IMPACT OF OSTWALD RIPENING ON RESIDUALLY TRAPPED CARBON DIOXIDE

A report submitted to the department of Energy Resources Engineering of Stanford University in partial fulfillment of the requirements for the degree of Master of Science

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I certify that I have read this report and that in my opinion it is fully adequate, in scope and in quality, as partial fulfillment of the degree of Master of Science in Energy Resources Engineering.

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Abstract

The stability of residually trapped CO2 is often taken for granted in the simulation studies used for predicting the long-term fate of CO2 in geological storage reservoirs. Ostwald ripening is one of the mechanisms that could potentially remobilize residually trapped CO2. This mechanism would cause the gradual growth of ganglia with low capillary pressures at the expense of ganglia with higher capillary pressures. The growth of ganglia becomes an issue if the ganglia start expanding in the vertical direction. In porous media, capillary pressure at the top of a column of gas is directly related to the column height. Above a critical height, the capillary pressure at the top of the column could overcome the capillary entry pressure of the pores directly above it, and induce gravitational remobilization. Capillary heterogeneities at the pore scale are known to affect large-scale migration of gas plumes however. Ostwald ripening will be driven by differences in capillary pressure between ganglia, and subsequent diffusion of dissolved CO2 through the aqueous phase. In a bulk liquid medium, a bubble of gas is observed to be spherical. The capillary pressure of a spherical bubble of gas is inversely proportional to the bubble radius. In porous media on the other hand, the gas phase (observable through microtomographic imaging) takes the form of ganglia with complicated shapes and sizes. Capillary pressures of individual gas ganglia are thought to depend not on total ganglion volume, but rather on pore geometry and topology. A stable equilibrium where disconnected ganglia of different sizes share the same capillary pressure can be imagined. Critical questions relate to understanding and measuring the distribution of capillary pressure in isolated, disconnected ganglia, as well as studying their evolution in time. The goal of this study is therefore two-fold.
We develop reliable methods to estimate the capillary pressure distributions for populations of disconnected ganglia of gases that are trapped during imbibition experiments in sandstones. Multi-resolution X-ray microtomography datasets from air-water spontaneous imbibition experiments in sintered glass beads and sandstone samples were acquired at the Advanced Light Source, in the Lawrence Berkeley National Laboratory. A series of computational techniques to process microtomography images; estimate curvature at the interface between two immiscible fluids; and then link these curvature estimates to the capillary pressures of the ganglia were developed based on these data sets. The work flow we develop allows us to estimate curvature distributions for disconnected gas ganglia and assess the reliability of the estimates. Pore structure as well as resolution are found to have a significant impact on curvature estimation. The capillary pressures of disconnected ganglia are also found to be controlled by neighboring pore throat radii. The capillary pressure at different locations on interface of a single ganglion is found to be similar, such that the average capillary pressure for a ganglion is well defined and displays little variability. The distribution of the average capillary pressures for disconnected ganglia is quantified in the different samples and across samples in order to assess the potential for Ostwald Ripening.

A second research effort presented in this report focuses on simulating the evolution of multi-ganglia systems governed by ripening mechanisms in porous media. Using reduced dimension representations of the pore space, we study evolution in the context of simple physical laws to find equilibrium positions and guide physical intuition. The final equilibrium situation as well the time scales for evolution are found to be highly dependent on system initialization as well as on pore structure. The simulations also highlight the different evolution regimes of a multi-ganglia system in the bulk and porous medium settings.
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Chapter 1

Introduction

1.1 Background

Carbon Capture and Storage is a technology that has the potential to greatly reduce carbon dioxide emissions Metz et al. (2005). Geological storage is the process by which CO$_2$ is injected into the subsurface, where it is expected to remain trapped for hundreds to thousands of years. Technical and economic viability are key to its success. A general representation is that four trapping mechanisms operate when CO$_2$ is injected in porous rocks: structural, residual, solubility and mineral trapping Bachu (2008); Benson and Cole (2008).

Although significant efforts have been deployed over the last decade to increase the performance and predictability of carbon dioxide sequestration in deep formations, questions still remain due to the complexity of the fundamental science that underlies the behavior of supercritical CO$_2$ in brine-filled rocks. A key issue that still needs to be addressed is the long-term reliability of residual trapping, which is a major process for storage security in the reservoir. Residual CO$_2$ trapping occurs when water imbibes back into the rock, typically after injection stops. As the water imbibes back into the rock, the gas phase is disconnected into isolated ganglia through the mechanism of snap-off (Figure 1.1). From then on, the stability of residually trapped CO$_2$ is often taken for granted in the simulation studies used for predicting the long-term fate of CO$_2$. It is indeed assumed that residual trapping will permanently immobilize
the CO$_2$ until it is dissolved or mineralized. However, there is little experimental data either from laboratory experiments or from natural analogues to validate this hypothesis.

Figure 1.1: Conceptual model for snap-off - adapted from Holtz et al. (2002)

A mechanism that could have a significant impact on the long-term evolution of residual trapping is Ostwald ripening, which would cause the gradual growth of ganglia with low capillary pressures at the expense of ganglia with higher capillary pressures. In the context of geological storage, the growth of ganglia may become an issue if the vertical expansion of the ganglia eventually results in a capillary pressure high enough to induce gravitational remobilization upward.

CO$_2$ has a lower density than water, which makes it naturally buoyant in geologic formations. Seals are therefore necessary for the CO$_2$ to remain underground. Certain types of rock can act as seals by acting as both permeability and capillary barriers. Permeability affects the rate at which fluids flow through the rock. The capillary entry pressure of a rock is linked but not equivalent to its permeability. In the case of CO$_2$ and brine (salty water), the capillary entry pressure of a rock represents the difference in pressure between the two fluids that is necessary in order for the CO$_2$ to start entering the rock.
The fluids of interest in this report are brine and CO$_2$. In most geologic settings, brine is the wetting fluid and CO$_2$ is the non-wetting fluid. If we consider a vertical column of CO$_2$ in a reservoir with height $H$, the difference in pressure between the brine and the CO$_2$ at the top of the column is the capillary pressure $P_c = \Delta \rho g H^1$.

The capillary entry pressure of the pores just above the column of CO$_2$ is defined as $P_{entry} = \frac{2\sigma \cos(\theta)}{r_{pore}}$.

For a given pore radius $r_{pore}$, we can now define the critical height $H_{lim}$ as:

$$H_{lim} = \frac{2\sigma \cos(\theta)}{\Delta \rho g r_{pore}}$$  \hspace{1cm} (1.1)

This is the height of a column of gas such that the gas can enter the pore directly above it. In Figure 1.2 (a), we plot this height over a representative range of diameters, and Figure 1.2 (b) provides common pore diameters for reservoir and seal rocks to compare. Note that the $y$-axis of Figure 1.2 (b) is a direct representation of whether a given rock is a good capillary barrier and the $x$-axis of Figure 1.2 (b) is a direct representation whether a given rock is a good permeability barrier. The critical height in Figure 1.2 (a) will tell us at what pressure the gas starts to remobilize in the reservoir rock and the permeability in Figure 1.2 (b) will tell us how mobile the gas phase is.

The values obtained for $H_{lim}$ may seem small, especially for reservoir rocks. Real rocks are not homogeneous, however and have pore sizes that fluctuate around a mean pore size, as is shown in Figure 1.3. This heterogeneity in rocks has been referred to as capillary heterogeneity and could potentially block the capillary rise of CO$_2$ Krevor et al. (2011). Quantitative modeling approaches to study capillary heterogeneity like Li and Benson (2014) also demonstrate how pore scale effects can influence large scale migration.

\footnote{$^1\Delta \rho$ is the density difference between the brine and the CO$_2$, $g$ is the acceleration due to gravity}

\footnote{$^2\sigma$ is interfacial tension, $\theta$ is the contact angle and $r_{pore}$ is the radius of the pore}
CHAPTER 1. INTRODUCTION

(a) Evolution of the critical height $H_{\text{lim}}$ with pore diameter


Figure 1.2: Comparing the critical height for remobilization to common pore diameters

Figure 1.3: Log-normal distribution for pore radii, for three scale parameters ($\Sigma$) and the same location parameter ($\mu = -10$)
1.2 Problem statement

Consider two immobile bubbles of gas in a liquid saturated in dissolved gas. Laplace’s law states that the difference in pressure between the bubbles and the surrounding liquid, called capillary pressure, is proportional to the mean curvature of the surface of the bubbles. In a liquid and in the absence of any interaction with a surrounding structure, bubbles of gas tend to assume a spherical shape, to minimize their surface area. The difference in pressure between the surrounding liquid and the bubbles is inversely proportional to the size of the bubbles. The larger the bubble, the lower its capillary pressure. A system of multiple bubbles in a bulk liquid is therefore fundamentally unstable, since the small bubbles have higher capillary pressures than the larger ones. By diffusion of the gas through the liquid, the smaller bubbles will disappear at the expense of the larger bubbles. This well-known phenomenon is usually called Ostwald Ripening. In its most basic form, the question we are asking in this report is whether the same thing happens in a porous medium.

To make things clearer in the context of carbon storage, we place ourselves in a post-injection situation where viscous forces no longer play a significant role. It is generally assumed that bubbles of gas are disconnected by re-imbibition of brine through the gas phase Iglauer et al. (2011); Tanino and Blunt (2012); Andrew et al. (2014b); Chaudhary et al. (2013). We will take this hypothesis as a starting point. We consider a location far from the injection site. Only Fickian diffusion is considered as a driver for remobilization in this study. Ostwald ripening will be driven by differences in capillary pressure, and is inherently a pore scale process. Although extensively studied in the bulk case, it is often neglected in porous media. Capillary pressures in the porous medium are strongly related to the local pore network topography and geometry, which make their precise determination and evolution complex.

Considering purely diffusion-driven processes, can isolated bubbles aggregate into clusters large enough to induce gravitational remobilization?
1.3 Report outline

In this report, we describe a series of research efforts that aim at assessing the potential for diffusion-driven remobilization of disconnected gas ganglia in porous media, in the context of the long-term stability of carbon storage. In chapter 2, we present some theoretical considerations on the Ostwald Ripening mechanism. We describe the mechanism in the absence of interactions with a porous medium and numerically solve for evolution on a simple case with two spherical bubbles. We then give some theoretical insights on why equilibrium situations for the mechanism with multiple ganglia seem possible in the porous medium case. In chapter 3, we develop a method to estimate the capillary pressure distributions for populations of gas ganglia in porous media, using synchrotron images of residually trapped disconnected ganglia. The method takes advantage of advances in X-ray imaging to estimate the pressures of the ganglia, where sensors cannot be placed. In chapter 4, we test the multi-ganglia equilibrium hypothesis we made in chapter 2 and build simulation models to study the evolution of systems governed by ripening mechanisms in porous media. Finally, we make some concluding remarks in chapter 5.
Chapter 2

Theoretical considerations on the Ostwald Ripening process

In this chapter, we present the governing equations for Ostwald ripening in the bulk (or free) liquid setting in order to identify the key drivers for the process, as well as estimate characteristic evolution time scales. We then comment on the key differences in the porous media setting, and give some insights on why multi-ganglia equilibria seem possible.

2.1 Ostwald Ripening of gas bubbles in a bulk liquid

The Ostwald Ripening mechanism has been extensively studied in a homogeneous medium where dispersed particles of a second phase exist in a saturated solution, and where the bigger particles tend to grow at the expense of the smaller ones. Approximate solutions for the rate of growth and dissolution in oversaturated and undersaturated solutions were derived by Epstein and Plesset (1950). In the setting of Ostwald Ripening however, it is assumed that the solution is exactly at saturation. This is the case of Greenwood (1956), which studies the growth of solid particles in liquid solutions, and whose expression for growth is closest to the one we derive in
this section. The classic work Lifshitz and Slyozov (1961) analyzes the precipitation
of grains of a second phase in a supersaturated solution, and the subsequent growth
or coalescence of the larger grains at the expense of the smaller ones when the degree
of supersaturation of the matrix becomes very small. This work as well as a more
modern approach to the theory of Ostwald Ripening was reviewed and extended
by Voorhees (1985). Liquid-gas solutions were specifically targeted by Schmelzer
and Schweitzer (1987), using a thermodynamic approach based on the Gibbs free
energy of the bubbles. The main conclusion was that multi-bubble systems in an
otherwise homogeneous medium are thermodynamically unstable. In this section, we
analyze the evolution of a simple two-bubble system in a homogeneous medium. We
present the equations that govern the Ostwald Ripening mechanism and solve them
numerically in our simplified setting. This allows us to estimate characteristic time
scales for the Ostwald Ripening mechanism in the bulk case as well as identify its key
drivers.

2.1.1 Problem statement

We place ourselves in an idealized setting to study the Ostwald Ripening mechanism.
In this setting, we consider two spherical bubbles of gas that are in a liquid solution.
The bubbles are immobile. The solution is assumed to be saturated with dissolved
gas. A schematic is provided in Figure 2.1. We assume that the bubbles may not
move, but they can exchange mass with the surrounding liquid via dissolution or
exsolution. The mechanism is well described by three fundamental laws:

• Laplace’s law links the difference in pressure between the gas and the surround-
ing liquid to the curvature of the surface of the gas, or in this simple case, the
inverse of the radius of the bubbles

• Henry’s law\(^1\) links the pressure of the gas to the concentration of dissolved gas
inside the liquid, at the interface between the two. The link is proportionality.

---

\(^1\)Henry’s law assumes that the solution is dilute
• In the presence of a concentration gradient, Fick’s law describes the mass transport of solute gas by diffusion through the liquid.

Based on these laws, it is known that the system is thermodynamically unstable (Schmelzer and Schweitzer (1987)). Gas will dissolve from the smaller bubble into the liquid, migrate to and exsolve in the larger bubble. In this section, we describe the evolution of such a system. We derive a system of coupled equations on the radii of the two bubbles that governs the growth of the larger bubble at the expense of the smaller bubble. We then solve this system for evolution numerically, and use the results to estimate characteristic evolution time scales. These time scales will give a sense of how fast Ostwald Ripening occurs in the bulk case, to serve as a benchmark when we study the ripening mechanism in the porous medium case.

![Figure 2.1: Idealized setting for Ostwald Ripening](image)

2.1.2 Governing equations for the two-bubble model

We now derive the governing equations for the system we just described (see Figure 2.1). The two bubbles will be denoted by \( a \) and \( b \).

**Laplace equation for capillary pressure** With \( P_{a,b} \) the pressure in bubble \( a, b \); \( P_l \) the pressure inside the liquid (note this is also the saturation pressure); \( \sigma \) the surface tension and \( R_{a,b} \) the radius of bubble \( a, b \):

\[
P_{a,b} = P_l + \frac{2\sigma}{R_{a,b}} \quad (2.1)
\]
We then relate the pressure inside each of the bubbles to the concentration of dissolved 
gas at the interface between the liquid and the gas, using Henry’s law:

**Henry’s Law** with \( C_{a,b} \) the concentration at the interface between the liquid and 
bubble \( a, b \); \( C_s \) the saturation concentration (or solubility) and \( H \) Henry’s constant 
such that \( P_s = HC_s \) and \( P_{a,b} = HC_{a,b} \):

\[
C_{a,b} = C_s + \frac{2\sigma}{HR_{a,b}}
\]  
(2.2)

The third and final fundamental law we apply governs the mass transfer rate:

**Fick’s Law** the norm of the diffusion flux is \( D \frac{\partial C}{\partial x} \) with \( D \) the diffusivity. With the 
concentrations in \( \frac{kg}{m^3} \), a first order approximation for the flow of mass from one bubble 
to another can be written as:

\[
\frac{\partial m}{\partial t} = DA \frac{\Delta C}{x}
\]  
(2.3)

with \( A \) the area available for diffusion and \( x \) the distance between the bubbles. We 
consider that \( A \) is the surface made available by the throat between the two pores.

Using these three equations, we now derive a system of coupled equations on the 
radii of the two bubbles:

**System of equations for** \( R_{a,b} \) with \( \rho \) the density of the gas, we also have:

\[
\frac{\partial m_{a,b}}{\partial t} = \frac{\partial (\rho \frac{4}{3} \pi R_{a,b}^3)}{\partial t} = 4\pi \rho R_{a,b}^2 \frac{\partial R_{a,b}}{\partial t}
\]

From (2.2) we have \( \Delta C = \frac{2\sigma}{H} \left( \frac{1}{R_b} - \frac{1}{R_a} \right) \) (we will consider the mass entering bubble 
\( a \)), so

\[
4\pi \rho R_a^2 \frac{\partial R_a}{\partial t} = DA \frac{2\sigma}{H x} \left( \frac{1}{R_b} - \frac{1}{R_a} \right)
\]

If we choose to express \( H \) as \( \frac{P_s}{C_s} \) and make the additional assumption that the ideal gas
law holds; \( P_s = \frac{RT\rho^2}{M} \) and we find an expression equivalent to the one in Greenwood (1956),

\[
4\pi\rho R_a^2 \frac{\partial R_a}{\partial t} = D(\frac{A}{x}) \frac{2M\sigma C_s}{RT\rho} \left( \frac{1}{R_b} - \frac{1}{R_a} \right)
\]

since we have \( \frac{\partial m_a}{\partial t} = -\frac{\partial m_b}{\partial t} \), this leads us to the following symmetrical system for \( R_{a,b} \):

\[
\begin{align*}
\frac{\partial R_a}{\partial t} &= \alpha \frac{R_a^2}{R_b^2} \left( \frac{1}{R_b} - \frac{1}{R_a} \right) \\
\frac{\partial R_b}{\partial t} &= \alpha \frac{R_b^2}{R_a^2} \left( \frac{1}{R_a} - \frac{1}{R_b} \right)
\end{align*}
\]

(2.4)

where we introduced the coefficient

\[
\alpha = \frac{1}{2\pi RT} \frac{A}{x} \frac{MD\sigma C_s}{\rho^2} \quad [m^4.s^{-1}] \quad (2.5)
\]

This coupled system of equations shows that a two bubble system such as the one in Figure 2.2 (a) is thermodynamically unstable. Even a slight difference in the radii can only amplify in time until the smaller radius goes to zero. In the bulk case, the stable situation is the one in Figure 2.2 (b).

Figure 2.2: A two-bubble system governed by the Ostwald Ripening mechanism in a bulk liquid is thermodynamically unstable

\[\text{with } T \text{ temperature, } M \text{ molecular mass and } R \text{ the ideal gas constant.} \]
Dimensionalizing the system  We introduce the dimensionless radii $R_{a,b}^*$

$$
\begin{cases}
R_{a}^* = \frac{R_a}{R_0} \\
R_{b}^* = \frac{R_b}{R_0}
\end{cases}
$$

(2.6)

where $R_0$ is a characteristic radius (we can take the average of the initial radii, for example) for the system. We substitute $R_{a,b}$ with $R_0 R_{a,b}^*$ in the system of equations to get

$$
\begin{cases}
\frac{\partial R_{a}^*}{\partial t} = \frac{\alpha}{R_0^4} \left( \frac{1}{R_{a}^*} - \frac{1}{R_{b}^*} \right) \\
\frac{\partial R_{b}^*}{\partial t} = \frac{\alpha}{R_0^4} \left( \frac{1}{R_{b}^*} - \frac{1}{R_{a}^*} \right)
\end{cases}
$$

(2.7)

And we can check that $\lambda = \frac{\alpha}{R_0^4}$ has the dimension of a frequency:

$$
\lambda = \frac{AMD\sigma C_s}{2\pi RT\rho^2 R_0^2} \quad [s^{-1}]
$$

(2.8)

The dimensionless system reads

$$
\begin{cases}
\frac{\partial R_{a}^*}{\partial t} = \frac{\lambda}{(R_{a}^*)^2} \left( \frac{1}{R_{b}^*} - \frac{1}{R_{a}^*} \right) \\
\frac{\partial R_{b}^*}{\partial t} = \frac{\lambda}{(R_{b}^*)^2} \left( \frac{1}{R_{a}^*} - \frac{1}{R_{b}^*} \right)
\end{cases}
$$

(2.9)

We can rewrite $\lambda$ such as to clearly identify the defining terms:

$$
\lambda = \frac{1}{2\pi} \frac{DA C_s}{x} \frac{\sigma}{\rho R_0^3 R_0 P_s}
$$

(2.10)

The first term ($\frac{DA}{x}$) is a characteristic flow rate for the diffusion process. The second one ($\frac{\rho R_0^3}{C_s}$) is the volume of brine that is necessary to dissolve the gas in a spherical gas bubble with radius $R_0$. It compares the solubility to the mass of a bubble of gas with radius $R_0$. The last term ($\frac{\sigma}{R_0 P_s}$) is the ratio of the pressure exercised by capillary forces on a gas sphere of radius $R_0$ to the saturation pressure $P_s$. Note that $P_s$ is also the partial pressure of the gas in the liquid.
2.1.3 Estimating characteristic time scales from the two-bubble model

The characteristic frequency $\lambda$ can be used to extract characteristic time scales for the coupled system of equations we have just described. We identify three parameters that depend on the pore structure and initialization of the bubbles: the area available for diffusion $A$, the distance between the two bubbles $x$ and the characteristic radius $R_0$. The other parameters are thermodynamic quantities that depend mainly on the temperature and pressure conditions under consideration. Figure A.1 gives a phase diagram for CO$_2$ and Figure A.2 gives the evolution of density and solubility with temperature and pressure, as well as the impact of water salinity on solubility. For interfacial tension and densities, we use numerical values from Table 1 in Chiquet et al. (2007), and for the diffusivity constant of CO$_2$ in water, we use numerical values from Table 2 in Cadogan et al. (2014). We take three cases for temperature and pressure conditions to explore the sensitivity of the characteristic time $\tau = \frac{1}{\lambda}$ to the parameters $A$, $x$ and $R_0$. The thermodynamic properties for each case are listed in Table 2.1. Figure 2.3 (a-c) give the characteristic time $\tau$ when each of the three parameters of interest varies ($A$, $x$, $R_0$)$^3$.

To validate the definition of the characteristic frequency, we numerically solve the coupled system of equations on the radii for evolution using Matlab. We give ourselves an initial set of radii $R_{a*,0}$ and $R_{b*,0}$ as well as a time step $\delta t$ and for $n > 0$ we repeatedly update:

$$
\begin{align*}
R_{a*,n+1} &= R_{a*,n} + \delta t \frac{\lambda}{(R_{a*,n})^2} \left( \frac{1}{R_{b*,n}} - \frac{1}{R_{a*,n}} \right) \\
R_{b*,n+1} &= R_{b*,n} + \delta t \frac{\lambda}{(R_{b*,n})^2} \left( \frac{1}{R_{a*,n}} - \frac{1}{R_{b*,n}} \right)
\end{align*}
$$

(2.11)

The radii are updated according to this system of equations until one of the two bubbles disappears (the corresponding radius is zero). A plot of the evolution of the radii over time is given for a sample case in Figure 2.3 (d).

The time scales we estimate based on the characteristic evolution time $\tau$ are seen

$^3$The plot in Figure 2.3 (a) is made as a function of the the disc diameter so that this plot can be compared against Figure 1.2
Table 2.1: Numerical values chosen to estimate the characteristic frequency \( \lambda \). We also use \( M = 44.0095 \text{ g/mol} \) and \( R = 8.314 \text{ J/K/mol} \)

\[
\begin{array}{|c|c|c|c|}
\hline
P (\text{MPa}) & 5 & 15 & 30 \\
T & 307.4 & 323.6 & 363 \\
\sigma (\text{mN/m}) & 44.3 & 32.6 & 25.9 \\
\rho (\text{kg/m}^3) & 126.3 & 691.5 & 693.3 \\
D (10^{-9} \text{ m}^2.\text{s}^{-1}) & 2.75 & 3.64 & 6.60 \\
C_s (\text{kg.m}^{-3}) & 40 & 50 & 60 \\
\hline
\end{array}
\]

(a) Variation of \( \tau \) with characteristic radius \( R_0 - r_A = 40; x = 600\mu m \)

(b) Variation of \( \tau \) with distance between bubbles - \( r_A = 40\mu m; R_0 = 50\mu m \)

(c) Variation of \( \tau \) with diameter of disc available for diffusion - \( x = 500\mu m; R_0 = 50\mu m \)

(d) Solving for evolution of the coupled system - \( \tau = 2 \times 10^7 \text{s}, R_a^0 = 50\mu m, R_b^0 = 60\mu m, R_0 = \frac{R_a^0 + R_b^0}{2} \) and \( \delta t = 10^5 \text{s} \)

Figure 2.3: Estimating characteristic time scales for the two-bubble model in the bulk case
to vary in a very wide range. The pressure and temperature conditions have less impact on the characteristic time than the area and length along the diffusion path and the characteristic radius $R_0$.

### 2.2 Ostwald ripening in porous media

Several attempts were made to describe the Ostwald ripening process in the presence of a solid matrix. However it is often studied in a context where other mechanisms like a constant pressure decline in the liquid play a significant role [Yortsos et al. (1989); Li and Yortsos (1995); Dominguez et al. (2000)]. The presence of a pressure decline leads these authors to neglect the first order term that was the one responsible for ripening in the case of a homogeneous medium (see in particular Greenwood (1956)). Ripening has also been studied in a context where cluster growth stops or is strongly inhibited once there is significant interaction with the porous matrix walls, for viscous polymers and crystals growing in a solid matrix for instance [Schmelzer et al. (1995); Möller et al. (1998)]. More recently, ripening was evoked for applications similar to ours in Andrew et al. (2014a). Micro-tomography images were used to estimate the capillary pressures of CO$_2$ ganglia and parametrize the pore space using distance maps. Gravitational remobilization was discussed using a reformulation of the capillary and Bond numbers. Ostwald ripening was mentioned as a mechanism by which ganglion volume to surface area ratios could increase, leading to potential remobilization. The authors plotted ganglion surface area to volume as a function of volume (Figure 14 in Andrew et al. (2014a)) and observed that the surface area to volume ratio initially decreased with volume but then remained relatively constant for ganglia with larger volumes. From this observation they concluded that as ganglia span multiple pores, interfacial area relates almost linearly to volume and there is no energy gradient to drive the process of Ostwald Ripening.$^4$ This is not how we understand the problem, as the link between the surface area to volume ratio and the driver for Ostwald ripening is not clear to us. Whereas the surface area to volume

$^4$It should be noted that there are extremely few "large" ganglia in the experiments presented in Andrew et al. (2014a).
ratio can be directly related to curvature in the bulk setting, this is no longer the case in the porous media.

### 2.2.1 Differences Between Ostwald Ripening in Porous Media and Bulk Liquids

We assume the same three physical laws as in the bulk situation that was just described. Specifically, these are Laplace’s law, Henry’s law, Fick’s law. One key difference makes evolution in the porous medium case much more difficult to predict. In the presence of a solid matrix interacting with the two fluids in consideration, the morphology of the solid walls determine the capillary pressure. Laplace’s law is assumed correct for unsupported interfaces, but curvature now depends on the solid structure. We define an unsupported interface as the interface between the two fluids that is at "sufficient distance" from the solid. In particular, for thin films, Laplace’s law as we wrote it in the previous section is no longer valid.

Laplace’s law is derived by applying mechanical equilibrium to a spherical cap between two phases (see Dullien (2012) section 2.1). With $R$ the mean radius of curvature of the interface\footnote{$rac{1}{R} = \frac{1}{2}(\frac{1}{R_1} + \frac{1}{R_2})$ where $R_1$, $R_2$ are the principal radii of curvature of the cap.} and $\sigma$ the surface tension, Laplace’s law states that the difference in pressure $P_c$ between the two fluids is:

$$P_c = \frac{2\sigma}{R} = 2\sigma\kappa$$ \hspace{1cm} (2.12)

where we introduced $\kappa = \frac{1}{R}$ the mean curvature of the surface. In the case of simple geometries, like a cylindrical tube with radius $r$ (see Figure 2.4), the effect of the structure on the interface is described by the following expression for capillary pressure $P_c$ (see Dullien (2012) section 2.3), with $\theta$ the contact angle:

$$P_c = \frac{2\sigma \cos(\theta)}{r}$$ \hspace{1cm} (2.13)

In more complex geometries, the relationship between the volume of a ganglion
and its shape in the structure or resulting capillary pressure can be extremely complicated (Bear (2013) section 9.2.3). Even in the case of simplified representations of porous media, like the models described in chapter 4, this relationship is non-trivial to determine. However, the link between shape (or more exactly interfacial mean curvature) and capillary pressure defined by Equation 2.12 is assumed to always remain true for unsupported interfaces.

This conceptually simple, fundamental difference is what makes predicting the evolution of processes governed by the Ostwald Ripening mechanism so much more difficult in porous media than it was in the bulk case. The object of the approach presented in chapter 4 is to numerically solve for the evolution of porous media systems in relatively simple geometries.

### 2.2.2 Multi-ganglia equilibria in porous media

In the bulk liquid setting from section 2.1, a situation with multiple bubbles is thermodynamically unstable. The only possible equilibrium is the situation where all the gas aggregates into a single bubble. In porous media, the situation is more complex. Since differences in capillary pressure, or equivalently curvature, are the driver for the Ostwald Ripening mechanism, then a multi-ganglia equilibrium is necessarily one where all the ganglia have the same capillary pressure, or equivalently the same interfacial curvature.

**Simplified setting** We first consider the simple two-bubble system in Figure 2.5 (a). According to Laplace’s law, the capillary pressure of the bubble on the left
CHAPTER 2. OSTWALD RIPENING PROCESS

must be higher than the one of the bubble on the right, since the curvature of the unsupported interface is much lower on the right. Since we assume the pressure is the same everywhere in the liquid, and using Henry’s law, this capillary pressure gradient translates into a concentration gradient. Fick’s law implies that mass will transfer from the left to the right. Gradually, the interface on the left will recede towards the left as the bubble is shrinking, and the one on the right will advance towards the left as the bubble is growing, until the curvatures of both surfaces are equal, as shown in Figure 2.5 (b). The situation in Figure 2.5 (b) is stable, since an advance of the one of the interfaces towards the left or right will translate into a concentration gradient that will pull the interfaces back towards the equilibrium position. Now consider a system

![Figure 2.5: Simple two-bubble system in a porous medium](image)

(a) Disequilibrium situation  (b) Stable equilibrium situation

with $n$ bubbles in porous media. As was mentioned before, predicting the evolution of such a highly non-linear dynamic system is very complicated. Nonetheless, we make two hypotheses in the following.

Multi-ganglia equilibria exist in porous media  In the very simplified setting we show in Figure 2.5, a stable equilibrium exists for some given gas saturations, and even for a range of saturations. We hypothesize that there also exists multi-ganglia equilibria in more complicated pore geometries, and also for a range of saturations. In nature, there can be a great number of available pore throat radii of a given size\(^6\),

\[^6\text{Equilibria are really defined by an interface radius, but since the interface radius and the pore throat radius are linearly related by the cosine of the contact angle, equilibria can also be defined in terms of a pore throat radius here. In the setting for chapter 4, where the pore throat is locally}\]
which means it is possible to find saturations such that a multi-ganglia system with those saturations is at equilibrium, the requirement for equilibrium being that the ganglia must have interfaces that all have the same radius of curvature, or equivalently all have the same capillary pressure. This does not mean that there exists equilibria with multiple ganglia for every saturation, nor that every initial condition leads to a multi-ganglia equilibrium. On the contrary, the fact that bubbles cannot form in the Ostwald Ripening setting (where the pressure in the liquid is constant and uniform) implies that most equilibria will be reached only if the system is initialized very close to them.

Multi-ganglia equilibria are likely to be locally stable. In the same way that the equilibrium depicted in Figure 2.5 (b) is stable (in the sense that after a perturbation the system will return to its original equilibrium), we hypothesize that there are multi-ganglia equilibria that are likely to be stable. If the initial state of the system is close enough to a multi-ganglia equilibrium state, than we therefore hypothesize that this equilibrium will be attained and the ganglia will remain disconnected. This hypothesis stems from two observations. The first is that if a multi-ganglia equilibrium is defined by a pore throat radius that is available a great number of times in the pore space, than it is likely that the pore throat radii that are in a neighborhood to that pore throat radius are also available a great number of times. In other words, pore throat radius distributions are likely to be continuous. The second observation is that where there are interactions with a structure, decreasing the mass of a ganglion will generally result in a decreasing capillary pressure or equivalently an increasing radius, which has a stabilizing effect. The opposite was true in the bulk liquid case.

assumed to have the shape of a conical frustrum, the angle of the conical frustrum plays a role in the link between the interface radius and the pore throat radius, so an equilibrium with multiple ganglia is defined by one equilibrium interface radius that could correspond to multiple pore throat radii.

7we will illustrate this observation with simulations in chapter 4
Chapter 3

Capillary pressure estimation using microCT imaging

In the previous chapter, differences in curvature, or equivalently capillary pressure, were identified as one of the main drivers for Ostwald Ripening. In porous media, measuring the capillary pressure of individual disconnected ganglia is difficult, since we cannot place sensors in the ganglia. In this chapter, we describe a technique to measure pore-scale capillary pressures in order to assess the potential for Ostwald Ripening. Specifically, the aim is to assess how different are the capillary pressures of a population of ganglia, and in different rock samples.

3.1 Motivation

Due to significant developments over the last decades and its non-destructive characteristic, X-ray microtomography has become the foremost imaging technique to visualize and quantify pore-scale structures and processes, and provide input for pore-scale modeling [Blunt et al. (2013); Cnudde and Boone (2013); Wildenschild and Sheppard (2013); Schlüter et al. (2014)]. Previous studies that investigated residual trapping at the pore-scale using X-ray microtomography include Prodanović et al. (2007); Kumar et al. (2010); Iglauer et al. (2011); Tanino and Blunt (2012); Chaudhary et al. (2013); Georgiadis et al. (2013); Andrew et al. (2014b). In particular, all of these
studies show that the residually-trapped nonwetting phase takes the form of ganglia with various sizes and complicated irregular shapes, highlighting the complexity of the nonwetting and wetting phase interface geometry, as well as of the contact angle at the intersection of both fluids with the solid surface. Armstrong et al. (2012) first proposed a method to calculate interfacial curvature using synchrotron-based X-ray microtomography images of water and oil in a glass beads packed column using a voxel size of 13 \( \mu \text{m} \). They compared reliable macro-scale capillary pressures measured via a pressure transducer to micro-scale capillary pressures measured via interfacial curvatures\(^1\). They concluded, in particular, that higher image resolutions were required as significant curvature errors resulted from the inadequate segmentation of small features. Andrew et al. (2014a) then applied the method described by Armstrong et al. (2012) to calculate interfacial curvatures of water and supercritical \( \text{CO}_2 \), (50C and 10 MPa) in a Ketton limestone using lab-based microtomography images with a pixel size of 3.5 \( \mu \text{m} \). The authors reported that curvature distributions for a single ganglion presented a single well-defined peak, representing a single capillary pressure across the entire \( \text{CO}_2 \)-brine interface. They also related capillary pressure measurements to local pore space topography and showed that capillary pressure was inversely proportional to the radius of the largest restriction surrounding the ganglion. In a recent publication aiming at identifying individual dynamic drainage events at the pore-scale using fast synchrotron-based microtomography images of sc\( \text{CO}_2 \)/brine in the same Ketton limestone with a voxel size of 3.64 \( \mu \text{m} \), Andrew et al. (2015) extended the pore-scale curvature measurement technique originally proposed by Armstrong et al. (2012) in order to be able to measure the smaller curvatures resulting from higher drainage capillary pressures. In particular they presented a method to select terminal menisci from the entire \( \text{CO}_2 \) ganglia interfaces using curvature anisotropy and compute the interfacial curvature using only these selected regions. One drawback from this method is it drastically reduces the number of points over which the curvature is estimated, resulting in lower confidence as measured by the standard error measurement.

We previously determined that capillary pressure gradients are the driver for Ostwald

\(^1\)calculated on the images using Avizo Software
Ripening\textsuperscript{2}. In order to assess the potential for Ostwald Ripening in porous media, we must measure pore-scale capillary pressure in real rocks. Since we cannot put sensors inside disconnected gas ganglia to measure the pressure there, we develop a workflow similar to that in Armstrong et al. (2012) to image disconnected ganglia in rocks and measure their interfacial curvature. Assuming Laplace’s law holds, we can use the interfacial curvature as a way of estimating capillary pressure.

The goal of the study presented here is to develop reliable methods for estimating the pore-scale capillary pressure of individual residually-trapped gas ganglia for different rock types, especially sandstones, and using high resolution images. A multi-scale synchrotron-based X-ray microtomography dataset of residually-trapped gas in sintered glass beads and sandstone samples (Boise and Fontainebleau) was acquired, with voxel sizes varying from 0.64 to 4.44 $\mu$m. The major difference of these experiments with previous work is the quantification of capillary pressure distributions in a population of bubbles.

### 3.2 Capillary pressure estimation method

#### 3.2.1 Description of supporting experiments

The experimental work described in this section was conducted by Dr. Marco Voltolini from the Lawrence Berkeley National Laboratory and Dr. Charlotte Garing from the Energy Resources Engineering department at Stanford University. The main purpose of this chapter is to describe the capillary pressure estimation technique that was developed for this report. Data from the experiments described in this section were used to develop and test the method. We provide a description of the experiments in this section as background information for the reader. Figure B.1 provides the nomenclature we use for the different sub-volumes that were analyzed.

**Samples for the experiments** The experiments were conducted on cylindrical plugs of about 6 millimeters in diameter cored in three different types of samples:

\textsuperscript{2}since we are assuming that the pressure in the liquid is uniform and constant
sintered glass-beads, Boise sandstone and Fontainebleau sandstone. They were selected for their significant difference in porosity and pore network morphology, as can be seen in Figure 3.2. In addition, all samples are assumed to be strongly water-wet. The glass beads sample is composed of soda lime beads with diameters ranging from 250 to 400 micrometers and presents the highest porosity and pore sizes. Although the focus is set on estimating capillary pressure distributions in sandstones, the glass beads sample was chosen to develop the curvature estimation method as large interfaces between the two fluids are expected. The Boise and Fontainebleau samples are quarry sandstones from Boise, Idaho (USA) and the Paris Basin (France) respectively. Fontainebleau sandstone is composed of well-sorted quartz grains only Bourbie and Zinszner (1985) whereas Boise sandstone contains a significant amount of feldspar and clay materials Zimmerman (1984). Helium pycnometry porosity measurements, $\phi_{He}$, were conducted on samples extracted from the same blocks in which the samples used in the experiments were cored. The respective values of porosity measured for the glass-beads, Boise and Fontainebleau samples are 0.40, 0.28 and 0.10 (Figure B.1). Mercury injection capillary pressure analysis (MICP) was also performed and the pore-throat diameter distributions are shown in Figure B.1. The corresponding mean diameters $d_{Hg}$ are listed in Figure B.1 as well.

**Experimental setup and protocol** The samples were wrapped in a shrinkable Teflon tube and mounted vertically on the rotating stage in the beamline hutch, as displayed in Figure 3.1. The inlet and outlet, both wrapped together with the sample to ensure fluid flow through the core, were connected to flexible tubing allowing rotation during scanning. Two valves were placed at the inlet and the outlet in order to isolate the sample. The inlet tubing was also connected to a small reservoir located above the setup so that gravity-driven imbibition could be performed: a solution of deionized water with a 0.7 mol/L potassium iodide contrasting agent was poured in the reservoir and could then flow at room pressure and temperature through the dry sample by gravity, leaving behind a fraction of trapped air. Both valves were closed after the brine had come out of the outlet valve and the system was left to equilibrate for 30 minutes before scanning.
The dataset was acquired at Beamline 8.3.2 of the Advanced Light Source (Lawrence Berkeley National Laboratory). In each case, a baseline scan of the dry sample was first acquired, then multiple scans at different resolutions were taken after the experiment. The entire dataset was acquired using two different set-ups of camera and lenses, leading to slightly different resulting voxel sizes for the Glass beads and Fontainebleau sandstone samples and for the Boise sandstone sample, as detailed below.

**Glass beads and Fontainebleau sandstone**  For both samples a set of 2049 projections was acquired using a PCO.Edge camera with Optic Peter 2X (3.28 µm), 4X (1.62 µm) and 10X (0.64 µm) using an energy of 25 keV.

**Boise sandstone**  A set of 1441 projections was acquired using a PCO.4000 camera with normal optics 2X (4.44 µm voxel size) and 5X (1.80 µm voxel size) using an energy of 32 keV and an exposure time of 800 ms and 1000 ms for the 2X and 5X scans respectively.

**Image reconstruction**  The reconstruction of the volumes was performed using two different procedures, depending on the contrast needed in the datasets: i) a standard filtered backprojection, using a Shepp-Logan filter Kak and Slaney (1988) applied to the flat-field corrected projections, ii) a single-distance phase retrieval algorithm on the projections which improves the contrast among the different phases and reduces phase contrast artifacts. The algorithm presented by Paganin et al. (2002) and implemented in the ANKAphase software package Weitkamp et al. (2011) was chosen for phase retrieval. The reconstruction was then performed using a conventional filtered backprojection algorithm with the Octopus software Dierick et al. (2004).

Cross-sections of the three-dimensional reconstructed images are presented in Figure 3.2. The voxels are coded in levels of grey depending on the X-ray beam attenuation. The solid matrix appears in light grey, the brine in medium grey and the air in dark grey.
CHAPTER 3. CAPILLARY PRESSURE ESTIMATION

(a) Photograph of the setup

(b) Illustration of the experiment

Figure 3.1: Experimental set-up at the microtomography beam line 8.3.2 of the Advanced Light Source, LBNL
Figure 3.2: Two-dimensional cross sections through the three-dimensional reconstructed volumes for the Glass beads, Boise sandstone and Fontainebleau sandstone data sets imaged with different magnification resulting in multiple resolutions: 2X-4X-10X, respective voxel sizes of 3.28µm-1.62µm-0.64µm, for the glass beads and Fontainebleau sandstone samples and 2X-5X, respective voxel sizes of 4.44µm-1.8µm, for the Boise sandstone sample.
Image segmentation  All segmentations were performed on the raw reconstructed scans directly, due to the high quality of the imaging process, except for the BS-2X data (Boise sandstone, voxel size of 4.44 µm) for which a non-local means edge preserving filtering was applied first in order to reduce the noise. The data were segmented into three phases in order to assign each voxel as either rock, brine or air using a combination of different methods depending on the level of complexity displayed by each image. The software used for the segmentation step were Fiji and Avizo Fire 9. Each smaller sub-volume investigated was re-segmented using the same method than for the larger volumes for more accurate results. The number of voxels belonging to the pore phase $V_p$ and belonging to the air phase $V_{air}$ are computed and since the entire number of voxels composing the analyzed rock volume $V_{tot}$ is also known, the total porosity $\phi(\mu\text{CT})$ and air saturation $S_{nw}$ can be calculated as $\frac{V_p}{V_{tot}}$ and $\frac{V_{air}}{V_p}$ respectively (see Figure B.1).

3.2.2 Image processing workflow for capillary pressure estimation

This subsection describes the workflow for the method developed to compute interfacial curvature of gas clusters using the segmented micro-CT images, where voxels belong to one of the three identified phases (rock, brine or gas). The main steps, shown in Figure 3.3, consist in finding and meshing the surface of the gas phase; restricting it to the interface shared with the brine phase; smoothing the resulting mesh; and calculating its curvature, as described in the following.

Meshing the air surface  The surfaces of the gas and brine phases are identified by using the MATLAB proprietary *isosurface* function, leading to a trigonal mesh representing the surface of the each of the two phases. To find the surface, we provide as input to the function an array of binary, three-dimensional data points identifying the phase whose surface we are constructing, and then prompt Matlab to generate the 0.5-isosurface for this data.
Figure 3.3: Image processing workflow presented for a cropped sub-volume of Boise sandstone (290*290*140 voxels with a voxel size of 1.80 µm). a) 2D raw image after reconstruction. b) 2D segmented image. Three phases are identified: the solid matrix (white), the air (black) and the brine (blue). c) 3D rendering of the separated air clusters, or ganglia. d) 3D rendition of the air ganglia together with the brine phase (light blue). e) Smoothed mesh for each ganglion - Interfaces with the brine phase are represented in red. f) The mean curvature is calculated for each voxel of selected air/brine interface. g) The curvature probability distribution functions are extracted for each gas ganglion. h) A mean curvature value can be calculated for each gas ganglion. The capillary pressure is calculated using the computed mean curvature and the appropriate surface tension value.

\[ P_c = 2 \cdot \sigma \cdot \kappa \]
\[ \sigma = \text{surface tension} \]
\[ \kappa = \text{average curvature} \]
Although it is hard to know what specific algorithm is used by Matlab, most modern-day isosurface reconstruction techniques are variations of the marching cubes algorithm described in Lorensen and Cline (1987). The idea behind this algorithm is relatively simple. We give ourselves a three-dimensional grid as well as scalar values at each point of the grid. The objective is to generate the isosurface for a given value of the scalar field. Isosurfaces are surfaces along which the scalar field is constant (elevation contour lines on a topographic map represent the same type of object in two-dimensional space). The algorithm reads eight neighboring points at a time (forming a cube), and determines the intersection of the isosurface with the cube if there is one. The intersection can take the form of one of 256 possible polygons within the cube. The exact location of the intersection of the surface with each of the edges of the cube is found by linear interpolation.

The specific isosurface construction technique that Matlab uses is not known to us, however testing the isosurface function by generating 0.5-isosurfaces in binary, three-dimensional data arrays consistently yields surfaces defined by points with coordinates that are either integer or exactly between integers. This will be very useful in finding the interface between two phases in data that has three phases, as is our case.

Finding the air/brine interface We generate the surfaces of the brine and air phases using the isosurface function, as was just described. The next step is to find the interface of the air phase and the brine phase. This is the region of the air surface that is also a part of the brine surface. We observed that applying the isosurface function to generate 0.5-isosurfaces outputs points with coordinates that are not subject to rounding errors. This gives us a simple way to generate the air/brine interface. We simply perform the intersection of the set of point coordinates that define the air surface with the set of points that define the brine surface to find the common vertices. At the end of this step, we obtain a mesh of points representing the surface of the air phase, as well as a list of vertices that also belong to the brine surface\(^3\).

\(^3\)This method is not very efficient, especially since generating the surface of the connected brine can be very slow; and this constrains the size of the input data. Modifying the isosurface generation code to directly find the interface between two phases in a cube with three phases would probably
CHAPTER 3. CAPILLARY PRESSURE ESTIMATION

Smoothing the surface

The mesh generated in the previous step is rough and unsuitable for curvature estimation. In the next step, the mesh is therefore smoothed using an implicit fairing method of the type described in Desbrun et al. (1999): we consider a mesh $X$ with $m$ vertices $x_i, i = 1 \cdots m$ and integrate the following equation over time:

$$\frac{\partial X}{\partial t} = \lambda L(X) \quad (3.1)$$

where $L(X)$ is the mesh Laplacian and $\lambda$ is a parameter (taken to be 1 in our applications). Sorkine (2006) is a good reference on Laplacian mesh processing. More precisely, we use an explicit Euler scheme to integrate Equation 3.1:

$$X^{n+1} = (I + \lambda \delta t L) X^n \quad (3.2)$$

We call $T_{\text{max}}$ the time for which the mesh is smoothed (this means Equation 3.2 will be used $\lfloor \frac{T_{\text{max}}}{\delta t} \rfloor$ times). Note that this scheme is stable as long as $\lambda \delta t < 1$. If this criterion is not respected, ripples start appearing on the mesh surface and amplify over time. Otherwise, we obtain a smoother and smoother mesh with every iteration. The results for this report were generated using an implementation of this type of fairing method by G. Peyre in MATLAB. A linear approximation of the mesh Laplacian is computed and used to disperse small disturbances and smooth high frequencies while keeping the main shape intact according to Equation 3.2.

Estimating the curvature of a mesh

We first redefine curvature in a broader context. Denote by $M$ an arbitrary smooth surface of $\mathbb{R}^3$: for any point $P$ on the surface $M$, we can define $n(P)$ the unit normal vector at point $P$. The derivative of $n$ at $P$ defines the shape operator (also called the Weingarten endomorphism), whose eigenvectors and eigenvalues are called the principal directions and principal curvatures. The trace and determinant of the operator are called the mean and gaussian curvatures. If we denote by $\kappa_1(P)$ and $\kappa_2(P)$ the principal curvatures at point $P$, the mean curvature is $\kappa(P) = \frac{\kappa_1(P) + \kappa_2(P)}{2}$ and the gaussian curvature is $\Gamma(P) = \kappa_1(P)\kappa_2(P)$. be a lot faster. We initially set about writing our own isosurface generation code but quickly decided the idea was best left for future work, since it was not the main focus of this project, and the speed of this portion of the workflow was not limiting.
Standard references are Federer (1959); Darboux (1896). Throughout this report, we generically use the term curvature several times. This is always the mean curvature $\kappa(P)$ at point $P$, as this is the curvature that appears in Laplace’s law for capillary pressure $P_c$.\(^4\)

A classic approach to compute the curvature of a mesh is to locally approximate it with a quadric surface. A quadric surface is the graph of any function that can be put into the form

$$f(x, y) = ax^2 + by^2 + cxy + dx + ey + f$$  \hspace{1cm} (3.3)

where $(x, y)$ are the cartesian coordinates and $a, b, c, d, e, f$ are constants. We use an implementation by D. Kroon that fits a least-squares quadratic surface of this type to the mesh in the neighborhood of each vertex and use the fact that the eigenvalues of the Weingarten endomorphism are also the eigenvalues of the hessian matrix of $f$, $H(f)$ (see chapter 9 of Katz (2012)) to compute mean curvature at each point $\kappa(P)$:

$$H(f) = \begin{bmatrix} 2a & c \\ c & 2b \end{bmatrix}$$ \hspace{1cm} (3.4)

We will refer to this technique as the quadric fitting method. A more recent technique uses an approach described in Cohen-Steiner and Morvan (2003) that redefines curvature in the context of normal cycle theory so that the definition now holds for polygonal surfaces. The result does not involve curvature directly but rather curvature measures. Specifically, equation (2) in Cohen-Steiner and Morvan (2003) defines a discrete mean curvature measure. This work builds on the observation that the curvature measures of a smooth surface can be obtained from an object associated to the surface called the normal cycle of the surface (see Wintgen (1982); Zähle (1986)), and that the definition of the normal cycle of a surface has a unique natural extension to the case of a polyhedral surface (a mesh). In that setting, the curvature measures of a mesh are therefore defined as the measures recovered from the normal cycle of the mesh. G. Peyre implemented an algorithm based on this result in MATLAB

\(^4\)\(P_c = 2\sigma\kappa\), with $\sigma$ the interfacial tension and $\kappa$ the mean curvature over the region of the surface that is of interest.
as well as other useful graph theory utilities. There is a tuning parameter for this method that corresponds to the number of neighbors over which the curvature tensor is averaged when it is calculated at each vertex. We will refer to this technique as the normal cycle method.

Whether we use the quadric fitting or normal cycle method, we obtain a mean curvature estimate for each vertex of the air/brine interface. The interface for the case in Figure 3.3 is plotted in sub-figure (f) where the colorbar represents the mean curvature values. In sub-figure (g), we plot the probability distribution functions that result from the curvature distributions for each ganglion. The probability distribution functions are estimated using a kernel density estimator (assuming a Gaussian kernel). We use a Matlab implementation of the estimator described in Botev et al. (2010). For all the pdf graphs we will show in this chapter, the area under each of the curves integrates to 1.

Estimating capillary pressures for the different ganglia For each separately identified gas ganglion, we can extract an average mean curvature value. According to the assumptions we are making, and in particular that Laplace’s law is valid for the unsupported interface of the gas ganglia, we can then relate this average mean curvature to the average capillary pressure for the ganglion under consideration using Equation 3.5 ($\kappa$ is the average mean curvature, $\sigma$ is the air/brine interfacial tension).

$$P_c = 2\sigma \kappa$$ (3.5)

3.2.3 Sensitivity analysis

In this section we describe a sensitivity analysis for the capillary pressure estimation method we have developed. Different sub-volumes are chosen along this section to illustrate the sensitivity analysis. The nomenclature we use here to designate these sub-volumes is the same as the one used in Figure B.1.
Sensitivity to the curvature estimation technique  Curvature calculations were performed on several isolated ganglia using the implementations of the quadric fitting and normal cycle algorithms and were compared to curvature estimates resulting from the commercial Avizo Fire software suite. As is shown in figure 3.4, the difference on the mean curvature values is very small between the three calculations, especially once some smoothing is applied to the mesh. In the remainder of this chapter, we use a value of 5 for the smoothing parameter $T_{\text{max}}$. For that choice, the difference in average mesh curvature is $8 \cdot 10^{-4} \mu m^{-1}$ when comparing the normal cycle method to the Avizo result and $1.7 \cdot 10^{-3} \mu m^{-1}$ when comparing the quadric fitting method to the Avizo result. For the results that are shown in the remainder of this chapter, interfacial curvature is computed using our own code with the normal cycle method for curvature estimation. Although the observed differences between the algorithms were consistently very small for the investigated sub-volumes, the quadric fitting method may be prone to more instability, as the algorithm requires inverting matrices that can be ill-conditioned.

Sensitivity to smoothing  In Figure 3.5 we show the results of our sensitivity study for the impact of the diffusion-based smoothing we apply to the raw mesh extracted from the three-dimensional image using Matlab’s isosurface method. The curvature estimates rapidly converge once a small amount of smoothing is applied, as previously reported by Andrew et al. (2014a). For the smoothing parameters of the procedure described in section 3.2.2 we choose a value $T_{\text{max}} = 5$ and $\delta t = 0.3$ for the datasets presented in section 3.3, corresponding to about 15 iterations of the heat diffusion procedure.

Sensitivity to number of neighbors  The second averaging effect is related to the parameter that controls the number of neighbors used when estimating the curvature tensor in the normal cycle method. Figure 3.6 shows that curvature estimates are very similar when selecting 6 or 60 neighbors for the calculation. The curvature probability distribution functions become less spread out when averaging on more neighbors, as expected. To use results that are as close as possible to the real data, we choose to
Figure 3.4: Comparison of the results from the different curvature estimation techniques as smoothing is increasingly applied to the mesh of an isolated air ganglion in the Glass Beads data set (the resolution is 1.62 µm). The parameter $T_{\text{max}}$ controls smoothing and is defined in section 3.2.2. Results for the normal cycle method are given in blue, for the quadric fitting method in orange and for the Avizo software suite in green. For each method we give the average of mean curvature over the mesh (this is the value we use to estimate the capillary pressure of the bubble) as a function of smoothing in the curves with symbol 'x'; the average difference between the normal cycle or quadric fitting method and Avizo in the curves with symbol 'o' and the standard deviation on the difference between the normal cycle or quadric fitting method and Avizo in the curves with symbol '*'. The normal cycle and quadric fitting methods are implemented in MATLAB by G.Peyre and D. Kroon respectively.
Figure 3.5: Sensitivity analysis for different parameters required for the curvature calculation method using the normal cycle algorithm performed on a single air ganglia isolated from the glass beads sample imaged with a voxel size of 0.64 µm (top row) and from the Boise sample images with a voxel size of 1.8 µm (bottom row). Impact of smoothing on the mean curvature (each pdf corresponds to one choice of numerical value for the final time $T_{max}$ of heat diffusion - the time step is 0.3). Curvature is estimated using the normal cycle method with 6 neighbors.
use 7 neighbors in the results presented in section 3.3.

Figure 3.6: Sensitivity analysis for different parameters required for the curvature calculation method using the normal cycle algorithm performed on a single air ganglia isolated from the glass beads sample imaged with a voxel size of 0.64 µm (top row) and from the Boise sample images with a voxel size of 1.8 µm (bottom row). Impact of the number of neighbors used when averaging for the mean curvature calculation (each pdf corresponds to one choice for the number of neighbors). We use diffusion-based smoothing with $T_{\text{max}} = 5$.

**Sensitivity to location on mesh** The local variation of the curvature estimation on the interface was also investigated in order to assess the impact of interface identification on the curvature calculation, as the air/brine interface presented by a single air ganglion may change depending on the image acquisition, resolution and processing. Assessing local variation is also a test of the validity of Laplace’s law for the unsupported interfaces. Since the pressure in the ganglia is assumed to be uniquely defined, the mean curvature of the interface should be the same everywhere as well. This analysis was conducted on the well defined air ganglia isolated from the glass
beads sample imaged with a voxel size of 0.64 μm (GB-10X dataset) and from the Boise sample imaged with a voxel size of 1.8 μm (BS-5X dataset). These are the same datasets as the ones used for Figure 3.5. For each isolated air ganglion, regions were selected randomly on the interface and the curvature was computed for the selected portions of the total interface, as displayed in Figure 3.7. Some numerical results are given in Figure 3.9, where the calculation using the entire interface is highlighted in grey.

The results show that the seven selected portions of interface of the isolated ganglia extracted from the GB-10X dataset present similar interfacial curvature distributions and mean values ranging from $0.016 \mu m^{-1}$ to $0.023 \mu m^{-1}$, with a mean of $0.021 \mu m^{-1}$ and a standard deviation of $0.002 \mu m^{-1}$. On average, the values calculated on the selected interfaces differ from the one calculated using the entire identified interface by a bit less than 10%. There is more discrepancy in curvature distributions between the different interfaces selected from the BS-5X dataset. The mean curvature values for the different portions of interface range from $0.027 \mu m^{-1}$ to $0.043 \mu m^{-1}$, with a mean of $0.034 \mu m^{-1}$ and a standard deviation of $0.007 \mu m^{-1}$ and differ from the one calculated using the entire interface by around 17%.

**Sensitivity to image resolution**  The effect of image resolution on the calculation of interfacial curvature was investigated by analyzing a same air ganglion that could be identified on two images of the same sample acquired with different image resolutions. The analysis was conducted on an isolated air ganglion for the glass beads sample imaged with a voxel size of 1.62 μm and 0.64 μm, GB-4X and GB-10X respectively (Figure 3.8 (a)), the Boise sample imaged with a voxel size of 4.44 μm and 1.80 μm, BS-2X and BS-5X respectively (Figure 3.8 (b)) and the Fontainebleau sample imaged with a voxel size of 1.62 μm and 0.64 μm, FS-4X and FS-10X respectively (Figure 3.8 (c)). Details regarding the curvature calculations are given in Figure 3.9.

For the glass beads sample the isolated air bubble present similar characteristics with both resolutions: the shape and volume of the bubble is almost identical and so is the interface with the brine phase and its curvature. The mean value $\kappa$ for interfacial curvature is $0.0219 \mu m^{-1}$ for GB-4X and $0.0226 \mu m^{-1}$ for GB-10X, leading
Figure 3.7: Local variation of the curvature estimation on the interface analyzed for a single air ganglia isolated from a) the glass beads sample imaged with a voxel size of 0.64 m (GB-10X) and b) the Boise sample imaged with a voxel size of 1.8 m (BS-5X). In each case, the Figure shows from left to right: a visualization of the selected portions of the interface (red), a visualization of the mean curvature values presented by the selected interfaces, and a plot of the corresponding curvature histograms. The details are provided in Figure 3.9 (b).
to similar mean capillary pressures $P_c$ of 3,148 Pa and 3,260 Pa for GB-4X and GB-10X respectively.

The results differ in the case of the sandstone samples. For both the Boise and Fontainebleau samples, the air ganglia identified present some discrepancy although the general shape is preserved and total volume is in the same order of magnitude. For all cases one can note that the volume is lower with higher resolution. Figure 3.8 (b) and (c) also show that the portion of the air surfaces that is shared with the brine phase is roughly located on the same parts of the air ganglia. However, due to a very different number of voxels representing the identified interfaces with the different image resolution (lower with bigger voxel sizes), the interface that remains after the image processing for the curvature calculation highly differs. For the Boise sample, the final mean value $\kappa$ is 0.0309 $\mu$m$^{-1}$ for BS-2X and 0.0483 $\mu$m$^{-1}$ for BS-5X, leading to capillary pressures $P_c$ of 4,450 Pa and 6,955 Pa for the BS-2X and BS-5X ganglia respectively. For the Fontainebleau sample, there are not enough voxels left after processing to estimate the curvature of the FS-4X ganglion. The FS-10X has a mean curvature of 0.124 $\mu$m$^{-1}$ which corresponds to a capillary pressure of 17,903 Pa.

Deleting the unsupported part of the interface  In order to deal with potential edge effects at the line of contact where there is a discontinuity in curvature due to the contact angle, an additional step was added to the processing. It consists in deleting from the mesh the vertices that belong to the rock/gas interface before applying smoothing and computing the curvature. Figure 3.10 (a) shows an isolated bubble from the GB-10X data set. If we keep all of the interface, the mesh displays higher curvature values near the triple contact line between the three phases (these can be seen as three red rings on the image). Observing these rings motivated the deletion of the supported part of the interface before applying smoothing and estimating curvature. On the Boise dataset, we do not observe these rings, probably because the triple contact line is not as well defined. On the Fontainebleau data set, we observe flat interfaces that are thought to be thin films of water. We also treat them as supported interfaces. Identifying the vertices that belong to the thin films is trickier.
Figure 3.8: Effect of image resolution on curvature estimation analyzed for a same air ganglion isolated from a) the glass bead sample imaged with a voxels size of 1.62 µm (GB-4X) and 0.64 µm (GB-10X), b) the Boise sample imaged with a voxel size of 4.44 µm (BS-2X) and 1.8 µm (BS-5X) and c) the Fontainebleau sample imaged with a voxel size of 1.62 µm (FS-4X) and 0.64 µm (FS-10X). In each case, the Figure shows from top to bottom for both resolutions: a 2D raw image, the 3D segmented air ganglia (with its volume in voxels and mm$^3$), the visualization of the interface in red (with its surface in pixels and mm$^2$), and the visualization of the mean curvature values presented by the interface. More detail is provided in Figure 3.9 (b).
Figure 3.9: a) Effect of image resolution: interfacial curvature analysis conducted on a same air ganglion isolated from images acquired with different voxel sizes for the glass bead (GB-4X, GB-10X), Boise (BS-2X, BS-5X) and Fontainebleau (FS-4X, FS-10X) samples, displayed in Figure 3.8. b) Location on the mesh: interfacial curvature analysis conducted on selected portions of the entire interface of air ganglia isolated from the glass bead (GB-10X) and Boise (BS-5X) samples, displayed in Figure 3.7. The calculation performed on the entire interface is highlighted in grey. For both a) and b) the Table lists the voxel size, the number of voxels of the interface used for the calculation, mean curvature \( \kappa \) [\( \mu m^{-1} \)] (mean value, standard deviation, and standard error of the mean) and corresponding capillary pressure \( P_c \) [Pa].

<table>
<thead>
<tr>
<th>µCT images</th>
<th>voxel size (µm)</th>
<th>nb voxels of interface</th>
<th>( \kappa ) (µm(^{-1}))</th>
<th>( P_c ) (Pa)</th>
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<tr>
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<td>1.62</td>
<td>13545</td>
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<td>0.64</td>
<td>83137</td>
<td>0.0226</td>
<td>0.0126</td>
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<td>0.0298</td>
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<td>0.0577</td>
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<tr>
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<td>-</td>
<td>-</td>
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<tr>
<td>FS-10X</td>
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<table>
<thead>
<tr>
<th>GB-10X isolated ganglia</th>
<th>voxel size (µm)</th>
<th>nb voxels of interface</th>
<th>( \kappa ) (µm(^{-1}))</th>
<th>( P_c ) (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GB-10X isolated ganglia</td>
<td>0.64</td>
<td>83137</td>
<td>0.0226</td>
<td>0.0126</td>
</tr>
<tr>
<td>GB-10X isolated ganglia</td>
<td>2025</td>
<td>0.0222</td>
<td>0.0207</td>
<td>4.59E-04</td>
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<td>GB-10X isolated ganglia</td>
<td>1631</td>
<td>0.0220</td>
<td>0.0219</td>
<td>5.42E-04</td>
</tr>
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<td>0.0214</td>
<td>3.40E-04</td>
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<td>BS-5X isolated ganglia</td>
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<td>0.0219</td>
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<td>BS-5X isolated ganglia</td>
<td>988</td>
<td>0.0301</td>
<td>0.0271</td>
<td>8.61E-04</td>
</tr>
</tbody>
</table>
To get rough estimates, we find the connected components of the mesh\(^5\) that have negative curvature values and delete those that have a large number of voxels. This procedure was found to yield reasonable results.

(a) Full mesh for the bubble from the GB10X data set  
(b) Mesh for the bubble from the GB10X data set, after deleting the supported interfaces

Figure 3.10: Deleting the supported part of the interface

### 3.3 Results and interesting findings

Detailed results for several sub-volumes of the three samples are provided in appendix B. For the purpose of the discussion in this section, we show results from selected sub-volumes and resolutions for the Boise and Fontainebleau in Figure 3.11. There are 49 ganglia in the Boise sub-sample and 157 ganglia in the Fontainebleau sub-sample.

It is important to note that the images shown here were obtained from a simple gravity-driven imbibition experiment. In an experiment where the gas and brine are forced into the rock at higher pressures and temperatures, it is possible the system could be initialized differently.

\(^5\)To find connected components in a mesh, we wrote a search procedure in Matlab based off of the Breadth-First Search (BFS) algorithm. We start at a vertex and add all the neighbors (and the neighbors of the neighbors) of the vertex to a connected component list. We loop on the list of vertices until they are all in a connected component. To find the connected components that have a negative curvature, keep the same procedure but only apply it to the vertices that have negative curvature.
Figure 3.11: Interfacial curvature analysis for the analyzed sub-volumes of the Boise and Fontainebleau sandstone samples imaged with a voxel size of 1.8 and 1.62 µm respectively. (a) and (d) shows the surface of the air ganglia, (b) and (e) show the unsupported interfaces between the air and the brine (colored using mean curvature) and (c) and (f) show the pdfs for mean curvature along each ganglion. Each curve in (c) and (f) corresponds to one ganglion in (a) and (d).
3.3.1 Measuring pore-scale capillary pressure

Impact of pore structure and resolution The ability to accurately characterize the trapped nonwetting phase and identify the interface shared with the wetting phase is an important factor to estimate capillary pressure distributions in rocks using interfacial curvature calculations on X-ray microtomography images. Estimation is found to be highly dependent on both the pore size and shape of the samples as well as on the resolution of the scans. Porous samples with relatively low pore body to pore throat aspect ratios (represented here by the glass beads sample) display large non-wetting and wetting phase features with clearly identifiable interfaces between the two fluids. The average pore throat diameter for the glass beads sample (estimated with MICP in Figure B.5) is much larger than the lowest image resolution (3.28 $\mu$m) and even the smaller features presented by the brine phase are more than one order of magnitude larger than this resolution.

If we consider that at least three voxels are required to correctly identify an object, then the images acquired with the 2X magnification (voxel sizes of 4.44 $\mu$m for Boise and 3.28 $\mu$m for glass beads and Fontainebleau) cannot identify features smaller than 10-13 $\mu$m. Figure B.5 (a) indicates that 20% and 30% of the pore throat radii are comprised below this threshold for the Boise and Fontainebleau samples respectively. Higher resolutions are therefore needed for a more precise characterization of the microstructure for the sandstone samples.

In order to have a better identification of the interfaces for curvature calculations, the highest resolution (0.64 $\mu$m) is necessary for rocks presenting similar pore and throat sizes as the Fontainebleau sandstone sample. It should be noted that using a higher resolution does raise issues however. The lower the resolution, the larger the volume that can be imaged. Additionally, using a higher resolution will result in the identification of thin films of water, which complicates curvature estimation. In the samples shown here, thin films were particularly observed on the Fontainebleau sandstone images. Along the surface of the gas phase that is in contact with the thin films, Laplace’s law is thought to no longer hold (and is observed to no longer hold in these images), so the portion of the interface that is in contact with them should be removed for the purpose of capillary pressure estimation.
Confidence intervals  In order to measure the reliability of our mean curvature estimates, we calculate confidence intervals for the estimation of the average mean curvature over the ganglia (see Kendall et al. (1946)). We do not know the true variance of the distributions we are sampling from, but we have an estimate for it which is the sample variance. For a number of samples that is greater than 30, the $t$-distribution and the normal distribution are very similar. The number of samples we have is always much larger than this, so we can calculate confidence intervals using the classic expression for the Standard Error Measurement $\frac{s}{\sqrt{n}}$ where $s$ is the sample standard deviation and $n$ is the number of samples. Assuming that the distributions we are sampling from are normal, there is a 95% probability that the true mean of the distribution we are sampling from is at most $c \mu m^{-1}$ away from the mean, with

$$c = 1.96 \frac{s}{\sqrt{n}} \approx 2 \frac{s}{\sqrt{n}}$$  \hspace{1cm} (3.6)

The standard error measurement (SEM) calculated in this way is found to be relatively low when compared to the mean curvature. For the Boise sandstone, the average SEM is $1.7 \cdot 10^{-3} \mu m^{-1}$, which corresponds to a confidence interval of $\pm 490$ Pa. The mean curvature value for a single ganglion is $0.032 \mu m^{-1}$, which corresponds to 4,617 Pa. For the Fontainebleau sandstone, the average SEM is higher at $1 \cdot 10^{-2} \mu m^{-1}$, which corresponds to a 95% confidence interval of $\pm 2,885$ Pa. The average mean curvature value for individual ganglia is $0.110 \mu m^{-1}$, which corresponds to a capillary pressure of 15,893 Pa. These confidence intervals give a measure of how well we can estimate the capillary pressure of an individual disconnected ganglion. As expected, the measurements are of better quality in the case of the Boise sandstone compared to the Fontainebleau sandstone.\(^6\)

### 3.3.2 Capillary pressure distributions

**Capillary pressures are controlled by pore structure**  For each ganglion, we measured an average mean curvature, that corresponds to a capillary pressure\(^7\). The

\(^6\)As a comparison, the glass beads confidence interval for the 3.28 µm resolution was $\pm 265$ Pa.

\(^7\)We use an interfacial tension of 70 mN/m between water and air.
mean capillary pressure in the ganglia is 4,617 Pa for the Boise sandstone and 15,893 Pa for the Fontainebleau sandstone. To a first order, this is in good agreement with the capillary entry pressures of the rocks as measured by Mercury Injection Curve Pressure (MICP) experiments (see Figure B.5). Andrew et al. (2014a) observed in a Ketton limestone that the curvature of the ganglia was controlled by the size of the neighboring throats. In the post-imbibition context of geological storage, it is therefore plausible that the capillary pressures of disconnected ganglia be to a first order well approximated by the capillary entry pressure of the rock. This does not mean that the system is at equilibrium, however.

Variability of capillary pressure across a ganglion In Figure 3.7 we selected regions from a ganglion at random to compare their average mean curvature. The numerical results were shown in Figure 3.9. In order to quantify the variability of measured capillary pressure across a ganglion, we use hypothesis testing (see Kendall et al. (1946))\(^8\) and form \(T\)-statistics in the following manner:

\[
T = \frac{\bar{\kappa}_i - \kappa^*}{SEM^i}
\]

where \(\bar{\kappa}_i\) is the average mean curvature we estimated for region \(i\), \(\kappa^*\) is the average mean curvature for the ganglion and \(SEM^i\) is the standard error measurement for region \(i\). If the computed \(T\)-statistic is greater than 1.96, then there is a 95% chance that the null hypothesis is false. Another way of understanding this \(T\)-statistic is through confidence intervals: if the mean capillary pressure for the ganglia is outside the confidence interval around the mean capillary pressure for a region, then with 95% probability they are not the same.

\(T\)-statistics are shown in Figure 3.12. For the glass beads ganglion we reject the null hypothesis in four out of seven cases. For the Boise ganglion however, we reject the null hypothesis in three out of four cases. From these tests we conclude that in the case of this Boise ganglion, the measured capillary pressure is not the same at the different regions of the ganglion. The \(T\)-statistic not only tells us that the regions

\(^8\)Specifically, we test the following null hypotheses (\(H_0^i\)): [The sample corresponding to region \(i\) is drawn from a distribution with a mean that is the average mean curvature for the ganglion].
are different from the average mean curvature for the ganglion, it also quantifies that
difference. In the following paragraph we will see that variability is even greater be-
tween different ganglia.

One possible explanation to the measured differences in capillary pressures is that
there are measurement errors. Estimating the curvature of the surface is the product
of a series of complicated image processing steps. Uncertainty is in particular associ-
ated with image reconstruction and segmentation. A second explanation is that the
interfaces are supported, and we can therefore not apply Laplace’s law to link mean
curvature to capillary pressure directly. If the capillary pressure variability across
individual ganglia is real, then either the pressure of the gas inside the ganglion is
non uniform, or the pressure in the liquid is non uniform, or both are non uniform.
Non uniform pressures do not appear likely however, especially since the brine phase
appears to be connected.

<table>
<thead>
<tr>
<th>Curvature (µm⁻¹)</th>
<th>Pressure (Pa)</th>
<th>T-statistic</th>
</tr>
</thead>
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<td></td>
<td>Mean</td>
<td>SEM</td>
</tr>
<tr>
<td><strong>Mean</strong></td>
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</tr>
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<td>0.022</td>
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</tr>
<tr>
<td></td>
<td>0.0213</td>
<td>4.92E-04</td>
</tr>
<tr>
<td><strong>GB-10X</strong></td>
<td>0.0232</td>
<td>6.00E-04</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
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<tr>
<td></td>
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<td>8.61E-04</td>
</tr>
</tbody>
</table>

Figure 3.12: Summary statistics for the variability of capillary pressure across one
ganglion (results from datasets in Figure 3.7)

---

9From Figure 3.7 we can infer that there is a greater chance the interface can be considered
unsupported in the glass beads case than in the Boise case.
Variability of capillary pressure across a population of ganglia  Here we discuss the variability of capillary pressure across a population of ganglia. In order to quantify how different the curvature is between ganglia, we form $T$-statistics in the following manner:

$$T = \frac{\bar{\kappa}_i - \kappa^*}{SEM_i}$$  

(3.8)

where $\bar{\kappa}_i$ is the average mean curvature we estimated for ganglion $i$, $\kappa^*$ is the average mean curvature for the population of ganglia and $SEM_i$ is the standard error measurement for ganglion $i$. This $T$-statistic will give a measure of how far the system is from an equilibrium state, since differences in mean curvature or equivalently capillary pressure govern the Ostwald Ripening mechanism and an equilibrium situation is one where all capillary pressures are the same. We plot this statistic for the sub-volumes in Figure 3.11 as a function of sample size in Figure 3.13. The null hypothesis is rejected in every case with at least 99% probability (the corresponding cut-off threshold for the $T$-statistic is 3). It is interesting to note that the absolute values for the $T$-statistics are much higher than they were for different regions of the same ganglion, which we take to imply that there is much more variability across the populations of ganglia than across individual ganglia. In any case, the differences in capillary pressure between the ganglia are statistically significant and will provide measurable capillary pressure gradients that should drive Ostwald Ripening.

Interfacial surface area to volume ratio  We plot the ratio of interfacial surface area to volume as a function of volume for each ganglion in Figure 3.14 (only the plot for the Boise sample is given, the Fontainebleau results are very similar). According to Andrew et al. (2014a), this can be used to assess the potential for Ostwald ripening as well. We observe that the ratio changes much less for larger ganglia than it does for smaller ones. Andrew et al. (2014a) concluded from this observation that larger clusters are not as energetically favorable in a porous medium as they are in a bulk liquid and there is no energy gradient to drive Ostwald Ripening. This is not our

10Specifically, we test the following null hypothesis for ganglion $i$ ($H_0$): [The sample corresponding to ganglion $i$ is drawn from a distribution with a mean that is the average of the average mean curvatures for the population of ganglia].
understanding of the problem, as the link between this ratio and the Ostwald Ripening is ambiguous in the porous media setting.

3.4 Future work

Estimating diffusion paths in real rocks  In the theoretical framework for this report, we assumed that mass transport between ganglia could be modeled by Fickian diffusion. If that assumption holds, than the time scales for evolution depend not only on capillary pressure gradients but also on the lengths and areas available for diffusion. In chapter 3, we developed a method to estimate capillary pressure gradients in rocks from microtomography images. Using the same data sets, future efforts could focus on determining the diffusion paths between ganglia, and in particular the length and available area along those paths. Having this additional information would enable us to estimate characteristic evolution times for these samples, as well as make better informed modeling assumptions for simulation of pore scale ripening processes.
Dealing with thin films  The presence of thin films was shown to make capillary pressure estimation significantly harder. A conclusive procedure was not found in this study to consistently deal with these thin films. One idea that was explored but may be worth pushing further is to create a procedure to identify the local thickness of the brine phase at each point of the brine/air interface. This requires writing a method to estimate the distance between a point and a mesh, and applying that to each point of the brine/air interface. We could then choose to reject some interfaces using an arbitrary threshold.
Chapter 4

Pore-scale simulation of Ostwald Ripening-type processes

In chapter 2, we identified capillary pressure as one of the key drivers for Ostwald ripening. We also highlighted the key differences between the bulk and porous media settings. As much as possible, we will call bubble a gas cluster that behaves as if it were in the bulk setting, and ganglion a gas cluster that interacts with the structure of the porous medium. A bubble assumes a spherical shape while the shape of a ganglion is more complex and is determined by its interaction with the solid. Apart from this difference in shape, bubbles and ganglia are the same object throughout this chapter. We use the two names to emphasize the different behavior of gas in the absence or presence of interaction with a structure.

In chapter 3, we assessed the potential for Ostwald ripening in different rock samples. The underlying assumption is that the situation of the gas phase during the scans is representative of a post-injection situation, after the brine has re-imbibed back into the region of the rock where the gas plume was injected. This moment in time is the initial condition in the context of this report. In this chapter, we attempt to predict evolution of the system from this initial condition. We build simulation models to test the insights that were given in chapter 2 as well as provide characteristic time scales for evolution.
4.1 Introduction

4.1.1 Motivation

Motivation for reducing the dimensionality of the porous medium representation

Solving the full Navier-Stokes equations in porous media at the pore scale in capillary-dominated regimes is difficult. One of the major hurdles faced by current methods (volume-of-fluid and level-set for example) are the numerical errors associated with the estimation of interface curvature. These numerical errors induce spurious currents, as described for example in Brackbill et al. (1992). Another drawback of solving the full Navier-Stokes equations is that this is computationally more expensive than reduced-dimension methods (see Blunt (2001); Raeini et al. (2012)). Additionally, flow is not expected to play a large role in the ripening mechanism. Finally, topology of the pore network should govern equilibrium or disequilibrium of a multi-cluster system, not cluster volume or mass. These considerations, in particular that topology is expected to dictate evolution of the system, suggest an alternative approach to modeling the problem. This alternative we choose is to simplify our representation of the porous medium so that the simulation of diffusive processes can be made much simpler.

A brief overview of pore network modeling
Blunt (2001) provides a review of pore network modeling from the 1950s to 2001. In traditional pore network modeling there are usually wide pores connected by narrower throats. The pores and throats are often represented by cylinders or spheres, but can only contain one phase. Our framework adopts the same type of representation but two phases can occupy the throats and bodies (we neglect thin films however). Blunt (2001) also points out that classic pore network models are likely to have limited predictive capabilities, since essential features of the pore space are missing. The main objective of the model we built for this report was to better understand the evolution of ripening systems. Pore network models have extensively been used to simulate the dynamic flow of fluids through porous media (see Oren et al. (1998) for example or more recently Valvatne and Blunt (2003)), as well as percolation type processes (Hunt (2001) provides a
review of such modeling) but much more rarely to simulate diffusive processes. One example is Dominguez et al. (2000), where random walkers are used to simulate diffusion through a pore network model. In the process we are modeling, one of the central hypotheses is that there is no flow. We also assume that the process is quasi-static. Those considerations led us to adapt classic pore network models to our setting. One of the main advantages of pore networks for our purpose is that manipulating them is computationally lightweight, especially compared to continuum-based approaches (like the volume of fluid or level-set methods).

Relation between ganglion shape and enclosing structure In the bulk case, the link between mass and shape of the interface is well-defined. In the porous media setting, that link is highly dependent on morphology of the pore space. When the structure has the shape of a cone, the relationship between the radius of the interface and the geometry can be derived analytically, as is shown in Figure 4.1. In this chapter, we will assume that we can always use this relation to define the shape of the interface. When the morphology of the pore structure has an arbitrary shape, we therefore assume it can be locally approximated as a conical frustrum at the location of the interface. In both of the approaches we present below, we reduce the representation of the pore space in this way so that our problem becomes one-dimensional. Another advantage of the dimensionality reduction is that determining the shape of the interface reduces to making choices on the equivalent radius we use at every point in the porous medium. Once we have that equivalent radius, determining the radius of the interface becomes a relatively simple geometry problem.

4.1.2 General framework for simulation

We keep the same fundamental laws as in chapter 2, namely Laplace’s law for unsupported interfaces, Henry’s law for the relation between pressure and concentration and Fick’s law to govern mass transport of solute in the liquid. The Ostwald Ripening mechanism can be decoupled in two different mechanisms that operate on very different time scales. This assumption is implicit in most previous work on the mechanism, both in the bulk and porous media settings (Epstein and Plesset
Figure 4.1: Meniscus in a conical capillary (adapted from Dullien (2012), Figure 2.11). The radius of the interface is \( R = \frac{r}{\cos(\theta + \phi)} \), where \( r \) is the radius of the tube at the location of the interface, \( \theta \) is the contact angle and \( \phi \) is the angle of the cone. Capillary pressure \( P_c = P_g - P_l \) is the difference between the pressure in the gas \( P_g \) and the pressure in the liquid \( P_l \). Laplace’s law states that \( P_c = \frac{2\sigma}{R} \) where \( \sigma \) is the interfacial tension for the fluids \((g, l)\) under consideration.

(1950); Greenwood (1956); Lifshitz and Slyozov (1961); Voorhees (1985); Schmelzer and Schweitzer (1987); Li and Yortsos (1995); Möller et al. (1998) to name just a few). One of these mechanisms is the diffusion of solute gas between the ganglia. This mechanism is expected to be relatively slow. When gas is exchanged between the gas phase and the liquid phase, via dissolution or exsolution, the mass of gas in the gas phase changes, and the gas ganglia must find shapes to accommodate this change in mass. This second mechanism, by which a gas ganglion finds a position such that it is at equilibrium with itself and the surrounding liquid, is much faster. In the bulk case, this mechanism is very simple, since the shape of the bubble is always spherical. To numerically solve for evolution of the system, we implicitly made the assumption that the bubble instantaneously changes its radius when its mass changes, to compensate. This changes its pressure. In the porous medium case, we state that assumption explicitly, as the relation between the change in mass of a ganglion and the resulting modification in its shape is much more complicated.

Accordingly, we use a sequential algorithm that decouples these two mechanisms. At each iteration in time, we first solve what we call an internal equilibrium problem for each ganglion. The pressure inside each ganglion is assumed to be uniform, so solving the internal equilibrium problem requires finding the position and shape of the
ganglion such that mass conservation is respected and the mean curvature along the unsupported interfaces is identical at every point. We then search in the pore space for the diffusion paths between the ganglia. We make the additional assumption that the diffusion process can be decoupled in a set of diffusive transfers between pairs of ganglia along each diffusion path we have found. Along each diffusion path, we compute a mass transfer rate. By superposition, the mass transfer for each ganglion will be the sum of the contributions of each of its neighbors. This gives us the mass that enters or leaves each ganglion during the current time step. The algorithm then moves to the next iteration in time. To illustrate, the flow charts in Figure 4.2 and Figure 4.3 compare how we solve for the evolution of such processes in the bulk and in the porous settings and emphasize the coupling of the ripening process.

4.1.3 A simple tube model

Before we tackle the general problem in a three-dimensional porous medium setting in section 4.2, we take the case of a pore space that is represented by a three-dimensional tube of varying diameter. This is the simplest version of the simulation framework we have defined previously.

**Geometry**  We denote the pore space by $\mathcal{P} \in \mathbb{R}^3$ and consider a curve $S(\mathcal{P})$, of lower dimension than $\mathcal{P}$. This curve is our representation of the pore space. We assume we are given a mapping $x \in S(\mathcal{P}) \rightarrow r(x)$ that defines the radius of the tube at position $x$ along the curve $S(\mathcal{P})$. A cross section of such a pore space is shown in Figure 4.4 (a). We assume here that the central axis of the tube $S(\mathcal{P})$ is a straight line, but the tube model could easily be used for a setting with a central axis that is not straight.

In the following we will distinguish by the indexes $r$ and $l$ whether we are considering an interface convex towards the right or left respectively. We define the angle between the wall and the horizontal as $\Phi_r(x) = -\arctan(\frac{\partial r}{\partial x})$ and $\Phi_l(x) = +\arctan(\frac{\partial r}{\partial x})$. The radius of the interface is

$$ R_{r,l}(x) = \frac{r(x)}{\cos(\theta + \Phi_{l,r}(x))} $$
Figure 4.2: This flow chart shows how we would go about solving for the evolution of a system governed by Ostwald Ripening in the bulk case. We show the process for one bubble. The algorithm repeats it for each bubble in the system at every time step. This flowchart also shows how the system is coupled. This procedure is the one we follow in subsection 2.1.2 to derive the governing equations for the two-bubble in bulk system. The same could be done for \( n \) bubbles (see Greenwood (1956) for instance). At each stage of the work flow, we can use simple analytical expressions for each of the terms. The problem is well-defined.
Ganglion pressure changes by $\delta P$

- Update capillary pressure gradients (Laplace)
- Update concentration gradients (Henry)
- Update mass transfer rates (Fick)

Ganglion mass changes by $\delta m$

- Update ganglion capillary pressure
- Update unsupported interface radius
- Update bubble volume

Non-trivial

Figure 4.3: This flow chart shows how we would go about solving for the evolution of a system governed by Ostwald Ripening in the porous medium case. We show the process for one ganglion. The algorithm repeats it for each bubble in the system at every time step. This flowchart also shows how the system is coupled. This procedure is the one we follow in chapter 4 to numerically solve for the evolution of systems of ganglia governed by ripening processes. Several of these steps become a lot harder than in the bulk case. In particular, finding diffusion paths to update the mass-transfer rates from the concentration gradients and updating the position of the ganglia after a change in mass, which will lead to a change in unsupported interface radius.
Note that $\Phi_{l,r} > 0$ corresponds to a converging tube and $\Phi_{l,r} < 0$ will correspond to a diverging tube.

(a) Two-dimensional cross-section of a tube

\[ x \to r(x) = 100 + 30 \sin(\frac{x}{70} - 1.5) \mu m \]

(b) Two ganglia in a tube

Figure 4.4: Representing ganglia in a simple tube model

**Representing ganglia** A ganglion is entirely defined by the location of its interfaces with the brine along the horizontal axis. We accordingly choose to represent a ganglion by a couple $(x, y)$, where $(x, y) \in \mathcal{S}(\mathcal{P})^2$. We will always assume that we have $x < y$. To illustrate, two bubbles defined by their interfaces are plotted in figure 4.4 (b). The volume of a ganglion defined by the couple $(x, y)$ is

\[ V(x, y) = \int_x^y \pi r(z)^2 \, dz + V_{cap,l}(x) + V_{cap,r}(y) \tag{4.1} \]

where $V_{cap,r,l}(z)$ is the volume of the spherical cap\(^1\) defined by the interface pointing right or left at position $z$:

\[ V_{cap,r,l}(z) = \frac{1}{3} \pi R_{r,l}(z)^3 (2 - 3 \sin(\theta + \Phi_{r,l}(z)) + \sin^3(\theta + \Phi_{r,l}(z))) \]

**Internal equilibrium problem for the tube model** A ganglion is considered to be at internal equilibrium if the pressure inside it is uniform. In particular, we

\(^1\)From http://mathworld.wolfram.com/SphericalCap.html
enforce that the capillary pressure defined by its interfacial curvature must be the same everywhere. For a ganglion defined by the couple \((x, y)\) to be at equilibrium with itself, the following conditions must therefore be met:

\[
R_l(x) = R_r(y) = R_{eq} \\
\Phi_l(x) > 0 \\
\Phi_r(y) > 0
\] (4.2)

Note that for two ganglia to be at equilibrium with each other, they must be at equilibrium with themselves and their defining radii must be equal.

We assume that the internal equilibrium problems are independent, so that each cluster can be treated separately. We therefore consider one cluster only in the following. Given a situation for which the cluster is at equilibrium at \((x^t, y^t)\) at time \(t\), we look for the new equilibrium position \((x^{t+\delta t}, y^{t+\delta t})\) if the cluster volume changed by \(\delta V_t\) over the time step \(\delta t\):

\[
R(x^{t+\delta t}) = R(y^{t+\delta t}) \\
V(x^{t+\delta t}, y^{t+\delta t}) = V(x^t, y^t) + \delta V_t
\] (4.3)

To solve this problem, one option is to write a damped Newton solver to find the roots of the mapping :

\[
\begin{bmatrix} x^{t+\delta t} \\ y^{t+\delta t} \end{bmatrix} \rightarrow \begin{bmatrix} R(x^{t+\delta t}) - R(y^{t+\delta t}) \\ V(x^{t+\delta t}, y^{t+\delta t}) - V(x^t, y^t) - \delta V \end{bmatrix}
\] (4.4)

Adding damping is not absolutely necessary but was found to make computations faster in our applications.

**Mass-transfer problem for the tube model** Now consider two ganglia \(a\) and \(b\) defined by \((x^a, y^a)\) and \((x^b, y^b)\). We always assume \(y^a < x^b\). We suppose they are initially at equilibrium with themselves, but not with each other. We consider the amount of diffusion that would occur over a time step \(dt\). The pressure gradient
between the two ganglia is

\[ \Delta P = 2\sigma \left( \frac{1}{R^a} - \frac{1}{R^b} \right) \]  (4.5)

Assuming concentration at the interfaces is \( P = HC \) (Henry’s law), we have a concentration gradient

\[ \Delta C = \frac{2\sigma}{H} \left( \frac{1}{R^a} - \frac{1}{R^b} \right) \]  (4.6)

Assuming Fick’s law for diffusion, we can express the mass transfer to ganglion \( a \) during \( \delta t \) as

\[ \delta m^a = \frac{\delta t D A(y^a, x^b) 2\sigma}{(x^b - y^a)} \frac{1}{H} \left( \frac{1}{R^a} - \frac{1}{R^b} \right) \]  (4.7)

where for \( x < y \) we define the available diffusion area as\(^2\)

\[ A(x, y) = \min_{z \in [x, y]} \pi r(z)^2 \]  (4.8)

We assume the density of the gas is a given constant and denote it as \( \rho \). The variation in volume of cluster \( a \) is therefore given by

\[ \delta V^a = \frac{\delta t D A(y^a, x^b) 2\sigma}{(x^b - y^a)} \frac{1}{\rho H} \left( \frac{1}{R^a} - \frac{1}{R^b} \right) \]  (4.9)

and of course we have \( \delta V^b = -\delta V^a \).

**The tube model is of limited practical use**  The tube model is a simplified setting in which the simulation framework we defined can be applied. As such, it is convenient to describe that framework. The tube model is of limited practical use however, since it cannot handle situations where the coordination number of the pore bodies is larger than two, something that is fairly common in real rocks (see Dullien (2012) section 1.2). Additionally, solving the internal equilibrium problem using a Newton solver is time-consuming. In the following section, we present a strategy to apply the same simulation framework to more realistic pore networks, where higher coordination numbers are possible, and an analytical form is given for the shape of

\(^2\)For a more precise treatment, one can also use an integral form of Fick’s law that will provide an analytical solution for a cone-shaped pathway.
the throats. In particular, we will assume the throats are conical, which simplifies the internal equilibrium problem considerably.

4.2 Modeling the pore space using graph network models

The choices we make here are motivated both by the physical system we are modeling as well as the need to generate representations of the pore space that are realistic. In section 4.4 we will describe generation methods for realistic pore spaces. The graph network modeling approach we describe in this section was implemented in Matlab using object-oriented programming. Most of the elements that are defined in the following are objects in that implementation.

4.2.1 Geometry

Two simple graph network models built using the guidelines we are about to define are represented in Figure 4.5 and Figure 4.6. Figure 4.5 (a) in particular gives some of the notation we will use in this section and when describing the sequential algorithm we use to solve for evolution. As far as possible, we will denote with an uppercase \( R \) the radius of an interface and with a lowercase \( r \) the radius of a geometric element of the pore space.

**Pore bodies** The nodes of the graph are what we call pore bodies. A pore body is assumed to be spherical. We give each body a position and a radius. The choice of a sphere to represent pore bodies is guided by the physical process we are modeling: in the absence of interactions with the walls, the shape of the gas phase will be spherical. In other words, the pore bodies that are represented in this manner are not necessarily spherical. The radius we are assigning to each body is really the radius of the largest spherical bubble that could fit in that pore. The size of that bubble defines the pore
body for our purposes, and its exact shape does not really matter.  

**Pore throats** The edges of the graph are what we call throats. A pore throat represents connections between one or more pore bodies. This is not standard for a graph, as edges are normally defined as pairs of vertices. Pore throats are assigned a radius and a position. This is the position and radius of the constriction that defines the throat. The default position for a throat is the barycenter of the positions of the bodies it connects, but that does not have to be the case (and if the throat only connects one body, than it is not possible). The pore space we are building will be used to perform simulations involving interfaces between a wetting and non-wetting phase. The state at any point in time of a system of ganglia will entirely be defined by the positions of the different interfaces. The available positions for the interfaces are made up of the union of the segments that define the edges of the graph. The throats of the pore space have the shape of collections of tubes of varying radius. The segments that define the edges of the graph are the central axes of the tubes. The radius of the tubes is assumed to vary piecewise linearly.

**Representing ganglia** As was just mentioned, a gas ganglion will entirely be defined by the positions of its interfaces with the brine phase. In a first implementation, we will consider that gas ganglia can occupy only one pore body. If a cluster of gas phase only occupies one body and has a volume that is smaller than the volume of the body, than it is called a bubble and assumes a spherical shape. If it has a volume that is larger, it penetrates the neighboring throats and is called a ganglion. The number of its interfaces is defined by the number of throats that connect to the pore.

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3 In the Maximal Inscribed Spheres (MIS) representation of the pore space we will describe later, the pore bodies would correspond to local maxima for the mapping from the position along the skeleton to the MIS radii. Or using the terminology in Silin and Patzek (2006), pore bodies are super masters.

4 In the Maximal Inscribed Spheres (MIS) representation of the pore space we will describe later, the pore throats would correspond to local minima for the mapping from the position along the skeleton to the MIS radii. Or using a terminology close to Silin and Patzek (2006), pore throats would be super slaves. One significant difference here compared to the description in Silin and Patzek (2006) is that we allow pore throats to make an arbitrary number of connections with pore bodies (our only requirement is that the number of connections be an integer greater than or equal to 1).
CHAPTER 4. PORE-SCALE SIMULATION

body.

Constraints on the pore space  The pore space is the graph that consists in a collection of bodies and a collection of throats (or nodes and edges). We impose a certain number of constraints on the geometric characteristics of the bodies and throats in order for the pore space to be considered valid for simulation. These constraints stem from concerns on the capillary pressure variable, and on the quasi-static nature of the simulations we wish to perform in the pore space.

We would like to model the interaction of the gas phase with the walls using the relation defined by Figure 4.1. According to that relation, a ganglion will be at a stable position if the tube is convergent. The divergent tube is the classic Haines jump case (Haines (1930)). To be in the convergent case as much as possible, we decide that bodies must have defining radii that are larger than all their neighboring throats. We now consider a bubble occupying a pore, and gradually increase its volume. As long as the volume of the bubble is smaller than the volume of the body, it keeps its spherical shape. We will also assume it is located at the center of the body. We assume that the bubble becomes a ganglion by touching the walls on all sides simultaneously, and that it enters all of the neighboring throats at the same moment. By enforcing that a body must have a defining radius that is larger than all its neighboring throats, we ensure that the mechanism by which the ganglion enters the pores can be described as a succession of quasi-static steps. There will be an instability when the volume of the ganglion is such that one of its interfaces in the throats reaches the point when the throat becomes divergent, but we choose to leave that case for later study. In the simple examples we present here, the ganglia will always have a volume that is between zero and the volume at which this instability occurs.

The capillary pressure variable, or equivalently the variable for the interface radius should be defined at every possible position for an interface between the wetting and non-wetting phases, and as much as possible be continuous. Inside the pore bodies, the interface radius is the same as the bubble radius. Inside the pore throats, the interface radius is defined by the pore geometry as $r \cos(\theta + \phi)$, where $r$ is the radius of
the tube at the position of the interface, $\theta$ is the contact angle and $\phi$ is the local angle that the tube generator makes with the central axis of the tube. We choose to constrain the pore space geometry such that the capillary pressure is continuous when a ganglion occupying a body grows enough to enter the neighboring throats. This gives us a condition on the radius of the throats where they intersect with the bodies, namely

$$\frac{r_{TB}}{\cos(\theta + \phi)} = r_B$$

(4.10)

These validity conditions that we choose to give ourselves may seem unnecessarily constraining. One of the reasons we use them is to ensure Laplace’s law remains valid at every point. In a real porous medium, there are points where Laplace’s law should be replaced with a version accounting for the presence of thin films or supported interfaces.

### 4.2.2 Sequential algorithm

In this subsection we define rules for evolution using the governing equations for the Ostwald Ripening mechanism. We use the same type of sequential algorithm that we introduced for the tube model. We define an internal equilibrium problem, which amounts to finding the position of a ganglion as a function of its mass, as well as a mass transfer problem to determine mass transfer rates as a function of the positions and pressures of the different ganglia in the network. One step that was trivial in the previous models is to find the diffusion paths between the ganglia. This is more complicated in the graph network model and we will accordingly give more detail.

**Internal equilibrium problem** We restate the internal equilibrium problem in the context of the graph network model and then derive a closed form solution. We consider a ganglion or a bubble that occupies a pore body. Given a certain mass, we can calculate the volume of that ganglion or bubble.$^5$ Solving the internal equilibrium problem consists in finding the position of the ganglion (as defined by the location of

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$^5$Throughout this report we assume density is constant, and that the fluids are incompressible. This framework would still work if we had another simple relationship between mass and volume.
Figure 4.5: Simple graph network - Example 1 - Two bodies connected by one throat. (a) Notation is the one we will use throughout this section. (c) At the intersection between the body and the throat the capillary pressure and interface radius are continuous, which forces the tube radius to be discontinuous. There is a discontinuity in capillary pressure in the middle of the throat. This is because the interface radius is the radius of an interface which is convex towards the converging part of the tube. The angles of the two conical frustrums that make up the throat are different, so the radius of an interface that is exactly in the middle of the throat is different depending on which body is occupied by the gas phase.
its interfaces), such that the pressure inside the ganglion is the same everywhere and the volume of gas in the ganglion is the one we have determined. Depending on the volume of the cluster, this problem has different solutions. We call $V_{cl}$ the volume of the cluster, $V_B$ the volume of the body and $V_B^{\text{max}}$ the maximum volume of gas that can fit into the pore body and its neighboring throats before a Haines jump occurs.

**Solution for $V_{cl} \in [0, V_B]$** Since the pore body is assumed to be spherical in shape with radius $r_B$, we have

$$V_B = \frac{4}{3} \pi r_B^3$$

(4.11)

The solution for the internal equilibrium problem is trivial in this case. According to the assumptions we made, the cluster takes the shape of a sphere (it is a bubble) with radius

$$R_{cl} = \left(\frac{3}{4} V_{cl}\right)^{\frac{1}{3}}$$

(4.12)

**Solution for $V_{cl} \in [V_B, V_B^{\text{max}}]$** We first introduce some additional notation. We consider a pore body with $n$ neighboring throats, as in Figure 4.7. We already defined
The radius of the body. For \( i = 1 \cdots n \), we define \( r_{T,i} \) the radius of throat \( i \), \( r_{TB,i} \) the radius of throat \( i \) at the intersection with the body, \( \phi_i \) the angle of throat \( i \). As the bubble volume grows, the interfaces will advance in each of the throats and remain stable until one of the throat constrictions is reached. The throat constriction that is reached first is the one that defines the largest interface radius (or the lowest capillary pressure). Note that this is not necessarily the throat with the largest constriction radius, since the interface radius also depends on the tube angle \( \phi_i \). The maximum volume of gas that can fit into the pore body \( V_B^{\text{max}} \) is therefore defined as the volume of gas such that the bubble reaches the first throat constriction.

We now also define some variables to describe the cluster. For \( i = 1 \cdots n \), we call \( R_i \) and \( r_i \) the radius of the interface, respectively the tube, in throat \( i \); \( h_i^{\text{max}} \) the length of throat \( i \); and \( h_i \) the position of the interface in throat \( i \) with \( h_i \in [0, h_i^{\text{max}}] \). For convenience we will use the relative positions \( x_i = \frac{h_i}{h_i^{\text{max}}} \in [0, 1] \).

With this notation, solving the internal equilibrium problem amounts to finding the positions \( x_i, i = 1 \cdots n \) of the interfaces in each throat such that the volume of the ganglion defined by those positions is \( V_{\text{cl}} \) and the interface radius \(^5\) at each of those positions is the same.

We write the relation between position and tube radius using linear interpolation:

\[
    r_i = (R_{T,i} - R_{TB,i})x_i + R_{TB,i}, \quad i = 1 \cdots n
\]

(4.13)

The relation between tube radius and interface radius is given by

\[
    R_i = \frac{r_i}{\cos(\theta + \phi_i)}, \quad i = 1 \cdots n
\]

(4.14)

The volume of the gas in throat \( i \) is the volume of the conical frustrum \( V_i^{\text{cf}} \) (we neglect the volume of the spherical caps):

\[
    V_i^{\text{cf}} = \frac{1}{3} \pi h_i \left[ r_{TB,i}^2 + r_{TB,i}r_i + r_i^2 \right]
\]

(4.15)

\(^5\)the interface radius is the inverse of the curvature, which is equivalent to capillary pressure

\(^7\)From http://mathworld.wolfram.com/ConicalFrustum.html
We are looking for the positions \( x_i \) such that the radii of the interfaces are all equal. We call \( R_{cl} \) the equilibrium interface radius. We have \( \forall i = 1 \cdots n, R_{cl} = R_i \) so

\[
\forall i = 1 \cdots n, \quad r_i = R_{cl} \cos(\theta + \phi_i)
\]  

(4.16)
as well as

\[
\forall i = 1 \cdots n, \quad h_i = h_{i}^{\text{max}} \frac{R_{cl} \cos(\theta + \phi_i) - r_{TB,i}}{R_{T,i} - r_{TB,i}}
\]  

(4.17)

Finally, we can express the volume of the ganglion as a function of the equilibrium interface radius:

\[
V_{cl} = V_B + \frac{1}{3} \pi \sum_i \frac{h_{i}^{\text{max}}}{r_{T,i} - r_{TB,i}} \left[ R_{cl} \cos(\theta + \phi_i) - r_{TB,i} \right]
\]

\[
\left[ r_{TB,i}^2 + r_{TB,i} R_{cl} \cos(\theta + \phi_i) + (R_{cl} \cos(\theta + \phi_i))^2 \right]
\]  

(4.18)

This last relation gives the volume of the ganglion as a cubic polynomial of the equilibrium interface radius. For \( V_{cl} \in [V_B, V_B^{\text{max}}] \) we can solve for the roots of this expression\(^8\) to find the equilibrium interface radius \( R_{cl} \). The position \( x_i \) of the interface in throat \( i \) is then given simply by

\[
\forall i = 1 \cdots n, \quad x_i = \frac{R_{cl} \cos(\theta + \phi_i) - r_{TB,i}}{R_{T,i} - r_{TB,i}}
\]  

(4.19)

Note that to find the maximum available volume \( V_B^{\text{max}} \) we do not need to solve an internal equilibrium problem. Since we know that for this volume the radius of the interface is the one defined by the limiting throat, we can directly calculate the volume \( V_B^{\text{max}} \) using Equation 4.18.

For \( V_{cl} > V_B^{\text{max}} \), a Haines jump occurs. In a first implementation, we choose to simply avoid this situation.

\(^8\)There are three possible solutions to this equation. In practice, we find there is only one solution in the interval \([R_{\text{min}}, R_{\text{max}}]\), where \( R_{\text{min}} \) is the interface radius defined by the limiting throat and \( R_{\text{max}} \) is the radius of the body \( r_B \).
CHAPTER 4. PORE-SCALE SIMULATION

Figure 4.7: Solving the internal equilibrium problem for the graph network model. (a) A pore body with five throats. (b) A cluster that is initialized at random with interfaces in each throat. The radii of the five interfaces are all different \(\{94, 55, 64, 100, 58\}\) µm for throats 1-5. (c) The solution to the internal equilibrium problem. We solve the problem for the volume of the cluster in (b). The radii of the five interfaces are now all the same (80 µm).
Finding diffusion paths  In the graph network case, finding diffusion paths is no longer a trivial problem. Given a set of ganglia in the pore space, we must find all the available diffusion paths between them. There can be one, multiple or no diffusion path between two given clusters. We use an algorithm that is based on the classic Breadth-First Search (invented by Lee (1961)) to find all the diffusion paths between two nodes of the graph. As we search, we record the length of the path and the minimum area along the path. We also avoid prevent the search algorithm from returning any cyclic paths (otherwise there could be an infinite number of diffusion paths returned by the algorithm).

Mass-transfer problem  We use the superposition approach that was introduced earlier to deal with the mass-transfer problem. We consider a system with \( n \) ganglia. Ganglia \( i \) has \( m_i \) neighbors that were found when looking for diffusion paths in the previous step. For each neighbor \( j, j \in [1 \cdots m_i] \) we can calculate the mass transferring from ganglion \( j \) to ganglion \( i \) using the interface radii of the two ganglia \( R_j \) and \( R_i \), the minimum area along the diffusion path \( A_{ij} \) and the length of the diffusion path \( x_{ij} \) using:

\[
\frac{\partial m_{ij}}{\partial t} = \frac{D A_{ij}}{x_{ij}} \frac{2\sigma}{H \left( \frac{1}{R_j} - \frac{1}{R_i} \right)} \tag{4.20}
\]

For each ganglion we sum the contributions from each path in which it appears, counting mass positively if it is flowing in the ganglion. This gives us the net mass influx \( \frac{\partial m_i}{\partial t} \) to ganglion \( i, i \in [1 \cdots n] \):

\[
\frac{\partial m_i}{\partial t} = \sum_{i=1}^{m_i} \frac{\partial m_{ij}}{\partial t} \tag{4.21}
\]

\(^9\)There is potentially a problem with the superposition if parts of two distinct diffusion paths overlap. Since the CO\(_2\) is dilute in the brine, this should not be too much of an issue.

\(^{10}\)When one of the volumes of the ganglia is small enough such that it becomes a spherical bubble whose projected area is smaller than the area \( A_{ij} \), we use that instead.

\(^{11}\)\( D \) is the diffusivity constant, \( H \) is Henry’s constant, \( \sigma \) is the surface tension.
We verify that mass is conserved at each iteration by checking that the sum of all the net influxes is zero at every moment in time:

$$\sum_{i=1}^{n} \frac{\partial m_i}{\partial t} = 0 \quad (4.22)$$

**Automatic time stepping** Some parts of the simulations require shorter time steps than others, so we introduce an automatic time-stepping routine. When no event has occurred for a certain number of time steps (an event is typically the disappearance of a bubble), the time step is automatically increased. When a bubble disappears, the time step is decreased until the disappearance occurs exactly at the end of a time step. The reason we must do this is that we are essentially assuming the system does not change too much over the course of a time step. The disappearance of a bubble introduces many changes, in particular with regards to the available diffusion paths. Another reason it is important to have bubbles disappear at the end of time steps is to ensure mass conservation is never violated (if bubble disappears in the middle of a time step, some mass is lost). The characteristic time $\lambda$ that was defined in the two-bubble problem in chapter 2 was found to give an order of the time scales involved in bubbles disappearing. This characteristic time can therefore be used to initialize the time step (we use a fraction of $\lambda$ in our applications).

### 4.3 Findings

All of the results we show in this subsection use the values from Table 2.1 with a pressure of 15 MPa and a temperature of 323.6 K. Multi-ganglia equilibria are found for different cases. The equilibrium situation is found to be dependent on initialization. Pore structure is found to have a great impact both on equilibrium and on the time scales for evolution. A key insight from these simulations is that the relationship between a change in the mass of a ganglion and its capillary pressure is inverted from the bulk to the porous media settings. In the bulk setting, a decrease in mass will increase capillary pressure. In the presence of a structure, a decrease in mass will usually decrease capillary pressure. In other words, when the gas assumes
the shape of bubbles, the capillary pressures will move farther and farther apart with time, and the driver for the mechanism will only increase, whereas in the presence of a solid matrix, the capillary pressures will move closer and closer together, and the diffusion process will gradually slow. This also implies that the time scales for the disappearance of a bubble are much smaller than when two ganglia equilibrate.

Validating the model against the bulk case  In a graph network model with initialization of the gas phase such that there are two spherical bubbles that never interact with the walls, the results should be the same as the ones we obtain in the bulk case. Notable differences between the two models include:

- The area and length we use for diffusion in the bulk model are always the same, whereas they change at every iteration for the graph network case.

- For the graph network model, we introduced an automatic time-stepping scheme to make iterations faster.

Figure 4.8 shows the results from a comparison between the two models. They are in good agreement, despite the differences we just mentioned.

Example graph network model case  We show an example graph network model case in Figure 4.9. The orange cluster disappears and is absorbed by the two other clusters. Initially, the orange and blue clusters have the same radius, so they are not exchanging mass. But as soon as the orange ganglion shrinks (mass is transferred to the green ganglion), it starts exchanging mass with both of the other ganglia. It is interesting to note that the interface radii of the green and blue clusters behave differently as their mass grows. The green cluster penetrates the neighboring throats and is a ganglion, so its increasing mass results in an increasing capillary pressure or equivalently a decreasing interface radius. The blue cluster is a bubble for the entire duration of the simulation and its increase in mass results in an increasing radius or equivalently a lower capillary pressure. It becomes easier and easier for the blue cluster to grow as its pressure only decreases. It is the opposite for green cluster. This can be seen in Figure 4.9 (f), where we show the net volume influx for each cluster.
Figure 4.8: Comparing results from the graph network model to those from the bulk model. We initialize the system in both cases with bubbles that have radii of 50 and 60 μm. In the graph model, the bubbles are each in pore bodies that have a 100 μm radius and are separated by a 400 μm throat (since the bubbles are in the middle of the bodies, the distance between them is actually initially 490 μm). The throat constriction has a 20 μm radius. The initial condition is shown in (a). The bulk model is initialized with radii of 50 and 60 μm. The radius of the disc available for diffusion is set to 20 μm, and the diffusion length is set to 500 μm. The evolution in time of the two radii in both models is shown in (b) and are in good agreement. We use values from Table 2.1 with a pressure of 15 MPa and a temperature of 323.6 K.
Initially the green cluster is growing faster, but as soon as the blue and orange clusters have different interface radii, the growth of the blue cluster only accelerates in time until the orange cluster disappears. When the orange cluster disappears, the diffusion paths change, as the blue and green clusters now "see each other". The blue cluster slowly grows at the expense of the green cluster until an equilibrium position is found.

**Impact of initial conditions** In Figure 4.10 we show how initial conditions impact evolution in the porous medium case. The pore graph network model geometry is the same as the one in Figure 4.9 but the gas phase is initialized differently. The bubble in green has an initial volume that is smaller, and we add a ganglion in the pore body that was previously empty. As is shown in Figure 4.10, these initial conditions lead to an equilibrium situation where all of the gas is located in one spherical bubble (the blue bubble). Intuitively, we could have expected that a rock with a higher gas phase saturation is more unstable and is more prone to diffusion-driven gravitational remobilization. To further illustrate that evolution is much harder to predict in the porous medium case than it was in the bulk case (and can be counter intuitive), we use a gas saturation that is lower in Figure 4.10 than it was Figure 4.9 (19% for Figure 4.10 versus 33% for Figure 4.9). The evolution of the red ganglion is interesting in that its radius initially increases, since losing volume leads to a retreat in the tube and therefore a decrease in capillary pressure. When it becomes a bubble however, losing mass makes its volume smaller and the process accelerates.

**Impact of pore structure** In Figure 4.10 we show how the pore structure impacts the evolution of multi-bubble systems governed by the ripening mechanism. We take a pore structure where some ganglia are close together (blue, orange, green, red ganglia in Figure 4.10 (a)) and do not communicate very well with another (the bubble in lavender). The bubble in blue is not much closer than the lavender one but the area available for diffusion is much larger (the diffusion area scales with the square of the throat radii). In the first part of the simulation (shown in Figure 4.10 (c) and (d)), the orange green and red ganglia are absorbed by the blue one (and by the lavender one but to a much smaller extent). At the end of the first part of the simulation, the
CHAPTER 4. PORE-SCALE SIMULATION

(a) Finding diffusion paths for cluster 1

(b) Initial situation

(c) Equilibrium situation

(d) Capillary pressures

(e) Interface Radii

(f) Net volume influx

Figure 4.9: Results for a simulation in a graph network model. There are three clusters, that we will denote by 1 (orange), 2 (green) and 3 (blue). (a) Diffusion paths for the orange cluster. (b) Initial and (c) Equilibrium situations. (d) Capillary pressure in each ganglion, (e) Interface radius for each ganglion (this is the interface radius at each iteration after internally equilibrating) and (f) Net volume influx for each ganglion. We use values from Table 2.1 with a pressure of 15 MPa and a temperature of 323.6 K.
Figure 4.10: Results for the same graph network model geometry as in Figure 4.9, but with different initial conditions. (a) Initial and (b) Equilibrium situations. (c) Capillary pressure in each ganglion and (d) Interface radius for each ganglion. We use values from Table 2.1 with a pressure of 15 MPa and a temperature of 323.6 K.
blue cluster is a ganglion that has penetrated about halfway in its only neighboring throat. During the much slower second part of the simulation, the blue and lavender ganglia slowly equilibrate. This process can also be separated into two stages. In the first stage, the lavender cluster is a bubble, and the process accelerates as time advances. When the lavender cluster starts interacting with the walls, penetrates the throat and becomes a ganglion, the equilibration process continues, but slows gradually. The rate at which the system is evolving at an instant in time is well captured by the plots that show the net volume influx to each ganglion (Figure 4.10 (g) and (h)).

4.4 Future work

A natural extension of the work described so far would be to generate more realistic pore network models. Possible approaches mentioned in Blunt (2001) include using experimental data like in Fischer and Celia (1999), simulation of sedimentation and compaction processes based on microtomographic images like in Bakke et al. (1997) or statistical reconstruction algorithms to generate random pore networks like in Idowu (2009).

4.4.1 Simulating in random pore networks

A first option is to use a procedure akin to the one in Idowu (2009) to generate random pore networks that are statistically representative of real rocks. We give ourselves distributions for pore body and pore throat radii, as well as the coordination number (number of neighbors) of the bodies. The procedure we use is as follows:

1. Choose number of bodies and size of cube that contains the network.

2. Generate bodies at random locations in the cube, under the constraint that the bodies are at least at a certain distance from each other. Each body is assigned a radius and coordination number from the corresponding distributions.
CHAPTER 4. PORE-SCALE SIMULATION

(a) Initial situation

(b) Equilibrium situation

(c) Capillary pressures - From 0 to $5 \times 10^7$ s

(d) Capillary pressures - From 0 to $1 \times 10^{10}$ s

(e) Interface Radii - From 0 to $5 \times 10^7$ s

(f) Interface Radii - From 0 to $1 \times 10^{10}$ s
CHAPTER 4. PORE-SCALE SIMULATION

Figure 4.10: Results for a second graph network model geometry. (a) Initial and (b) Equilibrium situations. (c) Capillary pressure, (e) Interface radius and (g) Net volume influx for each ganglion for the first part of the simulation. (d) Capillary pressure, (f) Interface radius and (h) Net volume influx for each ganglion for the full simulation. We use values from Table 2.1 with a pressure of 15 MPa and a temperature of 323.6 K.

3. Loop over the bodies. If the current body still has $k$ connections to make, connect it to its $k$ nearest neighbors. Decrease the number of connections each of its neighbors has to make by one. Iterate until all the bodies have made all their connections. Each of the connections is a throat and is assigned a radius from the appropriate distribution.

Figure 4.11 shows the results from a simulation in a network generated in this way with 25 bodies.

4.4.2 Generating representative geometries

Extracting the skeleton of the pore space A second idea to generate pore networks is to extract the skeleton from microtomography images of rocks. Skeletonization techniques aim to represent the porous medium (and reduce dimensionality) using elements from its mathematical morphology. This could be the medial axis, or alternatively the skeleton, as defined in Silin and Patzek (2006) and Lindquist et al. (1996). Whatever representation we choose, we consider that along this reduced
Figure 4.11: Simulating ripening in random pore networks. The pore body radii are drawn from a lognormal distribution with parameters $\mu = -9.8$ and $\Sigma = 0.3$ (that corresponds to a mean radius of 58 $\mu$m), the pore throat radii are drawn from a lognormal distribution with parameters $\mu = -10.4$ and $\Sigma = 0.3$ (that corresponds to a mean radius of 32$\mu$m).
representation (that will be a set of curves in 1D or a set of surfaces in 2D), we obtain an equivalent radius giving a measure of the size of the pore space around that point. If we can obtain a set of curves and equivalent radii, than we can convert that to our setting relatively easily. We briefly expand on the skeleton concept.

We denote by $\mathcal{P}$ the pore space, a set of $\mathbb{R}^n$. In our application we will have $n = 2$ or $n = 3$. Initially our representation of the pore space is $\mathcal{P}$ which has dimension $n$. We denote $\mathbf{r} \in \mathbb{R}^n$ the position vector in the cartesian space. A ball of radius $R$ centered at $\mathbf{r}_0$ is defined as $B_R(\mathbf{r}_0) = \{ \mathbf{r} \in \mathbb{R}^n : ||\mathbf{r}_0 - \mathbf{r}|| \leq R \}$. A ball at $\mathbf{r}_0$ is called a maximal ball at $\mathbf{r}_0$ if it satisfies the following conditions:

- $B_R(\mathbf{r}_0) \subseteq \mathcal{P}$
- There is no ball $B_{R}(\mathbf{r}_0')$ such that $B_R(\mathbf{r}_0) \subset B_{R}(\mathbf{r}_0') \subseteq \mathcal{P}$

The skeleton of $\mathcal{P}$ is the set of all the points of $\mathbb{R}^n$ that are the center of a maximal ball. The medial axis concept is slightly different but similar to the skeleton. From now on we suppose we are given $\mathcal{S}(\mathcal{P})$ a representation of the pore space, either the skeleton or something similar. Note that in two-dimensional space our representation will be a set of curves, and in three-dimensional space a set of surfaces. If we start with a three dimensional space, we assume we can reduce it twice to get a set of curves (this would be the skeleton of the skeleton).

A good reference is the procedure detailed in Silin and Patzek (2006). This leads to a stick-and-ball representation of the pore space, which should not be complicated to adapt to the our setting.
Chapter 5

Discussion

5.1 Main findings

In chapter 2 we highlighted capillary pressure as one of the main drivers for Ostwald ripening. The main difference between the bulk and porous media settings is the link between the volume of the gas phase and its shape. This key difference makes evolution difficult to predict. In chapter 3 we presented a technique to measure the interfacial curvature distributions for populations of disconnected gas ganglia. The capillary pressures were found to be controlled by the pore throats of neighboring radii, and to a first order, to be well approximated by the capillary entry pressure of the rock. The variability of capillary pressure across a population of bubbles, and even more so across the different rock types, was used to assess the potential for Ostwald Ripening. In chapter 4, we describe a simulation-based approach to predicting the evolution of multi-ganglia systems in porous media governed by the ripening process. A key insight from these simulations is that the relationship between the change in mass of the gas phase and its subsequent change in capillary pressure is inverted from the bulk to the porous media settings. This feedback mechanism destabilizes the system in the bulk case and stabilizes it in the porous medium case. Additionally, the equilibrium situation (and whether it involves multiple ganglia) was found to be highly dependent on pore structure as well as gas phase initialization.
5.2 Gravitational remobilization

The key question in this report is whether aggregation of the gas phase by diffusive processes can result in connected phases large enough to induce gravitational remobilization. In chapter 1, we defined a critical height such that the capillary pressure at the top of the gas phase would be enough to overcome the capillary entry pressure of the pores directly above it. This capillary pressure was the product of different densities of the gas and brine phases. In chapter 3, we measured capillary pressures that were well approximated by the capillary entry pressure of the rock (to a first order). If that is the case in real rocks in a post-injection setting, than the necessary height to induce remobilization could be a fraction of the critical height we defined earlier.

If the initial state of the ganglia is defined by the entry pressure of the rock, even small increases in the capillary pressure can result in mobilization. In other words, connected clusters, even over shorter distances, can be mobilized by gravitational forces. This connected height could be a small fraction of the column height needed to overcome the entry pressure due simply to the creation of a connected gas phase (by exsolution for example). It should be noted that this shorter connected height no longer has anything to do with a gravitational segregation effect, so the gas phase wouldn’t even need to expand in the vertical direction. It would simply need to slightly increase its capillary pressure. Which is the usually the case if its mass increases, as was observed in chapter 4, be it in the vertical or horizontal direction.

5.3 Ostwald ripening in heterogeneous rocks

In chapter 3, the capillary pressure distributions are significantly different from one sample to another. This indicates that there is a much greater potential for Ostwald Ripening in heterogeneous rocks than there is in homogeneous rocks. Another of the conclusions from this report is that inside a region of rock that is fairly homogeneous, equilibrium situations seem possible and that the time to reach those putative equilibria are very dependent on the diffusion lengths and areas. An interesting question
would be to study meso-scale heterogeneities in the context of Ostwald ripening. If we consider a starting point where the residual saturation of disconnected gas ganglia is uniform in a reservoir, and take two regions of rock $A$ and $B$ that are relatively homogeneous, but have different properties, as measured for instance by their MICP curves, we would assume from this study that an equilibrium is attained in each of those regions of rock, but that the equilibria are substantially different. From chapter 3, we can infer that at a first order, the equilibrium in each region is defined by the entry pressure of each region (or by the capillary pressure that is defined by the dominant pore throat radius), as is shown on Figure 5.1. These are points $A_0$ and $B_0$. Since the capillary pressure is higher at $A_0$ than at $B_0$, we expect gas to migrate from $A$ to $B$ through the ripening process. The saturation in region $A$ will decrease as that in region $B$ gradually increases. We could probably even derive a condition based on the properties of the two rocks such that all the gas in region $A$ ends up in $B$. This condition should be: if the saturation increase in region $B$ that results from adding all the gas in region $A$ corresponds to a capillary pressure that is lower than the entry pressure of region $A$ (the capillary pressure defined by point $B_{lim}$ in Figure 5.1), then all the gas in region $A$ ends up in $B$. This is also the condition such that the gas phase remains disconnected, or has a vertical height that is at least smaller than the height of region $B$.

Averaging effects may imply that the pore-scale considerations we focus on in this study can be neglected, as is assumed for instance in Goldobin and Brilliantov (2011) to derive the governing equations for the diffusive transport of gas in reservoirs. Upscaling results in this report, for example using the idea in the previous paragraph, could serve as a basis for testing the assumptions made there and in related studies.

# 5.4 Micro model validation

Experimentation using micro models could inform some of the questions raised by this report, as well as validate some hypotheses. In particular, observing Ostwald Ripening in rocks is expected to be very difficult. Using microtomography imaging to observe Ostwald ripening supposes that the samples can be reliably imaged several
times over the course of an experiment. It also supposes that all the parameters for
the experiments can be precisely maintained during the entire experiment duration.
Preventing pressure leaks over the course of the expected experiment durations could
be a barrier to performing such experiments with accuracy. In micro models, control-
ling the parameters is much easier, and so is the imaging process.

Another research effort that could be pursued through experimentation in the envi-
ronment of micro models is to test the hypotheses that are made in this report for the
modeling of ripening processes in porous media, in particular in the graph network
approach. One simple question would be to understand what happens when a bubble
grows in a geometry like that shown in Figure 5.2 (a) past the diverging point of the
cone (point A in the figure). This type of experiment would aim at understanding
how the Haines jump phenomenon happens in a quasistatic setting. Another would
be to explore the interaction of the bubble with the walls of a cone where the angle
$\Phi$ is such that $\theta + \Phi > 90$ degrees ($\theta$ being the contact angle).
(a) Haines jump case in a quasistatic setting

(b) Cone with angle such that $\Phi + \theta > 90$ degrees

Figure 5.2: Ideas for micro model experiments to test modeling assumptions in chapter 4
Bibliography


Appendices
Appendix A

Some properties of carbon dioxide

Figure A.1: Phase diagram for CO₂ - from Metz et al. (2005)
APPENDIX A. SOME PROPERTIES OF CARBON DIOXIDE

(a) Density variation with temperature and pressure - from Metz et al. (2005)

(b) Solubility in water as a function of pressure and temperature - from Kohl and Nielsen (1997)

(c) Decrease in solubility with increasing water salinity - from ENICK and KLARA (1990)

Figure A.2: Other relevant CO₂ properties
Appendix B

Capillary pressure estimation results

In this appendix we detail some of the results that were obtained from applying the processing work flow we described in chapter 3 to larger sub-volumes of the data sets.

Figure B.1 summarizes the characteristics of each sub-volume, including the number of ganglia presenting interfaces large enough to be used for the computation of mean curvature, referred to as ”nb interfaces”, and the values of the mean curvature $\kappa$ and corresponding capillary pressures $P_c$ for the entire sub-volumes. The mean capillary pressure values can then be compared with the Mercury Injection Capillary Pressure (MICP) curves, converted from air/mercury to brine/air and displayed for each sample in Figure B.5 (b). Additional details are presented in Figure B.2, Figure B.3 and Figure B.4 for selected sub-volumes of the glass beads, Boise and Fontainebleau samples respectively. Results are displayed in the same manner in all figures: each column corresponds to the results for a given sub-volume, where the first image is a visualization of the disconnected air ganglia, the second is a visualization of the air/brine interfaces, the third is a visualization of the curvature values at each point of the unsupported interfaces. On the last image, each curve represents the probability distribution function (pdf) for the curvature values of one of the considered air ganglia.
### APPENDIX B. CAPILLARY PRESSURE ESTIMATION RESULTS

#### Figure B.1: Characteristics of i) the three rock types: porosity $\phi_{He}$ measured with Helium pycnometry and mean pore-throat diameter $d_{Hg}$ [$\mu$m] estimated using MICP and ii) the sub-samples investigated using multi-scale X-ray microtomography: name of the sub-sample, voxels size (length of the side of the cube forming the voxel [$\mu$m]), volume [mm$^3$], computed porosity $\phi_{\mu CT}$ and air saturation $S_{nw}$, number of separated air ganglia, number of these ganglia presenting an interface with the brine phase large enough for the interfacial curvature analysis, mean curvature $\kappa$ [$\mu$m$^{-1}$] (mean value, standard deviation, and standard error of the mean) and corresponding capillary pressure $P_c$ [Pa].

<table>
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<th>Rock sample</th>
<th>$\phi_{He}$ (-)</th>
<th>$d_{Hg}$ ($\mu$m)</th>
<th>$\mu$CT images</th>
<th>V (mm$^3$)</th>
<th>$\phi_{\mu CT}$ (-)</th>
<th>$S_{nw}$</th>
<th>nb air ganglia</th>
<th>nb interfaces</th>
<th>$\kappa$ ($\mu$m$^{-1}$)</th>
<th>$P_c$ (Pa)</th>
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<td>49</td>
<td>38</td>
<td>-</td>
</tr>
<tr>
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<td>14</td>
<td>FS-4X</td>
<td>1.62</td>
<td>18</td>
<td>0.07</td>
<td>0.69</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
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<td>14</td>
<td>FS-4X*</td>
<td>1</td>
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<td>0.72</td>
<td>157</td>
<td>107</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<td></td>
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<td>0.06</td>
<td>0.75</td>
<td>26</td>
<td>20</td>
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**NOTE:** The table provides a comprehensive overview of the characteristics of the three rock types and the sub-samples investigated, including porosity, mean pore-throat diameter, volume, computed porosity, air saturation, number of air ganglia, number of interfaces with the brine phase, curvature, and capillary pressure.
Glass beads subsamples (GB-2X*, GB-4X*) Figure B.2 (c) and (g) highlight the similarity of curvature values presented by the interfaces considered for the calculation. For both sub-volumes, the distributions of curvature values for each isolated air ganglia (Figure B.2 (d) and (h)) show that the interfaces of all identified ganglia present similar local values of mean curvature that are close to the average mean value for the ganglia. The standard deviation of curvature values for a given air ganglion ranges from $0.008 \, \mu m^{-1}$ to $0.020 \, \mu m^{-1}$ with a mean of $0.009 \, \mu m^{-1}$ for GB-2X*, and from $0.008 \, \mu m^{-1}$ to $0.079 \, \mu m^{-1}$ with a mean of $0.011 \, \mu m^{-1}$ for GB-4X*. On average, the standard error of the mean for a single air ganglion is $1.2E^{-4} \, \mu m^{-1}$ and $2.3E^{-4} \, \mu m^{-1}$ for GB-2X* and GB-4X* respectively. The distributions graphs (Figure B.2 (d) and (h)) also show that the curvature values for each isolated air ganglia are similar one to another, with values ranging from $0.009 \, \mu m^{-1}$ to $0.024 \, \mu m^{-1}$ with a mean value of $0.015 \, \mu m^{-1}$ for sub-volume GB-4X* and from $0.006 \, \mu m^{-1}$ to $0.011 \, \mu m^{-1}$, with a mean value of $0.008 \, \mu m^{-1}$ for sub-volume GB-2X* (Figure B.1). The standard deviation of the mean curvature presented by the different air ganglia is $0.002 \, \mu m^{-1}$ and $0.008 \, \mu m^{-1}$ for GB-2X* and GB-4X* respectively. The corresponding mean capillary pressures $P_c$ are 1,107 Pa and 2,139 Pa for GB-2X* and GB-4X* respectively. These estimations are in the order of magnitude of the entry pressure of about 2,000 Pa calculated from the MICP measurement on the glass beads sample in Figure B.5 (b).

Boise subsamples (BS-2X+, BS-5X+, BS-5X*, BS-5X°) Figure B.3 (c), (g), (k) and (o) display visualizations of the curvature values presented by the interfaces considered for the calculation for BS-2X+, BS-5X+, BS-5X* and BS-5X° respectively. The corresponding curvature pdfs per air ganglia are shown in Figure B.3 (d), (h), (l) and (p). The results are detailed point by point for the three sub-volumes of the sample imaged with a voxel size of 1.8 \mu m, and then for the sub-volume of the sample imaged with a voxel size of 4.44 \mu m (BS-2X+), which represents the exact same volume as BS-5X+. Figure B.3 (h), (l) and (p) show that the interfaces of all disconnected air ganglia present more broadly distributed local values of mean curvature around the average mean value for the ganglia than for the glass beads sub-volumes presented above: the standard deviation of curvature values for a given
Figure B.2: Interfacial curvature analysis for the analyzed sub-volumes of the glass beads sample imaged with a voxel size of 3.28 µm (GB-2X* - graphs a) to d)) and of 1.62 µm (GB-4X* - graphs e) to h)). a) and e) the disconnected air ganglia are represented with different colors. b) and f) the total air phase is represented in navy blue and the interfaces with the brine phase are colored in red. c) and g) the mean curvature is plotted for each portion of interface used for the calculation. d) and h) the mean curvature distribution is plotted for each separated air ganglia that presents interfaces large enough for the calculation.
APPENDIX B. CAPILLARY PRESSURE ESTIMATION RESULTS

Air ganglia is higher. Mean curvature ranges from 0.020 \( \mu \text{m}^{-1} \) to 0.871 \( \mu \text{m}^{-1} \) with a mean of 0.068 \( \mu \text{m}^{-1} \) for BS-5X+, from 0.017 \( \mu \text{m}^{-1} \) to 0.705 \( \mu \text{m}^{-1} \) with a mean of 0.066 \( \mu \text{m}^{-1} \) for BS-5X*, and from 0.019 \( \mu \text{m}^{-1} \) to 0.641 \( \mu \text{m}^{-1} \) with a mean of 0.061 \( \mu \text{m}^{-1} \) for BS-5Xo. It can be noted that the results are very similar for the three sub-volumes. On average, the standard error of the mean for a single ganglia is 1.8E\(-3\) for BS-5X+ and BS-5X* and 1.7E\(-3\) for BS-5Xo. When compared with BS-5X+, BS-2X+ presents wider distribution curves: the standard deviation for a single ganglion ranges from 0.013 \( \mu \text{m}^{-1} \) to 2.195 \( \mu \text{m}^{-1} \) with a mean of 0.234 \( \mu \text{m}^{-1} \), which is more than three times higher. The distributions graphs (Figure B.3 (h), (l) and (p)) show that most air ganglia/brine interfaces display similar distribution of interfacial curvature values. The mean curvature values for a single ganglion range from 0.010 \( \mu \text{m}^{-1} \) to 0.122 \( \mu \text{m}^{-1} \) with a mean value \( \kappa \) of 0.040 \( \mu \text{m}^{-1} \) for sub-volume BS-5X+, from 0.009 \( \mu \text{m}^{-1} \) to 0.285 \( \mu \text{m}^{-1} \), with a mean value \( \kappa \) of 0.054 \( \mu \text{m}^{-1} \) for sub-volume BS-5X* and from 0.014 \( \mu \text{m}^{-1} \) to 0.129 \( \mu \text{m}^{-1} \), with a mean value \( \kappa \) of 0.032 \( \mu \text{m}^{-1} \) for sub-volume BS-5Xo (Figure B.1). For BS-2X+ the mean curvature values range from 0.001 \( \mu \text{m}^{-1} \) to 0.276 \( \mu \text{m}^{-1} \), with a mean value \( \kappa \) of 0.042 \( \mu \text{m}^{-1} \), which is very close to the value calculated for BS-5X+. The standard deviation of the mean curvature presented by the different air ganglia is 0.020 \( \mu \text{m}^{-1} \) for both BS-5X+ and BS-5Xo and is a bit higher for BS-5X* with a value of 0.033 \( \mu \text{m}^{-1} \). The corresponding average capillary pressures \( P_c \) range from 4,617 Pa to 7,803 Pa with a mean value of about 6,000 Pa, for the sub-volumes with a voxel size of 1.8 \( \mu \text{m} \). The average capillary pressure \( P_c \) for sub-volume BS-2X+ is 6,071 Pa, which is close to the value calculated for BS-5X+. Figure B.5 (b) displays the MICP measurement for the Boise sample (grey line) with an entry pressure around 6,000 Pa.

**Fontainebleau subsamples (FS-4X*, FS-10X*)** Although Figure B.4 (c) and (g) show that both sub-samples FS-4X* and FS-10X* present rather similar interfacial curvature, the distributions of curvature values for each isolated air ganglia differs (Figure B.4 (d) and (h)): whereas for FS-4X* most ganglia present similar distributions, the distributions presented by the air ganglia for FS-10X* vary from a ganglion to another and the deviation is also larger. These results include however
Figure B.3: Interfacial curvature analysis for the analyzed sub-volumes of the Boise sandstone sample imaged with a voxel size of 4.44 m (BS-2X⁺ - figures a) to d)) and of 1.8 µm (BS-5X⁺ - figures e) to h), BS-5X⁻ - figures i) to l) and BS-5X° - graphs m) to p)). a), e), i) and m) the disconnected air ganglia are represented with different colors. b), f), j) and n) the total air phase is represented in navy blue and the interfaces with the brine phase are colored in red. c), g), k) and o) the mean curvature is plotted for each portion of interface used for the calculation. d), h), l) and p) the mean curvature distribution is plotted for each separated air ganglia that presents interfaces large enough for the calculation.
all the interfaces that remain after deleting from the mesh the vertices that belong to the rock/air interface as explained in subsection 3.2.2, which is the procedure that was successfully applied to the glass beads and Boise images. A high fraction of flat air/brine interfaces appear on the images in the case of the Fontainebleau sandstone, due to the presence of thin films between the air phase and the rock. These interfaces, which are likely to be supported by the solid, significantly lower the mean interfacial curvature values of air ganglia and were therefore removed for the curvature calculation. The standard deviation of curvature values for a given air ganglion ranges from 0.006 \( \mu m^{-1} \) to 1.309 \( \mu m^{-1} \) with a mean of 0.205 \( \mu m^{-1} \) for FS-4X* and from 0.039 \( \mu m^{-1} \) to 0.213 \( \mu m^{-1} \) with a mean of 0.099 \( \mu m^{-1} \) for FS-10X*. The standard error of the mean, for a single ganglion, is on average one order of magnitude higher for FS-4X* (1.0E\(-2\) \( \mu m^{-1} \)) than for FS-10X* (3.1E\(-3\) \( \mu m^{-1} \)). From one air ganglion to another the mean curvature values vary from 0.001 \( \mu m^{-1} \) to 0.625 \( \mu m^{-1} \) with a mean value \( \kappa \) of 0.110 \( \mu m^{-1} \) for FS-4X* and from 0.048 \( \mu m^{-1} \) to 0.349 \( \mu m^{-1} \), with a mean value \( \kappa \) of 0.147 \( \mu m^{-1} \) for FS-10X*. The standard deviation of the mean curvature presented by the different air ganglia is 0.113 \( \mu m^{-1} \) for FS-4X* and 0.093 \( \mu m^{-1} \) for FS-10X*, which is about four times larger than for the Boise sub-volumes. The standard errors for the Fontainebleau sub-volumes are also one order of magnitude higher than for the Boise sub-volumes (Figure B.1). Finally, the estimated mean capillary pressures \( P_c \) are 15,893 Pa for FS-4X* and 21,110 Pa for FS-10X*. As for the other samples analyzed, these estimations are in the order of magnitude of the entry pressure of about 15,000 Pa calculated from the MICP measurements (Figure B.5 (b)).
APPENDIX B. CAPILLARY PRESSURE ESTIMATION RESULTS

Figure B.4: Interfacial curvature analysis for the analyzed sub-volumes of the Fontainebleau sandstone sample imaged with a voxel size of 1.62 µm (FS-4X∗ graphs a) to d)) and of 0.64 µm (FS-10X∗ graphs e) to h)). a) and e) the disconnected air ganglia are represented with different colors. b) and f) the total air phase is represented in navy blue and the interfaces with the brine phase are colored in red. c) and g) the mean curvature is plotted for each portion of interface used for the calculation. d) and h) the mean curvature distribution is plotted for each separated air ganglia that presents interfaces large enough for the calculation.
Figure B.5: (a) Cumulative volume-weighted pore-throat size distribution obtained by MICP for the Glass beads (blue line), Boise sandstone (grey line) and Fontainebleau sandstone (pink line) sample. The dominant diameter size (intrusion of half of the pore volume) is $101 \mu m$, $31 \mu m$ and $14 \mu m$ for the Glass beads, Boise and Fontainebleau samples, respectively. The voxel sizes for the different image acquisitions ($2X$ $3.28 \mu m$ for the Glass beads and Fontainebleau samples, and $4.44 \mu m$ for Boise sample / $4X$ $1.62 \mu m$ for the Glass beads and Fontainebleau samples and $5X$ $1.8 \mu m$ for Boise sample / $10X$ $0.62 \mu m$) are displayed with dotted and dashed vertical lines. (b) Capillary pressure curves for air/water on the sintered glass beads sample (blue line), Boise sandstone (grey line) and Fontainebleau sandstone (pink line), converted from Hg/air MICP measurements. The entry pressures are about 2,000 Pa for the glass beads sample, 6,000 Pa for Boise sandstone and 15,000 Pa for Fontainebleau sandstone. Graphs provided by Dr. Charlotte Garing.