



Characterising mineral surfaces and probing the impact of ageing in crude oil using AFM

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Declaration of Originality

I hereby certify that the material in this thesis is the result of my own original research. All consulted materials have been properly acknowledged and the literature used referenced.

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Abstract

The crude oil adsorption on model mineral surfaces such as mica and calcite has been investigated using the atomic force microscopy technique to determine the nanoscale characteristics of crude oil particles such as asphaltenes. In order to proceed with studying more complex surfaces, such as reservoir rocks, one needs to be able to distinguish the features of the rocks from those of crude oil particles. Crude oil is composed of four different fractions known as SARA fractions of crude oil. The images obtained from AFM showed that the asphaltenes of crude oil in fact do adsorb onto the mica discs, and the asphaltene aggregates tend to form agglomerates. Additionally, it was found that different crude oils form agglomerates with different features, and the adhesivity and stiffness differ from crude to crude. On a calcite surface, which is positively charged, crude oil formed a film when the surface was submerged into crude oil and aged at a temperature of 70 °C and pressures above 10 bar. This proved that the surface charge of the surface, which crude oil's aromatic compounds come into contact with, plays a key role in the manner in which crude oil will wet that surface in the absence of any other compounds, such as water. Once these patterns were established, in order to further enhance knowledge in this field, Ketton rocks were flushed with brine and imaged in order to establish whether water films could be imaged with AFM or not, and indeed, this was a success, and water films were successfully detected. Then came the ultimate goal of this project, which is to determine whether crude oil's aromatic fractions, such as asphaltenes and resins, will wet the originally water-wet rock surface and alter the wettability of the rock's surface in favour of oil.

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“The scientific man does not aim at an immediate result. He does not expect that his advanced ideas will be readily taken up. His work is like that of the planter - for the future. His duty is to lay the foundation for those who are to come, and point the way.”

Nikola Tesla

Publications

The work and results of the experiments of this thesis project which are currently undergoing publication process are noted here in chronological order:

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Nomenclature

All symbols used in this thesis are defined where they first appear. For the reader's convenience, the principal meanings of the commonly used notations are presented in the lists below. Though many of the symbols are specific to the chapter where they are introduced, in certain cases, symbols introduced in previous chapters might be employed with the same meaning in following chapters.

Abbreviations

AFM Atomic Force Microscope

SEM Scanning Electron Microscope

TEM Transition Electron Microscopy

STM Scanning Tunneling Microscope

SPM Scanning Probe Microscopy

SFA Surface Force Apparatus

QI Quantitative Imaging

FD Force Distance

3D Three Dimensional

2D Two Dimensional

RPM Rotations per minute

EOR Enhanced Oil Recovery

PAH Polycyclic Aromatic Hydrocarbon

PA Petroleum Asphaltenes

CA Coal Asphaltenes

CT Computed Tomography

FT Fisher-Tropsch

SRD Stochastic Rotation Dynamics

QMR Quantitative Molecular Representation

NMR Nuclear Magnetic Resonance Spectroscopy

GCD Gas Chromatography Distillation

QMR Quantitative Molecular Representation

GPC Gel Permeation Chromatography

MD Molecular Dynamics

LBM Lattice Boltzmann Method

FIB-SEM Focused Ion Beam-Scanning Electron Microscope

Roman letters

q	Volumetric flux per unit area (m s^{-1})
k_s	Medium permeability (m^2)
K_{sat}	Saturated permeability (m^2)
L	Length (m)
$K_{\text{r,w}}$	Relative permeability (m^2)
P_c	Capillary pressure (bar)
R	Radius of fitted sphere (milli-Darcies)
K_{eff}	Effective permeability
K	Absolute permeability
K_r	Relative permeability
S	Specific surface area (m^2)
D	Equivalent diameter (m)
S_{avg}	Average fluid film thickness (nm)
F	Acting force on cantilever (N m^{-1})
k	Cantilever spring constant (N m^{-1})
x	Cantilever vertical displacement (m)

Greek letters

ϵ	Porosity
γ	Interfacial tension (mN m^{-1})
θ	Contact angle ($^\circ$)
ϕ	Bulk porosity
μ	Dynamic viscosity (Pa s)
Γ	Surface coverage fraction
ΔP	Pressure drop (Pa)

Chapter 1

Introduction

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1.1 Introduction

Energy has been one of the most controversial subjects ever since the discovery of fire by man and has increased substantially due to the Industrial Revolution. The vast majority of the energy that people produce and use today comes from fossil fuels like crude oil. Heavy oil, comprising extra heavy oil and bitumen, is appealing because of its vast reserves [17, 78]. Approximately 30% of the global oil resources consist of conventional oil, while the remaining portion is comprised of heavy oil, extra-heavy oil, and bitumen. Recovering and refining heavy oil is more challenging and expensive compared to ordinary oil due to its high viscosity and heavier molecular compositions [212, 146]. Enhanced oil recovery (EOR) is a crucial method for extracting heavy oil, particularly during the first stages of development, unlike traditional light oil. In the process of solvent-injection enhanced oil recovery (EOR), solvents are used to decrease the viscosity of heavy oil. However, the effectiveness of solvents varies depending on the specific oil field. Therefore, it is essential to comprehend the constituents of oil and how their properties are altered when solvents are introduced. This understanding is crucial for assessing the efficacy of various solvents [146].

The role of crude oil does not end in providing energy, but it also sources more than 50%

of chemicals used in today's everyday life [244]. Therefore, even if countries switch from fossil fuels to renewable, crude oil would still be essential for the chemical and other markets.

While fossil fuels are essential for supplying energy and raw materials in various industries, there have been notable advancements in the creation of environmentally friendly fuels and raw materials for chemical manufacturing. The Fisher-Tropsch (FT) method has facilitated significant progress in developing biofuels, allowing for the manufacture of environmentally friendly gasoline and feedstock. The FT operations utilise a stepwise polymerisation process to convert synthesis gas with a specified hydrogen-to-carbon monoxide ratio into hydrocarbon liquids and waxy solids. Water is produced as a byproduct during this process. As previously stated, the process takes place with the assistance of an iron or cobalt catalyst under moderate pressures (about 20 to 50 bar) and temperatures (200 to 350 °C) [93]. Initially designed for coal-to-oil conversion, the technique has since been enhanced by recent technological breakthroughs to enable oil production from biomass.

Oil production consists of three main phases: primary, secondary, and tertiary [218] [240]. In reservoir engineering, the goal is to produce oil as efficiently as possible. Often, it is possible to recover more oil. However, it could be more cost-intensive. This phenomenon is significant when discussing the role of wettability and asphaltenes. Generally, it is believed that one can recover more oil from a water-wet reservoir than from an oil-wet reservoir. This is due to the need to displace oil from the matrix rocks into the fractures connecting to the wells. Consequently, one of the main mechanisms for recovering oil from fractured reservoirs is the imbibition of water into the rocks, followed by the displacement of oil (from rocks that are preferentially water-wet [185]).

In the primary production period, only 5-30% of the original oil in place (OOIP) can be recovered by the native pressure energy stored in the reservoir [218]. Techniques such as water, steam, and gas injection are now used to enhance the recovery rate of crude oil. However, there are limitations. The more water injected in the reservoir, the lower the oil-water ratio becomes, and at some point, the recovery of crude oil is no longer cost effective [33, 32, 49, 218]. This issue is linked to unfavorable wettability of the reservoir rock.

The wettability of reservoir rock has been proven to be a key factor in enhanced oil recovery (EOR). Therefore, changing the wettability of the reservoir rock in favor of one fluid can play a vital role in enhanced oil recovery. Wettability is not a property of the rock alone but of the crude oil/brine/rock system. In terms of crude oil, surface active components, such as precipitating asphaltenes or resins, may change the wettability of the rock. Therefore, the

asphaltenes/resins ratio, which relates to the colloidal stability of asphaltenes in the crude, and the ratio of saturates/aromatics, which indicates the ability of the oil to dissolve asphaltenes, are assessed.

Some of the critical economic issues in the petroleum industry today are linked with asphaltenes [63, 66, 64, 65]. This is because all conventional and light oil fields have passed their production peak. Therefore, today, we are turning toward more heavy crude resources, which tend to contain higher proportions of asphaltenes. This causes a significant issue in the oil industry: the abundance of asphaltenes in oil reserves, primarily in the heavy oil fields. Asphaltenes are sometimes nicknamed as the cholesterol of the oil industry [52]. This is because they can have unwanted phase transition and sediment near the well-bore regions of the reservoir and production tubing, therefore hindering production, transportation, and refining. This results in increased extraction and transportation costs to the point where some fields become economically unfeasible.

Asphaltene's interfacial interactions with reservoir rocks impact the rock's wettability, hindering oil recovery [265]. This offers a focal point for enhanced oil recovery (EOR), which motivates this PhD project.

Understanding asphaltenes, the reason behind their phase transition, and the impact of this phase transition on rock wettability will have a vital role in the future of Enhanced Oil Recovery (EOR). Atomic Force Microscope (AFM) allows force spectroscopy and surface imaging at the nanoscale, and this technique has become a popular method for assessing wettability as force curves give information about adhesion force, which can be then converted into information about wettability [86, 165, 266].

1.1.1 Thesis Outline and Chapter Structures

This thesis consists of nine chapters, each chapter is briefly introduced here and how it fits within the overall purpose of the project and write up of this thesis is highlighted.

Chapter 2

This chapter looks broadly into reservoirs, crude oil, and its essential fractions before focusing on its polar components, asphaltenes, and resins and their behaviors and, thus, its negative

impacts on crude oil production, refining, and transport processes. This chapter introduces the fundamentals that motivated this project, such as reservoir rocks and their mineral compositions, crude oil, and its fractions, and how the matrix has a principal role in oil recovery.

Chapter 3

The third chapter will introduce this project's experimental methods, equipment, and procedures. Atomic Force Microscopy, the backbone technique used in this project, is introduced, and various imaging modes are described along with each mode's advantages. Scanning Electron microscope is also introduced briefly with the fundamental working principle of this equipment. In this work, much of the crude oil used has been aged to try to revert the properties of the crude oil to how it is in an oil reservoir. This ageing technique and ageing cell are also fully described in this section, along with detailed steps required in ageing samples appropriately, and why this method was used is also described.

Chapter 4

This is the first results chapter and characterises the mineral surfaces and rock samples used in this research project are introduced in this chapter. Their important characteristics and relevance to reservoir and oil recovery are discussed, along with reasons they became choice surfaces for the investigation of this project. Mica, calcite, and ketton rocks are described in this section, and AFM images are provided to help the reader visualise the samples better.

Chapter 5

Having introduced the AFM, minerals used in this project, and ageing technique, this chapter combined all the elements it reports in detail on how the introduction of crude oil which is then left to age, changes the topographical features of important minerals commonly found in reservoir matrix, namely mica, and calcite. This chapter looks at three different crude oils and two separate mineral surfaces, and thereby it allows a fair conclusion to be drawn in comparing crude oil adsorption on mineral surfaces and how effective the ageing technique is in producing reservoir-mimicking conditions. It concludes the difference between the different crude oils on the same mineral surface whilst making a comparison between crude oil adsorption differences

across the different mineral surfaces.

Chapter 6

During experiments conducted in Chapter 5, when ageing mica in the presence of calcite in the ageing cell using one of the crude oils, it was observed that there were crystals on the surface of the mica. Using SEM, these crystals were identified to be gypsum and therefore gave motivation for the experiments of this chapter. Ageing process on mica was repeated in crude oil when calcite was present in one cell and absent in another cell. This was undertaken in order to establish two things: firstly, whether the discovery of crystals is a genuine finding and thereby a reproducible result, and secondly, whether the presence of calcite in the ageing cell plays any role at all in the formation of the gypsum crystals. This is because gypsum and calcite are in the same mineral family, and both are calcium-based.

Chapter 7

Since the ageing technique is a lengthy process and it takes a month for the samples to be ready for experiments, a fast sample-producing technique was tested and developed in this project whereby crude oil undergoes serial dilution in order to reach a concentration dilute enough to leave deposits for investigation under AFM without making the surface too adhesive as that can be a problem for samples being imaged under AFM. This will be highlighted in more detail in the chapter.

Chapter 8

This chapter builds on the knowledge gained from the results of Chapter 5 and looks at Ketton rock, which is a limestone-based rock obtained from a quarry in Rutland in the UK by itself when the rocks are flushed with brine. The AFM is then used to see whether water films with AFM can be detected or not. Water films were detected, which were then measured for thickness and modeled for further visualisation. The relevance of this chapter in the overall project is that in the reservoir, oil and water (brine) coexist, and therefore ageing a brine-flushed ketton rock can give a solid simulation of what a reservoir rock matrix looks like at a nanoscale.

Chapter 9

This chapter builds on chapter 8. The ketton rocks, which were flushed with brine, were subsequently aged in three separate crude oils for a month and then imaged using AFM. This was done in order to establish whether the crude oil depositions onto rocks displace water adsorbed on the surface of the rock or not, this is a theoretically investigated topic, and the novelty of this project is that it built a method along with the steps used to produce reliable experimental data which showed the subsequent consequence of water film detection using AFM and then displacement of water films with crude oil on the surface of the rocks at nanoscale.

Chapter 10

Conclusions across the previous experimental chapters of this thesis are combined here to give a unified and summarised conclusion for this Ph.D. project. Further works required to build a better outlook for industry and science are also pointed out, along with recommendations on possible outlook built-ups.

Chapter 2

Literature review

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In this chapter, various topics are discussed in a particular order, which helps to build the background to this project's results and importance. Reservoir formation and life cycle, the chemistry of crude oil, and its most essential components and characteristics are then defined. A deeper look into asphaltenes is then made to present the current thinking on the structure of asphaltenes along with their importance. Wettability is then discussed to set the scene for the final chapters of this thesis.

2.1 Oil Reservoirs

An *oilfield* is a term that refers to one or a group of reservoirs contained in a defined area that belong to a single geological structural feature. A hydrocarbon reservoir does not resemble an underground fluid storage, i.e., a lake, but rather crude oil is accumulated and contained between grains of sand or other porous rock formations. A reservoir, therefore resembles a rigid and finely perforated sponge [89].

2.1.1 Crude Oil Reservoir Components

Remains of microorganisms that live in water, and to a lesser extent, land organisms, that are carried down to the sea by the rivers and plants that grow on the seabed of the oceans, are enmeshed in silt and fines that will settle at the bottom of the sea basins. Rich in organic materials, these deposits become the source rocks for forming crude oil. The sediments grow thicker and sink to the ocean floor under the gravitational pull of their weight. As more deposits pile up, the weight of the deposits beneath them increases by several thousandfold. Simultaneously, the temperature increases by up to a few hundred degrees, forming a 'pressure cooker' environment.

The mud and sand harden into shale and sandstone. At the same time, carbonate precipitates and skeletons harden into limestone, and the remains of the deceased organism are converted into fossil fuels. After the formation of the crude oil liquid, it flows up towards the earth's upper crust as it has a lower density than brine solutions, which saturates the interstices of the sand, shale, and carbonate rocks that constitute the rock formation, which is why in every hydrocarbon

reservoir, crude oil and gas (formed by the degradation of the crude oil into shorter-chain alkanes and water) coexist. This upward flow continues until there are no more microscopic pores facilitating the flow of crude. At this point, the reservoir is formed as the crude flow encounters an impermeable shale or a dense layer of rock, which does not allow the crude to flow upwards. The oil has become trapped at this stage, and a hydrocarbon reservoir is created [199].

Thus, once the fossil fuels are formed in an appropriate reservoir rock matrix, a trapping mechanism becomes crucial to ensure the hydrocarbon fuel mixture formed does not escape to the surface of the earth through buoyancy and other forces. Billions of crude oil barrels can be recovered from a reservoir rock, but if the trapping mechanism is not in place, no reservoir will be found but only oil-stained rock matrix [95, 112, 189].

2.1.2 Formation of Hydrocarbon Reservoirs

The reservoir rock, along with the fluids in the rock matrix, comprise the main principle components of any crude oil reservoir.

The formation of a hydrocarbon reservoir depends on several criteria, all of which need to be satisfied for the reservoir to develop. The first and most important ingredient is the source, which is the core of the formation of fossil fuels. Single-celled aquatic life forms are thought to be the source that feeds the formation of fuels. The reservoir can be thought to be a 'pressure cooker' in which the remains of organisms will be cooked into crude oil, and like any cooking process, the hydrocarbons can be overcooked or underdone, and just like many other practical circumstances, the formation of oil is not optimal. [96].

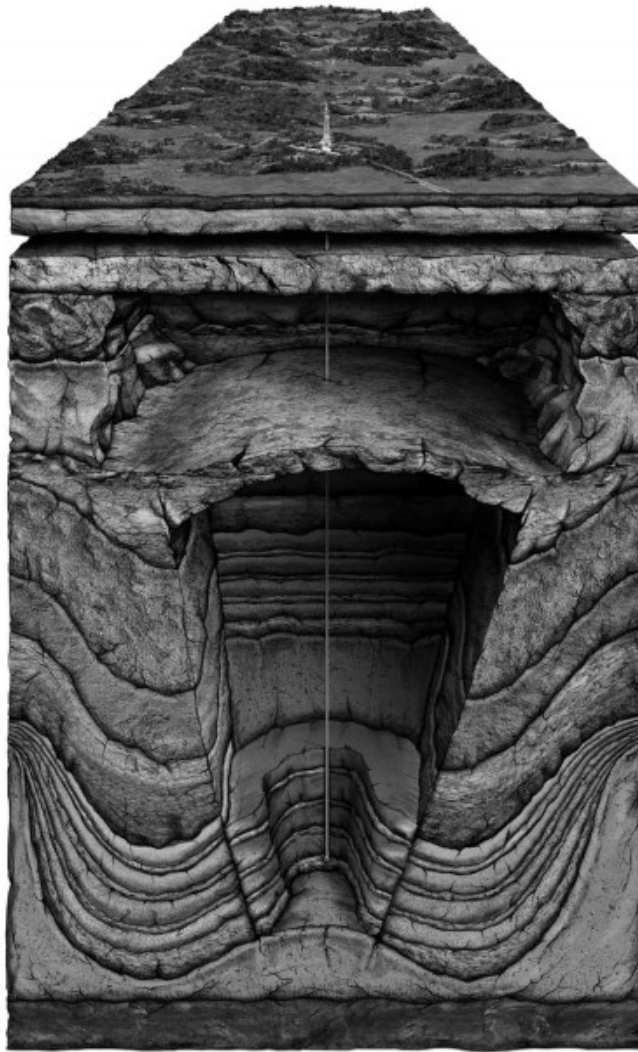
The second ingredient needed is a conduit from the source rock to a reservoir rock to allow the formation, trapping, and flow of the crude oil within the matrix. Most hydrocarbons are formed in source rocks, which are not suitable for modern and current production systems. As for production, hydrocarbons need to be able to flow into wells, and the rate of flow must be sufficient enough to make extraction economically profitable.

Petroleum reservoirs are usually discovered in sedimentary rocks. Rarely, crude oil is discovered in metamorphic or fractured igneous rocks. This is because metamorphic or fractured igneous rocks are formed at high temperatures and pressure conditions, which are not optimal for petroleum formation. Additionally, they do not possess the interconnected porous matrix

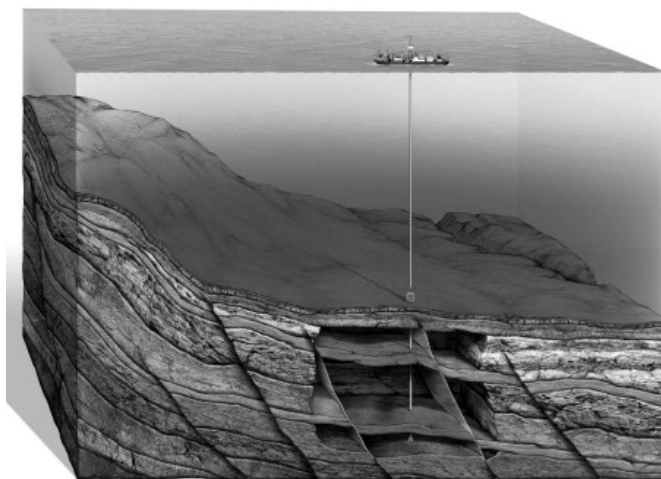
space that can facilitate the flow of the oil from the porous media to the wellbore [95, 96].

2.1.3 Geological Reservoir Categories

Hydrocarbon reservoirs result from sedimentary processes that occurred millions of years ago. Given the geology of the earth, some of these sedimentary deposits now exist in great depths beneath the earth's surface where land is; such reservoirs are called onshore fields, as shown in figure 2.1. Some reservoirs, however, exist at depths beneath the seabed. Such reservoirs were formed initially where land was but now are located beneath the seabed as, over the years, the geography of the earth has changed. Though once all lands were connected, separation occurred, and thus, some of the hydrocarbon reservoirs formed years ago are now located beneath the sea. Such reservoirs are referred to as offshore reservoirs [307].



(a) Onshore Reservoir



(b) Offshore Reservoir

Figure 2.1: Offshore vs Onshore reservoirs schematic representation, adopted from [\[307\]](#).

2.1.4 Reservoir Classifications and Reservoir Fluids

Reservoirs are classified based on their fluid dynamic behaviour and, additionally, the reservoir rock matrix itself; the reservoir rock plays a crucial role in the production levels a reservoir can achieve, and minerals that form the surface of the rock play a key role in the recovery rate through their wetting properties and their interaction with polar active components of crude oil (asphaltenes and resins).

Reservoir Rock Characteristics

Reservoir rock is a matrix that traps hydrocarbons within itself, while its porous media allows the hydrocarbon to flow freely within the matrix. The sealing mechanism of the impermeable cap rock prohibits hydrocarbon flow towards surface layers, while the pores and throats of the matrix facilitate the flow paths for the accumulated petroleum [39, 2]. Reservoir rock matrices come in different configurations, from tight rocks to dense rocks and loose sands. Rocks are classified into two overall categories: conventional and unconventional rocks. In conventional rocks, grains are bound together via several minerals such as calcite, silica, and clay [39, 61]. Conventional rocks have suitable storage and conductivity, facilitating the reservoir's accumulation and flow of hydrocarbons. In contrast to conventional reservoirs, unconventional reservoirs are spread across a large area with no indicative trap geometry. Additionally, the hydrocarbon reserves in such reservoirs have a low density and are trapped through strong capillary forces; thus, natural flow through buoyancy is no longer an option. Therefore, unconventional reservoirs require physical changes to the properties of the rock matrix or the fluid, which directly impact their flow capability. Such methods involve steam injection or fracking [187].

The two most important properties of the reservoir rocks that play a critical role in the exploitation and production of hydrocarbons from the reservoir are porosity and permeability of the rock. A reservoir rock, in essence, is a subsurface storage volume with sufficient porosity and permeability that permits migration, accumulation, and finally storage of the petroleum under adequate conditions [310, 158].

Porosity

The reservoir needs sufficient porosity, which is vital to how much hydrocarbon can be stored there. Porosity is a measure of the void spaces (pore volume) per overall bulk volume of the reservoir rock, where the void space is the net volume difference between the bulk volume and the volume occupied by grains. Total porosity and effective porosity are the two subdivisions of rock porosity. Only effective porosity is essential for oil industry and reservoir engineering purposes, as it explains and accounts for only the interconnected pores through which hydrocarbons can flow within the system. Therefore, effective porosity is the adequate volume from which hydrocarbons can be recovered. Since oil and water are found together in most hydrocarbon reservoir matrices, hydrocarbon porosity is also introduced as a way to measure how many interconnected pores are filled with hydrocarbons [55]. Oil and gas may also coexist in the reservoir; quantitatively, hydrocarbon porosity is defined as below:

$$\Phi = \frac{\text{Void Space}}{\text{Bulk Volume}} \quad (2.1)$$

The void space is the difference between the bulk volume and the matrix grain volume. As such, the porosity can alternatively be expressed in the form:

$$\Phi = \frac{\text{Bulk Volume} - \text{Grain Volume}}{\text{Bulk Volume}} \quad (2.2)$$

Permeability

Permeability is a measure of the connectivity of the pores of the rock in the subsurface, as the rock matrix must be a porous medium to be permeable. Thus, permeability indicates how easily hydrocarbon fluids can flow through the rock pore matrix. Darcy's law defines the flux of liquid flow through a porous medium; the flux is directly correlated with how permeable the medium is.

$$q = -\frac{k \Delta p}{\mu L}, \quad (2.3)$$

Where q represents volumetric flux per unit area ($q=Q/A$, where Q is volumetric flux and A

is the cross-sectional area.), μ is the fluid viscosity, Δp is the pressure drop along the length L , and k is the permeability of the medium. Reservoir permeability can be divided into primary and secondary categories, where the deposition and lithification of the sedimentary rocks define primary permeability. In contrast, the secondary permeability of the matrix results from alteration within the rock matrix through sedimentation, fracturing, and solution [299, 122, 46, 143].

Since in a hydrocarbon reservoir, one or more fluids can coexist in more than one phase, the permeability of the rock is also classified into absolute and relative.

Permeability is absolute when rock pores are occupied and saturated with only one fluid and no other fluids or phases are present. However, relative permeability occurs when more than one fluid is present in the porous rock matrix. Thus, often in hydrocarbon reservoirs, more than one fluid across multiple phases coexists, resulting in the impact of one fluid over another. Hence, in reservoirs where more than one fluid exists in the porous media, the permeability of the rock to any of the phases is referred to as the effective permeability [143]. Effective permeability may be related to absolute permeability through the following:

$$K_{eff} = K K_r, \quad (2.4)$$

where K_{eff} is the effective permeability, K is the absolute permeability, in milli-Darcies, and K_r is the relative permeability to the fluid, dimensionless.

It is sporadic that reservoir rocks are homogeneous in their physical properties or uniform in thickness [299]. Variation in geological processes of erosion, deposition, folding, and lithification, amongst other processes, often dictates that reservoir rocks are heterogeneous and not uniform in properties. As a result of the heterogeneity of the reservoir matrix, it is common practice to calculate the average permeability based on several factors. These factors include bedding direction, deposition environment, flow direction, and other factors [74, 189, 143].

2.1.5 Life Cycle of Reservoir

A producing oil reservoir can produce for over 100 years, though not all reservoirs will produce for so long, and all reservoirs go through a complete cycle from their inception until their abandonment, which is listed below:

1. Exploration: Exploration of fossil fuel plays is where the hydrocarbon reservoir's life begins [183, 260]. The plays constitute geologic structures that indicate possible hydrocarbon source accumulation, which incorporates the presence of a source rock and a reservoir rock matrix with migration pathways to allow the flow of petroleum with a cap rock. Through geophysical and geological studies, if evidence is gathered of potential oil and gas existence, then these plays will turn into prospects, and exploratory wells will be drilled, and should petroleum extraction occur, a new oilfield will be discovered. Historical data indicates that only around 30% of exploration wells lead to oil and gas extractions, of which some are unconventional reservoirs, of which the most well-known type is shale oil reservoirs. Unconventional reservoirs require efficient production as opposed to exploration as they cover a large area, and thus unconventional hydrocarbon reservoirs usually result in technical challenges for production.

2. Delineation: In order to assess the recoverable quantity and quality of the crude oil in the reservoir, along with the water and gas content, appraisal wells are drilled, which help evaluate the reservoir extent. Reservoir assessment is often finalised with petrophysical research and transient well tests.

3. Reservoir Development: At this stage, optimal reservoir production is achieved as oil and gas wells are produced with economical flows. Through analysing various scenarios and simulations, the appropriate location, placement, and well designs are chosen. [260].

4. Production: Crude oil is recovered through three mechanisms during the production life of a reservoir: primary (pressure of the reservoir is sufficient for this stage as pressure drop through drilling leads to pressure gradients within the reservoir which induce flow through porous rock matrix that is interconnected to the production well [16, 211], secondary and EOR, tertiary) [16].

Primary recovery allows the extraction of the subsurface oil through the native energy stored in the reservoir; extraction is encouraged by one or a combination of the following: i. oil drainage as a result of gravitational force (gravity drainage); ii. water-driven liberation from nearby aquifers; iii. vapour phase interchange from liquid inside the reservoir; iv. oil expansion (solution drive); and v. gas expansion (gas cap drive). [16, 168]. Though this stage is mainly driven by the pressure force of the reservoir, pumpjacks that use a piston to enhance pressure in the reservoir can be used to help increase the recovery rate at this stage of production. Recovery rate at this production stage is usually no more than 30% of the original oil in place (OOIP) [159, 44].

Once the natural drive mechanisms reduce over time, secondary efforts mostly involving water and gas injection or both are implemented to maintain the recovery rate of the reservoir [308, 257, 99]. During this stage of production, significant quantities of the OIIP are recovered, which adds another 15-30% volume recovered to that of the primary [298]. Reservoir characteristics such as wettability and capillary forces often hinder secondary recovery processes [69], and at this point enhanced oil recovery techniques (EOR) are initiated in order to keep extraction of oil from the reservoir going [328, 140, 81, 82].

Carbon dioxide injection (generally supercritical carbon dioxide as it sublimates under atmospheric pressure [150]) Subject to water-flooding earlier, thermal energy application to heavy oil reservoirs is among the EOR techniques utilised in the industry, which can help increase the recovery rate of a reservoir to 75% of the OOIP [260, 207]. It is worth noting that while secondary recovery methods are built around sweeping oil through injection of water or gas in the wells without any alteration of the hydrocarbon properties, EOR techniques are built around altering the actual properties of the hydrocarbons in the reservoir, such as density and viscosity of the crude oil, which helps make flow easier [259, 136]. Statistical data indicates an overall recovery rate of 25-50% across the three production phases worldwide [260].

5. Abandonment: The production levels of a reservoir start to naturally decay, and other operating problems eventually bring the production level down to a point at which production is no longer economically feasible as the rate of return on the investment in the reservoir is below what is acceptable. At this stage, the reservoir has approached its final phase, which is known as abandonment [304, 275].

Declining well flow rate, increasing water production, high gas-to-oil ratio, and persistent workover of wells are cost-intensive and among the most common triggers of abandoning a reservoir [260].

2.1.6 Hydrocarbon Reservoir Phase Behaviour

The nature of hydrocarbon fluids is quite complex. Their behaviour in the reservoir rock is very different from what they do in the facilities used for surface production. This is mostly caused by the drop in temperature and pressure that occurs as fluids travel from the reservoir to the surface through the well.

A phase envelope, sometimes referred to as a pressure-temperature diagram, is typically used to comprehend these complex systems. This diagram is depicted in figure 2.2. It makes an effort to portray the condition of a reservoir when the system's pressure decreases by looking at its production history. The numerous points from A to G depict various reservoirs at the time of their discovery or start of production [143].

The Bubble Point Level designates the point in the subsurface system when, as a result of a decrease in reservoir pressure, the very first gas bubbles begin to emerge from the oil. This is similar to the onset pressure of asphaltene precipitation in several aspects. The system's gas saturation rises while oil saturation falls once bubble-point pressure has been passed. [143].

For reasons that will be explained in more detail later, retrograde condensates cannot be used in gas mixtures.

The key point is when the bubble point line and the dew point line intersect. Because it is impossible to classify or categorise these fluids as simply 'oil' or 'gas', they are known as 'critical fluids' and reflect the zone where the two phases may coexist. Reservoir systems are classified as liquid (oil) or vapour (gas), depending on which side of the critical point they are located. Moving further to the left of the critical point causes the oil system to become less gas-saturated and more 'dead' [143].

However, when the system moves further to the right from the critical point, it starts to get increasingly 'gassy' until it is only dry gas. Figure 2.2 shows the state of the reservoir fluid at different pressures and temperatures. As the reservoir is drilled, the pressure and temperature of the reservoir drop [143].

Point A

It depicts a reservoir that was found to exist at pressures substantially greater than the bubble point's pressure. The system pressure remains higher than the bubble point even as production increases and decreases [143].

Point B

It depicts a reservoir that was initially found at a pressure higher than the bubble point, but after a period of extraction, the system pressure has dropped to less than the bubble point. Given the two-phase region in which this system is now operating, simultaneous petroleum and gas will be generated. The volume (saturation) of the petrol phase increases quickly as the system pressure decreases, which may have a negative impact on the oil phase's mobility [143].

Point C

Symbolises a reservoir that was found to have a pressure lower than the vapour pressure. A gas cap, or region of high gas concentration (saturation), may have formed within such a system as a result of the gaseous phase migrating higher as a result of gravitational partitioning. Except if the overall network pressure gradient is inverted (by the injection of water, gas, or another fluid), a system of this type will always be in the two-phase zone. Unsaturated oil is what results next. [143].

Point D

This point indicates a system that is located to the right of the critical point and in the single-phase area. Due to the fact that its pressure degradation route doesn't really break the dew point curve, any such system is a complete gas system and will stay as such throughout production [143].

Point E

Describes a system that, at first, was located to the right of the critical point but was originally in the two-phase zone. Wet petrol systems are what such a system is known as. The system may cross the dew point line as the system pressure decreases as a result of production. In such a case, the oil that has been vaporised into the gas will condense out. It is constantly desired to keep the system pressure high enough to prevent condensation because this is an undesirable circumstance [143].

Point F

Illustrates a system that was initially in the single-phase gas area but was just to the right of the critical point. Small amounts of liquid phase are therefore present, but they have evaporated within the system. Upon crossing the dew point line, as the system pressure drops and due to differences in relative permeability, the liquid phase can condense out and could cause system capillaries to get clogged [143].

It is often preferred to maintain the system pressure significantly higher than the dew point pressure in such a system, known as a condensate, in order to prevent the vapourised liquid phase from condensing out.

Point G

Constitutes, as was said above, what is referred to as a 'critical fluid.' At this time, the physical characteristics of the liquid and gas phases, such as viscosity and density, are comparable. [143].

Each one of the systems listed above, with the exception of dry gas, is prone to asphaltene precipitation issues if the prerequisites are met.

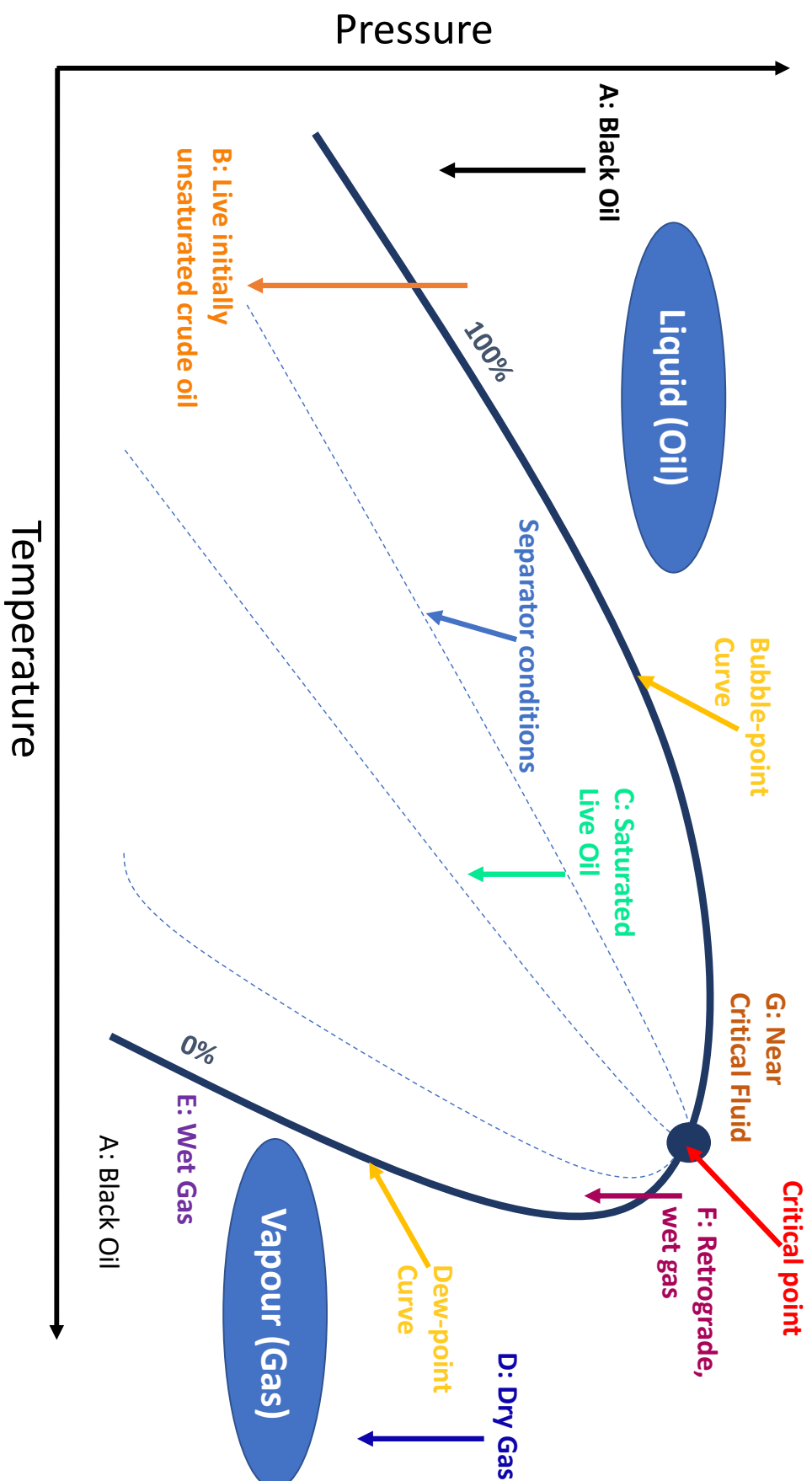


Figure 2.2: Chemogram of the Phase Envelope for Reservoir Fluids, points A-G are discussed in the text.

2.2 Chemistry of Crude Oil

The insufficient availability of whales triggered the very beginning of the modern crude oil industry we have today. Mankind has used artificial light sources throughout its development as a tool to reduce man's dependency on sunlight. Until 1859, oils obtained from animal fats were used as a light source by converting into beeswax candles or using whale oil. Whale oil produced the purest light compared to all previously available fuels, and therefore it became a luxury product. Thus, overhunting of whales to produce whale oil, which was the most profitable fuel source, led to a decline in the whale population, which in turn increased whale oil prices further. Surface-reaching oil was discovered around 4000 BC; this oil was used in the Middle East as an adhesive coating for road and building construction, along with waterproofing boats [89].

Crude oil was then used in China around 1000 BC and even refined at small scales for lamp and heating oil. It was only during World War I when Winston Churchill, then commander of the Royal Navy, decided to replace coal-powered vessels with more advanced and more rapidly responsive oil-powered military vessels. This action led to a dramatic increase in global demand for crude oil and turned this raw hydrocarbon resource into a strategically significant commodity that is known to all today.

Having noted the importance of crude oil in the current times for meeting the needs of humanity in terms of energy and feedstock production, it is worth noting that crude oil extraction is not indefinitely viable, and additionally, in the last 30 years or so, many issues with fossil fuel usage and production have been highlighted, which include the most noteworthy global warming and climate change. It is thus of paramount importance to keep in mind that although we still require fossil fuels, like with the whales, it is time to think beyond fossil fuels and into a green, sustainable future.

2.2.1 Crude Oil and Its products

Although originally oil was used as a source of heat and light, with mankind's development, so did the uses of this hydrocarbon. In 1903, oil powered the gasoline engine of the Wright Flyer, and in 1908, mass production of automobiles by Henry Ford created an even larger demand for middle distillate products (diesel, gas oil, and kerosene). With time, crude started to be refined into a more diverse portfolio of products, all serving a different purpose. By 1950, the

use of crude oil from lamp oil into transportation fuel was complete. Today, gasoline and diesel are frequently used to power cars and trucks, while residual fuel oil, more commonly known as bunker fuel, is used to power big vessels used to transport goods and fuels across the world's oceans. Jet fuel and kerosene are also used for fueling planes. Transportation products account for about two-thirds of crude oil consumption today.

The other third of products accounts for commodities such as bitumen, which is used as binder when mixed with small rocks and gravel to make road paving asphalt. This product facilitates the construction of large and inexpensive road networks used in today's age. Another major product worth noting is naphtha and LPG (liquefied petroleum gas). Naphtha is a product that can be used in blending pools of gasoline or as a feedstock for the petrochemical industry, while LPG is used as a heat source in countries with poor gas piping networks. LPG is also commonly used as a feedstock for petrochemicals.

2.2.2 Crude Oil's Assessment

Crude oil extracted from the reservoir is indeed a raw product that, in order to be used for different purposes, needs refining through a sophisticated refining process. Refineries are complex structures that facilitate the transformation of crude into finished products such as LPG, naphtha, gasoline, and other products.

The more sophisticated a refinery is, the less dependent its product production slate will be on the crude oil mixture that is being fed into it. The refineries complexity is measured through an index known as the Nelson Complexity Index [153, 220].

Crude oils have different colours, ranging from black, brown, or very light to almost colourless (condensate). Additionally, their viscosity varies significantly, as it can be water-like or honey-like. The more viscous a crude is, the heavier it is and hence more difficult to extract, refine, and transport. Depending on the reservoir a crude oil stems from, it can contain a variety of unwanted elements, such as sulphur, metals, sediments, water, and nitrogen. Sulphur is not desired as it has corrosive impacts, while the metal content of a crude oil can poison refinery units and catalysts [89, 161, 289].

There are several hundred known grades of crude oil produced currently, and all of them have certain specifications and characteristics, some of which are visible to the naked eye and

some of which need laboratory tests to be distinguished and identified. API, percentage sulphur, and distillation profile are among the most important commercial specifications of a crude oil, but in order to build these, one needs to understand the chemistry of the oil.

2.2.3 Crude Oil Chemistry

Crude oil is a highly complex and naturally occurring mixture of hydrocarbons that are fractionated into paraffin, cycloparaffinic (naphthelic), and aromatic groups. There is a small percentage of sulphur, as well as a trace of nitrogen and oxygen compounds. These fractions are comprised of two types of hydrocarbons:

Aliphatic Hydrocarbons

These are straight chain molecules with an open chain structure. This principle fraction can be divided into below classes:

- Alkanes: C_nH_{2n+2}
- Alkenes: C_nH_{2n}
- Alkynes: C_nH_{2n-2}
- Cyclic Aliphatics: C_nH_{2n}

Aromatic Hydrocarbons

The core of these hydrocarbons is formed based on benzene and its derivatives which consists of carbon rings fused together with high degree of delocalized electrons.

2.2.4 SARA Fractions

Typically, crude oil is composed of a percentage of dissolved gases (methane, predominantly), liquids, and solids. Due to the complex nature of the crude oil mixture, it is common for crude oil to be fractionated into four main components known as SARA (saturates, aromatics, resins,

and asphaltenes) fractions of crude oil [37, 276]. While previously a commonly employed method for characterising crude oil, it is important to acknowledge that recent scientific advancements and the capabilities of machine learning have made it possible to characterise crude oils at the molecular level.

Saturates

In saturated hydrocarbons, all carbon atoms are bonded to the maximum possible hydrogen atoms, and thus there is no carbon double bond present. Alkanes are indeed what are referred to as saturates; the most simple alkane is methane followed by ethane, propane, and butane [116]. This fraction exists predominantly in the liquid phase, with the exception of methane and butane molecules, which are in the dissolved gas state. Saturates play no significant role in stabilising asphaltenes, but they are a major fraction of crude oil [94].

Aromatics

More complex in structure than alkanes and the second main component of crude oils, which are more often than not nonpolar and have the characteristic of an unsaturated hydrocarbon ring with multiple carbon-carbon double bonds within the ring structure [155, 232, 233, 23]. Toluene, xylene, and phenol are the most common aromatic fraction [94].

Resins

Resins have a higher molecular weight than saturates and aromatics and have a more complex structure. Crude oil is an overall nonpolar liquid, which makes it insoluble in water [170]. Resins, though consist of an aromatic core with some aliphatic groups attached and also have polar groups attached [200].

Asphaltenes

Asphaltenes are the most complex structured fraction of crude oil, which exist as a solid phase and are suspended within crude oil. They are the most dense and largest molecules of crude oil [63]. Like resins, they are polar aromatic compounds and therefore surface-active. Saturates,

aromatics, and resins have a general structure by which they can be referred to and classified. But in the case of asphaltenes, due to structural complexity and the fact that there are many asphaltene structures, grouping this fraction into a specific structure family is very difficult [225]. Therefore, their solubility is used as the classifying factor for asphaltene molecules. Thus, asphaltenes are defined as the fraction of crude oil that is insoluble in alkanes such as n-pentane or, more commonly, n-heptane but soluble in aromatic solvents such as toluene [66]. In crude oil, the asphaltenes are frequently clustered together as asphaltene agglomerates, which also contain resins that stabilise the agglomerates against further aggregation [8].

2.3 Wettability and its alteration role in crude oil recovery

2.3.1 Definition and Impacting Factors

When oil in the reservoir is being extracted by water flooding, the wettability of the reservoir rock is a surface property that is of the utmost importance [51]. Wettability is the term used to characterise a solid phase's preference to be in contact with one fluid over another when exposed to the fluids [246, 30, 75].

The wettability of a porous rock reservoir is the tendency of the rock surface to come into contact with either the oil or the brine in the porous rock that it is exposed to. The rock's surface is referred to as "oil-wet" for preferential contact with oil; this is thought to be brought on by the adsorption of polar crude oil components, such as asphaltenes, on the normally water-wet mineral surface. Similarly, if the surface of the rock prefers to be in contact with water, the surface is said to be "water-wet." The fluid that covers the largest amount of rock surface and is most common within the pores will depend on whether the surface is inclined to hold water or oil [30]. Thus, in terms of oil recovery, it is desirable for the reservoir to be water-wet.

The fluid that covers the most rock surface and is predominant inside the pores will depend on whether the surface is inclined to attract water or oil [30]. The term 'intermediate wetting' or 'neutral wetting' refers to a rock's lack of a strong propensity to come into contact with either water or oil. As a key factor in determining the distribution and flow of fluid in a reservoir, the wettability of the rock-fluid system is crucial. Figure 2.3 shows an example of a porous material where oil and water coexist. The non-wetting fluid will be restricted to the centres of big pores or as agglomerates that stretch over many crevices, while the wetting fluid will cover the bulk

of the rock surface and occupy the smallest pores [30].

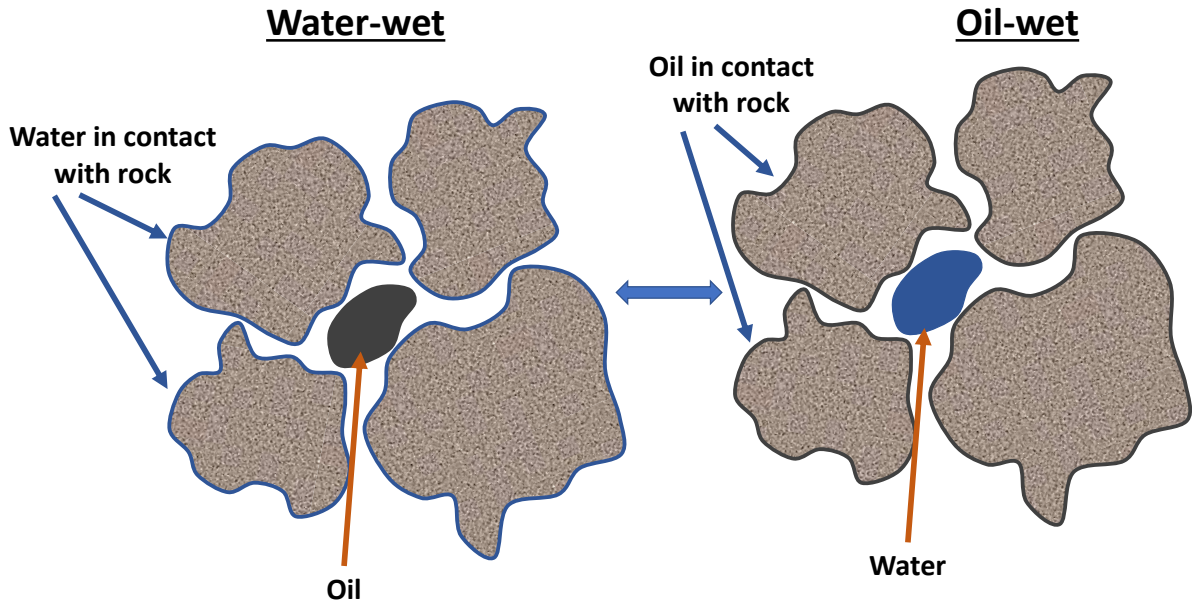


Figure 2.3: Schematic representation of oil- and water-filled porous media.

2.3.2 Rock chemistry and fluid constituents' effects on wettability

The individual system components (rock, crude, and brine) determine the strength of the various acting forces. The majority of minerals in reservoir rock were initially wet with water [30, 45, 129]. Only a few minerals, such as talc or graphite, are inherently hydrophobic [41, 264].

However, the adsorption of surface active substances known as asphaltenes can change a surface's wettability so that it becomes more oil-wet [57, 90, 98, 165].

2.3.3 Carbonate Reservoir's Wettability Structure

As introduced earlier, reservoirs are formed of two major components: the hydrocarbon fluids and the rock matrix itself. The reservoir rock mineral surface plays a key role in the volume of crude oil that can be recovered from a reservoir well [252, 148, 318]. More than 60% of the world's hydrocarbon reserves are stored in carbonate reservoir matrices [318, 296]. Literature studies show that the majority of carbonate rocks are categorised as oil-wet. [296, 71]. The typical oil recovery, however, is modest (around 40%) because of the unique properties of carbonate rocks. When the carboxylic acid found in crude oil is adsorbed on the positively charged calcite surface

found in carbonate rocks, an oil-wet state is created on the rock's surface. [253, 235, 160, 297].

2.4 Asphaltenes and Resins

2.4.1 Asphaltenes

Surface-active elements that can change surface wettability can be found in heavy crude oil fractions. Typically, they are polar chemicals that contain sulphate, oxygen, or nitrogen [30, 83]. As a result of these substances, the crude oils can be classified as basic or acidic [236].

However, it has been difficult to identify and correlate the precise contributions that these chemicals have made to wetting states due to their complexity. However, research that concentrated on the character of these compounds rather than their precise identification has revealed that asphaltenes and resins have a role in the preference for oil at the rock surface [88, 22].

Definition of Asphaltenes

Molecules naturally tend to exist in mixtures; crude oil is the most prominent mixture of all, with over 100,000 individual chemicals being present. However, crude oil is divided into four main fractions commonly known as SARA fractions of crude oil, which consist of saturates, aromatics, resins, and asphaltenes [37].

Of all these four fractions of crude oil, asphaltenes play a key role in organic deposition in both processing and recovering petroleum from the reservoir, [37] yet very little is known about this crucial fraction of crude oil. Asphaltenes are a large side group typically found in crude oil and coal.

Asphaltenes are not pure compounds but instead a complex mixture of thousands of different molecules, all of which have highly complex structures [267, 8, 177], therefore in order to define asphaltenes, one uses the method used to extract asphaltenes from crude oil in order to define this fraction of the crude oil [143].

Asphaltenes are said to be a fraction of the crude oil that is soluble in aromatic compounds such as toluene and insoluble in n-alkanes such as n-heptane (or other light alkanes such as n-pentane). They are also said to be the most heavy and polar components of the bitumen fraction of crude oil [143].

However, the most common way to describe asphaltenes is that they are highly condensed polyaromatic structures that contain heteroatoms (sulphur, oxygen, and nitrogen) [279, 27, 26, 28] and metals (such as vanadium and nickel), which exist in oil in suspension form often in an aggregated state [119]. The presence of sulphur, nitrogen, and oxygen in asphaltene molecules means that these molecules have a certain degree of polarity, thus making them a surface-active component of crude oil.

Drawn from the classical colloidal model, resins and other aromatic molecules hold the stack of asphaltenes (aggregates, agglomerates) in dispersion in crude oil; this gives rise to the colloidal state of asphaltenes [288, 176, 205, 303] shown in figure 2.4. However, it is worth noting that in this thesis and within the scientific community, the classic colloidal model is now succeeded by the Yen-Mullins model. [101].

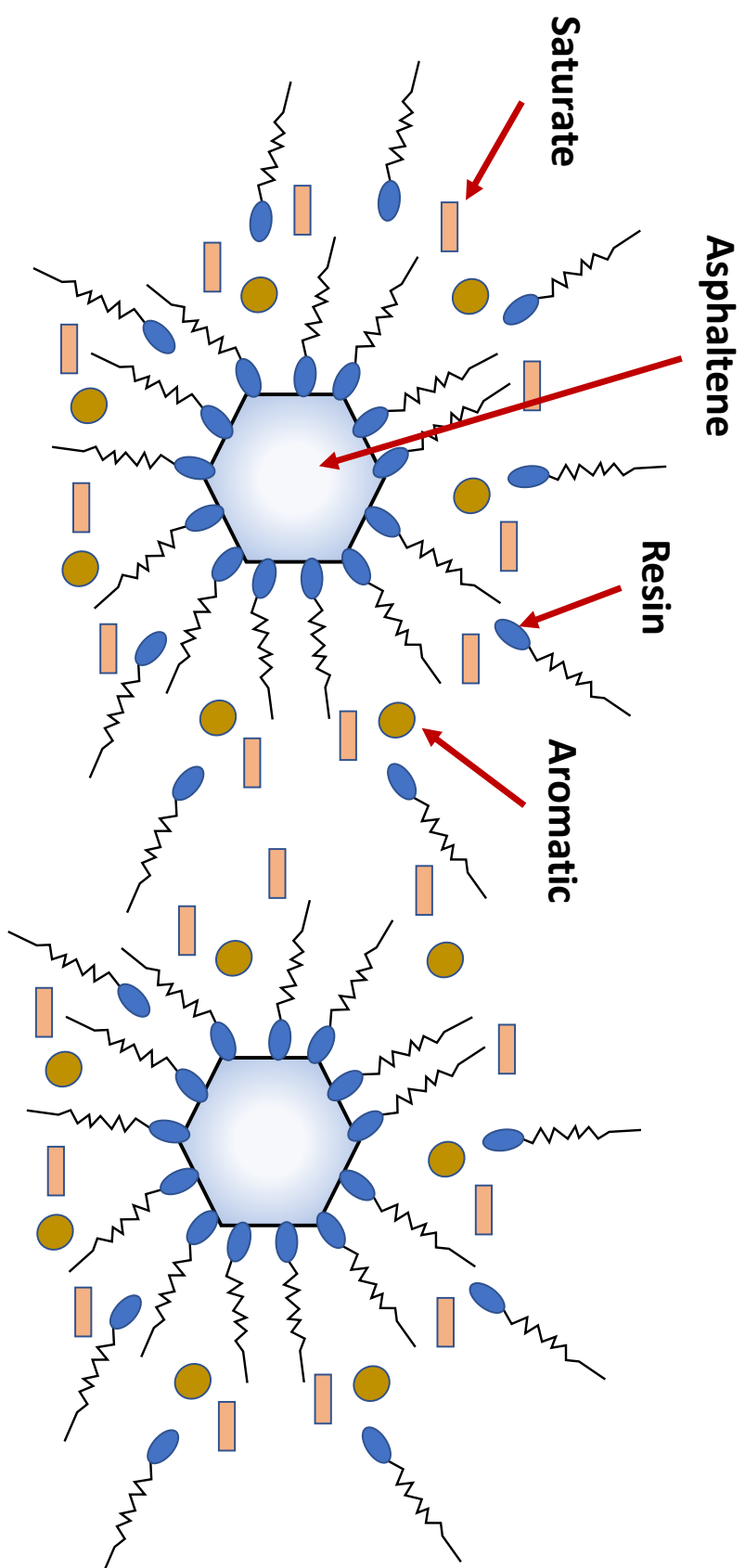


Figure 2.4: Representations of asphaltene molecules stacked and stabilised by resins and aromatics in crude oil. Illustration of force balances in stabilising the asphaltenes in solution [37, 230].

2.4.2 Characteristics

Structure

Asphaltene molecules have a very complex structure, and determining the asphaltene structure itself is an active research area. However, with recent technological advancements and improvements in atomic force microscopes, the atomic structure of individual asphaltene molecules in real space was visualised for the first time [265], which can be seen in figure 2.5. In figure 2.5, bright straight lines correspond to carbon-carbon bonds; these images were taken in liquid helium to prevent bond vibrations at very low temperatures.

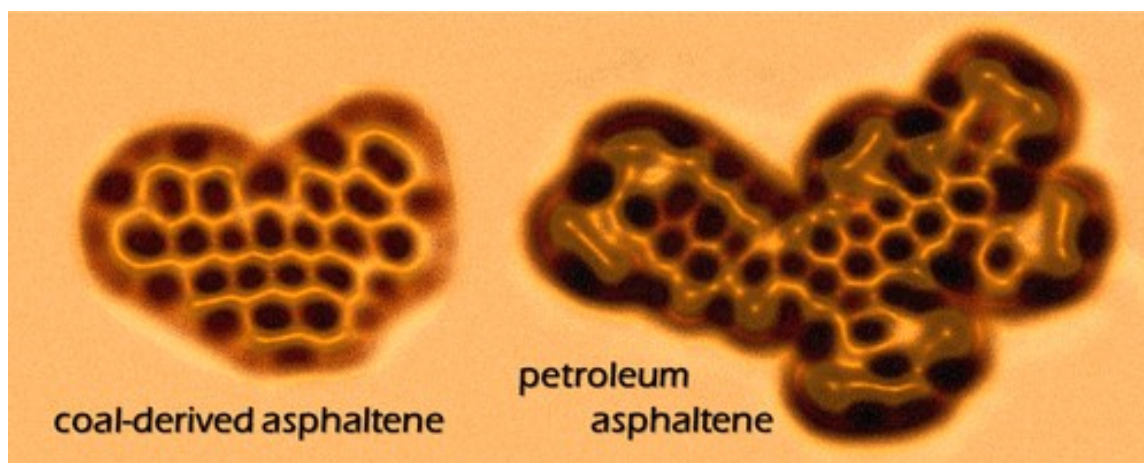


Figure 2.5: Asphaltene structure derived from AFM imaging. [265]

Asphaltenes are made of many distinct chemical species with unknown compositions [212]. Recent studies combining AFM and scanning tunnelling microscopy (STM) shed light on the atomic structure of asphaltenes [265]. Asphaltene molecules are made of an aromatic core in the centre with tangential alkane chains. The central core of asphaltenes can sometimes itself be divided into separate polycyclic aromatic hydrocarbons (PAH), which are connected through a single bond, proving the presence of archipelago-type molecules. Although asphaltenes with several PAHs core have been observed, the most dominant asphaltene molecular architecture is said to have a single aromatic core [265].

In addition to the fact that no two asphaltene molecules are identical, the molecular structure of asphaltene also depends on the origin of the sample. Petroleum-derived asphaltenes (PAs) show a presence of a long chain side group, which is not observed in coal-derived asphaltenes (CAs). This long chain side group leads to PA molecules having a greater extent of three-dimensional character compared to CA molecules [265]. However, nowadays the most widely

accepted asphaltene model is the Yen-Mullins model (this model is presented in figure 2.6). This model characterises the asphaltene structure of a crude oil as a function of the size and behaviour of the crude oil itself [213].

Precipitation

Asphaltene precipitation is the process by which asphaltene molecules go through a phase change from solution to solid and form a separate phase in oil, where they remain as a suspension. Asphaltene precipitation is a result of changes in temperature and pressure in the reservoir, a phenomenon that occurs near the well bore, where the pressure drops. It is also found that asphaltenes differing in character will have different asphaltene precipitation onset pressures [151].

Additionally, crude oils that contain large amounts of saturates are more susceptible to pressure-induced asphaltene precipitation [151, 37]. Field asphaltene precipitation can be largely reversed in a matter of minutes through applying pressure [151]. Also, solvent treatments can be employed for reversing pressure-induced asphaltene precipitations; however, this is subject to adequate turbulence to break up asphaltene particles[228].

Flocculation

One of the key characteristics of asphaltenes, which results in the plugging of pipes and wells over time, is that they flocculate as a result of changes in pressure and temperature [292]. Asphaltene flocculation is the process by which precipitated asphaltene particles come together to form larger agglomerates called flocs [143]. This process is sometimes referred to as aggregation or agglomeration. Flocs formed as a result of this process will coexist in the liquid oil as a separate phase (like an emulsion) [143]. These flocs may then cause plugging of the pores in the reservoir.

Adsorption

Adsorption of asphaltene molecules refers to the process by which precipitated asphaltene particles adhere to the surface of the reservoir rock's porous structure; it begins at the production well and propagates throughout the production chain [8]. Multiple factors are said to have an influential impact on the adsorption of asphaltenes, such as the electrokinetic charge of the asphaltenes, streaming potential, etc [176]. The adsorption of asphaltene molecules prior to

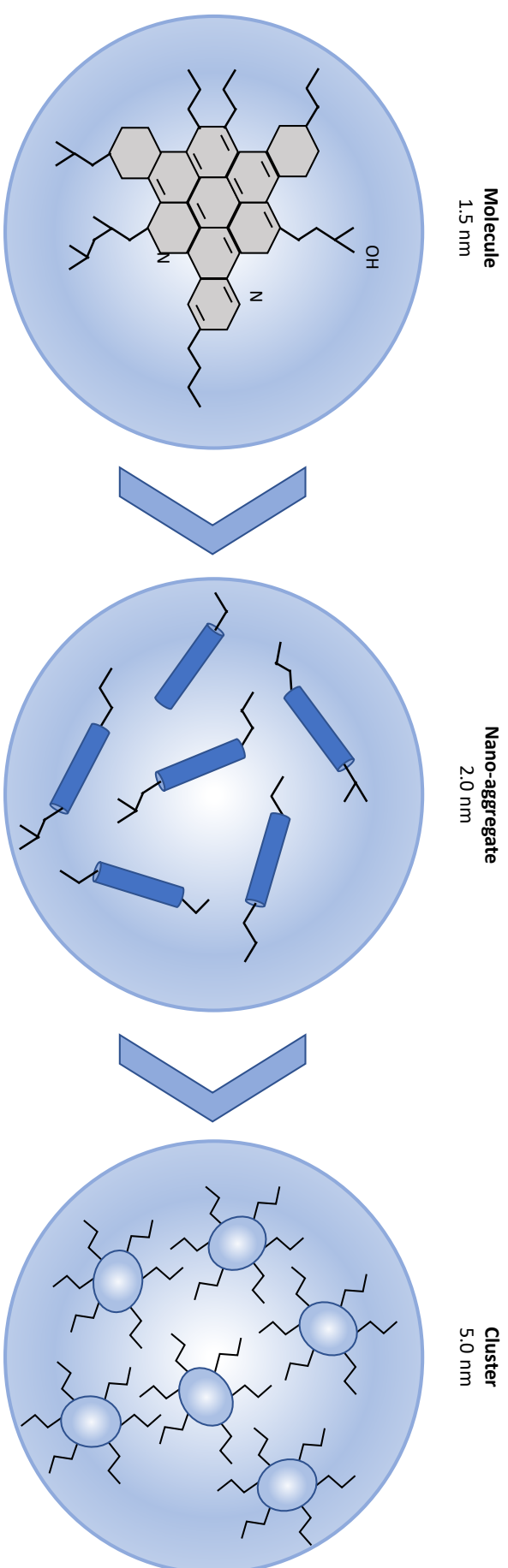


Figure 2.6: Yen–Mullins asphaltene showing from left to right the following: Light Oil with low asphaltene concentration (Isolated Molecules), Black Oil with moderate asphaltene concentration (Nanoaggregates) and Heavy Oil with high asphaltene concentration (Aggregated Clusters). [94, 213]

precipitation has also been observed [18]; this is called direct adsorption. However, whether the precipitated asphaltene deposits or not depends on the charge of both aggregates and the surface in which aggregates are in contact. This is due to the fact that dissimilar charges between the fluid and the contacting surface result in attractive forces, and like charges result in repulsive interactions between the fluid and the contacting surface [143].

Rock Pores Blockage by Asphaltenes

Reservoir rock is considered to be a porous media and therefore deposited asphaltenes may lead to plugging of the rock pores in the event where size of the asphaltene agglomerates become larger than the hydraulic radius of the rock pore [8, 143].

Entrainment

One scenario that may occur with deposited asphaltenes is pore plugging, which happens when the size of aggregates exceeds the average hydraulic diameter of the rock. However, this effect may be offset and counteracted if the local fluid velocity is high enough to force aggregates through the pores or have a shearing effect on the aggregates (break them up) [143]. Through the breaking up of aggregates into smaller flocs, part of the asphaltenes that previously were plugging the pores will be entrained via the flowing medium [143]. A schematic of all events mentioned is presented in figure 2.7. It is worth noting that micro-fluidics experimental data combined with multi-scale simulation allowed for the investigation of asphaltene deposition in a glass capillary. The results of such experiments were then compared with stochastic rotation dynamics (SRD) computer simulations. The dimensionless conductivity of the capillary was determined by directly comparing the results of the experiment and simulation. The colloidal asphaltene particles' interaction potential well depth was determined by comparing it to the capillary flow experiment, thereby establishing its effective value. [53].

2.4.3 Cholesterol of Oil Industry

In today's oil industry, asphaltenes have gained a reputation as a key cause of significant losses in profitability within the industry. The main issue with asphaltenes is their undesirable phase transition from crude oil solution to solid particles, which precipitate and deposit, hence hin-

dering the production and processing of crude oil [37, 265]. Precipitated asphaltenes can adhere to any equipment or pipe they come in contact with; this includes most of the components in the oil production facility, such as well bores [204], pipe lines [208], transport and pumps [265], storage units [175] and even refining equipment such as heat exchangers [191].

Asphaltene deposition is not limited to the wellbore region and processing; it also occurs in the reservoir rock matrix itself [37]. It is well known that the interactions between the surface active components of crude oil (asphaltenes and resins) and reservoir rock surfaces lead to wettability alteration of the reservoir rock, and it has been stated that once asphaltenes and resins adsorb on the surface of the reservoir rock matrix, they will alter the wettability of that surface in favour of the oil phase permanently [42, 43]. This change in wettability due to asphaltene deposition is not well understood and therefore offers a focal point for enhanced oil recovery techniques and further research. Therefore, all the issues that have been stated so far have given asphaltenes their reputation and their nickname as the 'cholesterol of the oil industry' as they can have unwanted impacts on all the stages of oil production and the reservoir itself.

2.4.4 Chemistry of asphaltenes

2.4.5 Asphaltenes' fundamental chemistry and structure

The very intricate structure of asphaltenes is still a topic of current investigation. Due to their complexity, it has been exceedingly challenging to determine their molecular weight range and exactly what phase they are in when they are present in crude oils [286, 14, 231]. Yet, it is known that numerous distinct chemical species, whose constituents are not fully understood, are present in asphaltenes [212].

Numerous earlier investigations have shown that there is internal interaction between asphaltenes in addition to between the asphaltenes and the other elements of the crude oil in ways that are still not known exactly, which contributes to the complexity of these structural relationships. It is thus not unexpected that several models have been put out in an effort to determine the real condition of asphaltenes in crude oil, given these complications. It is worth noting that molecular dynamics (MD) simulations provide the capability to forecast the molecular-level behaviour of asphaltenes. It is crucial to utilise asphaltene molecule architectures in these simulations that accurately reflect experimental results. A novel quantitative molecular representation (QMR) technique has been developed, enabling the simulation of asphaltene

molecular structures that align with existing experimental data, including mass spectrometry, nuclear magnetic resonance (NMR), and elemental analysis [131].

Self-Association of Asphaltenes

Although the 'Colloidal Model' was first comprehensively detailed by Pfeiffer and Saal (1940) [230], Nellensteyn effectively laid the groundwork for it in 1923. However, Pfeiffer and Saal succeeded in adequately developing the preceding Nellensteyn (1923) [219] framework into a more convincing and clear argument. Dickie and Yen (1967) [85] advanced a further modification of the colloidal model in which they hypothesised that asphaltenes were composed of layered aromatic sheets onto which resins were adsorbed. They came to the conclusion that steric repulsion between resins is what causes asphaltenes to disperse in crude oil. The most important and note-worthy Asphaltene self-association models have been collected and presented in figure 2.8, which has been adopted from Hassanzadeh and Abdouss (2023) [128]. The reader is referred to this excellent review paper should further information be required on these models.

2.4.6 Resins, asphaltenes stabiliser

The molecules known as resins are what keep the asphaltene agglomerates (also known as aggregates). The polar heads of the resins encircle the asphaltene agglomerates, while their aliphatic tails extend into the oil medium. It is possible to oxidise the resins to produce asphaltenes [124]. Their properties include being lighter fractions (than asphaltenes), insoluble in ethylacetate at ambient temperature, but soluble in regular heptane [277]. They are black in colour, display a semi-solid character, and have an adhesive quality. Resins fundamentally resemble asphaltenes; however, they have a reduced molecular weight. Resins are also classified as a solubility subclass, with constituent counts in the tens of thousands, varying types and shapes, but all sharing the same solubility and adsorption characteristics. Resins get their characteristics from solvent extraction. The resin portion has more of the asphaltenic compounds with higher molar masses when heavier n-alkanes, like n-heptane, are used, but the resin fraction contains less of these compounds when lighter n-alkanes, like n-pentane, are used. Petroleum fluids with a high resin concentration are typically thought to be more stable (i.e., less likely to precipitate asphaltenes), while those with a low resin content are thought to be less stable. In order to identify whether a fluid is stable or not, Stankiewicz et al. (2002) [290], as shown in figure 2.9 devised a technique based on SARA analysis that cross-plots two ratios (Saturate/Aromatic vs. Asphaltene/Resin).

According to this, the bulk of experimental and field research supports the hypothesis that greater resin concentrations provide more stability and lower resin concentrations result in less stability; however, there have also been recorded outliers [201, 202].

Several asphaltene stability prediction models are defined below as per the literature, but the main one used for the purpose of this PhD project is the Colloidal Instability Index model. It is also worth noting that Shell Digital Rock used the same model for assessment of the crude oil's stability and then compared it to the empirical Stankiewicz graph.

Colloidal instability index (CII)

The crude oil system is regarded by the Colloidal Instability Index (CII) as a colloidal solution made up of several fictitious components. It can be mathematically described as the ratio of the sum of the contents of saturates and asphaltenes to the sum of the contents of resins and aromatics [20, 21, 123, 37, 205]. You can determine CII by using the below equation:

$$CII = \frac{Saturates(wt\%) + Asphaltenes(wt\%)}{Resins(wt\%) + Aromatics(wt\%)} \quad (2.5)$$

Stability Index (SI)

Other relevant models include the stability index (SI) model, which is a well-known parameter for defining asphaltene stability in a crude oil solution. This index is simply defined as a ratio of asphaltenes to resins (A/R). If the derived SI value is less than 0.35, then crude oil is considered to be stable; otherwise, it is considered to be unstable [251, 205, 123].

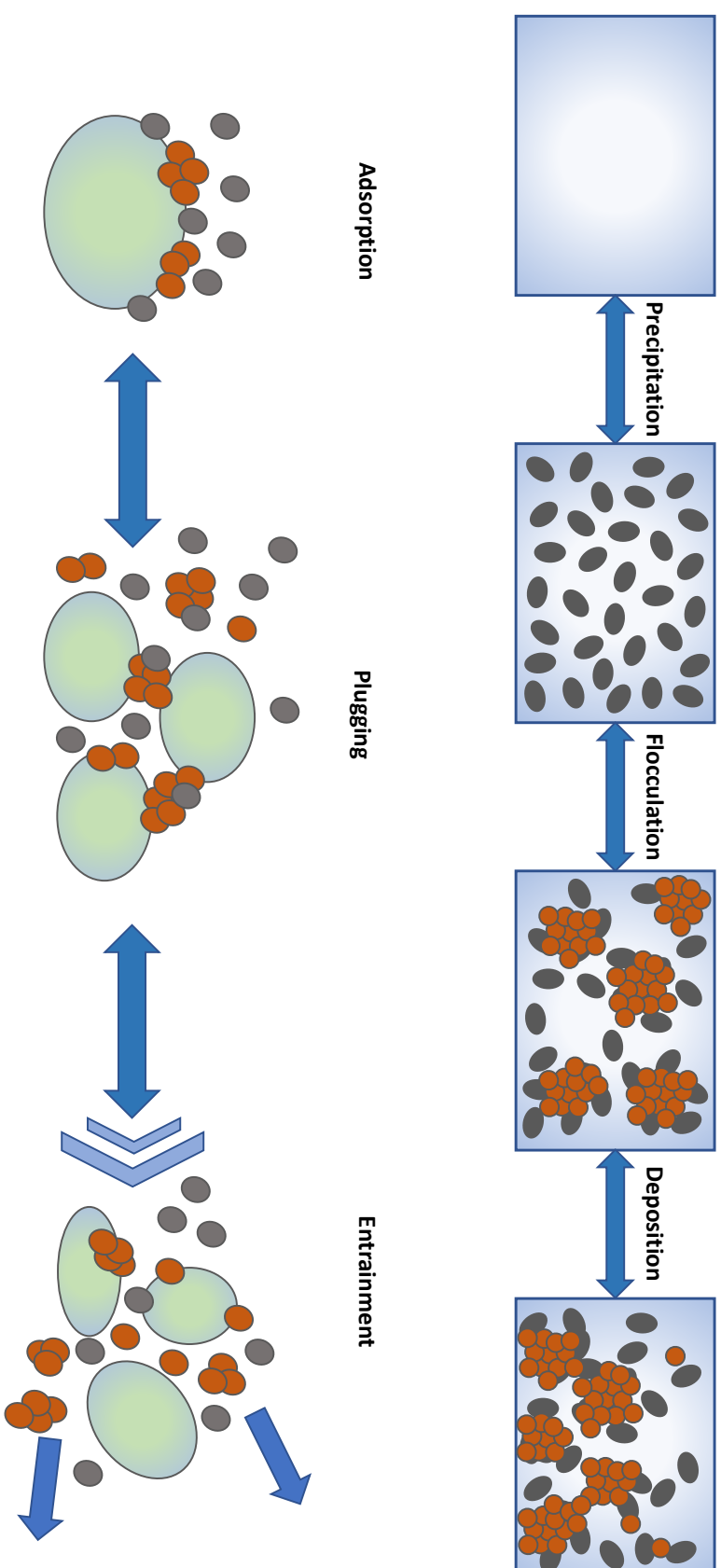


Figure 2.7: Schematics of various states asphaltenes can exist in crude oil, Adopted from [143].

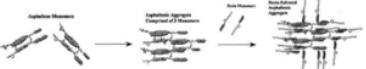
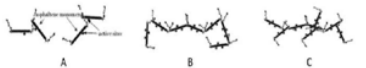
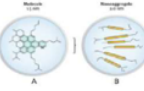
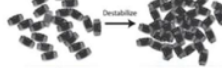
No	Model Names	Schematic Image	Description
1	Colloidal-micelle		A) Asphaltene micellization in polar aromatic solvents. B) Asphaltene aggregation from micelles.
2	Steric-colloidal		Colloidal aggregation of the archipelago model of asphaltene in the attendance of resins.
3	Polymeric		A) High temperatures, suitable solvent B) Low temperatures, poor solvents (linear aggregation) C) Low temperatures, poor solvents (random, branched aggregation)
4	Yen		Straight lines represent asphaltene aromatic groups, and zigzag lines represent alkanes with: A. Crystallite, B. Chain bundle, C. Particle, D. Micelle, E. Weak link, F. Gap and hole, G. Intracuster, H. Intracuster, I. Resin, J. Single layer, K. Petroporphyrin, L. Metal.
5	Yen-Mullins		A. Molecule B. At low concentrations, asphaltene molecules form nanoaggregates in the form of a disordered stack of aromatics (<10 numbers). C. At higher concentrations, nanoaggregates accumulate to form nanoclusters (<10 numbers).
6	Gray		Asphaltene supramolecular contains all the parts and interactions desired in the Gray and other models. Colors represent these interactions: blue = acid/base and hydrogen bonding; red = metal co-ordination complex; orange = a hydrophobic part; green = π - π stacking.
7	Fractal		A. Soluble/stable asphaltenes B. Insoluble/unstable asphaltenes

Figure 2.8: List of self-association models of asphaltene.. [128]

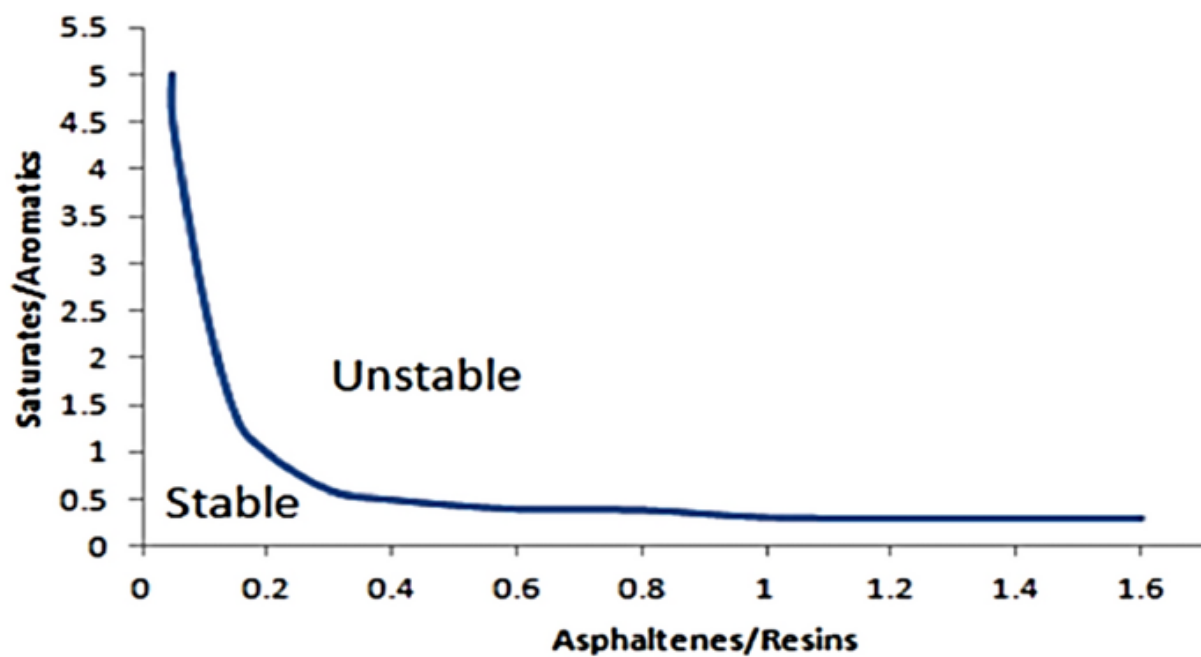


Figure 2.9: Stankiewicz plot which is obtained from many experimental data on various crudes obtained from [229]

Colloidal Stability Index (CSI)

This model builds on CII but with a new parameter introduced, this model is formed on the foundation that asphaltene content of an unstable crude oil is likely to be more polar than that of a stable crude oil [123, 251, 205]. CSI can be calculated through equation presented below:

$$CSI = \frac{\epsilon^{sat} \text{Saturates}(wt\%) + \epsilon^{asph} \text{Asphaltenes}(wt\%)}{\epsilon^{res} \text{Resins}(wt\%) + \epsilon^{arom} \text{Aromatics}(wt\%)} \quad (2.6)$$

ϵ represent dielectric constant and for various component of SARA components of crude oil it takes a fixed value tabulated below pending whether the oil is stable or not [21]. The values dielectric constant (ϵ) takes is tabulated in table 2.1.

Table 2.1: Dielectric constant values for stable and unstable crude oils [118, 21, 20].

Sara fraction	Stable crude (ϵ)	Unstable crude (ϵ)
Saturates	1.921	1.921
Asphaltenes	5.5	18.4
Resins	4.7	3.8
Aromatics	2.379	2.379

Chapter 3

Methodology

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3.1 Atomic Force Microscope (AFM)

AFM is a high-resolution analytical technique that changed the scientific world when it was first introduced in the 1980s. It enabled the imaging of surfaces at an atomic scale in liquids [156] (Bruker, 2017) [134]. AFM was invented in 1986 by Binnig, Quate, and Gerber, and it produces images of surface topography at the nanoscale. AFM is a type of scanning probe microscopy (SPM), and it is best known for its ability to produce topographical maps of the sample at the atomic level [134]. The first type of SPM was scanning tunnelling microscopy (STM), which employed quantum effects inducing an electrical current that flows between the tip and surface of the sample [108].

STM was invented by Binnig and Rohrer, and it was the first microscopy technique that allowed researchers to produce images at the atomic and molecular scale. However, STM had a disadvantage that opened the pathway for the invention of AFM, and that was the fact that it relied on measuring a tunnelling current for producing images, which therefore limited the range of samples that one could analyse with this equipment to those that could conduct electricity. AFM uses changes in force between the tip of the cantilever and the surface to produce images rather than measuring the changes in the tunnelling current as the tip is scanned over the surface of the sample. This gave AFM the upper hand in comparison to other SPM techniques, which allow imaging in liquids where surfaces may exist naturally, such as minerals in crude oil reservoirs [261].

In summary, the AFM was created in 1986 as a technique for visualising surface topography and measuring forces at the atomic scale [48]. Because surface forces are measured directly rather than abstracted into contact angles, it is a practical way to investigate wettability. Additionally, it is quite helpful for revealing details about a sample's mechanical characteristics and force interactions at the nanometer scale. In order to measure forces at a sample surface as it scans over it, the apparatus uses a sharp tip at the end of a flexible cantilever that, in effect, functions as a spring for a known force constant. The tip is manipulated using a piezoelectric scanner on the X, Y, and Z axes. A laser beam is reflected off the cantilever's back onto a position-sensitive quadrant photodiode, as shown in figure 3.1, and this allows researchers to determine whether the cantilever is bending towards or away from the sample as a consequence of intermolecular

interactions of attraction or repulsion. With cantilever deflection, the angle of the laser beam reflected varies, and its location on the photodiode is used to determine the deflection signal. A control computer's feedback loop receives this signal.

High-resolution topographical pictures may be obtained with the AFM, which can also provide details on a sample's mechanical characteristics, such as its stiffness and elasticity. The JPK Instruments Nanowizard 4 nanoscience AFM [134], depicted in figure 3.2, was used for all measurements in this work. This AFM has a new quantitative imaging (QI) mode that enhances imaging capabilities while also being simple to use; this mode is covered in more detail in Section 3.1.3. An optical camera is installed on the device to help with orientation during measurements. Since it is a very sensitive piece of equipment, it is enclosed with acoustical foam on the inside to lessen vibrations that are carried through the air.

3.1.1 principle of AFM Methodology

Before the invention of AFM, the interactions between surfaces were measured using the mica surface forces apparatus (SFA) [190]. The interactions are measured between two mica surfaces; the technique, however, is only applicable to transparent, atomically smooth surfaces. Like AFM, SFA relies on the bending of a cantilever spring to produce a force profile of the experimental subject but is limited to only investigating interactions between mica substrates. The range of force interactions that can be measured via SFA is similar to that of AFM.

At the core of this imaging technique is a plate spring known as the cantilever. The cantilever is mounted onto a silicon-made chip at one end, and at the other end, it holds a pyramidal or cone-shaped tip, which is used to measure forces between the tip and the sample. The chip holding the cantilever is mounted to a cantilever holder placed in a piezoelectric scanner, which moves the probe in x, y, and z directions, allowing surface scanning. When the sample and tip come into contact with one another, the cantilever bends or deflects depending on the type of interactions between the tip and the sample, whether they are repulsive or attractive. So, in simple terms, the idea behind the AFM is that the local forces between the tip and sample are either repulsive or attractive, and that is converted to the bending of the cantilever. These deflections towards or away from the surface are measured using a laser beam that reflects from the back of the cantilever, and its position is monitored by the position-sensitive photodiode.

This allows one to be able to detect the deflections of the cantilever as it approaches the

surface of the sample at different points. In order to turn these laser reflections into an electrical signal, a photo detector is used, which usually has four quadrants: A, B, C, and D, which are represented in figure 3.1. There are four quadrants so that the laser spot position can be calculated in both vertical and horizontal directions. With the cantilever deflecting, the angle at which the laser beam is reflected on the photo detector changes and lies in a different spot among the four quadrants. The signals from the four quadrants are compared, and an electrical signal is produced. This happens at each point (pixel) where the tip and the cantilever are brought into contact, and from the electrical signals, an image of the entire sample is produced to give insight about the height of the sample in different regions. Using the QI mode, in addition, the adhesion and stiffness (related to the elastic modulus) at each point (pixel) are also monitored.

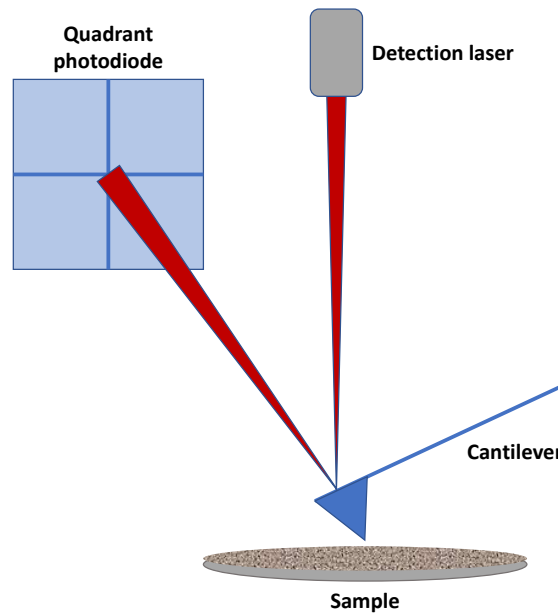


Figure 3.1: Force curve obtained by cantilever interactions with sample's surface at different stages upon approach and retract from the surface.

3.1.2 AFM setup

Selection of Appropriate Probe

Since the force distance profile used to produce an image from the sample depends on the deflection of the cantilever, which in turn affects the reflection of the laser beam on the photodetector, choosing the appropriate cantilever with the correct spring constant can significantly affect the results obtained and the quality of the image. From figure 3.3, we see that the force needed to

deflect the cantilever is linearly proportional to the cantilever deflection through a spring constant k . This linear relationship is described by Hooke's law. Shape and size of the cantilever are among the factors that affect the value of k . As the cantilever gets shorter and thickens in size, the spring constant k increases in value, and the resonant frequency increases. Typically, the spring constant can range from 0.1 nN/nm to 100 nN/nm. An AFM probe has a sharp tip, which has a few important features. One of these features is the tip height, which is in the range of 2.5-15 μm and the other feature of the tip of importance is the radius of curvature, which is in the range of 2-20 nm [320]. The cantilever is usually supported by a chip, which allows the operator to handle the cantilever with tweezers. One needs to always bear in mind that the probes are extremely fragile; therefore, one should be very careful handling the probes to avoid any damage.

Assembling

In order to start the AFM, the probe needs to be mounted onto a cantilever holder. The cantilever holder facilitates the laser beam passing through it as it is made of transparent glass and therefore allows the laser beam to shine on the back of the cantilever for imaging. The loaded cantilever holder is then mounted onto the AFM head and positioned above the sample. One can then turn the laser on and adjust the mirror to adjust the laser beam location on the cantilever until the maximum sum signal is obtained from the position-sensitive photodiode. This maximum signal sum refers to the sum of the signals from all four quadrants of the photodiode. The laser is then generally centred at the intersection point of the four segments of the photodiode, which essentially zeros the signal.

3.1.3 imaging using AFM

Approaching the sample surface

The cantilever can now be calibrated for sensitivity and spring constant by determining the resonance frequency of the cantilever. Once the probe is calibrated, one can now start approaching the surface. Initially, the AFM head can be lowered manually to be brought reasonably close to the surface, but this needs to be done with experience as the probe can crash into the sample if brought too close. Once close enough to the surface, the AFM head can automatically approach

the surface by using the piezoelectric z-drive. Alternatively, one can allow the equipment to approach the surface from the beginning, although it will take longer than approaching manually. If the height of the sample is unknown or the operator is inexperienced, the automatic mode of approach is strongly recommended to prevent damage to the sample and probe. The next step is to choose the appropriate imaging mode that is most suited to both the sample at hand and the results that need to be obtained.

Modes of imaging

The JPK instrument provides four alternative imaging modes each with their own advantages and unique strengths.

1. Contact mode: As the name suggests, in this mode, the cantilever tip is in direct physical contact with the surface of the sample, and the vertical deflections of the cantilever as a result of surface roughness are used to produce an image. This mode is most suited to samples that have a hard and flat surface; otherwise, the tip of the cantilever may remove adsorbed materials and damage the surface of the sample. However, the advantage of using contact mode is that the scanning time is much faster than other modes.
2. Dynamic Mode: This is an alternative imaging technique whereby the cantilever oscillates (vibrates) above individual points on the surface of the sample. The main difference between dynamic mode and contact mode is the measurements used to obtain the image. In contact mode, static deflections of the cantilever are used to produce an image, whereas in dynamic mode, the oscillations of the cantilever are measured and used to induce images. This is composed of two main types, as described below:
 - (a) Tapping Mode (Intermittent Contact Mode): In this mode, the cantilever oscillates close to resonance (constant amplitude) and comes into contact with the surface of the sample intermittently at the lowest point of its oscillation, lightly tapping on the surface of the sample, hence the name tapping mode. This mode is more suitable for soft samples where contact mode is not ideal.
 - (b) QI Mode: This imaging mode was based on the same principles of force spectroscopy. This is the most recently developed imaging technique which has a few advantages compared to its predecessors. This technique produces a complete force distance curve at each pixel of the image and besides height measurements it reveals other

quantitative data such as adhesion and mechanical properties of the sample such as stiffness through the measured slope of the force distance curve. In this technique the tip of the cantilever approaches the surface of the sample and is indented into the surface with a pre-set force (set point) depending on the nature of the sample, once indented the cantilever retracts to a pre-set vertical position called z-length at a pre-set speed called pixel time. There will be no lateral forces between the tip and the surface of the sample as the cantilever retracts making this imaging mode suitable for very soft and sticky samples or samples on which the adsorbed material is loosely attached to (such as asphaltenes). QI mode is the most suitable imaging mode for very sticky samples such as polymers or crude oil and its derivatives (asphaltenes) (JPK Instruments AG, 2018) [9] and this was the dominant mode used in this work.

Figure 3.3 illustrates many important features when analysing images. When a surface is treated with crude oil, the nature of these force distance curves will change as long as the substance introduced to the surface is adsorbed onto the surface. Additionally, these force distance curves can indicate whether or not the cantilever tip picks up crude oil substances from the surface. This happens when the adhesion area becomes round bottom-shaped; therefore, instead of getting a snap-off at point D, we get a more gradual release.

3.1.4 Force Spectroscopy

Although AFM is mostly known for its high-resolution imaging techniques at the nanoscale, one can use it to conduct force spectroscopy experiments. This is particularly useful to learn about interactions between a specific material and a specific surface. In this mode, a grid is laid on a specific part of the sample, and a complete force distance curve is produced as the probe approaches (extended) the surface and subsequently is retracted from the surface. The force curve at each point on the grid reveals information about the interactions between the tip and surface of the sample at different separation distances between the two counterparts. Essentially, this mode is similar to the QI mode, but the force distance curve is obtained more slowly, so higher-quality curves are obtained. However, the experiment is much slower, so whereas in QI mode, a 256x256 image is obtained in 8 minutes, a similar-sized force spectroscopy image would take nearly 24 hours, so a lower-resolution image, say 32x32, is obtained. This mode is used to get quantitative information about the statistics of the force profiles rather than for imaging.

As illustrated in figure 3.3, upon the extension of the tip towards the surface of the sample, the force is said to be zero because there are no interactions between the tip and sample and hence no deflection of the cantilever. However, in cases where long-range forces interact with the tip, the cantilever can deflect towards or away from the surface depending on the nature of the force interaction. As the tip gets closer to the surface of the sample, short-range forces such as DLVO (in aqueous) and van der Waals start to dominate and bend the spring; this continues until the contact point is reached. Once the tip is in contact with the surface, it pushes against the surface of the sample, resulting in a repulsive force that increases proportionally with the distance travelled by the probe as the cantilever deflects upwards. This region is said to be the contact region. The tip is pushed against the sample until a pre-set force, known as the set point, is reached. Once the set point is reached, the probe starts to retract from the sample, and although the probe is moving away from the surface, the tip remains in contact with the surface due to adhesion forces, which keep the cantilever deflected towards the surface, as illustrated in figure 3.3. The probe is fully retracted to its original position once the adhesion force is fully overcome and the tip is separated from the sample.

The specimen is approached by the AFM tip, which is depressed until a specific force is reached, fully retracted, and then the process repeats until the next pixel is reached, allowing the measurement of mechanical sample parameters like stiffness and elasticity. The cantilever does not deflect at greater tip-sample separation because there are no detectable tip-sample interactions. As this separation becomes closer, other intermolecular forces start to work; short-range attractive forces like capillary forces or van der Waals will induce a leap to contact as the cantilever's spring constant is surpassed.

When the cantilever makes repulsive contact with the sample, it is deflected upward until the predetermined force, also known as the setpoint, is attained. When the tip is removed from the surface, adhesive forces between the tip and the surface keep the tip in place due to their similar hydrophilicity, causing the cantilever to deflect downward until a snap-off occurs upon further increase in separation, at which point the cantilever returns to its initial undisturbed position.

By using Hooke's equation (see eq. 3.1) to translate the detector signal into a force value and adjusting the piezo displacement for the cantilever's bending, it is possible to get an actual force vs. distance curve from figure 3.1. By measuring the force curve from the tip's contact with a reference, spotless, incompressible surface, such as a glass slide, it is possible to calibrate

the tip and acquire these values.

$$F = -k x, \tag{3.1}$$

Where F is the force acting on the cantilever, k is the cantilever spring constant, and x is the cantilever vertical displacement.

The slope of the repulsive part of the force curve, which yields a number in nm/V, reflects the bending of the cantilever when the tip is in contact with the surface. This quantity, known as the sensitivity, is used to multiply the detector signal in volts and convert it to nm. To get the actual vertical tip position, subtract the cantilever's deflection in units of length from the piezo height.

The Thermal Tune technique is used to calibrate the cantilever's spring constant [142, 76]. The JPK AFM software graphs the thermal fluctuations of the cantilever versus frequency to provide a thermal noise spectrum. The cantilever's resonance frequency will be represented by the plot's maximum amplitude, which depends on the spring constant. As a result, the spring constant is determined by fitting the thermal noise plot with a Lorentz function [9]. By utilising these calibrated numbers to adjust the force curve, a force-distance curve can be created using Hooke's law.

3.1.5 Force Mapping

Another way to extract information about the interactions between the tip and the sample is to conduct a force mapping image. This mode is very similar to the adhesion map produced by the QI imaging technique; however, the main difference between the two lies in the algorithm of the tip motion and the sample rate, which both allow a higher scan velocity in QI mode. However, for more representative force data, a force mapping image is more recommended. The advantage of this technique over force spectroscopy is that it is much quicker to analyse the data obtained and can quickly compare and contrast results. In force spectroscopy, many force distance curves are obtained, and they need to be either analysed individually or batch processed and then compared with another sample. However, in force mapping, once an adhesion map of the sample is obtained, one can use the force data to produce a histogram and compare that to other samples.

3.1.6 Processing Force Curves for water films measurements

First, calibrated values of sensitivity and spring constant acquired as described in Section 3.1.4 are manually entered into the programme prior to force-distance curve analysis, automatically converting deflection numbers to force if not used prior to measurements. The removal of offsets and tilts is then accomplished by using a baseline fit. As a result of long-range forces, interference with the laser alignment, surface heterogeneity (for rough surfaces), and other environmental variables, measured forced-distance curves often exhibit various degrees of tilt. In order to eliminate any offset in vertical deflection at the part of the curve where there is no contact between the tip and the surface, the baseline is automatically removed.

The zero force line is then placed as the zero location of the x-axis when the contact point is also identified. To determine the exact height at the set point force, a linear fit may be used on the slope or constant compliance area of tip-sample contact. Manual adjustment of the fit range is possible and is particularly helpful for non-linear slopes [9]. The height signal, which combines the cantilever's actual movement towards the sample and its deflection, is then adjusted for cantilever bending to identify the location of the vertical tip.

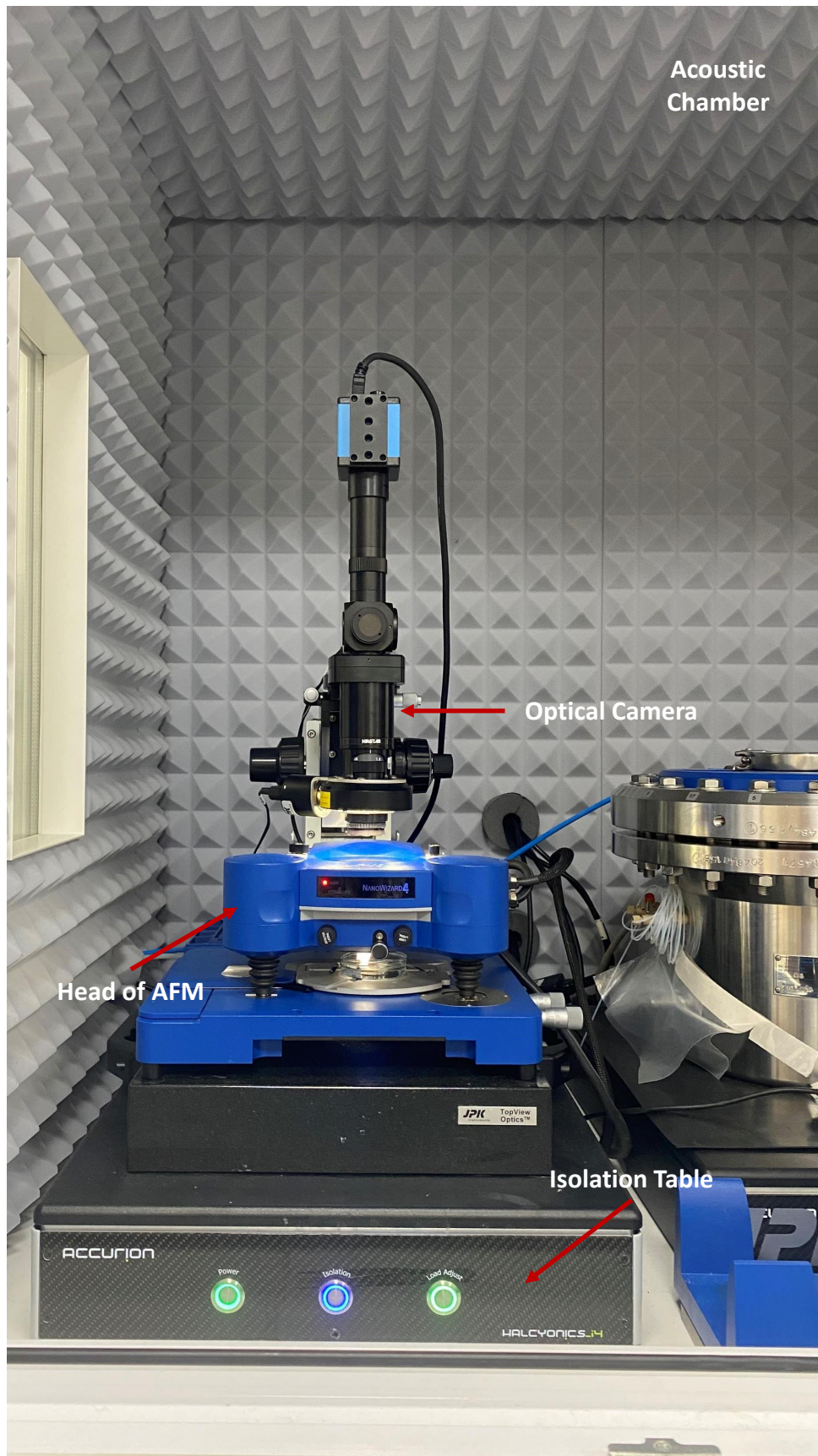


Figure 3.2: AFM chamber and the set up used for imaging in this project.

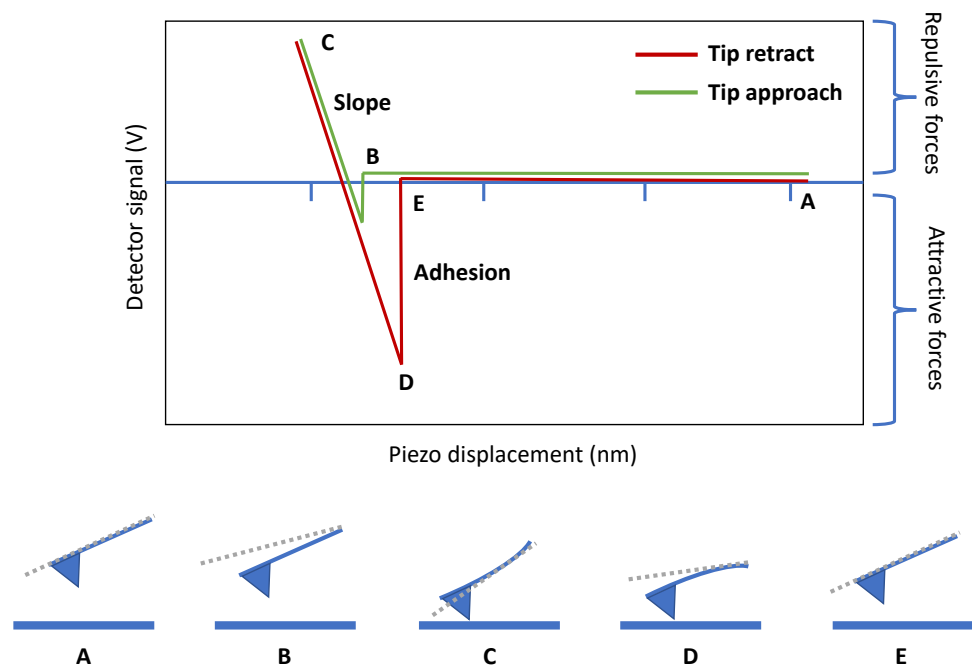


Figure 3.3: Force curve obtained by cantilever interactions with sample's surface at different stages upon approach and retract from the surface.

3.2 Scanning Electron Microscopy (SEM)

3.2.1 SEM History

In 1937, a scientist by the name of Manfred von Ardenne invented a microscope with high resolution via raster scanning a demagnified and finely focused electron beam. Using the scanning of the electron beam by Ardenne was an attempt to improve results obtained via a transmission electron microscope (TEM) in two ways: firstly, to produce images with a higher resolution than those obtained via TEM, and secondly, to mitigate the problems with chromatic aberration inherent to real imaging using the TEM technique.

3.2.2 Principle of the SEM

SEMs use an electron beam, which produces signals, allowing the sample to be imaged with resolution at the nanometer scale. Electrons are fired from a filament and collimated into a beam in the electron column. The electron beam interacts with atoms at various depths within the sample, and in turn, various types of signals are produced, including secondary electrons, back-scattered electrons, and X-rays.

3.2.3 Electron significance in SEM

Figure 3.4 shows various classes of X-rays and electrons produced by the interaction of the electron beam with the sample. All these different types of signals carry different but useful information about the sample and allow the operator to select which signal to capture. Once the high-energy electrons reach the sample, several electrons and X-ray signals are produced.

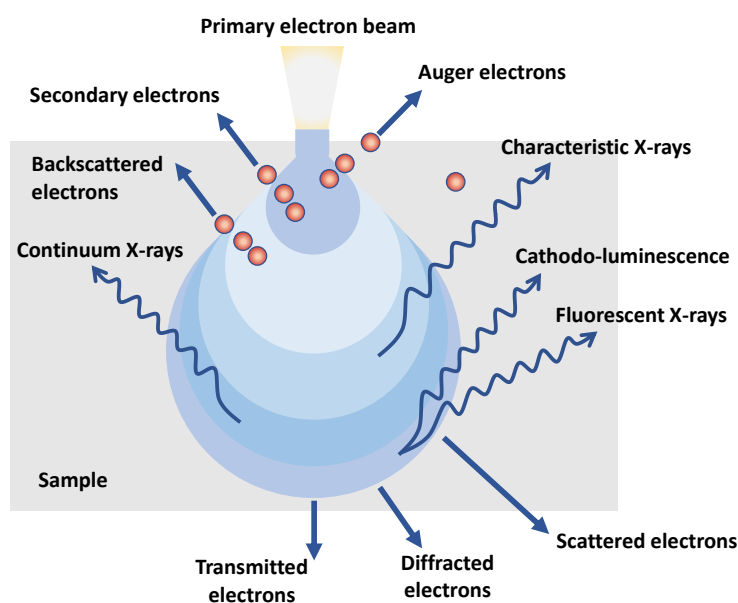


Figure 3.4: Signals produced via the electron beam interaction with the sample.

3.2.4 Back-scattered electrons (BSE)

These electrons originate from deep within the sample (a few microns under the surface) and interact strongly with the sample. They are high in energy and are scattered out of the sample, losing a small amount of energy. The image produced by these electrons is lower in resolution, but it provides useful compositional information about the sample. Back-scattered electrons are reflected back after elastic interactions between the electron beam and the sample.

3.2.5 Secondary electrons (SE)

These electrons are lower in energy in comparison with back-scattered electrons and are emitted from depths within a few nanometers beneath the sample's surface. They originate from the

atoms forming the sample and are a result of inelastic interactions between the sample and the beam of electrons shining on the sample via the SEM. These electrons are sensitive to the surface structure of the sample and thus provide topographic information about the surface of the sample. Back-scattered electrons come from deep within the sample, while secondary electrons originate from the surface of the sample; thus, each type of electron gives different information about the sample. BSE images are highly sensitive to differences in atomic number, and the higher the atomic number of the element detected, the brighter it appears in the image obtained, while SE imaging provides more detailed information about the topographical feature of the surface of the sample.

3.2.6 X-rays

Characteristic X-rays are produced as a result of outer orbital electrons replacing the lower orbital electrons emitted in the form of a SE and moving from a higher energy orbital. The electron releases energy in the form of X-rays; therefore, the X-rays are a direct product of the electrons fired at the surface. X-rays emitted from the sample give information about the elemental composition of the surface through energy dispersive X-ray spectroscopy (EDX). This is extremely relevant, as we will see in Chapter 6 of this project. Therefore, the formation of X-rays from SEM is a result of the electron beam ionising the sample.

3.3 BSE imaging Mode

Back-scattered electrons' origin is from a broad region within the interaction volume (the region where the electrons interact with the atoms of the sample). BSEs are a product of the elastic collisions of electrons with atoms, which result in a change in the electron's trajectory. Electrons are much smaller particles than atoms, and thus atoms scatter the electrons hitting them; the larger the atoms are, the bigger their scattering impact is on the electrons colliding with them; this is referred to as the "billiard-ball" model. Larger atoms, therefore, produce a higher signal than smaller atoms.

The number of back-scattered electrons that reach the detector is directly proportional to their Z number. The dependence of the number of back-scattered electrons on the atomic number helps facilitate differentiating between different phases, providing images that carry information

on the sample's composition. Additionally, BSE images can provide valuable information on crystallography, topography, and the magnetic field of the sample.

The most common BSE detectors are solid-state detectors, which usually contain p-n junctions, and their working principle is based on the generation of electron-hole pairs by the back-scattered electrons that escape the sample and are absorbed by the detector. The energy of the back-scattered electrons dictates the number of electron-hole pairs. The p-n junction is connected to a pair of electrodes, one of which attracts the electrons, while the other pair attracts the holes. This leads to the generation of an electrical current, which depends on the amount of back-scattered electrons absorbed.

The BSE detectors are placed above the sample, centred around the electron beam in a doughnut arrangement to allow the electron beam to reach the sample, which allows maximum collection of the back-scattered electrons, and they consist of symmetrically divided parts. When all parts of the detectors are activated, the contrast of the image depicts the atomic number (Z number) of the element. Alternatively, a topographical image of the sample can be retrieved if only specific quadrants of the detectors are activated.

3.3.1 SE imaging Mode

In contrast to back-scattered electrons, secondary electrons are formed from the surface or near-surface regions of the sample as a result of inelastic interactions between the primary electron beam and the sample. Thus, they have less energy than BSEs. They are used to inspect the topographical features of the sample image.

The most common detector used in the detection of secondary electrons is the Everhart-Thornley detector. It incorporates a positively charged scintillator inside a Faraday cage, which attracts the secondary electrons. The scintillator then accelerates the electrons it attracts and converts them into light, which is sent to a photomultiplier for amplification. In order to increase the efficiency of detecting secondary electrons, the SE detector is placed at the side of the electron chamber at an angle.

3.3.2 Advantages and Limitations of this technique

Advantages of SEM

Since various electrons are produced via the electron beam of the SEM and each type of electron gives different information about the sample, this makes the SEM a very versatile tool that provides valuable solutions for different applications.

Disadvantages of SEM

Since the imaging chamber of the SEM is under vacuum, the sample being placed in the chamber needs to fit certain conditions. Firstly, it needs to be small enough to fit in the specimen chamber; if it is not conductive enough, certain treatments may be necessary in order to increase their conductivity and stabilise them in order to prevent the buildup of charge on the sample, which would give rise to blurring of the image.

Additionally, given the vacuum required in the SEM, the sample needs to be dry and liquid-free, and therefore this may be an issue for imaging biological samples such as tissue samples, so this imaging mode is not the most suitable for such samples. Additionally, powdered samples need to be fixed to a rigid stub in order to be placed in the sample chamber.

3.3.3 SEM protocol for this project

The rock samples were characterised, and their minerals were identified using scanning electron microscopy (SEM). An energy dispersive X-ray (EDX) examination was performed using a Thermo Fisher Scientific Quanta FEG 650F SEM with two Bruker X-Flash 6/30 electron dispersive spectrum detectors. Initially, complimentary pictures shot at 5 kV and less than 60 Pa were provided using low-vacuum SEM.

Using backscattered electrons (BSE), pictures were created with variable contrast levels to represent various mineral elements. High atomic number heavy metals appeared lighter in the back-scattered images. Compounding using EDX, a method that allows for the elemental examination of rock samples, provided details on chemical compositions. Through the interaction of x-rays with the sample surface, mineral elements were detected. This allowed the mineralogy

of the crystals observed in chapter 6 to be detected, and this allowed the identification of these crystals.

Thermo Fisher Scientific's Maps Min programme was used to acquire the images, and Nanomin analysed the spectra data. Its foundation is the combination of x-ray scanning and a mineral deconvolution algorithm, which enables imaging, mineral content identification, and the creation of high-resolution mineral maps with quantifications [239, 125]. There is a spectral table in the Mineral Reference Editor.

Nanomin utilises a library of each mineral to determine the mineral composition per pixel [103].

3.4 Ageing Technique

3.4.1 Ageing Cell Mechanism

Calcite, mica, and the quarry rock Ketton were exposed to a crude oil mixture under elevated temperatures and pressures. Therefore, in order to expose the samples studied in this project to conditions similar to those of the reservoir, an ageing cell shown in figure 3.8 was utilised, which allows the sample to be placed in crude oil at pressure and temperatures higher than those of the ambient. The ageing cell is built to withstand elevated pressures (up to 110 bar) at high temperatures, with a temperature limit of 130 °C shown in figure 3.9.

The ageing cell facilitates elevated pressure in its chamber by compressing the liquid placed in it and thereby reducing the volume of the liquid chamber. This leads to a pressure buildup within the sample chamber of the ageing cell, and when the ageing cell is placed in an oven and the temperature of the ageing cell is increased, the pressure of the ageing cell also increases. Thus, mineral samples placed in an ageing cell were exposed to crude oil in similar conditions to those in the reservoir.

3.4.2 Standard Operating Protocol of Ageing Cell

In order to safely raise the pressure of the ageing cell and increase the temperature after filling the ageing cell, certain steps need to be taken to ensure there are no leaks while the ageing cell's pressure gets elevated at ambient temperatures.

1. Firstly, multiple volume fillers are placed in the ageing cell's chamber in order to reduce the volume of crude oil needed to fill up the ageing cell as a measure of safety protocol. A metal ring, as shown in figure 3.5, is placed at the bottom of the ageing cell.

2. A metal cylinder shown in figure 3.6 is then placed on top of the metal ring in the ageing cell to further occupy the volume of the ageing cell. 3. Place the plug(s) with 6 cylindrical holes designed to vertically hold cylindrical samples such as ketton rocks in the middle of the metal insert.

3. plugs of 1 inch or 1 plug of 1.5 inch are used.



Figure 3.5: Metal insert to reduce the volume of the ageing cell's vessel.



Figure 3.6: Volume reducing cylinders placed in the ageing cell's vessel.

4. The ageing cell's essel: a large vessel is used for three plugs of 1.5 inches or nine plugs of 1 inch; a small vessel is used for one plug of 1.5 inches or three plugs of 3 inches. When multiple plugs are used, a Teflon disc, as shown in figure 3.7, is placed between the plugs to avoid capillary contraction between the plugs. This is especially important when handling brine-flushed Ketton rock samples, as capillary contact between the plugs can result in changing water saturation and, therefore, false results and reduced water film measurements.

5. Once all volume fillers are placed correctly in the ageing cell's vessel, the rest of the volume of the cell is filled with crude oil, and experimental samples are placed in the crude oil. A maximum of 80 cc of crude oil is used for the small vessel, and a maximum of 155 cc of crude



Figure 3.7: Teflon disc to avoid capillary contact between rock plugs.

oil is used for the big vessel. 6. At this stage, the ageing cell piston is placed on top of the vessel and screwed together until it is tight and can no longer turn. This needs to be done on a flat surface in a lab hood to avoid breathing in crude oil's fumes and spillages. 7. The pressure valve is then closed to allow for the pressure to be kept inside the vessel, and liquid and air can no longer escape the ageing cell as, at this stage, the cell becomes fully sealed. 8. Once the pressure valve is fully shut and the ageing cell is sealed, the pressure-building piston nut is screwed, which pushes the piston into the ageing cell's vessel and reduces the volume of the cell, in turn increasing the pressure within the ageing cell's chamber. The pressure of the cell at this point increased to anywhere between 10 and 20 bars, depending on the crude oil placed in the chamber (the volatile content of each crude oil differs slightly from the other). The pressurised cell is then monitored for a 24-hour period to ensure the pressure of the cell does not drop, there are no leaks, and the vessel is fully sealed. If the pressure does not drop at this stage, the cell is being placed in an oven set at 70 °C for a 28-day period. 9. If the pressure in the cell drops to room temperature and the piston nut is unscrewed to depressurise the vessel, then the pressure valve is unscrewed and the source of the leak is identified and fixed before pressurising the cell again.

3.4.3 Ageing cell's operating limits

The ageing cell is made of stainless steel, which is a non-reactive metal and does not interact chemically with crude oil, especially at elevated pressures and temperatures. Additionally, the

metal body of the cell is able to withstand the elevated pressures and temperatures to which the cell is exposed for a prolonged period of one month.

The ageing cell used in this project has a design pressure and temperature of 131 bar and 130 °C respectively, while the working pressure and temperature limit of the cell stand at 110 bar and 120 °C accordingly. The volume of the small vessel consistently used in this project is 80 ml. To reduce the volume of crude in the vessel, as a safety measure, metal beads were added to the vessel, as shown in figure [3.10](#).

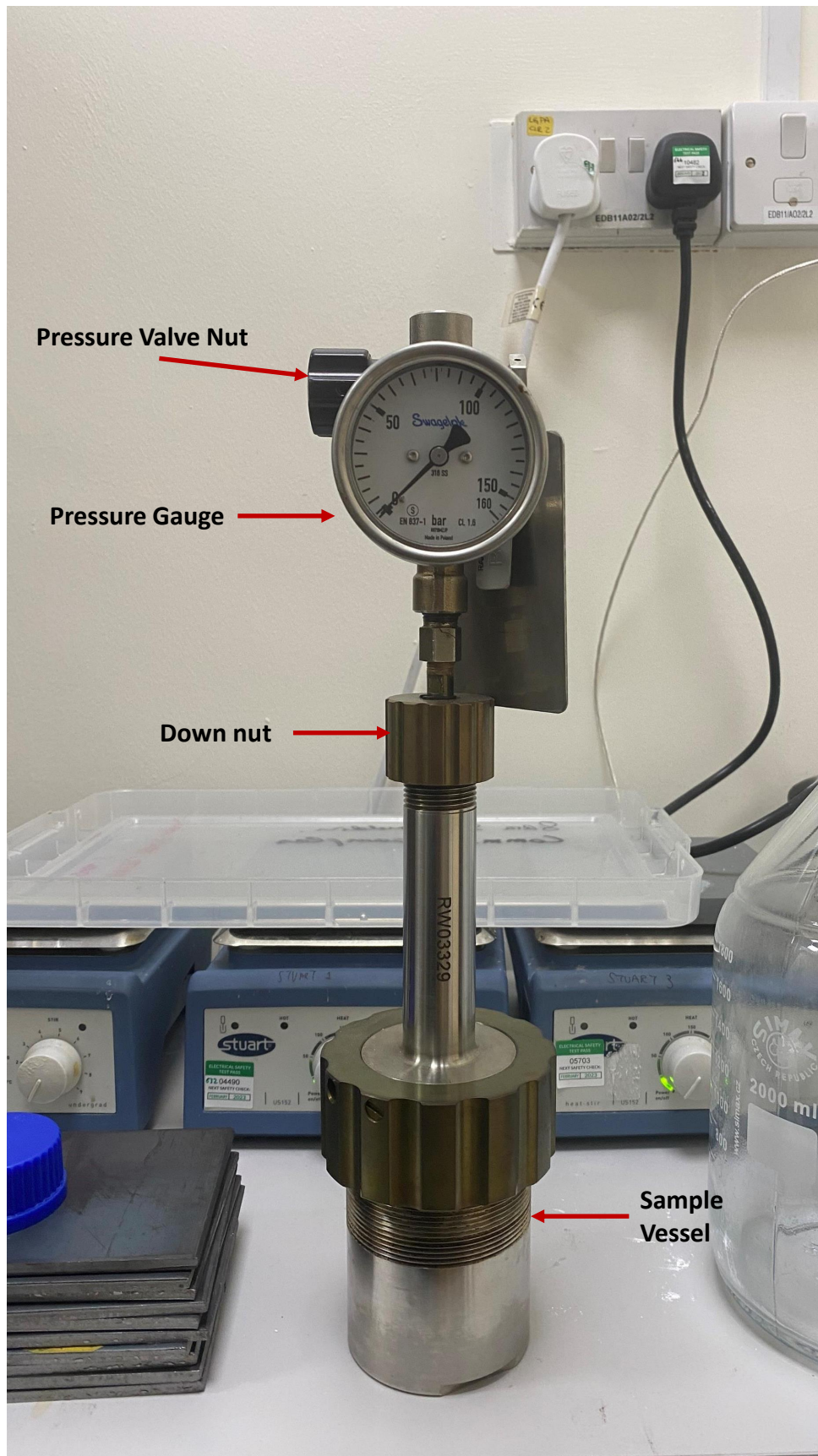


Figure 3.8: Ageing cell used for ageing samples in this project.

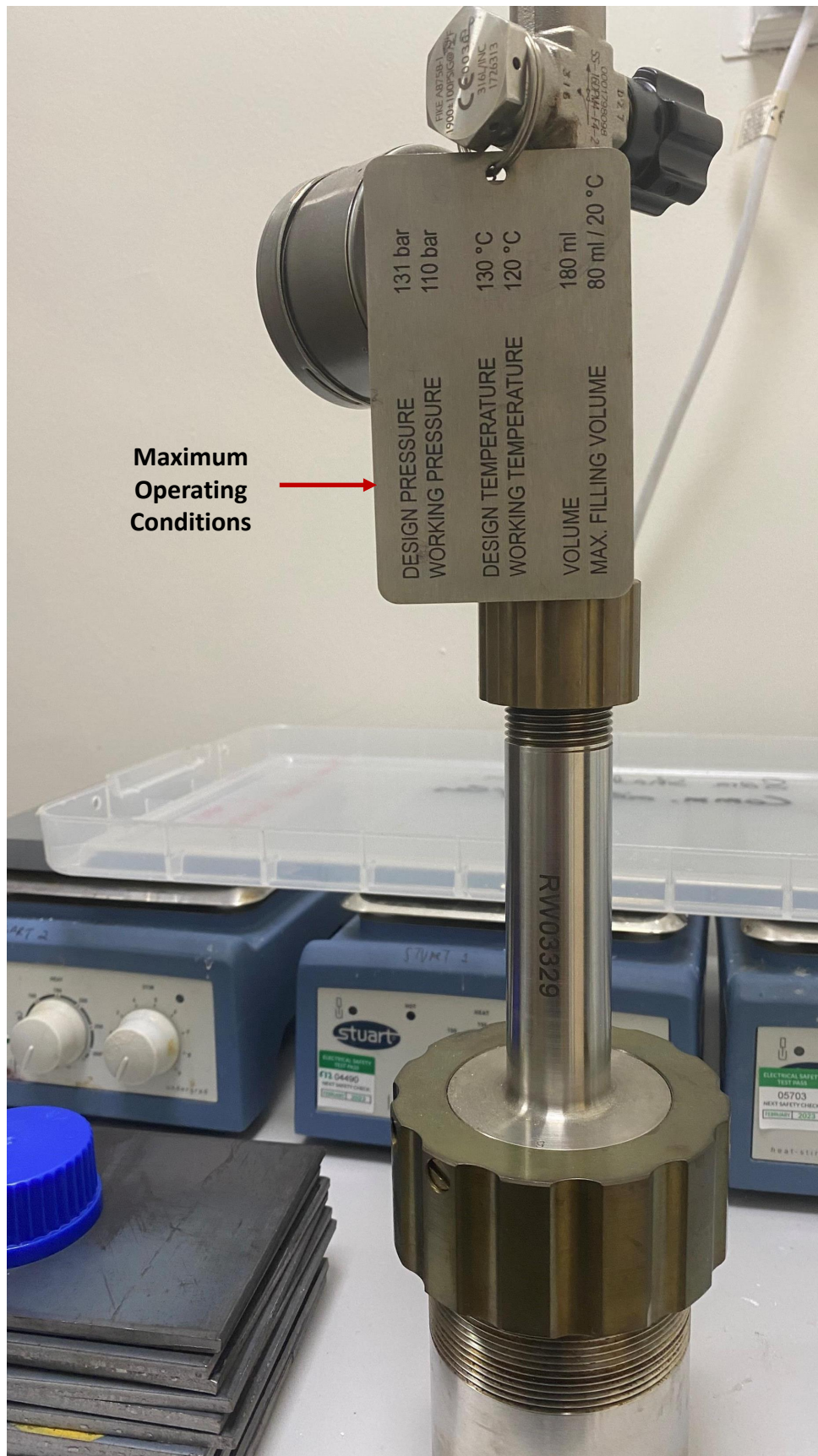


Figure 3.9: Maximum operating limits of the ageing cell used in this project.



Figure 3.10: Ageing cell's vessel in the fume cupboard, this figure represents the vessel when all volume occupiers are placed, sample is then placed and crude oil is poured on top till the remainder of the volume filled. Metals beads are there to reduce the volume of crude oil required to fill out the ageing vessel as maximum liquid can not exceed 80cc.

Chapter 4

Materials used for fundamental characterisation

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4.1 Reservoir's Mineralogy

Various rock types have different mineral compositions, which affect the surface charge of the rock and, in turn, the reservoir's inclination for wetting. Calcite surfaces in carbonate rocks have

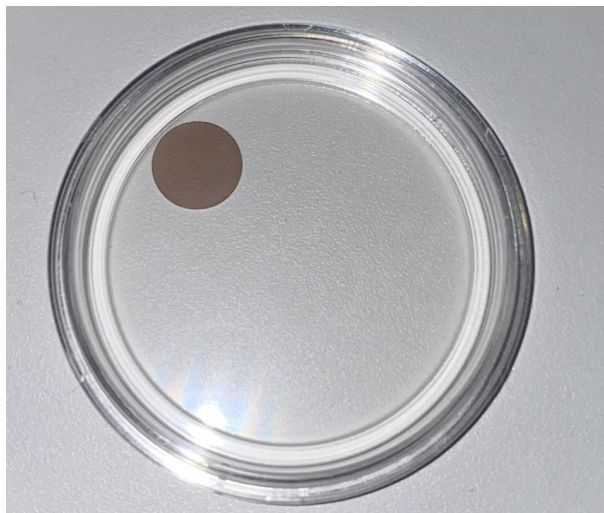
positive charges at neutral pH, whereas silicate and mica surfaces in sandstones have negative charges [33].

The charges in sandstone are negative [33, 32]. The flat planar surfaces of clay minerals, however, show negative charges, while their edge surfaces can have both positive and negative charges. Thus, which mineral is exposed to oil within the pore surfaces of the rock will determine its propensity for wetting, as well as how it is oriented in the case of clays, as clay possesses a negative surface charge on planar surfaces, while on the edges it can have either positive or negative charges [59, 206]. The adsorption of organic compounds with opposing charges will be more likely to occur on certain surfaces.

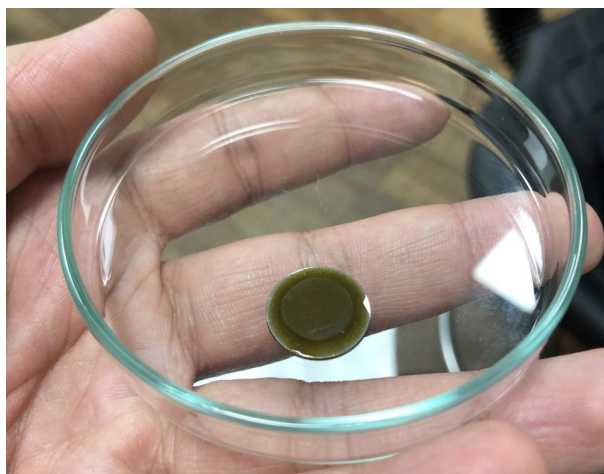
The majority of conventional reservoirs have either carbonate or sandstone mineral composition [197, 256]. Compared to sandstone, carbonate rock has a tendency to become more oil-wet [30, 71, 300]. There may be a connection between this and the two rocks' different surface charges. Calcite, the dominant mineral in carbonates, is positively charged and mildly basic, in contrast to silica, which often has a negative charge and is the primary component of sandstone rocks [45].

4.2 Mica

A typical hydrophilic anionic surface is muscovite mica, which has the generic composition $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ [278]. It is a silicate mineral that can create flat, even sheets that are fully cleavable, which accounts for its widespread usage in microscopic investigations of thin coatings. Tetrahedral SiO_4 sheets are interlayered with octahedral AlO_6 sheets, and the layers are all negatively charged. [196]. Due to its hydrophilicity and highly electropositive interlayer K^+ cations, muscovite mica interacts strongly with polar components [306]. Agar Scientific Ltd. sold us sheets of molecularly smooth muscovite mica with a 9 mm diameter. Mica is frequently employed in AFM studies because it is a suitable model for the faces of clays, such as kaolinite, which is an alumina silicate. Figure. 4.1 shows a mica sheet sample used in this project prior to ageing and after being exposed to crude oi. Mica discs measuring 9.9 mm in diameter were obtained from Agar Scientific Ltd., Parsonage Lane, Stansted, Essex.



(a) Mica Disc used in this project



(b) Mica Sheet exposed to crude oil during experiments

Figure 4.1: Mica discs used in this project

4.3 Asphaltenes adsorbed on Mica

Initially, asphaltenes separated from Mayan crude oil using pentane and heptane were then precipitated and formed in a solid state. 10 milligrammes of asphaltene were dissolved in toluene through volumetric flasks and serial dilutions. Mica discs were then cleaved in air, and the asphaltene solution was then immediately placed on the mica disc for the asphaltenes to adsorb onto mica. The sample was then placed in a fume cupboard to allow the solvent to evaporate, leaving behind the adsorbed asphaltenes. After 24 hours, just like the rest of the samples in this study, the sample was placed in a decane and imaged using AFM.

This experimental data was obtained in order to be compared to later stages of this project's data when crude oil is adsorbed onto mica's surface.

4.3.1 Height measured maps

Figure 4.2 shows the topographical features of asphaltenes adsorbed onto mica's surface at various scales. Asphaltenes have the most complex structure out of all molecules of crude oil and have a negative charge [25, 94]. Figures 4.2 (a) and (b) at 10 micron and 5 micron scales, respectively, show that the negative surface of mica is in fact not completely covered by asphaltenes due to repulsive charge interaction between the surface and asphaltenes. Figures 4.2 (c) and (d) at 5 microns and 2.5 microns scale, respectively, also reveal that asphaltenes formed an agglomerate, which is indeed an asphaltene-formed agglomerate. The spherical shape formed is due to the fact that spherical geometry minimises the contacting surface [250, 113] between asphaltenes and mica's surface. It is worth noting that the agglomerates are not 100% formed of asphaltenes but rather a mixture of crude oil fractions, which include asphaltenes, resins, and other fractions [52]. In figures 4.2 (a), (b), (c), (d), (e), and (f), the light regions indicate the presence of crude oil agglomerates, whereas the darker regions are clear mica. Figure 4.2 (a) and (b) at 10 microns revealed that crude oil agglomerates were formed on mica surfaces as we observed light coloured regions at an elevated height. Figures (c) and (d) were zoomed in on the light coloured regions of figures (a) and (b) to give high resolution images of the crude oil agglomerates on mica's surface. Figures 4.2 (e) and (f) were focused on the smooth rather than agglomerate covered regions of images (b) and (c), which show much smaller nano-aggregates.

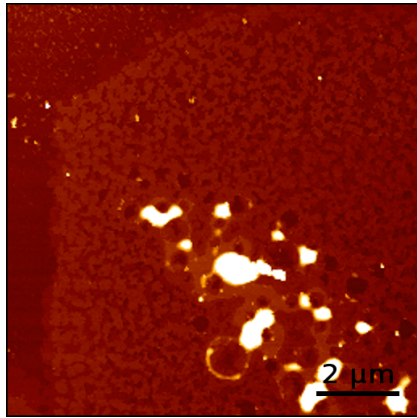
4.3.2 3D construction of asphaltenes on mica

Figure 4.3 (a) shows that the surface of mica is not uniformly covered by the negatively charged asphaltenes in 3D structure for better visualisations, while figure (b) reveals an agglomerate formed by asphaltenes.

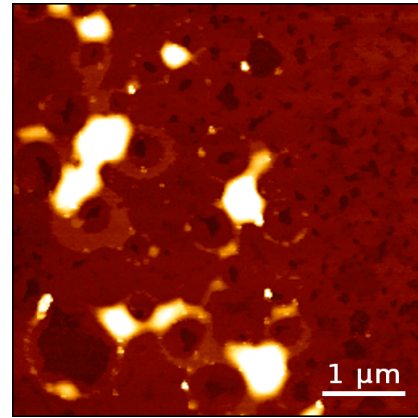
4.3.3 Cross sectional analysis on asphaltenes

Figures 4.4 (a) and (c) show the area of the agglomerates that were chosen for the cross-sectional analysis to be performed through the JPK analysis software. The cross-sectional analysis helps reveal the dimensions of the agglomerates, which can be used as a proxy for the crude oil agglomerates studied in this project, which will be revealed in chapters 5,6 and 7 of this project.

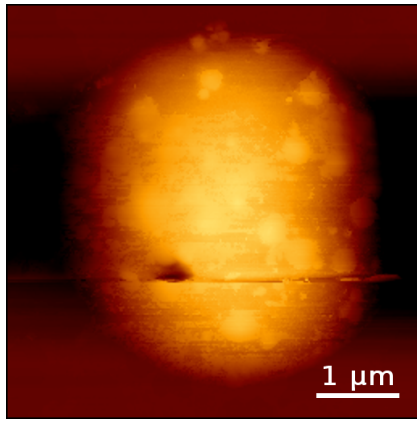
Graphs obtained through the JPK software analysis are shown in figures 4.4 (b) and (d).



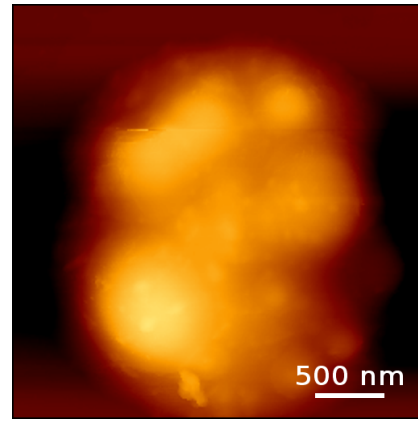
(a) Asphaltenes from Mayan crude adsorbed onto mica



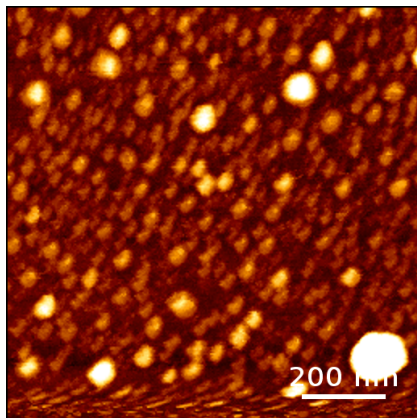
(b) Asphaltenes from Mayan crude adsorbed onto mica



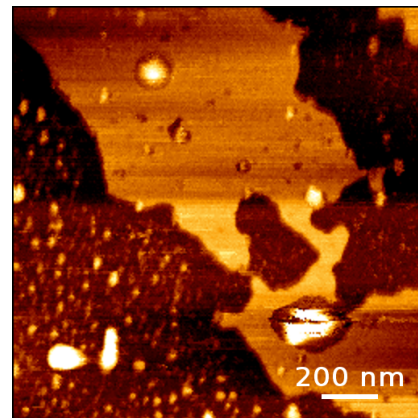
(c) Asphaltenes from Mayan crude adsorbed onto mica



(d) Asphaltenes from Mayan crude adsorbed onto mica



(e) Asphaltenes from Mayan crude adsorbed onto mica

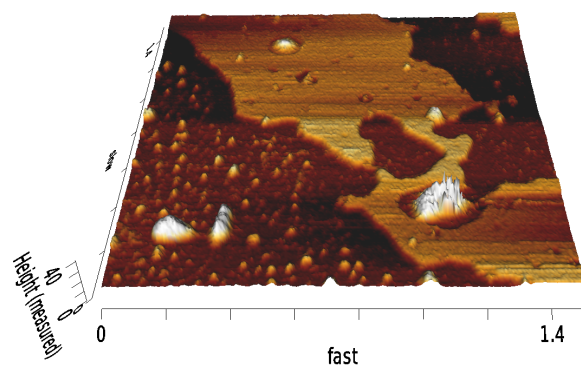


(f) Asphaltenes from Mayan crude adsorbed onto mica

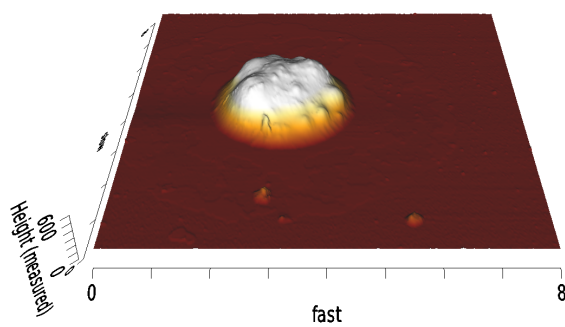
Figure 4.2: Height map topographical characterisations of diluted asphaltenes in toluene and adsorbed onto mica for characterising isolated asphaltenes on mica's surface. At larger scale figures such as (a) and (c), large agglomerates can be seen, while a closer look at smaller scale figures such as (e) and (f) reveals smaller aggregates and surface coverage by asphaltenes and other crude oil molecules. Similar observations were made in Imperial College [66].

Figure 4.4 (b) reveals that the height of the agglomerate shown in figure 4.4 (a) is nearly 500 nm and its diameter is 3 microns.

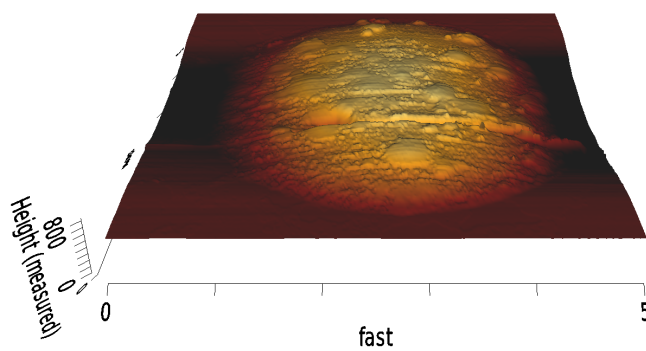
The cross-sectional plot in figure 4.4 (d) reveals that the height of the agglomerate shown in figure 4.4 (c) is around 20 nm and the length of this a is 443.8 nm.



(a) 3D 1.4 microns scale

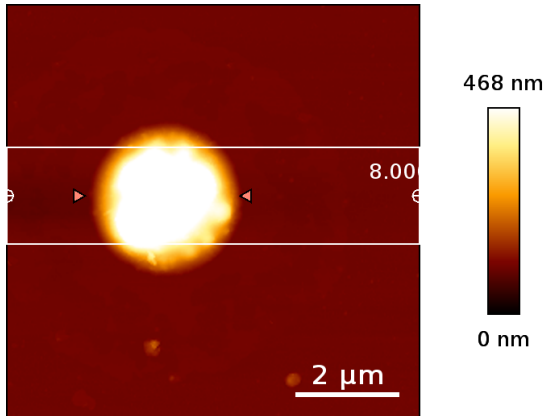


(b) 3D construction of asphaltene agglomerate

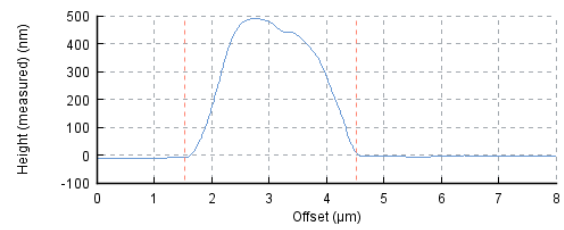


(c) Agglomerate of asphaltene deposit on surface of mica 5 microns

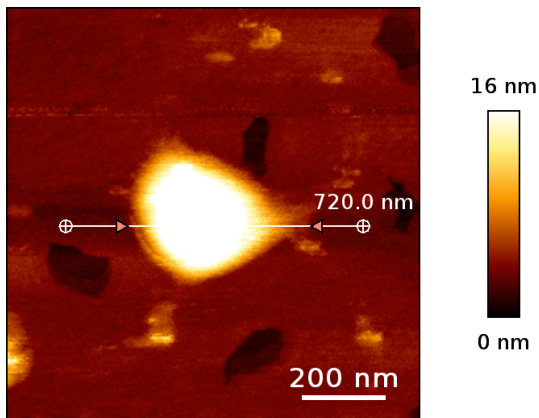
Figure 4.3: 3D construction from topographical maps of asphaltenes adsorbed onto surface of mica.



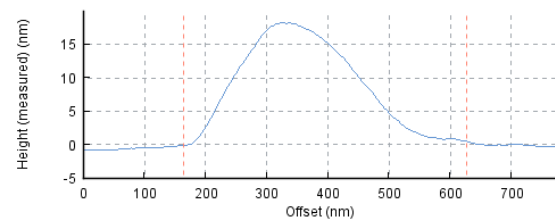
(a) Asphaltene topography showing the cross-sectional analysis



(b) Cross-sectional curves



(c) Asphaltene topography showing the cross-sectional analysis



(d) Cross-sectional curves

Figure 4.4: Cross sectional analysis performed on the asphaltene agglomerates for dimensions of these agglomerates to be recorded.

4.4 Calcite

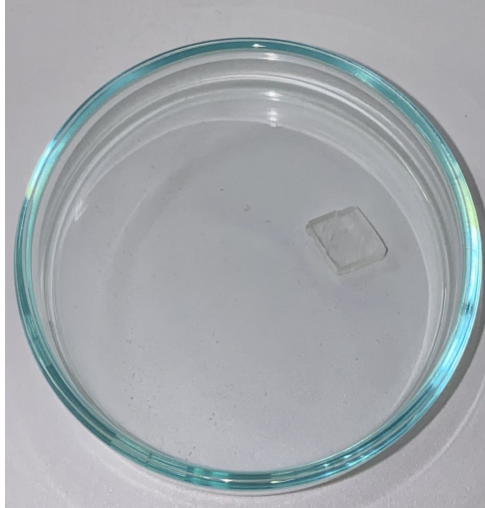
High-quality Icelandic Spar crystals of calcite shown in figure 4.5 from Mexico were purchased from Manchester Minerals UK. The mineral calcite, which is frequently found in carbonate reservoirs, has a positive surface charge [92, 40]. Calcium carbonate exists in several polymorphic crystal states, with calcite (CaCO_3) being the most stable one [246]. In order to comprehend the effect of crude oil's surface-active compounds on wetting patterns, it is crucial to understand how they interact with calcite [295]. Calcite can also be cleaved so that the surface being imaged has never been exposed to the elements. The cleavage plane exposed is the $\{10.4\}$ (1014) cleavage plane of calcite, and this is due to the way the calcite was consistently oriented when cleaving (as it is also the weakest cleavage plane [6]. Additionally the adsorption free energy will significantly vary based on the specific surface structure. Evidence indicates that the 10.4 face is the prevailing crystal face on the macroscopic calcite crystal [132]). Streaming potential methods have been used to measure the zeta potential of this plane and have been found to be positive with an iso-electric PH of up to 10.8 [13]. Calcite was cleaved in decane for this investigation, and then it was imaged in decane. This is due to the fact that calcite is only marginally soluble in water, making decane the more suitable solvent [138, 287].



Figure 4.5: A calcite crystal image showing the crystal prior to any cleaving operation.

The calcite crystals purchased are initially large, and for experimental purposes, the calcite crystal is cleaved using cleaver equipment by aligning the blade with the cleaving plane of the calcite, allowing a clean cut. The cleaving continues until all surfaces of the sample are fresh, free from any contaminants, and at a suitable size for imaging under AFM. Figure 4.6 (a) shows

one of the calcite samples imaged in this experiment. Figure 4.6 (b) represents a carbonate quarry rock used in this project for experiments conducted in chapter 8 and chapter 9. This rock is ketton quarry rock.



(a) Calcite sample cleaved to a suitable size for AFM imaging.



(b) Ketton rock sample drilled out of the main cylinder to a suitable size for AFM imaging.

Figure 4.6: Carbonate samples used in this project, mineral calcite and ketton quarry rock respectively.

4.5 Crude Oils used in this project and their characteristics

Three distinct crude oils were selected for this study, which will be called Crude A, B, and C moving forward in this thesis. These crude oils were provided by Shell B.V. as part of the Shell Digital Rock project.

All below properties and analysis were provided as part of Shell's digital Rock programme, courtesy of Shell B.V [111].

4.5.1 2D Gas chromatography

Gas chromatography in two dimensions, often known as GC–GC, was utilised to analyse the constituents of crude oil. This information will be used to identify the species, or subgroups of species, that are probably responsible for the various oil-substrate interactions. It will also serve as a more reliable basis for component lumping and the identification of pseudo-components in the development of modelling and simulation capability. After diluting the oil samples, 1 μl

of the mixture was injected via a high-temperature injector at 250 °C for two-dimensional gas chromatography analysis (GC–GC). This consisted of two columns arranged in series, the first of which contained an apolar stationary phase and the second of which was slightly polar, both of which led to a flame ionisation detector. Due to the weight-linear nature of the detector, the quoted relative amounts are weight percentages. A 10-second-worth of effluent was frozen after the first column and revalorized to proceed through the second column. Hence, separation is achieved using the first column’s boiling point, which is shown along the X-axis of the plotted results in figure 4.7, and the second column’s polarity, which is shown along the Y-axis in figure 4.7. Based on polarity, these statistics provide a quantitative differentiation between the relative amounts of several classes of constituents within boiling point fractions. In order to depict the fluid composition and related relative amounts, the output serves as a basis for component grouping. From the GC–GC analysis of these crudes presented in figure 4.7, the following conclusions can be drawn: When compared to crude B and crude C, crude A’s composition clearly differs in terms of the abundance of particular groupings, notably lacking the lower fraction range. The lower fraction range is where the relative deviations in the crude B and crude C profiles are most noticeable. The profile for crude A is frequently linked to oils with high levels of oxidised (biodegraded) chemicals, which could help to explain why it differs from crude B and crude C [111].

4.5.2 Density and Viscosity

Particularly significant properties for the numerical modelling techniques, which need precise fluid properties as input, are density and viscosity.

Table 4.1: Comparison between newly obtained density and viscosity to original reference data [111], for A, B and C at 20 °C.

Crude specimen	Density, ρ (kg/m ³)	Viscosity, η (Cp)
A	0.9347	88.425
B	0.8339	4.8731
C	0.8592	9.4672

4.5.3 TAN and TBN

Since they measure the total fraction of acidic and basic polar crude components, which are also known to have a tendency to be surface active and adsorb on solid interfaces, the total acid

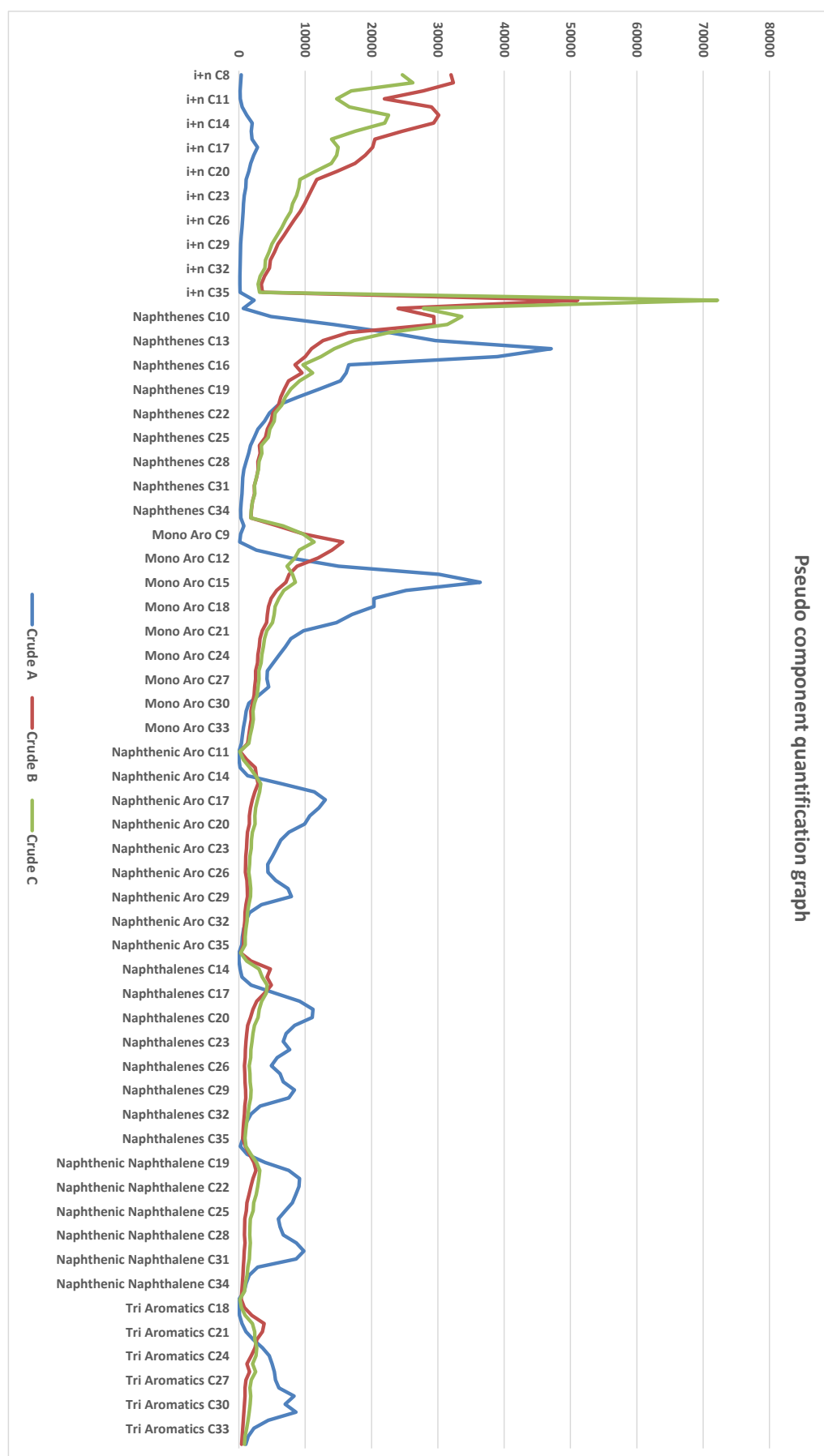


Figure 4.7: 2D gas chromatography plot of the crudes. [111]

number (TAN) and total basic nitrogen (TBN) are traditionally the crude oil parameters most commonly used to correlate with wettability alteration [33]. Crude A has a TAN value of 1.37, making it a naphthenic crude oil with a range of (0.5 to 5) mgKOH/g, which is relatively high.

Table 4.2: Total Acid Number (TAN) and Total Basic Nitrogen (TBN) measured for crude A, crude B and crude C.

Crude specimen	TAN SMS 2384 mgKOH/g	TBN SMS 1468 mg/kg
A	1.37	320
B	0.07	83.9
C	0.09	270.6

4.6 SARA Analysis of the crude oils used in this project

As introduced earlier, the ability of the oil to dissolve asphaltenes is shown by the saturates/aromatics ratio, which rises inversely with the oil's stability. The colloidal stability of asphaltenes in crude oil is related to the asphaltenes/resins ratio, which increases inversely with oil stability [251]. More than 230 crude oils with different amounts of asphaltene have had their relationship between those two ratios examined, and the results produce a stability threshold that is comparable to that in figure 4.8. Hence, based on the P-ratio and S-value, crude C would be considered a fluid with marginal stability, whereas crude A and crude B would be considered stable fluids.

Table 4.3: Basic properties of the crude oil used in this study.

Crude Oil Alias	API	Saturates	Aromatics	Resins	Asphaltenes
crude A	35.80	37.27	48.45	14.21	0.07
crude B	39.79	58.45	36.92	4.36	0.28
crude C	34.19	44.00	44.00	9.69	2.31

As mentioned in chapter 2.2.4, SARA fractions of crude oil and their relations to one another play a key role in stabilisation of asphaltenes in crude oil [7, 251]. There are several asphaltene stability models used to predict and evaluate the stability of asphaltene suspension in crude oil solutions, which are described below, and the models are discussed in detail in an earlier chapter 2.4.6.

For estimating the risk of asphaltene precipitation, Stankiewicz et al. (2002) [154] developed a plot between the ratios of saturates to aromatics and asphaltenes to resins. Figure 2.9 shows this plot, highlighting the stable and unstable regions.

The three crude oils employed in the experiments of this PhD project were also categorised as such for stability, and figure 4.8 shows the degree of stability of the crude oils used.

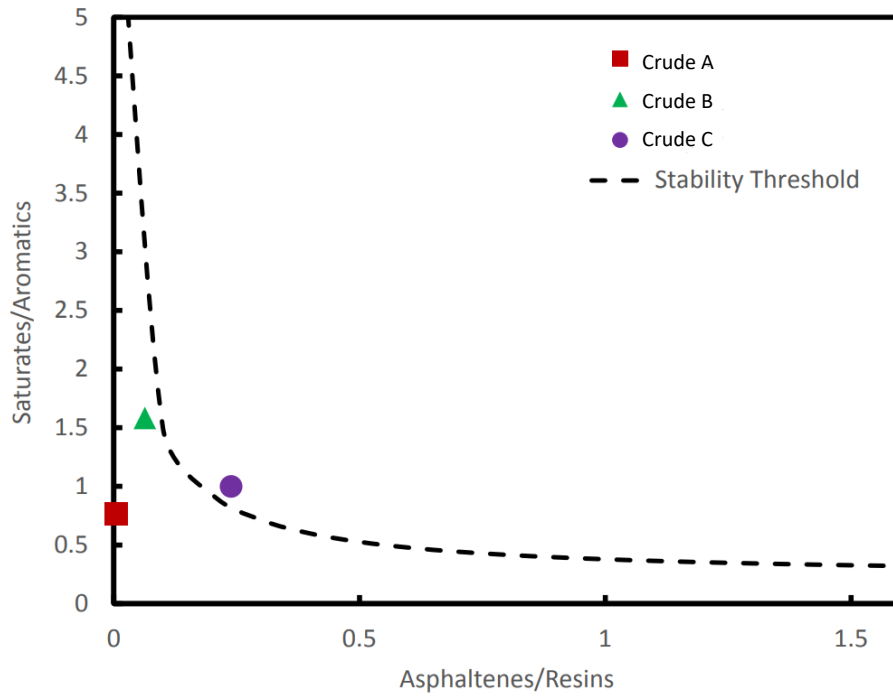


Figure 4.8: Stability curve of the crude oils A, B and C provided by Shell. [111]

4.6.1 Metals, Water and Sulphur analysis

In order to further elucidate the nature of the crude oils, the metal, water, and sulphur content of the three crude oils was assessed by Shell, and these data are reported in tables 4.4 and 4.5.

Table 4.4: Metal content of crude oils selected, crude A, crude B and crude C, reported with 10% precision if above detection limit.

	A	$\pm$	B	$\pm$	C	$\pm$
	mg/kg		mg/kg		mg/kg	
Ca	3.8	0.4	1.36	0.1	2.69	0.3
Fe	5.14	0.5	<0.25		0.94	0.3
Mg	0.53	0.05	0.18	0.02	0.15	0.02
Mn	<0.03		<0.03		<0.03	
Mo	0.42	0.04	0.21	0.03	0.25	0.03
Na	3.46	0.3	0.73	0.5	2.83	0.3
Ni	1.166	0.1	0.12	0.05	7.28	0.7
Si	0.51	0.5	0.56	0.5	1.4	0.5
V	0.44	0.3	<0.25		25.4	3
Hg	<0.001		<0.001		<0.001	

Table 4.5: Water and sulphur content of each crude are tabulated here, these are important parameters which have significant importance both from processing perspective and economic prospect of the crudes.

Crude specimen	WATER (ASTM D4928) weight%	SULFUR (ASTM D2622) weight%
A	0.04	0.149
B	0.01	0.792
C	0.02	1.265

Chapter 5

Application of Atomic Force Microscopy in investigating Aged Crude Oil Deposition onto Mica and Calcite

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5.1 Abstract

Crude oil precipitation and adsorption on model mineral surfaces, mica and calcite, have been investigated using atomic force microscopy (AFM) to determine the spatial characteristics of identified particles, specifically asphaltenes. Crude oils can be segmented into four different fractions: saturates, aromatics, resins, and asphaltenes (SARA). The analysis indicates that asphaltenes adsorb onto both mica and calcite, albeit differently. Adsorption on mica was primarily evident using aggregates, which formed distinct agglomerates. This is interpreted as a reinforced tendency, as the observed formation of progressively larger adsorbed agglomerates is consistent with interfacial energy minimisation of the respective negatively charged surfaces in contact. Respectively, agglomerates observed on calcite had more uniform coverage, in line with attractive interactions between negatively charged agglomerates and positively charged surfaces.

5.2 Introduction

Carbonaceous materials deposition on designed and naturally occurring surfaces during all stages of petroleum production greatly hampers operational efficiency. This has a significant economic impact. Carbonaceous compounds that are deposited commonly consist of asphaltene, while the deposition of other substances like waxes also presents a challenge. The problem arises from the colloidal form of crude oil and the fluctuating environmental conditions it undergoes throughout production [66].

Crude oils are traditionally composed of four fractions known as SARA fractions of crude oil [66]: saturates, aromatics, resins, and asphaltenes. This is because crude oils have different compositions, and therefore molecular characterisation is not readily available through experimental techniques [10]. This is due to the vast and large number of molecules present in any crude oil; thus, grouping molecules with similar characteristics is an experimental way to assess a crude oil. This characterisation is given in chapter 4.6. However, it is worth noting that

recently, computational methods have been developed to tackle this issue [147], and in fact, through machine learning, it is now the future to characterise crude oils at a molecular level through large-scale machine learning, however experimental data analysis still is required to form the most accurate data for further modelling to be based upon (Appendix H gives more information on machine learning and digital oil).

Some of the key economic issues in the petroleum industry today are linked with asphaltenes, which are the polar surface-active fractions of crude oil [37, 123]. This is because regardless of the asphaltene content of any specific crude oil, precipitation of asphaltenes is not avoidable most of the time. Blending crude oils, which is a common practice in refineries, is known to cause asphaltene destabilisation and precipitation also [282]. Asphaltenes precipitate naturally if the ratio of SARA fractions in crude oil allows it. [37, 123], additionally, sudden pressure [152] and temperature changes (known as pressure and temperature onset) in the reservoir can cause precipitation too. Asphaltenes are sometimes nicknamed ‘the cholesterol of the oil industry’ [52, 53]. This is because they can have an unwanted phase transition and precipitate near the well-bore regions of the reservoir and production tubing, clogging all the pipework and therefore hindering production, transportation, and refining [269, 127, 63, 66, 64, 65, 190]. This results in increased extraction and transportation costs, to the point where some fields become economically unfeasible for extraction. Asphaltene’s interfacial interactions with reservoir rocks impact the rock’s wettability by altering the wettability of the surface of the reservoir rock in favour of oil, therefore hindering oil recovery [37, 127, 265, 317, 144, 50, 194, 29, 31, 58, 164]. By asphaltenes adsorbing on the rock surface, the hydrophilic rock becomes more oleophilic and thus more oil-wet than water-wet [185]. Since the oil is attracted to the rock surface, its flow is hindered and thus remains in the porous rock medium. Wettability alteration (by use of surfactants, for instance) could lead to more optimum recovery in terms of volume and cost [58], as the wetting pattern on the reservoir rock surface can affect the flow of crude oil out of the porous media [36, 246, 165]. In the primary production period, only 5-30% of the original oil in place (OOIP) can be recovered by the native pressure energy stored in the reservoir [193, 68]. Techniques such as water flooding [184, 15], steam, and gas injection are now used to enhance the recovery rate of crude oil [273], but there are limitations.

Atomic Force Microscopy (AFM) allows imaging of surfaces at nanoscale resolution across mm-scale surfaces [130, 320]. This technique has recently begun to be used to assess wettability [241].

In this chapter, we have investigated the adsorption of crude oil precipitates, asphaltenes, and resins onto both mica and calcite model surfaces using AFM. This is because in carbonate reservoirs, surface-active components of crude oil are likely to adsorb onto the surface of the rock surface [194]. The key question is whether the mineralogy and surface charge of minerals lead to a different wettability pattern formed by crude oil, and additionally, whether a uniform coverage of the mineral surface itself is homogeneous or not.

5.3 Materials and methods

5.3.1 Atomic Force Microscopy (AFM)

At the core of this imaging technique is a plate spring known as the cantilever. The cantilever is mounted onto a silicon-made chip at one end, and at the other end, it holds a pyramidal or cone-shaped tip, which is used to measure forces between the tip and the sample. The chip holding the cantilever is mounted to a cantilever holder placed in a piezoelectric scanner, which moves the probe in x, y, and z directions, allowing the surface to be scanned. When the sample and tip meet one another, the cantilever bends or deflects, depending on the types of interactions between the tip and the sample, being repulsive or attractive. So, in simple terms, the idea behind the AFM is that the local forces between the tip and sample are either repulsive or attractive, which consequently deflect the cantilever. These deflections, towards or away from the surface, are measured using a laser beam that shines on the back of the cantilever and is reflected onto a position-sensitive photodiode.

The photodiode has four quadrants, A, B, C, and D, and the position of the laser spot can therefore be monitored in both vertical and horizontal directions. Moreover, if the spring constant of the cantilever is known (generally measured in the current experiments), the force of adhesion being experienced by the cantilever can be calculated. The summary of this can be seen in figure 3.1.

5.3.2 Quantitative imaging Mode

QI imaging mode was employed in this section to reveal the topographical features of the imaged surfaces. As described in the chapter, imaging mode is based on the same principles of force

spectroscopy. This technique produces a complete force distance curve at each pixel of the image. Besides height measurements, it reveals other quantitative data, such as the adhesion of the tip to the surface and mechanical properties such as stiffness through the measured slope at high compression. In this technique, the tip of the cantilever approaches the surface of the sample and is indented into the surface with a pre-set force (set point). Once indented, the cantilever retracts to a pre-set vertical position, called the z-length, at a pre-set approach speed, and it remains in contact with the surface at each pixel for a period referred to as the pixel time, which was approximately 10 ms.

There will be no lateral forces between the tip and the surface of the sample as the cantilever retracts, making this imaging mode suitable for very soft and sticky samples or samples to which the adsorbed material is loosely attached (e.g., asphaltenes). QI mode is the most suitable imaging mode for very sticky samples, such as polymers or crude oil and its polar components (asphaltenes) [1]. This was the dominant mode used in this work.

5.3.3 Characterising Topographical features of Mineral surfaces with AFM

In this study, we used AFM (Nanowizard 4, JPK Instruments, now Bruker) to image the structure of the rock surface down to nanometer resolution. The sample was scanned with a silicon tip (PPP-NCHAuD from NanosensorTM) on a $1\ \mu\text{m} \times 1\ \mu\text{m}$ area with a resolution of 512×512 pixels in quantitative imagingTM mode. The image was levelled, filtered using a median filter, analysed for curvature and roughness, and visualised with JPKSPM data processing software (JPK instruments). The same setting of imaging was used for larger-scale images.

5.3.4 Ageing Technique

Ageing is a well-established technique in the industry for preparing samples [234]. The method used in this project involved using an ageing cell (pressure cell), which is designed to withstand high pressures at high temperatures. The samples are placed into the ageing cell, and the metal container of the ageing cell is filled with crude oil. The cell is then pressurised at room temperature and then placed in an oven at $70\ ^\circ\text{C}$ for a one-month duration. The pressure of the cell rises as the temperature is increased, and the end pressure of the cell will be dependent on the crude oil used. In previous attempts at ageing minerals in crude oil, the crude was only heated and not pressurised. In this project, having the pressure cell allowed for elevated

pressure and temperature, which placed the mineral surface in close proximity to that of an actual reservoir.

Table 5.1: Equilibrium pressures of crude oils achieved at 70 °C in ageing cell.

Crude sample	Pressure (bar)
<i>Crude A</i>	35
<i>Crude B</i>	40
<i>Crude C</i>	25

5.3.5 Crude oils and chemicals

Crude oils

Crude oils used in this investigation were provided by Shell B.V. and were all part of the wider Shell Digital Rock programme. Some basic properties of the oils are shown in Table 5.2.

Table 5.2: Basic properties of the crude oil used in this study.

Crude Oil Alias	API	Saturates	Aromatics	Resins	Asphaltenes
crude A	35.80	37.27	48.45	14.21	0.07
crude B	39.79	58.45	36.92	4.36	0.28
crude C	34.19	44.00	44.00	9.69	2.31

Chemicals

1. Decalin from Sigma Aldrich with a purity of 98% was used to remove any non-adsorbed crude oil from the surface of the mineral after ageing. Decane from Sigma Aldrich with a purity of ≥ 95 was used as the solvent in which the surfaces were imaged and cleaved prior to ageing.
2. Decane was chosen as it is a product of crude oil and carries fewer health risks when evaporated. Additionally, calcite is soluble in water, so using decane as the solvent for which imaging was conducted was justified. Imaging in liquid, as opposed to air, carries the advantage of additional noise cancellation, and therefore the quality of the images obtained via AFM increases. However, the liquid used for imaging media needs to be transparent, so decane is the best alternative to using crude oil itself.

5.3.6 Minerals

Mica

Mica discs measuring 9.9mm in diameter were obtained from Agar Scientific Ltd., Parsonage Lane, Stanstead, Essex. Mica is known for having a flat surface at the atomic level; additionally, it can be readily cleaved, and a fresh surface free from contamination can be obtained for imaging [221]. Mica has a net negative surface charge [221, 314, 139] and is a mineral frequently found in reservoir rocks. The dominant component of sandstone reservoirs is quartz (silica), which is also negatively charged. Quartz cannot be cleaved as they have no cleavage plane. Mica has similar properties to those of clay minerals in sandstone reservoirs [165], which makes it an important surface to study for wetting patterns changes occurring in reservoirs because of crude oil adsorption on the surface [221, 314, 139, 241].

Calcite

High-quality Iceland Spar crystals of calcite from Mexico were purchased from Manchester Minerals, UK. Calcite is a mineral frequently found in carbonate reservoirs and has a positive surface charge [92, 40]. Calcite (CaCO_3) is the most stable polymorphic crystal state of calcium carbonate and is commonly found in carbonate oil reservoirs [246]. Therefore, the interaction between crude oil surface active compounds and calcite is extremely important in understanding the impact of the surface-active compounds of crude oil on wetting patterns [295]. Calcite can also be cleaved so that the surface of the calcite, which is imaged, has never been exposed directly to air. For this investigation, calcite was cleaved in decane and then imaged in decane. This is because calcite is slightly soluble in water, and therefore decane is the more ideal solvent.

Mica and calcite were investigated in this project. Both minerals are flat and were cleaved within the decane prior to each experiment to ensure the surface of the minerals was not contaminated. Additionally, mica and calcite have opposite charges, and this was important in showing whether charge influences how crude oil will deposit on the surfaces.

5.3.7 Experimental Procedure

A JPK Nano Wizard 4 Atomic Force Microscope, which allows the imaging of adsorbed crude oil components at nanoscale on relatively smooth surfaces, was used. The cantilever was cleaned using a UV/ozone plasma chamber for 20 minutes before any imaging was undertaken. The mineral surfaces were then cleaved in decane and imaged in decane under AFM using QI mode to characterise the pure mineral surface topographical features.

Mica and calcite were cleaved in decane across all sides to ensure a new surface is exposed free of contamination (the cleavage plane of calcite is 1014 known to have a positive charge [13] and mica is 001 known to have a negative charge [91]). After being cleaved in the decane, the samples were placed in an ageing cell filled with crude oil. The cell was then pressurised at room temperature and monitored for a few hours to ensure the cell pressure remained constant and there was no leak. The cell was then placed in the oven heated to 70 °C. The pressure of the cell rose until it reached the equilibrium pressure of the oil at 70 °C. This pressure was then recorded. The cell remained in the oven at the recorded pressure and temperature of 70 °C for four weeks. After 4 weeks, the samples were taken out of crude oil and placed in decalin for 5 minutes to remove any non-adsorbed crude oil from the surface. The samples were then stored in decane and imaged in decane.

Before imaging starts, the cantilever is calibrated in air to establish the force constant and sensitivity, and then recalibrated in decane for sensitivity. This is because air data are more accurate to use for processing, but decane data are needed for the AFM force curves to be accurately captured and represent real data. Topographical images of the surface of the sample were taken via AFM using the quantitative imaging mode. The cantilever used in the experiments was a silicon cantilever purchased from Windsor Scientific with the following model number: PPP-NCHAuD (length: 125 μm , width: 30 μm , force constant: 10–130 N/m).

The surfaces of the model samples had been imaged prior to introducing crude oil onto the surfaces. This is key to understanding what changes can be imposed on the surface properties of the minerals upon crude oil adsorption.

5.4 Result and discussion

5.4.1 Characterising Model Mineral surfaces with AFM

imaging pure Mica

To characterise the surface structures of mica, a freshly cleaved mica surface was imaged in decane. Table 5.3 is a summary of the features observed in the images obtained from the surface of the mica at two different scales of $10\mu\text{m}$ and $1\mu\text{m}$. The surface of mica is completely flat at the nanoscale, in accordance with the literature. Small particles measuring up to 1.95 nm were seen, which have similar stiffness as mica. These features can also be seen in the adhesion image, but not in the stiffness image, suggesting that the material giving rise to these features is probably mica and is a result of flaws in the cleaving. The adhesion of mica does not exceed 2.5 nN.

The similarity of the stiffness range is a result of the surface being pure mica. Figure 5.1 shows the mica sheet surface at 1 micron and 10 micron scale. The height measured maps (a) and (d) show the surface of mica is flat at nanoscale and does not exceed 2nm in height, while the stiffness maps (c) and (f) exhibit that the material has a rather uniform hardness to its surface, indicating that the material surface is mainly mica.

Table 5.3: Summarised quantitative and qualitative AFM gathered data on pure mica sample imaged in decane.

Scale \ Topographical properties	Surface features	Maximum height measured (nm)	Maximum adhesion (nN)	Stiffness range (N m^{-1})
10 microns	Flat	1.95	2.5	0.741 - 0.487
1 micron	Flat	1.82	2.27	0.678 - 0.450

imaging pure Calcite

The surface topology, adhesion, and stiffness of the calcite are shown in the images presented in figure 5.2 and summarised in table 5.4. Figure 5.2 reveals that the surface of the calcite is flat at the nanoscale but with a major difference to that of mica. The surface of the calcite is

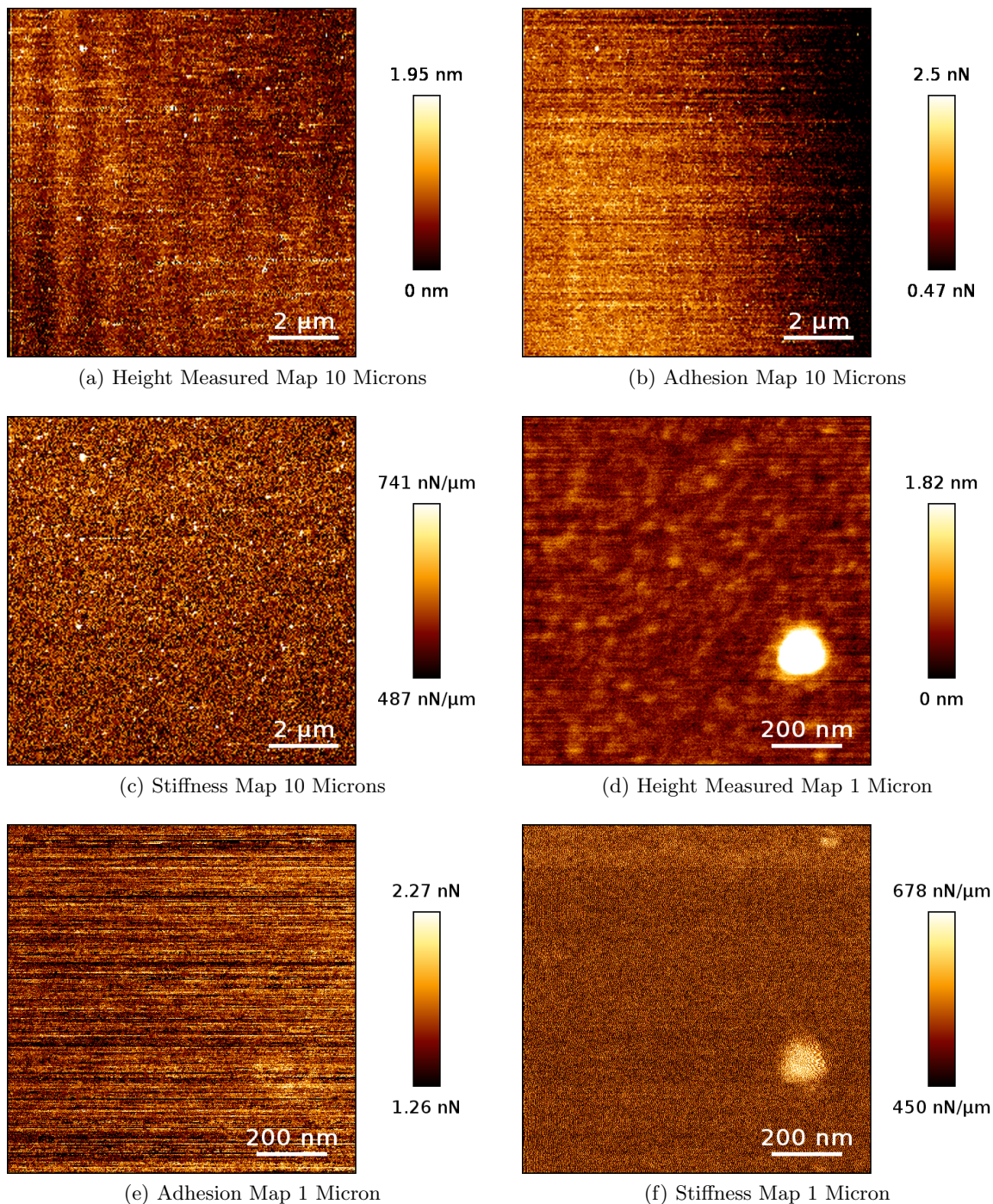


Figure 5.1: Mica sheet cleaved in decane and imaged in decane at 10 microns and 1 micron image scale showing roughness, adhesion and toughness of pure mica.

composed of numerous steps. However, each step itself is relatively flat. In order to characterise the surface and steps of the calcite better, a cross-sectional analysis was conducted across two separate height images of the calcite. The results are presented in Figures 5.3 a-c, which show the steps across the calcite surface clearly. From the height vs. offset plot Figures 5.3 (c), one can see where there is a sharp and almost vertical drop in height, indicating a step (kink)

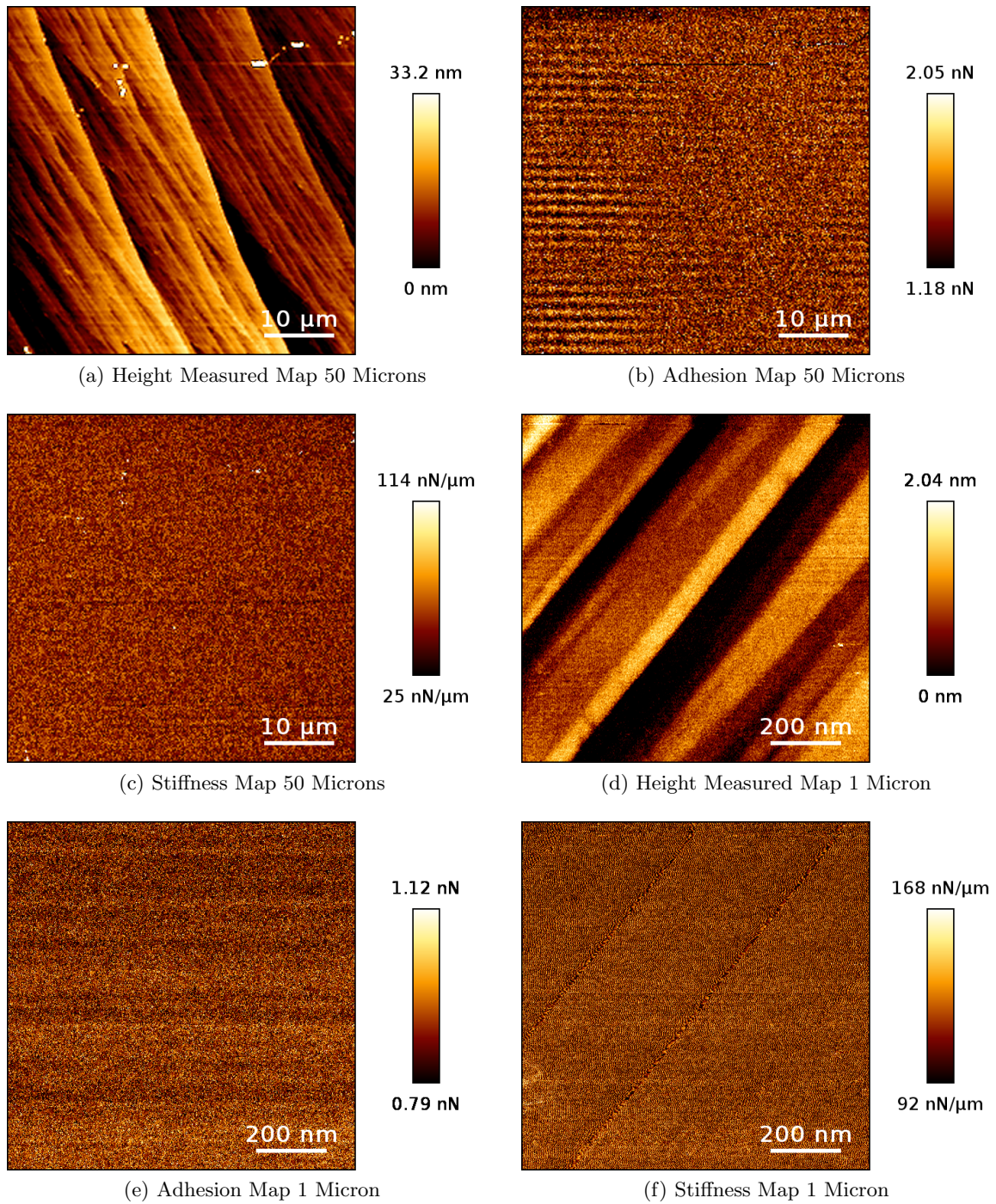


Figure 5.2: Calcite cleaved in Decane to prevent any dissolution and contamination, imaged in decane for minimal noise impact on imaging for characterising the pure carbonate surface under atmospheric temperature and pressure using AFM.

occurring in the surface of the calcite of the order of 1nm in height.

Table 5.4: Summarised quantitative and qualitative AFM gathered data on pure calcite sample imaged in decane.

Topographical properties Scale	Surface features	Maximum height measured (nm)	Maximum adhesion (nN)	Stiffness range (N m^{-1})
50 microns	Stepped, each step is flat	33.2	2.05	0.114 - 0.025
1 micron	Stepped, each step is flat	2.04	1.12	0.168 - 0.092

Calcite's Cross Sectional Analysis

Since the calcite's surface at the nanoscale is not as flat as mica but rather stepped, this is an important character to bear in mind when introducing crude oil onto the surface of calcite, as seeing the steps visually or not after crude oil is introduced onto the surface can give insight as to how well crude oil deposits cover the surface of calcite, as we will see shortly in this chapter. The inset of the figure 5.3(a) shows clearly that the surface of calcite is formed of flat steps that have dents and valleys; however, each step itself is atomically flat.

5.4.2 Aged mica samples

All crude oils formed distinct agglomerate depositions on the surface of mica. This was expected before running the experiments. Mica has a negative surface charge, as do polar components of crude oil, as stated in earlier chapters of this thesis (Chapter 2). Therefore, in order to minimise the repulsive interactions between the surface and the components, spherical deposits are formed, which reduce the contacting surface between the negative components to a minimum. The gap in the stiffness range confirms that the surface is formed of different components, as the lower range is closer to that of mica. Crude oil B formed the largest agglomerates at both the molecular level and the 10-micron scale.

Figures 5.4 show the topographical features of the aged mica in the crude oils. From figure 5.4 (a), (b), and (c), one can see that all crude oils formed agglomerates on the surface of mica, though crude oil C has more clustered agglomerates, in line with the fact that it is deemed to be the most unstable oil out of the three. Which is in line with the SARA analysis stability curve of these crude oils presented in figure 4.8.

Figure 5.5 represents the adhesion maps of the mica sheets aged in the crude oils; crude A is the least adhesive crude oil, while the aggregates formed by crude oil C are the most adhesive.

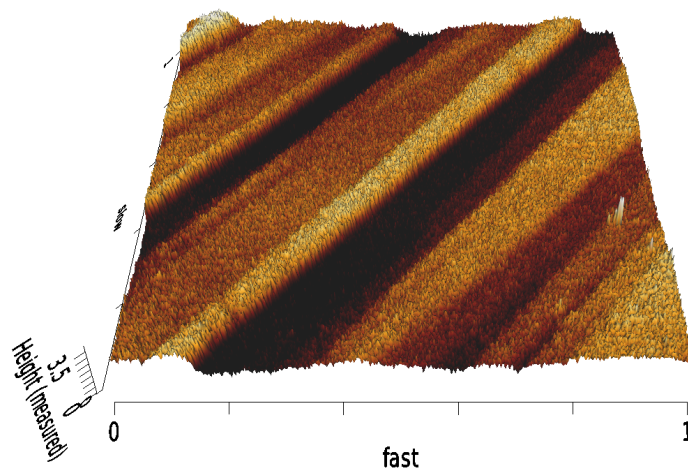
Figure 5.5 (a) and (b) also show that crude oil A and B have different adhesive properties; the adhesion in crude oil A shows that the agglomerates have the same adhesion as the background, while in crude oil B, the agglomerates have weaker adhesion than the background. Crude oil A has constant adhesion, whereas in B and C, the adhesion images pick out the height, as we see in figure 5.4.

Table 5.5: Summarised quantitative and qualitative AFM gathered data on Mica aged samples on 1 micron scale.

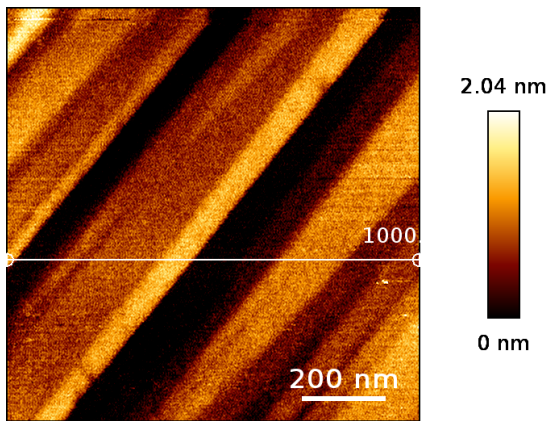
Topographical properties Crude Oils	Coverage Type	Maximum height measured (nm)	Maximum adhesion (nN)	Stiffness range (N m^{-1})
Crude A	Agglomerates	16.3	6.1	5.95 - 0.556
Crude B	Agglomerates	24.1	28.3	12.2 - 0.395
Crude C	Agglomerates	27	7.01	1.29 - 0.520

Table 5.6: Summarised quantitative and qualitative AFM gathered data on Mica aged samples on 10 micron scale.

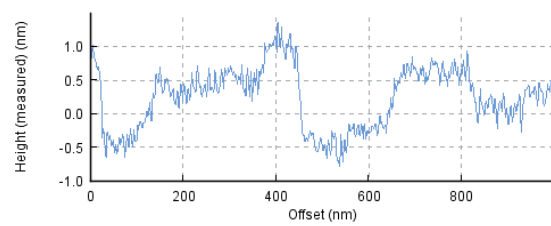
Topographical properties Crude Oils	Coverage Type	Maximum height measured (nm)	Maximum adhesion (nN)	Stiffness range (N m^{-1})
Crude A	Agglomerates	18.2	11.2	5.95 - 0.556
Crude B	Agglomerates	74	10.5	12.2 - 0.395
Crude C	Agglomerates	42.3	12.9	1.29 - 0.520



(a) 3D Image of Pure Calcite

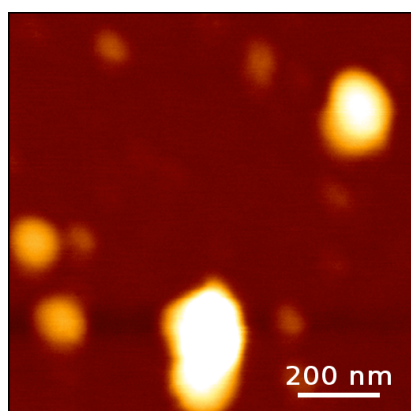


(b) Cross Sectional Line Through Calcite

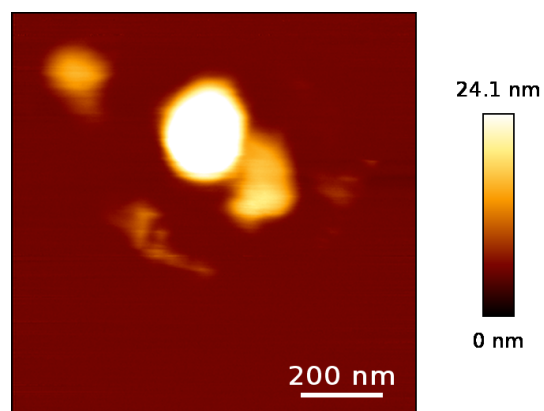


(c) Roughness Graph of Calcite

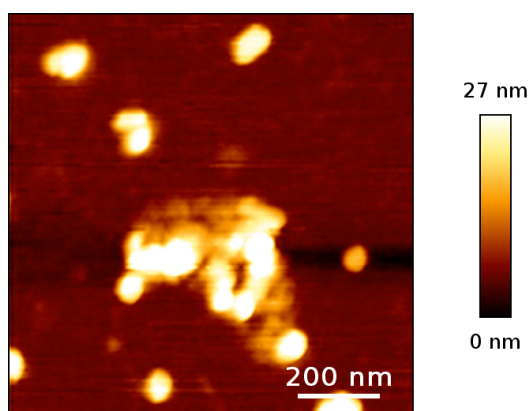
Figure 5.3: 3D Visualisation of Calcite's surface at nano scale, using cross sectional analysis to illustrate the stepped nature of calcite's surface better. (a) 3D Construction of Calcite's Surface at 1 micron; (b) Sectional line through which Graph c was based on; (c) Cross Sectional Graph of Calcite



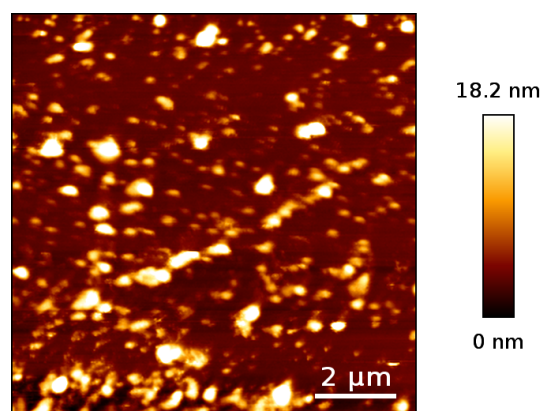
(a) Mica Aged in Crude A 1 micron



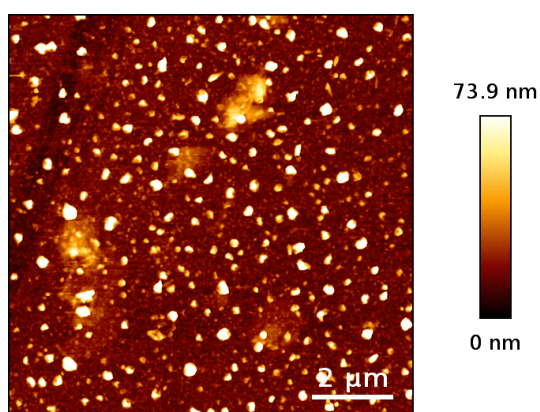
(b) Mica Aged in Crude B 1 micron



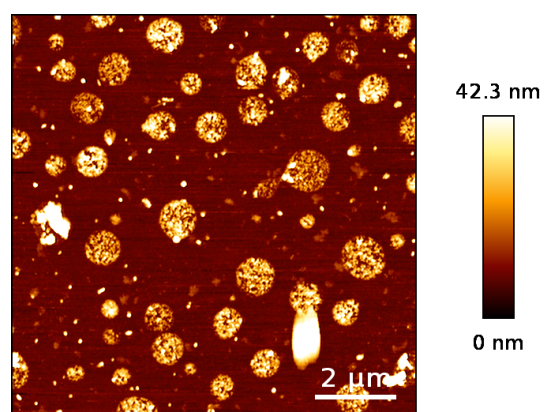
(c) Mica Aged in Crude C 1 micron



(d) Mica Aged in Crude A 10 microns



(e) Mica Aged in Crude B 10 microns



(f) Mica Aged in Crude C 10 microns

Figure 5.4: Height measured maps of mica aged in three separate crude oils of this project, showing the roughness alteration by crude oil on mica's surface and crude oil deposition visualisation on 1 micron and 10 microns scale.

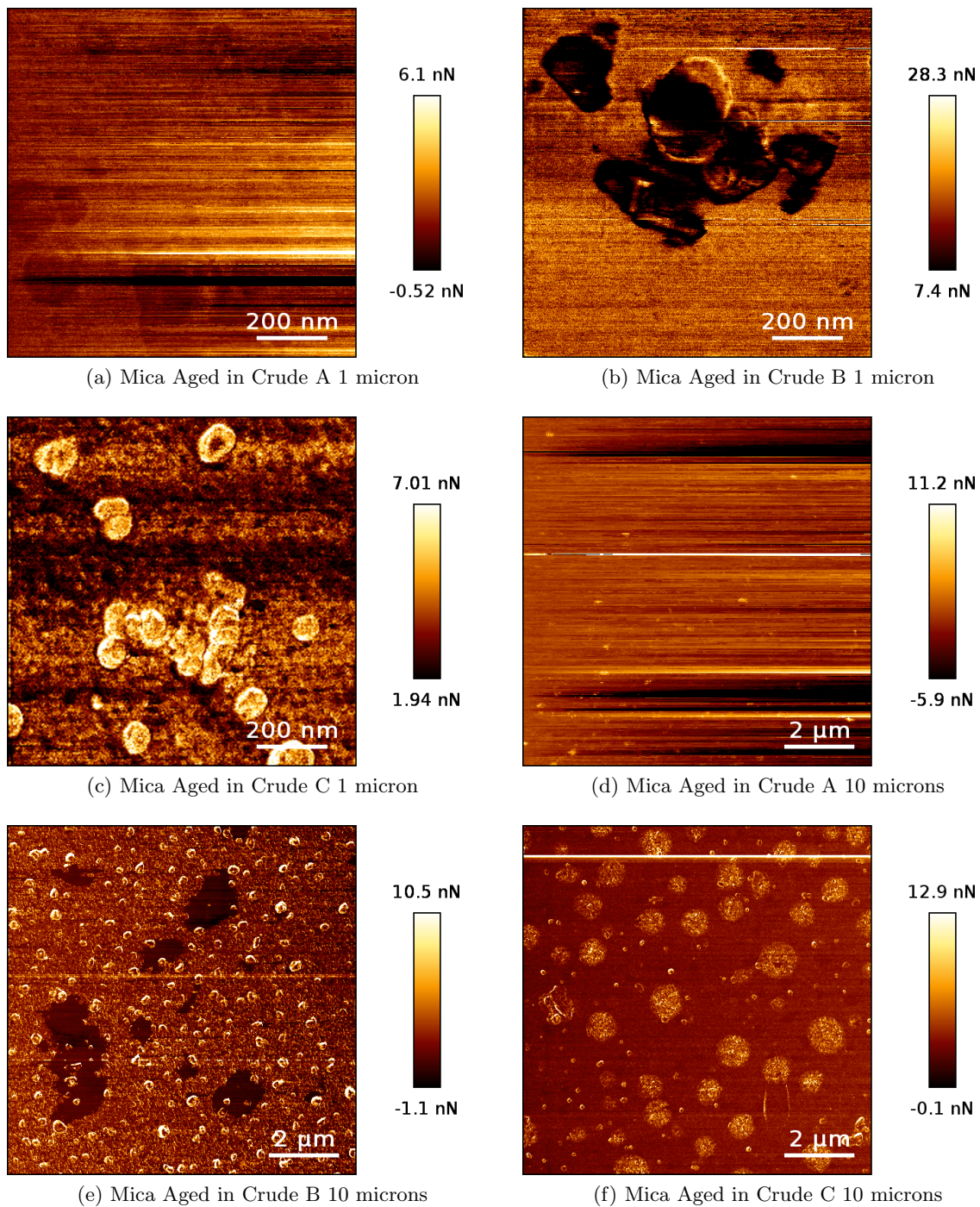


Figure 5.5: Adhesion maps of mica aged in three separate crude oils of this project, showing the adhesion alteration by crude oil on mica's surface specially around crude oil deposits.

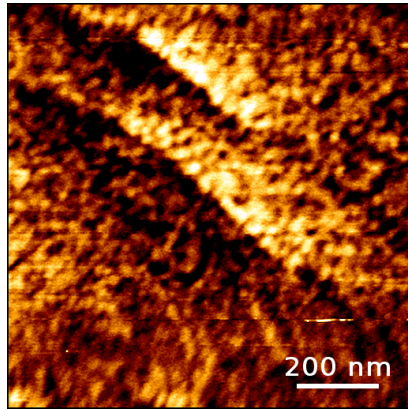
5.4.3 Aged calcite samples

At a larger scale, the surface of the calcite was uniformly covered in crude oil; however, the film itself was not homogeneous, which means that the thickness of the crude oil film varies across the surface of the calcite. This was confirmed by the tip of the cantilever being able to poke a hole through the surface of the film at various points in the films formed by crude oil A and B (similar AFM studies in Imperial College have also observed un-even surface of minerals and metals after being exposed to crude oil and asphaltenes [64]). Crude oil C, however, did not exhibit such behaviour; the surface was uniformly covered by crude oil; however, the thickness of the film was higher at some points than others, as agglomerates were observed on top of the crude film. The small gap in stiffness range across the three crude oils also indicates the uniform coverage of the surface by crude oil.

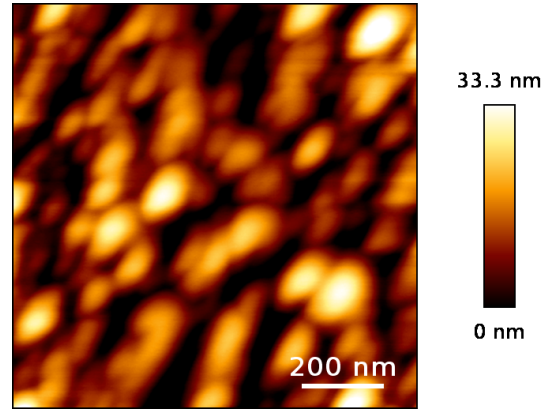
While all three crude oils uniformly covered the surface of calcite, crude oil C formed the thickest layer on the surface of calcite, and this is in agreement with the CII curve indicating crude oil C is the most unstable crude oil and forms the most precipitate from all three crude oils. Crude oil A formed the thinnest film, which is also in agreement with the CII, with crude oil A being the most stable crude oil and crude oil B forming a film between the two crude oils.

Figure 5.6 shows the coverage of the films, whilst figure 5.7 and figure 5.8 show the adhesion maps and stiffness maps of the aged calcite, respectively. Figure 5.6 shows that crude oil A forms the thinnest film on the surface calcite, but it has uniformly covered other calcite surfaces. Crude oil B formed a thicker film than crude oil A (Figure 5.6b and 5.6e), but the film is not as thick as crude oil C. The cantilever can penetrate the film, which becomes evident from the figures 5.6e and figure 5.6f. Crude oil C, however, formed the thickest film and also uniformly covered the surface of calcite; this again confirms that crude oil C is the most unstable crude oil in terms of asphaltene precipitation, and it indeed forms the most aggregates on both mica and calcite.

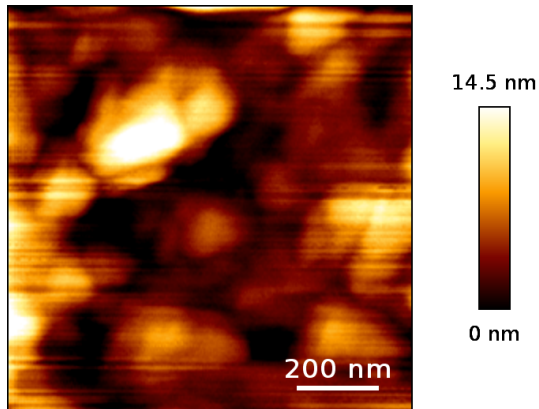
Table 5.7 summarises the most important features observed from crude oil deposition onto calcite at the molecular level, while Table 5.8 summarises the important topographical features of the crude oil deposition onto calcite at ten micron scale. All three crude oils formed a more uniform solid film across the surface of calcite; this is expected as the surface of calcite is positively charged and the forces between the polar components of crude oils and calcite are attractive. The range of stiffness is very small, which also suggests that the surface image was covered by the same material. This is also evident from figure 5.8 and figure 5.7.



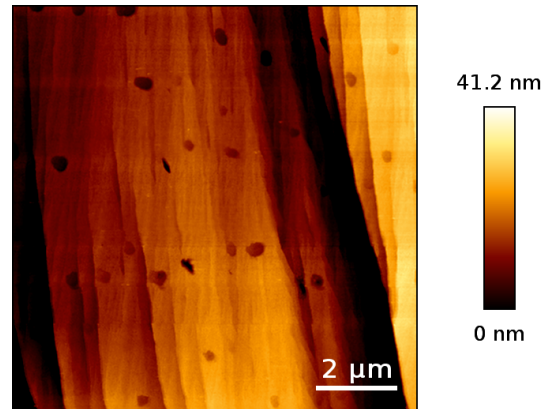
(a) Calcite Aged in Crude A 1 micron



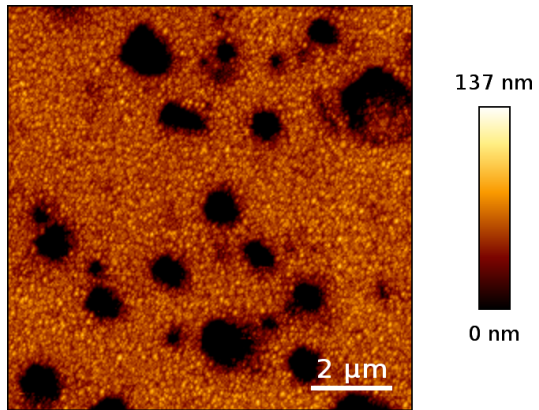
(b) Calcite Aged in Crude B 1 micron



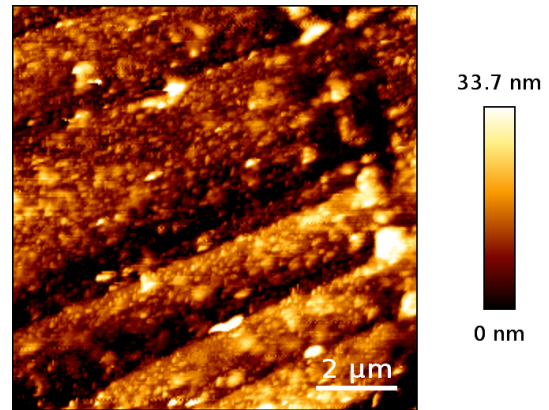
(c) Calcite Aged in Crude C 1 micron



(d) Calcite Aged in Crude A 10 microns

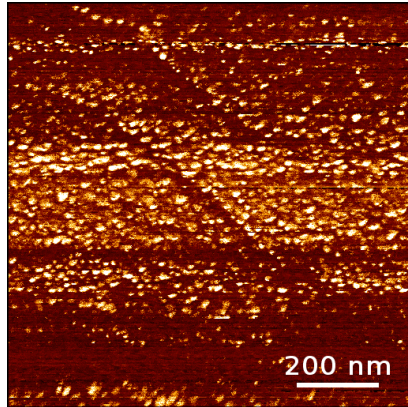


(e) Calcite Aged in Crude B 10 microns

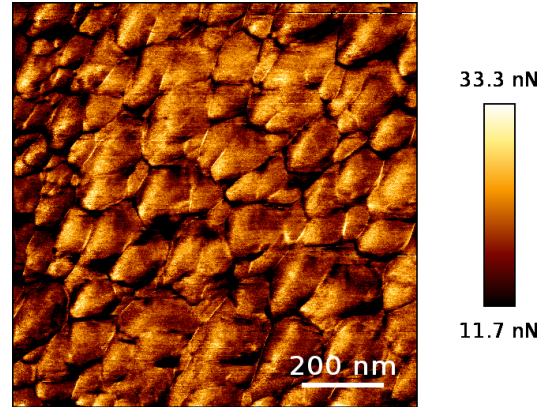


(f) Calcite Aged in Crude C 10 microns

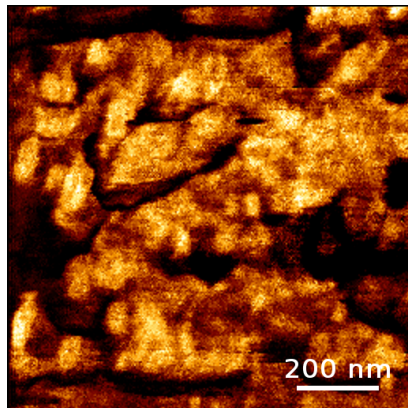
Figure 5.6: Height maps of calcite samples aged in three separate crude oils at $1\mu\text{m}$ and $10\mu\text{m}$



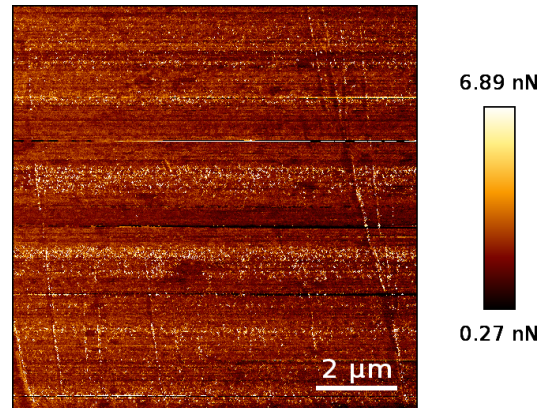
(a) Calcite Aged in Crude A 1 micron adhesion maps



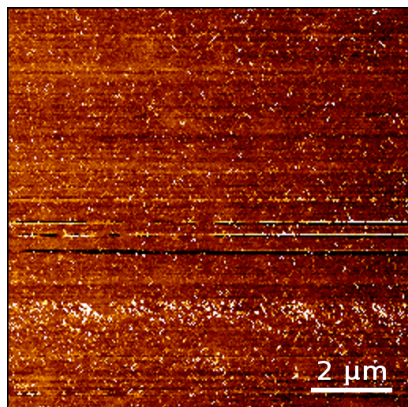
(b) Calcite Aged in Crude B 1 micron adhesion maps



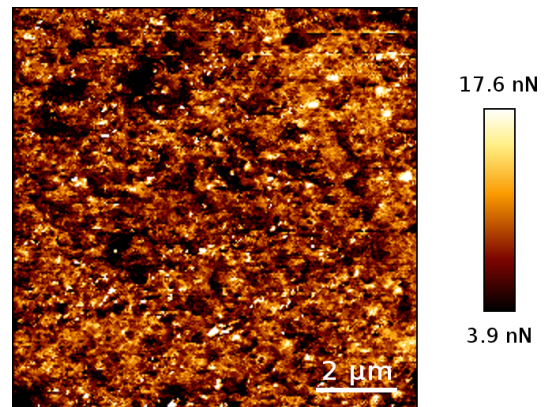
(c) Calcite Aged in Crude C 1 micron adhesion maps



(d) Calcite Aged in Crude A 10 micro adhesion maps

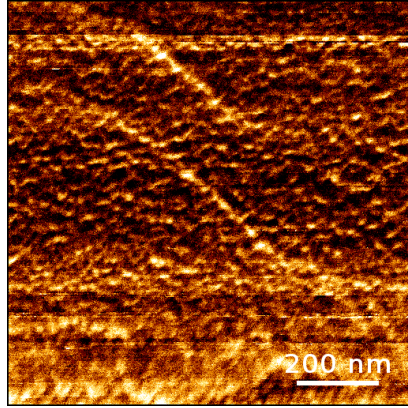


(e) Calcite Aged in Crude B 10 micro adhesion maps

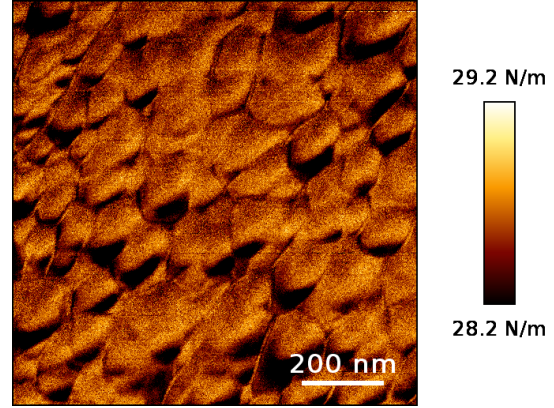


(f) Calcite Aged in Crude C 10 micro adhesion maps

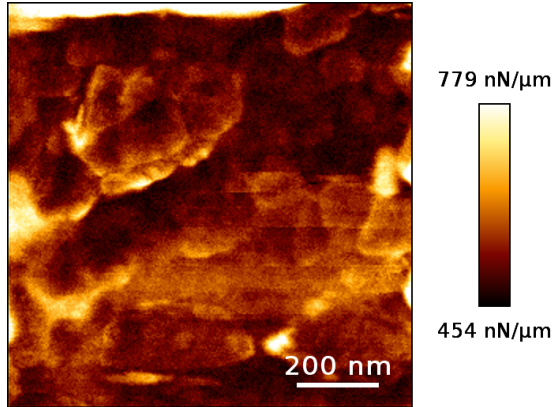
Figure 5.7: Adhesion maps of calcite samples aged in three separate crude oils at $1\mu\text{m}$ and $10\mu\text{m}$



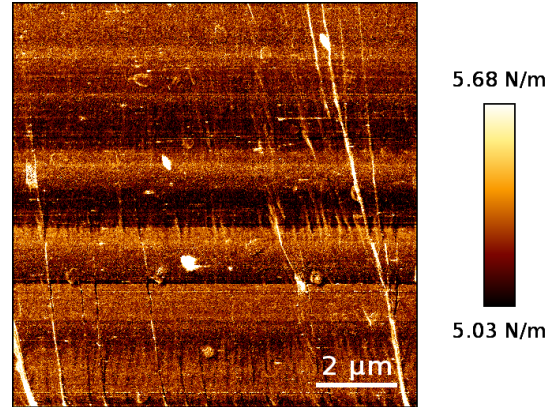
(a) Calcite Aged in Crude A 1 micron stiffness maps



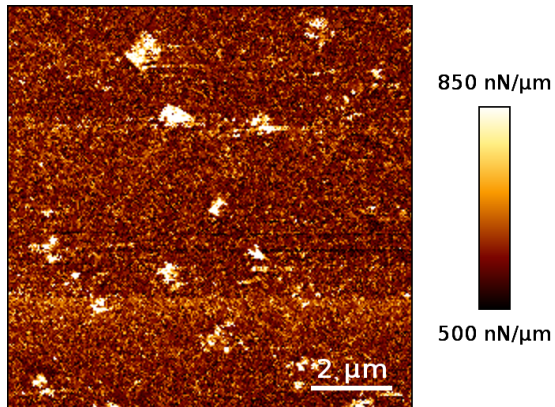
(b) Calcite Aged in Crude B 1 micron stiffness maps



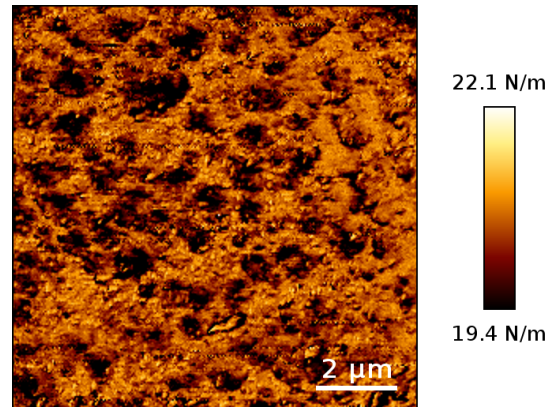
(c) Calcite Aged in Crude C 1 micron stiffness maps



(d) Calcite Aged in Crude A 10 micro stiffness maps



(e) Calcite Aged in Crude B 10 micro stiffness maps



(f) Calcite Aged in Crude C 10 micro stiffness maps

Figure 5.8: Stiffness maps of calcite samples aged in three separate crude oils at $1\mu\text{m}$ and $10\mu\text{m}$

Table 5.7: Summarised quantitative and qualitative AFM gathered data on calcite aged samples on 1 micron scale.

Topographical properties Crude Oils	Coverage Type	Maximum height measured (nm)	Maximum adhesion (nN)	Stiffness range (N m^{-1})
Crude A	Uniform/Agglomerates on thick crude film	2.62	7.96	4.58 - 4.32
Crude B	Uniform/Agglomerates on thick crude film	33.3	44.4	29.2 - 28.2
Crude C	Uniform/Agglomerates on thick crude film	14.5	18.4	1.01 - 0.454

Table 5.8: Summarised quantitative and qualitative AFM gathered data on calcite aged samples-10 micron scale.

Topographical properties Crude Oils	Coverage Type	Maximum height measured (nm)	Maximum adhesion (nN)	Stiffness range (N m^{-1})
Crude A	Uniform/Non-Homogenous	41.2	6.89	5.68 - 5.03
Crude B	Uniform/Non-Homogenous	137	37.1	30.5 - 26.7
Crude C	Uniform/agglomerates seen	33.7	29.1	1.35 - 0.810

5.5 Calcite Crude Film Cross Sectional Analysis

5.5.1 Cross sectional analysis on film formed by crude A

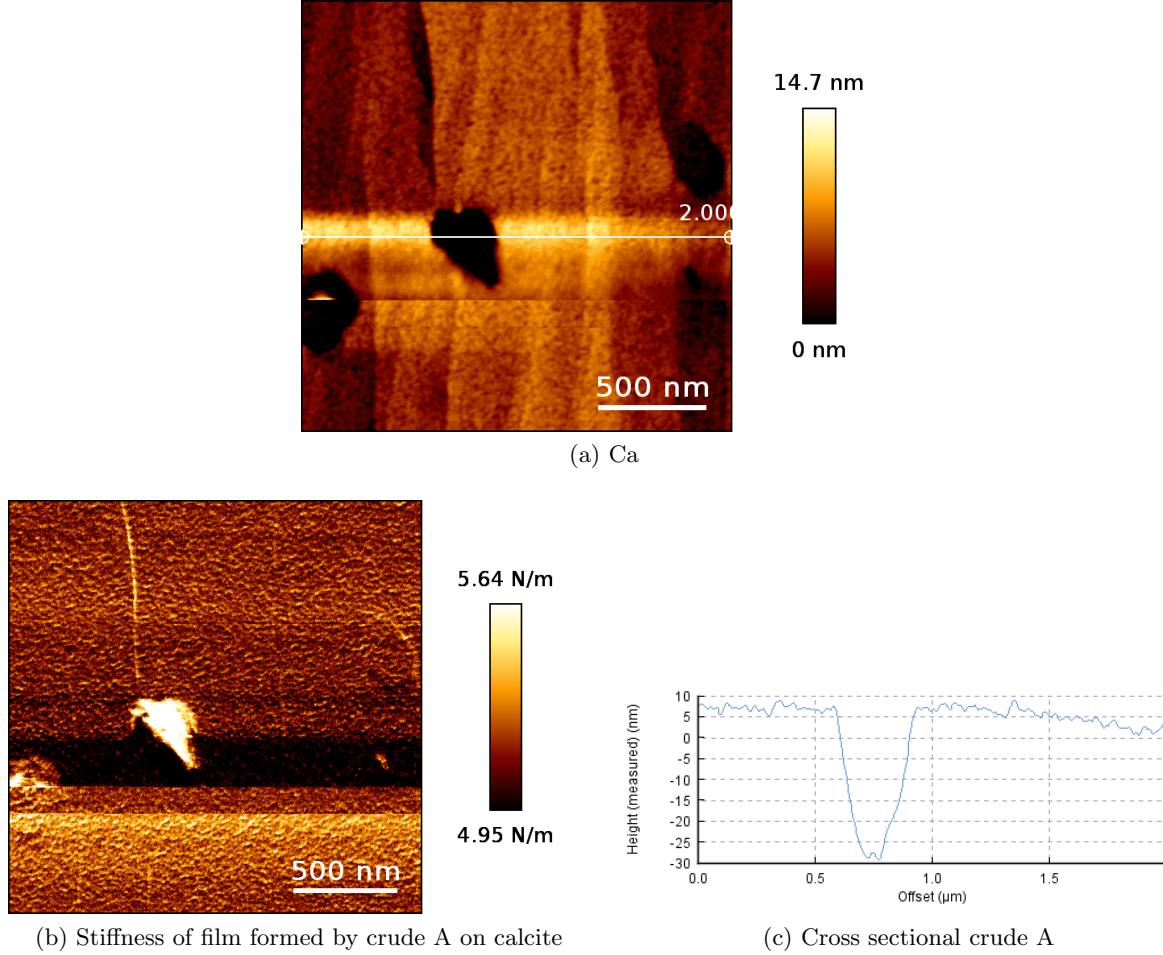


Figure 5.9: Cross sectional analysis performed on hole of crude A film formed on calcite's surface after being aged for a month.

Figure 5.9 (b) shows that the surface is harder where the hole was detected in the crude film, and therefore the cantilever's tip has touched the surface of the calcite at this hole. Therefore, a cross-sectional analysis on this hole gives an estimate of how thick the film formed by Crude A is, and figure 5.9 (c) shows that the depth of the hole detected in the crude film is 35 nm deep.

The film formed by crude A is therefore thinner than the film formed by crude oil B, as illustrated in figure 5.12. This is in agreement with the fact that Crude A is the most stable crude oil out of the 3 crude oils when comparing their stability on the stability curve shown in figure 4.8. Figures 5.10 and 5.11 show the 3D visualisation of the calcite surface aged in crude oil A which help observe the holes at 10 microns more clearly.

3D images of calcite aged in crude A

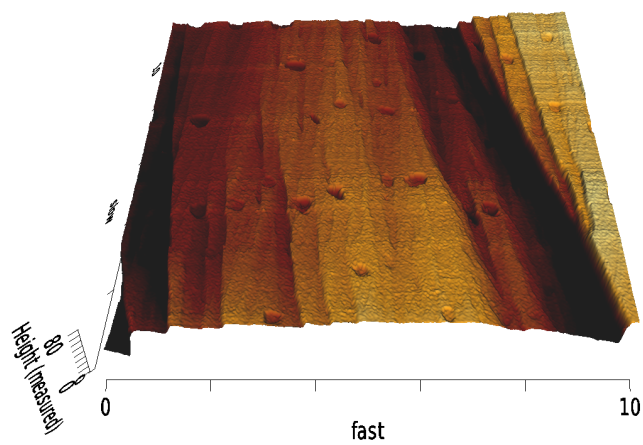


Figure 5.10: 10 micron scale 3D image of calcite's surface aged in crude A

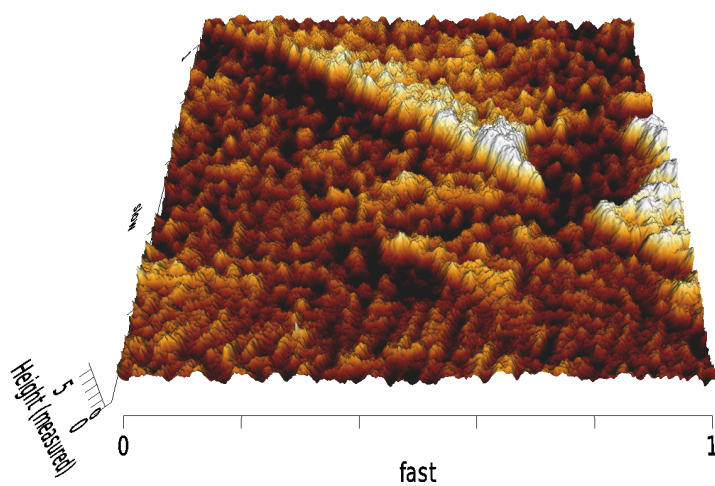


Figure 5.11: 1 micron scale image of the calcite surface aged in crude A

5.5.2 Cross sectional analysis on film formed by crude oil B

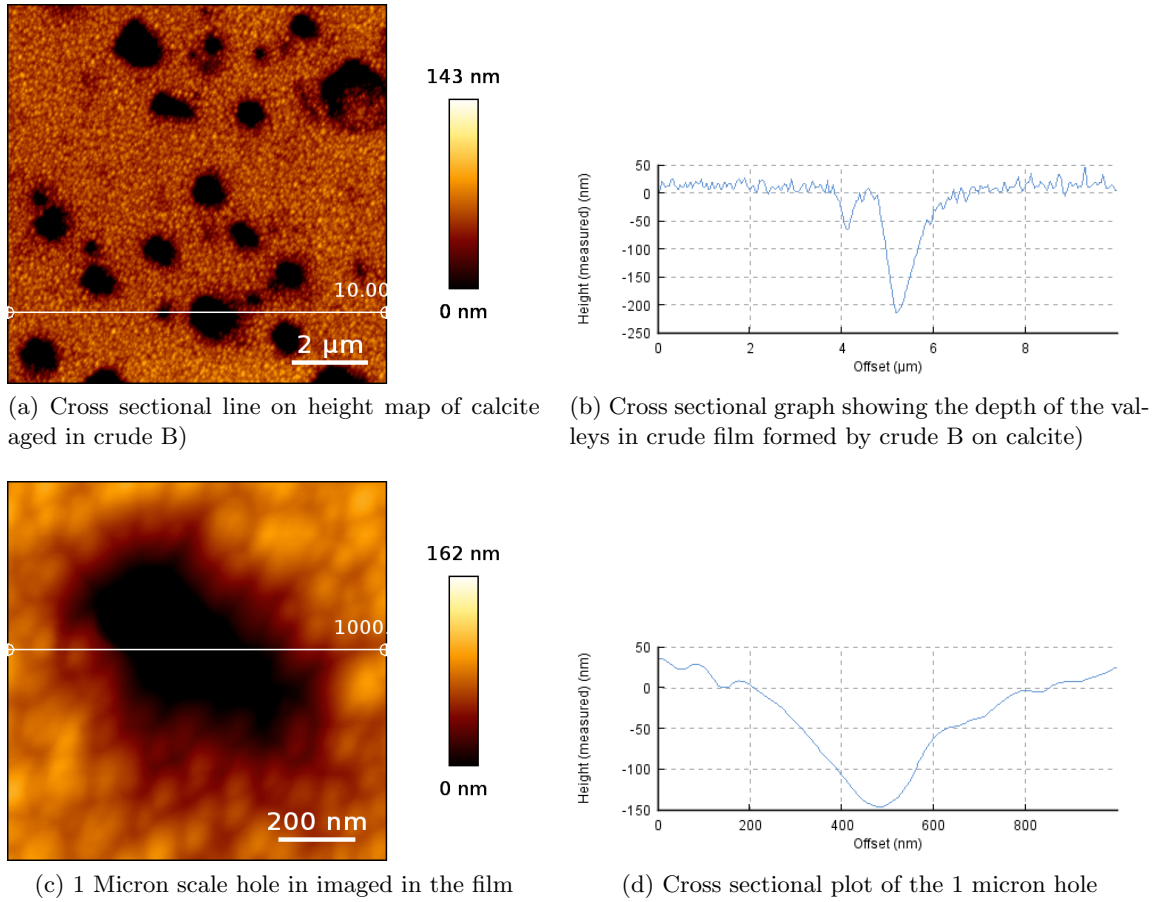
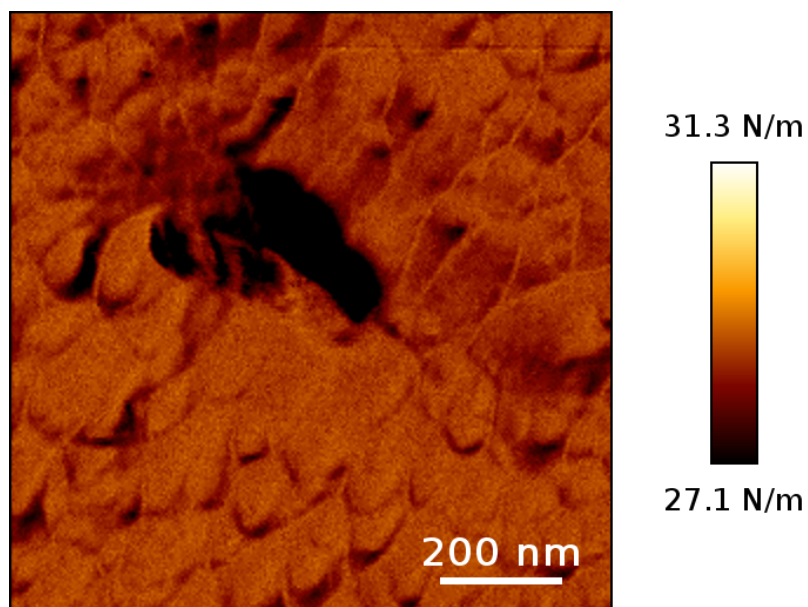


Figure 5.12: Cross sectional analysis of the film formed by crude B on calcite after being aged for a month.

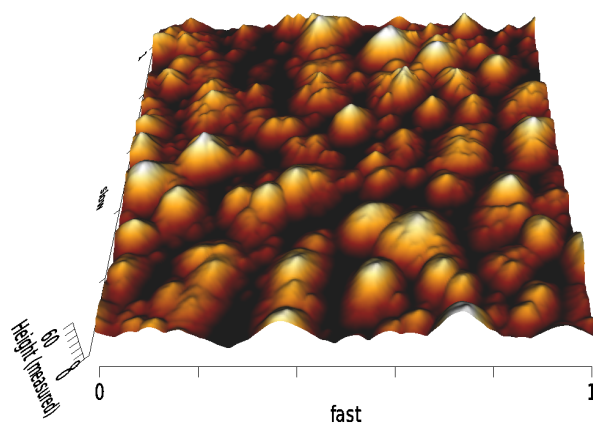
From the cross-sectional analysis conducted on the images shown in figure 5.12, it is evident that although the crude oil uniformly covers the calcite's surface, the film itself is not homogeneous and also not formed of a single layer but rather multiple layers.

Figure 5.12 (c) and figure 5.12 (d) show that crude film formed by crude oil B has a thickness of 200 nm and 150 nm, respectively. The bottom of crude oil B is softer than the bottom of the hole in crude oil A, as found at 1 micron. This confirms that crude oil A forms a thinner film than crude oil B, and this is in agreement with the SARA curve of the three crude oils, indicating that crude oil A is the most stable crude oil out of the three.

Figure 5.13(a) shows that the 150 nm film thickness, which is evident from the cross-sectional plot shown in the stiffness map of crude film formed by crude B on calcite figure 5.12 (d), is not the maximum of the thickness of the crude film since the hole that is closer to the surface of the calcite is not harder than the rest of the surface but rather softer.



(a) Stiffness Map of crude film of crude B on calcite with hole detected at micron scale



(b) 3D 1 micron scale construction of calcite's surface aged in crude B

Figure 5.13: Images obtained via AFM showing the Stiffness of hole observed in crude B film formed on calcite (a) and 3D construction on a 1 micron scale of the film (b)

5.5.3 Cross sectional analysis on film formed by crude C

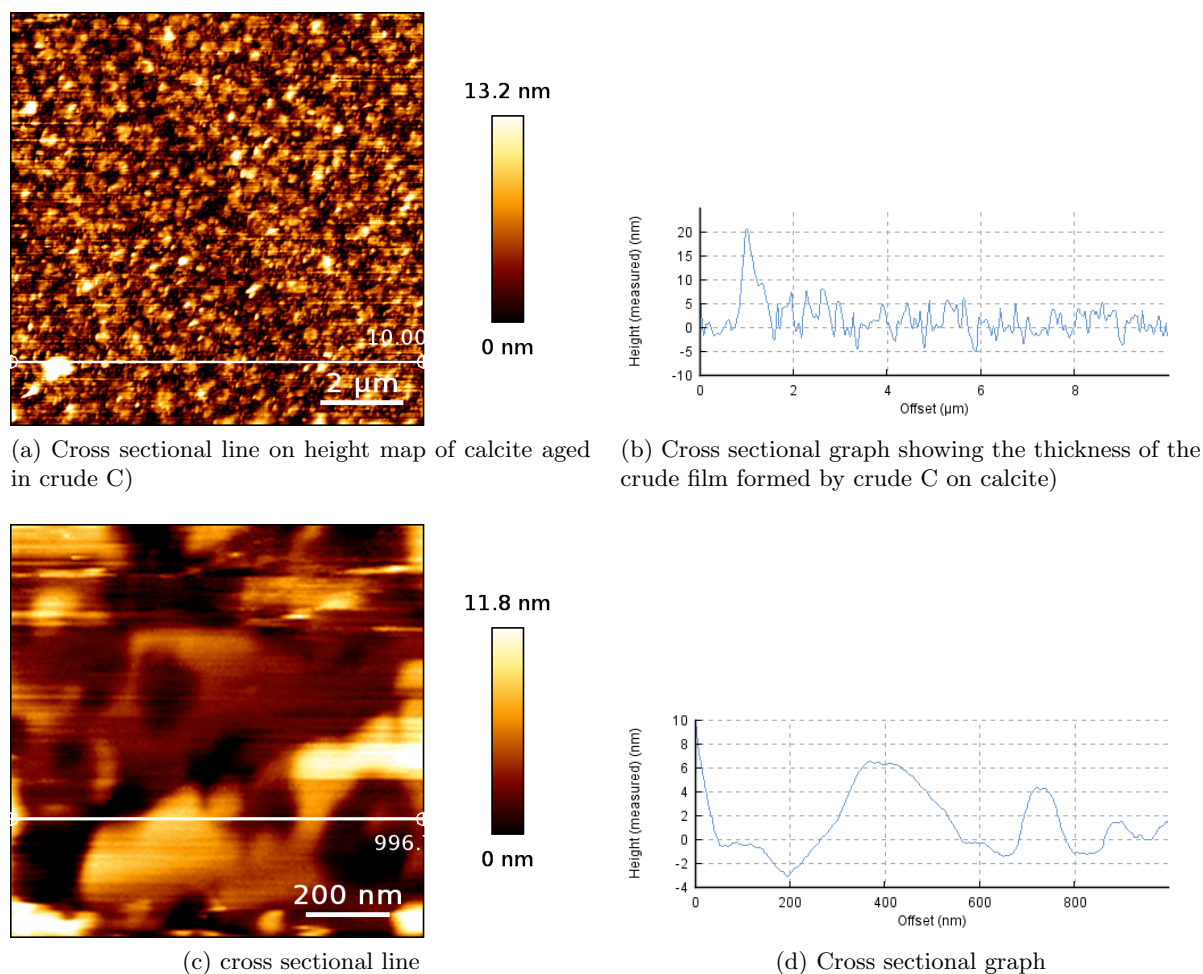


Figure 5.14: Cross sectional analysis of the film formed by crude C on calcite after being aged for a month.

Figure 5.14 shows that the film formed by crude C covered the surface of calcite more uniformly, and although the film is not homogeneous and it is composed of peaks and valleys, there are no clear holes such as seen with crude A and B. Crude C was the only crude that, when diluted and left on the surface of mica to dry, could not be imaged due to the high adhesion it created on the surface of the mica. From the original analysis conducted on all of the crude oils, based on the colloidal instability index of this crude, it was the only crude deemed unstable and prone to more asphaltene deposition. While one can see from this cross-sectional analysis that the crude film is formed of stacks of crude oil agglomerates, it is more difficult to determine the actual thickness of the crude film via this analysis since it does not appear that the underlying surface of calcite is reached, unlike the crude B study above. Figures 5.15 and 5.16 show the topographical feature of calcite surface post-ageing in crude oil C; the 3D representation shows the fact that crude oil C formed excess agglomeration on the surface more clearly to complement

earlier figures.

3D images of calcite aged in crude C

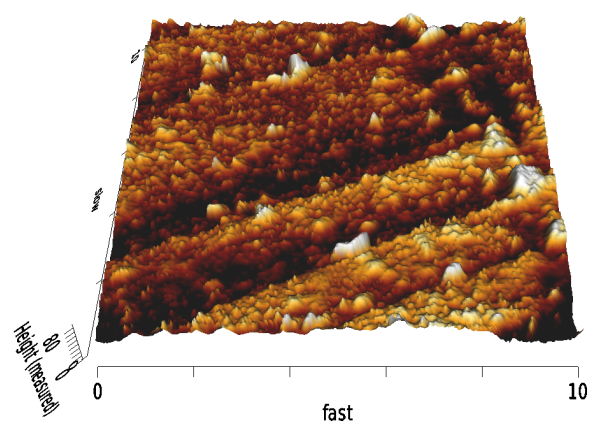


Figure 5.15: 10 micron scale 3D image of calcite's surface aged in crude C

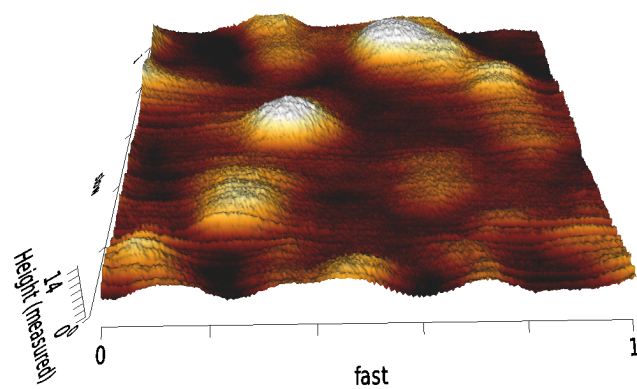


Figure 5.16: 1 micron scale image of the calcite's surface aged in crude C

5.6 Conclusion

Crude oil impacts the surface structure of minerals upon ageing. The mineralogy of a surface plays a key role in determining whether crude oil forms distinct agglomerates across the surface of the mineral or whether the oil deposits cover the surface of the mineral in a uniform manner. Crude oil formed agglomerates across the surface of the mica, whereas the surface of calcite was uniformly covered with a more solid crude oil film. This was largely due to the different surface charges of these minerals.

Different crude oils are broadly similar on the same mineral surface, but slightly different characteristics were observed. For instance, the crude oil film formed by crude A is thinner than crude oil B, but the difference between different crude oils on the same mineral surface is only restricted to the characteristic of the coverage. The key conclusion is that although crude oil uniformly covers the surface of the calcite, the crude oil film itself is not homogeneous. Additionally, the surface charge of the mineral with which crude oil will be in contact plays a key role in whether crude oil covers the surface entirely or not. Crude oil deposits on the surface of the calcite are predominantly asphaltene molecules; they play a key role in facilitating the adsorption of crude oil on the surface of the calcite by altering the wettability of the mineral from water-wet to oil-wet [194].

Crude oil deposition alters the wetting pattern on mineral surfaces; this can impact the flow of fluids, which is highly important from a reservoir engineering point of view [162].

Chapter 6

Serendipitous Discovery of crystals on Mica aged in Crude B in presence of Calcite

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6.1 Introduction

Studying mineral surfaces such as mica and calcite under ageing conditions with crude oil is important in understanding wettability changes occurring because of surface-active components of crude oil. Wettability is a key factor in crude oil recovery and extraction, as it directly impacts the flow of fluids in porous media [194, 33, 49, 50].

Ageing is a common technique within the oil industry research community to mimic the conditions of crude oil reservoirs [234]. The process of ageing requires an ageing cell that can withstand high pressures greater than 100 bar, and the temperature for ageing is 70 °C.

The pressure in the ageing cell rises until it reaches the equilibrium pressure of the crude oil at the temperature set, which is 70 °C. During this investigation, calcite and mica were placed in the ageing cell in crude oil for one month. An atomic force microscope (AFM) was used to image the mineral surfaces, and topographical images of the surfaces of the minerals were produced. Usually, the two surfaces never impact one another; however, in this crude oil, crude B crystals were observed on the surface of the mica when the mica was imaged with AFM.

Upon observing crystals, a scanning electron microscope (SEM) was used to identify the compounds forming the crystals.

The experiment was repeated in the absence of calcite, and no crystals were formed. The ageing was then repeated in the presence of calcite, and it was found that the initial observation of crystals on the surface of mica is reproducible in this crude oil. Mica itself is not frequently found in the reservoir rocks where crude oil is extracted; however, it has very similar properties to that of clay, which is frequently found in The surface chemistry of mica and clays is similar; they are both aluminosilicates. Mica, however, does not swell, but clay does. [186]. Additionally, sandstone reservoirs are predominantly composed of quartz, which is made of silicon dioxide [226]. Quartz and mica have similar surface chemistries and are both negatively charged above a pH of 3. Both have surface hydroxyl groups that are water-wet, with contact angles less than 20 degrees. [72, 169]. Therefore, the findings presented in this study are of particular importance, as crystallisation on the surface of clay in a reservoir would have potentially cost-barring impacts in an industrial setting.

6.2 Materials and methodology

6.2.1 Fluids and minerals

Crude oil

Crude oil B was exclusively utilised in this section's experiments because the formation of the crystals in the mutual presence of calcite in the ageing cell was only observed with crude oil B but not A and C. All of the properties of this crude oil can be found in chapter 4.5. It is worth noting that the results in this chapter were reproducible, and crystals were observed in two separate ageing experiments where the ageing conditions were controlled and the same.

Decalin

Decalin with 98% purity was purchased from Sigma-Aldrich; it was used to remove any non-adsorbed excess crude oil from mineral surfaces post-ageing. This would help prevent asphaltene precipitation once surfaces are placed in decane for imaging under AFM.

Decane

Decane with $\geq 95\%$ purity was purchased from Sigma-Aldrich. Decane is a product of crude oil and was used as the medium under which surfaces were imaged under AFM. Decane carries fewer health risks as opposed to toluene and decalin. Additionally, the media for which the sample is imaged using AFM needs to be clear and transparent to allow for the AFM laser to shine on the back of the cantilever.

Calcite

High-quality Icelandic Spar crystals of calcite from Mexico were purchased from Manchester Minerals UK. The original crystals were a few centimetres in width, length, and height. The original crystals were cleaved along the 1014 plane, using a specially designed blade cleaver, into smaller pieces, which were subsequently cleaved in decane to ensure all exposed surfaces were fresh and contaminant-free.

Mica discs

Mica discs measuring 9.9mm in diameter were obtained from Agar Scientific Ltd., Parsonage Lane, Stansted, Essex. The discs were cleaved in decane to expose a fresh surface before the introduction of crude oil onto the surface. Mica has an atomically flat surface, making it a suitable surface for AFM studies. Additionally, mica has properties like clay minerals found in sandstone reservoirs; therefore, studying mica is of relevance to oil industry research [165, 241, 314, 139].

6.2.2 Atomic Force Microscopy

Unlike traditional microscopes, which use electromagnetic waves such as electrons or photons to produce a magnified image, AFM produces images mechanically. An atomically sharp probing tip mounted on the end of a cantilever is raster-scanned over the surface imaged. The tip is brought close to the surface that is being imaged, and there are various intermolecular interactions between the tip and the surface, such as Van der Waals forces. These forces result in the deflection of the cantilever towards or away from the surface, pending whether nature is repulsive or attractive. These deflections are captured through a laser shining on the back of the cantilever deflecting; they are also recorded on a position-sensitive photodiode. From the signals produced by the photodiode, the computer produces extremely accurate topographical images of the surface down to nano-scale resolution [62, 246].

In this study, we used AFM (Nanowizard 4, JPK Instruments, now Brucker) to image the structure of the mica surface down to nanometer resolution. The measurements were conducted in decane as an imaging medium to minimise noise, and decane is a crude oil product, which is a clear solution. The sample was scanned with a silicon tip (PPP-NCHAuD from NanosensorTM) on a 10 μm x 10 μm area with a resolution of 512 x 512 pixels in quantitative imagingTM mode. The image was levelled, filtered using a median filter, analysed for curvature and roughness, and visualised with JPKSPM data processing software (JPK instruments).

Quantitative imaging mode

In contrast with contact mode, where the tip is raster-scanned over the surface of the sample, QI mode uses a force spectroscopy-like approach. The tip is intended to be inserted into the

surface of the sample with a predetermined force called set point; it spends time in contact with the surface at each pixel, called pixel time, and then the tip retracts to its original pre-set vertical height, called Z-length. This motion results in force curves produced at each pixel, and subsequently, additional quantitative data such as an adhesion map and stiffness map are produced. QI mode has several advantages compared with contact mode imaging. The first is that it produces more quantitative and mechanical data about the sample, such as adhesion and stiffness maps. Additionally, it is the most suitable way to image surfaces that have adsorbed materials loosely attached to the surface as it does not drag the sharp tip of the cantilever across the surface. Such imaging mode is suitable for imaging sticky surfaces such as crude oil adsorbed onto mica, as the adsorbed crude film on the surface of the mica is not damaged [265].

6.2.3 ageing mica in crude oil

Mica discs were cleaved in a decane to ensure no impurities on the surface, then placed in a crude oil solution in an ageing cell. The pressurised cell was then placed in the oven at 70 °C and the pressure of the cell was at 35 bar. The ageing cell was in the oven for a period of 1 month. The aged mica discs were then placed in decalin for 5 minutes and then placed in decane for imaging.

During this study, mica was aged in three different crude oils provided by Shell B. V. The aged mica samples were then imaged using an atomic force microscope, which produced topographical images of the surface of the aged samples. One of the crude oils not only deposited agglomerates of asphaltenes, but crystals appeared on the surface of the mica sample.

6.2.4 Scanning electron microscopy

In order to characterise and identify the mineralogy of the crystals observed on the surface of mica, scanning electron microscopy was utilised. The equipment used in gathering the SEM data set for this project was a Thermo Fisher Scientific Quanta FEG 650F SEM equipped with two Bruker X-Flash 6/30 electron dispersive spectra detectors, which aided in energy dispersive X-ray (EDX) analysis. Electrons are fired at the surface, X-rays are emitted, and the wave length of curves depends on the element from which they were emitted.

Image processing was done through Maps Min, and the spectra data was processed by

Nanomin, which is part of the software package within the Thermo Fisher Scientific suite. X-ray scanning combined with mineral deconvolution algorithms is what this processing method utilises, therefore allowing imaging along with mineral identification content as well as generating high-resolution mineral maps with quantification [239].

Selection and identification of areas of interest are commissioned via Nanomin, which allows identification of compositional differences. This allows isolating individual elements and minerals so that their spatial configurations can be mapped. A BSE background layer can also be used to map and identify an undetermined BSE mineral [239].

Therefore, overlaying a Nanomin mineral map on an SEM BSE image enables the identification of the mineral composition of the crystals imaged. Thus, the SEM-EDX analysis used as part of this project is an extremely useful tool for mineral identification. The SEM experiments and their data were done by Shell B.V., and Dr. Fons Marcelis conducted further SEM experiments on the aged mica disc with crystals formed on it in order to identify their mineralogy.

6.3 Results and discussion

6.3.1 imaging surface of mica prior to ageing

As seen in Chapters 4 and 5, mica has a flat surface at the nanoscale; the surface does not have any agglomerates or crystal-like features prior to being exposed to crude oil in the presence of calcite. There can be dust particles that may look similar to an agglomerate of crude oil deposit, but they are much shorter in height and width, and no adhesion energy features or stiffness are recorded for such contaminant or dust particles on mica's surface. In order to make a characteristic comparison between mica's pure surface and its being aged, table 6.3 summary is being used.

Table 6.1: Summarised quantitative and qualitative AFM gathered data on pure mica sample imaged in decane.

Scale \ Topographical properties	Surface features	Maximum height measured (nm)	Maximum adhesion (nN)	Stiffness range (N m^{-1})
10 microns	Flat	1.95	2.5	0.741 - 0.487
1 micron	Flat	1.82	2.27	0.678 - 0.450

6.3.2 Impact of ageing on surface of the mica in absence of calcite

Upon ageing in crude oil, spherical agglomerates appeared over the surface of mica. Rather than observing a uniformly covered mica disc, the crude was deposited in spherical agglomerates. This is due to the fact that mica is negatively charged, as are the crude oil polar fractions, i.e., asphaltenes and resins; therefore, in order to minimise the contact surface, the crude particles form a sphere. The surface of mica post-ageing became more adhesive, which is a result of the presence of crude particles. To understand the impact of ageing on mica, mica discs were cleaved in decane and, following ageing, washed with decalin and imaged in decane.

From figure 6.1 and figure 6.2, which are height-measured maps of the aged mica disc in the absence of calcite in the ageing cell, it is evident that without any calcite present in the ageing cell, only crude oil deposits in the form of distinct spheres are formed as a result of repulsive charge interactions between negatively charged mica's surface and the negatively charged crude oil molecules, i.e., resins and asphaltenes (crude oil is negatively charged due to the presence of the carboxylic acid groups [56]). Figures 6.3 and 6.4 are the adhesion maps of the aged mica, which show that the aggregates of crude B are more adhesive than the surface of mica, which is expected and thus verifies the results obtained. Figures 6.5 and 6.6 represent the stiffness maps of the same area shown in height maps and adhesion maps. They reveal that the aggregates have a stiffness between 0.395 and 0.885 nM/ μ m.

Table 6.2: Summarised quantitative and qualitative AFM gathered data on Mica aged samples on 1 micron scale.

Topographical properties Scale	Coverage Type	Maximum height measured (nm)	Maximum adhesion (nN)	Stiffness range (N m ⁻¹)
10 micron	Agglomerates of crude oil spherical	74	10.5	1.51 - 0.440
1 micron	Agglomerates of crude oil spherical	77.9	12.8	0.885 - 0.395

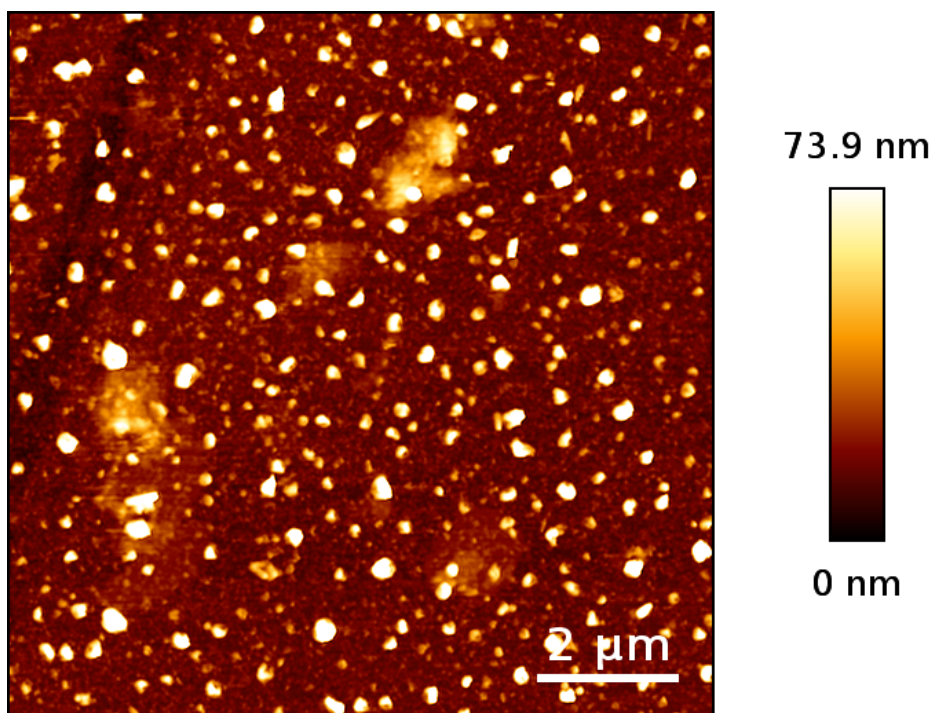


Figure 6.1: Height maps of mica aged in Crude Oil B, without Calcite present in the ageing cell, the mica was then washed with decalin to remove any excess crude from the surface of mica and then imaged in decane. 10 Micron scale

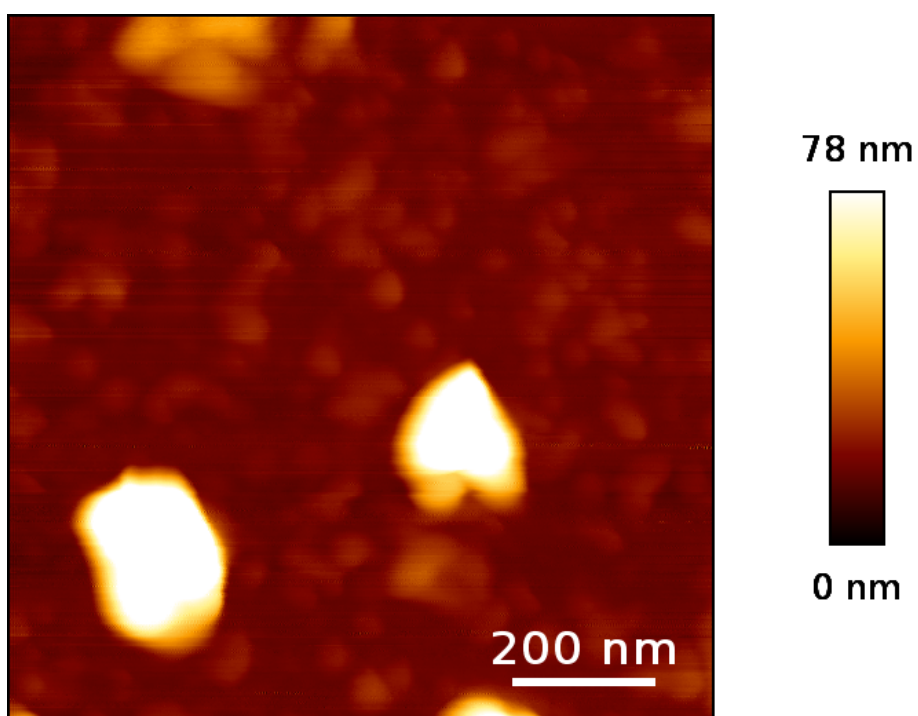


Figure 6.2: Height maps of adhesion map of mica sheet aged in crude B in absence of calcite in ageing cell. 1 micron scale

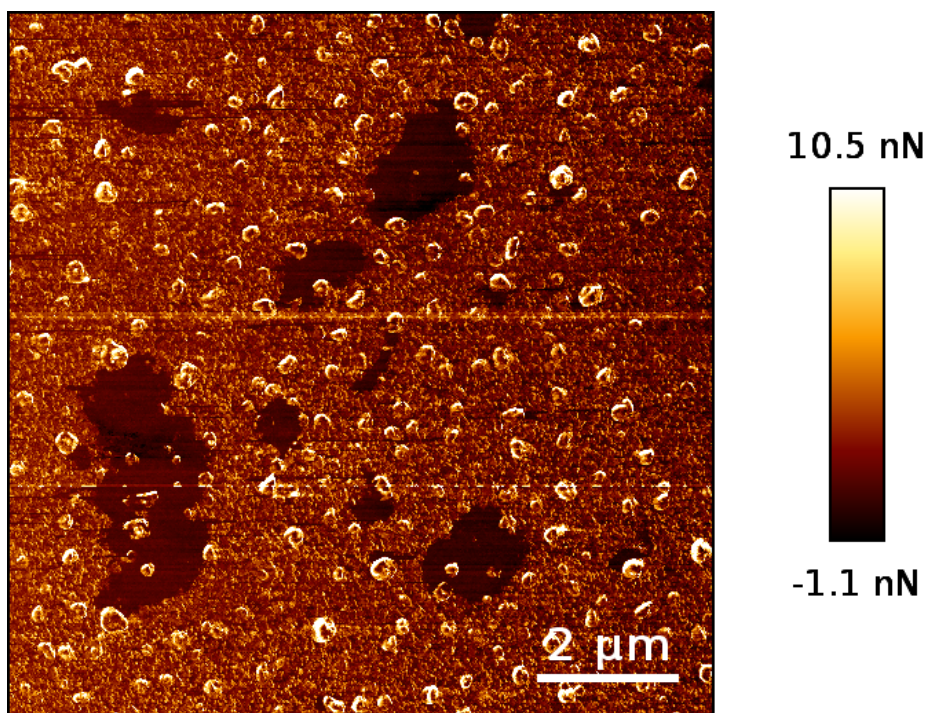


Figure 6.3: Adhesion map of mica sheet aged in crude B in absence of calcite in ageing cell. 10 micron scale

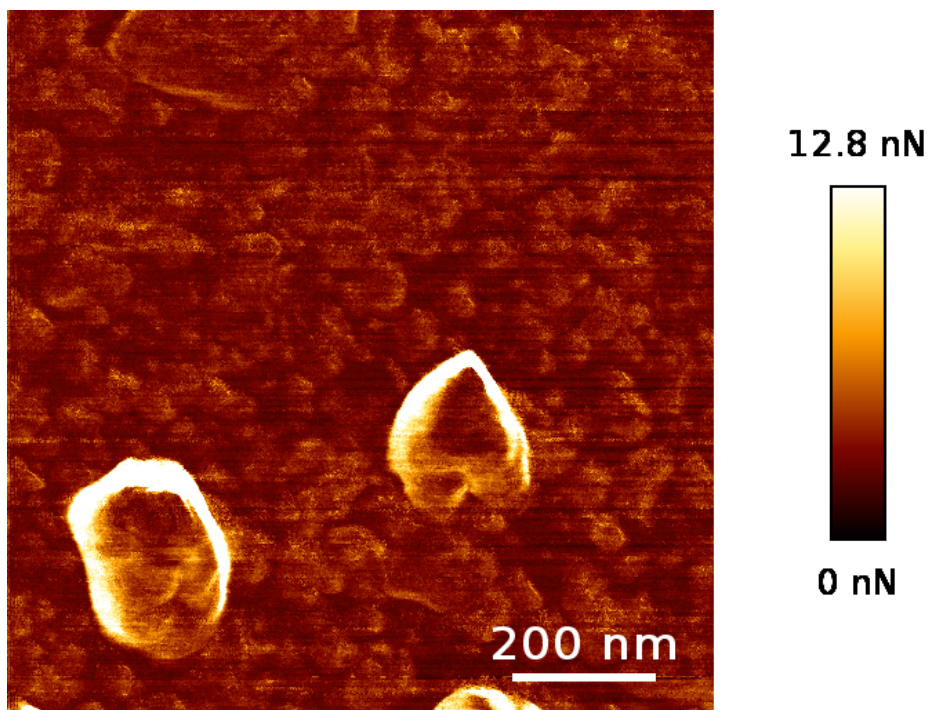


Figure 6.4: Adhesion map of mica aged in Crude Oil B, without Calcite present in the ageing cell, the mica was then washed with decalin to remove any excess crude from the surface of mica and then imaged decane. 1 Micron scale

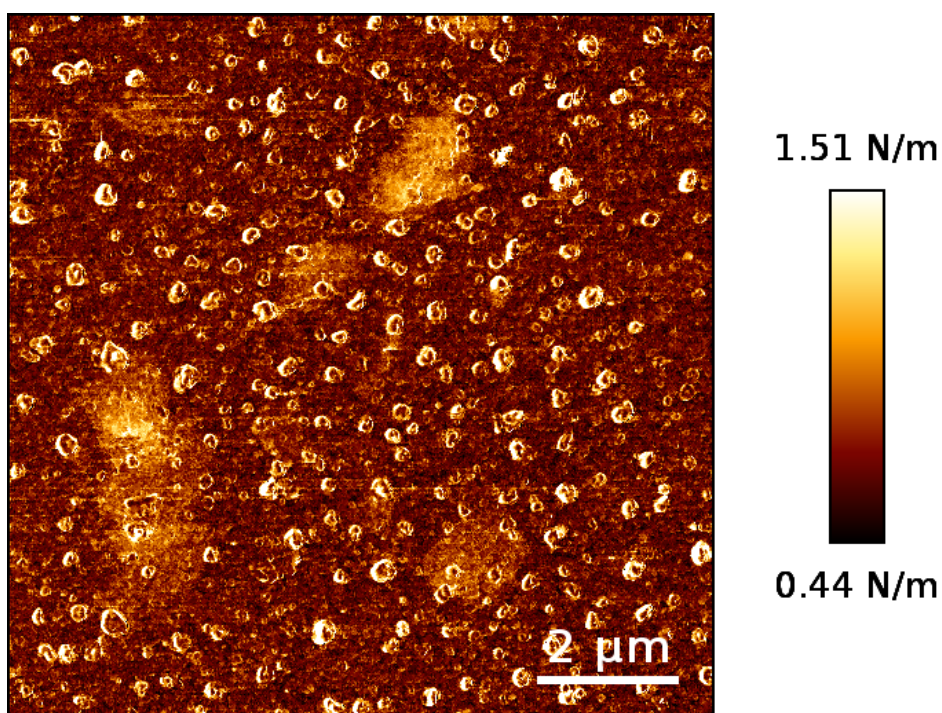


Figure 6.5: Stiffness map of aged mica sheet in crude oil B in absence of calcite crystals in the ageing cell imaged in decane under AFM at 10 micron scale

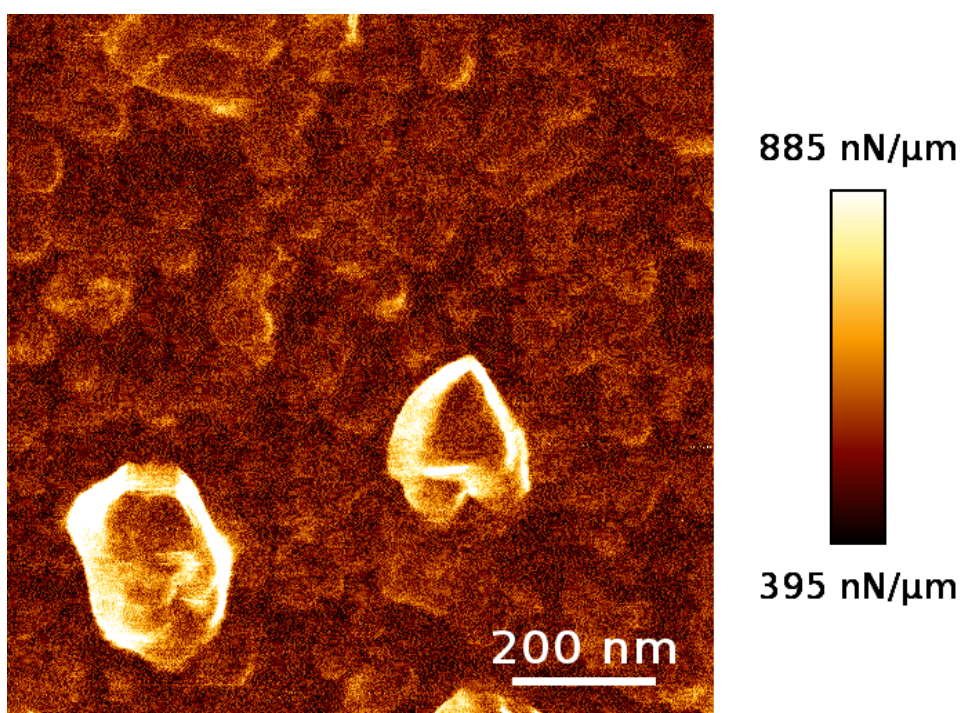


Figure 6.6: Stiffness map of aged mica sheet in crude oil B in absence of calcite crystals in the ageing cell imaged in decane under AFM at 1 micron scale

6.3.3 Formation of crystals on surface of mica in presence of calcite in ageing cell

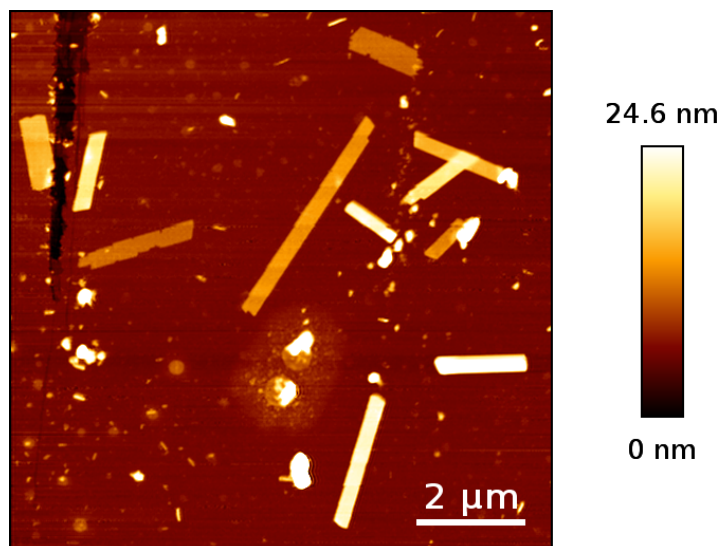
Once calcite was also placed in the ageing cell along with mica discs, not only asphaltene agglomerates were seen, but fine needle like shaped crystals were observed across the surface of mica. These crystals came in different sizes but were consistent in shape. The SEM images (see figures 6.14,6.13) reveal that the crystals contained calcium and sulphur, which indicated these crystals are most likely to be gypsum. In some instances, the crystals looked hexagonal; in others, they looked like a parallelogram. This is not because they are different in shape; rather, because of the plane in which they are lying differently on the surface of the mica. Figures 6.7,6.8 and 6.9 present the topographical features, adhesion maps, and stiffness maps of areas of mica imaged with crystals found at 10 microns and 5 microns scale.

Figures 6.8 and 6.9 confirm what we observe from the topographical map. The adhesion maps presented in figure 6.8 also show that the adhesion of the tip to the crystals is stronger than that of the substrate. Similarly, it is worth noting that the crystals appear slightly harder than mica, as they appear brighter in the stiffness map images presented in figure 6.9.

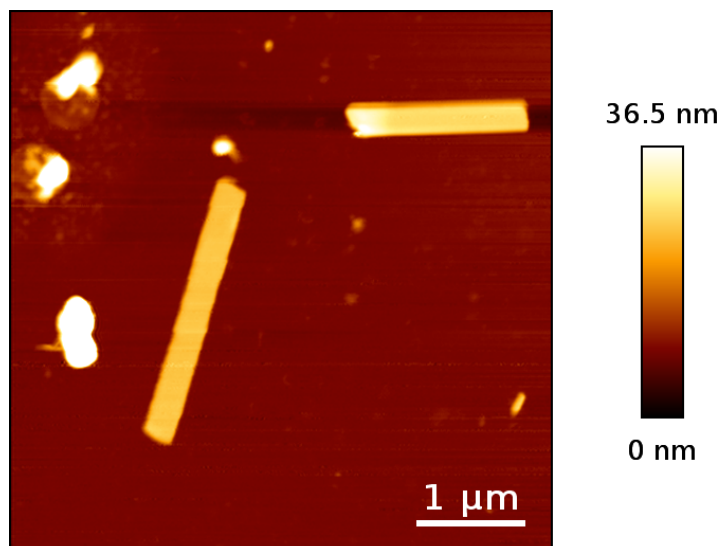
Figure 6.8 c is the adhesion map of the crystals at 5 micron scale. From the data on this map, a histogram was built, which showed the average adhesion force of the surface was 7.509 nN. The most adhesion is indeed on the surface of the crystals, which ranges from 22–27 nN. This may not be because the crystals are adhesive, but rather because the crude oil film covers the crystals in more adhesive areas. The maximum adhesion force of the surface captured for these samples was higher than that seen in pure and aged mica in the absence of calcite. Gypsum crystals are positively charged, and so are calcite crystals. Thus, more crude oil deposits are formed on the surface of these crystals and more on the overall surface of the calcite.

Table 6.3: Summarised quantitative and qualitative AFM gathered data on Mica aged samples on at different scales.

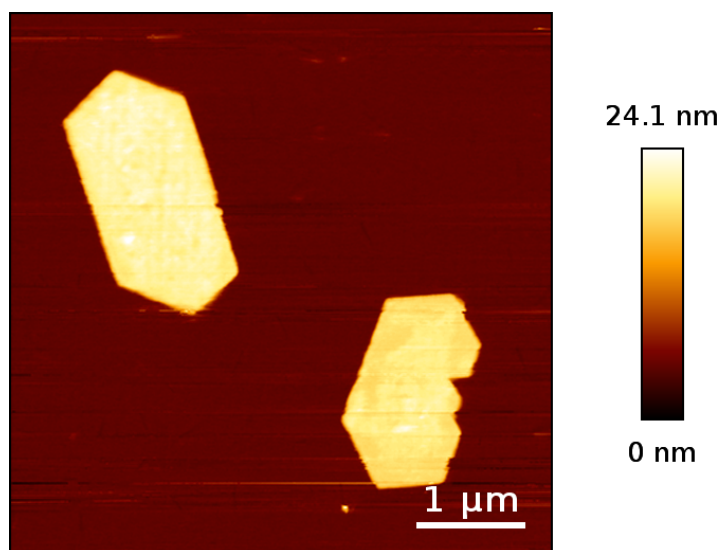
Scale \ Topographical properties	Coverage Type	Maximum height measured (nm)	Maximum adhesion (nN)	Stiffness range (N m^{-1})
10 microns	Distinct crystals crude oil Distinct crystals	24.6	34.7	12.1 - 10.2
5 microns	Agglomerates crude oil Distinct crystals	36.5	36.8	11.8 - 10.2
5 microns	Distinct crystals crude oil Distinct crystals	24.1	22.1	12.5 - 11.4



(a) Height Measured Map of Mica with crystals 10 microns

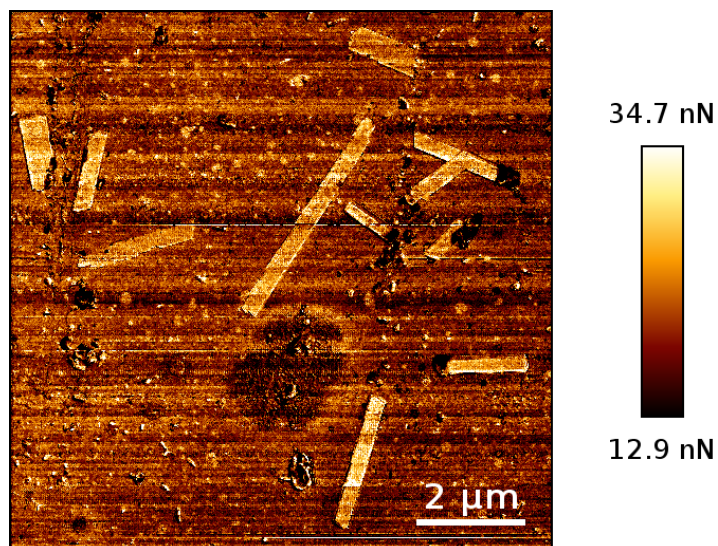


(b) Height Measured Map of Mica with crystals 5 microns

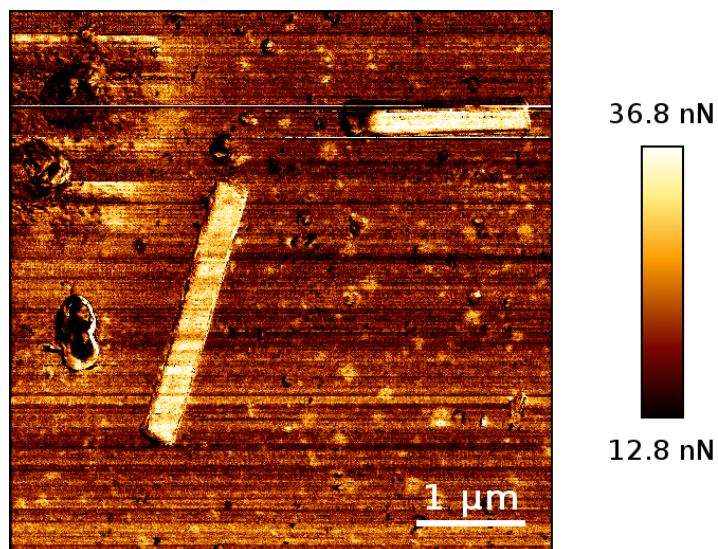


(c) Height Measured Map of Mica with crystals 5 microns

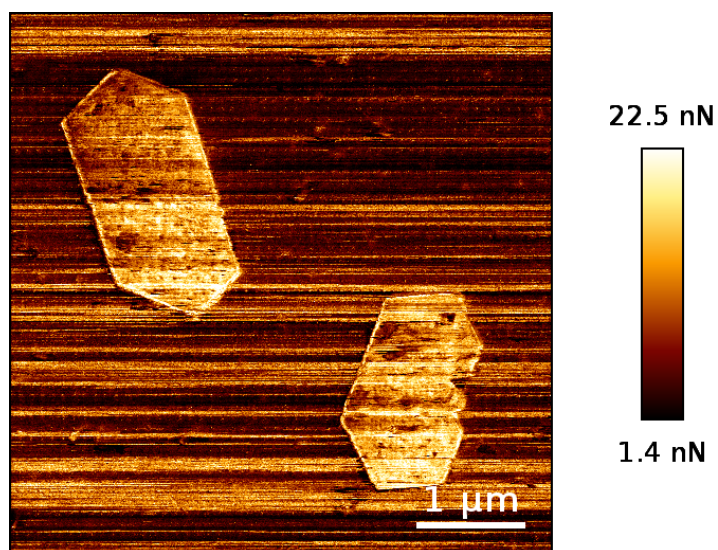
Figure 6.7: Height measured of mica aged in crude oil B in presence of calcite, crystals observed.



(a) Adhesion map of Mica with crystals 10 microns

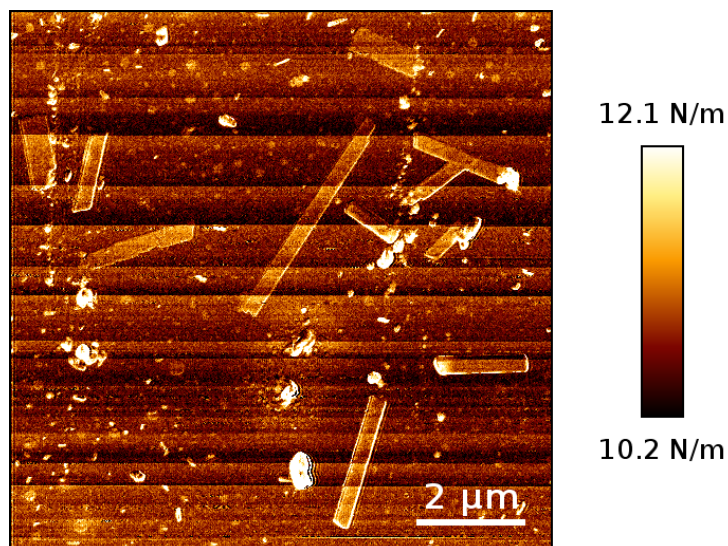


(b) Adhesion map of Mica with crystals 5 microns

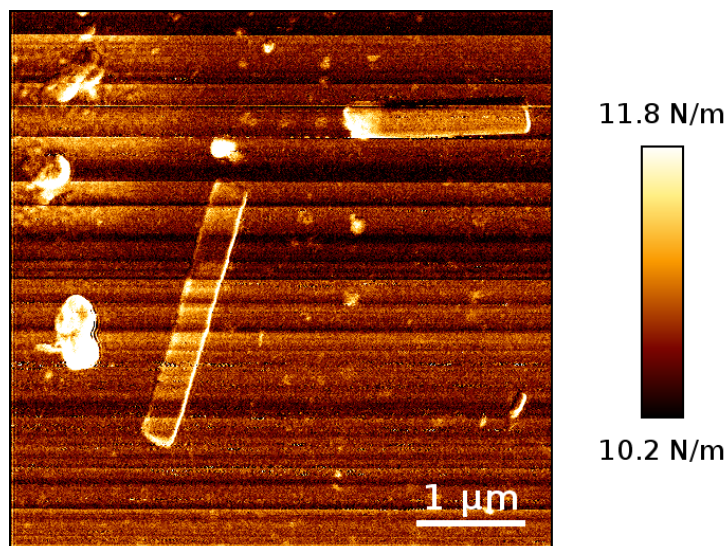


(c) Adhesion map of Mica with crystals 5 microns

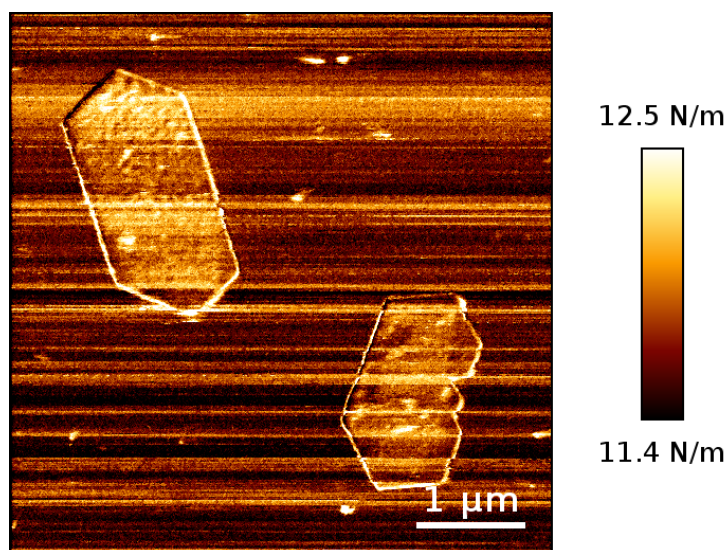
Figure 6.8: Adhesion map of mica aged in crude oil B in presence of calcite, crystals observed.



(a) Stiffness map of Mica with crystals 10 microns



(b) Stiffness map of Mica with crystals 5 microns



(c) Stiffness map of Mica with crystals 5 microns

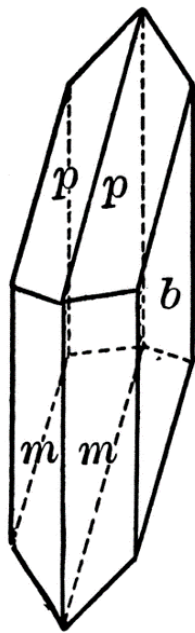
Figure 6.9: Stiffness map of mica aged in crude oil B in presence of calcite, crystals observed.

6.3.4 Crystals dimensional and cross-sectional analysis

The crystals varied in shape depending on the plane on which they were imaged, and their size also varied as they grew to different sizes on the surface of the mica. However, the stiffness of these crystals was always in the same range, indicating that the material they were made of was the same. Cross-sectional analysis using the JPKSPM data processing software (JPK instruments) allows the dimensions of a particular crystal found in the image to be measured. Cross-sectional analysis of a crystal imaged on a $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$ scale image revealed the following dimensions for the crystal: height: 20 nm, length: 800 nm, and width: 275 nm. Table 6.4 summarises the cross-sectional analysis data presented in figures 6.11 and 6.12.

Table 6.4: Cross sectional analysis of crystals on mica

Scale	Surface features	Maximum height measured (nm)	Maximum Width (μm)	Length range (μm)
5 microns	Hexagonal	15	1.235	2.426
1 micron	Parallelogram	20	0.300	0.875



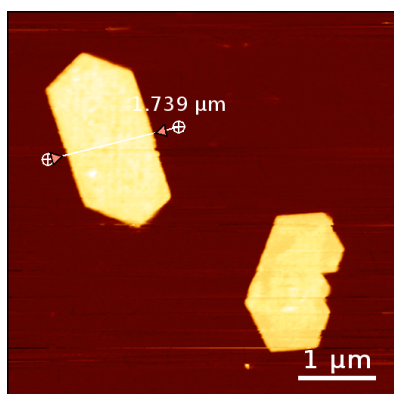
(a) Various planes of gypsum crystals. [3]



(b) Gypsum crystals at large scale. [4]

Figure 6.10: Figures a and b show the actual gypsum crystals grown at large scale visible to naked eye whilst showing various planes the crystals can lie on.

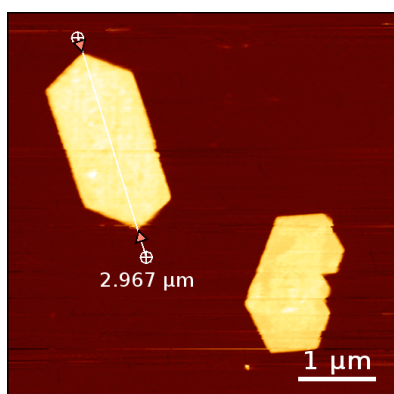
Figure 6.10 (a) shows that the gypsum crystal has various planes it can lie on, and thus, in some instances, a hexagonal crystal plane was recorded and in other instances, a parallelogram.



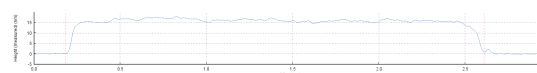
(a) Cross sectional line on height map of calcite aged in crude C)



(b) Cross sectional graph showing the thickness of the crude film formed by crude C on calcite)

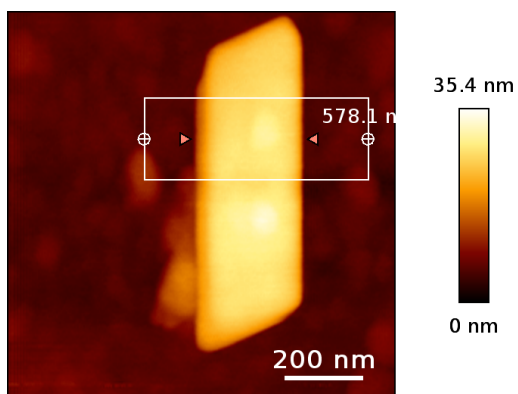


(c) cross sectional line

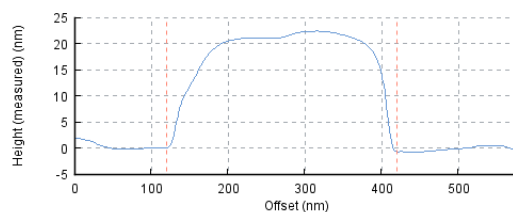


(d) Cross sectional graph

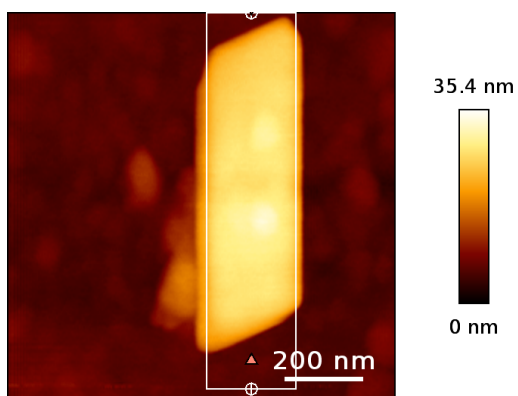
Figure 6.11: Cross sectional analysis of the film formed by crude C on calcite after being aged for a month.



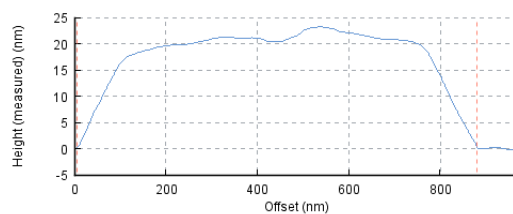
(a) Cross sectional line on height map of calcite aged in crude C)



(b) Cross sectional graph showing the thickness of the crude film formed by crude C on calcite)



(c) cross sectional line



(d) Cross sectional graph

Figure 6.12: Cross sectional analysis of the film formed by crude C on calcite after being aged for a month.

6.3.5 Mineralogy of crystals through SEM

SEM images confirmed the results obtained from the earlier AFM experiments, as the crystals were observed on the SEM images. The EDX images can reveal the chemical nature of the crystals and show that they are made of sulphur and calcium. It is proposed that the crystals are most likely gypsum.

SEM and EDX images revealed that the crystals are made of sulphur and calcium. Figures 6.14 and 6.13 help identify the crystals as gypsum. Chemically, gypsum is calcium sulphate dihydrate, which is a soft sulphate mineral; hence, in the stiffness maps obtained from AFM, they are of similar hardness as mica and even crude oil deposits.

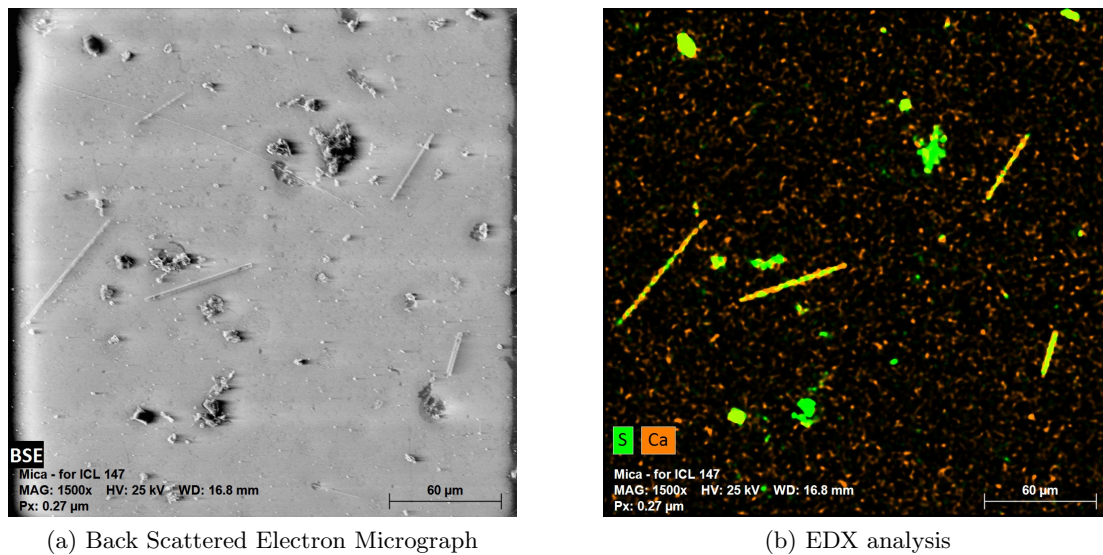
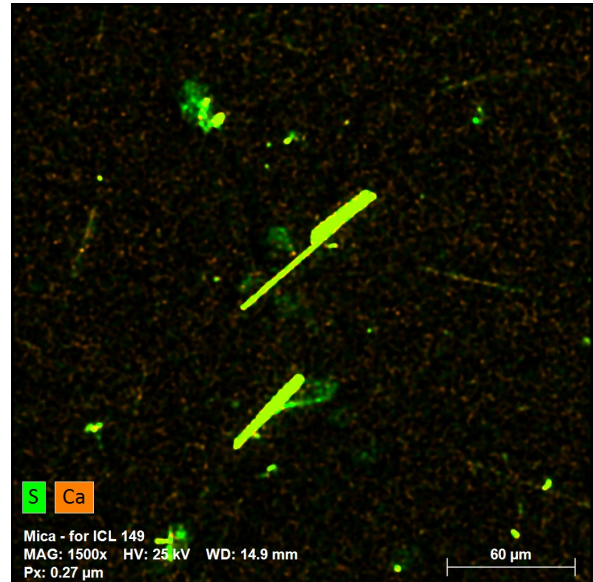


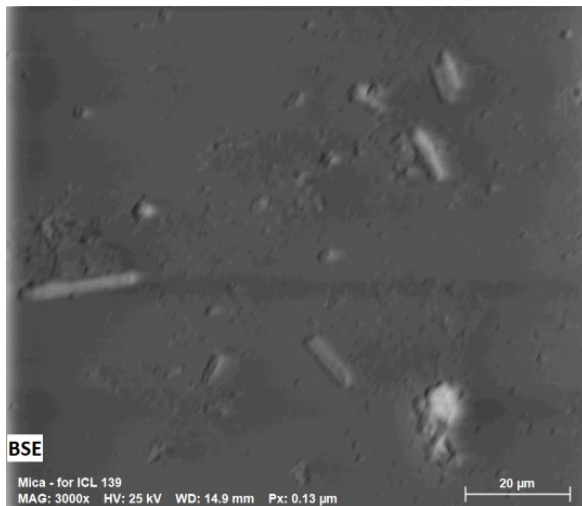
Figure 6.13: SEM image of the crystals with BSE background layering revealing the composition of the crystals observed. 60 microns scale



(a) Back Scattered Electron Micrograph



(b) EDX analysis



(c) Back Scattered Electron Micrograph



(d) EDX analysis

Figure 6.14: Back Scattered electron images obtained via SEM along with their EDX analysis of the crystals seen on the mica sample.

6.4 Conclusion

Ageing alters the topographical features of mica at the nanoscale. The formation of distinct agglomerates on the surface of mica is a result of the precipitation of surface-active components of crude oil; they are known to have the capability to alter the wettability of the mineral [194].

Additionally, the mineralogy of the surface of the mineral plays a vital role in the deposition pattern observed. Mica has a negative surface charge [314, 138, 221]; the repulsive interactions between the surface-active components of crude oil, which are also negatively charged, force the agglomerates to form in a spherical shape to minimise the contact surface between the components and surface. When calcite was present in the ageing cell, gypsum crystals were formed on the surface of mica. In the absence of calcite in the ageing cell, no gypsum crystals were formed on the surface of mica.

This means that calcite is a precursor to the formation of gypsum crystals on mica. Given that mica is frequently found in sandstone reservoirs and has similar surface features to clay, the formation of such crystals can block small pores in the reservoir rock matrix and hinder oil production. The key conclusion is that the presence of calcite in crude oil with mica can lead to blockage in the porous media of the reservoir rock matrix and therefore hinder the recovery rate.

Additionally, it is worth noting that the formation of crystals was only the case in crude oil B, and with crude C and crude A, no such crystals were recorded upon imaging the samples in the AFM. This also indicates that the formation of these crystals is related to the chemistry of the crude oil; however, from the analysis of the crude oils in Chapter 3, there was no distinct feature that would indicate as to why crude oil B facilitated the formation of these crystals. Another important thing to note here is that gypsum crystals appeared to be more adhesive than the surface of mica, and since both surfaces are minerals, this can be explained by the fact that calcite is positively charged, and this crude oil formed a film on the surface of the gypsum crystals, just as it did with calcite's surface, as shown in chapter 5. Thus, gypsum crystals are not themselves adhesive but rather covered with a thin crude oil film. Further crystal images can be found in Appendix C.

Chapter 7

Crude oil dilution in toluene, a faster alternative approach for adsorbing crude oil onto mineral surfaces

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7.1 Introduction

Wetting measures the attractive force of spreading one fluid to a solid surface in the presence of another immiscible fluid [150]. Therefore, wetting is crucial in controlling capillary pressure and relative permeability-saturation relationships in a porous medium such as the reservoir's rock matrix, which has a sponge structure with pores and throats in the micron and nanometer range. Wetting is typically described by the contact angle, which refers to the angle formed between the tangent to the interface between the liquid and vapour and the solid surface at the point where the three phases meet [141].

The contact angle is conventionally measured from the side of the liquid. The contact angle between a liquid and an ideal solid surface, which is perfectly smooth at the atomic level, chemically uniform, unreactive, and incapable of being deformed by the liquid, is conventionally determined using the Young equation [141]:

$$\cos\theta_{Young} = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma}, \quad (7.1)$$

The symbol θ_{Young} represents the Young contact angle, whereas γ_{sv} and γ_{sl} represent the interfacial tensions between the solid and vapour, and solid and liquid, respectively. γ represents the surface tension of the liquid. According to the Young equation, a solid surface with a high surface energy (i.e., high solid-vapor interfacial tension γ_{sv}) will have a small contact angle, while a surface with low energy will have a large contact angle [141]. It is worth noting that given the surface where the liquid is in contact with the solid is rough, Wenzel equation (1936) which defines the relation between roughness and wettability [?].

In addition to the chemical properties of the surface, the structural characteristics of the surface also impact how the fluids interact with the surface. The rougher a surface is, the more surface area is available [322, 309]. Capillary effects will also be more prominent on an uneven surface [67].

The ageing technique is one way to assess the impact of the surface-active components of crude oil on mineral model surfaces such as calcite and mica, as described in previous chapters. However, as ageing requires an ageing cell to facilitate a high temperature and pressure environment and it takes a month for the samples to be ready for imaging, this is a slow process, and it

is imperative to have a rapid method to be able to plan the research accordingly, as observing preliminary changes occurring on the surface can help researchers plan experiments ahead.

In this research project, a toluene dilution technique was tested to compare with the ageing technique, and also, at the beginning of the project, it gave an indication as to what should be planned for future experiments.

7.2 Materials and Methodology

7.2.1 Chemicals

Toluene

Toluene with 99.5% purity was provided by Imperial College London Chemical Store (produced by VWR). Toluene is an aromatic solvent in which crude oil can be dissolved, and it does not lead to asphaltene precipitation as it is not an n-alkane. Toluene is a suitable aromatic solvent as it carries fewer health hazards and is not known to have the same carcinogenic impacts as benzene.

Decane

A sample of decane with a minimum purity of 95% was acquired from Sigma-Aldrich. Decane is a colourless hydrocarbon derived from petroleum and belongs to the class of n-alkanes. Consequently, it poses fewer health hazards in comparison to aromatic compounds of crude oil. Since the media used for Atomic Force Microscopy (AFM) needs to be transparent for the AFM laser to reach the cantilever, decane was selected as an optimal solvent for imaging, as calcite is soluble in water and brine.

Crude oils

The characteristics of all crude oils mentioned in this chapter are thoroughly explained in chapter 4. The crude oils were supplied by Shell, together with their fundamental analysis data, as part of the digital rock programme.

7.2.2 Mineral surfaces

The experiments done in this chapter utilised the very same mica and calcite material that was detailed in Chapter 5, section 5.3.6.

7.2.3 Atomic Force Microscopy

In this chapter, AFM was employed in a similar fashion to its usage in chapters 5 and 6. The QI imaging mode was utilised to evaluate the minerals that were exposed to a solution of diluted crude oil in toluene. The imaging occurred in decane, a transparent and colourless solution. A prerequisite for AFM imaging is the requirement of a clear solution, where the laser beam can illuminate the back of the cantilever's tip without any deflection. Additionally, a dark solution would obstruct the passage of the laser beam.

7.3 Experimental Procedure

A JPK NanoWizard 4 Atomic Force Microscope, which allows the imaging of adsorbed crude oil components at the nanoscale on relatively smooth surfaces, was used. The cantilever was cleaned using a UV/ozone plasma chamber for 20 minutes before any imaging was undertaken. When mica was the surface being imaged, water was injected on the surface of the mica disc before imaging started. The cantilever was then calibrated in water before approaching the surface and imaging. If, however, the model surface that was being imaged was calcite, the calcite was placed in decane solution in a petri dish and placed underneath the AFM head.

The cantilever was then calibrated in air to establish the force constant and then recalibrated in decane for sensitivity. The measurements are done in decane here for calcite as opposed to water due to calcite's solubility in water. Topographical images of the surface of the sample were taken via AFM using the quantitative imaging mode. The cantilever used in the experiments was a silicon cantilever purchased from Windsor Scientific with the following model number: PPP-NCHAuD-10 (length: 125 μm , width: 30 μm , force constant: 10–130 N/m). The surfaces of the model samples had been imaged prior to introducing crude oil onto the surfaces; these results are presented in chapter 5.

This is key to understanding what changes can be imposed on the surface properties of the

minerals upon crude oil adsorption. In this study, an AFM (Nanowizard 4, JPK Instruments, now Bruker) was used to image the structure of the rock surface down to nanometer resolution. The measurements were conducted in a liquid (water or decane, depending on the mineral) to reduce the vibrational noise impact on the measurement. The sample was scanned with a silicon tip (PPP-NCHAuD from NanosensorTM) on a 10 μm x 10 μm area with a resolution of 512 x 512 pixels in quantitative imagingTM mode. The images were levelled, filtered using a median filter, analysed for curvature and roughness, and envisaged with JPKSPM data processing software (JPK instruments).

Mineral Surface Cleaving and imaging the fresh surface

To conclusively characterise wettability alterations because of crude adsorption, the mineral surfaces were cleaved in decane to ensure fresh surfaces exposed for imaging were contaminant-free and then imaged using QI mode in decane to ensure best quality imaging, as liquid as opposed to air offers noise cancellation.

Crude oil solution preparation via serial dilution

In this experiment, toluene was used to dilute crude oil. The target concentrations of crude oil in toluene were 100 mg/L, 10 mg/L, 1 mg/L, and 100 $\mu\text{g/L}$. In order to attain such minimal concentrations, a sequential dilution process was implemented, involving the following steps:

1. A 100 mg/L sample was created by pipetting the required volume of crude oil into a 50 ml volumetric flask and then diluting it with toluene.
2. In order to decrease the concentration of the 100 mg/L sample, 1 mL of the sample was transferred into a 10 mL volumetric flask, and the remaining volume of the flask was filled with toluene. This process will result in a dilution of the 100 mg/L sample by a factor of 10. The following specimen can be diluted by a factor of 10 appropriately. Subsequently, the solution that had been created was employed to adsorb crude oil onto the model surfaces.

Mica Preparation

Mica discs are flat and easy to handle and cleave. Before introducing any liquid onto the surface of the mica disc, the mica disc was cleaved using adhesive tape to leave behind a fresh surface of mica that had not been exposed to air. It is important to note that the cleaving process was done in decane to prevent any contamination on the fresh surface of mica. Once cleaved, 200 μL of solvent containing crude oil was injected on the surface of the mica. The mica disc is then placed in a sealed petri dish for a period of 24 hours in a fume cupboard to allow the crude oil components to adsorb onto the surface of the mica. The same sample could also be placed in an oven where the temperature was 100 °C rather than ambient; however, the surface of the samples in this case was rougher due to the nature of the drying conditions. All the images reported here were dried at room temperature and normal atmospheric pressure.

Calcite preparation

Calcite was cleaved using a specially designed cleaver with a blade in guillotine-like fashion at an angle that corresponds to the calcite cleavage plane. The calcite sample was placed in the cleaver filled with decane, and cleaving took place in the fume cupboard in decane solution to ensure the fresh surfaces were not exposed to air. The cleaver is comprised of a blade and a dish, allowing the calcite to be placed in the decane while cleaving. Once the calcite is cleaved, the freshly exposed surfaces of the calcite are placed in a solution of crude oil and toluene with the desired concentration, and the samples are sealed so that the solvent does not evaporate. The samples were then given 24 hours to dry before imaging in decane solution in the AFM. The entire procedure occurs at room temperature and pressure ($T = 20\text{ }^{\circ}\text{C}$, $P = 1\text{ Bar}$).

7.4 Results and Discussion

7.4.1 Characterising the Model Mineral Surfaces with AFM

7.4.2 Modeling the mineral surface prior to crude oil introduction

The characterisation of the model mineral surfaces was introduced in chapter 5, section 5.4.1, and thus the data will not be repeated. In summary, mica's surface is flat, and calcite's surface is stepped, with each step itself being relatively flat.

7.4.3 Crude oils A and B adsorbed on Mica via toluene

All crude oils have different properties from one another depending on their origin and composition. It is known that the asphaltene content and makeup of different crude oils are different. The surfaces of reservoir rocks are composed of many different minerals, which include mica and calcite. This section will shed light on the characteristics of the crude A and crude B crude oils deposited on the surface of mica while comparing these relatively light oils to a heavy Kazakh crude oil, which is very asphaltene-heavy and has a dough-like structure.

Crude oil A formed the fewest aggregates on the surface of mica compared to crude oil B; this is in agreement with the findings of chapter 5. Figure 7.1 and 7.3 compared with 7.2 and 7.4 (a) show that the aggregates formed by crude oil A are smaller than crude oil B, while on a 10 micron scale, figures 7.3 and 7.4 show that crude oil A barely formed any deposits on the surface of mica as the surface appears to be as flat as a naked mica surface. Figure 7.4 (a) on the other hand is showing crude oil B formed 3 distinct aggregates; this is in agreement with the fact that crude oil B is more unstable than crude oil A, which is a very stable crude, as pointed out by the fundamental analysis performed on all crude oils highlighted in chapter 4, section 4.6. The stiffness maps reflect how complex the surface is when the cantilever touches it.

Still, most importantly, it can also show whether the surface is covered by a softer or more rigid substrate or not, as long as the substrate adsorbed onto the surface has a different hardness. The stiffness maps shown in Figures 7.3 (c) and 7.4 also confirm that crude oil A barely formed any aggregates on mica's surface; the surface has a hardness within the range of 23-23.5 N/m,

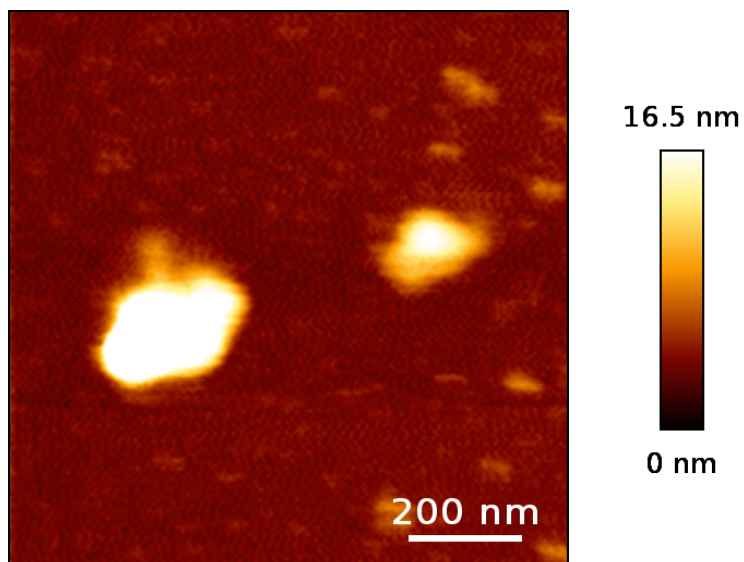
whilst crude oil B formed aggregates on the surface of mica, reducing the stiffness of the surface to 57-304 nN/ μm .

1. The maximum height of the surface reaches 18nm due to the presence of crude oil agglomerates (this height was achieved with crude oil B).
2. The surface of the mica shows good coverage with crude oil B, as the rest of the surface has an average maximum height of around 2.6 nm. From the analysis of the mica, the maximum height of naked mica can reach only 1.3 nm, and these figures are double that, which means the surface of the mica is covered with crude oil. This indicates that the methodology employed in adsorbing crude oil onto mica was effective with crude oil B.
3. From the adhesion data, the maximum adhesion obtained from crude oil B reached an average of 10 nN. This confirms that crude oil has indeed been adsorbed onto the mica disc, as adhesion of plain mica was measured as part of experiments presented in chapter 5 section 5.4.1, which was recorded to be no more than 2.5 nN. Therefore, this confirms that anything observed in the measured-height images is not an image artefact or contaminant.

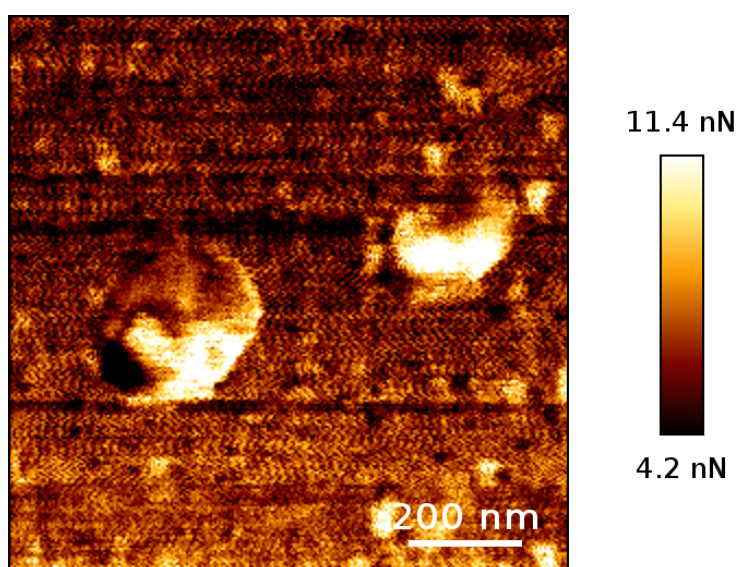
In order to characterise the crude oil agglomerates on the surface of the mica better, a cross-sectional analysis has been conducted, which compares the size, adhesivity, and hardness of these particles to those of dust particles observed on naked mica discs. Figures 7.2 (a) and 7.4 (a) give an insight into the size of the agglomerates from crude oil B crude.

Figure 2.4 shows the classical colloidal model of asphaltenes. Based on this model, many asphaltene molecules come together, forming a stack of asphaltenes in the core, which is surrounded by other fractions of crude oil [37]. Therefore, the large agglomerates that are observed in figure 7.5 are likely to be these asphaltene agglomerates of the colloidal model of asphaltenes presented in figure 2.4. Additionally, the surface of mica is negatively charged, as is the charge of asphaltene aggregates.

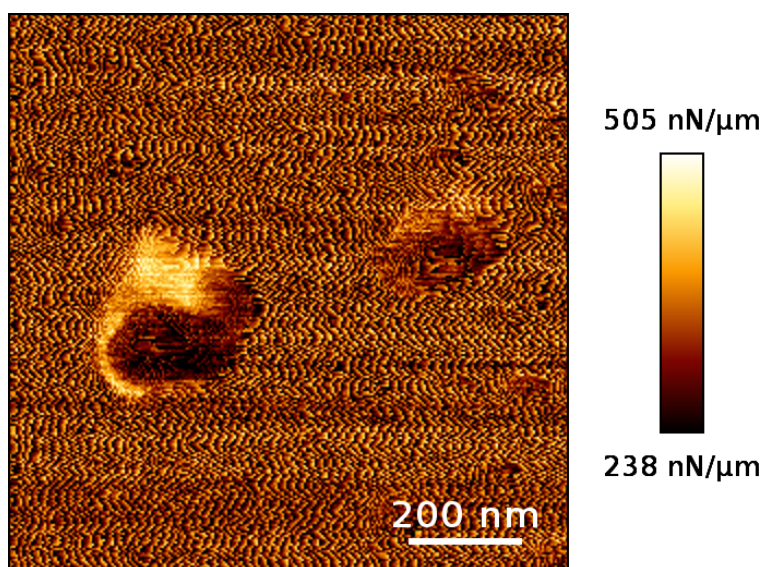
Therefore, in order to minimise the unfavourable interactions between asphaltene particles and the negatively charged surface of mica [73, 135], asphaltene molecules will come together in order to minimise the contact surface with mica. Table 7.1 gives a quantitative summary of the description given on crude oil A and B diluted deposits on the surface of mica.



(a) Crude A diluted in toluene 10 mg/l Maximum height Map

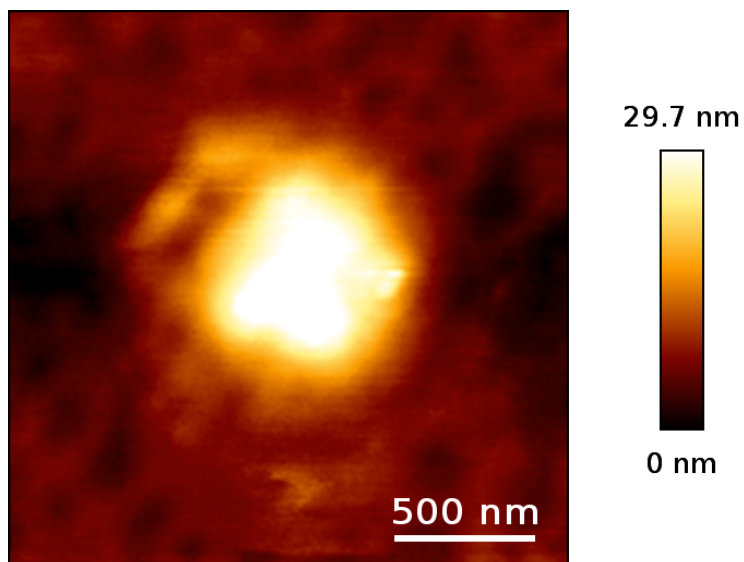


(b) Crude A diluted in toluene 10 mg/l Adhesion Map

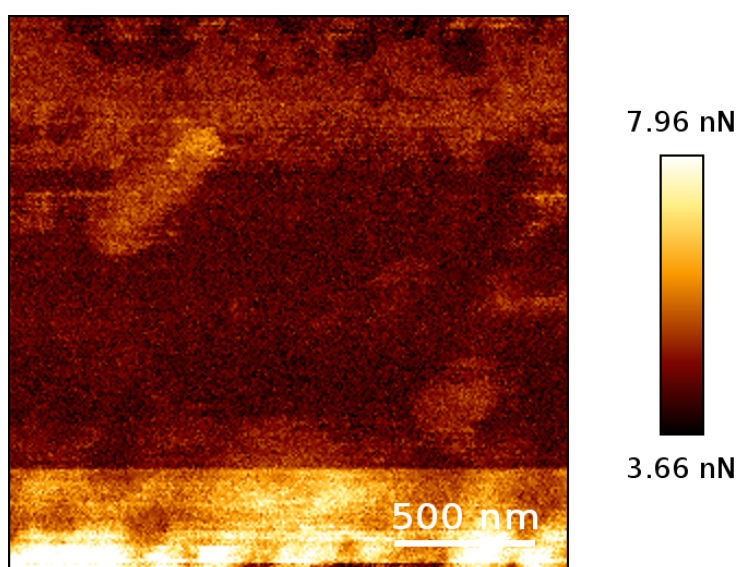


(c) Crude A diluted in toluene 10 mg/t Stiffness Map

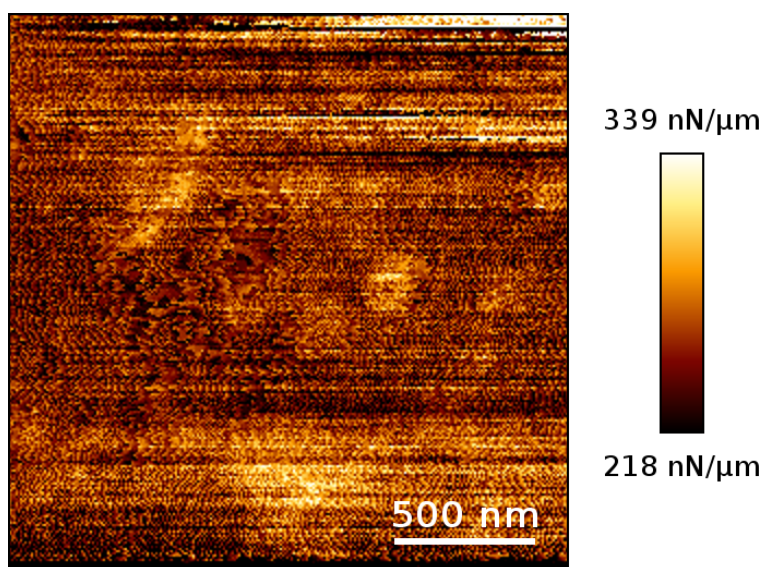
Figure 7.1: Crude oil A diluted in toluene, mica aged AFM imaged



(a) Crude B diluted in toluene 10 mg/l Maximum height Map

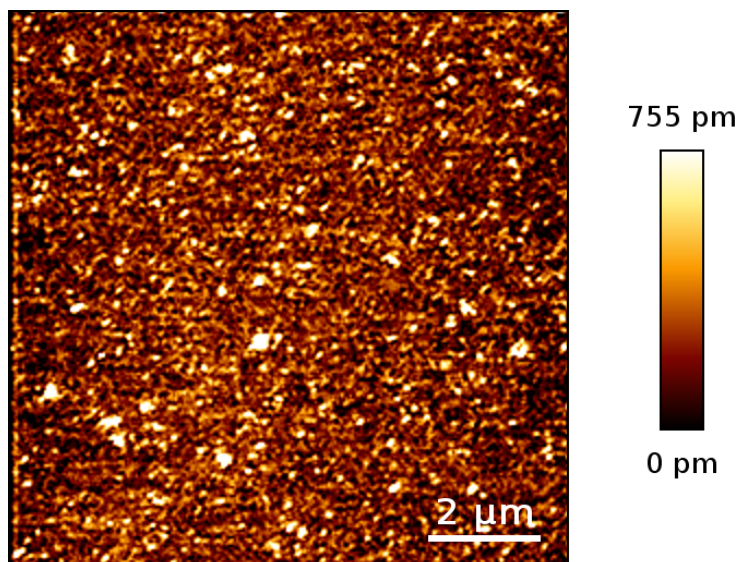


(b) Crude B diluted in toluene 10 mg/l Adhesion Map

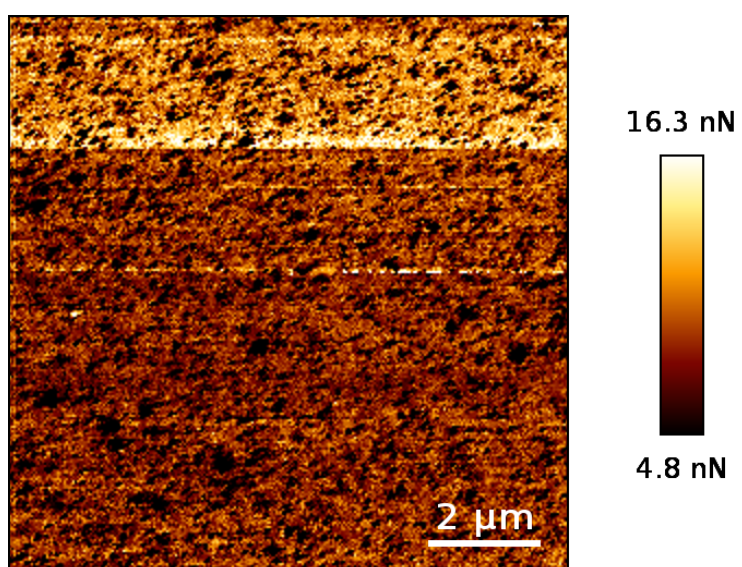


(c) Crude B diluted in toluene 10 mg/t Stiffness Map

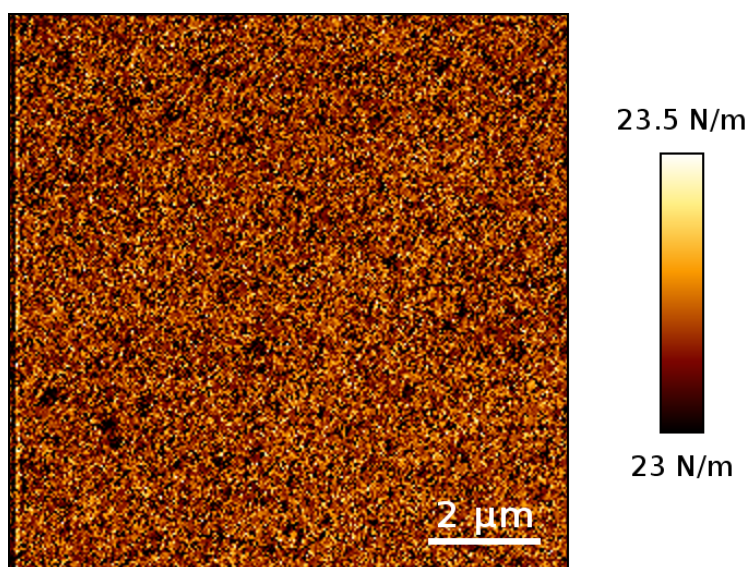
Figure 7.2: Crude oil B diluted in toluene, mica aged AFM imaged



(a) Crude A diluted in toluene 10 mg/l Maximum height Map

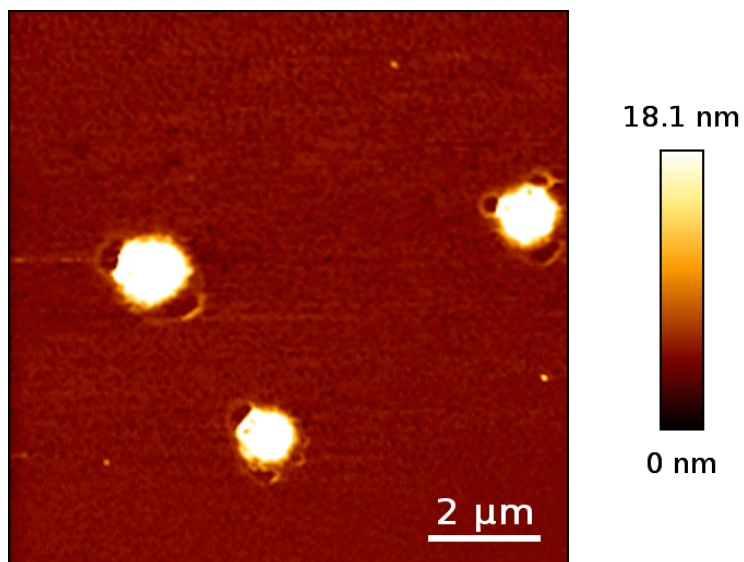


(b) Crude A diluted in toluene 10 mg/l Adhesion Map

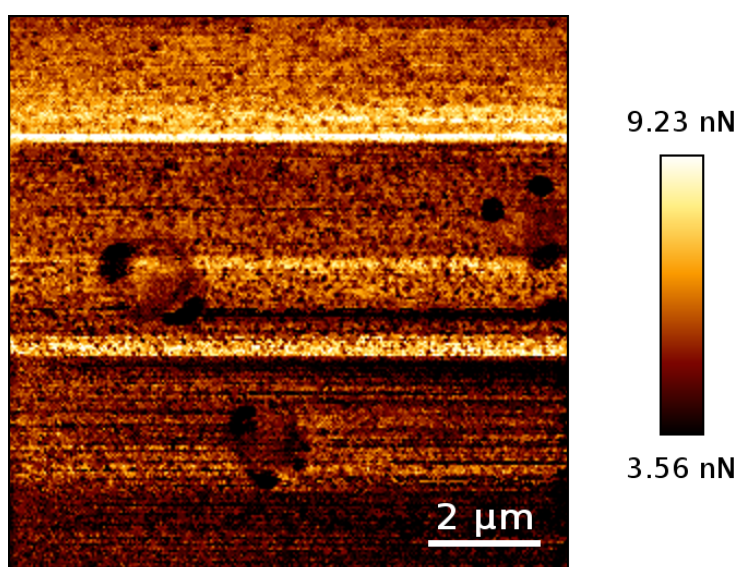


(c) Crude A diluted in toluene 10 mg/t Stiffness Map

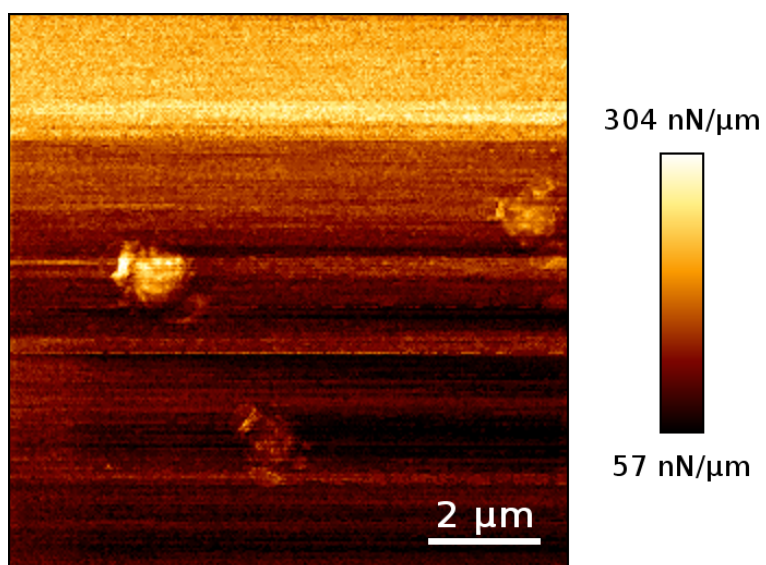
Figure 7.3: Crude oil A diluted in toluene, mica aged AFM imaged 10 micron scale



(a) Crude B diluted in toluene 10 mg/l Maximum height Map



(b) Crude B diluted in toluene 10 mg/l Adhesion Map

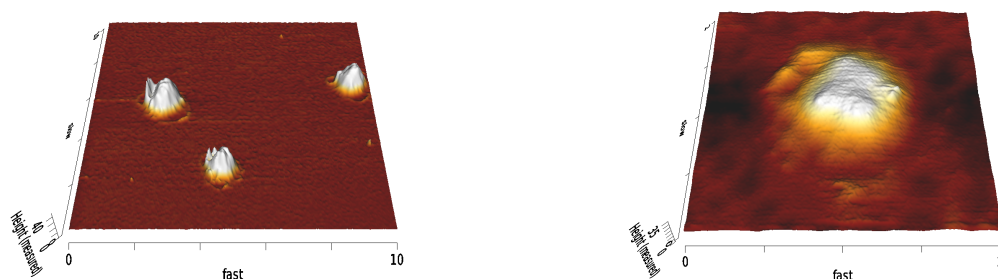


(c) Crude B diluted in toluene 10 mg/t Stiffness Map

Figure 7.4: Crude oil B diluted in toluene, mica aged AFM imaged 10 micron scale

Table 7.1: Summarised quantitative and qualitative AFM gathered data on mica diluted crude samples on 10 micron scale.

Crude Oils \ Topographical properties	Coverage Type	Maximum height measured (nm)	Maximum adhesion (nN)	Stiffness range (N m^{-1})
Crude A	Uniform/Agglomerates on thick crude film	1.1	3.62	0.577 - 0.442
Crude B	Uniform/Agglomerates on thick crude film	18.1	9.26	0.304 - 0.057



(a) Crude B agglomerates 10 microns scale topography (b) Crude B agglomerates 1 microns scale topography

Figure 7.5: 3D images of agglomerates seen formed on mica's surface when placed in toluene diluted crude B solution and imaged in decane.

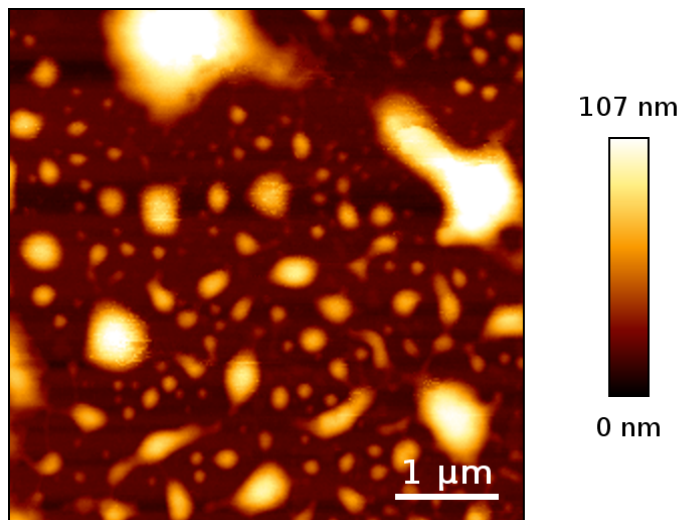
Crude oil C could not be imaged when adsorbed onto mica. This is because crude oil C is the most unstable crude oil out of the three crude oils provided by Shell. On retraction, the adhesion was so high that the AFM tip did not separate from the surface; thus, no image could be produced. (See appendix F for more insight).

7.4.4 Heavy Kazakh Crude Adsorbed onto mica

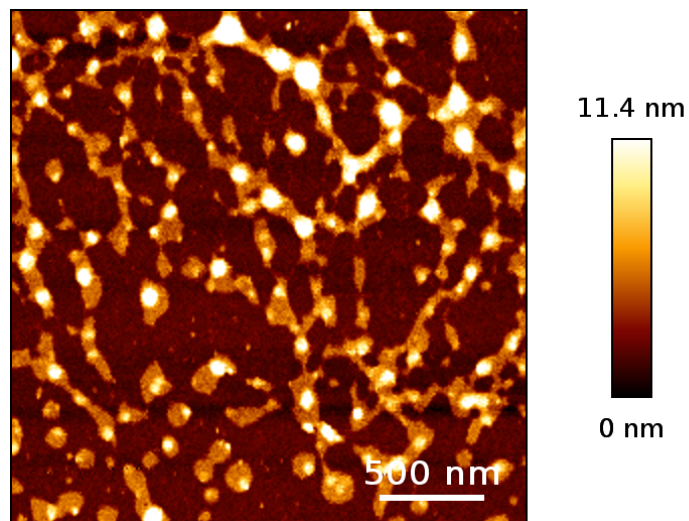
Crude A, B, and C are conventional oils, and although they have exhibited deposits on the surface of mica, a heavier crude from Kazakhstan, which has a very high viscosity and dough-like structure, was also diluted in toluene, and the solution was made up to 10 mg/l.

Height measured maps

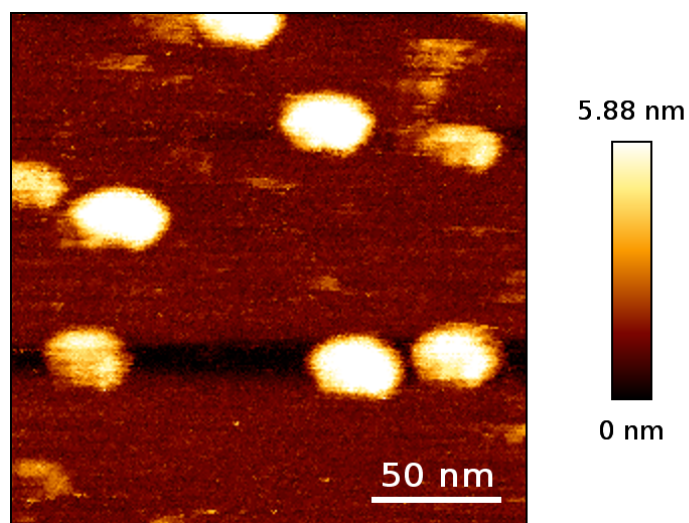
Figure 7.6a and 7.7a compared with figure 7.4 (a) show that the more asphaltene-heavy Kazakh crude clearly exhibited a bigger surface coverage compared to crude B. This is due to the fact that the heavier Kazakh crude is more rich in asphaltenes, which are the polar components of crude oil. These molecules have the capability to alter the wettability of a mineral surface in favour of oil molecules. Kazakh crude, which is more rich in asphaltene fraction, initially adsorbed onto the surface of mica, and by altering the wettability of the surface of mica in favour of oil, it facilitated more agglomerates to deposit onto the surface of the mineral.



(a) Heavy Kazakh Crude diluted on Mica 5 micron scale

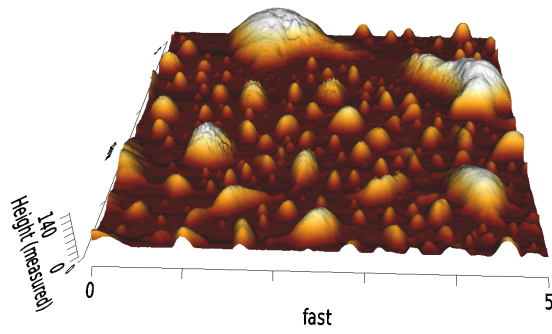


(b) Heavy Kazakh Crude diluted on Mica 2.5 micron scale

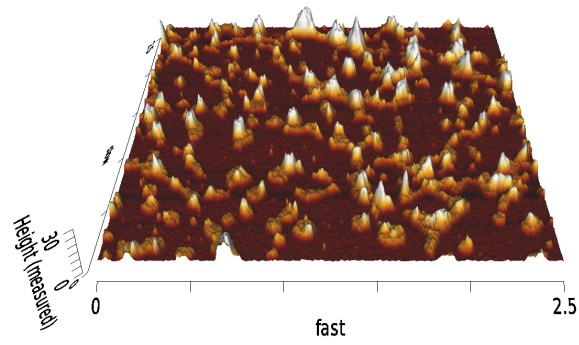


(c) Heavy Kazakh Crude diluted on Mica 0.25 micron scale

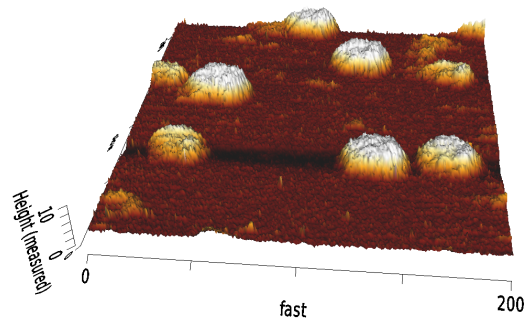
Figure 7.6: Topography of heavy Kazakh crude diluted in toluene and adsorbed onto mica in same manner as conventional crude oils.



(a) Heavy Kazakh Crude diluted on Mica 5 micron scale



(b) Heavy Kazakh Crude diluted on Mica 2.5 micron scale



(c) Heavy Kazakh Crude diluted on Mica 250 micron scale

Figure 7.7: 3D Topography of heavy Kazakh crude diluted in toluene and adsorbed onto mica in same manner as conventional crude oils.

Comparison of Agglomerates dimensions formed by each crude

For comparing the size and dimensions of the agglomerates formed by the conventional crude oils A and B and the heavy Kazakh crude with asphaltene agglomerates, cross-sectional analysis was conducted, which highlights the results shown in figure 7.8.

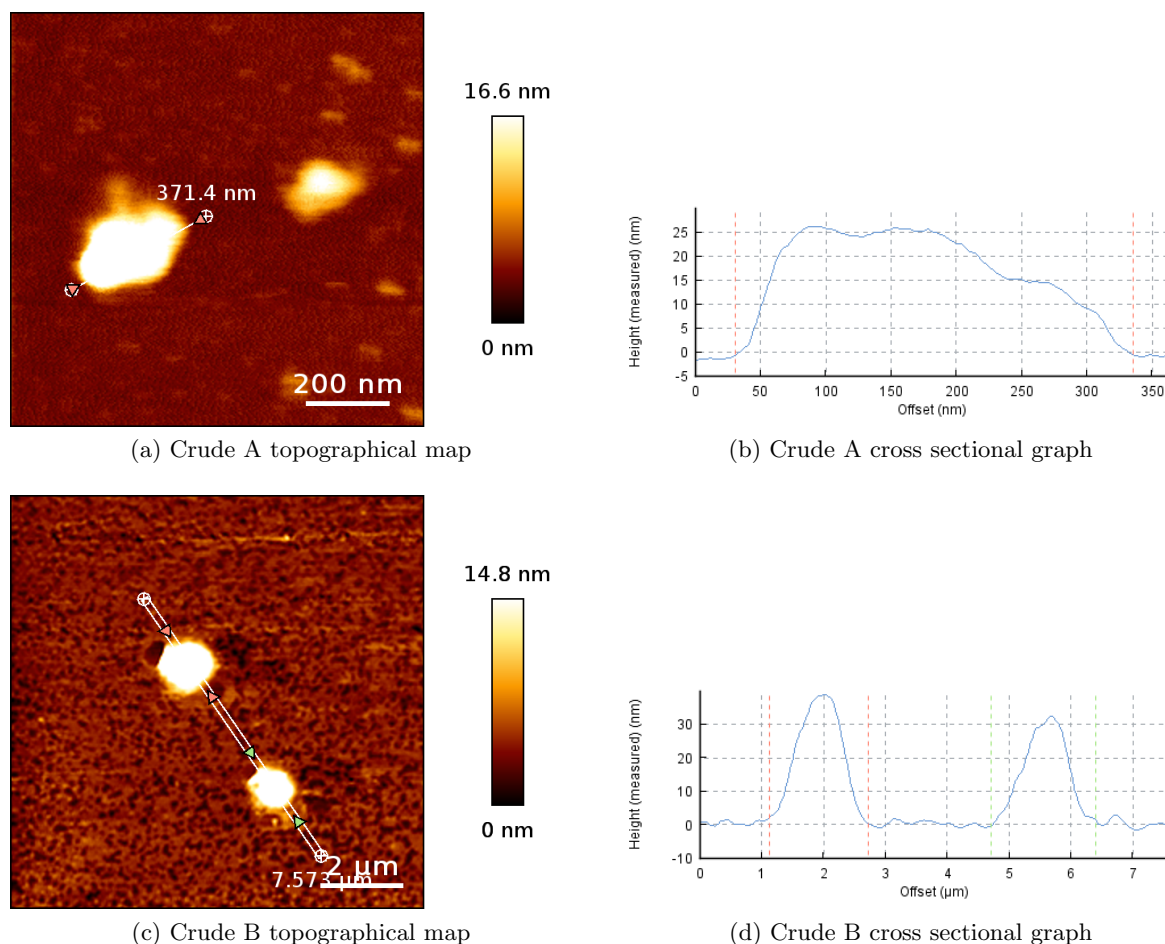


Figure 7.8: Cross sectional analysis on agglomerates formed by crude B and heavy Kazakh crude for comparisons.

Agglomerate formed by crude oil A, as shown in figure 7.8 (b), was found to be 305 nm in diameter and reached a maximum height of 25nm. Figure 7.8 (d) shows the cross-sectional analysis performed on agglomerates formed by crude oil B and the average diameter of the agglomerates found formed by crude B at 1520 nm. This finding is in agreement with the fact that crude B has higher asphaltene contents than crude A, as per the SARA analysis performed on the crude oils. To further complete the comparison of the crude oils studied via toluene dilution, cross-sectional analysis was also performed on heavy Kazakh crude and asphaltenes by themselves.

Figure 7.9 (d) illustrates the cross-sectional plot of the agglomerate formed by asphaltenes,

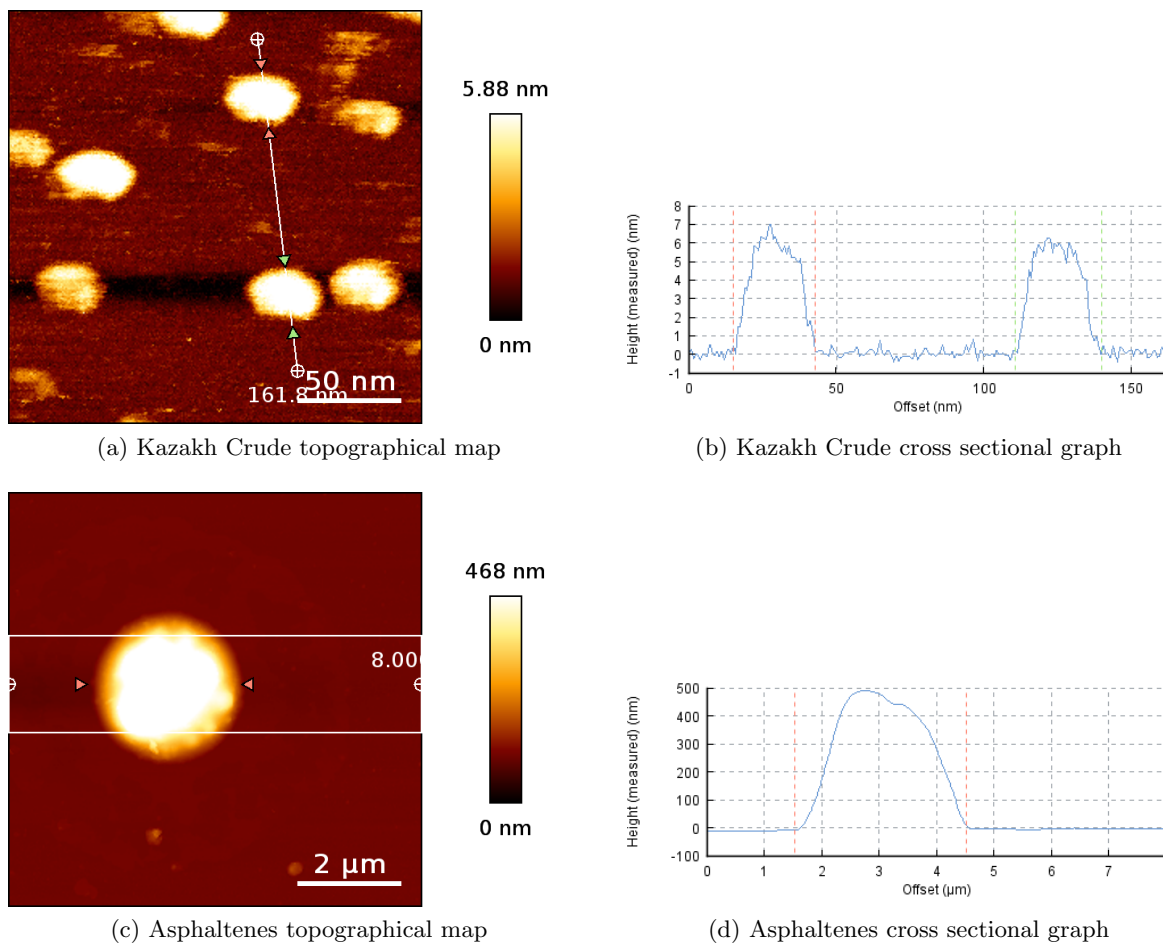


Figure 7.9: Cross sectional analysis on agglomerates formed by Kazakh crude and asphaltenes from Mayan crude oil for comparisons.

which were diluted in toluene and adsorbed onto mica. The diameter of this agglomerate is 3 microns wide and 500 nm tall. This agglomerate is purely formed from the asphaltene fractions of a Mexican crude oil, which was extracted from the crude oil by precipitating it in n-pentane and n-heptane solvents. Another pure asphaltene agglomerate was found to be 443.8 nm wide in diameter with a height of 20 nm. This agglomerate is much closer to the size of the agglomerates found in conventional crude oils A and B.

Figure 7.9 (b) demonstrates that the agglomerate formed by the heavy Kazakh crude is on average 28.44 nm wide in diameter and around 7 nm tall. These agglomerates were the smallest of all crude oils, but yet, this heavy Kazakh crude exhibited the largest coverage of mica's surface. This can be due to the fact that the heavy asphaltene content of this crude altered the wettability of the surface in favour of oil, which in turn allowed the negatively charged polar components of crude to cover the negatively charged surface of mica more readily. Kazakh crude oil deposited the most aggregates on the surface of mica; this is directly correlated with the fact that it has a higher asphaltene content compared to light crude oils A, B, and C. This explains a

significant industrial problem: the more asphaltene content a crude oil has, the more aggregates are formed on a mineral surface. When rocks become oil-wet, the recovery rate of the reservoir decreases [144].

Adhesion Comparisons of the crude oils and asphaltenes

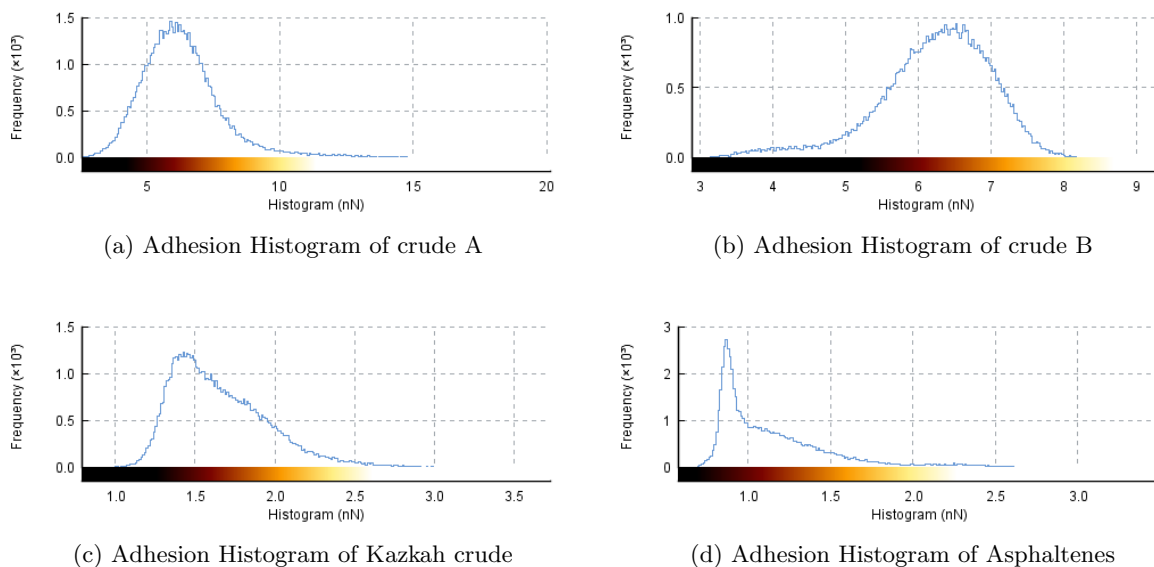
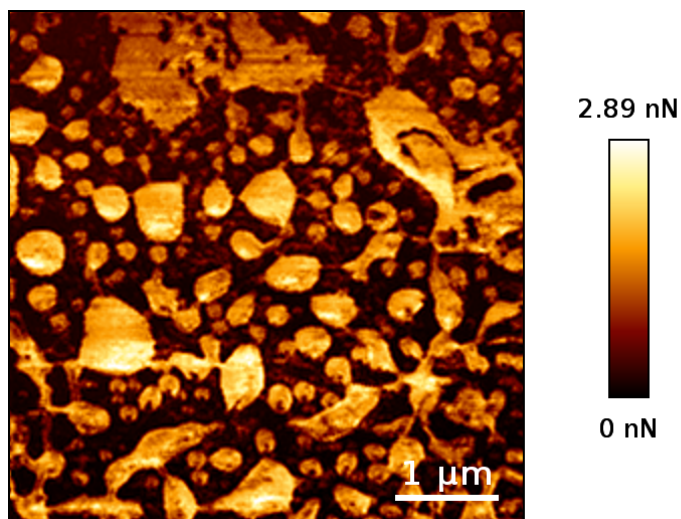


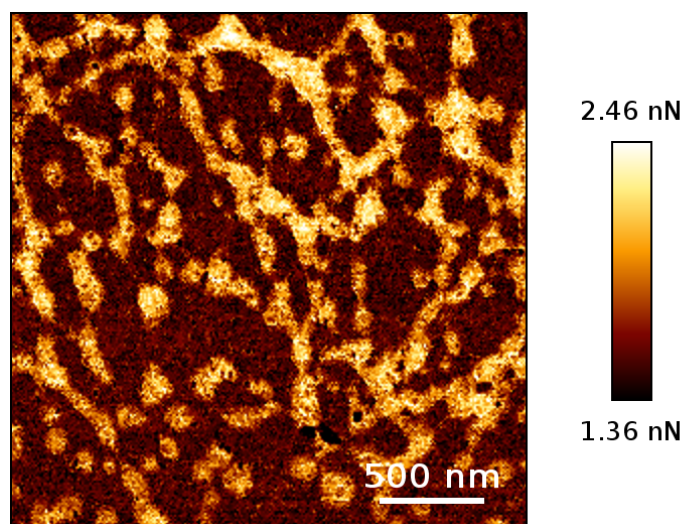
Figure 7.10: Adhesion histograms of the adsorbed crude oil on mica, showing the shift of adhesions.

Figure 7.10 shows the histogram plots obtained from the adhesion data of the various crude oils diluted in toluene and adsorbed onto mica; additionally, the asphaltene histogram is also plotted to be compared to all crude oils. The two conventional crude oils showed very similar average adhesion force values, with crude oils A and B having an average force of adhesion of 6.344 nN and 6.213 nN, respectively. Heavy Kazakh crude had an average force of adhesion of 1.684 nN, and asphaltenes showed the lowest force of adhesion of all adsorbents, with an average force of adhesion of 1.152 nN. It is worth noting that a heavy crude oil is considered heavy due to its high viscosity and not its asphaltene content.

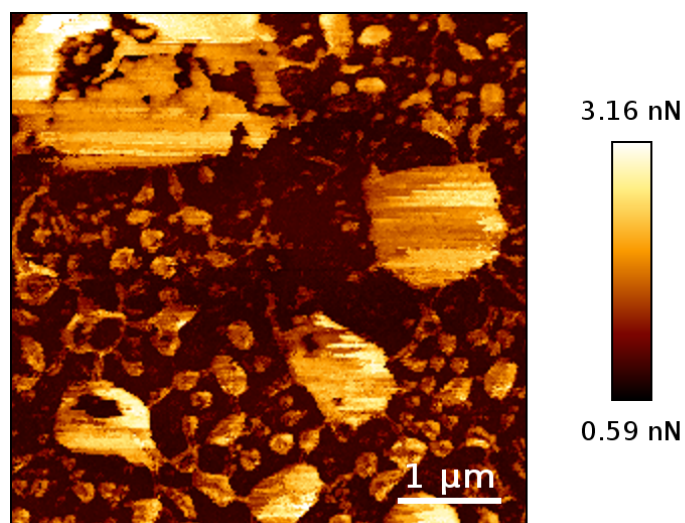
Figure 7.12 shows the stiffness maps of the Kazakh crude obtained, representing the same images shown in figure 7.11 but only their stiffness maps. The three images all indicate that crude oil deposits on the surface of mica are less hard than the surface of mica itself. This is the observation that is the result of diluting the crude oil in toluene and adsorbing it on a mineral surface.



(a) Adhesion map of Heavy Kazakh Crude diluted on Mica 5 micron scale

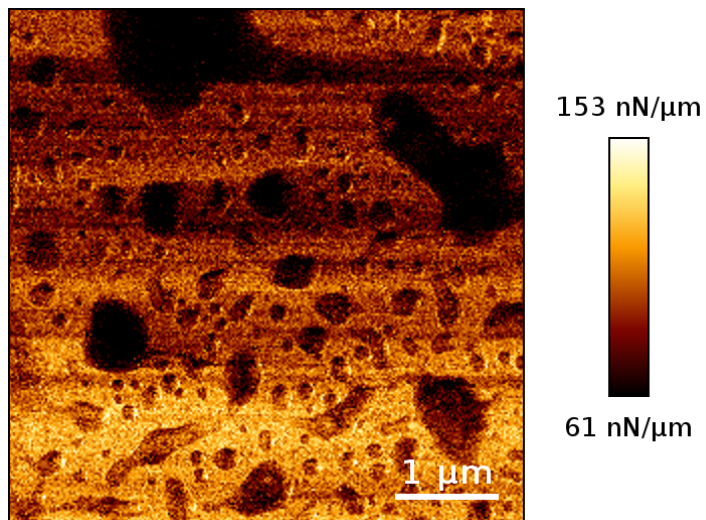


(b) Adhesion map of Heavy Kazakh Crude diluted on Mica 2.5 micron scale

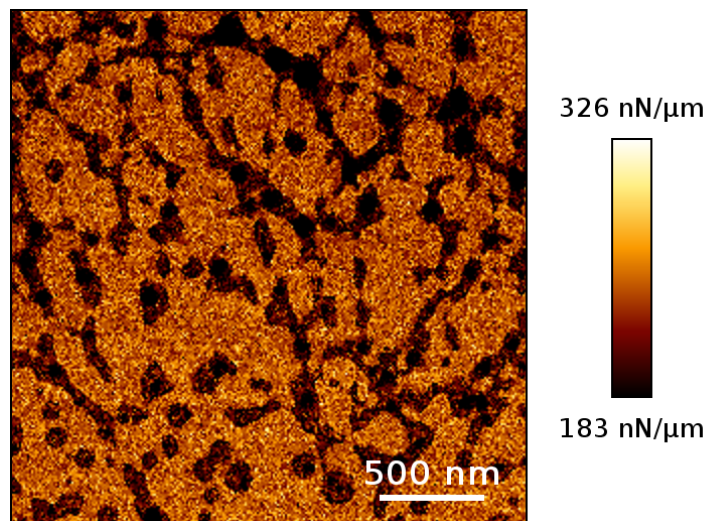


(c) Adhesion map of Heavy Kazakh Crude diluted on Mica 5 micron scale

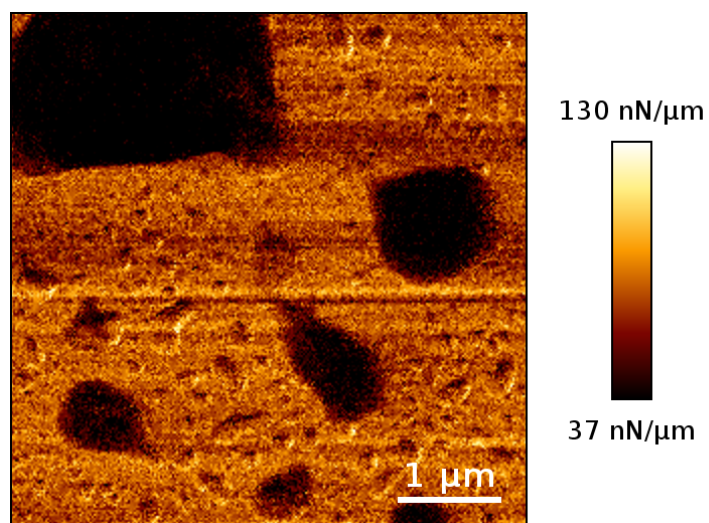
Figure 7.11: Various adhesion maps obtained from imaging the Kazakh crude adsorbed onto mica and imaged in decane using the AFM's QI Mode.



(a) Stiffness Map of Kazakh Crude on Mica



(b) Stiffness Map of Kazakh Crude on Mica



(c) Stiffness Map of Kazakh Crude on Mica

Figure 7.12: Various stiffness maps obtained from imaging the Kazakh crude adsorbed onto mica and imaged in decane using the AFM's QI Mode.

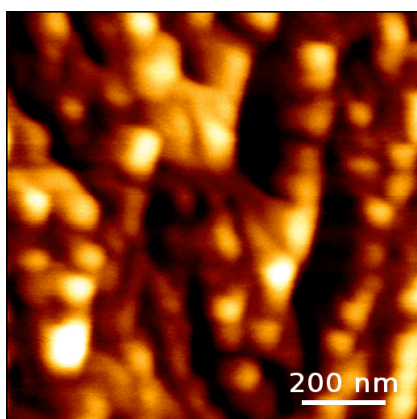
7.4.5 Crude oil adsorbed on Calcite

Calcite is positively charged as opposed to the negatively charged mica. Therefore, it is expected that deposits of oil will cover the surface of the calcite more uniformly. Height maps of calcite exposed to crude oils A, B, and C are presented in figure 7.13. On a 1 micron scale, all three crude oils show that they have formed a film on the surface of calcite as the surface is more smooth, while on a 10 micron scale, it becomes evident that the toluene dilution method is not as effective as the ageing technique since the stepped features of calcite's surface are visible (ribbon-like structures). This means that although the crude oils formed a thin film on the surface of calcite, the film is not thick and is comparable to the films observed via the ageing technique presented in chapter 5, section 5.4.3.

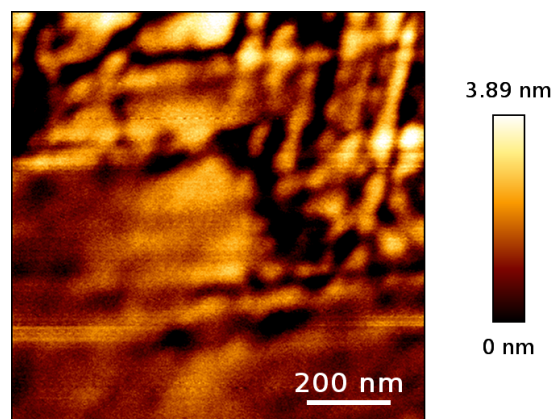
Figures 7.15 and 7.16 show the adhesion maps and stiffness maps, respectively, of calcite's surface after crude oil is adsorbed onto its surface through the toluene dilution technique at 1 micron and 10 micron scale. Figure 7.14 presents the 3D topography of the calcite's surface after being exposed to the crude oils. The 3D images allow the visualisation of the crude oil thin films well. Figures 7.13, 7.14, 7.15 and 7.16 all show one important feature, which is that the stepped nature of calcite is visible across all images, and therefore any adsorbed crude oil layer is very thin. It is important to note that these features of the calcite surface were not as visible when aged in crude oil, as shown in chapter 5.

Table 7.2: Summarised quantitative and qualitative AFM gathered data on calcite diluted samples on 1 micron scale.

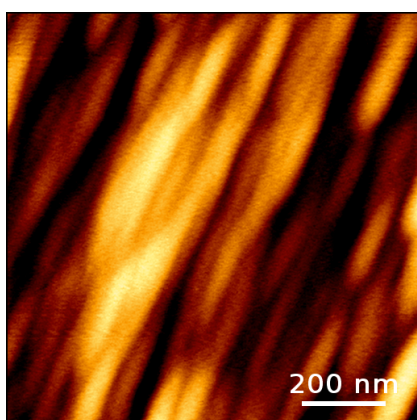
Crude Oils \ Topographical properties	Coverage Type	Maximum height measured (nm)	Maximum adhesion (nN)	Stiffness range (N m^{-1})
Crude A	Uniform/Agglomerates on thick crude film	10.9	31.9	28.6 - 28.1
Crude B	Uniform/Agglomerates on thick crude film	3.89	33.3	28.8 - 28.2
Crude C	Uniform/Agglomerates on thick crude film	8.11	106	28.7 - 28.1



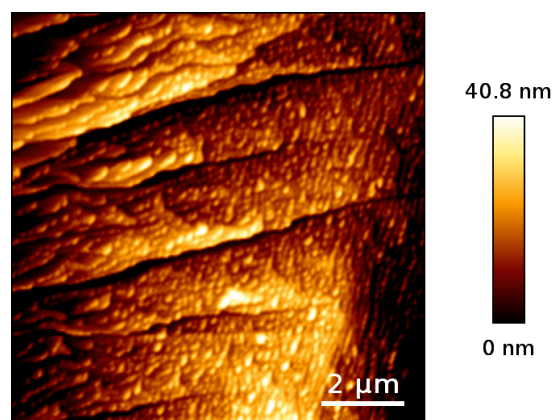
(a) Toluene Diluted on calcite topography crude A 1 micron scale



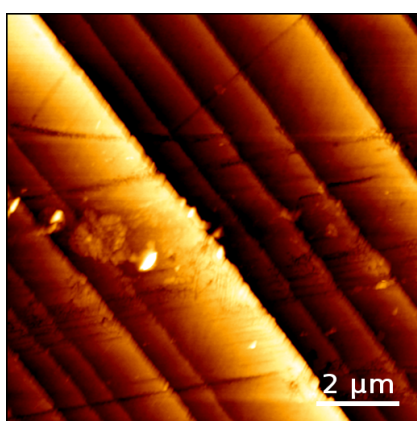
(b) Toluene diluted on calcite topography crude B 1 micron scale



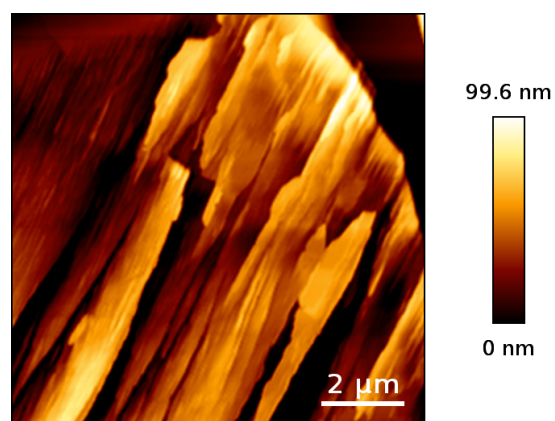
(c) Toluene Diluted on calcite topography crude C 1 micron scale



(d) Toluene Diluted on calcite topography crude A 10 micron scale

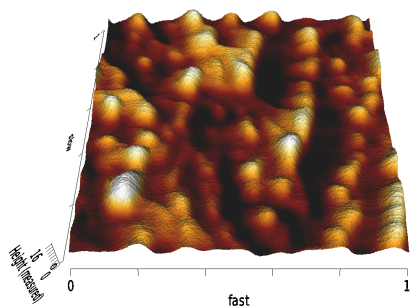


(e) Toluene Diluted on calcite topography crude B 10 micron scale

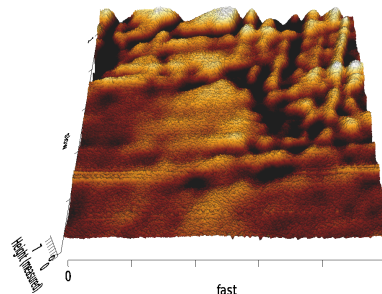


(f) Toluene Diluted on calcite topography crude C 10 micron scale

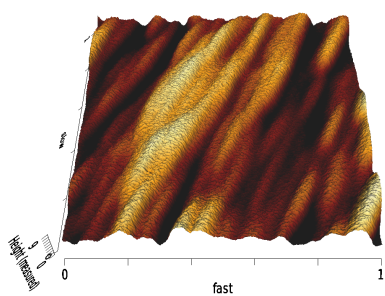
Figure 7.13: Summary of images in 1 micron and 10 microns scale of the topography of diluted crude oils evaporated on calcite and imaged in decane.



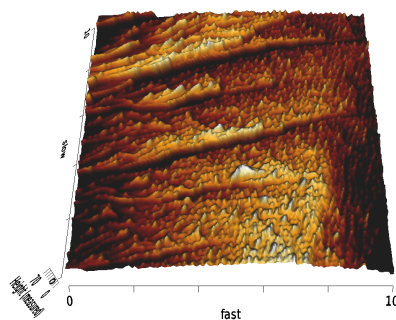
(a) Toluene Diluted crude A on calcite at 1 micron scale



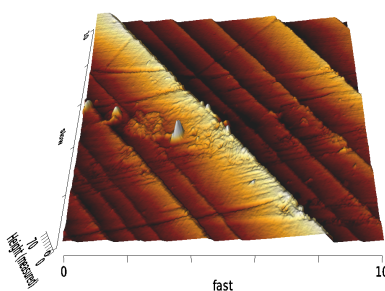
(b) Toluene diluted crude B on calcite at 1 micron scale



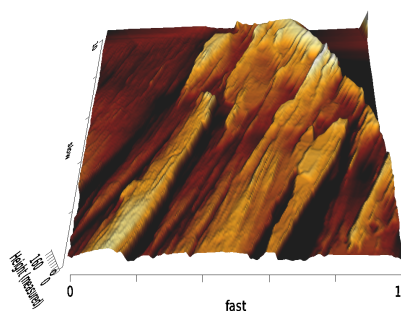
(c) Toluene Diluted crude C on calcite at 1 micron scale



(d) Toluene Diluted crude A on calcite at 10 micron scale

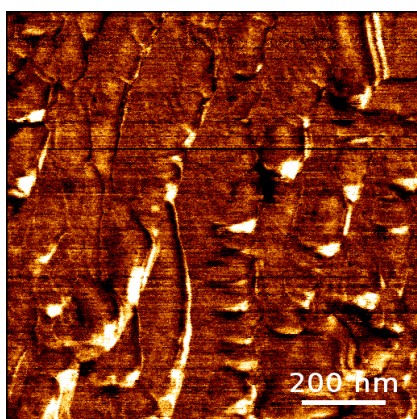


(e) Toluene Diluted crude B on calcite at 10 micron scale

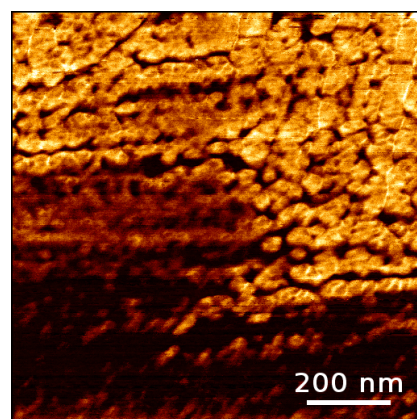


(f) Toluene Diluted crude C on calcite at 10 micron scale

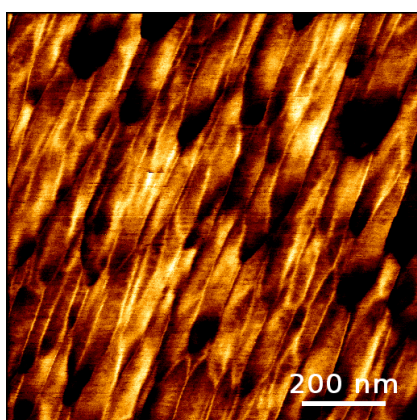
Figure 7.14: 3D Topographical of images in 1 micron and 10 microns scale of the topography of diluted crude oils evaporated on calcite and imaged in decane.



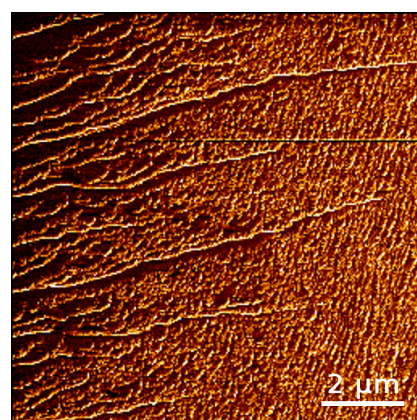
(a) Toluene Diluted Adhesion Map crude A 1 micron scale



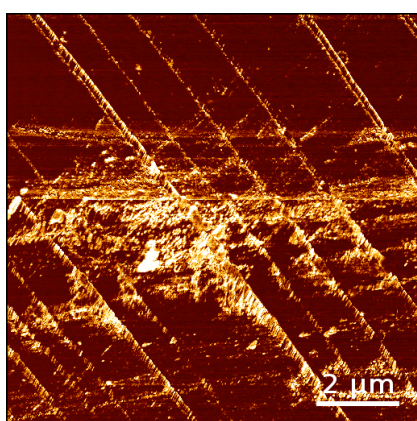
(b) Toluene diluted Adhesion Map crude B 1 micron scale



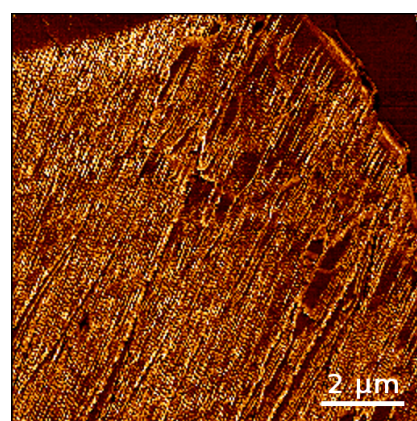
(c) Toluene Diluted Adhesion Map crude C 1 micron scale



(d) Toluene Diluted Adhesion Map crude A 10 micron scale

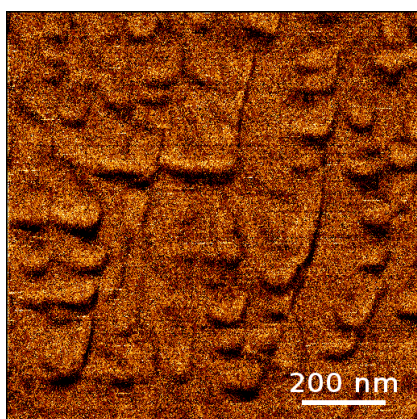


(e) Toluene Diluted Adhesion Map crude B 10 micron scale

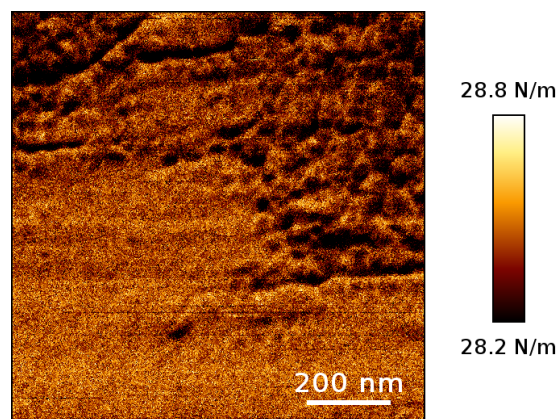


(f) Toluene Diluted Adhesion Map crude C 10 micron scale

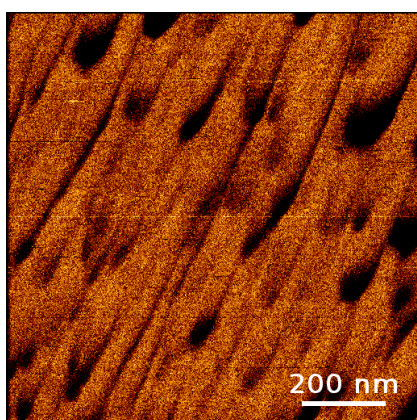
Figure 7.15: Summary of images in 1 micron and 10 microns scale of the adhesion maps of diluted crude oils evaporated on calcite and imaged in decane.



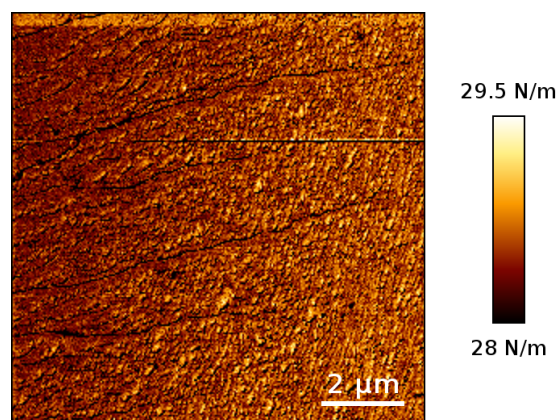
(a) Toluene Diluted Stiffness Map crude A 1 micron scale



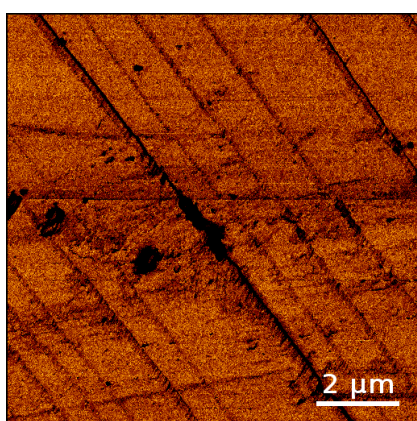
(b) Toluene diluted Stiffness Map crude B 1 micron scale



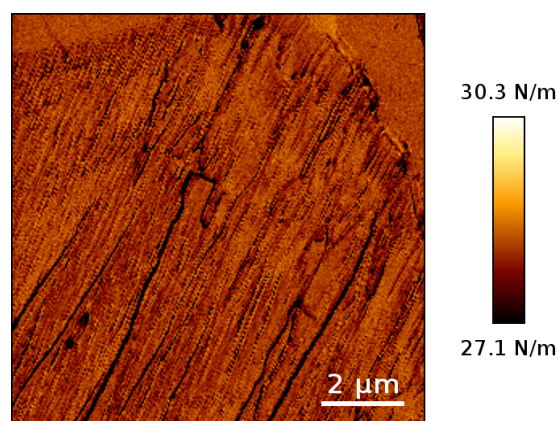
(c) Toluene Diluted Stiffness Map crude C 1 micron scale



(d) Toluene Diluted Stiffness Map crude A 10 micron scale



(e) Toluene Diluted Stiffness Map crude B 10 micron scale



(f) Toluene Diluted Stiffness Map crude C 10 micron scale

Figure 7.16: Summary of images in 1 micron and 10 microns scale of the Stiffness maps of diluted crude oils evaporated on calcite and imaged in decane.

Table 7.3: Summarised quantitative and qualitative AFM gathered data on calcite diluted samples on 10 micron scale.

Crude Oils \ Topographical properties	Coverage Type	Maximum height measured (nm)	Maximum adhesion (nN)	Stiffness range (N m^{-1})
Crude A	Uniform/Agglomerates on thick crude film	40.8	71.5	29.5 - 28
Crude B	Uniform/Agglomerates on thick crude film	34.5	26.5	29 - 28.1
Crude C	Uniform/Agglomerates on thick crude film	99.6	72.5	30.3 - 27.1

7.5 Comparison of Deposit Patterns between Mica and Calcite

On Mica, agglomerates were observed. There is no uniform coverage of the mica's surface. This is a result of the negative-repulsive interactions between the surface of the mica and crude oil's polar components. As opposed to mica, calcite has a positive surface charge, and therefore crude oil forms a more uniform film on the surface of calcite. From the results, crude C is more adhesive than crude A and B, and this is in agreement with the fact that crude oil C is the most unstable crude oil out of the three.

7.6 Limitations and Issues with method

Crude oil C is the most adhesive crude oil out of the three crude oils used in this study. When diluted in toluene and adsorbed onto mica, the surface of the mica became too adhesive, and the surface could not be imaged using AFM. This is a result of the adhesive surface interacting with the cantilever tip. This is a limitation to this method as the surface is not entirely dry; therefore, crude oil that has very adhesive deposits (such as crude oil C) cannot be imaged. Drying the sample in the oven will result in a rough surface, which is not something one can expect from the conditions in the reservoir.

7.7 Conclusion

Crude oil impacts the surface structure of minerals upon ageing. The mineralogy of a surface plays a key role in determining whether crude oil forms distinct agglomerates across the surface

of the mineral (Similar results were also obtained by other research groups in Imperial College London such as work done by Campen et al.2020 [65].) or whether the oil covers the surface of the mineral in a uniform manner. Crude oil formed agglomerates across the surface of the mica, whereas the surface of calcite was uniformly covered with a solid crude oil film. This was largely due to the different surface charges of these minerals. Different crude oils have slightly different behaviours regarding the same mineral. For instance, crude A produces a thinner crude oil film than crude B. The key conclusion is that although crude oil uniformly covers the surface of the calcite, the crude oil film itself is not homogenous.

In addition, the rapid method implemented in this project, initially by serial dilution of crude oil in toluene, is a method that saves time and indeed produces consistent results with the ageing technique. However, the details of the results were vastly different. This means that this technique is appropriate to give an idea of what is to be expected, but it is not a reliable technique for drawing conclusions, as ageing shows different key results that are not fully represented by this method. The deposit pattern on mineral surfaces by crude oil is dependent on the mineral surface characteristics, such as surface charge. The key conclusions to draw from the data gathered in this chapter are:

- Toluene dilution produces similar results for mica and calcite to the ageing technique; however, the size of aggregates and thickness of crude oil film formed on the surface of the minerals in this quick technique are not as presentable as the ageing technique.
- The surface charge of the mineral crude oil's surface active components come into contact with play a key role in the pattern they form on the surface of that mineral, as it is evident that repulsive charge interactions lead to distinct aggregate formation, as seen on mica's surface, while on calcite's positive surface, a more uniform film is formed due to attractive interactions between calcite's surface and negatively charged surface active polar components of crude oil (asphaltenes and resins).
- The stability of crude oil in maintaining the asphaltenes in a dissolved state is directly linked to the quantity of aggregates and the thickness of the film observed on the mineral surface.
- Heavy crude oils, characterised by greater viscosity due to higher asphaltene concentrations, tend to create a greater number of aggregates on the surface of mineral rocks. Due to the presence of asphaltenes, which are surface-active polar components of crude oil, the aggregates created will modify the wettability of the rock's surface in favour of crude

oil. This alteration negatively impacts the recovery rate from reservoirs, as observed and documented in the industry.

Chapter 8

In-situ 3D measurements of nano-scale liquid films along the internal surface of porous rocks

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8.1 Introduction

Multiphase flow processes in porous media play a role in a large range of applications, including filtration, swelling media, printing technologies, building materials, and fuel cells. In the subsurface, multiphase flow in porous media occurs during infiltration of rain, environmental remediation applications, transport of natural organic matter in soils or oil recovery, CO₂ sequestration, and hydrogen storage [223, 47, 222]. Thereby, two or more immiscible fluids, such as air, gas, water, and oleic phases, including petroleum hydrocarbons or crude, move through the porous material. The flow behaviour of one single fluid within a porous rock can be determined through the rock's permeability, defined by Darcy's law (Morris Muskat developed the multiphase flow. Darcy's law states that oil, gas, and water have all relative permeabilities, and this is widely used in sandstone and carbonate rocks [217].).

$$q = -\frac{k_s}{\mu} \frac{\Delta p}{L}, \quad (8.1)$$

Where q represents volumetric flux per unit area ($q=Q/A$, where Q is volumetric flux and A is the cross-sectional area.), μ is the fluid viscosity, and Δp is the pressure drop along the length L . k_s represents the permeability of the medium with units of (m²) [192].

Multi-phase flow in porous rock, on the other hand, is commonly described through a phenomenological extension, in which the proportion of the permeability through each fluid phase to the overall permeability of the rock is given as a function of saturation, providing a relative permeability-saturation relationship. The specific relative permeability-saturation relationship is dependent on the structural and chemical attributes of the system [49]. The chemical attributes define the preference of the solid to stay in contact with one fluid rather than the other, referred to as wetting. The more wetting fluid thereby tends to cover the solid surface, forming thin fluid films, while the contact with the non-wetting fluid is minimized. The wetting behaviour of a fluid-fluid-solid system is reflected through the contact angle given by the surface tensions between the solid and the fluids and the fluid-fluid interfacial tension [145]. Within the pore structure, wetting leads to the non-wetting phase predominantly residing within the pore centres and the wetting phase along the pore walls. However, of critical interest is the behaviour within

narrow pore throats—the connections between one pore body and another. These pore throats provide the pathways for the non-wetting phase to flow. Yet, the increased surface-to-volume ratio in these locations leads to an increased likelihood of snap-off events triggered by swelling of the wetting fluid films related to an increase in local pressure, which in turn leads to local pressure variation triggering re-connection of the non-wetting phase and an overall intermittent behaviour of coalescence and break-up of non-wetting ganglia [49, 249]. This behaviour is referred to as intermittency or ganglion dynamics (Haines jump). [323, 324] has been observed in many studies, including model systems such as microfluidics or glass beads [38, 80, 325] as well as dynamic micro-CT experiments [242, 248] and is considered responsible for the specific shape of relative permeability-saturation relationships [35, 263].

The assessment of this effect, however, is notoriously difficult. Most experiments only reveal that the process is happening. The underlying mechanism, which is related to the swelling and transport of the wetting phase through thin fluid films [245], is either poorly replicated where smooth model surfaces prevent the establishment of natural fluid configurations at this length scale or insufficiently represents the structural and chemical heterogeneity of a natural rock. Computational models trying to predict this behaviour can only overcome this restriction through the implementation of fitting parameters, which allow for replication of previously measured experiments but not for predictions [11, 60, 238].

In this study, we utilised atomic force microscopy (AFM), a tool able to detect topography and force distance relationships down to an atomic level [114, 283] by mechanical means, to measure the nano-scale fluid films responsible for the flow dynamics at the larger scale in situ along the internal surface of the rock. AFM is often used to characterise the wetting properties of fluid/fluid/solid systems, mostly through adhesion measurements where the force to pull off a functionalized tip represents one fluid from a model surface, reflecting the chemical attributes of the solid in the presence of another fluid [180]. In recent years, advancements in AFM have allowed for the assessment of nano-scale droplets, enabling the determination of contact angles down to the nano-metre level [84, 115, 261] and the assessment of the internal surface of rocks with their natural roughness [129, 246, 320].

Here, we use it to create a 3D visualisation of the nano-scale fluid films, to provide the necessary insights to upscale wetting characteristics from the molecular scale to the flow dynamics occurring at the pore scale, and for larger-scale computational models to work.

In summary this section is step by step as follow;

Hypothesis

Many naturally occurring and artificially created porous media are characterised by multiphase flow processes. Because porous rocks, like aquifers and other liquid reservoirs, are wet and have capillarity, water films are likely to form along the internal pore surface when fluid moves through them. These water films could affect how the displacing fluid advances when it is close to connate saturation. The microscale thickness, surface coverage, and connectivity of these water films, which fluctuate with capillary pressure, should determine the flow efficiency.

Experiments

After draining the medium with decane, we use AFM to examine the sub-pore-scale configuration of microscale water films on the rough pore surface of Ketton and Estailades rocks. The permeability through these films is then estimated using a film flow model after comparing the findings with a numerical simulation.

Discoveries

This chapter reveals that there is a significant relationship between capillary pressure and the surface coverage and connectivity of the water films. This could potentially determine the displacement efficiency at the start of imbibition, when the brine phase re-enters the pore space, and affect the permeability of the films by up to several orders of magnitude.

8.2 Methodology and Materials

Rock samples from the Ketton and Estailades were cut into cylindrical plugs with a diameter of 3.8 cm and a length of 5 cm, and pre-drilled subsamples with a diameter of 5 mm and a length of 2 cm inside each plug in accordance with Lin et al.'s description's [182]. As a result of its uniform pore distribution [24] and high degree of chemical homogeneity (>99% calcite), Ketton rock is a good choice for use as a reference material in imaging studies. While the chemical homogeneity of Estailades limestone is comparable, the pore space is more heterogeneous due to the presence of numerous smaller throats that serve as the connections between pores [24]. The samples were initialised by vacuuming them and flooding them with brine that had the

composition shown in Table 8.1.

Table 8.1: Brine composition used for flooding in this project (Shell’s standard brine [111]).

Component	Concentration (mg/L)
Na ⁺	13404
K ⁺	483
Mg ²⁺	1618
Ca ²⁺	508
Cl ⁻	24141
SO ₃ ²⁺	3384
HCO ₃ ²⁺	176

Following that, decalin was added to the samples by centrifuging them between 1300 and 7700 RPM in order to replace the brine. The rotational speed is then used to calculate the capillary pressure, with error margins describing the variation between the top and bottom of the sample. The below equation can be used to calculate the capillary pressure from the rotational speed:

$$P_c(r) = -\frac{\Delta\rho \omega^2 (r_2^2 - r^2)}{2}, \quad (8.2)$$

Where $\Delta\rho$ represents the difference in density between two fluids, $P_c(r)$ denotes the capillary pressure at any given radial point, ω represents the rotating speed, and r_2 indicates the distance to the outlet face of the plug [100].

This part of the sample preparation was performed by Shell in their labs, and the samples were then sent to Imperial for further experiments. The sub-samples were divided up after initialization and put into a decane for the AFM measurement. An AFM from JPK Instruments called the Nanowizard was the instrument used. Mounted on the probe holder was a PPP-NChAuD probe. By measuring force-distance curves over a 128x128 area, the images were produced using the QI mode.

8.2.1 Processing Force curves

In order to identify the presence of fluid films on porous rocks, as well as to ascertain their characteristics and quantify their contribution to flow, recorded force-distance measurements are used in conjunction with topographical data from AFM.

The JPK data processing software was used to process the obtained force-distance curves. To account for the effects of interference and thermal drift, baseline subtraction was used. The software then calculates the solid’s contact point. Additionally, the deflection is added to the height of the piezo extension in order to extract the tip’s vertical location. The FD curves are used to extract the fluid layer thickness using an automated MATLAB algorithm.

8.2.2 Numerical simulations

Using the commercial software Geodict’s PoroDict Pore-size Distribution tool, more numerical simulations were conducted (version 2022) [5]. The simulation data was further processed in the Dragonfly programme (version 2022.1) to produce the surface coverage and volumes.

8.3 Results and discussions

With the objective of characterising the shape of nano-scale fluid films in rocks and their properties regarding flow, we investigated two carbonate rocks: the oolitic Ketton, which is often used in micro-CT studies as a simple benchmark for studies on hydrocarbon production or sub-surface CO₂ storage due to its chemical homogeneity and homogenous pore structure (Andrew, 2015; Hudson and Clements, 2007), and Estailades limestone, a rock with a more heterogeneous pore structure but similar chemical homogeneity [34, 172]. The fluid films were established by initializing the sample first with wetting brine and then desaturated with non-wetting model oil using a centrifuge in a batch also used for other experiments [107].

The measurements were taken from within an open pore on the outside of the sample using the QI mode from JPK Instruments, a fast force spectroscopy mode in which the sharp probe mounted to a cantilever raster scans the surface, taking one full force distance curve by engaging and disengaging the sample at a fixed x-y position at each point.

Figure 8.1 (a) displays a typical force-distance (FD) curve that was captured while scanning fluid films. The various steps in the approach and retraction of the tip are listed from 1 to 7. In both approach (blue) and retract (red) curves, the presence of a fluid film is indicated by a pulling force on the tip that is brought on by an attractive force between the fluid film and the tip [227, 104, 261]. By locating a jump-to-contact point and a solid contact point in the approach curve, the fluid thickness can be estimated, with the difference in vertical tip position

(between steps 2 and 3) resembling the thickness. In the retract curve, a stronger downward force than in the approach is seen, and it lasts longer than the fluid thickness. It takes a certain amount of force to break the capillary neck during retraction, which is what causes this.

For an open pore on the surface of an Estailades rock sample, the height and adhesion images are displayed in Figures 8.1 (b) and (c). Regions with higher adhesion (bright) and regions with lower interaction can be easily distinguished in the adhesion image (dark). This shows that fluid films are present in the areas of rocks with high adhesion and absent in the areas with low adhesion. When the height and adhesion images are compared, it appears that the fluid films are only missing from the elevated crystal edges, which is consistent with the theory that the thin water film will break if the solid surface's curvature makes this possible [246, 163, 157].

8.3.1 AFM images showing the water films at different capillary pressures Ketton rock

The QI mode of the AFM was used in order to obtain the raw data from which the later models of this study were formed. The raw data reveal very important information about the Ketton rock, firstly the Ketton rock's topographical features. The adhesion maps obtained without any further masking for the formation of 3D-modelled water films reveal areas where water films are formed, as water will have a much higher adhesion than the rock's solid surface. This is due to the fact that the tip of the cantilever used throughout this PhD project was hydrophilic, which results in a strong force of adhesion when the tip is pulled away from the film. Additionally, QI Mode, which works on the same principle of force spectroscopy, allowed individual water film curves to be obtained, processed, and visualised.

Figure 8.2 (a) and (b) show the topographical features of ketton rock. This carbonate rock is more than 97% calcite; therefore, it is homogeneous. For better visualisation of these height maps, 3D images were also obtained, as shown in figure 8.7. The most important features are the adhesion maps shown in Figure 8.2 (c) and (d). Figure 8.2 (c), which corresponds to the adhesion map at low PC, consists of more lightly coloured areas than figure 8.2 (d). Light colours correspond to areas with higher adhesion. This is consistent with the initial expectation, as this ketton rock was flushed with decalin at a lower capillary pressure. Therefore, more water films, which exhibit higher adhesion areas, are as expected. In contrast, figure 8.2 (d) only shows high adhesion areas around the edges of the rocks, and in the valleys of the rock there is no light coloured area in the adhesion map, indicating much less water film remains on the surface of

the rock.

8.3.2 Water Films illustration via force curves obtained via AFM

The cantilevers used in this project were PPP-NCH-AuD, which are silicon-made, and the cantilevers tip is gold-coated; gold is a hydrophilic metal [272, 106]. This means the tip of the cantilever will dive towards the liquid film, and upon retraction, there will be a high force of adhesion required to pull away the cantilever from the surface due to the attractive nature of the forces between the gold tip and water film.

Figure 8.3 shows different force curve profiles obtained from different points of the adhesion map obtained from low capillary pressured ketton rocks. The critical feature of curves shown in figure 8.3 is that upon approaching the surface, the tip is attracted to the water film as the trace (approach) curve is not bent upwards but downwards. At this point, the tip comes into contact with the water film. The point at which the curve hits back against the zero-distance line is where the water film ends, and the tip touches the surface of the ketton rock. The areas with very little adhesion occur where the peaks are in the height map; this is because water is collected in the valleys between the ketton granules at nanoscale, and force distance curves at these points do not exhibit the same behaviour.

Figure 8.4 shows the same features as figure 8.3 but for high capillary pressured ketton rock, while figure 8.5 compares the force profiles of a low PC and high PC water film obtained from the ketton rocks. Figure 8.5 shows that the water films of a low PC ketton rock are thicker than those of a high PC. Figure 8.6 illustrates the difference between the force distance curves obtained from a dry surface and those obtained from a wet one.

8.3.3 The shape and size of nano-scale films

For accurate quantification of the fluid films we reconstructed a 3D representation from the topographical and spectroscopic information. The topographical image represents the configuration of the solid. The spectroscopic data reveals the position of the fluid in relation to the solid.

Along with a distribution plot of film thickness, Figure 8.8 displays the reconstructed 3-dimensional results of the water distribution for both Estailades and ketton limestones at the

corresponding capillary pressures. In contrast to samples initiated under higher capillary pressure, which have thin and poorly connected fluid layers, samples initiated under low capillary pressure have thick, well-connected fluid layers. In addition to having a larger thickness under lower capillary pressure, the films have a tendency to cover a larger portion of the solid surface [271]. Corner flow is more likely to be facilitated by connected fluid films under low capillary pressure rather than by re-configuring the fluid layer.

Through a computational model that displays fluid distribution in a structure using an algorithm that fits spheres into the void spaces inside the solid, the physics governing the formation of fluid films can be approximately understood. According to the Young-Laplace equation [246], the respective spheres' capillary pressures can be related:

$$P_c = -\frac{2\gamma \cos \theta}{R}, \quad (8.3)$$

R is the radius of the fitted spheres, θ is the contact angle of water in n-decane with the rock surface, and γ is the interfacial tension between water and decane, which is approximately 50 mN/m [327]. According to Savulescu et al. [261], the average contact angle value for a calcite-brine-decane system is 21° . Solid topologies from all four samples were used in the simulations, with spheres growing in radius by 20 nm at every step. In Figure 8.9, along with the experimentally determined values, we show the fluid volume and surface coverage as a function of the capillary pressure. The percentage of the solid that is covered by the water film is indicated by the surface coverage. It is important to note that, particularly when comparing the Estailades samples, the numerical results from the two distinct samples of the same rock are different. This demonstrates how the parameters are affected by the local topology of the solid surface.

In comparison to the experimental results, the simulation results predict significantly higher surface coverage and brine volume. The dissolution of water into the decane is one potential outcome that results in water loss in the experiments. At a mole fraction of 5.7×10^{-4} , the solubility of water in decane has been determined [262]. We assume that dissolution only has a minor impact on the fluid film's thickness because the residual saturation of water is significantly higher than this.

We therefore anticipate that the numerical simulation's limitations are primarily to blame for the deviation. Surface-fluid interactions, such as electrostatic double layer effects [274], are

not taken into account. Additionally, the upper edges of the solid topology are occasionally left with a nonphysical water film because the sphere fitting isn't perfect for filling them.

8.3.4 Implications on permeability and flow at connate water saturation

Water's ability to flow through porous media is determined by its relative permeability, which is particularly crucial when it comes to connate water saturation. Corner flow is made easier by the water films, which cause snap-off incidents. This has a significant impact on the flow paths because it reduces the connectivity of the non-wetting phase [248].

The relative permeability of dry soils determines how much water they can hold when it rains [179]. Since the water cannot be effectively transported into the soil layer in this situation, a low relative permeability could result in surface flooding [121]. The thickness and connectivity of the water film affect the local relative permeability of water in near-connate conditions. The relative permeability for macroscopic (>10 nm thickness) water films can be calculated using [173]:

$$k_{r,w} = -\frac{4}{k_s \pi D} (1 - \epsilon) \delta^3 \Gamma, \quad (8.4)$$

with k_s the saturated permeability, ϵ the porosity, δ the average fluid film thickness, and Γ the surface coverage fraction. Contrary to what was previously believed [173], the film does not completely cover the solid surface, so we added a surface coverage fraction. Only connected water films are taken into account by this parameter. The imaginary grain diameter, known as the equivalent diameter, or D , is equal to the specific surface area (the surface area per unit volume). One can calculate the equivalent diameter by using:

$$D = \frac{6}{S} \quad (8.5)$$

S stands for the rock sample's specific surface area. On the Digital Rocks Portal, segmented micro-CT images are used to determine the specific surface area [173]. They are obtained from voxelized images, which we assume capture the surface as if we had a flat scan area (voxel sizes for Estailades and ketton are 3.1 microns and 5 microns, respectively). We observe that specific surface areas estimated from measurements of nitrogen adsorption can be up to two orders of

magnitude larger [167].

From the connected fluid volume, we can estimate the permeability as a fraction of the single-phase permeability through the rock. The water layers initiated under high capillary pressure contain many isolated patches, so we estimate that only around 60% of the film is connected. The properties of the porous matrix of the limestone samples are shown in the S.I.. The following relative permeabilities are found:

Table 8.2: Properties of the solid matrices.

Property	Estailades	ketton
Porosity	0.29	0.24
Saturated permeability (m^2)	1.3×10^{-13}	7.1×10^{-12}
Equivalent diameter (μm)	601	1004

Table 8.3: Comparison of relative permeabilities from film model.

Sample	Relative Permeability
Estailades ($P_c = 1.3$ bar)	5.88×10^{-9}
Estailades ($P_c = 0.26$ bar)	3.02×10^{-4}
ketton ($P_c = 0.36$ bar)	2.78×10^{-9}
ketton ($P_c = 0.15$ bar)	3.80×10^{-7}

8.4 Comparison with theoretical models

The physics controlling the formation of such fluid films can be described through a computational model displaying fluid distribution in structure using an algorithm that fits spheres into the void space. If the contact angle is known, the respective spheres can be related to capillary pressures following the Young-Laplace equation [246]. Figure 8.10 shows the results of the computational model for the water film coverage determined from the in-situ measurement and the max and min capillary pressure the four samples have experienced during the centrifuging.

8.5 Conclusion

The findings support the existence of tiny water films on porous rocks' internal surfaces that can help corner-flow [248]. We discover that the overly simple assumption that there is a thin continuous layer of water along the surface that is used in many computational models is too simplistic [173, 157]. According to the sample's preconditioning, we discover that the water coverage along the pore walls' surface varies in continuity and depth. In the past, a numerical model based on the Young-Laplace equation was used to estimate these variations [246]. However, the experimental data reveals a departure from this model, which is probably the result of unaccounted-for effects like disjoining pressure. As a result of the significant variation in coverage and connectivity, the relative permeability of water (in the matrix and not isolated) changes by up to 5 orders of magnitude, supporting our hypothesis that these variations have a significant impact on flow characteristics.

In order to evaluate the factors that affect fluid displacement processes on a sub-pore scale, this section of this PhD project used a novel technique to directly measure fluid films on porous rocks in 3D. The evaluation of fluid film permeability aids in the comprehension of larger-scale displacement processes like snap-off [49]. The next step will involve studying in-situ dynamics of fluid films during displacement processes using the available techniques such as micro-CT. Future research should concentrate on analysing how film configurations affect flow by including these phenomena in the existing numerical flow models, and this is what the final chapter of this thesis will investigate.

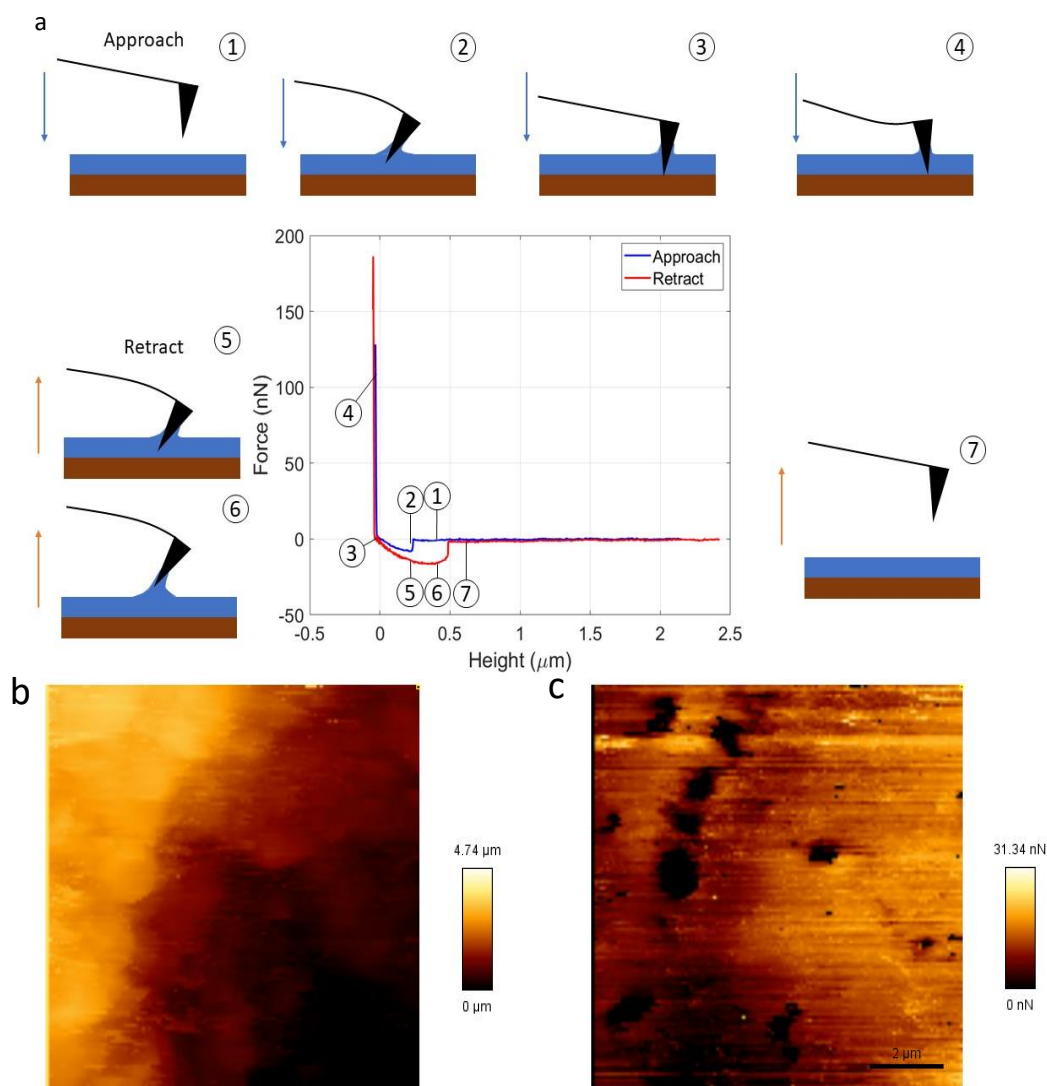
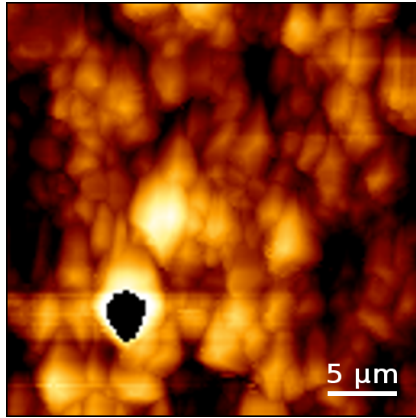
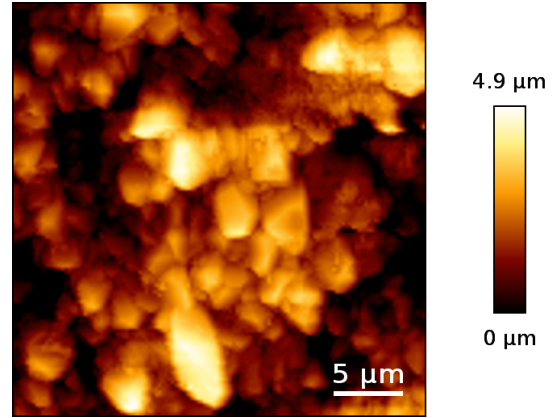


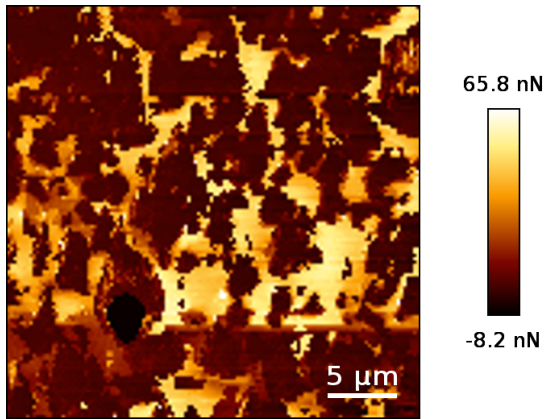
Figure 8.1: Conceptual illustration of the AFM tip's ascent (blue curve) and descent (red curve). The force on the tip as a function of the tip height in relation to the surface is how the force-distance curve is expressed. Capillary forces pull the tip downward as it approaches the film in the following order: (1) tip approaches film; (2) fluid meniscus forms around it; (3) solid contact point; (4) tip is pushed against solid; (5) tip retracts; and (6) capillary forces continue when tip is above fluid level. Image of surface height in 1B. Image of adhesion 1C (mapped from point 6).



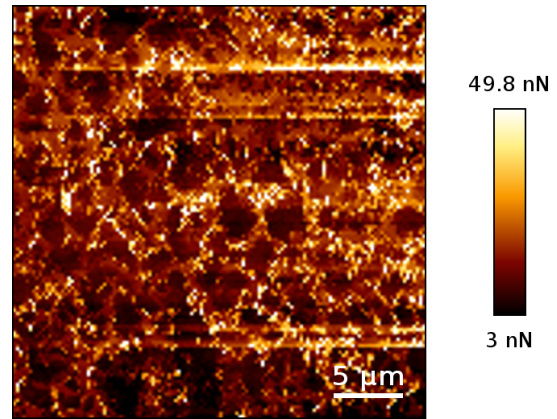
(a) Low PC Ketton Rock Height Map



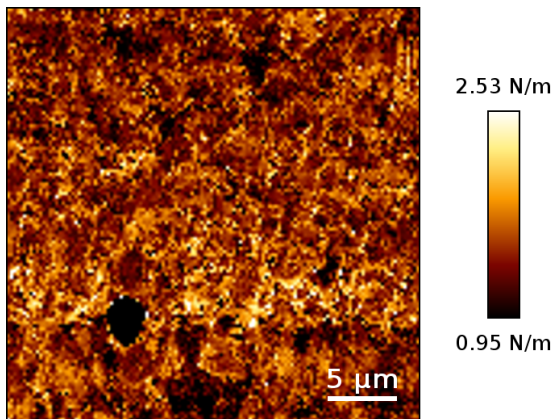
(b) High PC Ketton Rock Height Map



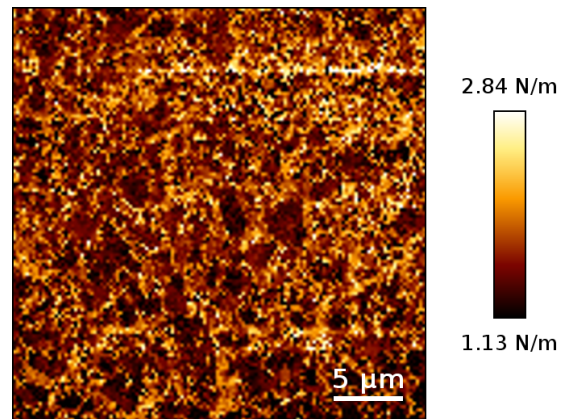
(c) Low PC Ketton Rock Adhesion Map



(d) High PC Ketton Rock Adhesion Map

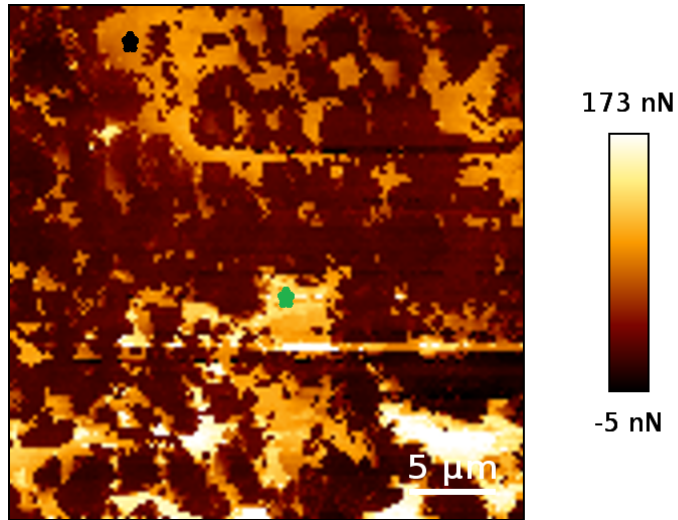


(e) Low PC Ketton Rock Stiffness Map

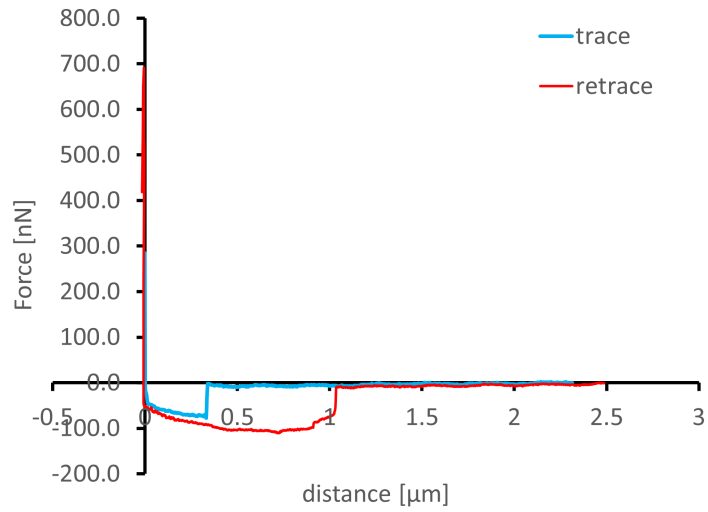


(f) High PC ketton Rock Stiffness Map

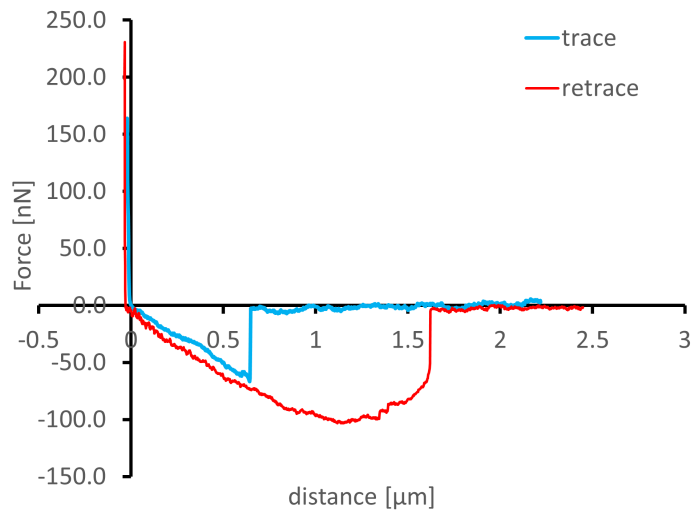
Figure 8.2: Images obtained from ketton rocks which were brine flushed, then flushed with decalin and stored in decalin at different capillary pressures.



(a) Low PC ketton rock's adhesion map

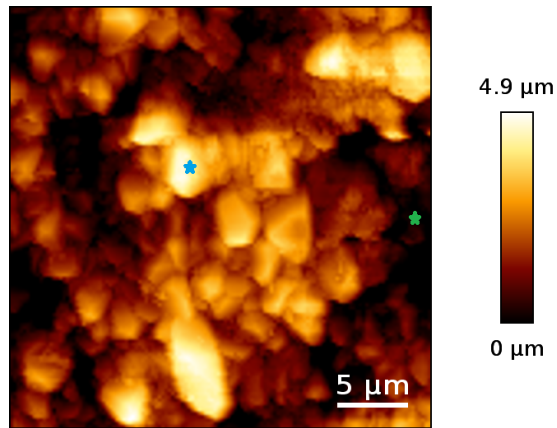


(b) Force Distance curve black star

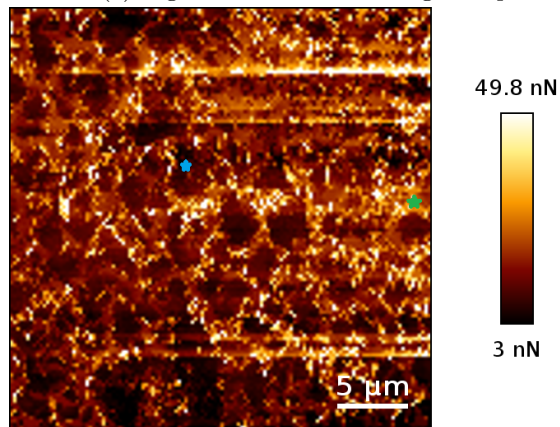


(c) Force Distance curve green star

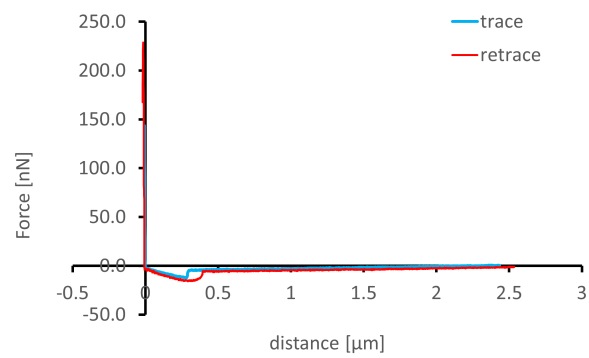
Figure 8.3: Force distance curves obtained from the different high adhesion areas of the low pc ketton rock.



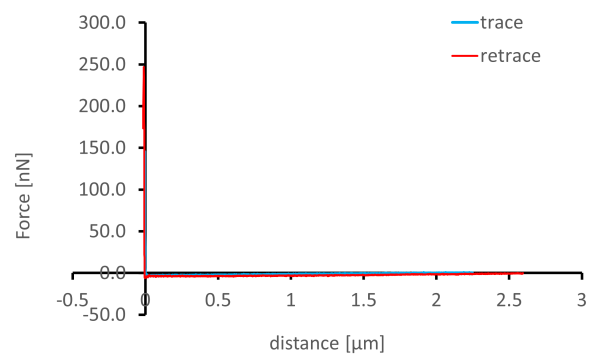
(a) High PC ketton rock's height map



(b)
High
PC



(c) Force Distance curve green star



(d) Force Distance curve blue star

Figure 8.4: Force distance curves obtained from the different high adhesion areas of the high pc ketton rock.

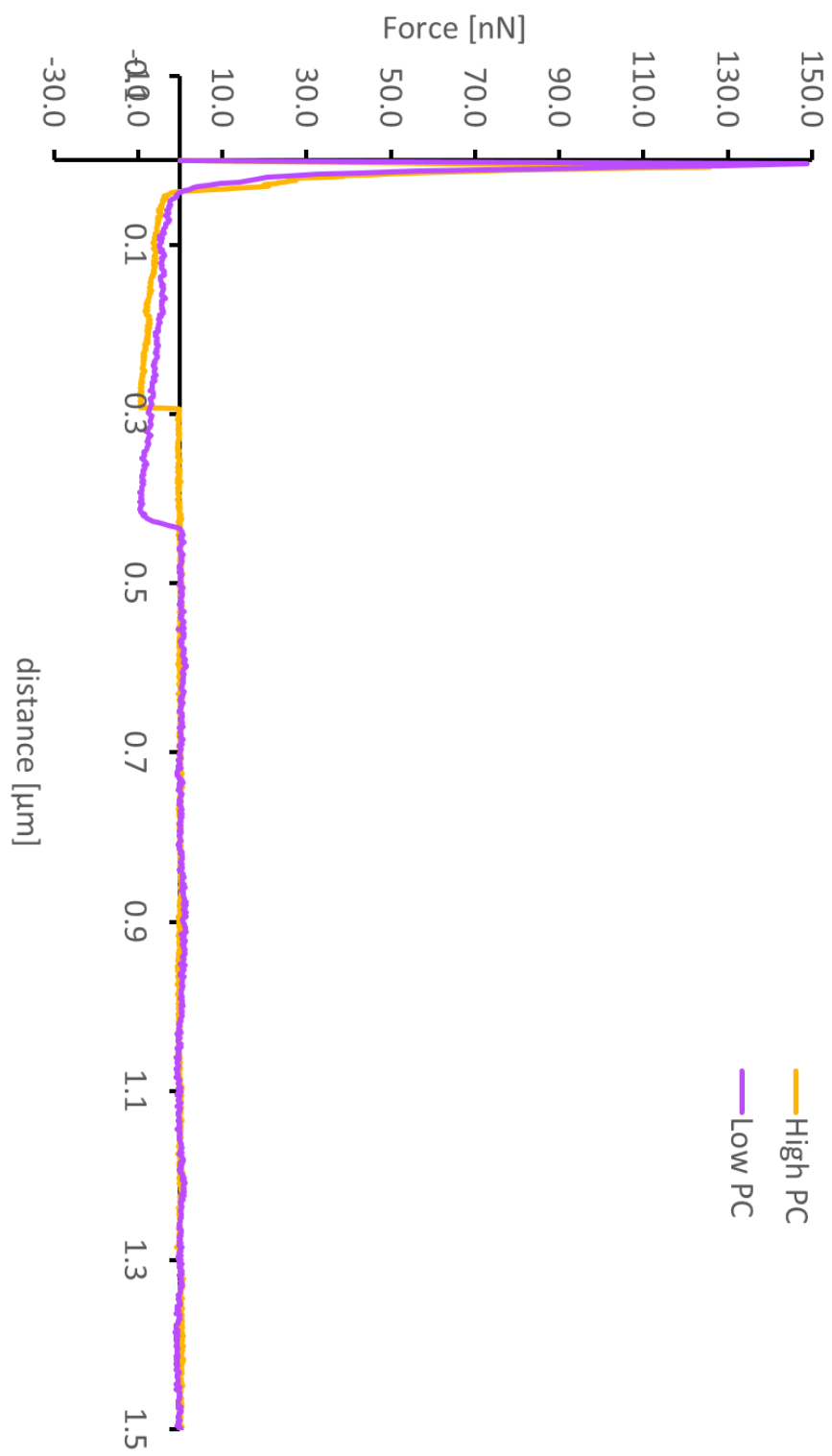
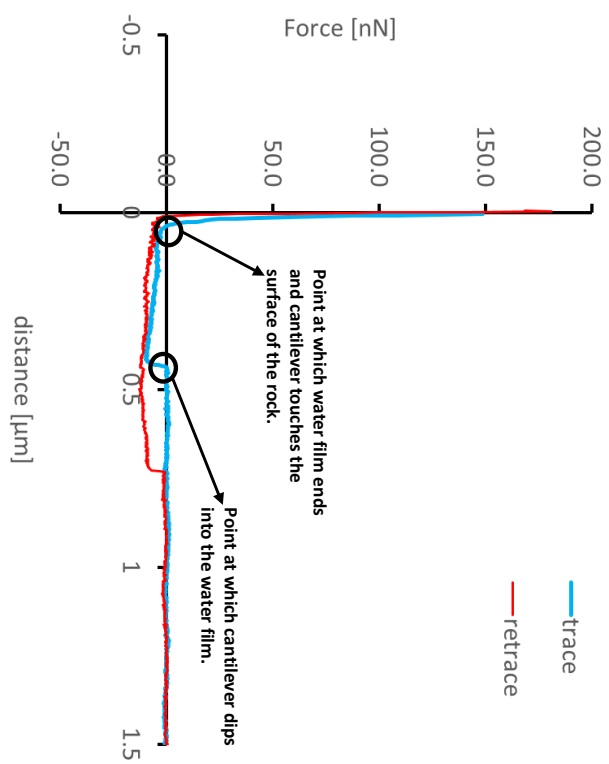
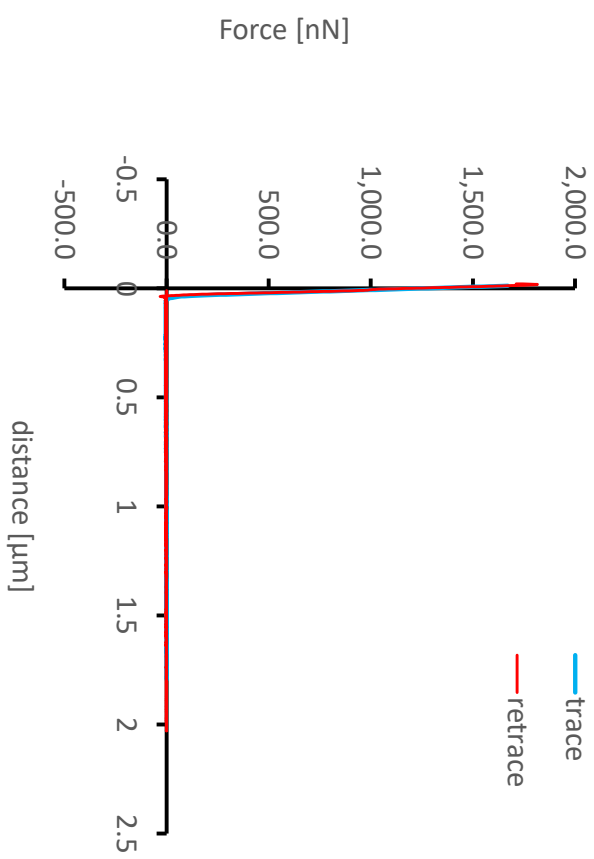


Figure 8.5: Approach curves which highlight the water film thickness, just to illustrate that the higher the capillary pressure of decalin flushing after brine injection, the narrower the water films gets.



(a) Water Film Force Curve



(b) Solid Film Force Curve

Figure 8.6: Comparison of force distance curves when the cantilever touches a liquid film versus a solid film or surface.

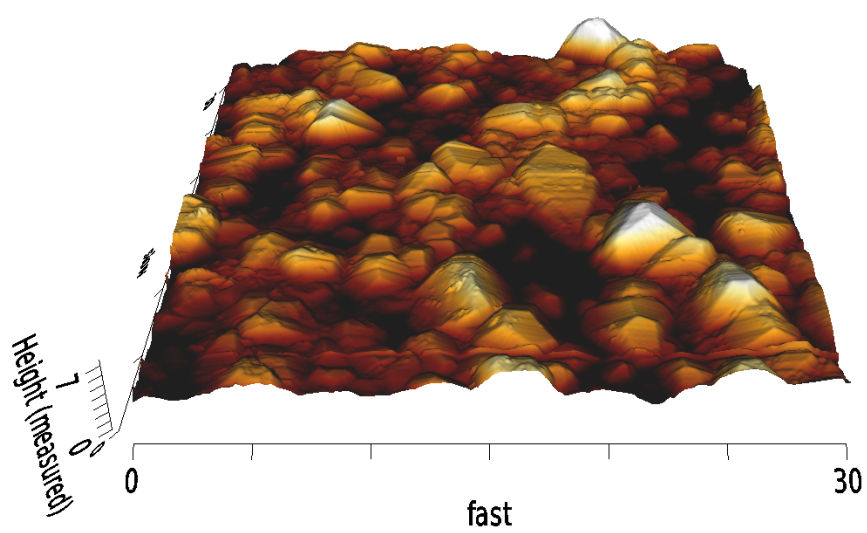


Figure 8.7: 3D image constructed from height maps and processed in JPK software.

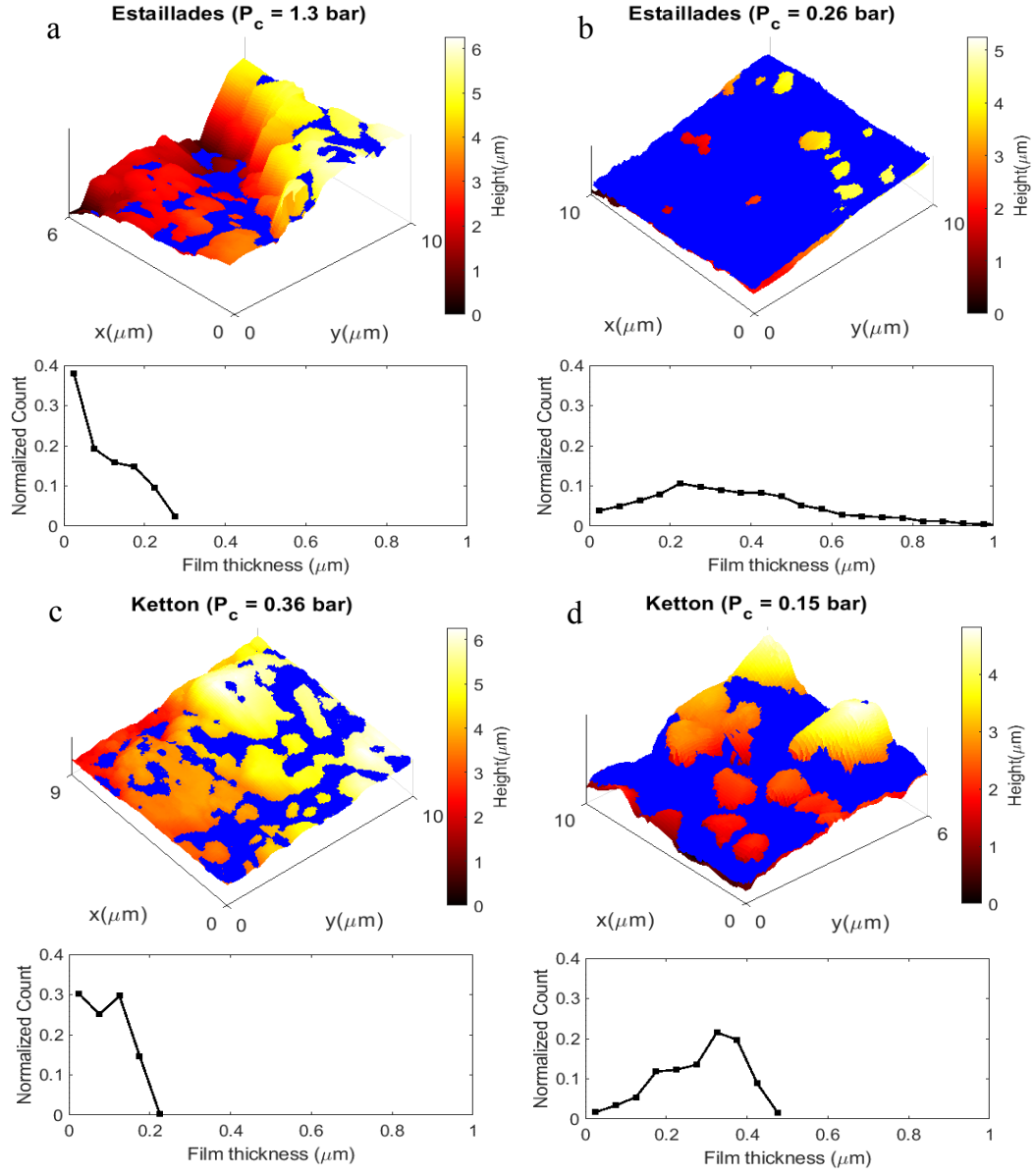
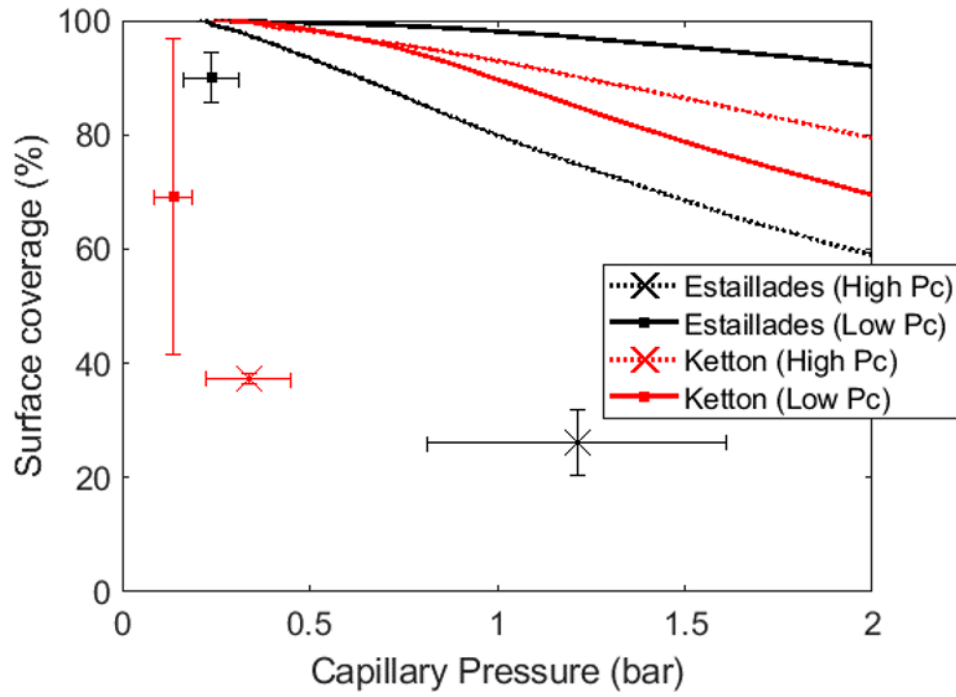
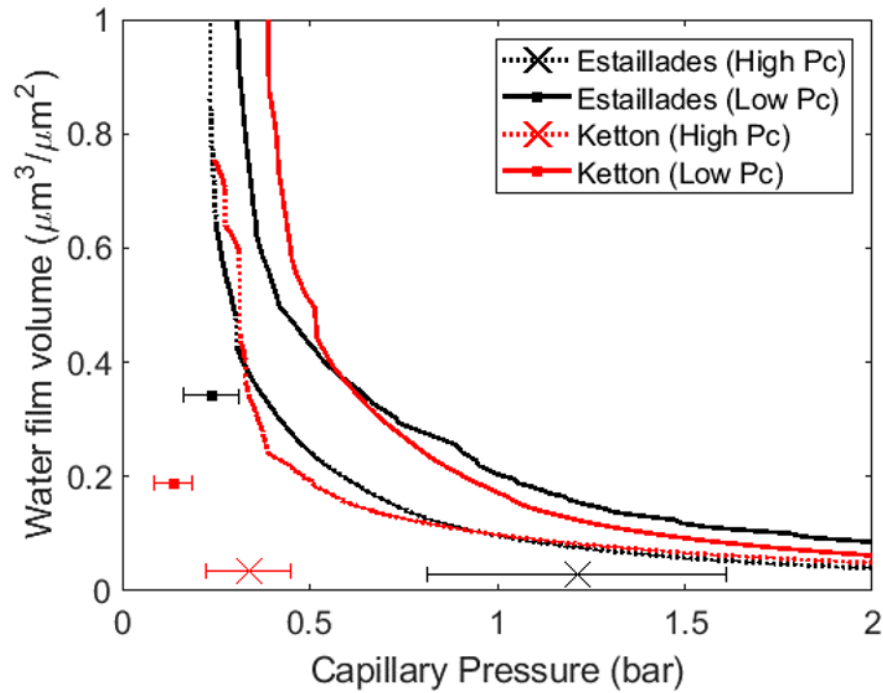


Figure 8.8: A water film coverage (the 3D images);and water film thickness distributions (graphs) for Estailades and ketton at low and high capillary pressure are presented. in this figure.



(a) Surface coverage vs Capillary pressure



(b) Water film volume vs Capillary pressure

Figure 8.9: Surface coverage (a) and water volume per scan area comparison using simulation (lines) and experimental (markers) data (b). The capillary pressure difference between the two ends of the samples during centrifugation is shown by the horizontal error bars. Vertical error bars show how far the median filtered data has deviated from the original.

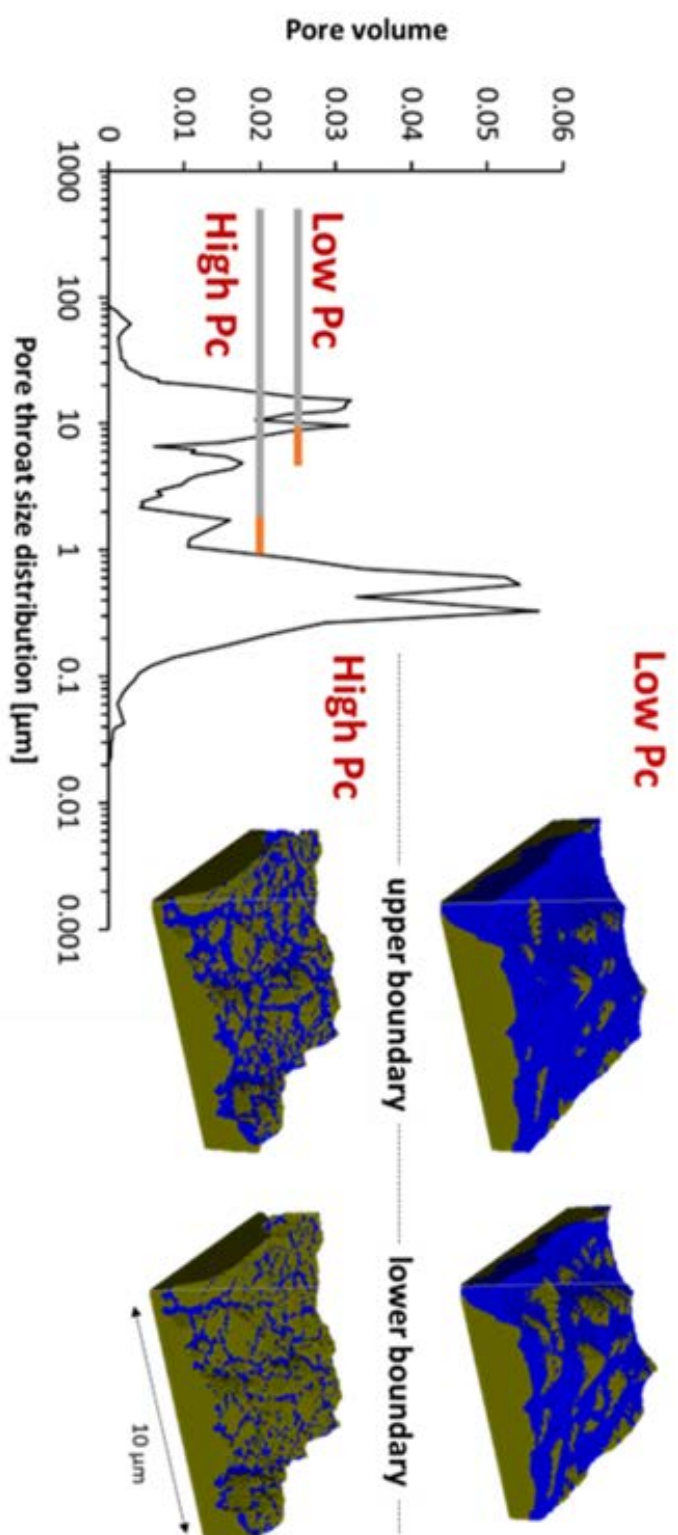


Figure 8.10: Pore size distribution for Estailades rock, the horizontal bars correspond to the pores which should be filled with water at high and low capillary pressures. The images show calculated water films on the 3D image of Estailades at low and high capillary pressures.

Chapter 9

New insights on rock alteration by oil – an in-situ investigation at the nano-scale using AFM

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9.1 Chapter Background

In hydrocarbon reservoirs as well as oil spills into the environment, the alteration of rock by the adsorption of oleic compounds is known to have an impact on flow dynamics in the subsurface

and to control the efficiency of oil recovery and environmental remediation. This process, often referred to as ageing [258, 237], alters the wetting state, the preference of one fluid to stay in contact with the surface in the presence of another fluid. In narrow pores of porous medium, the change in wetting manifests as a change in the pressure gradient needed to move a fluid/fluid interface. Thus, the wetting alteration may trigger changes in pore-scale displacement events: piston like [174] and snap-off [174, 87] reported for oil-filling events to happen much slower in mixed-wet systems than the Haines jumps observed in water-wet systems [209]. At the Darcy scale, ageing manifests in the change of relative permeability and capillary pressure-saturation functions used to assess a reservoir’s production capacity or remediation efficiency. This process can potentially change otherwise favourable conditions for oil recovery to insufficient ones.

The polarity of oil and rock, asphaltene precipitation, and disjoining pressure effects are molecular mechanisms contributing to ageing. Furthermore, chemical and structural heterogeneities are considered at larger length scales. [247].

In computational models, all these processes are lumped into fitting parameters such as contact angles and shape factors [97, 70]. Contact angle variations are thereby supposed to reflect the molecular attributes of the wettability alteration, assuming that the process can be fully described through the adjustment of surface tension between the two fluids and solids. Shape factors account for structural attributes, with the potential to inhibit oil-rock contact considered essential to the alteration of the surface.

In experimental work, ageing is addressed in various ways. In some studies, the reservoir core with the original fluids obtained from the drilling is used, acknowledging potential contamination but assuming that this remains the best approximation of the original conditions. Others clean the entire core and aim to restore the conditions by reintroducing the liquids and exposing the sample again to reservoir temperature and pressure. Thereby, theories about the underlying mechanisms vary. Computational models aiming to predict the pore-scale flow behaviour address the alteration of rock by the oil mainly through a change in contact angle.

However, recent observations suggest a more complex relationship between crude oil and water interactions at the oil-water interface. It was initially thought that oil does not wet the rock surface at the oil-water interface. Thus, it does not change the original wetting pattern and water film distribution on the surface of the rock matrix in the reservoir’s porous structure [181, 19, 281].

In this study, AFM was employed to study the process of wetting alteration by oil.

AFM was used in order to detect the water films on the surface of the Ketton and Estailades quarry rocks in Chapter 1.1.1.

To the best of my knowledge and the research conducted so far, the data in this chapter provide the first in-situ measurements addressing the wettability alteration of rocks by oil using AFM. This section presents a novel methodology to scan the internal surface of a porous rock after treatment with crude oil close to connate water saturation and after water flooding at the nm scale to determine the underlying mechanisms.

9.2 Materials Methodology

9.2.1 Rocks and Fluid Samples

In this study, we used the same quarry rocks as chapter 1.1.1 Ketton carbonate, which is an oolitic limestone [210] and Estailades carbonate. The composition of the brines and the results of the SARA analysis, TAN, TBN relative permittivity, viscosity, and density at 20 °C for the different crude oils used in this study are displayed in the experimental tables 2.1.4, 4.2, 4.6, 8.1, 8.2, 8.3.

9.2.2 Sample Preparation

The rock samples were first vacuumed, then saturated with brine, and then desaturated with decalin using a centrifuge. Two Ketton samples were centrifuged at 1300 RPM and 2000 RPM. Subsequently, the capillary pressures were determined from the rotational speeds as per the previous chapter.

One sub-sample of each sample was placed in a decane for measurements to determine nano-scale fluid configurations prior to the wettability alteration and into crude oil for treatment. Additional sub-samples were submerged into the three different crude oils used in this project with properties described in chapter 4 and aged for 4 weeks at a temperature of 70 °C. At this elevated temperature, equilibrium pressures were achieved as described in chapter 5, table 5.1.

Furthermore, two Estailades samples were centrifuged between rotation speeds of 1300 and 7700 RPM (it is worth noting that Shell performed all brine flooding in their laboratories). Also, sub-samples were taken for these samples to investigate nano-scale fluid configuration prior to treatment with crude. Additional sub-samples were treated with crude B for micro-CT flooding experiments. After the water flood experiments, the nano-scale fluid configurations at residual oil saturation were investigated to complement the micro-CT study.

9.2.3 AFM measurement and data processing

Nanowizard 4 AFM (JPK Instruments, now Bruker) was used to visualise the structure of the rock surface and liquid and solid films down to nanometer resolution. The measurements were conducted in approachable adjacent pores not affected by drilling (see appendix G). The samples were scanned with a silicon tip (PPP-NCHAuD from NanosensorTM) in quantitative imaging mode. The images were levelled, filtered using a median filter, and analysed using the JPKSPM data processing software (JPK instruments). The force-distance curves were compared with the water-film force-distance curves in order to see whether oil displaced the water film on the surface of the Ketton rocks after the ageing process.

Due to its simple bead-pack-like structure, Ketton rock is better suited for AFM studies, easing the identification of suitable locations for AFM scanning. Due to the higher complexity of Estailades, the approach of the internal surface of a pore fails frequently. However, with respect to flow dynamics occurring during water flow, Estailades is considered more representative of reservoir conditions.

9.3 Results and Discussion

AFM measurements were obtained for dry samples of Ketton and Estailades discussed in subsection 9.3.1, for Ketton and Estailades close connate water saturation prior to the exposure to crude which are described in subsection 9.3.2, for Ketton rock close to connate water saturation after exposure to crude (discussed in subsection 9.3.3) and for Estailades rock at residual oil saturation which is discussed in subsection 9.3.4.

9.3.1 Challenges imaging a rock using AFM, Natural Roughness of the rocks

Figure 9.1 shows the AFM measurements obtained from the natural internal surface of the two carbonates, Ketton (a,b,c) and Estailades (d,e,f), investigated. Figure 9.1g shows an example of a scanning location, with the probe monitored by the laser (violet dot) focusing on a grain surface of the rock. The height images (a,d) represent the structure. In each sample, only a few individual crystals are visible. Hence, the images cannot be considered representative. The adhesion images (b,e) reflect the attraction the tip experiences when scanning the surface at a particular location, and the slope (c, f) represents the resistance of the surface when it is pushed against it by the piezo. Adhesion and slope can be indicative of the mineralogy, e.g., if different minerals have varying surface charges or hardness [321, 293, 311].

The two carbonates used in this study show a rather homogeneous composition and hence only minor variation in these parameters. Yet, distinct regions of higher and lower adhesion or slope are observed. This is mainly due to imaging artefacts: The tip is approaching each position with fixed x and y piezos, while the z piezo keeps moving. If the tip lands on a parallel surface as schematically drawn in figure 9.1 h-I, one obtains a force distance curve reflecting the very forces described before (figure 9.1 i). However, on a tilted surface, the tip might get in contact with a larger surface area (figure 9.1 h-II), slip (figure 9.1 h-III), or get stuck (figure 9.1 h, IV), increasing the tip-rock contact area and adhesion or appearing softer than it actually is manifesting in a lower slope, as shown by the force distance curve in figure 9.1 j.

We highlight these effects to indicate the uncertainties of this measurement. Generally, the more steep the surface in relation to the movement direction of the tip and the narrower the hole, the more likely it is affected by an error. Each measurement was taken at a different location, as at this scale, finding the same spot after the sample has been moved for treatment is impossible with the techniques available. Accordingly, the data presented in this study is for qualitative interpretation and cannot be used quantitatively.

9.3.2 Nano-scale fluid coverage close to connate water saturation

The measurements in figure 9.2 show the samples, Ketton (a-f) and Estailades (fg-l), close to connate water saturation prior to exposure to the crude. The presence of the water film can be seen in the adhesion image. This is as capillary action pulls down the water-wetting tip. The force distance curves shown in figure 9.2 show the recorded response for a case where no (m), a

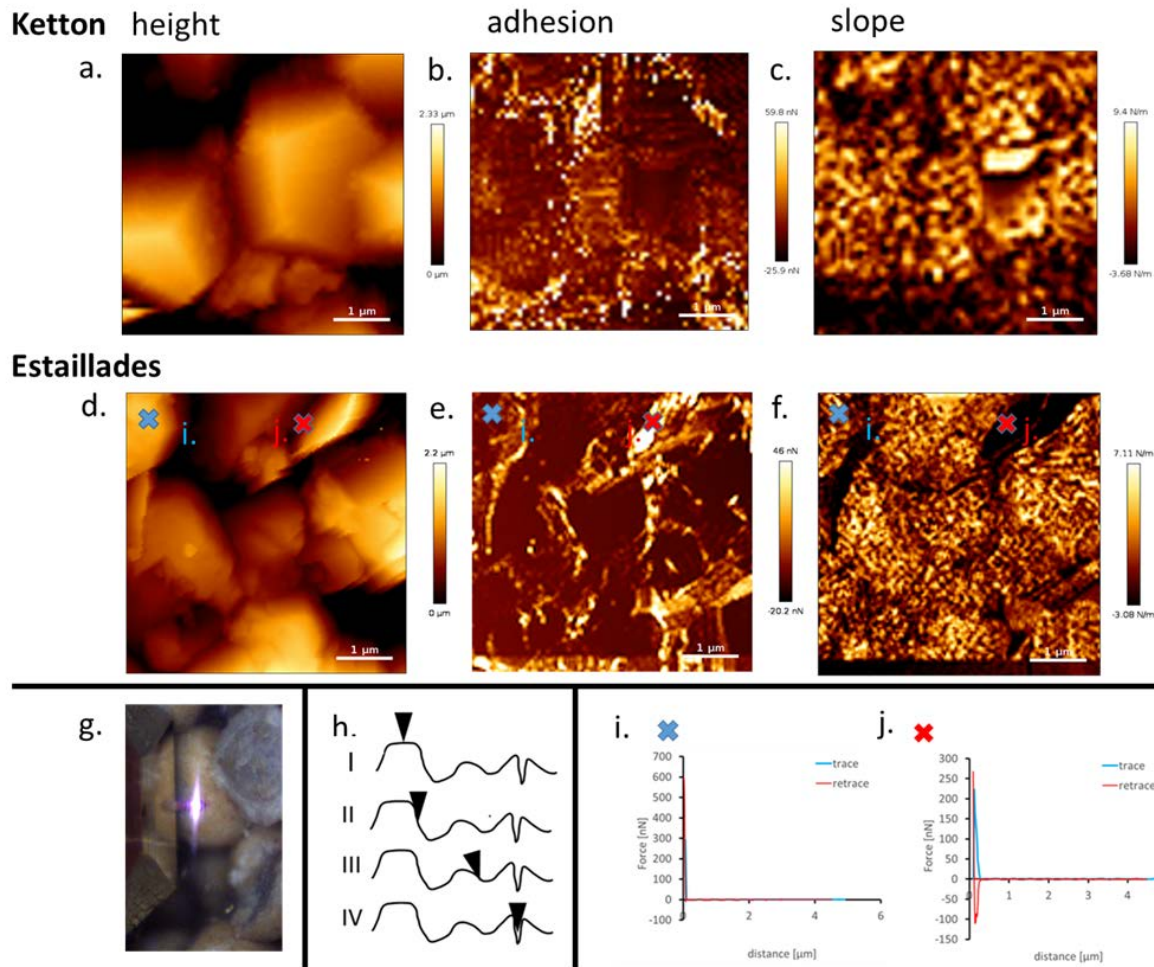


Figure 9.1: The surfaces of Ketton carbonate (a-c) and Estailades carbonate (d-f) were measured with AFM. a,d reflect the topography, b,d the adhesion, and e,f the slope of the respective surface. g displays the positioning of the AFM probe on the surface of a grain. The roughness of the surface can cause the AFM tip to expose a larger area to the surface, slip or get stuck (h), effect the recorded force-distance curves (i, j), and create image artefacts that need to be considered in the interpretation.

thick (n), or a thin film is present (o), and p is a schematic of the AFM probe at different stages of the approach and retract in the presence of the water film. This relationship has already been observed in model mineral-oil-water systems, as well as for lubricants and micocylage.

Overall, the measurements of low capillary pressure samples (Ketton: figure 9.2 a,b,c and Estailades: figure 9.2 g,h,i) show higher adhesion responses, with up to 62 nN and 56 nN, respectively, than the high capillary pressure samples (Ketton: figure 9.2 d,e,f and Estailades: figure 9.2 j,k,l) with up to 22.6 nN and 11.3 nN, which hinds to deeper layers. Also, water coverage, reflected by the area of higher adhesion in the images figure 9.2 b,h,e,k, appears higher for low capillary pressure samples than high capillary pressure samples. The water coverage at the measured location in the high capillary pressure Ketton sample appears so low,

that the measured adhesion response in the displayed image is of insufficient quality to prove its existence (figure 9.2 h).

Overall, the observations are in line with the coverages modelled in Ruecker et al. 2020 [246]. This chapter further investigates and looks into alterations caused by the ageing process on water film distributions seen on Ketton rocks recorded in chapter 1.1.1.

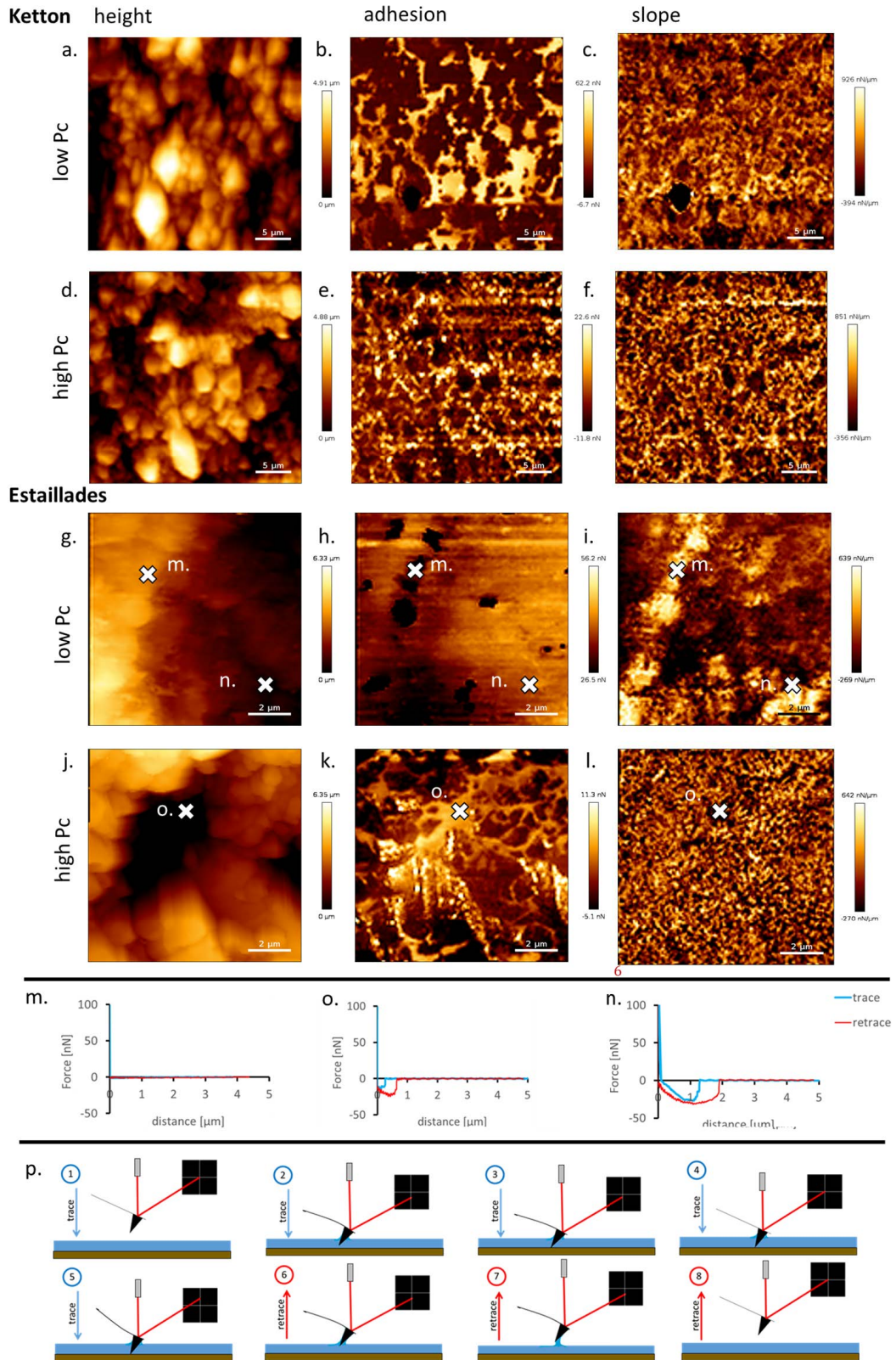


Figure 9.2: Topographic, adhesion, and slope images of water films after centrifugation for high and low capillary pressures for Ketton (a-f) and Estailades (g-j), respectively. The force-distance curves (m, o, n) illustrate how the tip interacts with the fluid-fluid interface and effects the adhesion response due to capillary effects during the tip retraction. p illustrates the movement of the tip through the water film.

9.3.3 Nano-scale observations of the rock alteration by oil

Figure 9.3 shows the measurements for the low capillary pressure Ketton samples (figure 9.3 a,b,c) and high capillary pressure samples (figure 9.3 d,e,f) after ageing in crude B. The low capillary pressure sample again displays a higher adhesion than the high capillary sample. However, surface coverage is more difficult to derive for this sample. The force-distance curves appear different as the samples age. Figure 9.3 e,f,g,h display some examples. In contrast to the measurements obtained before ageing, the tip appeared repulsive to the fluid-fluid interface. We interpret this as surface active components from the crude not only adhering to the crude-solid interface but also arranging along the fluid-fluid interface, forming a layer that tends to resist the AFM-tip from pushing through.

In figure 9.3 e, the force-distance curve indicates that the tip is not able to penetrate until very close to the surface. However, the adhesion it experiences when retrieving hints at the presence of a water film. A potential explanation could be that during approach, the tip pushing against the layer along the fluid-fluid interface pushes the water underneath aside. However, once in contact with the tip, the capillary force starts acting, causing the adhesion response observed during retraction. In figure 9.3 f, the tip first reacts repulsive as in figure 9.3 e, yet significantly less.

The tip pushes through the fluid-fluid interface, and capillary forces pull it down before it reaches the rock surface, and the retract curve shows strong adhesion, too. We believe such observations may happen where the layer of surface active components is thin or close to non-existent. Figure 9.3 g and h show examples of a force distance curve without a response in adhesion during retract. We interpret these as locations without the presence of water films. However, these can also be distinguished into FD-curves with (figure 9.3g) and without (figure 9.3 h) repulsion responses during the approach. Given the similarity of figure 9.3g to figure 9.2m, we believe that these locations display oil-rock contacts without any layer of surface active components. Whilst figure 9.3 h with Baring differences between hPC and lPc were identified:

- The long range of deflection of the cantilever towards the sample during the disengagement at many positions accumulating in the dips of the surface topography is indicative of a water film underneath the oil, as described in figure 9.3 on the samples that were not exposed to crude.
- This behaviour does not appear in the samples aged with crude A or crude C. However,

in this sample, as in the B-aged samples, the cantilever often first deflects away from the surface before it reaches contact during approach, which could be due to the presence of a soft repulsive layer.

- Furthermore, the F-D curves indicating the presence of a water film show distinct features during the approach: Here, the cantilever often first deflects away from the surface and then towards the surface before reaching contact. This could mean that the fluid/fluid interface is covered by a layer of crude oil components. Sometimes, the probe deflects multiple times back and forth before it engages with the surface, which might relate to pinning effects along the tip.

However, due to image artefacts related to surface structure and capillary action of the fluids present on the tip, many force distance curves appear distorted, allowing only for qualitative interpretation.

9.3.4 The impact of oleic alteration on flow dynamics at the nano-scale

After ageing the brine-flushed Ketton rocks in three separate crude oils, it became evident that ageing alters the wettability of the rock and changes the water film distributions originally recorded on the surface of the rock. It is evident that crude oil's polar components (asphaltenes and resins), as shown in earlier chapters of this thesis, precipitate out of the solution and adsorb onto the surface of the rock or mineral. Once adsorbed, they alter the wettability of the rock in favour of the oil phase, displacing the water adsorbed onto the surface of the rock at the oil-water interface and thus making the surface of the rock "oil-wet" instead of water-wet." Figures 9.4, 9.7, and 9.10 represent raw topographical features of crude A, B, and C, respectively. The topographical height measured maps across the three sets all show the oolitic structure of the Ketton rock. Water films were recorded and analysed to assess potential water-oil orientation at the detection point. Figures 9.5 and 9.6 show no evidence of water films on the surface of the rock after Ketton rocks, which were originally flushed with brine and afterwards aged in crude A.

This is because no force-distance curve indicating a water film, as shown in section 8.3.2 earlier, was seen across multiple images, and this was the case for both low PC and high PC decalin flushed rocks. However, figures 9.8 and 9.9 show that water films have been preserved and have withstand the ageing process when Ketton rocks were aged in crude oil B; however,

the frequency of detecting the water films and the thickness of water films detected have been significantly reduced. Crude oil C showed no evidence of any water films; this was as anticipated as crude oil C was known to be unstable, and after seeing the data with crude oil A, crude oil C confirmed the hypothesis mentioned earlier.

Figures 9.11 and 9.12 show various force-distance curves at different depths of the rock's surface where water films were likely and unlikely to be found on both low PC and high PC samples. It is worth noting an important feature that confirms the formation of crude oil film on the carbonate surface of the Ketton rock: the upward deflection of the FD upon the approach of the cantilever's tip towards the surface of the sample. Because the tip of the cantilever is made of silica, which is negatively charged, an upward deflection away from the base line on the FD represents repulsive force between the sample and the tip. Since no such curves were recorded on calcite and Ketton's positively charged surfaces, such curves can only be triggered by oil coverage on the surface of the rock (since oil films formed by polar surface active components of crude oils are negatively charged).

9.4 Conclusion

This study presents novel AFM approaches to investigate the alteration of rock by oil at the nanometer scale along its naturally rough internal surface. The results showed that water films can prevail in the wetting alteration process. However, only one out of three crudes provided evidence for such water films. The surface active components of the oil were found to inhomogeneously attach to the fluid-fluid and fluid-solid interfaces in the respective samples. The measurements after the water flood further revealed water entrapped by an oil layer as well as regions of different adhesion following a pattern similar to the water distribution observed prior to the wetting alteration. Previous studies at a larger scale demonstrated that the flow behaviour very much depends on the exact oil, brine, rock composition, temperature, pressure, and flow history [24, 31, 33, 254]. The variability of observations may relate to the alteration mechanisms and resulting fluid configurations observed at the nano-metre scale presented in this study. Further studies of this kind may help to understand which pore-scale and core-scale responses relate to the nano-scale effects described. Such results would help in developing more sophisticated modelling tools to predict reservoir development or environmental remediation projects.

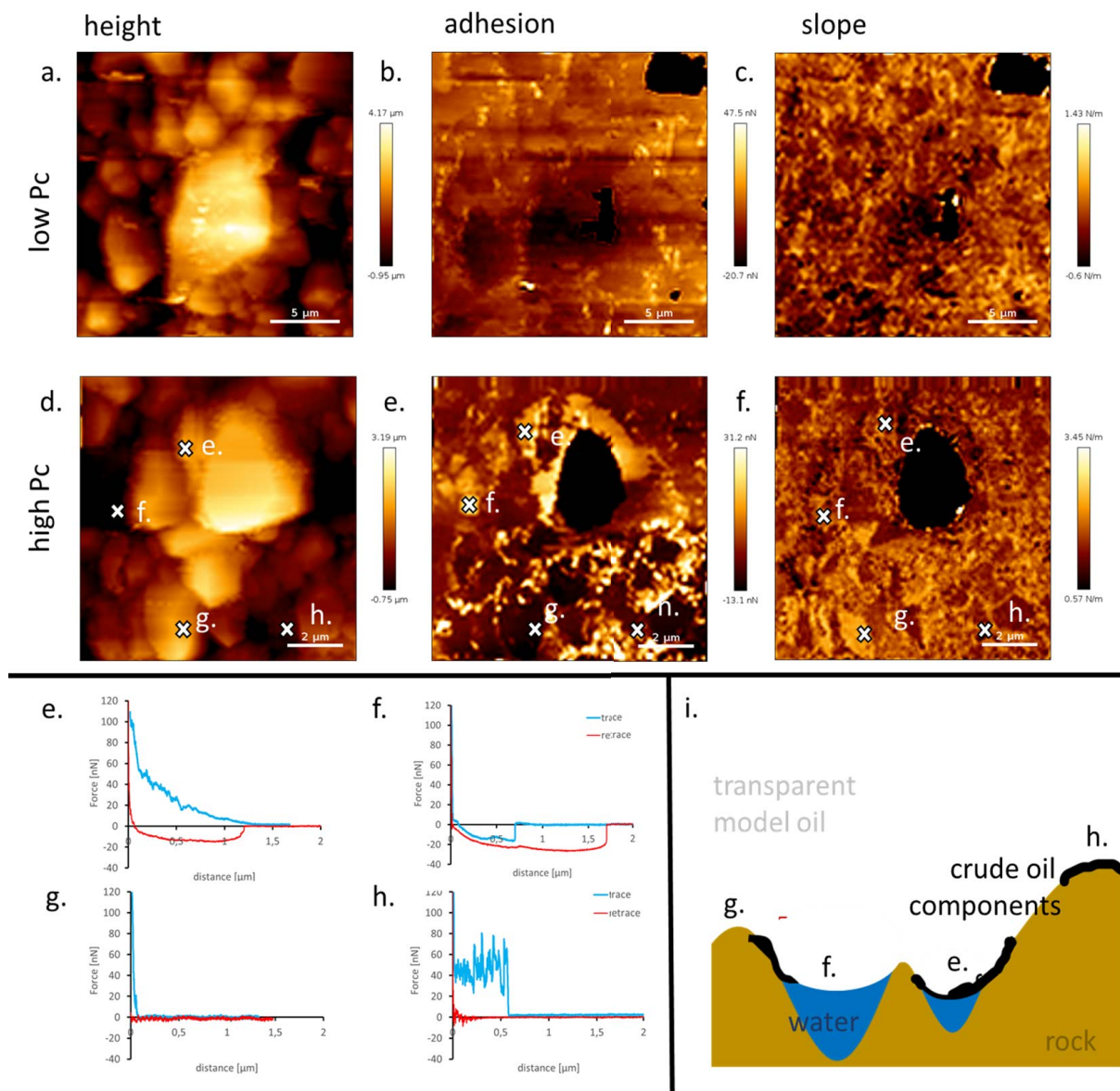
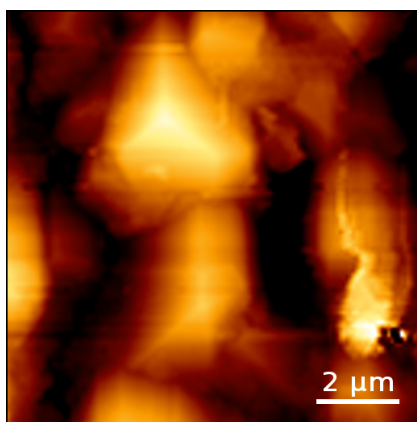
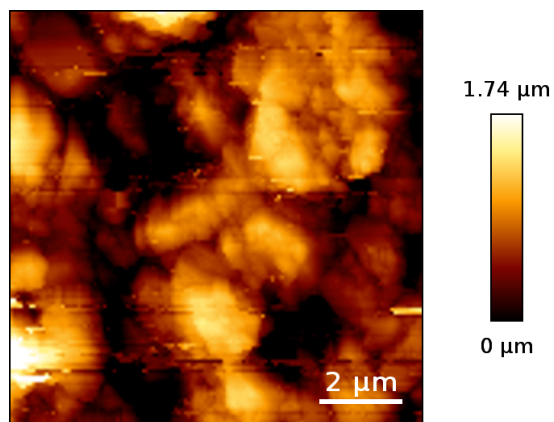


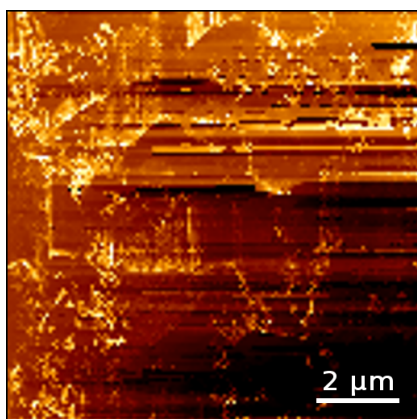
Figure 9.3: Topographic, adhesion, and slope image of Ketton rock aged with crude A after centrifugation for low (a,b,c) and high (d,e,f) capillary pressures. The force-distance curves (e,f, g, and h) illustrate different types of force-distance curves (observed), which we believe correspond to the ageing states illustrated in i.



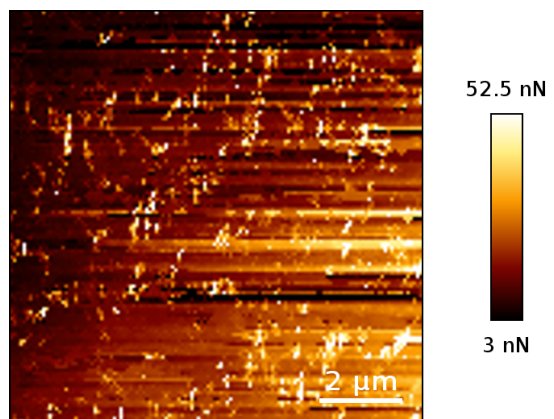
(a) Low PC Ketton Agen aged Rock Height Map



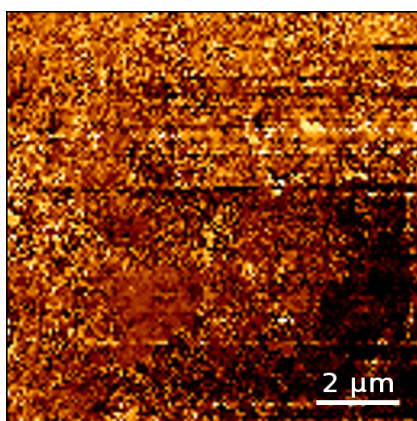
(b) High PC Ketton Agen aged Rock Height Map



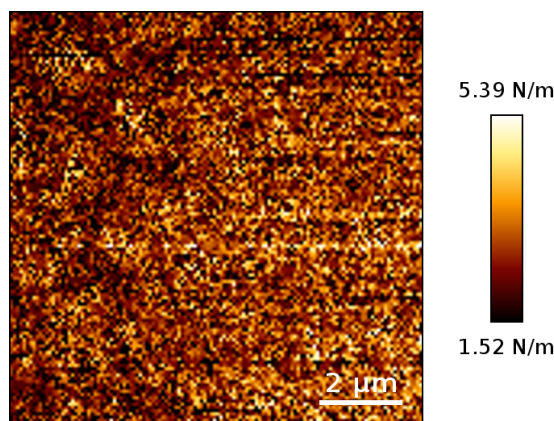
(c) Low PC Ketton Agen aged Rock Adhesion Map



(d) High PC Ketton Agen aged Rock Adhesion Map

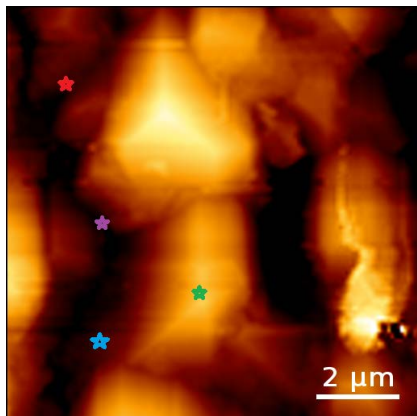


(e) Low PC Ketton Agen aged Rock Stiffness Map

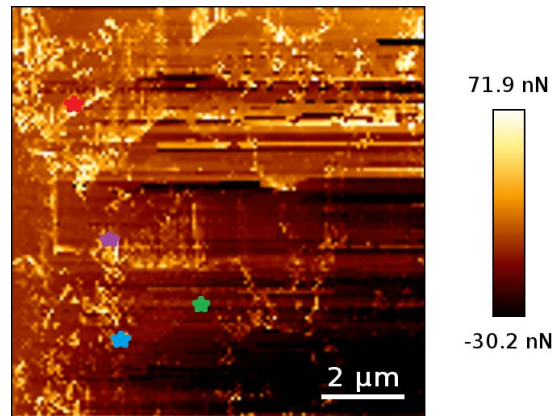


(f) High PC Ketton Agen aged Rock Stiffness Map

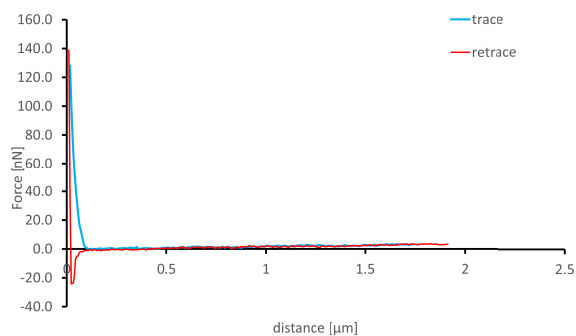
Figure 9.4: Ketton rock AFM images, these rocks were flushed with brine, then flushed with decalin at a lower and high capillary pressure and finally aged with crude A.



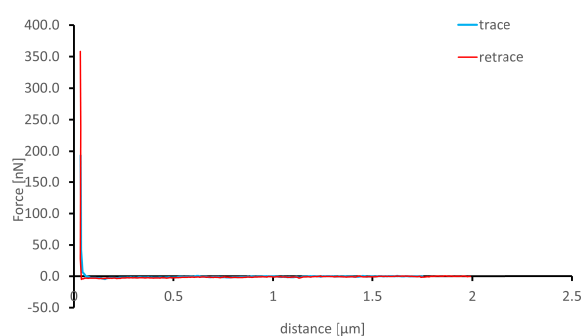
(a) Low PC Ketton crude A aged Rock Height map marked



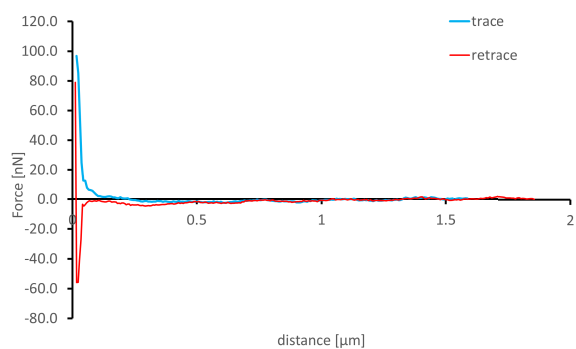
(b) Low PC Ketton crude A adhesion map marked



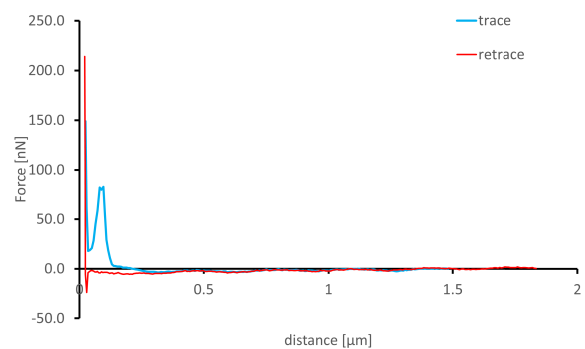
(c) Force distance curve at blue star



(d) Force distance curve at green star

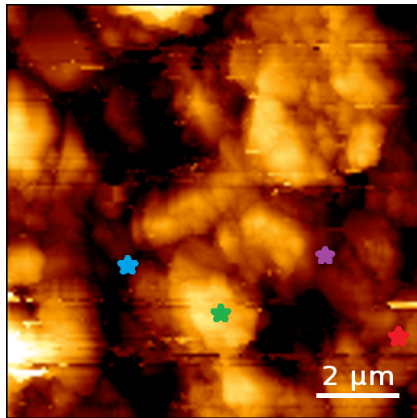


(e) Force distance curve at red star

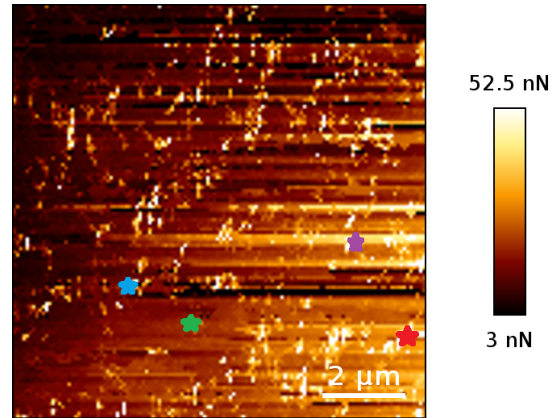


(f) Force distance curve at purple star

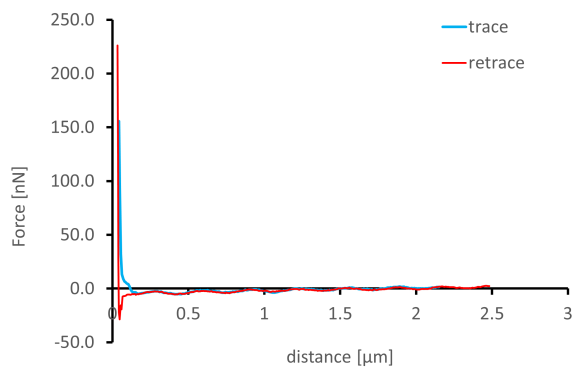
Figure 9.5: Various force distance curves illustration at different points of the adhesion and height measured map for low PC aged in crude A Ketton rock.



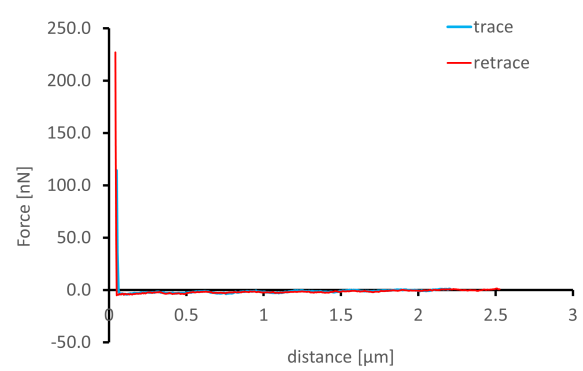
(a) High PC Ketton crude A aged Rock Height map marked



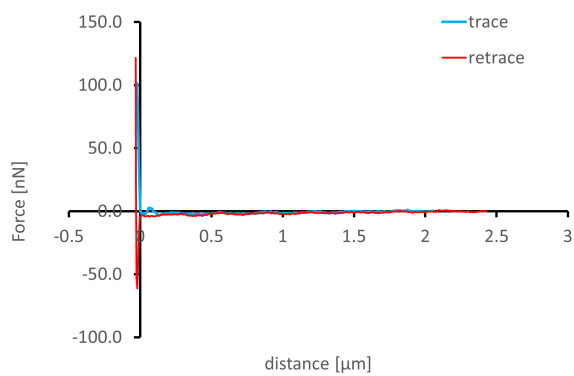
(b) High PC Ketton crude A adhesion map marked



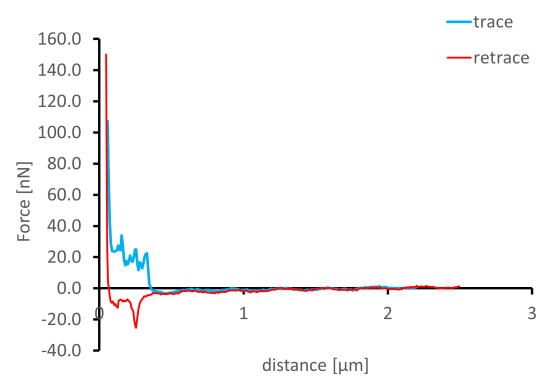
(c) Force distance curve at blue star



(d) Force distance curve at green star

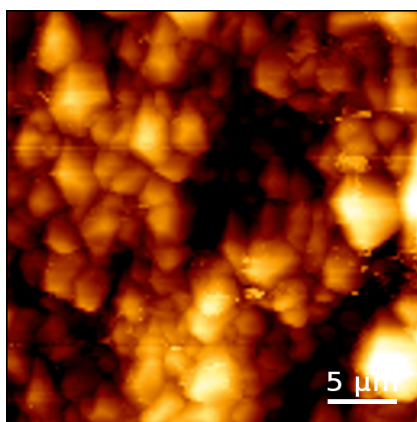


(e) Force distance curve at red star

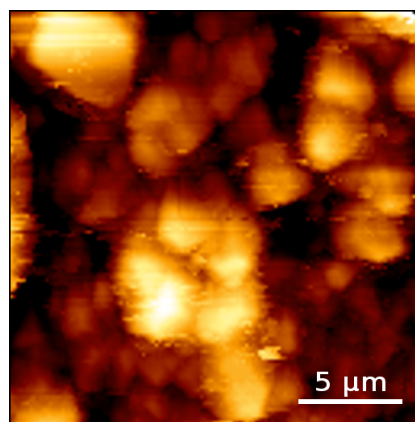


(f) Force distance curve at purple star

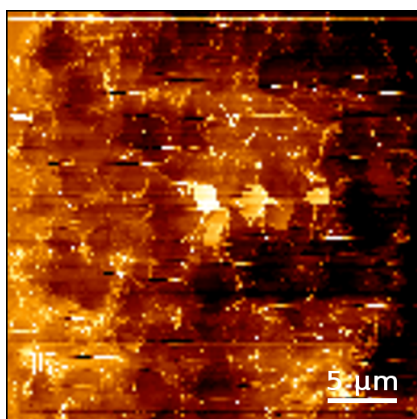
Figure 9.6: Various force distance curves illustration at different points of the adhesion and height measured map for high PC aged in crude A Ketton rock.



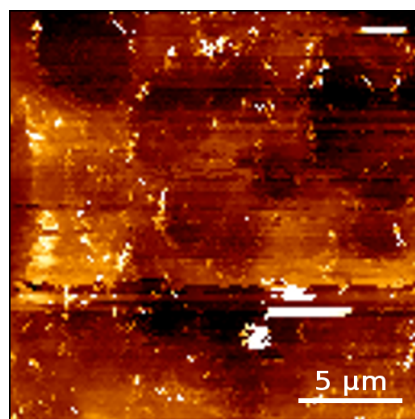
(a) Low PC Ketton crude B aged Rock Height Map



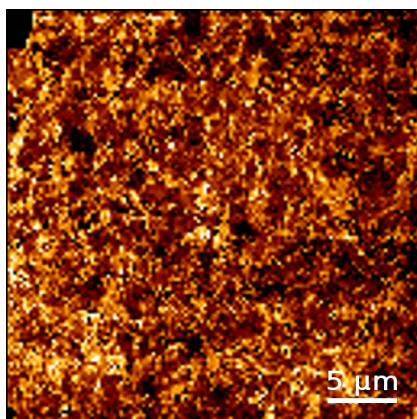
(b) High PC Ketton crude B aged Rock Height Map



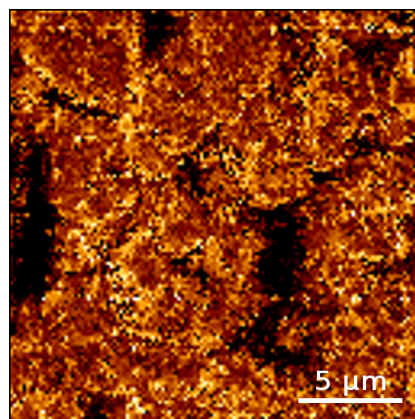
(c) Low PC Ketton crude B aged Rock Adhesion Map



(d) High PC Ketton crude B aged Rock Adhesion Map

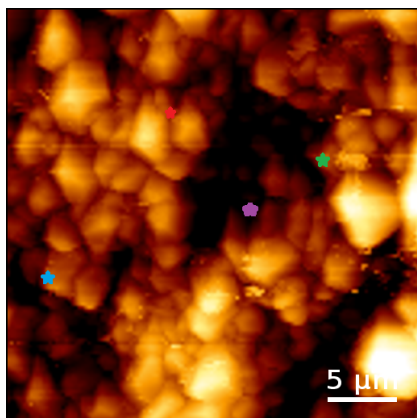


(e) Low PC Ketton crude B aged Rock Stiffness Map

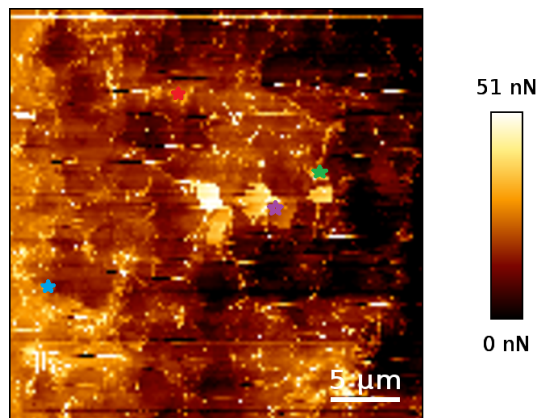


(f) High PC Ketton crude B aged Rock Stiffness Map

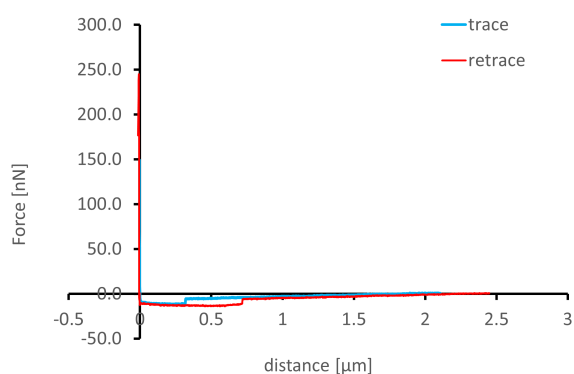
Figure 9.7: Ketton rock AFM images, these rocks were flushed with brine, then flushed with decalin at a lower and high capillary pressure and finally aged with crude B.



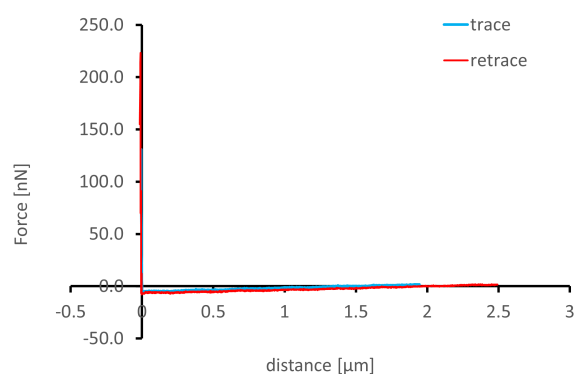
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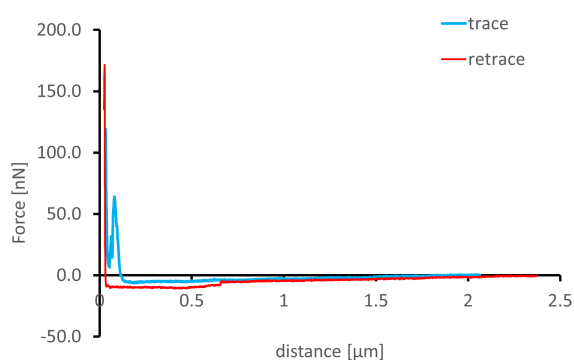
(b) Low PC Ketton crude B adhesion map marked



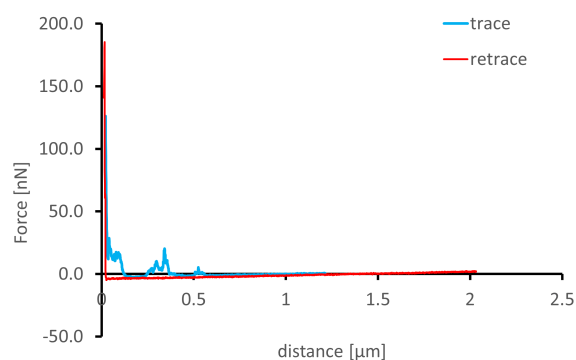
(c) Force distance curve at blue star



(d) Force distance curve at green star

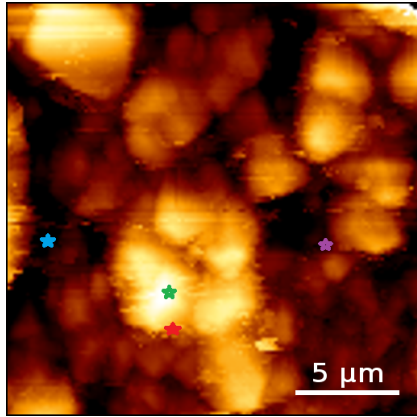


(e) Force distance curve at red star

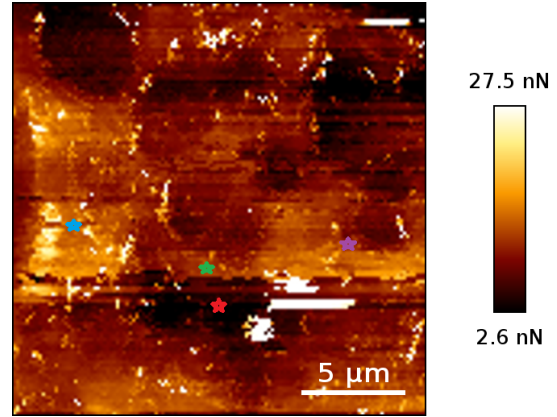


(f) Force distance curve at purple star

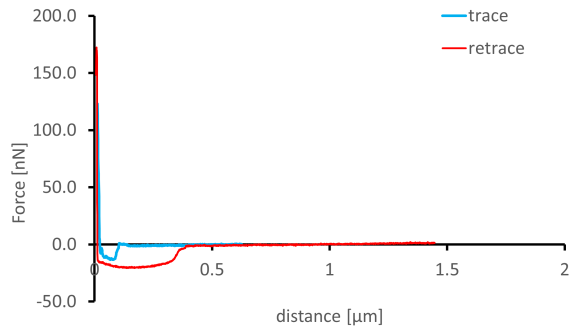
Figure 9.8: Various force distance curves illustration at different points of the adhesion and height measured map for low PC aged in crude B Ketton rock.



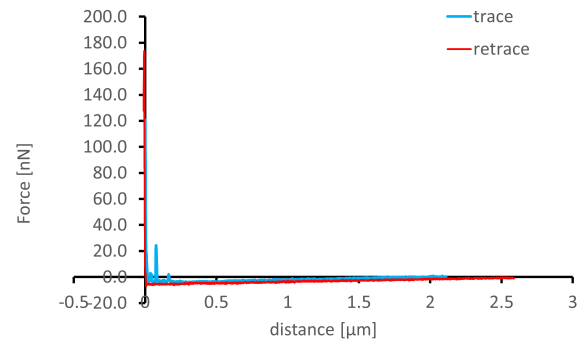
(a) High PC Ketton crude B aged Rock Height map marked



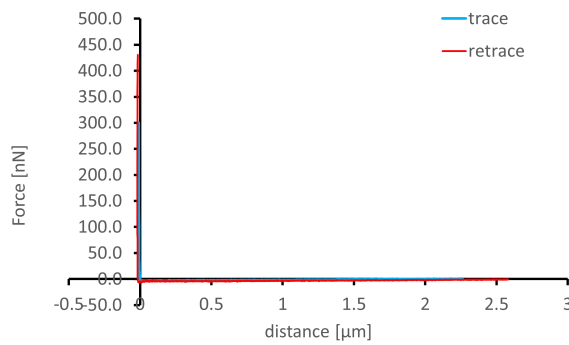
(b) High PC Ketton crude B adhesion map marked



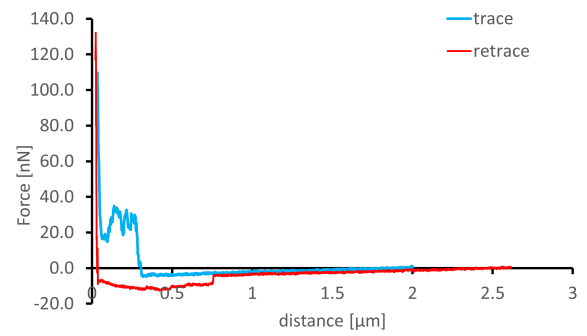
(c) Force distance curve at blue star



(d) Force distance curve at green star

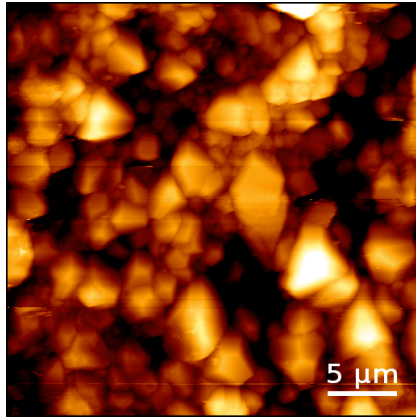


(e) Force distance curve at red star

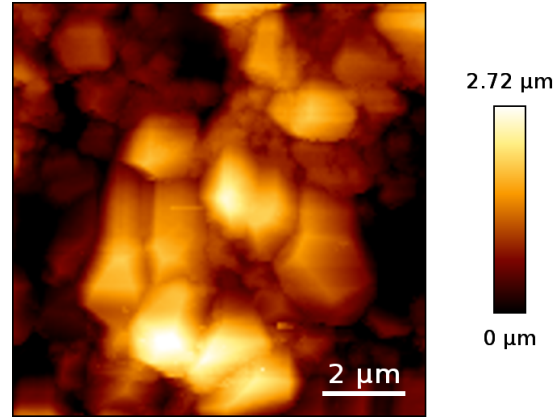


(f) Force distance curve at purple star

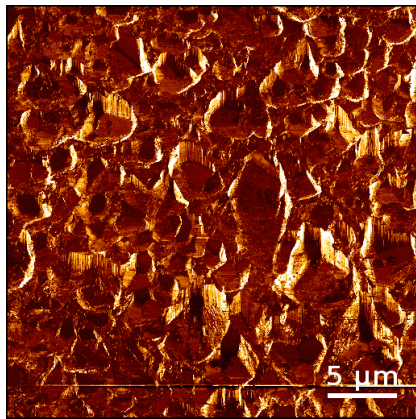
Figure 9.9: Various force distance curves illustration at different points of the adhesion and height measured map for high PC aged in crude B Ketton rock.



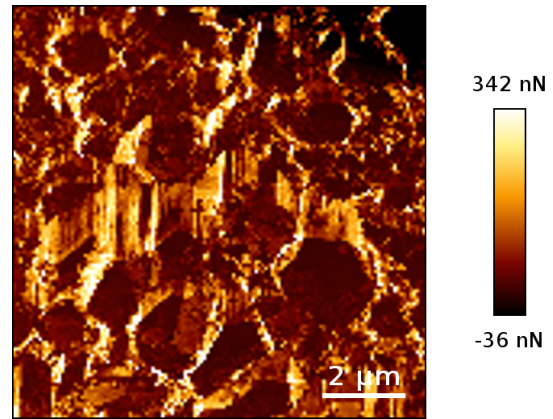
(a) Low PC Ketton crude C aged Rock Height Map



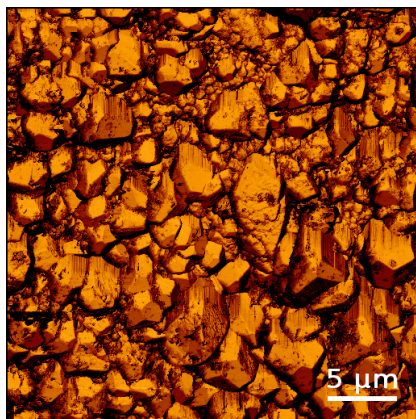
(b) High PC Ketton crude C aged Rock Height Map



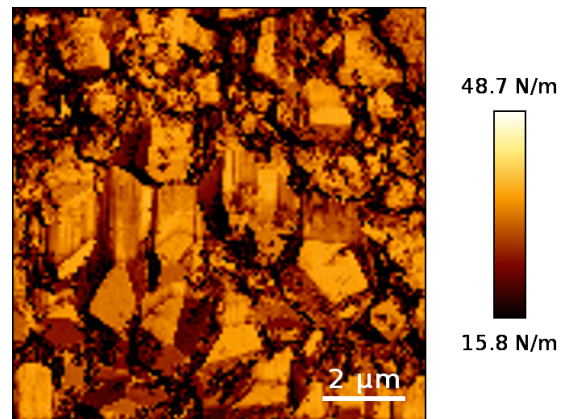
(c) Low PC Ketton crude C aged Rock Adhesion Map



(d) High PC Ketton crude C aged Rock Adhesion Map

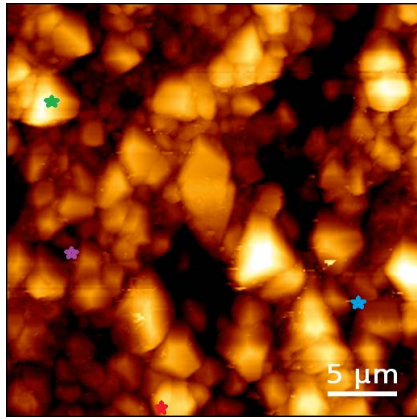


(e) Low PC Ketton crude C aged Rock Stiffness Map

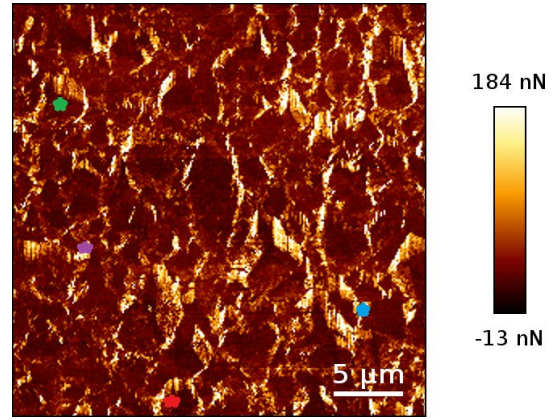


(f) High PC Ketton crude C aged Rock Stiffness Map

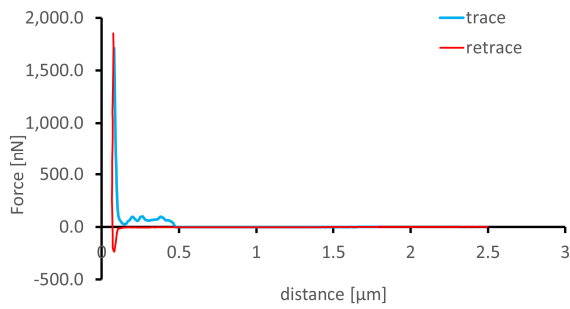
Figure 9.10: Ketton rock AFM images, these rocks were flushed with brine, then flushed with decalin at a lower and high capillary pressure and finally aged with crude B.



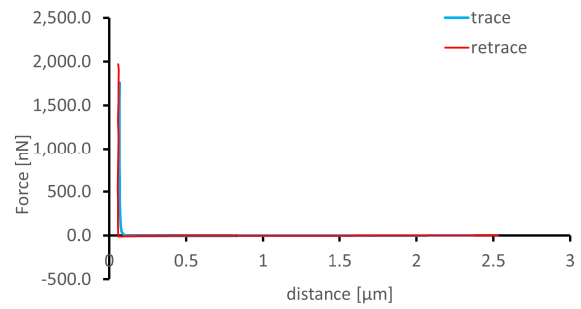
(a) Low PC Ketton crude C aged Rock Height map marked



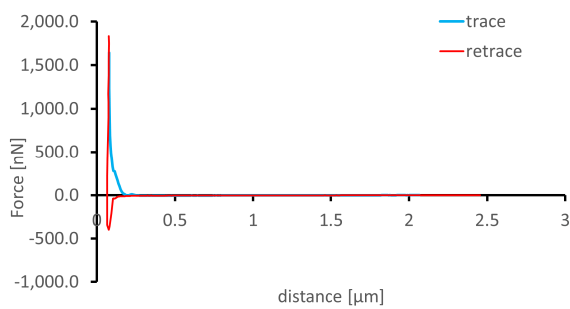
(b) Low PC Ketton crude C adhesion map marked



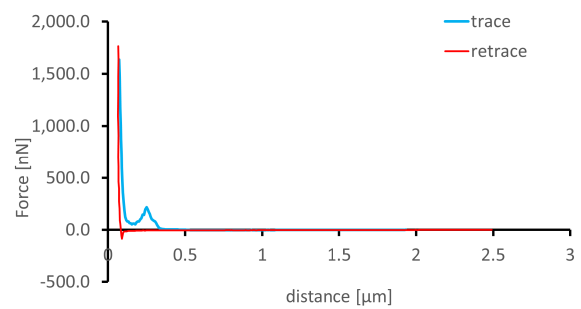
(c) Force distance curve at blue star



(d) Force distance curve at green star

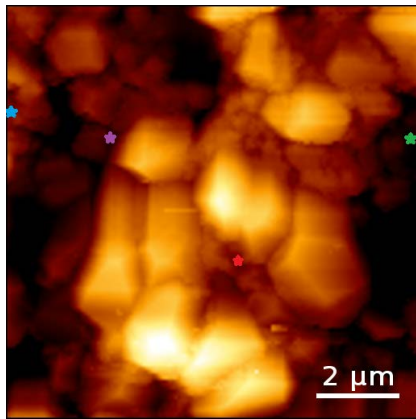


(e) Force distance curve at red star

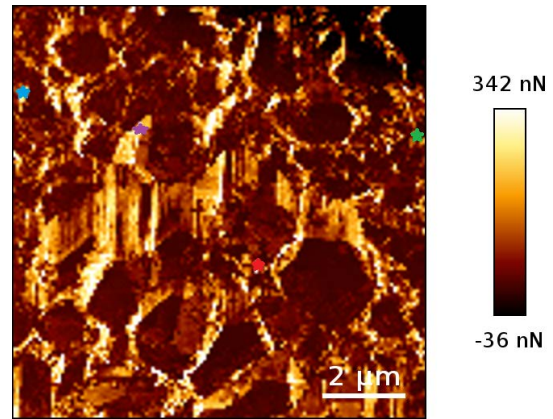


(f) Force distance curve at purple star

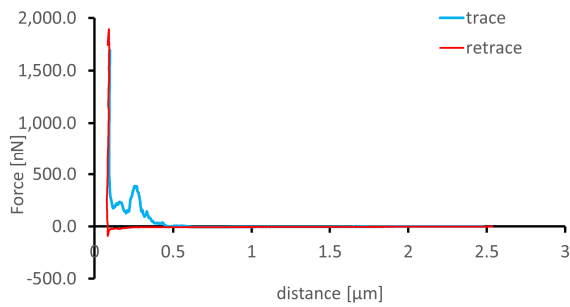
Figure 9.11: Various force distance curves illustration at different points of the adhesion and height measured map for low PC aged in crude C Ketton rock.



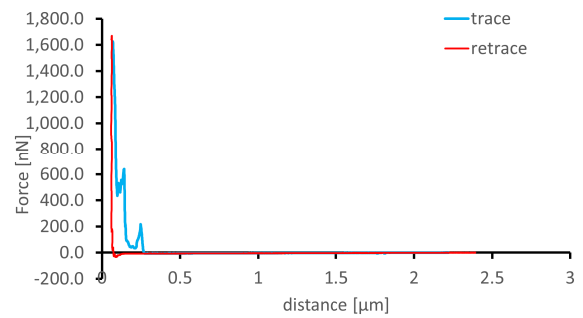
(a) High PC Ketton crude C aged Rock Height map marked



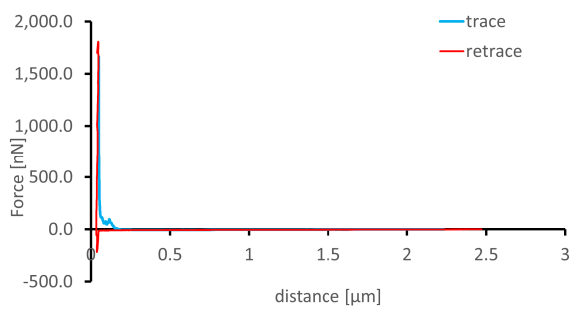
(b) High PC Ketton crude C adhesion map marked



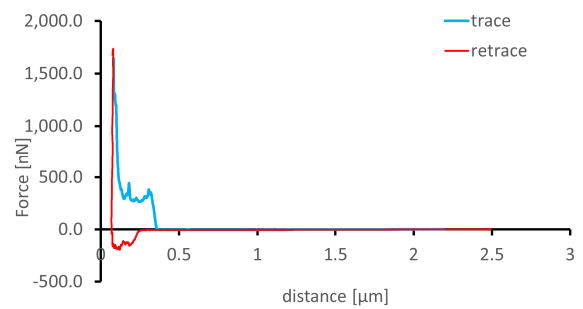
(c) Force distance curve at blue star



(d) Force distance curve at green star



(e) Force distance curve at red star



(f) Force distance curve at purple star

Figure 9.12: Various force distance curves illustration at different points of the adhesion and height measured map for high PC aged in crude C Ketton rock.

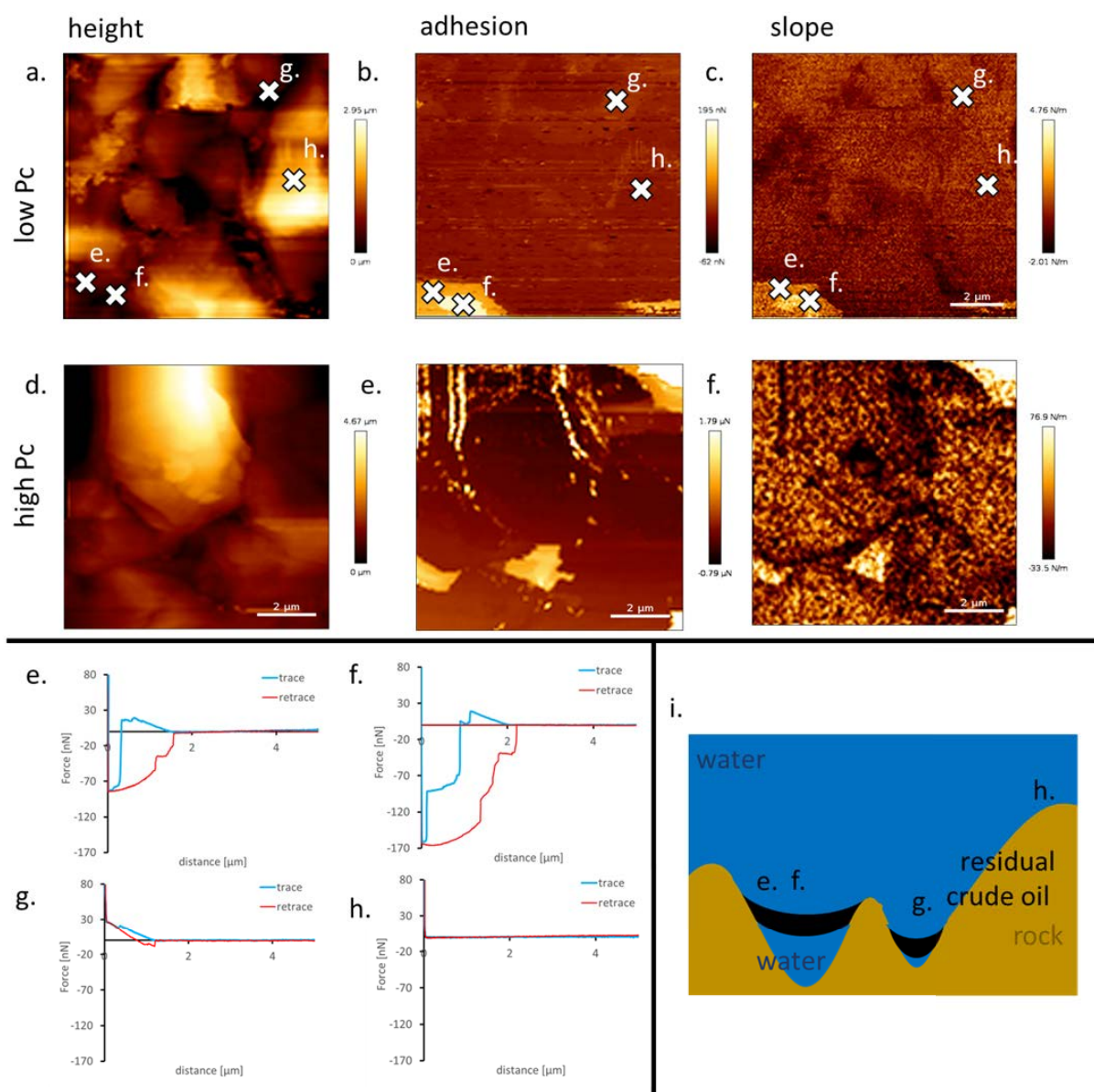


Figure 9.13: Estailades rocks, which were aged, were flushed with brine after ageing and imaged in decane using AFM. i represents the different configurations we interpret from the respective images and force distance curves. It appears that oil is remaining predominantly in valleys, entrapping a small amount of water underneath, with no sign of oil components adhering to the tips of the solid rock.

Chapter 10

Conclusions and future outlooks

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As part of this thesis, a series of experimental investigations along with their specific purpose, methodology, data, and conclusions were presented with the aim of shedding more clear light on the ageing impact on mineral surfaces and quarry rocks. As part of this chapter, an overall summary of each section's findings will be presented while connecting each finding to one another in a specific order, helping one understand the order of the sections of this thesis and the overall conclusion of this thesis.

10.1 Topographical features of model mineral surfaces of mica and calcite prior to the introduction of crude oil on the surface

In one of the initial phases of this project described in Chapter 5.4.1, mica and calcite were firstly cleaved in decane and imaged in decane using AFM. This was of paramount importance in enabling the surfaces to be characterised by themselves in order to clearly identify changes introduced by crude oil on the surface.

10.1.1 Aims

- To characterise the topographical features of mica prior to the ageing process.
- To characterise the topographical features of calcite prior to the ageing process.

Key findings

- The maximum height recorded for the mica was 1.95 nm, but having created a histogram from the topographical image of the mica obtained from AFM, the actual average height of the mica's surface is 0.2 nm, which makes the mica's surface one of the most atomically flat surfaces.
- On the contrary, calcite's surface was formed of steps; each step however itself was quite flat; the maximum height measured on the calcite surface was 33.2 nm; however, this is more of a gap between steps; the steps themselves had a flat surface, such as mica.

10.2 ageing impact on mica and calcite's surface

After having established key features of the mica and calcite at nanoscale, such as their topographical features, adhesion of their surfaces, and stiffness maps, the surfaces were aged in three different crude oils as described in Chapter 5. This was done in order to establish two things:

1. To establish the impact of ageing on mica and calcite and to compare the two to see

whether the mineral's surface charge impacts the way crude oil adsorbents spread on the surface of that mineral, given that mica's surface is negatively charged and calcite's surface is positively charged.

2. To see if different crude oils have significantly different features on the same mineral surface, this is important, as it will help future modellings to either generalise independently of crude oil's properties or determine whether any modelling for wetting predictions needs to take into account key crude oil's properties.
3. To establish the difference in wetting pattern observed on mica, which is more frequently found in sandstone reservoirs, versus calcite, which is the mineral mainly forming the carbonate reservoirs.

Key findings

- On the surface of mica, crude oil formed agglomerates as opposed to calcite, where a solid crude oil film covered the entire surface. The various surface charges of these minerals played a large role in this.
- On the same mineral surface, various crude oils are generally similar, but a few minor differences were seen in their characteristics. For instance, the crude oil film produced by crude A is thinner than the crude oil film produced by crude B, but the distinction between the various crude oils on the same mineral surface is only limited to the characteristics of the coverage. Another important measure found is that crude C, which is the unstable crude oil from the SARA curve, indeed covered the surface of calcite so well that there were no points at which the cantilever of the AFM could penetrate the film fully, which was a distinct feature seen with the more stable crude oils A and B (conceptually, one can assume that the cantilever can continue penetrating the film until a solid surface is reached, but there is a z limit here, which is a limit of the expansion of the piezo of the AFM, which is only 10 microns.).
- The main finding is that although the crude oil uniformly covers the calcite's surface, the crude oil film itself is not homogeneous. In addition, the surface charge of the mineral that the crude oil will come into contact with has a significant impact on whether or not the crude oil completely covers the surface.

10.2.1 Water film detection via AFM on Ketton and Estailades quarry rocks

After studying calcite's surface prior to and after ageing in various crude oils, quarry rocks Ketton and Estailades were chosen to establish and mimic reservoir conditions by injecting these quarry rocks with brine, and then the brine was displaced at various capillary pressures by decalin to remove some of the water films formed on Ketton rocks. This is because in reservoirs, oil, brine, and gas coexist; therefore, any alteration occurring via crude oil's polar components depositing on the surface of the rock is best established in the presence of oil and brine simultaneously in order to establish whether, after deposition of the crude polar components, the surface becomes oil- or water-wet. Ketton rocks are oolitic limestone quarry rocks, which means they are chemically homogeneous ($>99\%$ calcite) and hence suitable for basing experimental conclusions on. In chapter 8 of this thesis, Ketton rocks flushed with brine and then decalin were studied using AFM in order to detect and characterise water films.

Aims

1. To detect water films using AFM, characterise the water film force distance curves.
2. To compare the low-PC and high-PC decalin-flushed Ketton rocks. When the displacing fluid is approaching connate saturation, these water films may hinder its progress. The micro-scale thickness, surface coverage, and connectivity of these water films all of which vary with capillary pressure—should determine the flow efficiency.

Key findings

- Capillary pressure and the surface area and connectivity of the water films are significantly correlated, meaning water films found on low PC decalin flushed Ketton rocks were thicker and much more extensive, as shown in figures 8.2 and 8.5 of Chapter 8.
- When the brine phase first re-enters the pore space, this could potentially determine the displacement efficiency and have a significant impact on the films' permeability, possibly by several orders of magnitude.

Conclusion

1. The investigation of 3D fluid films on the internal surface of porous rocks at the nano- and micrometre scale is presented in Chapter 8 as a novel workflow (As this is the first AFM study to investigate this effect, earlier studies using X-ray tomography were unable to pick up this effect due to the resolution limitations of the technique, which is of the order of 1–5 microns.).
2. The findings support the hypothesis that corner-flow, which is thought to be the cause of a sharp decline in displacement efficiency during strong (more wetting) imbibition processes compared to weak imbibition, occurs in the presence of nanoscale fluid films.
3. Chapter 8 presented a method to evaluate the factors affecting fluid displacement processes on a sub-pore scale by directly measuring fluid films on porous rocks.
4. Understanding snap-off processes, which require that the wetting fluid be transported into a pore at a rate that is higher than the non-wetting fluid, is enabled by the assessment of permeability in fluid films.
5. Because the structure of a porous reservoir is often very complicated, it can be hard to come up with a single value for the irreducible water saturation. However, direct permeability calculations don't need an estimate of this parameter. Therefore, it's crucial to consider the configuration of sub-pore-scale fluid films, including the film's surface coverage, when calculating permeability for models under low brine saturation conditions.

10.2.2 ageing impact on water-film distributions of porous rocks after brine injection and detection

Having established water film distributions in porous quarry rocks such as Ketton, in order to establish whether in reservoirs oil's polar components such as asphaltenes and resins indeed precipitate on the surface of the rock and alter the wetting distribution on the surface of the rock, making it more oil-wet, these brine-flushed quarry rocks were then aged using the ageing process described in Chapter 3.4. Therefore, chapter 9 describes the impact of ageing on water film distributions initially detected and established in chapter 8. Like preceding chapters, the same three crude oils were employed in chapter 9 in order to see whether water films can preserve their position on the surface of the rock during the ageing process in any of the crude oils.

Aims

- To see whether water films can be detected after brine flushed Ketton rocks undergo ageing process.
- To characterise and form potential scenarios from force distance curves obtained from AFM imaging of the quarry Ketton rock after ageing in crude oil.
- To observe whether brine can displace the oil adsorbed on surface of rock during ageing process.

Findings

- According to the results obtained, the oil's surface-active components form a continuous layer.
- The outcomes demonstrated the ability of water-films to withstand the wetting alteration process. However, only one out of three crudes provided evidence for such water-films.
- Following a water flood, measurements on an Estailades sample under comparable conditions revealed water trapped by an oil layer as well as regions with varying adhesion that followed a pattern resembling the water distribution seen before the wetting alteration.

Conclusion

1. The study presented novel AFM approaches to investigate the alteration of rock by oil at the nanometer scale along its naturally rough internal surface. The results showed that water films can prevail in the wetting alteration process. However, only one out of three crudes provided evidence for such water films. The surface active components of the oil were found to inhomogenously attach to the fluid-fluid and fluid-solid interfaces in the respective samples.
2. The measurements on an Estailades sample under comparable conditions after a water flood revealed water trapped by an oil layer as well as regions of different adhesion, all of which followed a pattern resembling the water distribution seen before the wetting alteration.

3. The measurements after the water flood further revealed water entrapped by an oil layer as well as regions of different adhesion following a pattern similar to the water distribution observed prior to the wetting alteration. Previous studies at a larger scale demonstrated that the flow behaviour very much depends on the exact oil, brine, rock composition, temperature, pressure, and flow history [24, 31, 33, 254]. The variability of observations may relate to the alteration mechanisms and resulting fluid configurations observed at the nano-metre scale presented in this study.
4. Further studies of this kind may help to understand which pore- and core-scale responses relate to the nano-scale effects described. Such results would help in developing more sophisticated modelling tools to predict reservoir development or environmental remediation projects.

10.2.3 Serendipitous finding of gypsum crystals on mica during ageing process with calcite present in ageing cell

In chapter 6 of this thesis, novel data were presented that showed that when mica and calcite were simultaneously undergoing an ageing process, long and needle-shaped crystals were formed and observed on the surface of mica. This was only the case when ageing occurred in crude oil B, while mica and calcite were aged together. However, when mica and calcite were aged together in crude oils A and C, neither crystals were recorded nor observed.

Aims

- The original purpose of the experiments conducted for this chapter was to observe the impact of crude oil B on mica and calcite.
- Crude oil A showed that on mica, crude oil agglomerates were formed; likewise, crude oil C presented the same pattern, while on calcite, a uniform coverage of crude oil film was seen on the surface of the calcite. In both cases, mica and calcite were aged together in the crude oil in order to save time as the ageing process takes four weeks to complete.
- When crystals were recorded on the surface of mica, which was aged in crude oil B, the main aim of this chapter was to explain the precursor for this crystal formation.

- In order to establish whether the crude oil B itself contains these crystals and they just precipitated on the surface of mica or whether the presence of calcite was the reason behind the formation of these crystals, the experiment was repeated with one ageing cell containing only mica discs and another ageing cell containing both minerals, calcite and mica, like the originally planned experiment.

Findings

- Upon ageing the mica by itself in crude oil B, there were no crystals observed on the mica's aged surface.
- When the experiment was repeated as per the original experiment's method of ageing both minerals in the same ageing cell, crystals were observed again on mica's aged surface.

Conclusion

1. Having observed no crystals on mica's surface after being aged in crude oil B in the absence of calcite mineral, it was confirmed that crude oil B by itself is not forming these crystals on the surface of mica.
2. On the contrary, crystals were once again recorded on the surface of mica when calcite was present in the ageing cell. This confirms that calcite is indeed the precursor for the formation of these crystals on the surface of mica.
3. In order to establish the mineralogy of these crystals, SEM and EDX analyses were employed, which confirmed the original hypothesis that these crystals are none other than gypsum crystals due to their calcium and sulphur content. This is also in agreement with the presence of calcite in ageing cells as a precursor to the formation of these crystals.
4. The findings of this chapter are novel, and no such recordings were ever made before. This introduces an important but undermined damage factor in reservoirs. At nanopore levels of the reservoir rock matrix, especially in sandstone reservoirs where the mineralogy of the reservoirs is not as homogeneous as in carbonate reservoirs and many minerals coexist, the formation and growth of these crystals at subpore levels on a nanoscale can cause pore blockages and, in turn, hinder and reduce the rate of recovery from the reservoir.

10.2.4 An alternative to ageing for prompt results

Aim

- In chapter 7 of this thesis, an alternative method to ageing was implemented with the aim of establishing some preliminary results one can expect from any potential ageing experiment outcome.
- This is simply due to the fact that the ageing process takes four weeks to complete, and while waiting for any ageing results, it is important to know whether the chosen crude oil for the ageing experiment is indeed capable of impacting the surface of the chosen mineral at the nanoscale with clear evidence of the changes.

Findings

- In order to bypass waiting for ageing data, crude oils A, B, and C were all diluted in toluene, as asphaltene and resins are soluble in aromatic compounds [149, 255].
- Crude oil agglomerates were recorded on the surface of mica, and on the surface of calcite, a more uniform coverage of crude oil was recorded.
- Crude oil C diluted in toluene could not produce any results on mica; this is because the mica's surface became too adhesive, with the crude oil's C deposits visible on the surface of mica under a microscope. This is in agreement with the SARA analysis and CII curve of the three crude oils, which showed crude oil C to be the only unstable crude oil from the three crude oils, which means it has the most potential for depositing on the surface of any mineral it comes in contact with.

Conclusion

1. The toluene dilution method produces results similar to those of the ageing process; however, the ageing process produces more detailed data as it mimics the conditions at which a mineral surface is exposed under reservoir conditions.
2. Crude oil C is indeed the most unstable crude oil out of the three crude oils selected for this PhD project, and this is in agreement with the SARA analysis performed on the crude oils prior to this project's experiments by Shell B.V.

3. This method can be employed if the crude oil used is not too adhesive or highly unstable. Toluene accommodates asphaltene dissolution, and such solutions become highly concentrated with asphaltene molecules. Asphaltenes in the crude oil solution themselves are stabilised by resins and aromatic fractions, preventing excessive precipitation.

10.2.5 Overall Conclusion

To summarise the project's overall conclusion, before pointing out any future work needed to further enhance our understanding of the ageing process and its impacts on reservoirs' wettability patterns, which in turn will impact sub-pore level flows and recovery rates, the following points are made:

- The ageing process impacts the wettability of mineral surfaces through the facilitation of the deposition of crude oil's polar components (asphaltenes and resins). Crude oil forms agglomerates on the surface of mica, while it uniformly covers the surface of calcite.
- The mineral's surface charge also plays a key role in the wetting pattern observed on the surface of the mineral after it undergoes an ageing process. Mica has a naturally negative surface charge, while calcite has a positive surface charge. The polar components of crude oil are negatively charged, and these components are asphaltenes and resins that deposit on the surface of the mineral.
- Water films can be detected using AFM, from which a novel workflow for investigating and producing 3D fluid films in situ on the internal surface of porous rocks at the nanoscale was developed. The results back up the idea that corner-flow, which is thought to be the reason why displacement efficiency drops sharply during strong (more wet) imbibition processes compared to weak imbibition, happens when nanoscale fluid films are present. The pressure at which brine is flushed through the rock core impacts the amount of water film remaining on the surface of the rocks.
- After ageing the Ketton rocks with three separate crude oils, it is confirmed that the oil's polar components indeed precipitate out of crude oil and deposit on the surface of the rock. They alter the wettability of the rock in favour of the oil phase, making the rock's surface more oil-wet, and therefore, at the oil-water phase boundary, the water is displaced by oil, thus reducing the amount of water film one can detect on the surface of the rock post ageing. However, in the case of crude oil B, there was evidence of water films remaining on the surface of the rock, and thereby, in certain cases, one can expect the water films to withstand the ageing impact on the surface of the rock, but the overall assumption of oil not displacing water at the oil-water interface in modelling is too simplistic.

10.3 Outlook and future work frame recommendations

This PhD project broke ground on building an experimental methodology for ageing mineral model surfaces such as mica and calcite, as well as more complex and porous quarry rocks such as Ketton rocks, which are oolitic carbonate rocks suitable for modelling potential carbonate reservoirs' conditions. It also confirmed the impact of ageing on various surfaces, along with how it impacts water film distributions in porous media. But science is alive, and it needs to grow at every stage to further enhance humanity's knowledge on this topic. To break more scientific ground, which will help future engineers build more accurate models, the below recommendations are made to give an insight into future work needed to further complete our understanding of ageing on more model surfaces. Moreover, how it can potentially be reversed to allow a better recovery rate of crude oil, which is needed as a source of chemicals and energy for future generations to come, in more sustainable and less energy-intensive ways.

1. Though carbonate rocks and calcite were well studied in this project, helping to model carbonate reservoirs, sandstone reservoirs, which are sedimentary rocks composed of sand-sized granules, are another widely found reservoir rock matrix. Therefore, it is important to build the same framework for sandstone reservoirs. Although feldspar, mica, and various other minerals are held together via silica or another cement in a sandstone reservoir matrix, quartz is the mineral the sandstone reservoirs are predominantly made of [312, 105]. Therefore, replacing mica with quartz as a model mineral surface for the ageing process is a certain experiment required, while replacing Ketton rocks with bentheimer [226] as the quarry rock for the core flooding experiment is what is required to model sandstone reservoirs.
2. Core flooding an aged rock holding oil inside its pores with water and measuring the amount of crude oil one can remove will help build a better understanding of the actual recovery rate impacts ageing has at larger scales. Comparing various crude oils with different properties is also suggested to help build the relationship between wetting alteration and crude oil's specific properties more directly. Combining this with x-ray tomography will also help the researchers visualise the interaction between water and oil and how water may or may not displace the originally oil-aged surface.
3. It is well known that resins that resemble a surfactant structure can stabilise asphaltenes in solution; thus, using a surfactant with an oleic head and a hydrophobic tail can potentially misplace oil on the surface of the rock, allowing the surface of the rock to become once

again water wet [126]. This will help the recovery rate increase significantly and thereby increase the amount of oil available to mankind, especially in non-conventional reservoirs, as conventional reservoirs have largely passed their production peak. Such findings can help recover oil using more sustainable and less energy-intensive methods such as steam injection or gas injection.

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Appendix A

Pure calcite further topographical
images to complement the main
text's images

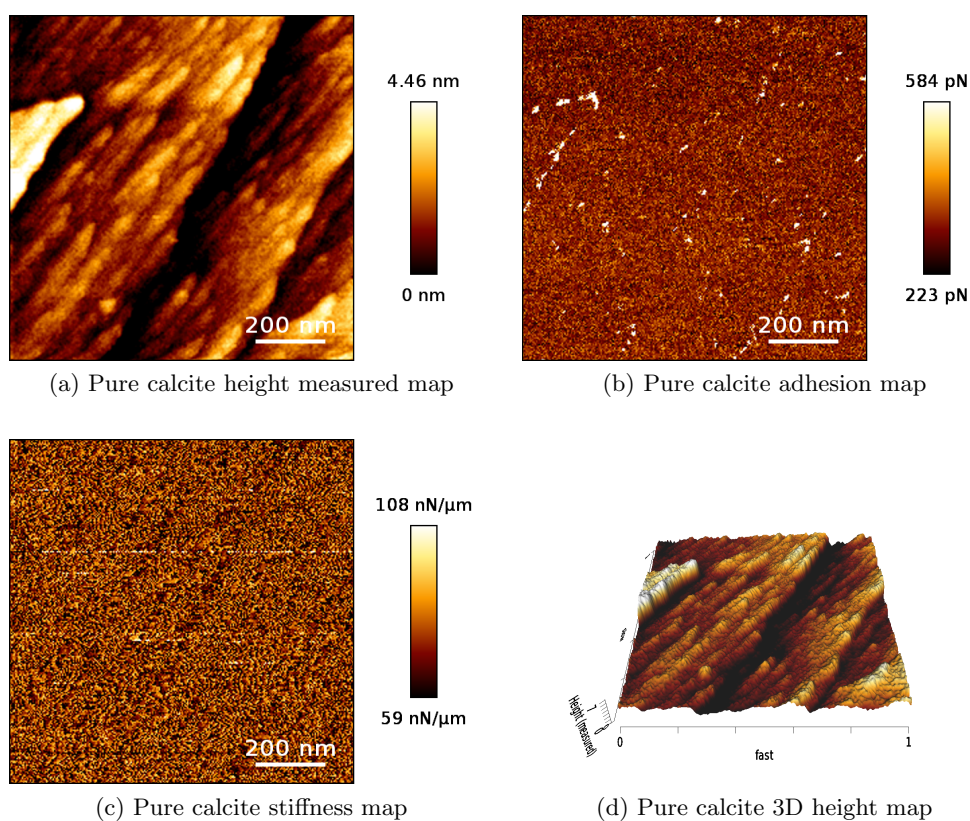


Figure A.1: Further image illustrating the stepped nature of calcite.

Appendix B

Aged mica further images to complement the main figures

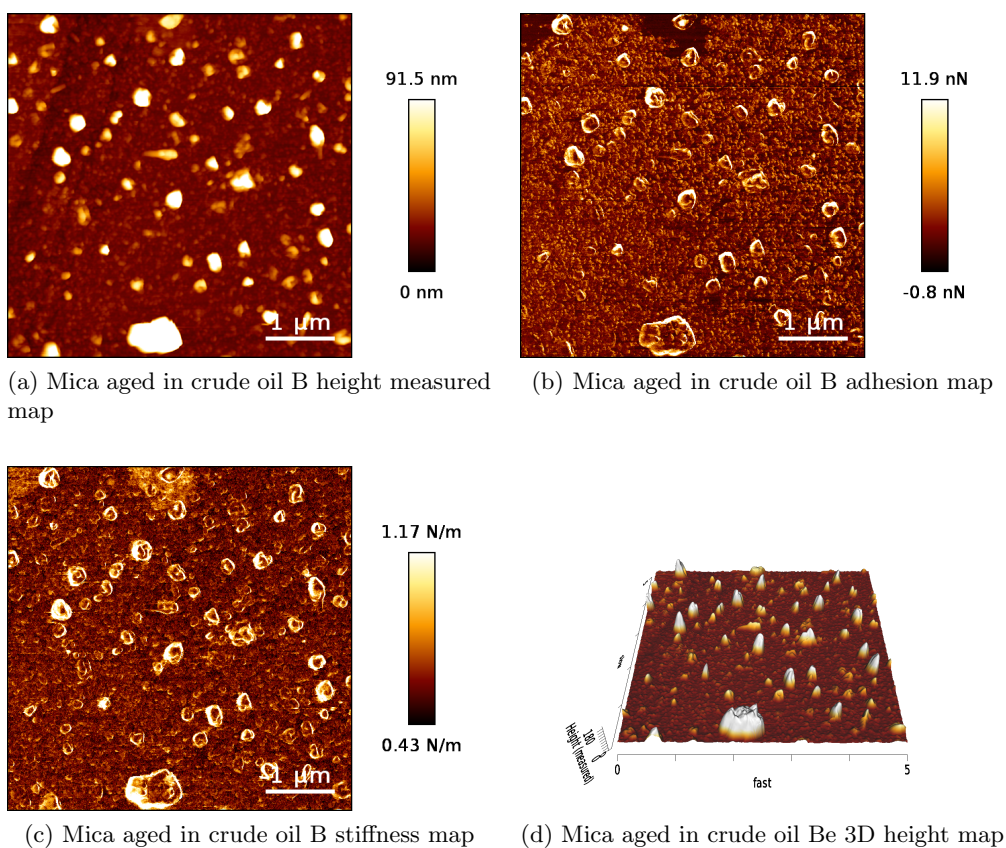


Figure B.1: Mica aged in crude oil B in absenc of calcite.

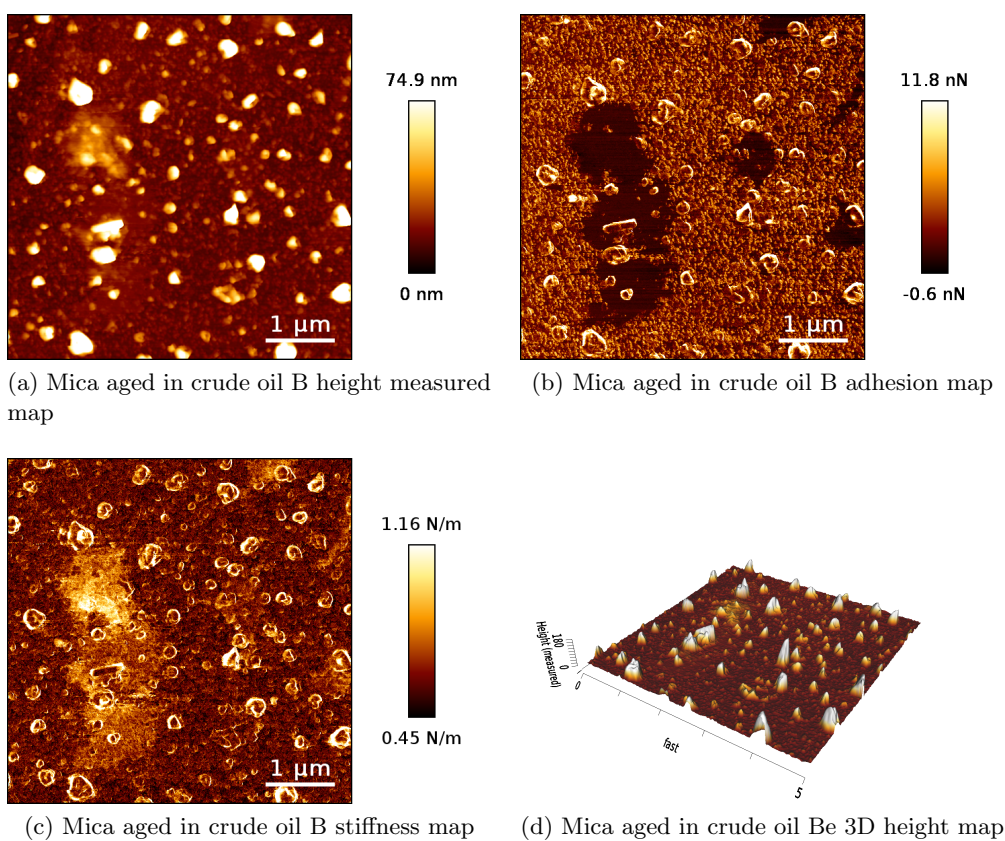


Figure B.2: Mica aged in crude oil B in absenc of calcite.

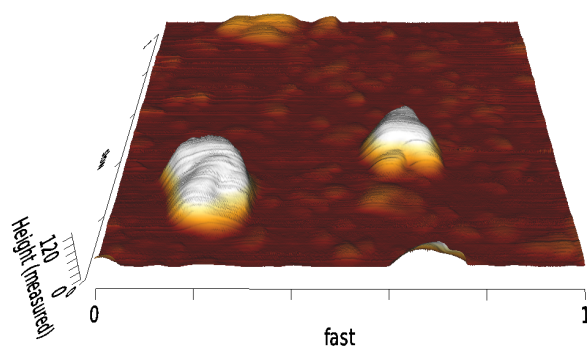


Figure B.3: 3D image of the aggregates formed by crude oil B on surface of mica when aged for a month in absence of calcite in aging cell.

Appendix C

Complementary gypsum crystals images for Chapter 6

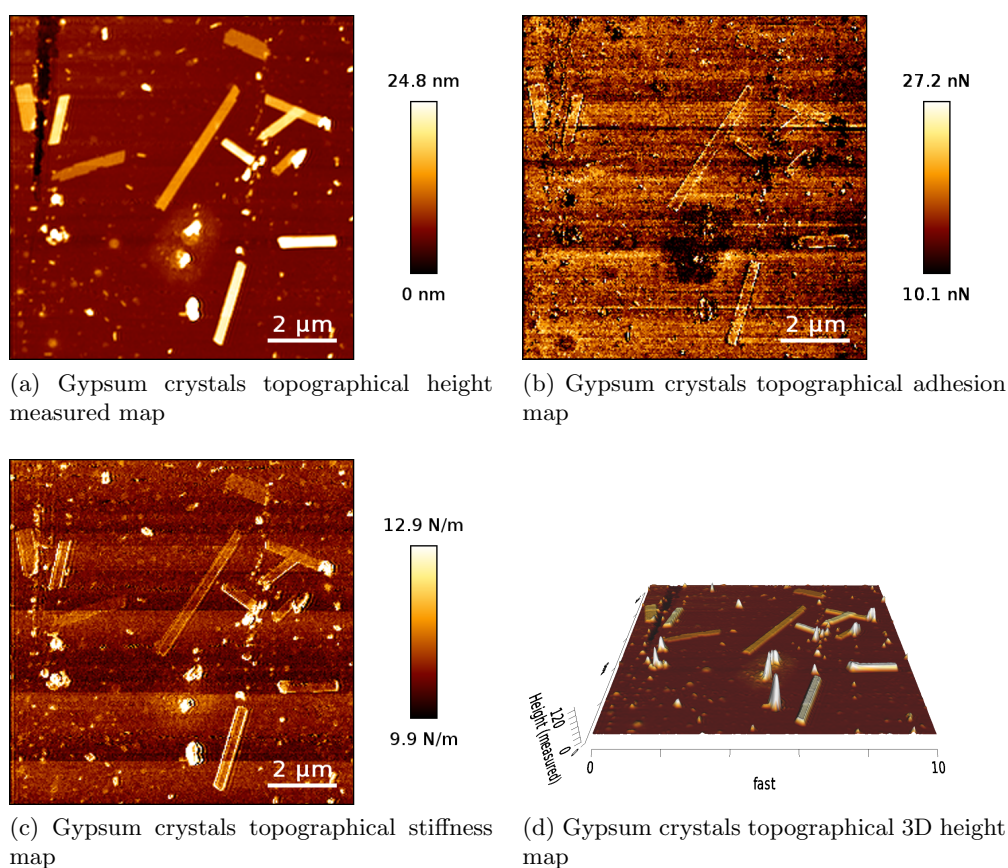


Figure C.1: Further images complementing gypsum crystals images in chapter 6.

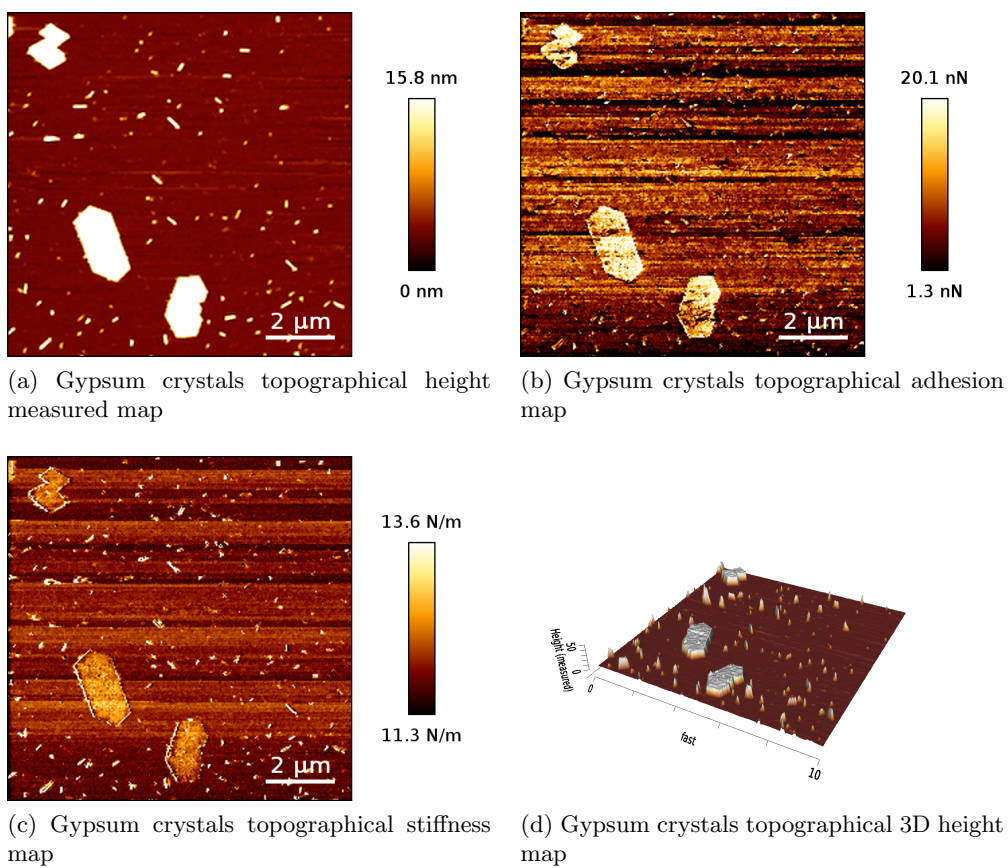


Figure C.2: Further images complementing gypsum crystals images in chapter 6.

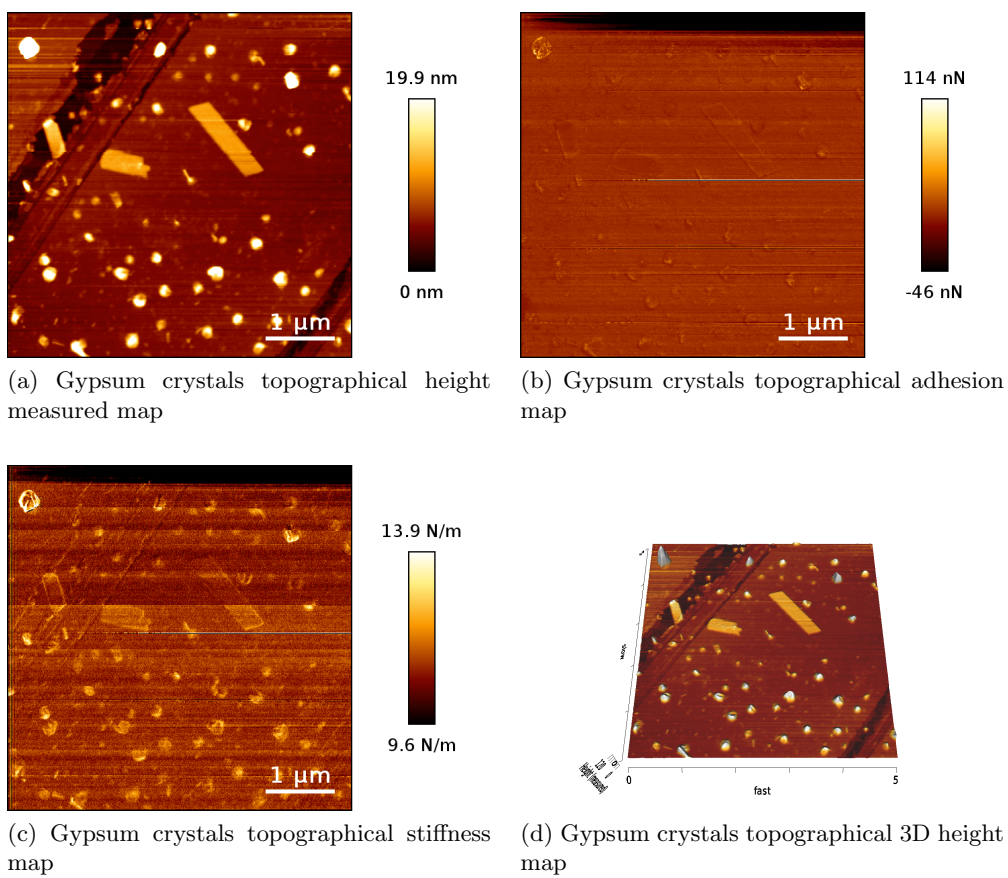


Figure C.3: Further images complementing gypsum crystals images in chapter 6.

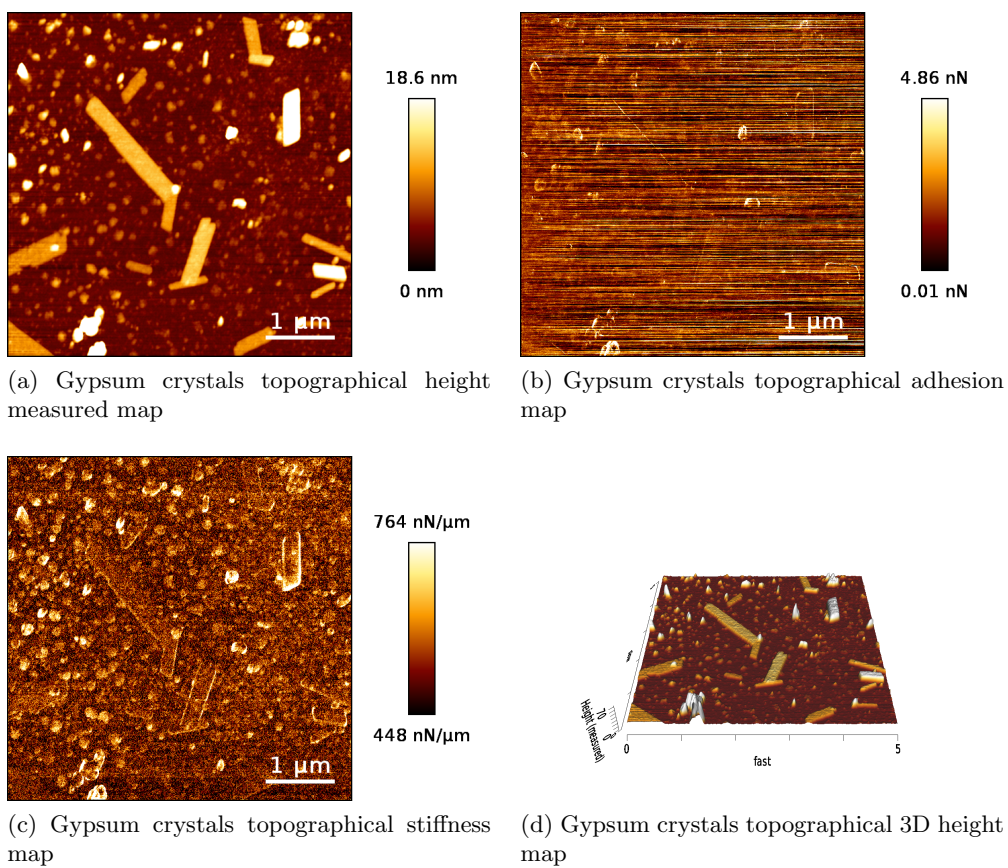
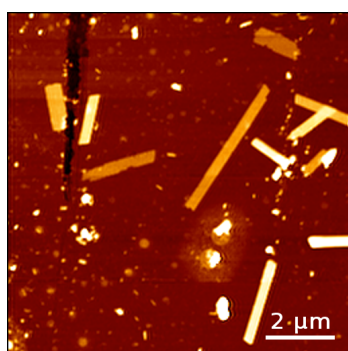
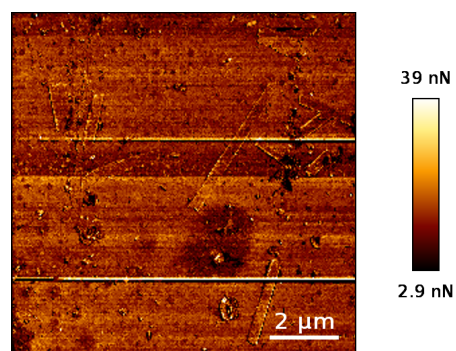


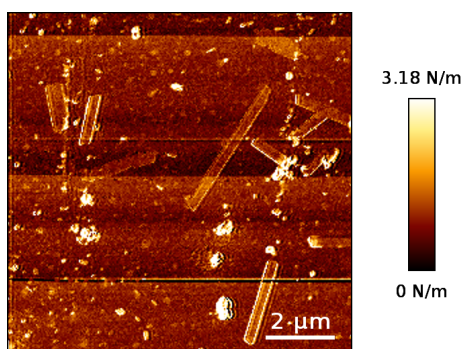
Figure C.4: Further images complementing gypsum crystals images in chapter 6.



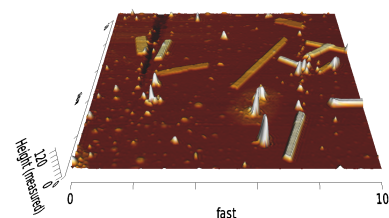
(a) Gypsum crystals topographical height measured map



(b) Gypsum crystals topographical adhesion map



(c) Gypsum crystals topographical stiffness map



(d) Gypsum crystals topographical 3D height map

Figure C.5: Further images complementing gypsum crystals images in chapter 6.

Appendix D

Measurement errors

Artifacts like the one in Figure D.1 can result in a measurement loss. The algorithm may be unable to locate a jump-to-contact point if the approach curve bends upwards as it approaches. The generated fluid layer maps underwent a median filter in order to correct for these artefacts. Plotted as an estimated vertical error is the involved departure from the initial result. These force-distance artefacts made it difficult to accurately determine the fluid-thickness in certain areas of the samples.

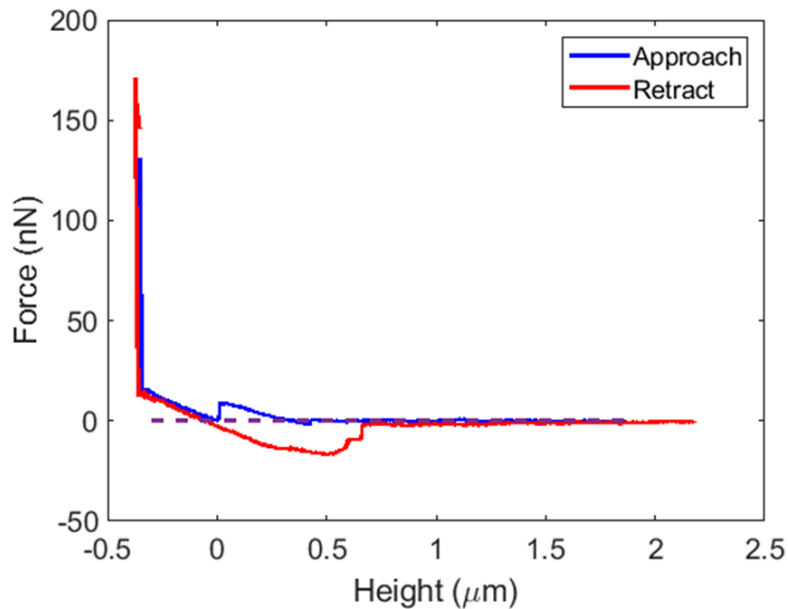


Figure D.1: Artifact of the force-distance curve: the approach curve bends upwards towards the jump-to-contact point, which is undetermined.

Appendix E

Numerical simulation artifacts

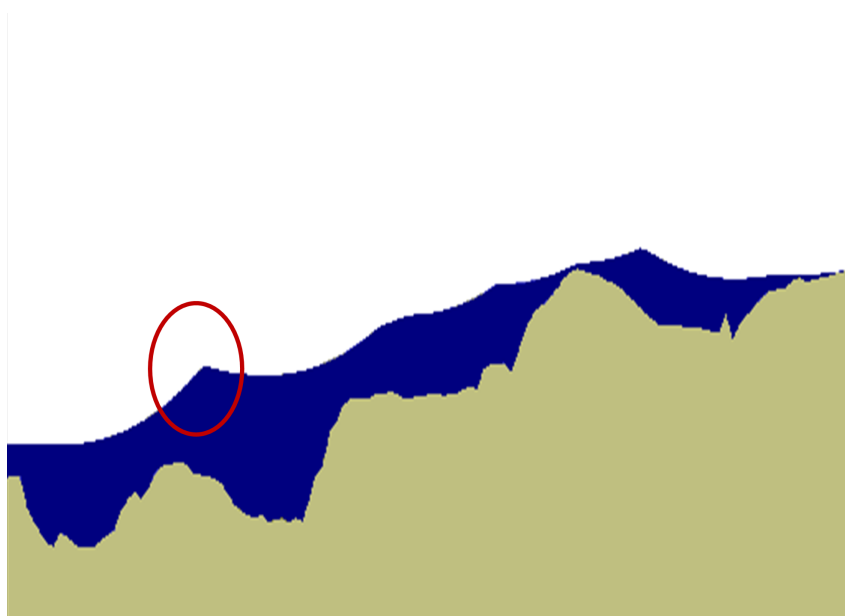


Figure E.1: The water film produced by the numerical simulation is displayed as a 2-dimensional slice. Because of some nonphysical edges produced by the sphere-fitting method, the simulation predicts a higher film volume than was actually measured.

Appendix F

Microscope image highlighting oil droplets on surface of mica after exposure to crude oil C

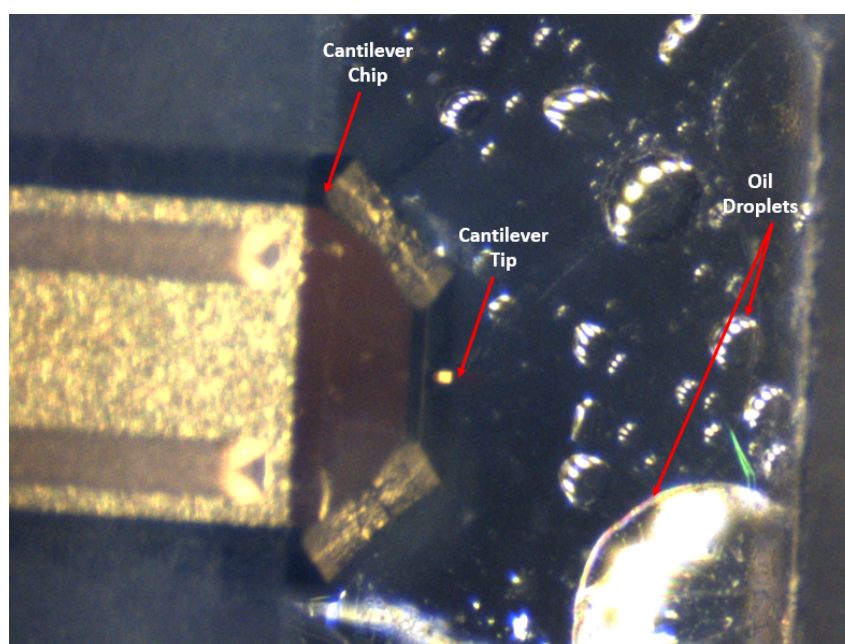


Figure F.1: Droplets can be seen formed on surface of mica after being exposed to crude oil C via toluene dilution technique, the surface was too adhesive for imaging.

Appendix G

Ketton rock under optical microscope of AFM highlighting healthy versus damaged grains which can be imaged

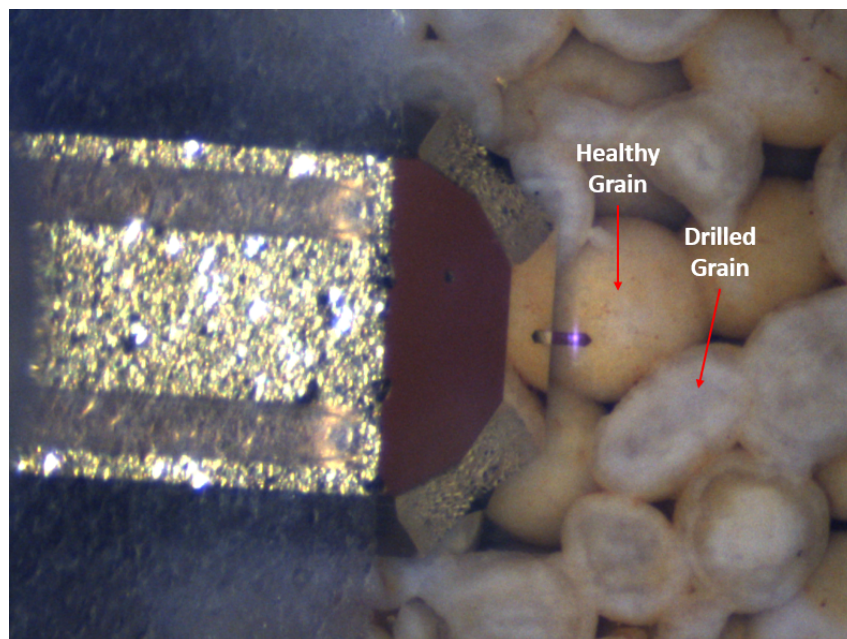


Figure G.1: Ketton rock under optical microscope, the healthy grains can be imaged under AFM, the grains cut by drilling process cannot be imaged.

Appendix H

Machine Learning and Digital Oil

The construction of a "digital field" in the oil and gas business, which refers to a geological reservoir model, was developed in the 1990s through advancements in 3D seismology [178]. This method has been well-documented, with a review by Matsuoka in 2013 [198]. The ability to obtain 3D photographs of sedimentary basins and oil reserves, along with the essential logging information on the sediments, has now become feasible and useful. The development of digital rock occurred in the 2000s through the utilisation of X-ray computed tomography (CT), focused ion beam-scanning electron microscope (FIB-SEM), and other technologies [301]. One can comprehend both the overall and surface chemistry of minerals, as well as the pore structure [301]. In addition, researchers have integrated fluid dynamics simulation techniques, such as the lattice Boltzmann method (LBM), with pore event modelling to investigate the displacement mechanism of two-phase flow in porous media [313]. Digital oil is a representation of crude oil using several representative molecules that are built based on analytical data. By utilising the comprehensive molecular model of the crude, it becomes convenient to analyse various fluid properties of the crude, including density, viscosity, diffusion coefficient, heat capacity, thermal conductivity, mechanical properties, and phase behaviour. These properties have been extensively studied by Iwase et al. (2018a, 2018b, 2019), and Liang et al (2019) [178, 147, 146, 12, 137, 294, 289]. Furthermore, it facilitates the examination of asphaltene aggregation, deposition, and precipitation at the molecular level, as well as wax precipitation, alterations in wettability, emulsions, and the use of chemicals to increase oil recovery (EOR) [178, 77]. Figure H.1 depicts a schematic diagram illustrating the concept of digital oil, digital rock, and digital field, as well as the significance of digital oil in conducting multiscale simulations to understand the intricate behaviours of complex materials in an oil field. This presentation will elucidate the potential advantages of

utilising advancements in petroleum chemistry to develop digital oil models specifically for use in petroleum engineering applications.

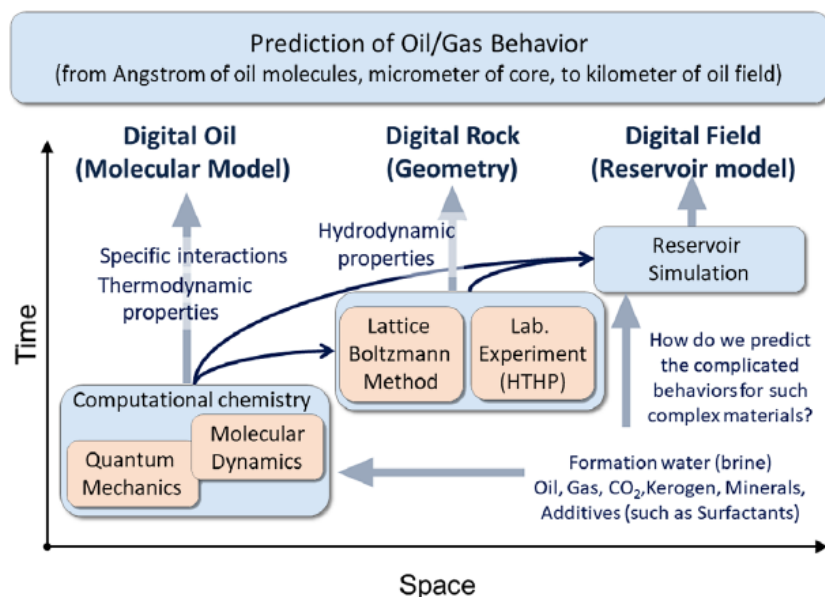


Figure H.1: Submission of digital oil proposal and schematic plan for multiscale simulations. Adopted from [178].

Oil science has made significant progress in the last fifty years [215, 277]. The atomic force microscopy (AFM) and scanning tunnelling microscopy (STM) techniques have been employed to uncover the structure of the molecules of asphaltenes [265]. Zahl and Zhang (2019) [326] have made efforts to differentiate the heteroatoms in aromatic compounds for AFM imaging. The presence and proportions of petroleum acids and bases containing oxygen and nitrogen heteroatoms have been acknowledged for a long time [79, 102, 188, 243, 315]. The sulphur compounds can be separated and examined using infrared spectra following the oxidation of sulphides to sulfoxides [224, 120]. The sulphur compounds in petroleum can be directly determined and quantified using K-edge X-Ray absorption spectra, X-Ray photoelectron spectroscopy, and X-ray fluorescence sulfur-in-oil analyzer [280, 109, 117, 305, 110, 270]. The chemical composition of various components of crude oils has been examined using gas chromatography (GC), GC-mass spectrometry (MS), and ^1H and ^{13}C NMR spectra [268, 291, 285, 284]. The molecular architecture of asphaltene has been more precisely characterised, with the dominating structure being the island-like arrangement [85, 213, 214, 319].

Due to progress in computational technological advances, molecular modelling and molecular dynamics (MD) simulations are now extensively utilised in petroleum engineering research [77, 54, 131, 132, 147, 146, 178, 289, 133, 171, 12, 216, 302, 166, 203, 316]. MD simulations offer the advantage of providing unique insights that cannot be obtained just through experiments.

In theory, a molecular representation of crude oil should include all of its components. However, it is challenging to identify and include all of these components, particularly in the case of heavy crude oil [195]. Therefore, it is necessary to adequately streamline molecular models. An effective method involves utilising a combination of representative molecules derived from measurements of the entire sample [52, 54]. Digital oil is a molecular representation of crude oil, where it is depicted as a combination of representative molecules from different fractions [289, 147, 178]. The QMR process for asphaltenes, resins, and heavy fractions was carried out using the Asphaltene Factory software for simulation created by Boek et al. (2009) [54, 52, 53]. Figure H.2 displays a schematic diagram of the enhanced oil recovery (EOR) study utilising the digital oil model.

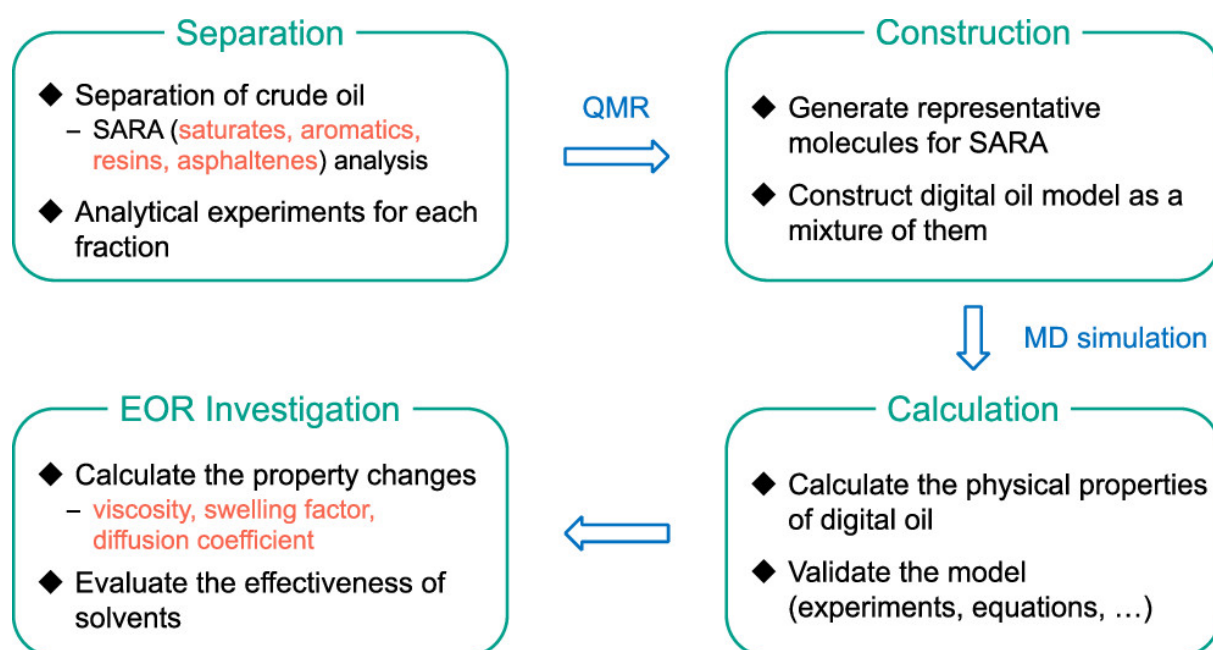


Figure H.2: The diagram illustrates the experimental setup for the enhanced oil recovery (EOR) investigation using a solvent-based approach and digital oil. *Adopted from [146]*

Figure H.3 illustrates the comprehensive process, which involves the segregation of unrefined oil, examination of each component, and development of the molecular structures. Figure H.3 (b) was created using the methodology outlined in reference (34). CHNS refers to elemental analysis, MM (GPC) refers to molecular mass measurement using gel permeation chromatography, ^1H and ^{13}C NMR spectroscopy provide information about the structural characteristics of hydrogen and carbon atoms, QMR stands for quantitative molecular representation based on average data such as average molecular mass, and extended QMR takes into account the mass distribution obtained from GCD experiments. Extended Quantitative Structure-Activity Relationship (QMR) techniques have the capability to produce molecular structures that do not contain aromatic rings. The missing components were identified by GCD tests [146].

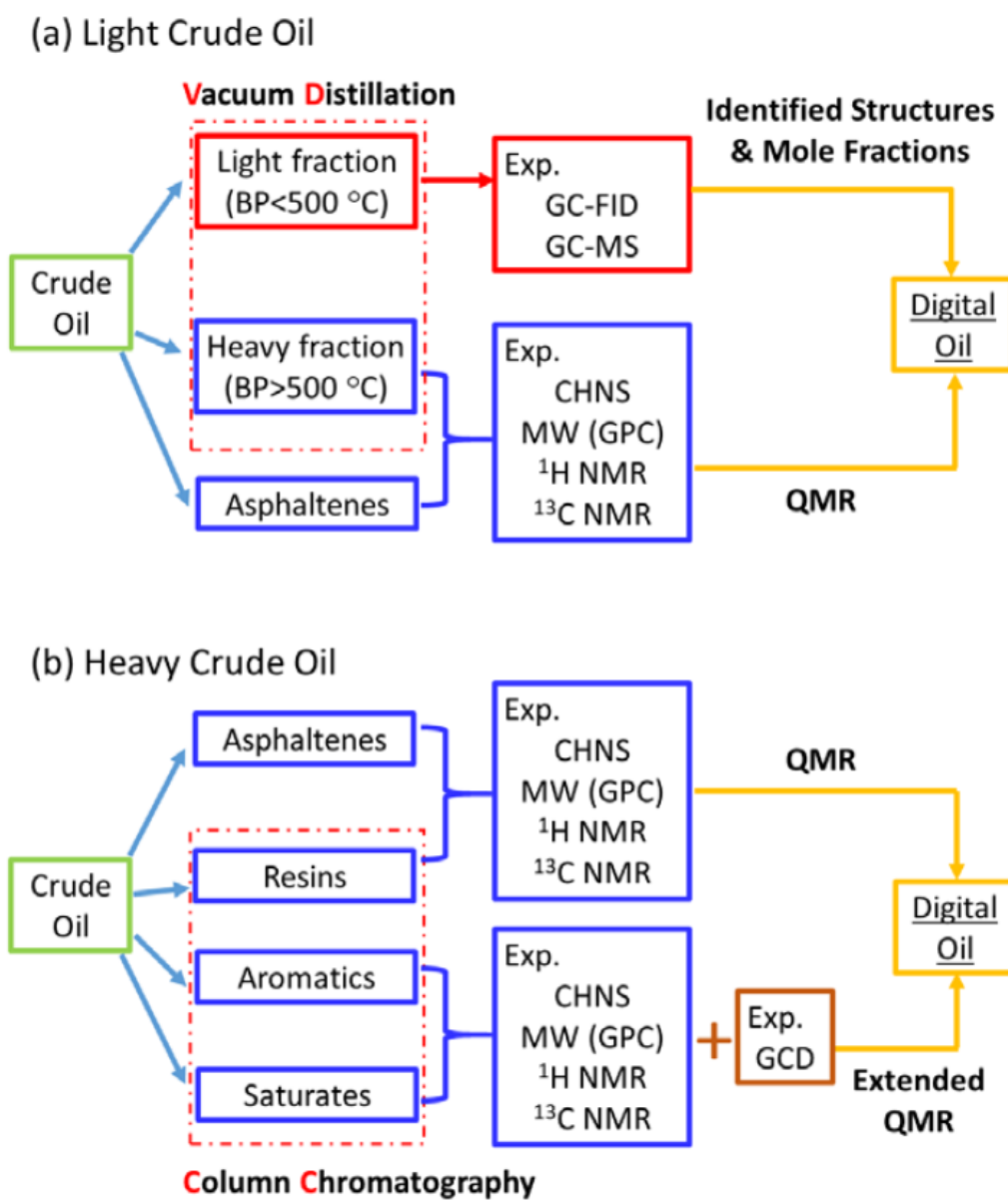


Figure H.3: The diagram illustrates the experimental setup for the enhanced oil recovery (EOR) investigation using a solvent-based approach and digital oil. *Adopted from [146, 178]*