AUTOMATIC IN SITU CHARACTERIZATION OF PORE MORPHOLOGY AND WETTABILITIES

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Declaration of Originality

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Ahmed Ahed Marouf Al-Ratrout
July 2nd, 2018
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Ahmed Ahed Marouf Al-Ratrout

July 2nd, 2018
This PhD’s Thesis is dedicated to:

Parents,
My Wife – my love,
My kids: Sultan, Meera and Hamdan,
My Brothers (Nour-Allah and Mohammed) and Sisters (Manal and Ahlam),
My Family-In-Law,
Supervisors,
Teachers,
Colleagues,
Friends,
Imperial College London,
Beloved Country - United Arab Emirates,
Hosted Country - United Kingdom
And Humanity.
Abstract

In many important processes, that control CO$_2$ storage in aquifers, oil recovery, and gas exchange in leaves, for instance, flow is controlled by the interaction of immiscible fluids with a rough surface. In this thesis, we present new automated methods for measuring \textit{in situ} contact angle ($\theta$), fluid/fluid interface curvature, rock surface roughness and pore morphology, applied to segmented pore-scale X-ray images. We first identify and mesh the fluid/fluid and fluid/solid interfaces. A Gaussian smoothing is applied to this mesh to eliminate artefacts associated with the voxelized nature of the image, while preserving large-scale features of the rock surface. Then, for the fluid/fluid interface we apply an additional local uniform curvature smoothing and adjustment of the mesh. We then track the three-phase contact line, and the two vectors that have a direction perpendicular to both surfaces: the contact angle is found from the dot product of these vectors where they meet at the contact line. This calculation can be applied at every point on the mesh at the contact line. We automatically generate contact angle values representing each invaded pore-element in the image with high accuracy.

We validate the developed approach using synthetic three-dimensional images of a spherical droplet of oil residing on a tilted flat solid surface surrounded by brine with different resolutions of known curvature and contact angle. We show that we are able to estimate contact angle to within 3$^\circ$ and curvature with error less than 9\% when the sphere is 2 or more voxels across, which indicates that with a 2 $\mu$m voxel size we can accurately capture curvatures as high as 0.5 $\mu$m$^{-1}$ and contact angles on pores 4 $\mu$m across.

We then apply the developed methods to study the \textit{in situ} distributions of contact angle and oil/brine interface curvature measured within mm-size rock samples from a producing hydrocarbon carbonate reservoir imaged after waterflooding at elevated temperature ($60^\circ$–$80^\circ$) and reservoir pressure (10MPa) using X-ray micro-tomography [Alhammadi et al., 2017b]. We
analyse their spatial correlation on a pore-by-pore basis using a novel approach combining the automated methods for measuring contact angles and oil/brine interfacial curvature, with a recently developed method for pore network extraction [Raeini et al., 2017]. Also, we studied the contact angle and interfacial curvature correlation on a ganglion-by-ganglion basis using a ganglia labelled images. The automated methods allow us to study image volumes of diameter approximately 1.92 mm and 1.2 mm long, obtaining hundreds of thousands of values from a dataset with 435 million voxels. We calculate the capillary pressure based on the mode oil/brine interface curvature value, and associate this value with a nearby throat in the pore space. Then, we quantify rock surface roughness and assess its impact on the wettability of the rock. Rougher surfaces are associated with a wider range of local contact angle. Finally, we establish a methodology to characterise pore morphology (wall curvature) in complex porous materials to determine their potential for developing fluid layer flow in mixed-wet systems. We apply this on mm-sized three-dimensional images of a beadpack, a sandpack, two sandstones (Doddington and Bentheimer) and six carbonates (Portland, Ketton, Estaillades and the aforementioned 3 reservoir samples from the Middle East [Alhammadi et al., 2017b]), representing porous media with an increasing degree of pore-scale complexity.

In this thesis, we demonstrate the capability of our methods to distinguish different wettability states in the samples studied: water-wet, mixed-wet and oil-wet. The measured contact angle and oil/brine interface curvature in the Middle Eastern reservoir samples are spatially correlated over approximately the scale of an average pore. There is a wide distribution of contact angles within single pores. A range of local oil/brine interface curvature is found with both positive and negative values. There is a correlation between interfacial curvature and contact angle in trapped ganglia, with ganglia in water-wet patches tending to have a positive curvature, and oil-wet regions seeing negative curvature. We observed a weak correlation between average contact angle and pore size, with the larger pores tending to be more oil-wet. Also, we identify a distinct pore-morphology signature where unconsolidated media have a large majority of pores with positive curvature, while consolidated media tend to be composed of more pores with negative curvature. In unconsolidated media there is no impact of relative pore size on pore curvature, in contrast to consolidated media for which we observe a tendency for the small pores to have negative pore curvature, while the large pores have positive ones. Both pore morphology and wettability have a large impact on the potential for layer flow. The signature of consolidated media having a wide range of positive and negative curvatures promotes layer
flow in mixed-wet systems. Importantly, this allows us to understand the tendency for the large pores in mixed-wet systems to have the positive fluid interfacial curvature, while small pores show a broader range of both positive and negative fluid interfacial curvature.
List of Publications

Journal Articles


**Conference Proceeding Papers**

**Presenting Author**


7. **AlRatrout, A.**, Bijeljic, B., and Blunt, M. J., *In situ* pore-scale characterization of contact angle, Imperial College Consortium on Pore-Scale Modelling, January 2016, Imperial


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5.18 **Pore wall curvature signatures.** Histograms of normalized pore curvature (red) and pore diameter (blue) of (A) a beadpack, (B) a sandpack, (C) Ketton, (D) Bentheimer, (E) Doddington, (F) Estaillades, (G) Portland, (H) WW sample, (I) MW sample and (J) OW sample. The beadpack and sandpack are have pores with positive curvature, while the rest consist of pores with both negative and positive curvature. The smaller pores tend to have negative curvature while large pores have values close to zero.

5.19 **Pore curvature visualizations.** Three-dimensional view of pores from sample-2 with diameters of 13.8 µm (A), 14.2 µm (B), 126.2 µm (C), 138.2 µm (D), 13.7 µm (H), 19.9 µm (G), 53.5 µm (F) and 58.5 µm (E). The mode curvature in the small pores (A-B) is positive and in (H-G) is negative.

5.20 **Relationship between the variation in pore curvature and ganglion interface curvature.** The measured pore curvature and oil/brine interface curvature, as a function of pore diameter and ganglion volume, respectively, for (A) WW, (C) MW and (E) OW samples. In (B), (D) and (F), we present a ganglion in WW, MW and OW samples, respectively. The measurements of the ganglion of (B), (D) and (F) are indicated with green circles on (A), (C) and (E).

5.21 **Flux number and pore diameter correlation** The estimated flux number which is the ratio of the sum of the diameters of the throats connected to a pore divided by the pore diameter, as a function of pore diameter for (A) a beadpack, (B) a sandpack, (C) Ketton, (D) Bentheimer, (E) Doddington, (F) Estaillades, (G) Portland, (H) WW sample, (I) MW sample and (J) OW sample. The smaller pores, with negative curvature (round shape), tend to have smaller flux number (more isolated) while large pores, with positive curvature (star shaped), tend to have larger flux number (more connected).

5.22 **Pore wall curvature signatures.** Signature pore morphology figures combining histograms of pore diameter (blue) and plots of pore flux number as a function of normalized pore curvature (red dots) of (A) a beadpack, (B) a sandpack, (C) Ketton, (D) Bentheimer, (E) Doddington, (F) Estaillades, (G) Portland, (H) WW sample, (I) MW sample and (J) OW sample. The smaller pores tend to have low pore flux number while large pores have high values. This is in agreement with the signature shown in Figure 5.18.
Nomenclature

$\theta$  Contact Angle

$\alpha$  Weight factor for the adjacent vertices, $j \in \text{adj}(i)$

$\beta$  Gaussian relaxation factor

$\gamma$  Curvature relaxation factor

$\kappa$  Interface curvature

$\kappa_i$  Vertex curvature

$\langle \kappa_i \rangle$  Vertex curvature smoothing operator

$\mathbf{R}$  Real number

$\mathbf{R}^3$  Real number in three dimension space

$\mu$  Viscosity/mean value

$\mu\text{m}$  micro-meter, unit

$\mathcal{K}$  Quadrilateral simplicial complex

$\Psi$  The mean of the measured value in spatial correlation, used Eq. ?? and Eq. ??

$\overrightarrow{p_i c_{f_j}}$  Vector connecting $c_{f_j}$ to a vertex at position $p_i$

$\overrightarrow{p_i c_{f_j}}$  Vector connecting a vertex at position $p_i$ to the adjacent face center $c_{f_j}$

$\overrightarrow{p_i c_{e_j}}$  Vector connecting adjacent $c_{f_j}$ to adjacent $c_{e_j}$

$\pi$  Mathematical constant approximately equal to 3.14159, used in Eq. 5.11
Ψ Measurement value in a spatial correlation, used Eq. 5.3 and Eq. ??

ρ Correlation coefficient, used in Eq. ??

σ Surface tension coefficient/standard deviation

σ² Variance of a measured distribution

A_i Vertex area defined as the sum of adjacent calculated \( A_j \)

b_i Distance to the calculated average of the positions of adjacent vertices used in Gaussian and curvature smoothings

d_i Distance of the average displacements during the Gaussian and curvature smoothings used to move back the vertices to the average of their original positions to avoid shrinkage in the interfaces.

\( F_C \) Capillary force

n_i Vector normal to vertex defined by the calculated vertex area \( A_i \)

n_l Vector normal to the bounding contour line of an interfacial element \( (l) \)

o_i Original position of vertex \( i \), before a smoothing process

p_i Final position of vertex \( i \), after a smoothing process

q_i Temporary position of vertex \( i \), during a smoothing process

s_i Interface tangent vector

z Zone of mesh \( M \) that represents an interface, which is a set of \( n \) faces, \( z := \{f_1, f_2, \ldots, f_n\} \)

\( z_1 \) face-zone of mesh \( M \) that represents oil/rock interface

\( z_2 \) face-zone of mesh \( M \) that represents oil/brine interface

\( z_3 \) face-zone of mesh \( M \) that represents brine/rock interface

\( \theta_i \) Contact angle computed at vertex \( i \)

\( \theta_{adv} \) Advancing contact angle

\( \theta_{rec} \) Receding contact angle
NOMENCLATURE

\[ \varepsilon \] Statistical length

\[ ^\circ C \] Celsius degree, unit

\[ A_j \] Triangular area, between vectors \( \overrightarrow{p_i c_f} \) and \( \overrightarrow{c_{e_j} c_f} \), adjacent to vertex at position \( p_i \)

\[ A_n \] Nominal area

\[ A_p \] Pore area

\[ adj(i) \] Total adjacent vertices to a vertex \( i \)

\[ c_{e_i} \] Edge center

\[ c_{e_j} \] Adjacent edge center

\[ c_{f_i} \] Face center

\[ c_{f_j} \] Adjacent face center

\[ dV \] Volume of a control volume

\[ E \] Set of edges, \( E := \{ e \in \mathcal{E} \} \)

\[ e \] edge of a face \( (f) \) and a set of two connected vertices, \( e := \{ p_1, p_2 \} \)

\[ F \] Set of faces, \( F := \{ f \in \mathcal{F} \} \)

\[ f \] face of mesh \( M \) and a set of four connected edges, \( f := \{ e_1, e_2, ..., e_4 \} \)

\[ i \] Vertex

\[ j \] Adjacent vertex to a vertex \( i \)

\[ k_r \] Relative permeability

\[ l \] Boundary line of an interfacial element

\[ L_{\text{grain}} \] Grain length estimated using Eq. 5.11

\[ M \] Multi-zone extracted mesh from multi-phase segmented images

\[ N \] Total number of measurements

\[ P_c \] Capillary pressure

xxvi
r₁, r₂ Principal radii of curvature

\( R_a \) Curvature-based roughness parameter

\( R_c \) Mean radius of curvature

\( R_p \) Pore radius in voxels

\( R_p \) Pore radius

\( R_s \) Pore roughness ratio

\( R_κ \) Curvature radius kernel

\( R_{Gauss} \) Gaussian radius kernel

\( r_{i→j} \) Distance between the measurements at positions \( i \) and \( j \), used in Eq. ??

\( S \) Interface surface/rock surface area in Eq. 5.11

\( S \) Single-zone extracted mesh from dry segmented images

\( stdCA \) Standard deviation of the measured contact angle distribution, used in Eq. ??

\( V \) Vertex set/Image volume in Eq. 5.11

\( V_{BR} \) Brine/rock interface vertex set

\( V_{CL} \) Contact line vertex set

\( V_{OB} \) Oil/brine interface vertex set

\( V_{OR} \) Oil/rock interface vertex set

2D Two dimensions

3D Three dimensions

\( % \) percentage

\( ® \) Registered trademark

CCS Carbon Capture and Sequestration

CO₂ Carbon dioxide
NOMENCLATURE

CT  Computed tomography
h  Radius of a capillary tube
kg  Kilogram, unit
km  Kilo-meter, unit
m³  cubic meter, unit
mm  Milli-meter, unit
mPa-s  Millipascal-second, unit
MW  Mixed-wet sample
OW  Oil-wet sample
pH  Potential of hydrogen, unit
USBM  U.S. Bureau of Mines method for indicating wettability
wt%  weight percentage
WW  Water-wet sample

Subscripts

κ  Curvature
a  Apparent
adv  Advancing
BR  Brine/rock interface
c  Capillary (in $P_c$) and curvature (in $R_c$)
Gauss  Gaussian
i  Vertex
j  Adjacent vertex to a vertex $i$
n  Nominal
NOMENCLATURE

\( OB \) Oil/brine interface

\( OR \) Oil/rock interface

\( p \) Pore

\( rec \) Receding

\( S \) Interface surface

**Superscripts**

\( ^\circ \) Degree

\( ^{th} \) Ordinal indicator
1. Introduction and Research Objectives
1.1 Introduction

Determining how carbon dioxide can be stored securely in underground aquifers, quantifying the rate at which oil and gas are recovered from hydrocarbon reservoirs and shale, the performance of fuel cells and catalysts, the efficiency of gas exchange in leaves and lungs, how well fabrics resist or soak up water, and the design of water-repellent surfaces, all crucially depend on wettability: how fluid phases interact with solid surfaces within porous structures. From a fundamental point of view, it is still unknown how wettability controls the fluid configurations in porous materials and what drives the formation of fluid layers leading to either enhanced or impeded flow and transport [Datta et al., 2014, de Gennes, 1985, Reynolds et al., 2017, Sanchez et al., 2005, Sun et al., 2005, Zhao et al., 2016].

The interaction of fluids with a rough surface is traditionally described using the Wenzel [Wenzel, 1936] and Cassie-Baxter [Cassie and Baxter, 1944] models that are used to calculate a single effective contact angle on a rough surface [Hirasaki, 1991, Lafuma and Quéré, 2003]. This approach has been used to interpret the transition from water-wet to water-repelling conditions in human skin, leaves, insect wings and feathers, for instance, and on manufactured surfaces [Bromberg et al., 2017, Nychka and Gentleman, 2010, Sanchez et al., 2005, Sun et al., 2005]. However, this work deals with external surfaces and does not quantify the typical wetting states within a material and the relationship with surface roughness: for example, what are the contact angles and fluid arrangements inside a leaf, lung tissue or rocks, and how does this affect fluid flow?

In porous rocks where portions of the solid surface have undergone a wettability alteration caused by the direct contact of surface-active components with the solid [Buckley et al., 1989] it has been suggested that separated water-wet and oil-wet regions of the pore space are present [Blunt, 2017, Kovscek et al., 1993] and this has been observed directly using atomic force microscopy in chalk [Hassenkam et al., 2009]. The advent of high-resolution X-ray microtomography has made it possible to image the rock and fluids within the pore space at micron resolution (see, for instance [Berg et al., 2013, Pak et al., 2013, 2015]) and from this to determine contact angles directly at high temperatures and pressures representative of deep underground reservoirs [Andrew et al., 2014, Khishvand et al., 2016, 2017, Pak et al., 2015]. The behaviour is somewhat different from the theory: a wide distribution of contact angle is seen, even in
CHAPTER 1. INTRODUCTION AND RESEARCH OBJECTIVES

Figure 1.1: A schematic of wettability and length scales in porous media flows. The right-hand figures show images of oil retained within the pore space of water-wet and oil-wet (water repellent) samples, described later in this thesis. In a water-wet rock, the oil is trapped in quasi-spherical ganglia with contact angles less than 90°. For an oil-wet rock, oil is retained in layers that follow the surface roughness with both positive and negative values of the curvature $\kappa$. This allows the oil to flow to low saturation, facilitating recovery at the km scale (left figure). The middle figures show how the samples are selected from cm-scale cores extracted from a reservoir.

The range of observed contact angles is likely to be a result of the roughness of the rock surfaces. However, methods to quantify roughness have been concerned with the external surfaces of objects and are not directly applicable to porous materials [Lai et al., 2014, Leach et al., 2008, Mah et al., 2011, Xie et al., 1999].

1.1.1 Research Objectives

X-ray methods are now widely used as they allow non-destructive imaging of the rock and fluids in the pore space under varying pressure, temperature, salinity and/or wetting conditions [Andrew et al., 2013, 2014, Idowu et al., 2015]. X-ray imaging has been used to measure...
fluid/fluid interface curvature [Andrew et al., 2014, Armstrong et al., 2012, Singh et al., 2016] and contact angle [Andrew et al., 2014, Klise et al., 2016, Scanziani et al., 2017] between immiscible fluids at the pore scale. Also, recent studies have employed some of these methods for the in situ characterization of wettability and pore-scale multiphase displacements in natural porous media [Khishvand et al., 2016, 2017, Lv et al., 2016]. However, measuring contact angle and fluid/fluid interface curvature in typical micro-CT images with low resolution (large voxel size) and for complex rocks is still not routine and all these methods are either cumbersome or may introduce significant errors generated by voxelization artefacts.

Also, one of the important parameters defining wettability is the macroscopic rock surface roughness at the pore scale. However, to date, the correlation of surface roughness with contact angle and fluid/fluid interface curvature at the pore scale has not been studied. This is of great importance for the understanding of multiphase flow properties: such correlations have a major impact on relative permeability and recovery, predicted using pore scale modelling, but have never been directly measured [Al-Dhahli et al., 2012, Bakke and Øren, 1997, Blunt, 2001, Fatt, 1956, Piri and Blunt, 2005, Valvatne and Blunt, 2004].

Furthermore, natural porous materials display a wide range of pore shapes as a result of the different chemical and physical processes by which they are formed [Bensaude-Vincent et al., 2002]. Pore morphology, especially wall curvature, is a vital parameter in designing porous materials [Sanchez et al., 2005], and can play a key role in understanding wettability alteration and fluid configurations in multiphase flow applications [Blunt, 2017, Kovscek et al., 1993]. In mixed-wet systems, the fluid configurations can be controlled by the local pore morphology or roughness. Hence, it would be of great interest if one could a priori determine signature of pore morphology of a porous medium which would uniquely define potential for either enhanced or impeded flow and transport.

The aim of this work is to provide an automated rapid method to provide an accurate characterization of pore-scale wettability (contact angle), fluid/fluid interface curvature, surface roughness and pore morphology. We apply the new approach to segmented pore-scale X-ray images. This method fits a smoothed surface with locally uniform curvature to fluid/fluid interfaces and records its intersection with the solid. This approach removes the subjectivity associated with the aforementioned methods, while providing many hundreds of thousands of measurements throughout the sample. This opens up new possibilities to characterise wetta-
bility at the mm-scale. However, to date, the spatial correlation of wettability has not been studied, nor its relation to fluid/fluid interfacial curvature, surface roughness and pore size. This is of great importance for the understanding of multiphase flow properties: such correlations have a major impact on relative permeability and recovery, predicted using pore-scale modelling, but have never been directly measured [Al-Dhahli et al., 2012, Bakke and Øren, 1997, Blunt, 2001, Fatt, 1956, Piri and Blunt, 2005, Valvatne and Blunt, 2004].

1.1.2 Novel Contributions and Scientific Achievements

The algorithms developed in this study used the [OpenFOAM, 2014] platform for the numerical implementation of our work. The main achievements in this research are:

1. A novel automated rapid and accurate approach to quantify in situ wettability, fluid/fluid interface curvature, surface roughness and pore morphology in pore-scale images. Later in this thesis, we show that we are able to estimate contact angle to within $3^\circ$ and curvature with error less than 9% when the sphere is 2 or more voxels across, which indicates that with a 2 $\mu$m voxel size we can accurately capture curvatures as high as $0.5 \mu m^{-1}$ and contact angles on pores 4 $\mu$m across.

2. A new automated approach for combining the measurements of contact angle, fluid/fluid interface curvature, pore wall curvature and surface roughness to pore-segmented and ganglion-labelled images. A pore-segmented image can be extracted by a pore-network modelling technique [Dong and Blunt, 2009, Lindquist and Venkatarangan, 1999, Lindquist et al., 2000, Raeini et al., 2017, Silin and Patzek, 2006], in this study we use a generalized network extraction algorithm [Raeini et al., 2017] to generate pore-segmented images. We can allocate measurements to each pore and ganglion.

3. Two new methods developed to analyse surface roughness applied on pore-scale micro-CT images. The results indicate that roughness is correlated with in situ measurements of contact angle and fluid interfacial curvature on carbonate rock samples with different wettability states. In oil-wet carbonates oil layers follow the rock/fluid interface (roughness), while in the water-wet carbonate no correlation of oil-water curvature with roughness is observed.
CHAPTER 1. INTRODUCTION AND RESEARCH OBJECTIVES

4. A novel method developed to characterize the signature of pore morphology in complex porous materials. A wide range of positive and negative curvatures promotes layer flow in mixed-wet systems. Importantly, this allows us to understand the tendency for the large pores in mixed-wet systems to have positive fluid interfacial curvature, while small pores show a broader range of both positive and negative fluid interfacial curvature.

5. For the first time, the spatial correlation of in situ contact angle and oil/brine interface curvature has been studied in carbonate rock samples from a producing oil reservoir with different wettabilities - water-wet (WW), mixed-wet (MW) and oil-wet (OW). The results show that the contact angle and curvature are correlated over approximately a pore size.

6. For the first time, in situ contact angle and fluid/fluid interface curvature on a pore-by-pore and ganglion-by-ganglion bases have been studied. The mode curvature of trapped ganglia is correlated with the contact angle.

1.1.3 Thesis Structure

The unifying theme of this thesis is the development of characterization of in situ wettability automatically. It provides new insights into physics of the wettability development inside complex materials.

This thesis is organised as follows:

Chapter 2 introduces a review of the literature relevant to this work and background information is presented related to wettability, fluid/fluid interface curvature, surface roughness and pore morphology.

Chapter 3 describes the workflow of the method devised to obtain contact angle and fluid/fluid interface curvature distributions automatically, and the generated pore-segmented image and other related properties. In this section we also briefly describe the altered wettability experiments [Alhimmadi et al., 2017b] used for testing our method, see Section 3.3.
Chapter 4 we validate the accuracy of contact angle and fluid/fluid interface curvature measurements on synthetic three-dimensional images of a spherical droplet of oil residing on a tilted flat solid surface. Also, we validate our surface roughness measurements on pore structure using surface mapping. Then, validate the allocation of measurements of contact angle, fluid/fluid interface curvature and surface roughness for each pore.

Chapter 5 demonstrates the application of our methods to in situ wettability, surface roughness and pore morphology measurements in X-ray images of three limestone rock cores. Also, we discuss the results of the calculated capillary pressure distribution and contact angle spatial correlation, and their relation to pore size. Moreover, we discuss the relationships between wettability, oil/brine interface curvature and surface roughness and pore morphology.

Chapter 6 presents the main conclusions and accomplishments of this research and provides suggestions for future work.
2. Literature Review


2.1 Background

Wettability is a characteristic that reflects complex fluid/rock interactions [Punase et al., 2014, Wang and Gupta, 1995], and which determines the microscopic distribution of fluid phases in the pore space. It determines, for instance, the efficiency of fuel cells, the security of geological carbon dioxide storage, hydrocarbon recovery, remediation of ground water contamination and gas exchange in leaves [Anderson, 1986a, Blunt, 2017, Morrow, 1990, Wan et al., 2014]. In the context of oil recovery, it controls the pore-scale arrangement of fluids in the rock which in turn effects the macroscopic properties describing multiphase flow in porous media, such as capillary pressure \( P_c \) and relative permeability \( k_r \) [Anderson, 1986a, Bradford and Leij, 1996, Goda and Behrenbruch, 2011]. Therefore, quantifying wettability is vital for correctly modelling fluid flow and displacement processes in porous media.

Wettability can be inferred through indirect averaged measurements on cm-sized rock samples in the laboratory, commonly expressed using the Amott [Amott, 1959] and USBM indices [Donaldson et al., 1969], or by studying relative permeability characteristics [Anderson, 1986b]. At the pore scale, wettability is defined in terms of the contact angle between the fluids residing in the pore space [Blunt, 2017]. Conventionally, laboratory contact angle measurements are made using smooth mineral surfaces, typically quartz and calcite to represent sandstones and carbonates, respectively [Adamson and Gast, 1997, Goda and Behrenbruch, 2011, Good, 1979, Neumann and Good, 1979, Santini et al., 2013]. However, reservoir rock contains other minerals and rough surfaces, while fluid distributions are established by a displacement, which means that equilibrium measurements on chemically pure surfaces may not be representative of the contact angle in a reservoir rock under flowing conditions [Donaldson et al., 1969]. Furthermore, the contact angle and fluid/fluid interface curvature may vary across the pore space due to differences in surface roughness, mineral complexity and displacement type [Radke et al., 1992]. Figure 2.1 provides a simple view of a single pore showing, schematically, the contact angle and curvature for water-wet and oil-wet systems. Furthermore, contact angles hysteresis due to surface roughness, advancing contact angles \( \theta_a \) during imbibition displacement process (increase in water saturation) are typically found to be significantly larger than receding contact angles \( \theta_r \) during drainage displacement process (reduction in water saturation). In Morrow [1975] several models have been developed for this contact angle hysteresis by measuring both
advancing and receding angles in a number of smooth and roughened Teflon tubes and relating these to the intrinsic contact angle as measured at rest on a smooth surface. Although one would expect to see no difference between advancing and receding contact angles in completely smooth tubes (referred to as Class I model), some hysteresis was observed (Class II model). Morrow explained this by minor inaccuracies in the tube manufacturing process. Following roughening of the tubes, substantially more hysteresis was observed (Class III model). Also, recent studies have investigated the effect of contact angle hysteresis on capillary pressure using sandstones Raeesi et al. [2014] and effect of surface roughness in capillary tubes of uniform cross-section Raeesi et al. [2013]. Due to fact that surface wall heterogeneities, including structural (surface roughness) and chemical ones, contact angle cannot be represented by a single static contact angle Anderson [1987], Andrew et al. [2014], Hiemenz and Rajagopalan [1979], Morrow [1975] Our main objective in this study is to measure micron-scale roughness in each individual pore and investigate its relationship with the measured contact angle and curvature of fluid/fluid interfaces. In situ measurements, however, are difficult and have remained a challenge, since it is necessary to elucidate the pore-scale configurations of fluids at representative conditions inside a rock sample [Brown and Fatt, 1956, Morrow, 1975].
Figure 2.1: **Contact angle and interfacial curvature variation in pores.** A schematic view of a pore in two systems with different wettability states: The micron-scale rock surface roughness (or curvature) may cause variations in the contact angle ($\theta$) and oil/brine interface curvature ($\kappa$). An example of contact angle variation is illustrated on the water-wet pore (left), where the contact angle $\theta_1 \sim 60^\circ$, $\theta_2 \sim 30^\circ$ and $\theta_3 \sim 80^\circ$, but the curvature is constant and positive, as the oil bulges out into the water indicating locally a positive capillary pressure. The curvature of the oil layer in the oil-wet pore (right) follows the curvature of the rock surface, which is negative ($-\kappa$) where there is a convex surface and positive ($+\kappa$) where the surface is concave.

The advent of micron-resolution imaging tools has made it possible to study the pore-scale arrangement of fluid phases [Andrew et al., 2013, Pak et al., 2015, Reynolds et al., 2017]. In particular, X-ray methods are now widely used as they allow non-destructive imaging of the rock and fluids in the pore space under varying pressure, temperature, salinity and/or wetting conditions [Andrew et al., 2013, 2014, Idowu et al., 2015]. X-ray imaging has been used to measure contact angles in capillary tubes [Hashmati and Piri, 2014]. However, to date, few studies have measured contact angle and fluid/fluid interface curvature in rock samples. For contact angle measurements, Andrew et al. [2014] measured contact angle \textit{in situ} in a sample of Ketton limestone for a water-wet CO$_2$/brine system where the contact angles were measured manually on a raw image of the plane perpendicular to the three-phase contact line. This approach has been used to study contact angles in sandstones and bead packs [Garing et al.,...
2017, Khishvand et al., 2016, 2017, Lv et al., 2016, Tudek et al., 2017]. The problem with this approach is that it is time-consuming and may introduce subjective bias. Scanziani et al. [2017] extended this approach by fitting a circle on the fluid/fluid interface and a line to the fluid/rock interface on two-dimensional slices perpendicular to the three-phase contact line. Klise et al. [2016] developed another automated contact angle measurement that was applied to fluids in a bead pack with varying wettability characteristics. In this approach planes were fitted to the fluid/fluid and rock/fluid interfaces and the angle between them computed. The latter two methods, however, were developed based on fitting planes/lines to voxelized images. Measuring contact angle in typical micro-CT images with low resolution (large voxel size) and for complex rocks is still not routine and all these methods are either cumbersome or may introduce significant errors.

For fluid/fluid interface curvature, Andrew et al. [2014], Armstrong et al. [2012], Singh et al. [2016] and Li et al. [2018] have used Avizo Fire® to measure interfacial curvature, where the curvature measurement is applied on a smoothed surface using just a Gaussian smoothing technique. The issue with this approach is that Gaussian smoothing alone is not adequate to preserve the physical nature of fluid/fluid interface; for instance, a typical spherical droplet residing on a solid surface would be expected to have a constant curvature, but this constraint is not introduced into the method.

## 2.2 Physical description

Figure 2.2 provides a simplified view of our approach applied in a circular capillary tube, where the fluid/solid and fluid/fluid interfaces are shown. We assume that the fluid/fluid interface has a constant curvature that is related to the local capillary pressure through the Young-Laplace equation:
Figure 2.2: **Physics of wettability measurements.** A schematic view of two fluids in a cylindrical tube with a contact angle $\theta$.

\[
P_c = P_{\text{fluid}1} - P_{\text{fluid}2}
\]
\[
= \sigma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) = \kappa
\]  \hspace{1cm} (2.1)

\[
P_c = \frac{2\sigma}{R_c}
\]  \hspace{1cm} (2.2)

where $P_c$ is capillary pressure, $\sigma$ is the interfacial tension, $r_1$ and $r_2$ are the principal radii of curvature and $\kappa$ is the total curvature of the fluid/fluid interface. $R_c$ is the mean radius of curvature and $\theta$ is the contact angle.
2.2.1 Interface curvature

The following theory has been adopted in this work for estimating local curvature values for vertices belonging to a surface: in Figure 2.3 a volume element enclosing an interfacial surface $S$ shown in Figure 2.3 of a volume, $dV$ as indicated in Figure 2.2, containing an interface between oil and brine. The curvature at vertex position $q_i$ can be calculated by dot product with the vertex normal $n_i$ and vector $s$ which is normal to the contact line $l$ tangent to the interface $S$.

![Diagram of Fluid/fluid interface curvature theory](image)

**Figure 2.3: Fluid/fluid interface curvature theory.** A schematic of a control volume ($dV$), as indicated in Figure 2.2, containing oil and brine as two immiscible fluids, separated by and interface surface ($S$) and bounding contour line ($l$).

The capillary force active on the interface can be defined, in terms of capillary pressure $P_c$ applied on interface surface area $A_s$, which is equivalent to the active tension force $t_s$ applied on contact line $l$ that encloses interface surface, as:

$$F_C := \int_{A_s} P_c \cdot dA_s = \oint_{l} t_s \cdot dl \quad (2.3)$$

where, the interfacial tension force active on the interface can be defined as:

$$t_s = \sigma \cdot s_s \quad (2.4)$$
where $\sigma$ is the interfacial tension scalar in the direction of $s_s$ tangent to interface surface $S$ and normal to contact line $l$. From the Young-Laplace equation (Eq. 2.1):

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

(2.5)

where $\kappa$ is the curvature value of the interface surface. We can calculate $\kappa$ for the interface surface using:

$$\kappa = \frac{1}{A_s} \oint_{l_s} s_s \cdot dl$$

(2.6)

And similarly, we can estimate $\kappa$ for the contact line $l$ using:

$$\kappa = \frac{1}{dl} \oint_{l} s_s \cdot n_l$$

(2.7)

### 2.2.2 Contact angle

The physical heterogeneities of roughness complexity in the solid rock wall can vary in scale. This scale can vary from the macro-scale that represents the topological solid boundaries which forms the actual pore-element structure, down to micro-scale due to micro-porosity ($\mu \phi$), which normally falls below the resolution of the image. A literature review on the numerical and experimental contact line/angle dynamics can be found in Meakin and Tartakovskiy [2009] and Blunt [2017].

For measuring contact angles in three-dimensional micro-tomography images of more complex surfaces, such as a reservoir rock surface, we define normal vectors at the contact line and perpendicular to the fluid/fluid and fluid/rock interfaces, see Figure 2.4. At a contact point of the contact line, the equation to calculate the contact angle lies between two vectors; contact point – interface and contact point – solid, can be written as:

$$\theta = \pi - \cos^{-1} \left( n_{z_2} \cdot n_{z_3} \right)$$

(2.8)

where, $n_{z_2}$ is the vector normal to the fluid interface ($z_2$) at the contact line, and $n_{z_3}$ is the normal vector to the solid wall at the contact line.
2.2.3 Surface roughness

Many methods in the literature used to quantify rock roughness have been applied only on the external side of rock faces. These methods are based on either empirical [Mah et al., 2011, 2013], statistical [Belem et al., 2000, Hong et al., 2008, Leach et al., 2008] or fractal characterizations of the rock surface [Jiang et al., 2006, Xie et al., 1999]. Although these methods might be applicable to 2D profiles, they cannot capture the roughness of a 3D surface, and combining several methods is required [Hong et al., 2008, Leach et al., 2008]. The geometry of a surface can be considered to be comprised of two distinct components; one that may be referred to as the shape in terms such as waviness or curvature, and a random component sometimes referred to as unevenness [ISRM, 1978]. The unevenness of the rock surface at the pore scale is mostly beyond the resolution of micro-CT images, and its impact on the apparent contact angle and curvature may be small compared to the rock surface waviness or curvature. Recent studies have measured roughness from the curvature of a rock surface [Lai et al., 2014, Lavoué, 2009]. However, these methods are either applied on large-scale rock faces or the external surface of other objects.

In this work, we propose two methods to measure the rock surface roughness at the pore-scale. The first measures the local curvature of the rock surface. We smooth the extracted rock
surface using the curvature smoothing method that we developed in this work to eliminate all the voxel-induced artefacts of the image while retaining macroscopic concave and convex features. The second method is based on measuring the rock surface roughness ratio coefficient ($R_s$). This coefficient was originally defined by El-Soudani [1978] as the ratio between the actual area $A_t$ and the nominal area $A_n$:

$$ R_s = \frac{A_t}{A_n}, \quad \text{with} \quad R_s \geq 1 $$

The nominal surface is defined here as a surface that does not have irregularities and is geometrically perfect, so for example a nominal area of a rectangular projection on a flat rough surface is calculated by multiplying the length and width. To date, the calculation of $R_s$ has only been applied to surfaces that are macroscopically flat [Belem et al., 2000, ISRM, 1978, Mah et al., 2011, 2013]. To apply this method to rock pores, where the surface is not flat but rather curvy and quasi-spherical, we use for $R_s$ the area of inscribed spheres that represent the size of the pores which are extracted from micro-CT images using a generalised network model approach [Raeini et al., 2017]; details of these calculations are provided in Chapter 4.

Furthermore, we will use the *in situ* measured distributions of contact angles and curvature for oil/brine interfaces within mm-size water-wet (WW), mixed-wet (MW) and oil-wet (OW) carbonate rock samples [Alhammadi et al., 2017b] to analyse their correlation with rock surface roughness on a pore-by-pore basis. The measured contact angles are for a reservoir rock/crude oil/brine system measured at the high temperatures and pressures encountered in deep subsurface formations. Furthermore, we will relate measured values of the rock surface roughness, the contact angle and oil/brine curvature deviations to the pore sizes extracted by a generalized pore-network modelling approach [Raeini et al., 2017].

Next, in Chapter 3, we discuss the mathematical approach of our algorithm.
3. Numerical methods
3.1 3D contact angle and interfacial curvature measurements

We now describe how to apply our concept and the steps of our algorithm to measure contact angle and fluid/fluid interface curvature in three-dimensional pore-space images.

3.1.1 Surface extraction

In this step, we show how we extract a surface mesh from a segmented voxelized image. We use a method originally developed for extracting a single zone mesh for dry (solid only) images from Raeini et al. [2014]: here we generate a multi-zone mesh for representing multiple contacted phases. The extracted mesh $M$ is a vertex set $V$ given by $(\mathcal{K}, \mathbf{p})$, where $\mathcal{K} \subseteq 2^V$ is a quadrilateral simplicial complex, and $V \rightarrow \mathbb{R}^3$ is a function, which maps every vertex $i \in V$ to its position $\mathbf{p}_i$, see Liu et al. [2002] and Vollmer et al. [1999]. In a three-dimensional voxelized image, typically, vertices are found at a voxel corners. In Figure 3.1, we illustrate the different types of mesh elements that can be extracted.

![Figure 3.1: Mesh elements from a voxelised image. A) A set of two vertices forming an edge, $e$. B) A set of edges forming a face, $f$. C) A set of faces bounding a voxel.](image)

In this work, we let $E := \{e \in \mathcal{K}\}$ be the set of edges and $F := \{f \in \mathcal{K}\}$ be the set of faces of $M$. Each $e := \{\mathbf{p}_1, \mathbf{p}_2\}$ is a set of two connected vertices, and each $f := \{e_1, e_2, ..., e_4\}$ is a set of four connected edges. Also, the mesh $M$ is divided into three face-zones: $z_1$ represents the oil/rock interface, $z_2$ is the oil/brine interface and $z_3$ is the brine/rock interface in an oil-brine system. The set of vertices that belong to each zone will be denoted as $V_{OR}$, $V_{OB}$ and $V_{BR}$.
respectively. In addition, \( V_{CL} := \{ p_i \in \{ z_1 \cap z_2 \cap z_3 \} \} \) is the set of vertices which are shared by all three face-zones representing the three-phase contact line. Figure 3.2 illustrates the process of generating the mesh \( M \).

![Image](81x563 to 514x716)

**Figure 3.2: Mesh extraction from multiphase images.** A schematic view that shows the steps of mesh generation. A) In a segmented image, voxels are assigned to different phases. B) Generate connected vertices, edges and faces at interfaces. C) The final mesh with multiple face-zones, \( M := \{ z_1, z_2, z_3 \} \).

In this work, each vertex in the set \( V_{CL} \) is constrained to have a single edge connection with a neighbouring vertex of each zone. To achieve this, we add a face between each contact line edge and each zone and remesh maintaining four vertices for every face. This is to avoid contact line movement complexities during the smoothing step which is discussed next.

### 3.1.2 Interface area and normal vectors

The extracted mesh \( M \) from the previous step is used here as an input data for smoothing. We first define some geometric properties of the mesh before describing the smoothing process itself. All vertices are given a label \( i \). A face centre \( c_{f_i} \), is determined by averaging the position of all adjacent vertices \( p_j \) belonging to the same face, by using:

\[
c_{f_i} = \frac{1}{n_{p_j}} \sum_{p_j \in f_i} p_j, \quad p_j \in f_i
\]

(3.1)

where \( n_{p_j} \) is the number of vertices comprising the face. Then, an edge centre \( c_{e_i} \), is determined by averaging the position of two vertices belonging to this edge:

\[
c_{e_i} = \frac{1}{2} \left( \sum_{p_j \in e_i} p_j \right)
\]


\[ c_{e_i} = \frac{1}{2}(\mathbf{p}_1 + \mathbf{p}_2), \quad \{\mathbf{p}_1, \mathbf{p}_1\} \in e_i \quad (3.2) \]

Further, the calculated \( c_{f_i} \) and \( c_{e_i} \) are used to define two vectors connecting adjacent \( c_{f_j} \) and \( c_{e_j} \) to a vertex at position \( \mathbf{p}_i \):

\[ \overrightarrow{\mathbf{p}_i c_{f_j}} = \mathbf{p}_i - c_{f_j}, \quad \{\mathbf{p}_i, c_{f_j}\} \in c_{f_j} \quad (3.3) \]

\[ \overrightarrow{c_{e_j} c_{f_j}} = c_{e_j} - c_{f_j}, \quad \{c_{e_j}, c_{f_j}\} \in c_{f_j} \quad (3.4) \]

The triangular area, \( A_j \), between vectors \( \overrightarrow{\mathbf{p}_i c_{f_j}} \) and \( \overrightarrow{c_{e_j} c_{f_j}} \) is (see Figure 4):

\[ A_j = \frac{1}{2}(\overrightarrow{\mathbf{p}_i c_{f_j}} \times \overrightarrow{c_{e_j} c_{f_j}}) \quad (3.5) \]

At each vertex \( i \), the adjacent vertices are recorded and we label them as \( j \). The total number of adjacent vertices to each vertex \( i \) is labelled as \( \text{adj}(i) \). We then define \( A_i \) as the sum of adjacent areas, that may include multiple face-zones:

\[ A_i = \sum_{j \in \text{adj}(i)} A_j \quad (3.6) \]
Figure 3.3: Mesh geometric properties calculation. The analysis is performed on the mesh, $M$. A). At each vertex at position $p_i$, the adjacent vertices $p_j$, are also shown. B). Calculation of each vertex area vector $A_{p_i}$ using the calculated adjacent face centres $c_{f_j}$ and edge centres $c_{e_i}$.

We then calculate vertex normals [Thürmer, 2001]. These normals are defined by the area $A_i$ (see Figure 3.4):

$$n_i = \frac{A_i}{|A_i|} \tag{3.7}$$

We also record which face zone the normal belongs to. Then, we apply a correction for the normals of vertices belonging to the contact line ($i \in V_{CL}$) using the nearby vertices that belong to the oil/brine interface ($i \in V_{OB}$), by applying a linear extrapolation using:

$$n_i = \frac{4}{3}n_i - \frac{1}{3}n_j, \quad i \in V_{CL}, j \in V_{OB} \tag{3.8}$$

This is necessary to keep the local curvature of oil/brine interface near the contact line as uniform as the overall curvature. Also, a normal vector to an edge $n_e$, is determined by averaging the vertex normals belonging to this edge. This parameter will be used later for
computing curvature $\kappa$. We calculate $\mathbf{n}_e$ by:

$$\mathbf{n}_e = \frac{1}{2} (\mathbf{n}_1 + \mathbf{n}_2), \quad \{\mathbf{n}_1, \mathbf{n}_2\} \in e_i \tag{3.9}$$

We follow for our smoothing algorithm the convention that $\mathbf{o}_i$ denotes the input vertices at their original positions, $\mathbf{q}_i$ are the current positions before the application of volume preservation, and $\mathbf{p}_i$ the new, modified positions after one iteration of the algorithm, e.g. a smoothing algorithm starts with vertex positions $\mathbf{o} =: \mathbf{q}$ and maps the current positions $\mathbf{q}$ onto $\mathbf{p}$ in one step. Also, the kernel radius ($R_{Gauss}$) of Gaussian smoothing defines the number of iterations in one step. This process of smoothing can be applied iteratively until the result is satisfactory. Next we discuss this smoothing displacement of vertices $\mathbf{o}_i \in \{V_{OB}, V_{BR}, V_{OR}, V_{CL}\}$ of all face-zones in more detail.

Figure 3.4: Multi-interface mesh extraction. Artificial image representing a hemispherical oil droplet whose diameter is 10 voxels (each voxel is $1/10^{th}$ of the sphere diameter), residing on a flat rock surface, forming a contact angle of $90^\circ$ with a surrounding brine phase used to illustrate the algorithm: A) Extracted mesh $M$ with multiple face-zones. B) Point normals defined for each vertex $i$.

### 3.1.3 Volume-preserving Gaussian smoothing

We apply Gaussian smoothing as a Laplacian smoothing [Liu et al., 2002, Vollmer et al., 1999], and then we use an additional step to approximately preserve the volume of the segmented phases [Taubin, 1995]. Through maintaining the volumes of the fluid phases, we also approximately preserve the curvature, which, as we show later, is needed to define contact angle accurately. During this smoothing, the positions of vertices is changed, $\mathbf{o}_i \mapsto \mathbf{p}_i$, while pre-
serving the volume of fluids and rock, and leaving the topology of $\mathcal{K}$ their extracted mesh $M$ unchanged.

Figure 3.5: **Vertices displacement during Gaussian smoothing.** Vertex movement during one iteration of Gaussian smoothing. A) Movement from original positions towards calculated average positions $o_i \mapsto q_i$, Eq. (3.11), and B) from calculated average positions towards new positions $q_i \mapsto p_i$, Eq. (3.14).

The following mathematical steps are used to apply volume-preserving Gaussian smoothing. As shown in Figure 3.5-A, the distance $b_i$ to the calculated average of the positions of adjacent vertices is determined by:

$$b_i = \frac{\sum_{j \in adj(i)} \alpha_j o_j}{\sum_{j \in adj(i)} \alpha_j} - o_i$$  \hspace{1cm} (3.10)

where $\alpha_j$ is a weight factor for adjacent points, calculated by:

$$\alpha_j = |A_{o_j}| + 0.3|A_{o_i}|$$  \hspace{1cm} (3.11)

where the areas are found from Eq. 3.6. This weight is chosen to make the distance between the vertices more uniform (than having $\alpha_j = 1$). Then, the vertices $i$ are moved to $q_i$ by the distances $b_i$ using:
\[
q_i = \begin{cases} 
    o_i + \beta (b_i \cdot n_i|_{z_3}) n_i|_{z_3}, & i \in V_{CL} \\
    o_i + 0.8\beta (b_i \cdot n_i) n_i + 0.2\beta b_i, & i \in M
\end{cases}
\] (3.12)

here \(\beta \in \{0 \rightarrow 1\}\) is used as a relaxation scalar to better control the movement of vertices: later we show a sensitivity analysis to demonstrate the optimal value, and the values of the other parameters introduced later, which give the best results. In this thesis we use \(\beta = 0.1\). The term \((b_i \cdot n_i)n_i\) projects \(b_i\) in the direction perpendicular to the \(V_{OB}\). Also, we only smooth contact line vertices \((i \in V_{CL})\) in the direction of \(n_i|_{z_3}\) to prevent lateral distortion of the contact line.

Then average of the displacements during the Laplacian smoothing step is calculated as follows:

\[
d_i = \frac{\sum_{j \in \text{adj}(i)} \alpha_j (q_j - o_j)}{\sum_{j \in \text{adj}(i)} \alpha_j}
\] (3.13)

Finally, the points are moved back proportional to their average displacement in the Laplacian step \((d_i)\) to new positions \(q_i \mapsto p_i\) by:

\[
p_i = \begin{cases} 
    q_i - (0.3(d_i + (d_i \cdot n_i|_{z_3}) n_i|_{z_3})), & i \in V_{CL} \\
    q_i - (0.3(d_i + (d_i \cdot n) n_i)), & i \in M
\end{cases}
\] (3.14)

Here, \(d_i\) tends to move the vertices to the average of their original positions both laterally and in the direction of \(n_i\) for all interfaces. This movement prevents the shrinkage in the interfaces which is a common problem with the Laplacian smoothing alone [Liu et al., 2002, Vollmer et al., 1999]. This approach is shown in the pseudo-code algorithm-1.
Algorithm 1 Gaussian smoothing algorithm

1: //initialize points with original positions
2: p = o
3: repeat
4:   repeat
5:     for all i ∈ M do
6:       a = adj(i);
7:       if a ≠ 0 then
8:         //calculate weight factor α_j
9:         α_j = |A_o_j| + 0.3|A_o_i|
10:        //calculate the average distance b_i
11:         b_i = \frac{\sum_{j \in \text{adj}(i)} \alpha_j o_j}{\sum_{j \in \text{adj}(i)} \alpha_j} - o_i
12:        //mapping to the calculated average positions o_i ↦ q_i
13:        if i ∈ V_CL then
14:          q_i = o_i + β(b_i \cdot n_i)n_i
15:        else
16:          q_i = o_i + 0.8β(b_i \cdot n_i)n_i + 0.2βb_i
17:        end if
18:     end if
19:   end for
20: //calculate the average distance towards average original positions
21: for all q_i do
22:   d_i = \frac{\sum_{j \in \text{adj}(i)} \alpha_j d_j}{\sum_{j \in \text{adj}(i)} \alpha_j}
23: end for
24: until < R_{Gauss} = 0 >
25: //move vertices back for volume preservation
26: if i ∈ V_CL then
27:   p_i = q_i - (0.3(d_i + (d_i \cdot n_i)|_{z_3})n_i|_{z_3})
28: else
29:   p_i = q_i - (0.3(d_i + (d_i \cdot n)n_i))
30: end if
31: until < iteration = 0 >
At this step, the volume preserving Gaussian smoothing, as shown in Figure 3.6 is adequate to eliminate voxel artefacts. However, the smoothed mesh $M$ does not have a constant curvature, which is inconsistent with the Young-Laplace equation (Eq. 2.1). Thus, in the next step, we apply a curvature smoothing on vertices belonging to the oil/brine interface ($V_{OB} := \{p_i \in \{z_2\}\}$) and the contact line ($V_{CL}$) sets.

### 3.1.4 Volume-preserving curvature smoothing

In this step, we correct the vertex positions $p_i$, so that the interface has a uniform curvature. We move the vertices $i \in V_{OB}$ proportionally to the difference between their curvature and the curvature of the adjacent vertices. We apply this only on the oil/brine interface and the contact line, $i \in \{V_{OB}, V_{CL}\}$.

**Interface curvature**

The curvature at vertex position $q_i$ can be calculated from the sum of the dot product of the vertex normal $n_j$ and vector $s_j$ which is normal to the contact line and tangent to the oil/brine interface.
As in the Gaussian smoothing, we denote the position of points at the beginning of the curvature smoothing iteration by $o_i$. During the curvature smoothing, we will map them onto new positions $o_i \mapsto p_i$, $i \in \{V_{OB}, V_{CL}\}$. Again, this process will have two steps: first, we move the vertex position proportional to the difference between the vertex curvature, $\kappa_i$, and the average computed curvature of adjacent vertices $\kappa_j$, so the overall oil/brine interface and contact line curvature is almost constant. Then, the vertices are moved back closer to the average of their original positions to approximately preserve volume, as shown in Figure 3.8.
Figure 3.8: **Vertex displacement during curvature smoothing.** Illustrative steps showing vertex movement to impose a more uniform curvature. A) From the original positions of the smoothed Gaussian surface vertices are displaced towards calculated average positions $\mathbf{o}_i \mapsto \mathbf{q}_i$ (Eq. 3.21) based on the curvature estimated at each vertex, followed by B) movement towards new positions $\mathbf{q}_i \mapsto \mathbf{p}_i$ (Eq. 3.22) to preserve volume.

We can use two approximations to compute the interface tangent vector, $\mathbf{s}_i$, at the centre of edges connecting each point to its adjacent points. The first approximation is to use the direction of the vector connecting the point $\mathbf{o}_i$ to the adjacent point $\mathbf{o}_j$:

$$
\overrightarrow{\mathbf{o}_i \mathbf{o}_j} = \mathbf{o}_i - \mathbf{o}_j, \quad \{\mathbf{o}_i, \mathbf{o}_j\} \in e_j
$$

(3.15)

Another approximation is to use the cross-product of the interface normal vector and the vector connecting edge centre to the face centre $\mathbf{n}_e \times \overrightarrow{c_je_f}$. In this thesis, we combine these two approximations, as follows:

$$
\mathbf{s}_i = 0.5(\mathbf{n}_e \times \overrightarrow{c_je_f}) + 0.5|\overrightarrow{c_je_f}| \frac{\overrightarrow{o_i o_j}}{|\overrightarrow{o_i o_j}|}, \quad \{i, j\} \in V_{OB}
$$

(3.16)

Then, for the same vertices, curvature is estimated for all vertices belonging to the contact line using:

$$
\kappa_{iCL} = \sum_{j \in \text{adj}(i)} \frac{|(\mathbf{s}_i \cdot \mathbf{n}_i) - (\mathbf{s}_i \cdot \mathbf{n}_j)|}{|\overrightarrow{o_i o_j}|}, \quad \{\mathbf{n}_i, \mathbf{n}_j\} \in e_j, \quad \{i, j\} \in V_{CL}
$$

(3.17)
Also, for vertices belonging to the oil/brine interface:

$$
\kappa_{OB} = \sum_{j \in \text{adj}(i)} [(s_i \cdot n_i) - (s_i \cdot n_j)] / \sum_{j \in \text{adj}(i)} \alpha_j \mathbf{O}_j, \quad \{n_i, n_j\} \in e_j, \quad \{i, j\} \in V_{OB}
$$

(3.18)

Then we compute a smoothed curvature for the contact line $\langle \kappa_i \rangle_{CL}$ using:

$$
\langle \kappa_i \rangle_{CL} = 0.5 \left( \sum_{j \in \text{adj}(i)} \alpha_j \kappa_j \sum_{j \in \text{adj}(i)} \alpha_j + \kappa_{i_{CL}} \right), \quad \{i, j\} \in V_{CL}
$$

(3.19)

For vertices belonging to both the oil/brine interface and the contact line $\{i, j\} \in \{V_{OB}, V_{CL}\}$ we use:

$$
\langle \kappa_i \rangle_{OB} = 0.5 \left( \sum_{j \in \text{adj}(i)} \alpha_j \kappa_j \sum_{j \in \text{adj}(i)} \alpha_j + \kappa_{i_{OB}} \right), \quad \{i, j\} \in V_{OB}
$$

(3.20)

Here $\alpha_j$ is a weight factor for the adjacent points: in this thesis we use $\alpha_j = 1.0$ and $\alpha_j = 0.01$ for vertices belonging to the contact line and oil/brine interface, respectively. The number of repetitions of Eq. 3.19 and Eq. 3.20 defines the curvature smoothing kernel radius $(R_{\kappa})$.

Moreover, we calculate $\langle \kappa_i \rangle^*_{OB}$ using Eq. 3.20 extending $R_{\kappa}$ by a factor of two through doing the calculation twice. Then, we estimate the displacement distances $b_i$, using:

$$
b_i = \begin{cases} 
0.5(\kappa_i - \langle \kappa_i \rangle_{OB}) + 8.0(\langle \kappa_i \rangle_{OB} - \langle \kappa_i \rangle^*_{OB})] n_i |_{z_2}, & i \in V_{OB} \\
0.5(\kappa_i - \langle \kappa_i \rangle_{OB}) + 8.0(\langle \kappa_i \rangle_{OB} - \langle \kappa_i \rangle^*_{OB})] n_i |_{z_3}, & i \in V_{CL}
\end{cases}
$$

(3.21)

where $w_k = \gamma(\sqrt{\frac{\kappa_{i_{OB}}}{\langle \kappa_i \rangle_{OB}}})$ is a weighting factor to control the movement of a vertex. The term $\langle \kappa \rangle$ is a measure of average curvature near the vertex $i$, and $\langle \kappa \rangle^*$ is a measure of the average curvature further away from the vertex $i$. Here, $\gamma \in \{0 \to 1\}$ is a relaxation factor, and we
used $\gamma = 0.05$ as the optimal value for $i \in \{V_{OB}, V_{CL}\}$ in this thesis; see the sensitivity analysis in section-4.1. Then the vertices $i$ are moved to positions $o_i \mapsto q_i$:

\[ q_i = \begin{cases} 
  o_i + b_i, & i \in V_{OB} \\
  o_i + b_i(n_i|z_2 - (n_i|z_2 \cdot n_i|z_3)n_i|z_3), & i \in V_{CL} 
\end{cases} \tag{3.22} \]

To preserve the original volume of the oil/brine interface ($V_{OB}$), the vertices in positions $q_i$ are pushed back towards the average of original positions $o_i$, as shown in Figure 3.9-B, by the average of the final displacements $d_i$, which can be determined by:

\[ d_i = \frac{\sum_{j \in \text{adj}(i)} \alpha_j (q_j - o_j)}{\sum_{j \in \text{adj}(i)} \alpha_j} \tag{3.23} \]

Then, the vertices $i$ are moved to new positions $q_i \mapsto p_i$, by having:

\[ p_i = \begin{cases} 
  q_i - 0.3\gamma(d_i + 0.7(d_i \cdot n_i|z_2)n_i|z_2), & i \in V_{OB} \\
  q_i - 0.3\gamma(d_i + 0.7(d_i \cdot n_i|z_3)n_i|z_3), & i \in V_{CL} 
\end{cases} \tag{3.24} \]

Figure 3.9 shows the final outcome after applying curvature volume-preserving smoothing on the Gaussian smoothed oil/brine interface of mesh $M$. 
Figure 3.9: **Volume-preserving curvature smoothing.** Artificial image as shown in the previous figures. A) Smoothed mesh \( M \) with Gaussian volume-preserving smoothing, and after the application of curvature volume-preserving smoothing on vertices belonging to the oil/brine interface and contact line \( (i \in \{ V_{\text{OB}}, V_{\text{CL}} \} ) \), for B) 5 iterations, C) 10 iterations and D) 100 iterations.

A compact form of the previous steps is given in the pseudo-code algorithm-2. The smoothed mesh surface \( M \) is used to measure the contact angle for each vertex that belongs to the contact line set \( (i \in V_{\text{CL}}) \), which is discussed in the next section.

### 3.1.5 3D Contact angle calculation

In this step, we use the smoothed mesh \( M \), and compute the contact angle on each vertex that belongs to the contact line set, \( i \in V_{\text{CL}} \). The normal vectors, Eq. 3.7 and Eq. 3.8 in section-3.1.2, are computed on the vertices comprising the contact line. Each vertex is represented with two vectors normal to the oil/brine interface and the brine/rock interface, as shown in Figure 3.10.
Algorithm 2 Curvature smoothing algorithm - Part 1

1: //initialize points with original positions
2: \( p = o \)
3: repeat
4: for all \( i \in M \) do
5: //define vector \( o_i o_j \)
6: \( o_i o_j = o_i - o_j, \quad \{ o_i, o_j \} \in e_j \)
7: //define vector \( s_i \)
8: if \( \{ i, j \} \in \{ V_{OB}, V_{CL} \} \) then
9: \( s_i = 0.5(n_e \times c_{ej} c_{fj}) + 0.5|c_{ej} c_{fj}| o_i o_j \)
10: end if
11: //estimate curvature \( \kappa_i \)
12: if \( \{ i, j \} \in \{ \} \) then
13: \( \kappa_{iOB} = \frac{\sum_{j \in \text{adj}(i)} ([s_i \cdot n_i] - [s_i \cdot n_j])}{\sum_{j \in \text{adj}(i)} \alpha_j} \)
14: else if \( \{ i, j \} \in \{ \} \) then
15: \( \kappa_{iCL} = \frac{\sum_{j \in \text{adj}(i)} ([s_i \cdot n_i] - [s_i \cdot n_j])}{|o_i o_j|} \)
16: end if
17: repeat
18: //smoothing oil/brine interface curvature \( \langle \kappa_i \rangle_{OB} \)
19: if \( \{ i, j \} \in \{ \} \) then
20: \( \langle \kappa_i \rangle_{OB} = 0.5\left( \frac{\sum_{j \in \text{adj}(i)} \alpha_j \kappa_j}{\sum_{j \in \text{adj}(i)} \alpha_j} + \kappa_{iOB} \right) \)
21: end if
22: //smoothing contact line curvature \( \langle \kappa_i \rangle_{CL} \)
23: if \( \{ i, j \} \in \{ \} \) then
24: \( \langle \kappa_i \rangle_{CL} = 0.5\left( \frac{\sum_{j \in \text{adj}(i)} \alpha_j \kappa_j}{\sum_{j \in \text{adj}(i)} \alpha_j} + \kappa_{iCL} \right) \)
25: end if
26: until \( \langle \kappa_i \rangle < R_k = 0 \) >
Algorithm 3 Curvature smoothing algorithm - Part 2

27:  //calculate the average distance $b_i$ towards calculated new positions $q_i$
28:  if $i \in V_{OB}$ then
29:      $b_i = w_k \left[ 0.5(\kappa_i - \langle \kappa_i \rangle_{OB}) + 8.0(\langle \kappa_i \rangle_{OB} - \langle \kappa_i \rangle_{OB}^*) \right] n_i|z_2$
30:  else if $i \in V_{CL}$ then
31:      $b_i = w_k \left[ 0.5(\kappa_i - \langle \kappa_i \rangle_{OB}) + 8.0(\langle \kappa_i \rangle_{OB} - \langle \kappa_i \rangle_{OB}^*) \right] n_i|z_3$
32:  end if
33:  //mapping to the calculated new positions $o_i \mapsto q_i$
34:  if $i \in V_{OB}$ then
35:      $q_i = o_i + b_i$
36:  else if $i \in V_{CL}$ then
37:      $q_i = o_i + b_i(n_i|z_2 - (n_i|z_2 \cdot n_i|z_3)n_i|z_3)$
38:  end if
39:  //calculate the average distance towards average original positions
40:  for all $q_i$ do
41:      $d_i = \frac{\sum_{j \in \text{adj}(i)} \alpha_j d_j}{\sum_{j \in \text{adj}(i)} \alpha_j}$
42:  //move vertices back for volume preservation
43:  if $i \in V_{OB}$ then
44:      $p_i = q_i - 0.3\gamma(d_i + 0.7(d_i \cdot n_i|z_2)n_i|z_2)$
45:  else if $i \in V_{CL}$ then
46:      $p_i = q_i - 0.3\gamma(d_i + 0.7(d_i \cdot n_i|z_3)n_i|z_3)$
47:  end if
48:  end for
49:  end for
50:  until $< \text{iteration} = 0 >$
Figure 3.10: **Contact angle measurements.** A) Three-phase contact line highlighted on the smoothed mesh $M$. B) Normal vectors defined on both the oil/brine and brine/rock interfaces for the contact line set, $i \in V_{CL}$. The cosine of the contact angle is calculated from the dot product of these two normals.

Then, the contact angle ($\theta_i$) for each vertex is calculated through the brine phase by:

$$\theta_i = \pi - \cos^{-1}(\mathbf{n}_{i|z_2} \cdot \mathbf{n}_{i|z_3}), \quad i \in V_{CL}$$

(3.25)

where $\mathbf{n}_{z_2}$ is a vector normal to the oil/brine interface ($V_{OB}$) and $\mathbf{n}_{z_3}$ is a vector normal to the brine/rock interface ($V_{BR}$). This calculation is repeated for all the vertices on the contact line.

### 3.2 Surface roughness

Our main objective in this study is to measure micron-scale roughness in each individual pore and investigate its relationship with the measured contact angle and the curvature of fluid/fluid interfaces.

#### 3.2.1 Curvature based roughness

In this work, we propose two methods to measure the curvature distribution on the extracted rock surface. This method has four main steps as follows: firstly, remove the oil phase (replace it with brine) from the multiphase segmented image and generate an image with two phases
(brine/rock) only. This will help us avoid the complexities of the three-phase contact line; we generate a single-zone mesh \( (S) \) to represent the rock surface, \( S := \{z_i\} \); we define some geometric properties, i.e. vertex area \( (A_i) \) and normal vector \( (n_i) \), of the mesh before describing the curvature smoothing process itself, mentioned previously in Section 3.1.2; then, we apply a volume preserving curvature smoothing on all vertices belonging to the generated mesh \( (i \in S) \), which removes the voxelized artefacts from the segmented 3D image and measures the curvature, \( \kappa \), for each vertex, as discussed previously in Section 3.1.4.

Finally, using the smoothed mesh \( S \), we estimate the local rock surface roughness for each vertex \( (R_{a_i}) \) as:

\[
R_{a_i} = \frac{1}{N} \sum_{j \in \text{adj}(i)} |\kappa_j A_j| \tag{3.26}
\]

where \( \kappa_j \) and \( A_j \) are the computed curvature and area of the adjacent vertices \( (j) \) on the rock surface, respectively, and \( N \) is the number of adjacent vertices. Note that \( R_a \) has units of length, while the roughness ratio, \( R_s \) is dimensionless.

Physically this roughness measures the distance that a local feature deviates from an ideal flat surface, consistent with classical definitions in the literature [Lai et al., 2014, Lavoué, 2009].

### 3.2.2 Pore roughness ratio

The pore nominal area is defined as that of the largest inscribed sphere in each pore, with radius \( r_s \): \( A_n = 4\pi r_s^2 \). The actual pore rock surface area \( (A_p) \) is computed for the rock surface mesh \( (S) \), using the vertex area method mentioned above. We associate the vertices to a unique pore index of the pore-segmented image generated by the network extraction. We obtain the pore area \( (A_p) \) by summing up all the vertex areas associated with the pore:

\[
A_p = \sum A_i |_{\text{pore}} \tag{3.27}
\]

Then, the roughness ratio \( (R_s) \) for each pore is, from Eq. 2.9:

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3.3 Description of the experimental method

We briefly describe altered wettability experiments [Alhammadi et al., 2017b] which are used to test our method. The experiments were conducted on three cores of 4.8 mm diameter and a length between 13 and 16 mm from a giant multi-billion barrel carbonate oil reservoir in the Middle East, which is mainly composed of calcite (96.5wt% ± 1.9wt%). The properties of the samples are listed in Table 3.1. The samples were exposed to different crude oils for varying times to reproduce three distinct wettability states. We will label the three samples water-wet (WW), mixed-wet (MW) and oil-wet (OW) in what follows. A light crude oil (from the same reservoir, ambient conditions density of 830 kg/m$^3$) was used to age the WW and OW samples, and a heavier, more viscous, crude oil (Arabian Medium, ambient conditions density of 870 kg/m$^3$) was used for the MW sample. A solution of 7wt% potassium iodide (KI) salt (purity ≥ 99.0%, Sigma-Aldrich, U.K) in deionized water was the aqueous phase, which provided an effective contrast between brine, oil and rock phases in a micro-CT scanner. The ageing protocols, core-flooding apparatus and the experimental procedure follow the same protocols described in Alhammadi et al. [2017b], to which the reader is referred for additional details.

1. CO$_2$ was injected into the clean and dry samples to displace air followed by brine injection to fully saturate the rock.

2. Subsurface conditions were established (60°C or 80°C and 10 MPa) and primary drainage (crude oil injection) was performed, followed by (only for MW and OW samples) aging over three weeks to alter rock wettability.

3. During brine injection the flow was reversed and 20 PV of brine was injected at a low flow rate of 15 µL/min, corresponding to a capillary number of $6 \times 10^{-7}$ for WW and OW and $3 \times 10^{-7}$ for MW: the difference in capillary number is due to the different viscosities of the two crude oils used. Fluids were allowed to reach equilibrium for two
Table 3.1: Properties of the WW, MW and OW samples, modified from Alhammadi et al. [2017b]

<table>
<thead>
<tr>
<th></th>
<th>WW</th>
<th>MW</th>
<th>OW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter, mm</td>
<td>4.75</td>
<td>4.75</td>
<td>4.75</td>
</tr>
<tr>
<td>Length, mm</td>
<td>16.3</td>
<td>13.6</td>
<td>13.1</td>
</tr>
<tr>
<td>Helium Porosity, %</td>
<td>27.0</td>
<td>30.5</td>
<td>31.7</td>
</tr>
<tr>
<td>Segmented porosity, %</td>
<td>20.8</td>
<td>20.2</td>
<td>20.4</td>
</tr>
<tr>
<td>Pore volume, µL</td>
<td>78</td>
<td>74</td>
<td>74</td>
</tr>
<tr>
<td>Initial water saturation, %</td>
<td>56.3</td>
<td>97.5</td>
<td>91.7</td>
</tr>
</tbody>
</table>

Table 3.2: Crude oil A and B properties, modified from Alhammadi et al. [2017b]

<table>
<thead>
<tr>
<th></th>
<th>Crude oil A</th>
<th>Crude oil B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 21°C, kg/m³</td>
<td>830 ± 5</td>
<td>870 ± 5</td>
</tr>
<tr>
<td>Saturates, wt%</td>
<td>55.25</td>
<td>33.54</td>
</tr>
<tr>
<td>Aromatics, wt%</td>
<td>38.07</td>
<td>52.88</td>
</tr>
<tr>
<td>Resins, wt%</td>
<td>6.22</td>
<td>9.3</td>
</tr>
<tr>
<td>Asphaltenes, wt%</td>
<td>0.46</td>
<td>4.28</td>
</tr>
</tbody>
</table>

hours before acquiring high resolution (2 µm/voxel) scans from which the in situ contact angle distributions and fluid saturations were measured.

### 3.3.1 Brine and crude oil properties

Two crude oils were used, crude oil A (a light oil from the same reservoir as the rock samples) and crude oil B (Arabian Medium) which is heavier: see Table 3.2 for an analysis of their composition performed by Weatherford Labs to measure the content of the heavier fraction contents in each crude oil, including resins and asphaltenes that contain polar components able to alter the rock wettability.

Also, to increase the image contrast for effective image segmentation, a brine solution was prepared using 7 weight percent of potassium iodide (KI) (purity 99.0%, Sigma-Aldarich, UK) mixed with deionized water. As a result, the brine density was 1052.1 ± 2.2 kg/m³ and a pH value of 6.91 ± 0.2 measured with FiveGo pH meter, Mettler Toledo.
3.3.2 Image processing

All images were acquired using the Xradia VersaXRM-500 X-ray micro-CT; an objective of 4X was used with an exposure time of 3.5 seconds and 5,000 projections. The X-ray radiation intensity was 5,000-10,000 counts/second. The tomograms were reconstructed using Zeiss Reconstructor Software. In Figure 3.11, we present 3D volume rendering and 2D cross-sections of the original raw images for the three samples. We did not observe blurry phases that indicate fluid movement during the imaging time. This indicates that the equilibrium time (2 hours) was adequate for the fluids to stabilized before scanning [Gray et al., 2015, Khishvand et al., 2016, Schlüter et al., 2017]. Then, the images were segmented into three phases (oil, brine, rock) from the raw micro-CT image using a machine learning-based image segmentation known as Trainable WEKA Segmentation (TWS) [Arganda-Carreras et al., 2017], which applies a feature-based segmentation. Fast-random algorithm and texture filters (mean and variance) were chosen and pixels from each phase (oil, brine and rock) were annotated manually to train a classifier model. No noise reduction filter was applied prior to segmentation to avoid averaging of voxel values especially at the three-phase contact line at which contact angle is measured. The trained classifier model recognizes characteristic shapes, facilitating the measurement of contact angle, and was used to segment the images, Figure 3.11. Detailed descriptions of the image processing and segmentation can be found in Alhammadi et al. [2017b].
Figure 3.11: **Image segmentation and validation.** (A-C) Three-dimensional rendering of the raw tomographic image with a voxel size of $2 \times 2 \times 2 \, \mu m$ for the WW, MW and OW samples, respectively, after waterflooding. (A1-C1) Two-dimensional horizontal cross-sections of the raw tomographic image. The phases are represented as oil (black), brine (dark grey) and rock (light grey). (D-F) Three-dimensional rendering of the segmented images. (D1-F1) Two-dimensional horizontal cross-sections of the segmented images. The segmented phases are represented here as oil (red), brine (blue) and rock (white). (A1-C1) and (D1-F1) are sub-volumes cropped out of raw tomographic images and segmented images, respectively. Modified from Alhammadi et al. [2017b].
CHAPTER 3. NUMERICAL METHODS

We apply our contact angle, oil/brine interface curvature and roughness measurement method to the images after waterflooding, see Figure 3.12. The size of the segmented images in voxels is $435 \times 10^6$ for all samples, for a part of the rock samples with a diameter of 1.9 mm and length of 1.2 mm (volume of approximately $3.4 \text{ mm}^3$); the total sample size in the experiments was a length of between 13 and 16 mm and a diameter of 4.8 mm. We could not look at the entire rock sample volume due to image artefacts.

3.4 Generalized pore-network model extraction

To analyse the contact angle measurements on a pore-by-pore basis, we use a generalized pore-network model [Raeini et al., 2017] to generate a segmentation of the void space allowing contact angle measurements to be linked to specific pores. The void space is divided into individual pores, see Figure 3.13. The algorithm first finds the distance map which is computed for each void voxel (the distance between the centre of a voxel and the centre of the nearest solid voxel minus half the voxel length), see Figure 3.13.B. Then maximal spheres are found - the largest sphere centred on a voxel that can fit inside the pore space [Dong and Blunt, 2009]. This maximal sphere is used to generate a maximal sphere hierarchy: bigger spheres are marked as the parent of nearby partially overlapped smaller spheres [Dong and Blunt, 2009, Silin and Patzek, 2006]. The marked sphere parent defines a pore, where its centre defines the centre of the pore and its radius defines the pore radius ($R_p$). The maximal sphere is given a pore label and this label is also assigned to all children of the maximal sphere. Overall, this leads to a segmentation of the void space as shown in Figure 3.13.C.

Finally, to identify throats between connected pores, all the sets of voxel faces where, on either side, the two voxels are assigned to different pores are collected. Each set, that separates a two adjacent pores, defines a throat surface. Every void-space voxel is associated with a pore, Figure 3, and a throat, which is the throat surface first encountered in the direction of decreasing distance map. The calculations are described in Raeini et al. [2017], to which the reader is referred for additional details.
Figure 3.12: **Roughness, contact angle and oil/brine interface curvature measurements.** (A) Three-dimensional view of the raw segmented dataset of the oil-wet sample with a voxel size of 2 µm. (B) The oil (black) and brine (blue) phases are shown in a zoomed-in section of the image. (C) The curvature-based roughness measurement \(R_a\) on each vertex belonging to the rock surface after applying uniform-curvature smoothing: the smooth and rough areas are indicated by blue and red, respectively. (D) The smoothed mesh that is found after applying both Gaussian and curvature smoothing: the identified interface oil/brine (green) and oil/solid (red). (E) The measured curvature values of all vertices belonging to the oil/brine interface. (F) The extracted three-phase contact line. (G) Normal vectors are defined on both the oil/brine and brine/rock interfaces for the three-phase contact line set, \(i \in V_{CL}\). Using Eq. 3.25, the cosine of the contact angle is calculated from the dot product of these two normals.
Figure 3.13: Pore segmented extraction using a generalized pore-network model, Raeini et al. [2017]. Three-dimensional view of the sub-volume, as in Figure 3.12: (A) The raw segmented dataset. (B) The distance map computed the distance of each void voxel to the nearest solid voxel. (C) The void space separated into pores indicated by the different colours.

### 3.4.1 Associating measurements with pore-segmented images

In this step we allocate the contact angle and oil/brine interface curvature measurements to pores, Figure 3.14. The pore-index of each voxel from the pore-segmented image (Figure 3.14-A) is assigned to each vertex that has the same physical location, which belongs to the oil/brine interface and the contact line \( i \in \{ V_{CL}, V_{OB} \} \) of the smoothed image, Figure 3.14-B. Then, the measured oil/brine interface curvature and contact angles are filtered according to their pore-index to allocate the overall measured distributions into pore-by-pore based distributions. We can also associate any voxel to a throat, as mentioned above. We will also use other properties, such as pore and throat radius, to analyse the spatial distribution of contact angles throughout the rock sample and to calculate capillary pressure.

In the next chapter, we test the whole routine on digitized synthetic images and on a volume cropped from the WW sample. Both contact angle, oil/brine interface curvature and roughness are measured and allocated to pores.
Figure 3.14: A workflow for allocating the measured contact angle and oil/brine interface curvature to pores. Using both (A) the pore-segmented image and (B) the image where the total surface and oil/brine (green) and oil/solid (red) interfaces, are smoothed by both Gaussian and curvature smoothing. A combined view of the oil/brine interface curvature surface (C) and the three-phase contact line (D) with the associated pore indices is shown.
4. Validation of the numerical method
4.1 Synthetic Images

To test the accuracy of our method, the algorithm is first applied to a synthetic test case where the contact angle and fluid/fluid interface curvature are analytically defined. The test case represents a single spherical oil droplet on a tilted plane (with a slope of $y = x$), surrounded by brine, as shown in Figure 4.1. Contact points form a rim around the sphere where the solid, oil, and brine intersect. The oil/brine interface is shifted from the bottom left corner to the upper right corner to cover the full range of contact angle and to measure oil/brine interface curvature at different droplet sizes, as shown in Figure 4.3. Furthermore, we will demonstrate how exactly we allocate the measured contact angles and oil/brine interface curvatures from the entire image to the distributions of contact angles and oil/brine interface curvatures within single pores, as extracted by the generalized network model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Min</th>
<th>Max</th>
<th>Optimal parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaussian relaxation factor ($\beta$)</td>
<td>0.01</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Gaussian radius kernel ($R_{Gauss}$)</td>
<td>1</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>Gaussian iterations</td>
<td>10</td>
<td>500</td>
<td>40</td>
</tr>
<tr>
<td>Curvature relaxation factor ($\gamma$)</td>
<td>0.01</td>
<td>0.2</td>
<td>0.05</td>
</tr>
<tr>
<td>Curvature radius kernel ($R_c$)</td>
<td>6</td>
<td>48</td>
<td>12</td>
</tr>
<tr>
<td>Curvature iterations</td>
<td>20</td>
<td>1000</td>
<td>200</td>
</tr>
</tbody>
</table>

4.1.1 Contact angle measurement

Using this test case, the sensitivity of the six parameters used for smoothing techniques are evaluated; these parameters are: resolution, Gaussian relaxation factor ($\beta$), Gaussian radius kernel ($R_{Gauss}$), Gaussian iterations, curvature relaxation factor ($\gamma$), curvature iterations and curvature radius kernel ($R_c$). Six resolutions are defined by varying the number of voxels across the sphere, see Figure 4.1. The length scale of 1 voxel is set equal to $1/2$, $1/6^{th}$, $1/10^{th}$.
CHAPTER 4. VALIDATION OF THE NUMERICAL METHOD

Figure 4.1: Contact angle measurements validation. Example test cases with a spherical oil droplet residing on a tilted flat rock surface, with a slope of \( y = x \) (vertical angle= 45°), at six different voxel resolutions: (A) 1/2, (B) 1/6th, (C) 1/10th, (D) 1/14th, (E) 1/28th and (F) 1/56th. In this case, the theoretical contact angle through the surrounding brine (transparent phase) is 44°.

1/14th, 1/28th and 1/56th of the sphere diameter. Overall, the sensitivity analysis includes
2748 combinations of factors with the ranges shown in Table 4.1. For each combination, the theoretical contact angle is compared to the measured contact angles by calculating the root mean square error (RMSE). From the sensitivity analysis we selected the parameters shown in Table 4.1. As an example, for a 90° case with resolution 1/28th from Figure 4.1, with optimal parameters, Gaussian smoothing alone led to a RMSE of 4.6°, while using the curvature smoothing in addition led to a RMSE of 0.85°.

Figure 4.2: Contact angle measurements validation results. Theoretical contact angle compared to the calculated contact angle at six different voxel resolutions: (A) 1/2, (B) 1/6th, (C) 1/10th, (D) 1/14th, (E) 1/28th and (F) 1/56th of the sphere diameter (as shown in Figure 4.1). The error bars show the difference between the maximum and minimum value in the contact angle distribution. The dashed line indicates a 1:1 correlation.
Due to the stair-step voxel configuration (see 4.1) the calculated contact angle values around the contact rim are not a single value, but a distribution. The calculated contact angle (the median value along with the 100% confidence interval shown by the error bars) is plotted for each theoretical angle in Figure 4.2. The plots include contact angles that can be measured using all six resolutions. The algorithm tends to overestimate contact angle for less than 20°. The perimeter of the contact rim decreases to zero as the contact angle approaches 0°, which reduces the number of points used to calculate the median and confidence interval and can lead to errors, since there is little contact between the phases. Similarly, it is not possible to measure contact angles of 180° where there is no contact line. The theoretical contact angle is compared to the calculated contact angles by calculating the root mean square error (RMSE) averaged over all the contact angles studied except the zero° case. For the 1/2, 1/6th, 1/10th, 1/14th, 1/28th and 1/56th voxel resolution, the RMSE values are 2.3°, 3.0°, 2.2°, 1.6°, 2.1° and 2.5°, respectively.

4.1.2 Curvature measurement

We apply fluid/fluid interface curvature analysis on the test case previously used to validate the contact angle measurements. We use the same parameters listed in Table 4.1: as these choices are able to estimate contact angle to within 3° when the sphere is 2 or more voxels across.

The calculated curvature values for all vertices belonging to the fluid/fluid interface are shown in Figure 4.4. The median value along with the 100% confidence interval shown by the error bars is plotted for each theoretical curvature. The plots include curvature measured using all six resolutions. The algorithm tends to underestimate curvatures larger than 0.1 μm⁻¹ (droplet with diameter less than 10 voxels). The theoretical curvature value is compared to the calculated ones by calculating the normalized root mean square error (NRMSE) averaged over all the cases studied, except the zero degree case, divided by the true curvature. For the 1/2, 1/6th, 1/10th, 1/14th, 1/28th and 1/56th voxel resolution, the NRMSE values are 0.089, 0.073, 0.054, 0.055, 0.007 and 0.004, respectively.
Figure 4.3: Curvature measurements validation. Curvature measurements using example test cases with a spherical oil droplet residing on a tilted flat rock surface, with a slope of $y = x$ (vertical angle = 45°), at six voxel resolutions: (A) 1/2, (B) 1/6th, (C) 1/10th, (D) 1/14th, (E) 1/28th and (F) 1/56th. In this case, the theoretical contact angles through the surrounding brine (transparent phase) are 90° for (A), 60° for (B) and 44° for (C), (D), (E) and (F).
Figure 4.4: Curvature measurements validation results. Theoretical curvature compared to the calculated curvature at six voxel resolutions: (A) 1/2, (B) 1/6th, (C) 1/10th, (D) 1/14th, (E) 1/28th and (F) 1/56th of the sphere diameter (as shown in Figure 4.3). The error bars show the difference between the maximum and minimum value in the curvature distribution. The dashed line indicates the theoretical curvature value.
4.1.3 Curvature of oil spherical droplets

In this section, we apply the curvature measurements analysis on a spherical oil droplets image. We apply our measurements on similar resolutions of the previous case, so the image to set the length scale of 1 voxel equal to $1/2$, $1/6^{th}$, $1/10^{th}$, $1/14^{th}$, $1/28^{th}$ and $1/56^{th}$, similar to the resolutions of the test case discussed earlier in this section. The extracted surface at of the spherical oil droplets at different resolution is shown in Figure 4.5. Then, we also apply the same parameters listed in Table 4.1.
Figure 4.5: Spherical oil droplets image at different resolutions. A spherical oil droplets case at six different voxel resolutions: (A) $1/2^4$, (B) $1/6^{th}$, (C) $1/10^{th}$, (D) $1/14^{th}$, (E) $1/28^{th}$ and (F) $1/56^{th}$.
In this case, we calculated curvature values for all vertices belonging to surface of the oil spheres as shown in Figure 4.7. In this case, we observe that the algorithm tends to overestimate curvatures larger than 0.05 \( \mu m^{-1} \) (droplet with diameter less than 10 voxels across). For the \( 1/2, 1/6^{th}, 1/10^{th}, 1/14^{th}, 1/28^{th} \) and \( 1/56^{th} \) voxel resolution, the RMSE values are 0.2479, 0.078, 0.044, 0.033, 0.008 and 0.0007, respectively.

### 4.2 Pore-by-pore contact angle, curvature and roughness measurements

We use a sub-volume cropped out of WW sample (Figure 3.12.B and Figure 3.13.A). The number of voxels for this image is \( 1.3 \times 10^6 \) with a volume of approximately \( 0.01 \ mm^3 \). We use this image to measure the contact angle and oil/brine interface curvature and generate a pore-segmented image, see Figure 3.14.

First, we measure the distribution of oil/brine interface curvature and contact angle for the entire image (Figure 3.12.E and F, respectively.). Then, we allocate the measurements for each individual pore using the pore-segmented image, as discussed in Section 3.4.1. Figure 4.8 shows histograms of the measured contact angle and oil/brine interface curvature for all the pores that contain a three-phase contact.

In Figure 4.8 we also show the histograms of contact angle and oil/brine interface curvature discarding all the pores which contain small ganglia with fewer than 2000 voxels. These discarded oil ganglia may simply be segmentation artifacts in some cases, or the image resolution is insufficient to resolve their shapes accurately [Garing et al., 2017]. In any event, their small size makes the identification of accurate contact angle and oil/brine interface curvature values difficult: they represent ganglia that are smaller than half the average pore body size. Figure 4.9 shows some of these ganglia: even if the oil really does adhere to the rock surface in small blobs, we cannot reliably measure the contact angle for them. We require higher-resolution images to determine if these ganglia do exist and - if they do - their wettability. The oil saturation of the discarded blobs in the entire volume of WW, MW and OW samples (Figure 3.12. A) is 0.098%, 1.37% and 1.68%, compared to total oil saturations of 32.9%, 41.2% and 15.9%, respectively.
Figure 4.6: **Curvature measurements validation.** Curvature measurements using test cases with a spherical oil droplets at six voxel resolutions: (A) 1/2, (B) 1/6th, (C) 1/10th, (D) 1/14th, (E) 1/28th and (F) 1/56th.
Figure 4.7: Curvature measurements validation results. Theoretical curvature compared to the calculated curvature of the spheres at six voxel resolutions: (A) $1/2$, (B) $1/6^{th}$, (C) $1/10^{th}$, (D) $1/14^{th}$, (E) $1/28^{th}$ and (F) $1/56^{th}$ of the sphere diameter (as shown in Figure 4.5). The error bars show the difference between the maximum and minimum value in the curvature distribution. The dashed line indicates the theoretical curvature value.
Figure 4.8: Pore-by-pore contact angle and interfacial curvature measurements. Histogram plots showing distribution values of the measured contact angle and oil/brine interface curvature within each pore for all ganglia (A) and (C), and (B) and (D) excluding ganglia containing fewer than 2000 voxels.
CHAPTER 4. VALIDATION OF THE NUMERICAL METHOD

Figure 4.9: Oil ganglia with fewer than 2000 voxels elimination. Two examples of oil ganglia which contain fewer than 2000 voxels. These ganglia are labelled (A) and then discarded (B) from our analysis as it is not clear that they really represent oil and, in any event, the determination of their properties is difficult.

Table 4.2: The parameters used in measuring rock surface curvature.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curvature relaxation factor ($\gamma$)</td>
<td>0.05</td>
</tr>
<tr>
<td>Curvature radius kernel ($R_\kappa$)</td>
<td>10</td>
</tr>
<tr>
<td>Curvature iterations</td>
<td>800</td>
</tr>
</tbody>
</table>

4.2.1 Curvature-based roughness

We use a sub-volume cropped out of the WW sample (Figure 3.12-B). The number of voxels for this image is $3.35 \times 10^6$ with a volume of approximately $0.03 \text{ mm}^3$. We use this image to measure the rock (curvature-based) roughness. We first extract the rock surface mesh ($S$), and apply curvature smoothing to eliminate voxel artifacts while preserving the curvature features of the rock surface. Then, for each vertex in the smoothed surface ($i \in S$), we apply Eq. 3.26 to measure the rock surface roughness. We use the parameters listed in Table 4.2 for the curvature smoothing. These parameters are based on a visual sensitivity analysis conducted on the same image - lower values for these parameters are not sufficient to eliminate all the voxel artifacts, and higher values start to deform the macroscopic roughness.

The calculated roughness values ($R_a$) for all vertices belonging to the rock surface are shown in Figure 4.10. The colour map indicates the rough (red) and flat (blue) areas. The vertices
Figure 4.10: **Roughness measurement techniques.** (A) Curvature-based roughness ($R_a$) measurements using a sub-volume cropped out of the WW sample (Figure 3.12.B): the rough areas (high curvature) are indicated in red and the flat areas in blue ($R_a = 0$). (B) Roughness ratio ($R_s$) measurements: the ratio between the calculated pore area ($A_p$) and the calculated nominal area ($A_n$) of the inscribed sphere of the pore.
with high roughness values are highly curved (radius of curvature \( R_c \) is small) relative to its adjacent vertices. The vertices in the flat areas will have zero values, \( R_a = 0 \).

### 4.2.2 Pore-by-pore roughness ratio

For the analysis of the pore roughness ratio coefficient \( R_s \), first we measure the area of the rock surface \( S \) for the entire image. Then, we allocate the measurements for each individual pore using the pore-segmented image, as discussed in Section 3.4.1. Then, we sum the area associated with all vertices in each pore to calculate the pore area \( A_p \). Also, we calculate the nominal area \( A_n \) of the inscribed sphere of the pore. Additionally, we measure the distribution of the curvature and contact angle for the entire image. Then, we allocate the measurements for each individual pore. Figure 4.8 shows histograms of the measured curvature-based roughness \( R_a \) for all the pores. Further, we plot the roughness ratio coefficient \( R_s \) as a function of the pore diameter.

In the next chapter, we discuss the allocation of the measured contact angle and oil/brine interface curvature distributions and their spatial correlation across the entire image volume of the carbonate samples (WW, MW and OW) ignoring oil clusters containing fewer than 2000 voxels. Also, we discuss the relationship between the measured contact angle and oil/brine interface curvature with surface roughness. Moreover, we analyse pore wall curvature using the carbonate samples and other porous materials to discuss distinct pore morphology signatures.
5. Results and Discussion

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5.1 Introduction

The results are presented and discussed in seven sections as follows: in Section 5.2 we present the distributions of the contact angle and oil/brine interface curvature for each sample, and discuss the relationship between oil recovery and contact angle. Then, we allocate each measurement to a pore and throat, and to individual ganglia in Section 5.3. After that, we discuss the spatial correlation of the contact angle and oil/brine interface curvature in Section 5.4. Next, we discuss the correlation between contact angle, oil/brine interface and roughness in Section 5.5. Then, we present pore morphology signature of several samples with different level of complexities in Section 5.6. Finally, we discuss the correlation between wettability and pore morphology in Section 5.7.

5.2 Wettability and oil recovery correlation

We analyse the images obtained in each experiment after waterflooding. The algorithms for contact angle and oil/brine interface curvature are applied to measure several hundred thousand in situ contact angles and oil/brine interface curvatures, as shown in Figure 5.1.

For WW, MW and OW, the average contact angle values are 76°, 93° and 103°, and the oil/brine interface curvature median values are 0.0096 µm⁻¹, 0.0188 µm⁻¹ and −0.0052 µm⁻¹, respectively. These in situ measurements demonstrate the capability of our methods to distinguish between different wettability states in reservoir rock samples. We see a wide distribution of contact angles with values both above and below 90°. The distribution for WW sample is sharper: this rock has experienced less wettability alteration and hence retains more obviously water-wet characteristics. The MW and OW samples, which have experienced a more significant wettability alteration, have wider distributions of contact angle.

Moreover, the oil recovery is found to be a strong function of wettability (contact angle) and oil viscosity, Figure 5.2. The ratio of oil to brine viscosity for WW, MW and OW samples are 0.289, 0.834 and 5.64, respectively. However, we find that recovery is not simply inversely related to viscosity ratio: the highest recovery is seen in MW sample with an intermediate viscosity ratio, indicating that wettability also plays a key role in the behaviour. The WW sample showed a
Figure 5.1: **Histograms of all the contact angle and oil/brine interface curvature values.** Contact angle (A) and oil/brine interface curvature (B) measurements, average contact angle (C) and mode oil/brine interface curvature (D) averaged over each pore, and average contact angle (E) and mode oil/brine interface curvature (F) averaged over each ganglion, for the three samples: WW (blue), MW (green) and OW (red).
low oil recovery of 67.1% (remaining oil saturation of 32.9%). The maximum oil recovery of 84.0% (remaining oil 15.9%) was achieved by the MW sample with a mean contact angle close to 90° even though the oil viscosity is higher than in WW sample. The rapid deterioration in recovery was for the OW sample with a substantially more viscous oil to 58.6% (remaining oil 41.2%). Core-scale studies on sandstones [Jadhunandan and Morrow, 1995] have shown that optimal recovery was obtained for a rock that appeared neither strongly water-wet nor oil-wet. However, only the core-scale wettability index was measured, and the behaviour in terms of the pore-scale distribution of contact angle could not be assessed. At the pore scale, optimal recovery is found when the rock is not strongly water-wet, suppressing snap-off in small pores, which can trap oil, yet not so oil-wet as to confine all the oil to layers, which flow too slowly to provide significant recovery (1): as evident in Figure 5.2, the lowest remaining saturation is seen when the oil appears confined to only some of the smaller pores.

Next, we discuss more details of the correlation between measured contact angle and oil/brine interface curvature on both pore-by-pore and ganglion-by-ganglion bases.
5.3 Pore-by-pore and ganglion-by-ganglion correlation of contact angles and curvatures

We now generate pore-by-pore distributions of contact angle and oil/brine interface curvature. The pore networks extracted by the generalized network model consists of 4719, 5643 and 8858 pores, and 7510, 9467 and 17615 throats for the WW, MW and OW cases, respectively. Of these only 1092, 2930 and 5322 pores contain three-phase contact points, respectively. We then allocate each contact angle and oil/brine interface curvature value to a pore and throat and to individual ganglia; see Figure 5.1 C-F. The averaged distribution of contact angle are narrower than those shown in Figure 5.1 A-B on a voxel-by-voxel basis, but still indicate clearly the different wettability states of the three samples. For curvature, the ganglion-by-ganglion distributions discriminate better between the samples; higher (positive) curvatures are associated with lower (water-wet) contact angles.

The pore-averaged (mode) oil/brine interface curvature as a function of pore-averaged (arithmetic mean) contact angle is presented in Figure 5.3. The mode function is used to capture the most frequent curvature value of the oil/brine interface, which is used as most representative value for calculating local capillary pressure. We see a wide distribution of contact angle. The rocks studied are almost entirely calcite, and so the variation in contact angle is most likely due to local differences in pore-space morphology and rock surface roughness.

The images were analysed at the end of waterflooding. Most of the oil is trapped and has a local capillary pressure representative of when it was first disconnected, rather than the externally-imposed pressure at the end of the displacement. We see both positive and negative values of the oil/brine interface curvature. Negative values indicate that the water pressure is higher than the oil pressure and are observed in rocks where a significant fraction of the pore space is oil-wet, or have contact angles above 90° [Blunt, 2017], as evident in Figure 5.4. There seems to be only a weak correlation between contact angle and curvature with lower values of the curvature (and negative values) associated with larger contact angles (more oil-wet conditions). In a single pore there may be several disconnected sheet-like oil ganglia present; these ganglia may be associated with different contact angles and curvature, which obscures the correlation between them. However, we may expect there to be a stronger relationship between the contact
angles on a single ganglion, which may occupy several pores, and its curvature.

In Figure 5.5, we label each ganglion separately and calculate for each one the average contact angle and mode interfacial curvature. We found 126, 679 and 299 disconnected ganglia in the WW, MW and OW samples, respectively. We observe an approximately linear trend with a decrease of oil/brine interface curvature with increase of contact angle in the oil ganglia. In WW the curvatures are mainly positive and the contact angles are less than $90^\circ$, whereas for the other two samples both positive and negative curvatures are observed with a zero curvature associated, approximately with an average contact angle of $90^\circ$. One would expect oil on water-wet regions of the pore space to be trapped at a positive capillary pressure (positive curvature), while more oil-wet surfaces would trap oil at a negative capillary pressure.

Furthermore, we use the calculated mode oil/brine interface curvature ($\kappa$) to calculate capillary pressure ($P_c$) from the Young-Laplace equation:

$$P_c = \sigma \kappa \quad (5.1)$$

where $\sigma$ is the interfacial tension. The values for $\sigma$ are 19.56, 21.48 and 24.11 mN/m, for WW, MW and OW samples, respectively [Alhammadi et al., 2017b]. For each single throat associated with the oil/brine interface the calculated $P_c$ is plotted against the associated throat radius, as shown in Figure 5.6. The values of $P_c$ lie both above and below zero. The average capillary pressure values in Pa for the three samples are 1158.6, $-1022.9$ and $-3046.9$, respectively. The negative values in MW and OW indicate that the brine pressure is higher than the oil pressure when most of the oil is trapped and is indicative of a situation where much of the pore space is oil-wet with contact angles above $90^\circ$, as discussed previously.

There is no apparent correlation between throat radius and capillary pressure. This seems surprising as one might expect smaller radii to be associated with higher capillary pressures, but only if we ignore spatial variations in wettability: for instance, for a circular cylindrical tube of radius $r$, the capillary pressure is:
Figure 5.3: Pore-by-pore measurements for the entire sample volume. The smoothed oil surface, oil/brine (green) and oil/solid (red), in WW (A), MW (C) and OW (E) are used for contact angle and oil/brine interface curvature measurements. In the plots (B), (D) and (F), each point represents an average contact angle (on the x-axis) and a most frequent oil/brine interface curvature (on the y-axis) in a single pore for WW, MW and OW samples, respectively.
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Figure 5.4: A large pore (average pore diameter = 105 microns) from sample 2 with an average contact angle above 90° and negative averaged oil/brine interface curvature. The remaining oil is trapped in corners and crevices with negative interfacial curvature.

\[ P_c = \frac{\sigma \cos \theta}{r} \]  \hspace{1cm} (5.2)

In these experiments it would appear that there is a wide distribution of capillary pressure which is not readily associated with the throat radius, but is instead controlled by the local contact angles.

In Figure 5.8 we indicate the fraction of pores with average contact angles below 90° (water-wet) and above 90° (oil-wet) as a function of pore diameter. Here we see a tendency for the larger pores to be more oil-wet in samples MW and OW. This is consistent with in situ contact angle measurements made on cores after ageing [Khishvand et al., 2017].

We also study the fraction of pores with positive and negative oil/brine interfacial curvatures.
Figure 5.5: **Ganglion-by-ganglion measurements for the entire sample volume.** The oil ganglia-labelled images, in WW (A), MW (C) and OW (E) are used to associate the contact angle and oil/brine interface curvature measurements for each ganglion. In the plots (B), (D) and (F), each point represents an average contact angle (on the x-axis) and a most frequent oil/brine interface curvature (on the y-axis) in an oil ganglion for WW, MW and OW samples, respectively.
Figure 5.6: **Throat-by-throat capillary pressure measurements.** The mode oil/brine interface curvature ($\kappa$) value on the smoothed oil/brine interface in WW (A), MW (C) and OW (E) is used for calculating capillary pressure ($P_c$) using Eq. 5.1. In the plots (B), (D) and (F) each point represents a calculated $P_c$ (on the y-axis) associated with a throat which represented by its radius size in microns (on the x-axis).
Figure 5.7: Throat-by-throat and ganglion-by-ganglion contact angle and capillary pressure correlation for the entire sample volume. In the plots (A-B), (C-D) and (E-F) each point represents the associate capillary pressure and mean contact angle value for each throat and ganglion in samples 1, 2 and 3, respectively.
Here we see the opposite trend: for samples MW and OW - with more oil-wet conditions overall compared to WW sample - we see a weak tendency for the larger pores to contain ganglia with a positive curvature and capillary pressure. In Figure 5.9, we demonstrate an example of how the remaining oil can have positive and negative oil/brine interface curvature within a single pore based on the local curvature of the rock surface. The thin oil layers follow the peaks and valleys of the pore geometry, allowing both positive and negative curvatures of the oil/brine interface to be observed. The larger pores tend to bulge out into the rock — that is, they have a positive oil/brine interface curvature. The oil layers that follow the rock surface may assume this positive curvature.

5.4 Spatial correlation of contact angle and curvature

The spatial correlation ($\xi(r)$) of contact angle and oil/brine interface curvature across each sample, where $r$ is the distance between each two measurements is calculated as follows:

$$
\xi(r) = \frac{\sum_{j=1}^{N_j} \sum_{i=1}^{N_i} I_{ij} (\Psi_i - \Psi_j)^2}{2\sigma^2 \sum_{j=1}^{N_j} \sum_{i=1}^{N_i} I_{ij}} \quad (5.3)
$$

$$
I_{ij} = \begin{cases} 
1, & r - \varepsilon < r_{i\rightarrow j} < r + \varepsilon \\
0, & \text{otherwise}
\end{cases} 
\quad (5.4)
$$

$$
\sigma^2 = \frac{1}{N} \sum_{i=1}^{N_x} (\Psi_i - \overline{\Psi})^2 
$$

where $\Psi$ is a measurement value of the contact angle or oil/brine interface curvature, $\overline{\Psi}$ is the mean value, $r_{i\rightarrow j}$ is the distance between the measurements at positions $i$ and $j$, $\varepsilon$ is the statistical length - in this work we use the length of a voxel (2 microns), $\sigma^2$ is the variance of the measured distribution and $N$ is the total number of measurements. Note that here we study all the contact angle and oil/brine interface curvature values, not simply the pore or ganglion averages. The values of $\xi(r)$ are normalized to the theoretical values at infinite range (uncorrelated limit) by the calculated variance in Eq. ??.
Figure 5.8: Pore-by-pore wettability fractional analysis. Contact angle (A-F) and oil/brine interface curvature (G-L) as a function of pore diameter. The top row (A-C) shows the fraction of contact angles below (blue) and above (red) 90° for samples WW, MW and OW respectively. The second row (D-F) shows the histogram of contact angles above and below 90° for the three samples. Similarly, the third row (G-I) shows the fraction of oil/brine interface curvatures below (blue) and above (red) zero, while (J-L) shows the corresponding histograms. The average contact angle values show a tendency to be more oil-wet in the larger pores for samples MW and OW. However, the ganglia in the larger pores have a slight tendency to have a positive curvature, see Figure 5.9.
Figure 5.9: Impact of local pore morphology on oil/brine interface curvature. A large pore (average pore diameter = 100 microns) from OW sample with an average contact angle above $90^\circ$ and yet positive averaged oil/brine interface curvature. The remaining oil is comprised of ganglia with both positive and negative curvature.
The spatial correlation is shown in Figure 5.10. \( \xi(r) = 0 \) indicates a perfect correlation between two spatially separated values, whereas \( \xi(r) = 1 \) indicates no correlation and \( \xi(r) > 1 \) represents an anti-correlation. We observe that both the contact angle and oil/brine interface curvature are spatially correlated with a correlation length, which corresponds to when \( \xi(r) \) rises to approximately 1, of around an average pore diameter. For WW sample, the correlation length is the minimum pore diameter; for the MW sample it is closer to the average diameter whereas for OW sample, with the most oil-wet conditions, it is the maximum diameter for contact angle, although it is closer to the minimum diameter for curvature. This is an interesting result, as it shows that there is significant variation of the measurements within a single pore: while we can define a mean value, this does not necessarily indicate the value that is critical for displacement: the maximum contact angle value, or at least the one that gives the lowest capillary pressure (or oil/brine interface curvature), will limit the advance of water, while a minimum value or the highest capillary pressure controls drainage. Between pores, the measurements display a correlation which is more marked when the wettability alteration is most significant.

This result, for a mineralogically homogeneous rock, suggests that it is local pore morphology - the presence of small-scale roughness or micro-porosity - that controls the effective contact angle seen after waterflooding at the micron scale. There is a tendency for the larger pores to be more oil-wet, while we see a decrease in curvature as the contact angle increases towards more oil-wet conditions.

### 5.5 Pore-by-pore correlation of contact angles, curvatures and roughness

In Figure 5.11, we plot the roughness as well as variation of contact angle and curvature using the calculated standard deviation (std) for the measured distribution in each pore. Within each pore we still see a wide range of both contact angle and curvature. The sample-averaged (arithmetic mean) of the contact angle std values are 15°, 21° and 22°, the oil/brine curvature (mode) std values are 0.079 \( \mu m^{-1} \), 0.081 \( \mu m^{-1} \) and 0.1 \( \mu m^{-1} \), the curvature-based roughness \( (R_a) \) mode values are 0.15 \( \mu m \), 0.2 \( \mu m \) and 0.23 \( \mu m \), and the roughness-ratio \( (R_s) \) arithmetic average values are 5.4, 5.7 and 6, for the WW, MW and OW samples, respectively. The mode function is used to capture the most frequent value on the oil/brine interface, for calculating
Figure 5.10: Spatial correlation of contact angle and oil/brine interface curvature. Variograms showing the normalized functions for contact angle (A, C and E) and oil/brine interface curvature (B, D and F) spatial correlation, $\xi(r)$, for the images of WW (A and B), MW (C and D) and OW (E and F). Indicated by the dotted-dash, solid and dashed vertical lines are the characteristic lengths representing minimum, mean and maximum pore diameter size for all three samples.
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Figure 5.11: Distributions of the measurements on pore-space images. Histograms of the (A) variation of contact angle, and oil/brine interface curvature (B) using the standard deviation per pore. Also, the pore-averaged (mode) curvature-based roughness, $R_a$ (C) and pore roughness-ratio, $R_s$ (D) in each pore is shown for the three samples: WW (blue), MW (green) and OW (red).

local capillary pressure, and to capture the most frequent curvature-based roughness ($R_a$) value of the rock surface.

In Figure 5.12 we plot the rock curvature-based roughness ($R_a$), the rock roughness-ratio ($R_s$), the standard deviation of contact angle and the standard deviation of oil/brine interface curvature as a function of pore diameter. The standard deviation of contact angle reaches an approximately constant value for large pores, principally because we are averaging over many individual values. However, this is not seen for oil/brine interface curvature, where the variability approaches a constant value in large pores only for the oil-wet system (OW sample) and in the small pores in the water-wet system (WW sample). Oil layers in the oil-wet system follow the rock surface, while in the water-wet system oil is trapped in the centres of the pore with a
Figure 5.12: Pore-by-pore plots of roughness, contact angle and interfacial curvature variations as a function of pore-diameter. The curvature-based roughness ($R_a$) is shown in the top row (A-C), the roughness ratio ($R_s$) in the second row (D-F), the contact angle standard deviation (stdCA) in the third row (D-F) and the oil/brine interface curvature standard deviation in the forth row (G-I). The first, second and third columns represent WW, MW and OW samples, respectively.
more constant positive curvature, Figure 1.1.

Fig. 5.13 shows the point-by-point correlation between surface roughness and both contact angle and interfacial curvature as a function of the distance between the measurements. We consider two variables $x$ and $y$ that are measured at discrete points $i$ and $j$: $x$ is the solid surface roughness defined as $x_i = R_{ai}$, Eq. [3.26], while $y$ is either the contact angle, the fluid/fluid interfacial curvature or the roughness itself. We define dimensionless variables $\tilde{x}_i$ and $\tilde{y}_i$:

$$\tilde{x}_i = \frac{x_i - \bar{x}}{\sigma_x},$$  \hspace{1cm} (5.6)$$

where $\bar{x}$ is the average value of $x$ measured over the entire distribution:

$$\bar{x} = \frac{1}{N_x} \sum_{i=1}^{N_x} x_i,$$  \hspace{1cm} (5.7)$$

and $N_x$ is the total number of values of $x$. $\tilde{y}_i$ is defined in a similar manner. $\sigma_x$ is the standard deviation:

$$\sigma_x^2 = \frac{1}{N_x} \sum_{i=1}^{N_x} (x_i - \bar{x})^2.$$

(5.8)

Then we define a correlation $\xi(r)$ as:

$$\xi(r) = \frac{\sum_{j=1}^{N_y} \sum_{i=1}^{N_x} I_{ij} (\tilde{x}_i - \tilde{y}_j)^2}{2 \sum_{j=1}^{N_y} \sum_{i=1}^{N_x} I_{ij}},$$  \hspace{1cm} (5.9)$$

where $I_{ij}$ is an indicator function: if $r_{ij}$ is the distance between the locations $i$ and $j$ where $x$ and $y$ are measured, then $I_{ij} = 1$ if $r + \epsilon > r_{ij} > r - \epsilon$ and 0 otherwise, where $\epsilon = 1$ $\mu$m here. A value $\xi = 1$ represents no correlation and is expected for $r \to \infty$ and for variables that have no relationship with each other; $\xi = 0$ is a perfect correlation and would be seen at $r = 0$ if $x$ and $y$ were the same variable; $\xi > 1$ represents an anti-correlation. The value at $r = 0$ where $x$ and $y$ represent different quantities is a measure of how well they are related at the same location.

For the MW and OW cases, the roughness is anti-correlated with contact angle, Figs. 5.13(E) and (F), meaning that rougher surfaces are associated with lower values of the contact angle.
Figure 5.13: **Spatial correlations computed using Eq. [5.9].** (A-C) The spatial correlation of surface roughness \( (R_a) \). We see a correlation length of approximately a pore size. (D-F) The correlation between surface roughness and contact angle as a function of the distance between the measurements. Here a value of \( \xi > 1 \) indicates an anti-correlation in that greater roughness is associated with smaller contact angles. (G-I) The correlation between surface roughness and interfacial curvature. Here rougher surfaces, which tend to be more water-wet, are more likely to have a higher interfacial curvature \( (\xi < 1) \) for the MW and OW samples, consistent with the results in part (D-F). The vertical lines indicate the minimum pore diameter (dotted), average pore diameter (solid) and maximum pore diameter (dashed).
This explains two hitherto unobserved features of wettability, namely that the average contact angle is lower than that measured on a flat calcite surface at the same conditions and with the same fluids, and secondly why there is a wide range of contact angle. Water collects in grooves, invaginations and other high-curvature portions of the surface, see Fig. 1.1. The effective angle for a displacement is a combination of advance over this water in corners (with a zero angle) and over altered-wettability surfaces where oil has contacted the solid directly. The result is — on average — lower contact angles, albeit with a large variation — with a greater shift towards more water-wet conditions associated with rougher surfaces that are able to retain more water after primary drainage. For the WW sample, Fig. 5.13(D), the correlation is weaker since the wettability alteration is less significant. For interfacial curvature, Figs. 5.13(G-I), we see a positive correlation, in that more roughness, associated with slightly more water-wet conditions, is associated with larger curvatures.

In Figure 5.14 we study on a pore-by-pore basis the correlation (ρ) between the standard deviation of contact angle, oil/brine interface curvature and roughness: each point is calculated for a pore diameter interval of 10 µm, Eq. 5.10. We also define the correlations between pore-averaged values:

\[
\rho(d) = \frac{\sum_{i=1}^{N_p} I_i \tilde{x}_i \tilde{y}_i}{\sum_{i=1}^{N_p} I_i},
\]

where now the indicator function labels a pore with a diameter of a particular bin size, d. The sums are over the number of pores \(N_p\) while \(\tilde{x}_i\) and \(\tilde{y}_i\) represent pore-averaged values of either the variation in contact angle or curvature, and surface roughness respectively. Here \(\rho = 0\) indicates no correlation, while \(\rho = 1\) represents perfectly correlated variables.

With a complex pore geometry and fluid arrangement in a natural system we do not expect to have an exact relationship between the variables, nevertheless the following trends are clear. Figs. 5.13(A-C) show that the local surface roughness varies spatially with a correlation length that is around a pore size: we see variations of roughness both within and between pores, Fig. 5.11(C-D). This correlation is also seen for contact angle and interfacial curvature, Figure 5.12.

For the oil/brine interface curvature, WW sample shows little or no correlation between curvature and roughness. The reason for this is that the oil tends to reside as quasi-spherical droplets in the larger pores, see Figure 5.15, with an overall positive oil/brine interface curva-
Figure 5.14: Relationship between the variation in contact angle, interfacial curvature and surface roughness. The calculated correlation ($\rho$), Eq. ??, of curvature-based roughness ($R_a$) with measured contact angle and oil/brine interface curvature variation, as a function of pore diameter. Each column represents WW, MW and OW samples in order from left to right, respectively. Where $\rho = 1$ the two variables are strongly correlated.
ture indicative of the capillary pressure at which the oil ganglion was trapped.

Figure 5.15: **Roughness impact on contact angle and oil/brine interface curvature.** Two large pores cropped out from the OW and WW samples: The remaining oil layer follows the rock surface giving a negative average curvature in the OW sample, while in the WW sample the remaining oil ganglion fills the centre of the pore and tends to have an overall positive curvature.

In MW and OW samples, the variation in oil/brine curvature is more correlated with the rock surface roughness, Figure 5.15. In mixed-wet systems, oil layers form that tend to coat the solid surface. A rough surface experiences a wide variation in local curvature and hence we see a relationship between the variation of oil/brine interface curvature and surface roughness. This effect is more evident in the larger pores where a more representative fraction of the surface is covered with oil. Note that it is wrong to associate an oil-wet rock surface with a negative...
oil/brine interfacial curvature in a pore: consider an oil-wet drop on a surface surrounded by water - the drop has a positive curvature even when the contact angle is greater than 90°.

Similarly we see a correlation between the variation of contact angle and roughness that again is more evident in the larger pores, where more measurements can be taken. On a rough surface the effective angle, measured at the resolution of the image, may differ significantly from the intrinsic, local, angle at the molecular scale. We suggest that for rougher surfaces we see a greater range of contact angle since there are more deviations from the average than would be seen on a smooth surface. In Figure 5.16, we show the contact angle, oil/brine interface curvature and curvature-based roughness ($R_a$) measurements frequency in a pore. We observe larger pores to contain higher number of measurements as expected.

### 5.6 Pore wall curvature distribution

Pore wall curvatures were measured on pore-space images of a beadpack (each bead is 50 voxels across) [Finney, 1970, Prodanović and Bryant, 2006], Bentheimer sandstone - provided by iRok Technologies [2013], a sandpack, Ketton limestone, Doddington sandstone, Estaillades limestone and Portland limestone were obtained using the micro-CT scanning facilities at Imperial College London [2018] and the WW, MW and OW samples [Alhammadi et al., 2017b]. The images are segmented using a watershed segmentation algorithm using Avizo Fire®as image processing software; more technical details can be found in [Andrew, 2014]. The Bentheimer, Doddington, and Estaillades images have been previously analysed by Alhashmi et al. [2016], Bijeljic et al. [2013], Meyer and Bijeljic [2016], Raenie et al. [2012]. The automated algorithm provides several hundred thousand pore wall curvature values, as shown in Figure 5.17. Throughout the sample volumes we observe a range of curvatures largely positive values for the beadpack and sandpack, representing a solid phase that bulges out into the pore space, as would be expected for spherical, or nearly spherical, grains, to predominantly negative curvature in the limestones, which is indicative of ellipsoidal-shaped pore spaces. Further, we calculate the average diameter of grains ($L_{\text{grain}}$), defined in Mostaghimi et al. [2012], using:

$$L_{\text{grain}} = \frac{\pi V}{S}$$  \hspace{1cm} (5.11)
Figure 5.16: **Pore frequency of contact angle, oil/brine interface and roughness measurements.** Contact angle (A-C), oil/brine interface curvature (D-F), surface roughness (G-I) and pore volume in voxels (J-L). The larger pores show larger number of the contact angle, oil/brine interface curvature and roughness (R<sub>a</sub>) measurements.
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Figure 5.17: **Rock wall curvature measurements.** Three-dimensional view of (A) a bead-pack, (B) a sandpack, (C) Ketton, (D) Bentheimer, (E) Doddington, (F) Estailades, (G) Portland, (H) WW, (I) MW and (J) OW samples. The positive and negative curvatures are indicated by red and blue, respectively.

where $V$ and $S$ are the image volume and the rock surface area in the void space. A list of calculated values are in Table 5.1. We use the calculated average diameter of grains as the characteristic length to normalize pore surface curvature. In Figure 5.18, we plot histograms of normalized pore curvatures and pore diameter, which allows us to distinguish different pore morphology signatures.

In Table 5.1, we present for all the samples the image size in voxels, voxel size, median curvature value, measured helium porosity, calculated porosity from the segmented image and the gain length estimated using Eq. 5.11. There is a clear impact of degree of consolidation on curvature distributions: while the unconsolidated beadpack and sandstone are mainly comprised of pores with positive curvature, the pore morphology in consolidated sandstones and limestones is characterised by the existence of pores with both negative and positive curvature. We note that curvature values are less positive for a sandpack compared to a beadpack, while the limestones have more pronounced negative curvatures than the sandstones. In Figure 5.19, we visualize examples of small and large pores with positive and negative wall curvatures in an exemplar complex consolidated media (WW, MW and OW samples). We observe that pores with negative curvatures are more isolated from other pores than the pores with positive
Table 5.1: The image size in voxels, measured median surface curvature, porosities and estimated grain length.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Image size (voxels)</th>
<th>Voxel size (micron/voxel)</th>
<th>Pore curvature (µm⁻¹)</th>
<th>Helium porosity (%)</th>
<th>Image porosity (%)</th>
<th>L_{grain} (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beadpack</td>
<td>500³</td>
<td>1³</td>
<td>0.0806</td>
<td>-</td>
<td>35.2</td>
<td>50</td>
</tr>
<tr>
<td>Sandpack</td>
<td>450³</td>
<td>10³</td>
<td>0.0084</td>
<td>-</td>
<td>35.4</td>
<td>224.57</td>
</tr>
<tr>
<td>Ketton</td>
<td>1000³</td>
<td>3³</td>
<td>-0.0322</td>
<td>-</td>
<td>13.1</td>
<td>520.13</td>
</tr>
<tr>
<td>Dodgington</td>
<td>1000³</td>
<td>2.7³</td>
<td>0.0001</td>
<td>-</td>
<td>19.3</td>
<td>293.14</td>
</tr>
<tr>
<td>Bentheimer</td>
<td>1000³</td>
<td>3³</td>
<td>-0.0049</td>
<td>-</td>
<td>21.2</td>
<td>225.52</td>
</tr>
<tr>
<td>Portland</td>
<td>973 × 973 × 883</td>
<td>3.8³</td>
<td>-0.0378</td>
<td>-</td>
<td>7.2</td>
<td>569.48</td>
</tr>
<tr>
<td>Estaillades</td>
<td>1000³</td>
<td>3.3³</td>
<td>-0.0753</td>
<td>-</td>
<td>12.5</td>
<td>283.77</td>
</tr>
<tr>
<td>Samples 1</td>
<td>984 × 1014 × 601</td>
<td>2³</td>
<td>-0.0569</td>
<td>27.0</td>
<td>20.8</td>
<td>165.47</td>
</tr>
<tr>
<td>Samples 2</td>
<td>984 × 1014 × 601</td>
<td>2³</td>
<td>-0.1076</td>
<td>31.7</td>
<td>20.4</td>
<td>130.72</td>
</tr>
<tr>
<td>Samples 3</td>
<td>976 × 1014 × 601</td>
<td>2³</td>
<td>-0.0799</td>
<td>30.5</td>
<td>20.2</td>
<td>152.45</td>
</tr>
</tbody>
</table>

Figure 5.18: **Pore wall curvature signatures.** Histograms of normalized pore curvature (red) and pore diameter (blue) of (A) a beadpack, (B) a sandpack, (C) Ketton, (D) Bentheimer, (E) Dodgington, (F) Estaillades, (G) Portland, (H) WW sample, (I) MW sample and (J) OW sample. The beadpack and sandpack are have pores with positive curvature, while the rest consist of pores with both negative and positive curvature. The smaller pores tend to have negative curvature while large pores have values close to zero.
curvature: this is consistent with the surface being curved to enclose a region of the pore space. Pores with more connections (throats) to neighbouring pores tend to contain more walls with positive curvature: the throat are restrictions in the pore space and the pore wall therefore has to have one negative radius of curvature that bulges into the pore space. Moreover, in complex consolidated media (such as WW, MW and OW sample) the smaller pores tend to have a more negative curvature in contrast to the larger pores, which is to be expected, as curvature scales with the inverse of a characteristic length.

5.7 Impact of pore morphology and wettability on layer flow

In Figure 5.20, we plot the average mode oil/brine interface curvature for each ganglion versus the average mode pore wall curvature for the WW, MW and OW samples. The mode function represents the most frequent curvature value. For the WW sample, we observe that the ganglia curvature is positive regardless of the shape of the pore - an example is presented in Figure
Figure 5.20: Relationship between the variation in pore curvature and ganglion interface curvature. The measured pore curvature and oil/brine interface curvature, as a function of pore diameter and ganglion volume, respectively, for (A) WW, (C) MW and (E) OW samples. In (B), (D) and (F), we present a ganglion in WW, MW and OW samples, respectively. The measurements of the ganglion of (B), (D) and (F) are indicated with green circles on (A), (C) and (E).
Moreover, in the small pores the curvature values are higher than in the large pores, we anticipate this to be due to the higher entry pressure required. For the MW and OW samples, a range of positive and negative ganglia curvatures is seen - we observe that the thin oil layer tends to follow the curvature of the pore walls resulting in a wide range of positive and negative wall curvatures as well as the pores having mixed wettability: water-wet pores and oil-wet pores with contact angles below and above 90°. We illustrate this in Figure 5.20 with an example of an oil ganglion forming a thin layer in the OW sample which tends to be trapped in isolated pore corners and follows the pore wall curvature.

Figure 5.21: **Flux number and pore diameter correlation** The estimated flux number which is the ratio of the sum of the diameters of the throats connected to a pore divided by the pore diameter, as a function of pore diameter for (A) a beadpack, (B) a sandpack, (C) Ketton, (D) Bentheimer, (E) Doddington, (F) Estaillades, (G) Portland, (H) WW sample, (I) MW sample and (J) OW sample. The smaller pores, with negative curvature (round shape), tend to have smaller flux number (more isolated) while large pores, with positive curvature (star shaped), tend to have larger flux number (more connected).

There is a signature of pore morphology (pore curvature) on the oil layer flow - as in the three samples we observe that in the small pores the layer tends to be more more isolated and curvy than in the large pores. We define a flux ratio which estimates the ability for flow between pores, as the sum of the diameter of all the throats connected to a pore divided by the pore diameter. Pores with positive wall curvature are observed to have higher coordination number (more throats connecting a pore with neighbouring pores) and flux number, see Figure 5.21.

The signature of pore morphology using pore flux number and pore curvature is shown in Figure 5.22, which shows a similar signature shown in Figure 5.21. In this plot we include an analysis for all the rock samples considered in this section. In the MW and OW samples, the wide-range
of pore wall curvatures can demonstrate their potential for oil layer flow: this is seen in Figure 5.18 as the oil ganglia curvature tends to have similar curvature to the pore curvature. An example of this type of ganglia is presented in the same figure. Also, we notice that for the OW sample thicker oil layers exist along the pore-wall with negative curvatures.

Figure 5.22: Pore wall curvature signatures. Signature pore morphology figures combining histograms of pore diameter (blue) and plots of pore flux number as a function of normalized pore curvature (red dots) of (A) a beadpack, (B) a sandpack, (C) Ketton, (D) Bentheimer, (E) Doddington, (F) Estaillades, (G) Portland, (H) WW sample, (I) MW sample and (J) OW sample. The smaller pores tend to have low pore flux number while large pores have high values. This is in agreement with the signature shown in Figure 5.18.

This is a preliminary analysis of the relationship between surface roughness, fluid flow, pore size and layers. It is likely that the origin of the large range of contact angle observed in our reservoir rocks is surface roughness. This in turn accommodates layers of both oil and water allowing both phases to flow over a wide saturation range. When the average contact angle is close to 90° recovery is most favourable. Further work, as discussed in the next chapter, is required to develop a more quantitative and predictive understanding of the relationship between surface roughness, wettability and recovery.
6. Conclusions and future work

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6.1 Conclusions

This thesis presents an automated method to measure in situ contact angles, fluid/fluid interface curvature, surface roughness and a signature of pore morphology from three-dimensional pore-scale images. The algorithm was verified using single spherical oil droplet on a tilted plane as a test case over a range of resolutions and further demonstrated on micro-CT images of pore-scale multiphase flow experiments. Also, the distribution of contact angles measured by our method is consistent with manual measurements Andrew et al. [2014], and a point-by-point comparison between the manual method and our method has been tested in Alhammadi et al. [2017b] shows the results are in good agreement. However, the automated method is rapid - as an example using a single 2.2 GHz CPU processor, it provides 2196 data points in 1.6 minutes using the optimal parameters (see Table-4.1). The contact angle algorithm can be applied to any image with distinct solid and fluid phases.

We have applied image processing and pore-network analysis to three micro-CT images of oil and water obtained after waterflooding at representative reservoir conditions in carbonate rock samples from a producing oil field. We have measured the distribution of contact angle, oil/brine interface curvature and roughness. We have used a network analysis to assign contact angle, oil/brine interface curvature and roughness values to pores and throats.

We see a wide distribution of contact angles with values both above and below 90°. For the MW and OW samples with more mixed-wet or oil-wet conditions, there is a tendency for the larger pores to be oil-wet (average contact angles above 90°). We see no obvious correlation between contact angle, oil/brine interface curvature and throat size. However, there is a correlation between contact and oil/brine interface curvature on a ganglion-by-ganglion basis. For each trapped ganglion, the mode curvature decreases as the contact angle increases, with positive curvatures associated with water-wet conditions, and negative curvatures likely to be associated with oil-wet regions of the pore space.

The contact angle is spatially correlated with a correlation length of approximately the average pore size. There is also a wide distribution of contact angle within each pore.

The results of this study have some concerning implications for pore-scale modelling, where a pore-averaged contact angle and pore or throat size are used to compute capillary pressures.
and, by implication, oil/brine interfacial curvatures. However, further tests are needed before reaching definitive conclusions. Nevertheless, our results show that there is no evident relationship between these quantities in a representative reservoir system; instead it may be better to treat wettability on a ganglion-by-ganglion basis, but it is not clear how to do this a priori, before we know the final fluid distribution after a displacement. While pore-averaged contact angles could be assigned to pore network models, it is not clear that these will lead to a more accurate prediction of capillary pressure for pore-scale displacement than the rather ad hoc methods used currently. Perhaps it is more useful to consider the assignment of local oil/brine interfacial curvature directly into models as a way of estimating capillary pressures for displacement.

In rock with unaltered wettability, surface roughness drives the system to more water-wet conditions [Cassie and Baxter, 1944]. We have shown that in this case, the interfacial curvature is approximately constant and positive. The non-wetting phase (oil in this case) is trapped as quasi-spherical ganglia in the larger pore spaces. This is optimal for storage applications, such as carbon dioxide sequestration, where it is desirable to trap one phase in the pore space to prevent migration and escape. However, this is not ideal for oil recovery, or other processes, such as gas transport through membranes or in biological tissues, for instance, where it is necessary to allow the flow of both fluids.

However, in rocks with an altered wettability, we observe oil layers that tend to follow the local curvature of the surface. The range of contact angle and curvature increases with the degree of roughness, with the correlation more obvious in larger pores and for a stronger wettability change. The contact angle tends to be lower on rougher surfaces due to the accumulation of water in crevices which make the surface effectively less oil-wetting. We have a mixed-wet state with local contact angles both above and below 90°. This facilitates the flow of both phases, which is favourable for oil recovery [Alhammadi et al., 2017b]. It is well-understood that using surfactants or changing the brine salinity, oil recovery can be improved through changing the wettability [Jerauld and Rathmell, 1997, Morrow, 1990]. However, we suggest that a mixed-wet state is ideal, which contrasts with the current assumption that moving towards a more uniformly water-wet state is preferred [Morrow and Buckley, 2011].
6.2 Future Work

In this work the developed automated methods have been applied for estimating wettability, surface roughness and pore morphology signature in unconsolidated porous media and porous rocks. However, we hypothesize that in other porous materials, where it is desirable to allow both a liquid and a gas phase to flow over a wide range of saturation, the combination of wettability alteration and rough surfaces leads to a mixed-wet state. This could be tested, for instance, in leaves, lung tissue and multiphase catalysts, using the image and analysis methodology proposed here. Furthermore, such a wettability state could be designed to improve the performance of fuel cells [Grey and Tarascon, 2017], catalysts, membranes and other porous materials.

The contact angle measurement is sensitive to the contact line and fluid/fluid interface curvature in the segmented image, see supporting materials in Alhammadi et al. [2017a]. The developed automated method can be utilized to improve the segmented image - this can be achieved by optimizing the segmentation parameters, else other suggestion would be is to further develop the automated method by imposing some realistic constraints to the fluid/fluid interface curvature. To achieve this, further testing and validation are required on more complex geometries, such as a beadpack, a sandstone and Ketton.

Further, measuring in situ contact angles and fluid/fluid interface curvature in different types of core samples would allow researchers to define more realistic contact angle and fluid/fluid interface curvature distributions, which include natural variability and uncertainty, for reservoir characterization. These distributions could then be used to more accurately predict multiphase fluid flow in pore-scale models. Altered wettability systems that have undergone fluid displacement cycles are likely to have a wide range of contact angles and fluid/fluid interface curvature and should not be considered to be uniformly wetting or non-wetting.

Also, measuring surface roughness and defining its relationship to contact angle and fluid/fluid interface curvature measurements can help to assign/predict realistic contact angle and fluid/fluid interface curvature distributions in pores where there are no measurements.

Furthermore, the computational performance of the automated methods can be further optimized using multiple processors or Graphical Processor Units (GPU) in parallel.
Also, further applications can be developed to, for instance, predicting fluid configurations in other pores where there is no measurements, using unsupervised machine learning methods called generative adversarial networks (GANs) that allow simulation of probability distributions given a set of training data can Goodfellow et al. [2014]. This GAN technique can be used to model three-dimensional textures of rocks based on three-dimensional binary representations of porous media acquired at the micrometer scale Mosser et al. [2017]. We suggest to deploy GAN to model three-dimensional fluid configuration at a certain wettability conditions, and apply the developed automatic to measure contact angle and fluid/fluid interface curvature. In addition, another machine learning technique to reconstruct porous media using convolution neural networks Wang et al. [2018] that allow to enhance the resolution of three-dimensional micro-CT based image. We can apply the developed automatic method to measure nano-scale rock surface roughness on the regenerated super high resolution Wang et al. [2018].


Raeesi, B., Morrow, N. R., and Mason, G. Effect of surface roughness on wettability and displacement curvature in tubes of uniform cross-section. *Colloids and Surfaces A:*


