillary pressure. This was performed by increasing the pressure of the oil buffer domain, while maintaining the pressure of the water buffer domain constant, applying constant pressure boundary conditions [134] at $x = 0$ and $x = 348$, respectively.

Water injection was performed for three wettability states: uniformly water-wet (WW) cases with $\theta_i = 45^\circ$, uniformly oil-wet (OW) cases with $\theta_i = 135^\circ$, and non-uniform mixed-wet (MW) cases. For the mixed-wet cases, different contact angle values ranging from $45^\circ$ to $165^\circ$ were assigned for each pore region based on the oil saturation in a pore region after the drainage simulations — a higher contact angle was assigned for a pore with higher oil saturation (fraction of the void voxels filled with oil in each pore region) after drainage. The input contact angle for the mixed-wet cases had a pore volume weighted average of $90^\circ$ with a standard deviation of $30^\circ$. The contact angles of the mixed-wet cases are shown in Fig. 6.9. For the water-wet cases, water injection was started immediately after the end of drainage. For the oil-wet and mixed-wet cases, an aging period was simulated before water injection. This aging was performed by continuing the simulations for 20,000 time steps while maintaining the pressure boundary condition at the end of the drainage after altering the input contact angle. This allowed a new position of capillary equilibrium to be attained before water injection.

Figure 6.9. Input contact angles of the mixed-wet cases. Different contact angle values ranging from $45^\circ$ to $165^\circ$ were assigned for each pore region based on oil saturation in a pore region after the drainage simulations, resulting in a pore volume weighted average of $90^\circ$ with a standard deviation of $30^\circ$.

The capillary number was defined, as before, by $Ca = \mu q_t / \sigma$, where $q_t$ is the total flow rate.
of oil and water. In both drainage and water injection, at each capillary pressure, simulations were performed until \( \text{Ca} < 1 \times 10^{-6} \) to ensure capillary equilibrium. The increment of capillary pressure was chosen to maintain slow displacement, resulting in an average capillary number during displacement smaller than \( 10^{-5} \) for all the simulations. The simulated capillary pressures are shown in Fig. 6.10. The simulation output was obtained with 14 saturation points for drainage and 21 saturation points for water injection.

![Simulated capillary pressures for drainage (DR) and water injection with three wettability states: uniformly water-wet (WW) cases with \( \theta = 45^\circ \), uniformly oil-wet (OW) cases with \( \theta = 135^\circ \), and non-uniform mixed-wet (MW) cases for (a) the bead pack and (b) Bentheimer sandstone.](image)

**Figure 6.10.** Simulated capillary pressures for drainage (DR) and water injection with three wettability states: uniformly water-wet (WW) cases with \( \theta = 45^\circ \), uniformly oil-wet (OW) cases with \( \theta = 135^\circ \), and non-uniform mixed-wet (MW) cases for (a) the bead pack and (b) Bentheimer sandstone.

### 6.2.4. Energy efficiency and viscous dissipation

We evaluated the amount of viscous dissipation for the entire porous domain during drainage and water injection using the uniform input contact angle cases (DR, WW, and OW cases) in which the change in surface energy can be estimated based on Eq. 6.9 with \( \theta_t = \theta_i \) — for the mixed-wet cases a representative input contact angle for the system was not known a priori as the input contact angle varied pore-by-pore.

The change in the surface energy, \( \Delta E_{\text{surf}} \), was obtained from the simulation results as shown in Fig. 6.11. The fluid configurations were used to obtain \( \Delta V_w \) in Eq. 6.9, while the oil/water and water/solid interfaces were used to obtain \( \Delta A_{\text{ow}} \) and \( \Delta A_{\text{ws}} \) in Eq. 6.9. The oil/water interface was obtained by extracting a contour surface corresponding to \( \rho^N = 0 \) from the simulated color function, while the water/solid interface was obtained by applying 600 iterations of Laplacian smoothing to the boundary surface of water and solid nodes which originally had a staircase shape. As shown in the previous section, this can provide sufficient smoothness while maintaining the original shape of a surface [8]. Using Eq. 6.9 with \( \theta_t = \theta_i \) for sequential simulation outputs, the summation of the change in the surface energy, \( \Sigma \Delta E_{\text{surf}} \), was obtained.

To obtain the applied external work, \( \Delta W_{\text{ext}} \), the simulated fluid pressure and fluid configurations were used. The simulated capillary pressure, \( P_{\text{c}}^{\text{sim}} \), was obtained with

\[
P_{\text{c}}^{\text{sim}} = P_{\text{o}}^{\text{avg}} - P_{\text{w}}^{\text{avg}},
\]

where \( P_{\text{o}}^{\text{avg}} \) and \( P_{\text{w}}^{\text{avg}} \) are the average fluid pressure of oil and water in the porous domain.
$P_{\text{sim}}$ does not necessarily match the imposed capillary pressure shown in Fig. 6.10, because $P_{\text{sim}}$ includes disconnected phases, while the imposed capillary pressure is only responsible for connected phases. The summation of the externally applied work, $\Sigma \Delta W_{\text{ext}}$, was obtained using Eq. 6.10. When micro-CT images during flooding experiments are used, in which the fluid pressure is typically not available, this capillary pressure needs to be estimated from the measured curvature of the oil/water interface using Eq. 6.12. A description of the measurement of capillary pressure from the interface curvature and an assessment of its accuracy was presented in section 6.1.

![Figure 6.11. An example of simulated fluid configurations and extracted surfaces obtained from the water injection simulation on Bentheimer sandstone for the water-wet case.](image)

(a) Simulated 3D oil and water configurations. Here, oil and water are shown in red and blue, respectively. (b) The extracted oil/water interface. (c) The extracted water/solid surface. (d) The extracted oil/solid surface.

Fig. 6.12 shows the cross-plot between $\Sigma \Delta W_{\text{ext}}$ and $\Sigma \Delta E_{\text{surf}}$ during drainage and water injection. We assumed that any mismatch between $\Sigma \Delta W_{\text{ext}}$ and $\Sigma \Delta E_{\text{surf}}$ was consumed as viscous dissipation. These computed values fell in the region expressed by Eq. 6.4 as shown in transparent blue in the figure. From the figure, we can see that drainage is a process where positive applied work is converted to stored surface energy in the system, while water injection in the water-wet cases is a process where stored surface energy after the drainage is converted to work. Finally, water injection in the oil-wet cases is the same process as the drainage in a
water-wet state.

Figure 6.12. Energy balance during drainage and water injection. The summation of surface energy (∑∆E_{surf}) is plotted against the summation of applied external work (∑ΔW_{ext}). These quantities are normalized by the bulk volume of the porous domain of ∼1mm^3. (a) Drainage (DR) and water injection for the water-wet (WW) case and oil-wet (OW) case for the bead pack and (b) for Bentheimer sandstone. The region expressed by Eq. 6.4 is colored transparent blue. Linear regression lines to obtain the ratio of viscous dissipation, R, are shown by the dashed lines for each case.

Based on Eq. 6.16, the ratio of viscous dissipation to surface energy, R, was determined from the slope of the cross-plot between ∑ΔW_{ext} and ∑ΔE_{surf} (Fig. 6.12) as shown in Table 6.5. When the slope approaches unity, R approaches 0, meaning a high energy efficiency. In both porous media, for drainage and water injection in the oil-wet state, the amount of viscous dissipation was more than 30% of the surface energy, indicating a relatively low energy efficiency. Bentheimer sandstone with smaller porosity and a smaller pore size showed more viscous dissipation in these cases. For water injection in the water-wet cases, we obtained negative values of R, because the sign of the change in surface energy, ∆E_{surf}, is negative in these cases, while the sign of the energy dissipated, ∆E_{vis}, is always positive. The viscous dissipation for the bead pack and Bentheimer was 10% and 3% of the surface energy, respectively, indicating a high energy efficiency. The larger viscous dissipation in the bead pack resulted from faster displacement; the average capillary number during water injection in the water-wet state was Ca = 6 × 10^{-6} for the bead pack, whereas Ca = 2 × 10^{-6} for Bentheimer sandstone.
Table 6.5. Summary of the viscous dissipation ratio, $R$, obtained for the uniform input contact angle cases. $R$ was obtained using Eq. 6.16 from the slope of the cross-plot shown in Fig. 6.12.

<table>
<thead>
<tr>
<th>Case</th>
<th>Slope*</th>
<th>Viscous dissipation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bead pack</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drainage</td>
<td>0.75</td>
<td>$R = 33%$</td>
</tr>
<tr>
<td>Water injection in the water-wet state</td>
<td>1.11</td>
<td>$R = -10%$</td>
</tr>
<tr>
<td>Water injection in the oil-wet state*</td>
<td>0.69</td>
<td>$R = 45%$</td>
</tr>
<tr>
<td><strong>Bentheimer sandstone</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drainage</td>
<td>0.61</td>
<td>$R = 63%$</td>
</tr>
<tr>
<td>Water injection in the water-wet state</td>
<td>1.03</td>
<td>$R = -3%$</td>
</tr>
<tr>
<td>Water injection in the oil-wet state</td>
<td>0.55</td>
<td>$R = 83%$</td>
</tr>
</tbody>
</table>

* The slope was found from a linear regression on the points shown in Fig. 6.12: $R$ is $1/$slope $-1$.

6.2.5. A representative thermodynamic contact angle

We investigated a representative thermodynamic contact angle, $\theta_t$, for the mixed-wet cases where $R$ in Eq. 6.15 could not be directly determined from the simulations. This was conducted through the comparison between the angles obtained without considering the viscous dissipation ($R = 0$) and those obtained with $R$ for the uniformly oil-wet cases shown in Table 6.5 which should give a maximum bound for the mixed-wet cases.

Fig. 6.13 shows the computed $\theta_t$ as a function of normalized water saturation, $S_{w}^*$, which is defined by:

$$S_{w}^* = \frac{S_w - S_{wir}}{1 - S_{wir} - S_{or}},$$

(6.17)

where $S_w$ is the water saturation in the porous domain, $S_{wir}$ is the irreducible water saturation at the beginning of water injection, and $S_{or}$ is the residual oil saturation at the end of water injection. In the figure, the computed angles for $10\% \leq S_{w}^* \leq 90\%$ are shown, because the values at the beginning and the end of water injection could not be determined accurately due to the influence from the water-wet and oil-wet porous plates. The computed $\theta_t$ for the uniformly water-wet and oil-wet case are also shown in the figure. As expected, the computed $\theta_t$ showed a good agreement with the input contact angles as indicated by the dashed lines in the figure, because we determined the dissipation ratio, $R$, so as to satisfy the energy balance with the input contact angle, $\theta_i$, in section 6.2.4.

For these cases, we can make two observations. (1) For water injection in water-wet states which is represented by spontaneous imbibition with an increase of water saturation with positive capillary pressure, $\theta_t$ can be determined even ignoring viscous dissipation owing to the high
energy efficiency of the displacement — assuming $R = 0$ resulted in a difference of less than $5^\circ$ compared to values obtained accounting for viscous dissipation. (2) For water injection in oil-wet states which is represented by forced displacement with an increase of water saturation with negative capillary pressure, viscous dissipation needs to be taken into account to determine $\theta_t$ — ignoring this with $R = 0$ resulted in undetermined $\theta_t$ with $|\cos \theta_t| > 1$.

For the mixed-wet cases where each pore region had different input contact angles ranging from $45^\circ$ to $165^\circ$, we observed only a small impact of the assumed value of $R$ on the resultant $\theta_t$ with less than $10^\circ$ difference between the angles obtained with $R = 0$ and those obtained with $R$ of the oil-wet case. This can be understood from Eq. 6.15. In the mixed-wet cases, the displacement occurred at $P_c \sim 0$, hence $\kappa \sim 0$ (see Fig. 6.10). In this case, the contribution of the viscous dissipation ratio, $R$, becomes less significant compared to the term of $\Delta A_{ow}$ in Eq. 6.15.

In our simulations of the mixed-wet cases, displacement occurred at $P_c \sim -1000$ Pa which corresponds to the total curvature $\kappa = -40$ mm$^{-1}$ with our input interfacial tension of $\sigma = 25$ mN/m (see Eq. 6.12). This means that when micro-CT images during displacement in mixed-wet porous media are used to find the thermodynamic contact angle, if the capillary pressure obtained from the measurement of the total curvature is greater than $-40$ mm$^{-1}$ (a negative value whose absolute value is smaller than 40 mm$^{-1}$), Eq. 6.15 with $R = 0$ estimates a representative $\theta_t$ within $10^\circ$.

For both mixed-wet cases, $\theta_t$ increased with water saturation. This trend has also been observed experimentally where $\theta_t$ was calculated based on X-ray images of water flooding on mixed-wet rocks [14, 115]. This trend can be explained from the sequence of displacement. For mixed-wet media, water first fills water-wet pores, followed by more oil-wet elements with

![Figure 6.13](image-url)
a decrease of capillary pressure. Since the thermodynamic contact angle is obtained from the difference of two capillary equilibrium states, the angle obtained captures the displacement between these states. Fig. 6.14 shows the sequence of oil displacement for the mixed-wet cases during water injection. Here, all the pore regions were classified into five groups based on their input contact angle, which ranged from $45^\circ$ to $165^\circ$. For each group, the number of oil filled voxels were counted and normalized by its value at the beginning of water injection. As expected, pores with a lower contact angle filled first at a low water saturation, followed by invasion of more oil-wet pores at a high water saturation. Hence, we first observed a smaller contact angle corresponding to filling in water-wet pores, then a higher contact angle for invasion of more oil-wet pores at a high water saturation. Furthermore, there was less displacement even by the end of water flooding for the more oil-wet pores where more negative entry capillary pressure is required, since displacement in these regions is less favored.

![Figure 6.14. Sequence of oil displacement for the mixed-wet cases computed for (a) the bead pack and (b) Bentheimer sandstone. All the pore regions were classified into five groups based on their input contact angle, which ranged from $45^\circ$ to $165^\circ$. The number of oil filled voxels on the y-axis was normalized by its value at the beginning of water injection.](image)

**6.2.6. Spatial distribution of contact angle**

Since Eq. 6.15 is valid for an arbitrary control volume, we applied the equation to each pore region by taking each pore region as a control volume, to compute $\theta_t$ on a pore-by-pore basis. We used two sequential simulation results to compute $\theta_t$ for pores where displacement occurred between the two states. This was performed from the first to the last simulation output to cover as many pore regions as possible. Then, $\theta_t$ for each pore region was determined by an average value of the computed angles from different sets of two sequential results. The viscous dissipation was not considered in this calculation — we used $R = 0$ in Eq. 6.15. In cases where there was significant energy dissipation in a pore region by a rapid pore-filling event such as a Haines jump, we had an undetermined value of $|\cos \theta_t| > 1$ — these values were ignored in the analysis.
Fig. 6.15 shows the computed $\theta_t$ for each pore region. Here, we discarded those pores which were in direct contact with the porous plates. The input contact angle, $\theta_i$, and $\pm 15^\circ$ difference from $\theta_t$ are shown by the solid and dashed lines, respectively. A quantitative analysis on the difference between $\theta_t$ and $\theta_i$ is shown in Table 6.6. In both the bead pack and Bentheimer sandstone, $\theta_t$ was determined for pores accounting for more than 68% of the pore volume, of which more than 66% of the values were within $\pm 15^\circ$ of $\theta_i$. Among the six water injection cases, the mixed-wet state of the bead pack showed the lowest accuracy.

The main source of the error came from the overestimate of $\theta_t$ for water-wet pore regions where $\theta_i = 45^\circ$ (see Fig. 6.15b). Fig. 6.16 shows an example of pore regions where a significant discrepancy between $\theta_t$ and $\theta_i$ was observed. In this pore region, the fluid meniscus spanned multiple neighboring pores whose $\theta_i$ was greater than $45^\circ$. As a result, the threshold capillary pressure for filling was affected by the higher contact angles in these neighboring pore regions during a cooperative pore filling event [69]. Therefore, the thermodynamic angle of this pore was over-estimated. In contrast, for the Bentheimer sandstone which had a lower porosity than that of the bead pack, the oil/water interface existed mostly within single pore regions. Hence, this case resulted in a better accuracy with 83% of the estimated values of $\theta_t$ laying within $15^\circ$ of the input values. An example of pore regions of Bentheimer sandstone where the thermodynamic contact angle was accurately determined is shown in Fig. 6.17.

Overall, we have shown that the application of Eq. 6.15 with $R = 0$ to find the thermodynamic contact angle can be used to determine the wettability on a pore-by-pore basis. It provides an accurate estimate of the spatial distribution of the contact angle when the size of each oil/water meniscus involved in a displacement was confined to single pore regions, while the estimated angle was biased by higher contact angles of neighboring pores when the meniscus spanned multiple pore regions. Choosing a control volume for the thermodynamic calculation that accommodates the meniscus involved in each displacement event might improve the determination of the spatial distribution of the wettability.
Figure 6.15. Comparison of the computed thermodynamic contact angle, $\theta_t$, and the input contact angle, $\theta_i$, on a pore-by-pore basis. The computed $\theta_t$ for each pore region is plotted as a function of pore labels assigned for each pore region, while the input angle, $\theta_i$, are shown by the solid lines with the dashed lines indicating $\pm 15^\circ$ difference from the input value. (a), (b) and (c) show water injection in the bead pack pore for the water-wet (WW), mixed-wet (MW), and oil-wet (OW) cases, respectively. (d), (e) and (f) show water injection in Bentheimer sandstone for the water-wet (WW), mixed-wet (MW), and oil-wet (OW) cases, respectively.
Table 6.6. Summary of the thermodynamic contact angle, $\theta_t$, determined on a pore-by-pore basis.

<table>
<thead>
<tr>
<th>Case</th>
<th>No. pores</th>
<th>$\theta_i$ in pores all within the error*</th>
<th>$\theta_t$ in pores all within the error</th>
<th>Accuracy†</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[pores]</td>
<td>[pores] [pores] [%PV] [PV] [%]</td>
<td>[%]</td>
<td></td>
</tr>
<tr>
<td><strong>Bead pack</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water-wet (WW)</td>
<td>630</td>
<td>417 352 90% 85% 95%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixed-wet (MW)</td>
<td>630</td>
<td>364 197 80% 53% 66%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil-wet (OW)</td>
<td>630</td>
<td>340 249 68% 48% 71%</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Bentheimer sandstone</strong></td>
<td>414</td>
<td>220 192 83% 77% 93%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water-wet (WW)</td>
<td>414</td>
<td>194 148 73% 60% 83%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixed-wet (MW)</td>
<td>414</td>
<td>272 222 88% 77% 87%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil-wet (OW)</td>
<td>414</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The error bar was defined as $\pm 15^\circ$ difference from the input contact angle, $\theta_i$, for each pore region.
† Accuracy is defined by [%PV of pores where $\theta_t$ is determined within the error bar divided by [%PV of pores where $\theta_i$ is determined.

Figure 6.16. An example of pore regions where significant discrepancy between $\theta_t$ and $\theta_i$ was observed since the fluid meniscus for a cooperative pore filling event spanned several pore regions of different wettability. (a) A pore region with $\theta_i = 45^\circ$, while its $\theta_t$ was calculated to be $115^\circ$. Here, this pore is shown in yellow, while the walls of adjacent pores are colored by their input contact angle (blue: 45°, green: 75°, red: 105°). (b) The surface patch of the oil/water meniscus (yellow) relevant to the calculation of thermodynamic angle for this pore before and (c) after displacement. This interface existed over multiple neighboring pores for a cooperative pore-filling event whose $\theta_i$ ranged from 45° to 105° with a pore volume weighted average value of 91°.
Figure 6.17. A pore region taken from the mixed-wet case of Bentheimer sandstone in which a good agreement between the thermodynamic and input angle for a pore region was observed since the fluid meniscus was confined to a single pore. This pore had an input contact angle of 105°, while the thermodynamic contact angle was computed to 107°. (a) Water phase in blue and the pore surface in transparent gray. Oil is not shown here. (b) The oil/water interface shown in blue before and (c) after displacement.

6.2.7. Summary

- The original equation to calculate the thermodynamic contact angle, \( \theta_t \), from energy balance proposed by Blunt et al. [27] has been extended to account for the impact of viscous dissipation.

- For water injection in water-wet media, \( \theta_t \) has been accurately determined even ignoring the viscous dissipation, because of the high energy efficiency of the process. On the other hand, for water injection in oil-wet media, viscous dissipation had to be taken into account because of non-negligible viscous dissipation due to rapid pore-filling events such as Haines jumps.

- For water injection in mixed-wet media, we have shown that viscous dissipation does not have a significant impact on the calculation of \( \theta_t \) when the displacement occurs at \( P_c \sim 0 \). Assuming the viscous dissipation of the uniformly oil-wet case as an extreme, the \( \theta_t \) obtained changed by less than 10° compared to the values obtained ignoring viscous dissipation.

- An increasing trend in the computed \( \theta_t \) during the displacement was observed in mixed-wet media, which is consistent with experimental observations [14, 115]. This is because displacement first occurs in water-wet pores followed by invasion of more oil-wet pore regions. We also saw that there was less displacement overall in oil-wet pores, where the entry capillary pressure is more negative (less favored).

- Through the comparison between \( \theta_t \) and \( \theta_i \) for each pore region, we have shown that the method can be used on a pore-by-pore basis to characterize the spatial distribution of the wettability. The difference between these two angles becomes small when the meniscus involved in the displacement is confined to the control volume used for the calculation of \( \theta_t \).
7. Conclusions and future work
7.1. Conclusions

The following conclusions have been obtained from this work. Here, each number corresponds to the research objectives raised in section 1.3.

(1) Development of a wetting boundary condition

A wetting boundary condition which accurately models contact angle with lower spurious current compared to an existing method has been developed, see Chapter 2. This improved wetting boundary condition has been validated against analytical solutions using a flat, curved, and staircase solid surfaces, Chapter 3.

We have shown a method to model dynamic contact angle with our numerical model using capillary rise experiments, section 4.1. When the experimentally observed dynamic contact angle was used in the simulations, the match between the simulations and experiments was improved.

Furthermore, it has been demonstrated that our improved wetting boundary condition can simulate prescribed (input) contact angles for a dynamic problem with a wide range of capillary number: $Ca = 10^{-6} \sim 10^{-2}$, which is important when the input contact angle changes during simulations such as during low salinity water flooding.

(2) Simulations of mixed-wet media with spatially varying wettability

Water flooding experiments imaged with a micro-CT have been studied in section 4.2. The measured $in situ$ contact angle has been used as input in the numerical model. The simulated fluid configurations and fluid connectivity were compared with those obtained from the experiment.

The spatial heterogeneity of the contact angle distribution observed in the experiment had to be taken into account to accurately predict fluid occupancy as a function of pore size and fluid connectivity. However, directly applying pore-averaged measured values to each pore region did not improve the quality of the match.

Applying a higher contact angle than the pore-averaged measured value for oil-wet pore regions improved the agreement between the experiment and simulations. This physically makes sense because in a process when non-wetting phase displaces wetting phase, it is locally the largest contact angle that determines the threshold capillary pressure at which one phase can advance and displace another. As a consequence, using contact angle values near the maximum observed within each pore provided the most accurate reproduction of the experimental results.

Using the best matched simulation model to the experiment, the application of low salinity, surfactant, and polymer flooding has been studied. This has been performed through a parametric study with changing the fluid and/or rock properties of the best match case. Then, the mechanisms for each enhanced oil recovery method has been studied at the pore-scale.

Furthermore, a simulation for polymer flooding case in which only the viscosity ratio was changed while retaining the same capillary number as in the best matched case suggested that
the difference in recovery factor observed in the experiments of Alhammadi et al. [13] was mainly caused by wettability.

(3) Development of a wettability alteration model for low salinity water flooding

A wettability alteration model for low salinity water flooding has been developed in section 2.2.2. This model can mimic slow kinetics mediated by thin water films which cannot be resolved by the resolution of the simulation.

First the model was tested for a simple test case. Then, it was validated using two low salinity water flooding experiments in the literature in sections 5.2 and 5.3. It successfully simulated experimentally observed behaviors: the detachment of an oil droplet from a solid wall due to a decrease in adhesion force caused by wettability alteration toward more water-wet state, and the remobilization of trapped oil caused by a progressive development of thin water films through the corners of pore spaces.

(4) Mechanisms of additional oil recovery by low salinity water flooding

Using our numerical model on the pore structure of a Bentheimer sandstone, the mechanisms of additional oil recovery by low salinity water flooding have been studied in section 5.4.

In secondary mode low salinity water injection, the concentration was stabilized by the two-phase displacement front because the injected low salinity water did not mix with high salinity pore water disconnected by oil. This contributed to better oil recovery in secondary mode compared to that in tertiary mode.

Furthermore, we have shown that at a Péclet number of order $10^{-1}$, which is typical of reservoir conditions, the mixing between low and high salinity water is more dominated by diffusion than by advection. Hence, there was no significant impact of stagnant regions on the mixing.

(5) Validation of pore-scale image analysis methods and the assessment of their uncertainty

A method to measure interfacial curvature to obtain capillary pressure has been studied in section 6.1. We have proposed an optimum procedure for smoothing and removal of erroneous values around the three-phase contact lines as a best practice.

It has been shown that when the proposed method is used, local capillary pressure can be estimated within a $\pm 20\%$ error for a non-dimensional curvature $\kappa < 0.15$ voxel$^{-1}$.

Furthermore, a method to measure a thermodynamically consistent contact angle has been studied in section 6.2. First, the original expression given by Blunt et al. [27] has been extended to account for the impact of viscous dissipation.
Using our numerical model, we have shown that the viscous dissipation has no significant impact on the estimation of the thermodynamic contact angle for water injection in water-wet and mixed-wet media. In these cases, the thermodynamic contact angle obtained ignoring the viscous dissipation gives less than $10^\circ$ difference compared to that obtained with the largest possible amount of dissipation.

An increasing trend in the computed thermodynamic contact angle against water saturation as observed in experiments [14, 115] has been explained in terms of the displacement sequence. We also saw that there was less displacement overall in oil-wet pores, where the entry capillary pressure is more negative (less favored).

Furthermore, we have shown that the method can be used on a pore-by-pore basis to characterize the spatial distribution of the wettability, through the comparison between the obtained thermodynamic contact angle and the input angle in the simulations for each pore region.

### 7.2. Future work

The suggestions for future work are as follows:

- For a comprehensive workflow of pore-scale imaging and modeling which aims to have predictive capability, the use of pore network modeling is necessary since it is not feasible for direct numerical simulations to deal with entire image volume obtained from pore-scale imaging experiments (typically larger than $2000^3$ voxel$^3$) [26]. We have shown how we use and interpret the measured information of wettability from pore-scale experiments. Hence, it is a logical extension to test how the findings from this work are applied to pore network models. This could be started from a comparison of the simulated results between direct numerical simulation and pore network model.

- It is evident that the measurements of contact angle from CT images are a key technique for the pore scale imaging and modeling workflow. We suggest that the thermodynamic contact angle measurement on a pore-by-pore basis is the most appropriate method to obtain angles to be used in the modeling. Hence, it is recommended to test the method on experimentally obtained images. The images of unsteady-state experiments imaged with time-resolved high-resolution synchrotron X-ray is ideal for this purpose.

- It is reasonable to expect that the distribution of contact angle is correlated to the roughness of the rock surface and the configuration of oil in altered wettability states. Once the application of the thermodynamic contact angle on a pore-by-pore has been proved with experimental images, it is recommended to study the correlation of the contact angle to these parameters.

- The wettability alteration model used for low salinity water flooding can be used to numerically study the above point. In this case, contact angle should be altered depending
on a component responsible for wettability alteration defined in oil phase (surface active components such as asphaltenes).

- The method to measure interfacial curvature needs to be improved as it provides not only capillary pressure, but also input for the thermodynamic contact angle measurement. As long as we use the extracted interface from segmented images, we have shown that smoothing is the main source of error, while fitting of a quadratic form to compute principal curvatures works well. We suggest to use LB iterations as a method to smooth images. In fact, an ideal smoothing method to apply is a mean curvature preserving smoothing. The LB iterations can be used for this smoothing. This work can be defined as an optimization problem: segmented images from experiments are used as input fluid distribution, then we find the best input contact angle distribution which gives the smallest difference between the simulated and experimentally obtained fluid configurations — only when correct contact angle is used in the simulations, a good match is obtained. Furthermore, this also gives the measurement of geometrical angle and, of course, an accurate estimate of curvature and capillary pressure.

- We note that the numerical model developed for low salinity water flooding can be easily extended to a numerical model for both polymer and surfactant flooding. Depending on the concentration of solutes in water, the interfacial tension is changed for surfactant flooding, while the viscosity of water is changed for polymer flooding. If the non-Newtonian motion of polymer solution is necessary to study, a rheology model for non-Newtonian fluid in the LB model is available in the literature, e.g., Ashrafizaadeh and Bakhshaei [20] and Huang et al. [54].

- Lastly, it is of great scientific interest to study mixing of fluids (such as low salinity and high salinity brine) in multiphase conditions. We have shown that there is no significant impact of stagnant regions for low Péclet numbers considering typical reservoir conditions for low salinity water flooding. However it is useful to study mixing for a wide range of flow regimes with the numerical model developed in the study, which could be encountered in other engineering applications.
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URL: http://aip.scitation.org/doi/10.1063/1.869307

URL: http://doi.wiley.com/10.1002/2017WR022433
A. The transformation and diagonal relaxation matrices

A.1. The D3Q19 lattice velocity model

The transformation matrix $M$ for the D3Q19 lattice model is given as [35]:

$$
M = \begin{bmatrix}
1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
12 & -4 & -4 & -4 & -4 & -4 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
0 & 1 & -1 & 0 & 0 & 0 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 0 & 0 & 0 & 0 \\
0 & -4 & 4 & 0 & 0 & 0 & 0 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & -1 & 0 & 0 & 1 & 1 & -1 & -1 & 0 & 0 & 0 & 0 & 1 & -1 & 1 & -1 \\
0 & 0 & 0 & -4 & 4 & 0 & 0 & 1 & 1 & -1 & -1 & 0 & 0 & 0 & 0 & 1 & -1 & 1 & -1 \\
0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 1 & -1 & 1 & 1 & -1 & 1 & 1 & -1 & 1 & -1 \\
0 & 0 & 0 & 0 & 0 & -4 & 4 & 0 & 0 & 0 & 0 & 1 & -1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \\
0 & 0 & 0 & 0 & 0 & 2 & 2 & -1 & -1 & -1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & -2 & -2 & -2 -2 \\
0 & 0 & 0 & 0 & -4 & 2 & 2 & -1 & -1 & -1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & -2 & -2 & -2 \\
0 & 0 & 0 & 0 & 2 & 2 & 2 & 2 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & -2 & -2 & -2 \\
0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & -2 & -2 & -2 \\
0 & 0 & 0 & -2 & -2 & 2 & 2 & 2 & 2 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & -2 & -2 & -2 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -2 & -2 & 2 & 2 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & -2 & -2 & -2 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{bmatrix}
$$  \tag{A.1}

The diagonal relaxation matrix $S$ for the D3Q19 lattice model is given as:

$$
S = \text{diag}(0, s_1, s_2, 0, s_4, 0, s_4, 0, s_4, 0, s_4, 0, s_9, s_{10}, s_9, s_{10}, s_{13}, s_{13}, s_{16}, s_{16}, s_{16}),
$$  \tag{A.2}

where $s_1$, $s_2$, and $s_{10}$ are free parameters and we use $s_{1,2,10} = 1$; $s_9$ and $s_{13}$ are related to the kinematic viscosity, $\nu$, through Eq. 2.25 by $s_{9,13} = 1/\tau$; $s_4$ and $s_{16}$ are chosen to satisfy the
following relation:
\[
\Lambda = \left( \frac{1}{s_9} - \frac{1}{2} \right) \left( \frac{1}{s_k} - \frac{1}{2} \right) = \frac{3}{16}, \quad k = 4, 16. \tag{A.3}
\]
This \( \Lambda = 3/16 \) results in the boundary wall location implemented via bounce-back exactly in the middle between a fluid and wall node [62].

A.2. The D3Q7 lattice velocity model

The transformation matrix \( M_s \) for the D3Q7 lattice model is given as:
\[
M_s = \begin{bmatrix}
1 & 1 & 1 & 1 & 1 & 1 & 1 \\
0 & 1 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & -1 \\
6 & -1 & -1 & -1 & -1 & -1 & -1 \\
0 & 2 & 2 & -1 & -1 & -1 & -1 \\
0 & 0 & 0 & 1 & 1 & -1 & -1 \\
\end{bmatrix} \tag{A.4}
\]

The diagonal relaxation matrix \( S_s \) for the D3Q7 lattice model is given as:
\[
S_s = \text{diag}(s_0, s_1, s_2, s_3, s_4, s_5, s_6), \tag{A.5}
\]
where \( s_1, s_2 \) and \( s_3 \) are related to the molecular diffusion coefficient, \( D_s \), through Eq. 2.34 by \( s_{1,2,3} = 1/\tau_s \); \( s_0, s_5 \) and \( s_6 \) are a free parameter and set to \( s_{0,5,6} = 1 \); \( s_4 \) is chosen to satisfy the following relation:
\[
\Lambda = \left( \frac{1}{s_1} - \frac{1}{2} \right) \left( \frac{1}{s_4} - \frac{1}{2} \right) = \frac{1}{4}. \tag{A.6}
\]
This \( \Lambda = 1/4 \) provides good accuracy and stability in simulations [62, 70].