Distribution and depletion of lubricant on antifouling lubricant-infused surfaces

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Statement of Originality

The work presented in this Thesis was carried out by myself during February 2016 to July 2019 in the School of Chemistry and University of Sydney Nano Institute, at The University of Sydney, as part of the requirements for the degree of Doctor of Philosophy in Science. Additional work was carried out during a visit to Harvard University, Cambridge, MA May - November 2018. This Thesis has not been submitted for any degree or other purposes. I certify that the intellectual content of this Thesis is the product of my own work and that all the assistance received in preparing this Thesis and sources have been acknowledged.

__________________________  _______________________
Sam Peppou-Chapman            Date
For Jessica.

We always challenged each other so when you said you thought I didn’t have the patience to do research you inspired me to prove you wrong. I wish you could see the researcher you helped me become.
Abstract

In 2011, two papers were published a month apart describing the ability of a structured surface to trap a thin liquid layer. This layer imparts the properties of a liquid onto a solid, creating a new type of surface known as a lubricant-infused surface (LIS). These surfaces are exceptionally slippery — droplets easily roll off them, bacteria cannot settle on them, ice cannot adhere to them — making them ideal for use in numerous applications.

LIS represent a paradigm shift in the study of functional surfaces, with the past decade seeing thousands of papers published on the design, application, function and analysis of these surfaces. One particularly exciting avenue of research is the prospect of LIS repelling biofouling without needing toxic biocides. Antifouling paints containing banned tributyltin (TBT) remain the most successful biofouling technology to date. Unfortunately for LIS, the lubricant layer is not entirely immobilised and will deplete over time due to external forces.

This Thesis explores the properties of LIS made from Teflon wrinkles infused with silicone oil and relates their properties to the quantity and distribution of lubricant on the surface by developing techniques to quantify and map the lubricant on the surface. The antifouling performance of the Teflon wrinkles was tested against the settlement of marine bacteria, *Psuedoalteromonas spp.*, and by immersion in the ocean. The antifouling ability of these LIS was then related to the amount of lubricant present by measuring the volume of lubricant using a fluorescence technique. To further explore the effect of depletion, the distribution of lubricant was quantified using atomic force microscopy meniscus force measurements, which produce precise maps of lubricant thickness at the nanoscale. The effect of different depleting forces on LIS were tested and directly related to the distribution of lubricant on the surface. In particular, the effect of immersing and retracting the surfaces through an air-water interface (unavoidable if LIS are deployed in marine environments) was studied over time and for different lubricant-substrate systems.
Acknowledgements

First and foremost I must thank my supervisor, Professor Chiara Neto, for everything she has done over the course of my PhD. The work included in this Thesis wouldn’t be nearly as relevant or interesting if it weren’t for her regular input and advice. My gratitude goes far beyond her involvement in the scientific portion of this PhD as the culture she has fostered in the group is one of openness and collaboration which have made the last few years an absolute joy. I have learned a lot from you and will take those lessons with me forever. Next, I must thank Professor Truis Smith-Palmer who took me under her wing when I first started and showed me everything I needed to know about biology, bacteria and research outside of physical chemistry.

I feel very lucky to have worked in a great team throughout my PhD with a great group of collaborators and friends in the Neto Group and the KCPC. In particular I must thank Cameron Ware for all the foundational work he did on Teflon wrinkled LIS (and the picture of water droplets on a rose in Chapter 1), Liam Scarratt for always being there to compare notes as we tried to understand LIS, Chris Vega Sanchez for helping with anything engineering-related and being an amazing collaborator on projects not included in this Thesis, Liwen Zhu for teaching me everything I know about AFM, Ahmed Owais for always comparing notes on anything surface related, Jun Ki Hong for being the go-to for biological LIS questions, Felix Vuellers for being a great collaborator on dipping surfaces and Ming Chiu for always lending a hand when needed. I must also thank the undergraduate helpers that made projects possible over the years. Daniel Balzer for his help with the fluorescence measurements, Erin Humphries for her work making P4VP wrinkles and Simone Morris for her help making Teflon wrinkles and dipping samples.

A huge thanks goes to Professor Joanna Aizenberg and her wonderful group. The six months I spent in her lab taught me immeasurably about slippery surfaces and research more generally. Every member of the lab made my time there enjoyable and mentally stimulating, but specific thanks have to go to my main collaborators Dr Ida Pavlichenko, Nicole Black and Mike Kreder. A huge thanks also goes to my undergraduate helpers Minh-Chau Le and Qin Ji.

Of course, I couldn’t have got to this point without support from my family, but what I am really thankful for is something that happened many years ago when I was still in primary school. Back in the early days of the internet, I saw an ad for a free gift from Readers Digest and immediately signed up without really understanding the concept of a subscription as ‘Dr S. Peppou’. A free gift and a few months of Readers Digest later, I got a bill in the mail for the subscription and instead of punishing me, my parents helped me write a letter to clear up the situation (they did say free...) and get away with my little escapade. They did have one condition, however. I would have to earn the title I used unscrupulously and, a few decades later, this Thesis is the last step in fulfilling that promise.

Finally, I must thank my amazing partner Mina, who has been a constant source of support as we journeyed through our PhDs together.
Publications


Works Included In This Thesis

(i) is adapted in Chapter 3 of this Thesis. Together with Smith-Palmer, I designed and performed the bacterial biofouling experiments. I designed and performed the fouling field test. I prepared the the manuscript except for the first section on sample preparation and testing which was prepared by Ware.

(ii) is adapted in Chapter 4 of this Thesis. I designed and performed all experiments and prepared the manuscript.

(iii) is adapted in Section 4.9 of this Thesis. I collected and analysed all mapping data and Tonelli performed and analysed all other experiments.

(iv) inspired the dipping set-up used in Chapter 5 of this Thesis. I helped collect and analyse data, and write the manuscript with Vüllers.

(v) is adapted in Section 1.3 of this Thesis. I compiled all relevant literature and wrote the text.
In addition to the statements above, in cases where I am not the corresponding author of a published item, permission to include the published material has been granted by the corresponding author.

Sam Peppou-Chapman

As supervisor for the candidature upon which this thesis is based, I can confirm that the authorship attribution statements above are correct.

Chiara Neto

Date
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List of Abbreviations

AFM  atomic force microscope
CA   contact angle
CAH  contact angle hysteresis
Ca   capillary number
CVD  chemical vapour deposition
h    wrinkle height
IL   infused liquid
LIS  lubricant-infused surface or liquid-infused surfaces
P4VP poly(4-vinylpyridine)
PDMS poly(dimethylsiloxane)
PFPE perfluoropolyether
PSW  polystyrene wrinkles
QLS  quasi-liquid surface
SEM  scanning electron microscope
SPM  scanning probe microscopy
STM  scanning tunneling microscope
Tg   glass transition temperatuer
TBT  tributyl tin
TW   Teflon wrinkles
\(\gamma_{LA}\) lubricant/air interfacial tension
\(\gamma_{LW}\) lubricant/water interfacial tension
\(\lambda\) wrinkle wavelength
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CHAPTER 1

Introduction

All interactions in our physical world are mediated by the same thing: surfaces. Surfaces are responsible for all the favourable interactions in your life, such as the easy to clean Teflon-coated pan in your kitchen; and all the unfavourable interactions, such as the dust crusted on your car’s windscreen. In the first example, the low surface energy of the Teflon coating makes it difficult for food to stick to it. In contrast, the high surface energy of glass combined with the high surface area of dust particles and some water makes them an excellent combination for sticking together. Controlling these interactions is the goal of surface science.

We often talk about functional surfaces as if they are a great invention of researchers in the lab. In actuality, all surfaces have some functionality — they interact with everything they come into contact with in a specific way, be it desirable or undesirable. All we scientists do is merely harness and finesse this functionality to give desirable properties in specific situations. To achieve this, we use our understanding of the fundamental interactions of surfaces combined with sensitive characterisation techniques to fine-tune and test this functionality and, ultimately, extend our fundamental knowledge.

Unfortunately for us, we are no match for millions of years of evolution, no matter how clever we think we are. Through natural selection, nature has produced surfaces with truly remarkable properties: the surface of the lotus leaf self-cleans due to water beading up and rolling off (superhydrophobic surfaces); [6] some fish scales reject fouling underwater by being perfectly wet by water (superhydrophilic surfaces); [7] and the surface of the peristome of the *Nepenthes* pitcher plant which combines solid and liquid to create a surface that is slippery to one of nature’s best adherers, ant’s feet [8]. Inspiration from these remarkable natural surfaces is where many of the giant leaps in surface science have originated. Mimicry of these effects in the lab has inspired researchers to take their general concepts and produce surfaces with vast and varied functionalities.

Parallel to the pursuit of creating new functional surfaces is the pursuit of a deeper understanding of the nanoscale phenomena underlying their performance. Integral to this is the ability to
characterise these surfaces at the nanoscale. Typical surface characterisation techniques are restricted in their capabilities here, with conventional characterisation techniques looking at macroscopic effects and the diffraction-limit limiting optical techniques to the analysis of microscopic features. New techniques, such as those based on atomic force microscopy (AFM), allow for these limits to be broken and for a comprehensive picture of these phenomena.

This Thesis examines the manufacture, function and analysis of a recently developed class of functional surface: lubricant-infused surfaces (LIS). This Chapter introduces the fundamentals of wettability and the phenomena related to LIS. In particular, it focuses on functional surfaces with special wettability and how fundamental wetting phenomena are exploited to produce desirable properties. LIS are explored in detail with particular focus on the lubricant layer that imparts their desirable properties. A detailed review of the literature reveals the current state of understanding the interaction between the lubricant and the substrate and characterisation of the distribution and thickness of the lubricant layer. Finally, the concept of biofouling and atomic force microscopy (AFM) are introduced.

### 1.1 Wettability

The term wettability refers to how a liquid interacts with a solid — to what extent the liquid spreads on the surface (or, conversely, how much the solid is wet by the liquid). This is something we encounter every day: cooking oil spreads easily in our saucepans, rain (hopefully) beads up and rolls off your umbrella, paint forms a nice uniform layer when you paint it on your wall. The most straightforward measure of wettability is the macroscopic contact angle, which is the angle the edge of a droplet makes on a flat substrate in a given continuous phase (usually the atmosphere). A small contact angle indicates the liquid wets the solid, while a large contact angle indicates the opposite. Given the theoretical range of contact angles is $0^\circ$ (totally wetting, see Figure 1.1a) to $180^\circ$ (totally non-wetting), $90^\circ$ is generally the transition for a surface to be considered -philic or -phobic (although there are many other definitions [9]). For example, in the case of water, a solid with a contact angle below $90^\circ$ is considered hydrophilic (Figure 1.1b), while a solid with a water contact angle greater than $90^\circ$ is considered hydrophobic (Figure 1.1c).

#### 1.1.1 Static wetting

The most common wetting scenario involves three immiscible phases: the solid, the liquid and the gas. Where these meet, they form a three-phase contact line which dictates the shape of the droplet on the surface. The contact angle is formed from the balance of three interfacial
1.1 Wettability

**Figure 1.1.** a) A totally wetting substrate with $\theta_E = 0$, $S > 0$; b) A hydrophilic substrate with $\theta_E < 90$, $S < 0$; c) A hydrophobic substrate with $\theta_E > 90$, $S < 0$; d) A droplet moving along a inclined surface — the difference between the contact angle at the front ($\theta_A$) and the rear ($\theta_R$) is the contact angle hysteresis and the angle of the surface when the droplet just starts moving is the roll off angle.

energies: $\gamma_{LG}$, $\gamma_{SL}$, and $\gamma_{SG}$ where the subscripts refer to the solid (S), liquid (L), and gas (G). $\gamma_{LG}$ is also known as surface tension and is due to the cohesive force between molecules at the surface of the liquid. Young’s equation relates these to the contact angle for an ideal surface: \[10\]

$$\cos \theta_E = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$$ \hspace{1cm} (1.1)

If the liquid fully spreads on the solid, its contact angle is zero, meaning that left hand side of **Equation 1.1** becomes 1. Rearranging this, we find the spreading parameter, $S$,

$$S = \gamma_{SG} - (\gamma_{SL} + \gamma_{LG})$$ \hspace{1cm} (1.2)

When $S > 0$, total wetting occurs and when $S < 0$, partial wetting occurs. The spreading parameter is a measure of the energy change due to the disappearance of the solid/gas interface and the creation of a solid/liquid and a liquid/gas interface.

Combining **Equation 1.1** and **Equation 1.2** give the Young-Dupré equation which relates the spreading parameter to the contact angle:
\[ S = \gamma_{LG}(\cos \theta_E - 1) \]  \hspace{1cm} (1.3)

This gives \( S < 0 \) when \( \theta > 0 \).

### 1.1.2 Pressure due to a curved interface

A curved interface has an associated pressure due to the cohesive forces of the interfacial tension. This pressure is known as Laplace pressure and is directly related to the average curvature of the interface: [11]

\[ \Delta P = P_{\text{inside}} - P_{\text{outside}} \]  \hspace{1cm} (1.4)

\[ = \gamma_{LG} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \]  \hspace{1cm} (1.5)

Where \( r_1 \) and \( r_2 \) are the principal radii of curvature at the point of measurement.

Laplace pressure is responsible for several common phenomena such as capillarity and condensation in pores. [11] The liquid in a droplet, such as in Figure 1.2a, has a greater pressure than the atmosphere as it has positive curvature everywhere, \( P_{\text{inside}} > P_{\text{outside}} \). A negative curvature, for example a liquid in a pore (Figure 1.2b), gives a negative pressure inside the liquid, \( P_{\text{inside}} < P_{\text{outside}} \).

Laplace pressure is particularly important as length scale is reduced. As it has an inverse dependence on the radius of curvature, a smaller curvature produces a large pressure. At the macroscale, Laplace pressures are generally negligible, but at smaller length scales, they become increasingly important.

### 1.1.3 Dynamic wetting

The description in Section 1.1.1 applies to static droplets on a surface, but not dynamic systems. In a dynamic system, the contact angle is not its equilibrium value but is either higher or lower depending on whether the liquid is wetting a new portion of the surface (advancing, \( \theta_A \)) or dewetting from a previously wet portion of the surface (receding, \( \theta_R \)). [11] The easiest way to visualise this is to consider a droplet moving on an inclined surface as in Figure 1.1d. The advancing side of the droplet’s contact angle increases until the pressure inside the drop can overcome the force pinning the contact line in that spot. Similarly, at the
1.1 Wettability

Figure 1.2. a) The positively curved interface of a droplet means that the pressure inside the droplet is higher than atmospheric pressure, $P_{\text{inside}} > P_{\text{outside}}$; b) negative curvature, such as a liquid in a pore, means that the pressure in the liquid is less than atmospheric pressure, $P_{\text{inside}} < P_{\text{outside}}$. Note that only one radius of curvature is shown for clarity.

rear of the droplet, the pressure drops until the pinning force is overcome, and the contact line moves. The contact angle values where the contact line moves are known as the dynamic contact angles of the system and are a measure of how easily the liquid phase adheres to the surface. Often, the contact angle hysteresis (CAH, $\Delta \theta$) is used as a measure of the mobility of droplets on a surface:

$$\Delta \theta = \theta_A - \theta_R$$

(1.6)

A low CAH indicates that a surface can easily shed droplets, while a high CAH indicates that droplets are likely to pin in the surface.

1.1.4 Effect of intermolecular forces on thin films

As film thickness decreases to the nanoscale ($<100\text{ nm}$), the influence of short- and long-range intermolecular interactions becomes increasingly important. The stability of a thin film (on the order of a few nanometres) is not influenced by the macroscopic wettability of the substrate, but instead by the intermolecular interactions of the system. This is described by the interface potential $P(e)$, a function of film thickness $e$, that describes the transition of the properties of a liquid film from the macroscopic value ($\gamma_{LG}$) when $e$ is large ($>100\text{ nm}$) to the value of the substrate ($\gamma_{SG}$) as $e \to 0$. How this potential varies determines the behaviour of the film at these small scales. [11]

The disjoining pressure $\Pi(e)$ is defined as the derivative of this function with respect to $e$:

$$\Pi(e) = -\frac{dP}{de}$$

(1.7)
and is a quantity that can be measured experimentally. The thickness of a film under a given static pressure (e.g. applied via Sheludko ring [11]) allows $\Pi(e)$ to measured as a function of $e$.

When van der Waal forces dominate intermolecular interaction, we can use the Hamaker constant to estimate the interface potential:

$$P(e) = \frac{A}{12\pi e^2}$$  \hspace{1cm} (1.8)

Where $A$ is the Hamaker constant.

The Hamaker constant is a measure of the van der Waals interactions for a given system. In the case of thin films, the Hamaker constant describes the interaction of two semi-finite phases (phase 1 and phase 2 - the substrate and the atmosphere, for example) acting across of a finite medium of thickness $e$ (phase 3). This gives a Hamaker constant $A_{132}$, the sign of which determines the stability of the film from the van der Waal interaction.

$$E_{vdW} = -P(e)$$  \hspace{1cm} (1.9)

$$= -\frac{A_{132}}{12\pi e^2}$$  \hspace{1cm} (1.10)

If the Hamaker constant is positive, there is a negative (attractive) interaction between layers 1 and 2, meaning the film is unstable. If the Hamaker constant is negative, there is a positive (repulsive) interaction between layers 1 and 2, meaning the film is stable.

### 1.2 Surfaces with special wettability

Surfaces with special wettability are able to be either completely wet by or completely repel a fluid. The most widely studied of these are superhydrophobic surfaces which completely repel water. Similarly, superoleophobic surfaces repel oils and other low surface tension liquids. On the other end of the spectrum, there are superhydrophilic surfaces on which water spreads completely. Superoleophilic surfaces are generally not studied as the low surface tension of oil means that the majority of surfaces will allow it to spread fully. Theses extreme wetting surfaces have several favourable properties. For example, the -phobic surfaces are excellent self-cleaning and anti-adhesive surfaces on which foulants are not able to adhere and are removed by droplets shed from the surface.
1.2 SURFACES WITH SPECIAL WETTABILITY

1.2.1 Superhydrophobic surfaces

Superhydrophobic surfaces draw inspiration from the lotus leaf, which is composed of an array of rough waxy papillae, see Figure 1.3b. These papillae have a micro- and nanostructure which, combined with the hydrophobicity of the wax, produce a surface that is not wetted by water. [6] The very best of these surfaces have a water contact angle of 180° — that is to say, water does not wet them at all.

This is an impressive feat given that the most hydrophobic featureless surfaces (fluorinated surfaces, e.g. Teflon) have a maximum water contact angle of around 120°. [12] The remarkably high contact angles are achieved through the addition of structure. This was evidenced by the Kao experiments in 1996, which showed that a rough hydrophobic surface could produce water contact angles close to 180° and coined the term superhydrophobic. [13]

This was not the first time this behaviour was seen, however, with the seminal work of Johnson and Dettre noting that as the roughness of perfluorinated wax increased, there is a sudden jump to high contact angles and low hysteresis. [14]

Although roughness cannot change the intrinsic contact angle of a material (also called the microscopic contact angle), it can change the apparent contact angle (also called the macroscopic contact angle, which is measured through typical optical techniques such as goniometry). A droplet on a rough surface can exist in one of two states. If the droplet penetrates the roughness of the solid it is said be in the Wenzel state, [17] (Figure 1.3a) and its apparent contact angle is modified by the roughness:

$$\cos \theta^* = R \cos \theta$$  \hspace{1cm} (1.11)

Where $\cos \theta^*$ is the apparent contact angle (i.e. the measurable macroscopic contact angle), $\cos \theta$ is the intrinsic contact angle and $R$ is the roughness ratio defined as the ratio of the true area of the surface divided by the projected area of the surface.

If the droplet is suspended above the roughness, it is said to be in a Cassie-Baxter state, (Figure 1.3b) and its apparent contact angle is related to the surface roughness by modelling the surface as heterogeneous: [18]

$$\cos \theta^* = f_1 \cos \theta_1 + f_2 \cos \theta_2$$  \hspace{1cm} (1.12)

Where $\cos \theta^*$ is the apparent contact angle and $f_i$ is the fraction of the surface with contact angle $\theta_i$. In the case of superhydrophobic surfaces, one of the phases the droplet is in contact with is air, with $\theta_2 = 180^\circ$. Given that $f_2 = 1 - f_1$, Equation 1.12 simplifies to:

$$\cos \theta^* = f_1 (\cos \theta_1 + 1) - 1$$  \hspace{1cm} (1.13)
Figure 1.3. a) Wenzel’s model - a droplet on a rough surface where the liquid wets all portions of the topography - an example of which is the rose petal effect where droplets have a large contact angle, but are pinned; b) Cassie-Baxter’s model - a droplet on a rough surface is suspended on the topography - an example of which is the lotus effect, where droplets have large contact angle and are mobile. In both cases, $\theta^*$ is the apparent contact angle (i.e. the measurable macroscopic contact angle) and is calculated using Equation 1.11 and Equation 1.12, respectively. Roughness in the schematics not to scale.


Where $f_1$ is the fraction of solid in contact with the droplet relative to the projected surface area. Note that this factor is similar, but not equivalent, to the roughness factor in Equation 1.11 above, as the droplet never comes into contact with all parts of topography in the Cassie-Baxter state.
Droplets in the Cassie-Baxter state are mostly suspended on a thin air layer and so will have minimal contact angle hysteresis and a low roll-off angle, leading to self-cleaning properties. This is generally the desired state for superhydrophobic surfaces, but it is not a robust state. The air pockets that suspend the droplet are not thermodynamically stable [19] meaning that the entire Cassie-Baxter state is metastable. High static pressures and surface contamination can collapse this state to the Wenzel state, ruining the favourable properties of superhydrophobic surfaces. [19, 20]

Superhydrophobic surfaces are relatively easy to produce, only requiring surface structure (ideally nanoscale) and hydrophobic surface chemistry. This is due to the high surface tension of water, making it difficult for it to enter the pores of topography. As a result, several commercial coating products produce superhydrophobic surfaces, and they are commonly produced in undergraduate labs. [21–23]

1.2.2 Wetting on real surfaces

The wetting equations discussed above are formulated for an ideal surface and not real surfaces. The Young, Cassie and Wenzel equations are all derived for ideal surfaces that are perfectly homogeneous with the assumption thermodynamic equilibrium. This is, of course, not the case with real surfaces having imperfections, contamination, or other inhomogeneities that mean that the system is in a metastable state. Even an atomically flat surface (e.g. a crystal plane) will still have inhomogeneities from the fact that the surface is composed of an atomic lattice that will necessarily have defects which act as microscopic pinning sites for the three phase contact line. This is the origin of contact angle hysteresis on atomically smooth surfaces and is visible as microscopic ripples and distortions of the contact line of a static droplet. [24] As a result, the measured contact angle of a droplet on a flat substrate is not define by simply balancing the interfacial tensions as predicted by Young’s equation, but is instead influenced by microscopic pinning, chemical inhomogeneities, and contamination. Similarly, the Wenzel and Cassie-Baxter equations cannot accurately predict changes in contact angle from the addition of roughness since the initial surface is not ideal.

Additionally, a surface with zero contact angle hysteresis would predict zero interfacial friction between the liquid in the droplet and the surface, which is not physical. Simple thermodynamic arguments, [25] show that a surface without any contact angle hysteresis cannot exist: a finite interaction energy between the droplet and the surface ($\gamma_{sl}$) leads to a small contact angle hysteresis. Studies of near-ideally smooth surfaces have confirmed that attributing contact angle hysteresis cannot be attribute entirely to roughness and inhomogeneity. [26, 27]
1.2.3 Superoleophobic surfaces

Superoleophobic surfaces are non-wetting to oils and other low surface tension fluids. An ideally -phobic surface would be non-wetting to all liquids and is classed superomniphobic. This term is often used interchangeably with ‘superoleophobic’ in the literature, but surfaces described in this way do not always repel the lowest surface tension liquids (also know as super-spreading liquids). To make low surface tension fluids bead-up and roll-off, the surface must have roughness with re-entrant geometry as shown in Figure 1.4b. This means that the roughness goes in on itself, and the contact line cannot advance into the geometry. [28–31] To make a surface resistant to even super-spreading fluids, doubly re-entrant geometry is needed. In this case, even if the microscopic contact angle is 0°, the liquid cannot enter the topography, as shown in Figure 1.4c. [32] Although this is an incredible result, the practicality of this technique is limited by inherently complex manufacturing and low mechanical robustness of the resulting surface.

![Figure 1.4](image)

**Figure 1.4.** Geometry determines the minimum contact angle that can spread into topography. For simple geometry (a) liquid with $\theta_A \geq 120^\circ$ cannot spread into the topography. For re-entrant geometry (b) liquid with $\theta_A \geq 30^\circ$ cannot spread into the topography. For doubly re-entrant geometry (c) even fluids with contact angle of 0° cannot spread into the topography.

1.2.4 Superhydrophilic surfaces

Superhydrophilic surfaces are similar to superhydrophobic surface in that they are produced through the combination of surface chemistry and roughness. In the case of superhydrophilic surfaces, roughness is added to an inherently hydrophilic material, producing a zero apparent water contact angle. [9] Some flat materials may also have water completely spread on them (freshly cleaved mica, for example). These materials are considered to be hydrophilic and not superhydrophilic as the effect of the topography is a key factor in whether a surface is classed as superhydrophilic. [9] The wetting of superhydrophilic materials is described by Wenzel’s equation (Equation 1.11) as the liquid penetrates the topography. In this case, as
1.2 Surfaces with special wettability

the intrinsic contact angle is less than $90^\circ$, the roughness has the effect of further reducing the contact angle. In this way, capillarity can aid the spreading of water to produce a continuous film on the surface.

1.2.5 Wrinkled superhydrophobic surfaces

The Neto group previously developed a simple method to produce superhydrophobic surfaces through spontaneous wrinkling of polymer bilayers. [33] These surfaces are produced by spin coating a layer of Teflon AF onto a pre-stressed polystyrene substrate which is then annealed above the glass transition temperature ($T_g$) of the polystyrene, but below the $T_g$ of the Teflon AF. The underlying polystyrene substrate shrinks while the Teflon top layer stays rigid, spontaneously forming wrinkles, shown in Figure 1.5.

![Figure 1.5](image)

**Figure 1.5.** Pre-stressed polystyrene (PS) coated with a rigid Teflon AF layer (blue) is annealed, producing wrinkles. This turns the Teflon surface from being hydrophobic to superhydrophobic.

Nanoscale wrinkles form randomly as the substrate shrinks, with larger microscale folds forming if the shrinking is more pronounced or the wrinkles are sufficiently small. Figure 1.6 shows the morphology of the wrinkles and folds. Morphology is easily controlled through modification of spin-coating parameters. The size (height, width, peak to peak distance (also called wavelength, $\lambda$) is dependent on the thickness of the Teflon layer which is dependent on spin speed and polymer concentration. Sample preparation is consistent once parameters are optimised for the desired morphology. The formation of wrinkles is a consequence of the mismatch in Young’s moduli in the film ($E_f$) and the substrate ($E_s$). The wavelength of the wrinkles scales linearly with the thickness of the rigid top layer $h$: [34, 35]

$$\lambda \approx 2\pi h \left( \frac{E_s}{3E_f} \right)^{\frac{1}{3}}$$

(1.14)

The as-produced wrinkles are superhydrophobic with a static contact angle of about $170^\circ$ (Figure 1.5) and a very low roll-off angle $<5^\circ$. [33] They are also very durable, which makes
them an ideal platform for further study of non-wettable surfaces. Unfortunately, like all superhydrophobic surfaces, the trapped air layer is not stable and is susceptible to collapse. In Chapter 3, we will see this in action where superhydrophobic Teflon wrinkles are found to be susceptible to biofouling in seawater.

1.3 Lubricant-infused surfaces

A new class of bio-inspired surface with special wettability was introduced in 2011 simultaneously by Wong et al. [36] and Lafuma & Quéré [37] known as lubricant-infused surfaces (LIS). These are also known as liquid-infused surfaces, slippery liquid-infused porous surfaces (SLIPS) or some other combination of liquid/lubricant/infused/slippery. This Thesis will refer to these surfaces as LIS.

LIS draw inspiration from Nepenthes to produce synthetic slippery, anti-adhesive surfaces by immobilising a liquid layer on the surface. Nepenthes are a genus of carnivorous pitcher plants native to south-east Asia. [38] They are part of a subset of carnivorous plants known as pit-fall traps, so-called as they catch their prey by luring them onto their peristome (or lip) where the surface is too slippery and insects cannot grip, so they fall in and are digested. The peristome’s slipperiness is due to a trapped layer of liquid, in this case, water. When it rains, the micro/nano structure of the peristome traps a thin layer of water through capillarity which
the ants cannot grip on, causing them to slip in. See Figure 1.7 for a schematic of *Nepenthes* and an SEM of its peristome.

Like *Nepenthes*, the liquid layer on LIS provides a mobile interface on which foulants (liquids, bacteria, ice) cannot adhere. Unlike *Nepenthes*, the liquid layer is not necessarily immobilised through capillary forces, see **Section 1.3.2**

LIS are similar in many ways to superhydrophobic surfaces. Where superhydrophobic surfaces suspend water droplets on an air layer, LIS suspend water droplets on a liquid layer and the high mobility of droplets (*e.g.* small roll-off angles generally $< 10^\circ$) in both cases is due to minimisation of the effects of contact line pinning. Both classes of surface have many of the same properties and potential applications:

- As antifouling surfaces due to reduced adhesion [39–44]
- As anti-icing surfaces due to reducing adhesion or reducing ice formation [45–48]
- As anti-corrosive surfaces due to the protective air or liquid layer [49–54]
- As drag reduction due to reduced shear at the liquid/air or liquid/liquid interface [55–61]
- As droplet manipulation platforms due to high droplet mobility [62–67]

LIS have a distinct advantage over superhydrophobic surfaces, however, as the lubricant layer is much more stable than the air layer. As a result, LIS outperform superhydrophobic surfaces in almost every category. The incompressible liquid layer on LIS easily withstands high static pressures that collapse the air layer on superhydrophobic surfaces. [19, 20] Where low surface tension fluids can penetrate the roughness on superhydrophobic surfaces, LIS repel all fluids that are immiscible with the lubricant, see **Section 1.3.3**. As a result, LIS are often described as being *omniphobic* without the need for delicate re-entrant geometry, see **Section 1.2.3**. While contamination changes the wettability of superhydrophobic surfaces, it cannot penetrate through the lubricant layer, making LIS much more robust.

### 1.3.1 Interaction of lubricant layer with droplets

When a droplet is placed on a LIS, it interacts with the lubricant layer and not the surface directly. There are two main consequences of this: the formation of a wetting ridge and the possible formation of a cloaking layer.
1.3.1.1 The wetting ridge

The wetting ridge is a meniscus of lubricant drawn up around the base of the droplet through capillary action, see Figure 1.8. The formation of this wetting ridge is unavoidable, and its size is a function of the amount of lubricant present on the surface, the length of time a droplet has been on the surface, and the velocity of the droplet. [68] The wetting ridge is an annular ridge of lubricant pulled up around the droplet due to the out-of-plane component of the lubricant surface tension at the droplet contact line and is similar to the ridge seen around droplets placed on soft or elastic surfaces. [69]

Measuring the true contact angle of a droplet on a LIS is non-trivial as the wetting ridge hides the contact line and distorts the base of the droplet. For simplicity, reported contact angles are generally apparent contact angles, calculated as the intersection of the fit of the Young-Laplace equation for the top of the droplet and a baseline defined by the top of the substrate (this method is used throughout this Thesis). The size of the wetting ridge influences the actual contact angle of the droplet. [70]

The wetting ridge is a region of negative Laplace pressure owing to its negative curvature and so draws more lubricant into it over time. [68] The equilibrium height of the wetting ridge is determined by the balance of Laplace pressure and hydrostatic pressure, and the shape is a modified Bessel function of the second kind, approximated by $z = \exp(-r/l_c)$ where $r$ is the radial position and $l_c$ the capillary length, see Figure 1.9a. [71] The equilibrium size of the wetting ridge for a static droplet is related to the amount of lubricant on the surface, with a relatively long timescale to come to equilibrium (on the order of minutes, see Figure 1.9b). [72] For a moving droplet, lubricant is also drawn into the wetting ridge.
and deposited behind it, with the thickness entrained varying with velocity, analogous to the Landau-Levich-Derjaguin (LLD) problem. [68] This leads to depletion as some lubricant is lost with each drop that rolls off the surface. [68, 73] Somewhat paradoxically, more lubricant is lost with slower-moving droplets as these entrain more lubricant in their wetting ridge. [68] Although droplets moving on LIS oleoplane, [74] energy is lost through viscous dissipation in the wetting ridge, [75] causing droplet motion to be dependent on the size of the droplet. [76]

1.3.1.2 The cloaking layer

Depending on the combination of lubricant/droplet, the lubricant can spontaneously spread over the droplet in a thin cloaking layer. The spreading parameter for the lubricant over a water droplet in air is

\[ S_{ld(a)} = \gamma_{wa} - \gamma_{la} - \gamma_{wl} \]

where \( \gamma_{wa} \) is the interfacial tension between water and air, \( \gamma_{la} \) is the interfacial tension between lubricant and air and \( \gamma_{wl} \) is the interfacial tension between water and lubricant. If \( S_{ld(a)} > 0 \) (for example for silicone oil spreading over water \( S_{ld(a)} = 73 - 21 - 35 = 17 \text{ mN m}^{-1} \)), then a thin layer of lubricant will spontaneously cloak the droplet as this lowers the overall energy of the system. [77] The thickness of this layer is of the order of nanometres with estimates of around 20 nm for a PFPE lubricant on a water droplet found by balancing the Laplace pressure in the cloaking layer with the disjoining pressure. [71] Direct observation of the cloaking layer using white light interference shows that the layer is not homogeneous across the surface area of the droplet with thickness between 10–500 nm, see Figure 1.9c. [68] The presence of the cloaking layer has also been confirmed by confocal microscopy, [71] but its thickness cannot be quantified using this technique. The volume of lubricant in the cloaking layer is much lower than is contained in the wetting ridge and, as a result, the cloaking layer does not contribute substantially to the depletion of

\[ \text{Figure 1.8. When a droplet interacts with a lubricant layer, some lubricant is drawn up into a wetting ridge and there is the possible formation of cloaking layer.} \]
lubricant from the surface. [68] but is a concern for applications where droplets condense on LIS. [78, 79]

Figure 1.9. a) Direct observation of the shape of the wetting ridge (black line) using confocal microscopy with fits. Red: catenoid; green: nonoid. Reproduced from [71] under Creative Commons 3.0. b) The size of the wetting ridge increases in time when the drop is static or in motion. Scale bar = 0.5 mm. Adapted from [68] under Creative Commons 4.0. c) Visualisation of the cloaking layer using white light interferometry on a moving droplet. The thickness scale on the left is calculated and should be used only as a guide. Scale bar = 1 mm. Adapted from [68] under Creative Commons 4.0.
1.3.2 Design and manufacture of LIS

LIS can be categorised into three classes based on their method of immobilising the liquid layer: 1-dimensional, 2-dimensional and 3-dimensional (see Figure 1.10c). This Section discusses these methods of stabilisation and general manufacturing techniques before discussing literature related to the rational design of LIS.

1.3.2.1 1-Dimensional LIS

In 1D LIS, the surface structure is on the molecular scale (see Figure 1.10c). A thin layer of lubricant (thickness of the order of a few nm) is either stabilised through intermolecular interactions with a molecular monolayer bound to the solid substrate or is directly grafted to the solid surface. There are relatively few studies using this molecular infusion mechanism compared to manufacturing LIS through other means.

1D LIS are manufactured in two ways. In the first method, the lubricant is infused within a molecular layer grafted onto a solid substrate, to promote the adsorption of the lubricant on the substrate. In academia, these were first reported as a modification of medical equipment with a perfluorocarbon molecular layer and then infusion with relatively small perfluorinated molecules, such as perfluorodecalin. [80, 81] The increased interaction of the perfluorodecalin with the perfluorocarbon modified substrate allows for the liquid to be stabilised and reduce the adhesion of thrombogenic molecules and cells. Industrially, perfluorinated lubricants have been tethered to hard disk surfaces to increase lubricant retention [82] and thin polymer films used to immobilise silicone oil. [83] More recently, similar systems have been reported, but instead, use polydimethylsiloxane (PDMS)/silicone oil combinations [84] or using π-π or π-COOH interactions to immobilise lubricants. [85–87]

The second method to manufacture 1D LIS is to covalently attach long-chain molecules to the surface in such a way that they retain liquid-like features. This class of 1D LIS are known as Slippery Omniphobic Covalently Attached Liquid (SOCAL) surfaces [88] or quasi-liquid surfaces (QLS) [89] and have attracted increasing attention recently due to their potential to eliminate lubricant depletion. In this method, surfaces can be made to be slippery without having any liquid flowing, displaying very low contact angle hysteresis (< 1°). [90] Methods to create these surfaces include grafting PDMS chains to a silicon surface using heat [90–92], acid catalyst [93] or even no catalyst [94], growing PDMS chains from a surface [95–97] or grafting perfluoro- polymers [98] or polymer brushes to the surface. [91, 99, 100]
1.3.2.2 2-Dimensional LIS

In 2D LIS, a surface micro-/nanostructure is used to trap lubricant by capillary action (see Figure 1.10c). This is by far the most common type of LIS reported in the literature and, in general, most of the work discussed in this Thesis refers to this type of surface. Intermolecular forces may aid in retaining a thin layer of lubricant on the tops of surface features, and therefore the study of short- and long-range interactions is critical. [36, 101]

2D LIS are manufactured by first creating roughness with the correct surface chemistry and then infusing a lubricant into the roughness (for recent reviews see [102, 103]). The important feature of this type of LIS is that there is roughness, ideally on the nanoscale, [104] and that the surface is of the correct chemistry to repel fouling liquids. [77] The underlying substrate can be inorganic or organic, so long as the surface can be functionalised to allow for successful infusion. The factors determining the correct chemical combination of surface and lubricant are explored in Section 1.3.3.

1.3.2.3 3-Dimensional LIS

In 3D LIS, the inherent porosity of a 3D molecular network is used to trap and store lubricant (see Figure 1.10c). Here, compared to 2D LIS, an additional mechanism is acting: the storage of lubricant is driven by an increase in entropy gained in the swollen state of the polymer. [105] In this system, the lubricant is absorbed into a polymer or other material network of the correct chemistry and then leaves a lubricious overlayer on the surface. Although intermolecular forces are the only stabilising force for the liquid overlayer, lubricant held in the bulk can replenish lubricant lost on the surface. These surfaces are also known as organogels, [106] and have been previously studied in a number of applications. [107, 108] Exploiting their ability to excrete a lubricating layer for anti-adhesive properties is novel.

3D LIS require a polymer that can be swollen by the lubricant. The most common of these is PDMS soaked in silicone oil (known as iPDMS). The silicone oil swells the PDMS matrix through diffusion and forms a lubricious overlayer which is later excreted whenever the overlayer is removed. [105] Other polymer matrices have also been employed such as polyvinylidene fluoride (PVDF) [109, 110] and polyethylene [111]. Surfaces of this type draw inspiration from the mucous-excreting glands of toads that cause the animal to be covered in a protective mucous layer that is constantly replenished from said glands. These surfaces have even been produced with macroscopic cavities filled with lubricant that mimic the glands. [112] PDMS has also been successfully swollen with alkanes, [113] and fatty acids. [114] An alternative approach blends the PDMS precursor with the lubricating liquid before crosslinking the PDMS, allowing the lubricant to be excreted later due to syneresis. [115]
 Industrially, this form of lubrication has found application in a medical field where thin layers of PDMS are used to stabilise silicone oil or other lubricants on medical devices.[116–118]

Figure 1.10. The most common lubricants are PFPE (a) and PDMS (b). c) 1D LIS stabilise a lubricant layer without structure; 2D LIS use capilarity to stabilise lubricant; 3D LIS store lubricant in a 3D molecular network.

### 1.3.3 Rational design of LIS

The design of LIS is wholly dependent on its final application. Generally, LIS include a hydrophobic substrate and a hydrophobic lubricant, but this is not a requirement and there are many examples in the literature that use hydrophilic lubricants. [36, 48, 74, 100, 119–124] The choice of hydrophobic substrate and lubricant is due to LIS generally being designed to repel aqueous foulants (e.g. bacteria/ice) or to manipulate water droplets. The very first reports of LIS both discussed design criteria for successful LIS. Lafuma and Quéré [37] outlined the requirements for a liquid-infused rough surface to repel water, and they highlighted the importance of ensuring that lubricant infuses into the solid, is immiscible with water to ensure
it is repelled, and water does not sink through the lubricant to contact the solid surface. Wong et al. [36] also outlined three general criteria for successful design:

- The lubricating liquid must wick into, wet and stably adhere within the substrate.
- The solid must be preferentially wet by the lubricating liquid rather than the liquid that is to be repelled (working fluid).
- The lubricating and working liquid must be immiscible.

With these basic requirements in mind, many researchers have explored the science behind the perfect lubricant/substrate combination.

Wong et al. use interfacial energies to describe a stable infused state — one where the solid is preferentially wet by the lubricant rather than the liquid to be repelled (working fluid). [36] By considering three wetted states (working fluid wetting the substrate, lubricant wetting the substrate, and working fluid on top of the lubricant) and ensuring that the first state is always energetically less favourable than the other two states, they propose two conditions that describe a stable infused state:

\[
R (\gamma_l \cos \theta_l - \gamma_d \cos \theta_d) - \gamma_{ld} > 0 \quad (1.15)
\]
\[
R (\gamma_l \cos \theta_l - \gamma_d \cos \theta_d) + \gamma_d - \gamma_l > 0 \quad (1.16)
\]

Where the \( R \) is the roughness factor (actual surface area to projected surface area), \( \gamma_l, \gamma_d \) are the interfacial tension of lubricant/air and impinging droplet/air, respectively, \( \gamma_{ld} \) is the interfacial tension between the lubricant and impinging droplet and \( \theta_l, \theta_d \) are the static contact angles of the lubricant and droplet on the flat substrate, respectively. This framework correctly predicts several stable lubricant/substrate combinations. [36]

Using classic liquid wetting behaviour, Smith et al. describe how the relative wetting properties of the lubricant/substrate combination influence the lubricant configuration on the surface. [77] In addition to the formation of the a wetting ridge and a cloaking layer, they identified that a positive spreading parameter for the lubricant over the substrate (\( S_{ls} > 0 \)) is required for the lubricant to cover the topography. Smith et al. use the Young-Dupré equation to predict wetting:

\[
S = \gamma_{lw} (\cos \theta_E - 1) \quad (1.17)
\]

Where \( \gamma_{lw} \) is the surface tension of lubricant in the medium (water) and \( \theta_E \) is the equilibrium static contact angle of the lubricant on the substrate in the medium. If \( \theta_E = 0 \), the lubricant spreads on the surface and covers high topographical regions even when the overall lubricant level is below these features. Smith et al. showed this using laser scanning confocal microscopy and environmental scanning electron microscopy (see Section 1.3.6 for more details)
for lubricants with different spreading parameter. For the fully wetting case, they used silicone oil, and for the partially wetting case, they used an ionic liquid (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide – BMIm). Their results show that the lubricant coats the tops of hydrophobized silicon microposts for silicone oil, but not for BMIm. The authors then examine all the possible thermodynamic configurations for a solid/lubricant/air and solid/lubricant/water system as these represent the majority of wetting scenarios LIS will face, as in Figure 1.11a. The stability of a lubricant layer on a surface often changes when the surface is moved from air to another medium, e.g. underwater. A surface with a stable lubricant layer in air may result in water droplet pinning if the lubricant dewets under the droplet and the droplet can penetrate the surface texture. An example of this is a hydrophilic substrate infused with a hydrophobic lubricant on which a water droplet is placed: the water will cause the lubricant to dewet and will sink into the lubricant layer, contacting the surface and pinning. These wetting states have been verified computationally. [72]

For a stable LIS, the solid must be preferentially wetted by the lubricant and not by the working liquid to be repelled. The surface of common substrates that are hydrophilic, such as untreated ceramics or metals, needs to be modified to make them more amenable as LIS, for example through silanisation. [47, 77, 125, 126]

Simply considering the interfacial tensions of the system cannot account for all observed wetting phenomena on LIS. Rowthu et al. found that this framework could not predict the stability of a hexadecane droplet on PFPE-infused alumina surfaces and instead built a model that takes into account density, viscosity, capillary time, capillary height, van der Waals forces of attraction, evaporation rate, surface diffusivity, and molecular shape and dimensions. [121] Using this extended framework, the authors could account for all observed wetting phenomena on their surface.

One fundamental weakness of considering only surface energy to determine the stability of LIS is that these values are not published for an arbitrary system. Preston et al. use the van Oss–Choudary–Good equation [127] to predict surface energy and design LIS that can repel a given fluid. [79] Five criteria for successful LIS design are identified from surface-energy-based reasoning (the failure is shown visually in Figure 1.11b) and are defined for the design of LIS in heat exchanger applications:

(i) $S_{ld} < 0$, the lubricant does not spread over the droplet — the droplet is not cloaked.
(ii) $S_{dl} < 0$, the droplet does not spread over the lubricant — it forms droplets that can be shed.
Figure 1.11. a) The possible thermodynamic configurations of lubricant in air and underwater as outlined by Smith et al. [77] The lubricant cloaks the droplet on the surface if the spreading parameter, $S_{OW}$ (equivalent to $S_{sl(a)}$), of the lubricant on the droplet is zero or positive. The wetting configuration is a function of the spreading parameter of the lubricant over the solid in air and water ($S_{OS(a)}$ and $S_{OS(w)}$, respectively; equivalent to $S_{sl(a)}$ and $S_{sl(d)}$). Adapted with permission from [77]. Copyright 2013 Royal Society of Chemistry. b) The possible failure modes outlined by Preston et al. [79] for a lubricant/substrate/droplet system. Adapted with permission from [79]. Copyright 2017 American Chemical Society. c) The three wetting states presented by Daniel et al. [74] for a droplet on a LIS with a corresponding phase diagram as a function spreading parameter, $S$, and Hamaker constant, $A$. L1 is a stable lubricating layer, L2 is an unstable lubricating layer, and L3 is a non-existent lubricating layer. L1 scale bar: 0.1 mm, inset: 10 µm; L2 scale bar: 0.3 mm, inset 1: 15 µm, inset 2: 40 µm; L3 scale bar: 0.1 mm. Adapted with permission from [74]. Copyright 2017 Springer Nature.
(iii) $S_{ls} > -\gamma_l R$, the lubricant spreads into the structural features of the substrate (of roughness factor $R$) in the presence of the vapour of the droplet — the lubricant remains successfully infused in the substrate during condensation.

(iv) $S_{ls(d)} > -\gamma_{dl} R$, the lubricant does not spread into the structure of the substrate in the presence of the impinging droplet.

(v) $\gamma_{dl} > 0$, the lubricant and the droplet are miscible.

Where subscripts $l$, $d$, $s$ refer to lubricant, impinging droplet and substrate respectively; where $S_{xy}$ represents the spreading parameter for $x$ spreading over $y$ and $R = (r - 1)/(r - \phi)$ is a roughness factor calculated using the roughness, $r$, and the solid fraction, $\phi$, and is 0 for a flat substrate and 1 for a very rough substrate.

By considering interfacial energy as the sum of dispersive and van der Waals interactions (Lifshitz-van der Waals (LW)) and the polar interaction (denoted as superscript + and -), the interfacial energy between two phases is:

$$
\gamma_{AB}^{\text{total}} = \gamma_A^{LW} + \gamma_B^{LW} - 2\sqrt{\gamma_A^{LW}\gamma_B^{LW}} + 2\sqrt{\gamma_A^{+}\gamma_A^{-}} + 2\sqrt{\gamma_B^{+}\gamma_B^{-}} - 2\sqrt{\gamma_A^{+}\gamma_B^{-}} - 2\sqrt{\gamma_B^{+}\gamma_A^{-}}
$$

These five criteria for failure can be used to assess the stability of a given substrate/lubricant/droplet system. Preston et al. correctly predict the failure mode of several solid/lubricant/droplet combinations from both their own experiments and ones reported in the literature. Their model can be used to rationally design a surface for a specific application, but is optimised for heat transfer applications where criterion (i) is crucial. In other applications, criteria (i) may or may not relevant.

For example, they predicted that a strong polar interaction between the substrate and the lubricant would allow a LIS to repel impinging droplets with surface tension of $\gamma \approx 11 \text{ mN m}^{-1}$. They identified SiO$_2$ substrate and hexafluoroisopropanol (6F-IPA) lubricant as a candidate system and managed to repel butane ($\gamma \approx 13 \text{ mN m}^{-1}$). Prior to this, the lowest surface tension reported to be repelled by LIS was pentane ($\gamma \approx 17 \text{ mN m}^{-1}$). [36, 128]

Daniel et al. used nanoscale interactions to rationalise the wetting behaviour of a lubricant underneath a droplet. Accounting for van der Waals interactions, they built a phase diagram describing three lubrication states: stable, unstable (dewetted patches) and non-existent (denoted L1, L2, L3, respectively, see Figure 1.11c). [74] Daniel et al. used interference microscopy (see Section 1.3.6 for more details) to study the thickness distribution of lubricant underneath the droplet for 24 substrate/lubricant combinations and found for a stable and continuous lubricant layer, two criteria must be met: $S > 0$ and $A > 0$ (i.e. a lubricant that spreads on the surface and is stabilised by van der Waals interactions as indicated by a positive
Hamaker constant, $A$). Without the stabilising van der Waals interaction, the droplet will contact the surface as the lubricant layer is squeezed out due to Laplace pressure from the droplet’s curvature (L2 state). [74, 129] If the droplet does contact the substrate, this does not preclude the droplet from moving easily, with droplets in both L1 and L2 wetting states leading to oleoplaning on the substrate. For the L1 state, this occurs at any velocity, but only occurs after a threshold velocity for L2. [74] Like the spreading parameter, the Hamaker constant is often not useful for designing LIS *a priori* as it is difficult to estimate correctly for complex multi-component systems. Unknown Hamaker constants can be estimated using combinations of known Hamaker constants for single material systems. [130]

### 1.3.4 Lubricant choice

Although there is no clear ideal lubricant for all applications and correct lubricant choice depends on the application of the surface, certain classes of lubricant have emerged as favourites in the literature due to their inherent favourable properties. In particular, perfluoropolyethers (PFPEs) and linear polydimethylsiloxane (PDMS, also known as silicone oil or dimethicone) have emerged as clearly preferred. PFPEs are a class of perfluorinated compounds whose general structure is shown in Figure 1.10a. They have been used as lubricants in the aerospace industry for decades and are known for their chemical inertness, low surface tension and (in the longer chain length molecules) low vapour pressure. Similarly, silicone oil is known for its chemical inertness, low surface tension and low vapour pressure and is often used to lubricate mechanical devices with its structure shown in Figure 1.10b. These properties, along with their relatively low cost compared to PFPEs, [131] make silicone oil ideal for use in LIS. The properties of the common types of PFPE and silicone oil are presented in Table B.1.

PFPEs and silicone oil have unique chemical composition, leading to the favourable properties that make them popular lubricants. The carbon-fluorine bond is one of the strongest chemical bonds, due to the high electronegativity of fluorine that gives the bond a partial ionic character. [132] Multiple fluorine atoms bonded to the same carbon increase this effect as there is a higher partial positive charge on the carbon. Fluorine has very low polarisability, meaning that compounds that contain a lot of fluorine have very weak London dispersion force interactions. [132] This means that although perfluorinated compounds are non-polar, they are lipophobic in addition to being hydrophobic. As a result, they are immiscible with almost all common solvents. The weak intermolecular forces give perfluorinated compounds low surface tension and a low viscosity (compared to polymers with similar boiling points).

Silicone oil is comprised of a backbone of siloxane bonds ($-\text{Si} - \text{O} - \text{Si}-$) with methyl groups attached to each of the silicon atoms. The combination of the partially ionic siloxane
bond (about 40%, due to the low electronegativity of silicon [133]) and the low polarity methyl groups gives silicone oil a unique chemical character, compared to organic polymers. Its chemistry is neither purely hydrophilic, nor purely hydrophobic, nor is it a surfactant as there is not enough separation between the hydrophilic and hydrophobic portions. Rearrangement of chains so that the methyl groups are at the surface gives silicone oil an overall macroscopic hydrophobic character. [134] The large $\text{Si} - \text{O} - \text{Si}$ bond angle ($151.2^\circ$ [133]) and large Si-O bond length ($1.63 \text{ Å}$ [133]) gives a small torsional barrier for rotation about the backbone and a very low $T_g$ (150 K [134]). The partially ionic nature of the siloxane bonds combined with high bond energy (445 kJ mol$^{-1}$ [134]) gives silicone oil excellent chemical and thermal stability, while weak intermolecular interactions between the methyl groups give low surface tension.

Although the classes of lubricants mentioned above are the most popular, many other lubricants have been employed including those from highly available sources such as vegetable oils, [111, 119, 135–138] polyols, [120, 139] or even motor oil. [136] Edible lubricants enable the application of LIS in areas of food handling and processing, [140] while cheaper oils pave the way for scalability of LIS manufacture in large scale applications.

Ionic liquids have also been successfully used as lubricants. [71, 77, 110, 141–147] Ionic liquids have negligible vapour pressure, [77] but the molecular composition has to be modified to make them hydrophobic and repellent to water and, as such, all reported ionic liquids include a fluorinated anion. While most of LIS applications seek to repel aqueous foulants and, as such, employ hydrophobic lubricants, specific applications can call for the use of hydrophilic lubricants. [36, 74, 100, 119–123, 139, 148] One example of a situation where infusion of a hydrophilic liquid is beneficial is repelling oil underwater. In this case, the underlying surfaces are superhydrophilic and infused with water. [122, 123] Hydrophilic lubricants have also been employed on anti-icing surfaces with Ozbay et al. showing that an 85% solution of glycerol infused into hydrophilic filter paper reduces ice accretion much more effectively than a hydrophobic lubricant infused into a hydrophobic filter paper. [120]

For many of these lubricants, a major concern is chemical stability. Long term application of LIS requires the lubricant to be stable over a long period. While some lubricants may have beneficial environmental or medical properties, this often comes at the cost of chemical stability. For example, plant oils lose around 30% of their oxidative stability after 12 months storage. [149]

An overview of lubricants found in the literature and their properties are presented in Table B.1 and Table B.2.
1.3.4.1 Critical contact angle for infusion

One advantage of 2D LIS is that they use capillarity to aid infusion. A lubricant with non-zero contact angle can stably infuse into 2D LIS if its contact angle on a flat substrate of the same chemistry is below a critical value $\theta_c$. This is the hemiwicking criteria for a liquid to enter a porous solid. [37, 77, 150]

\[
\cos \theta_c = \frac{1 - \phi}{r - \phi} \tag{1.19}
\]

where $\phi$ corresponds to the fraction of the solid surface wet by the liquid, and $r$ is the roughness ratio. The $\phi$ factor is estimated using the Cassie-Baxter equation (Equation 1.12) and roughness ratio $r$ is defined as the ratio of true surface area to apparent surface area.

The critical contact angle for infusion is dependent on not only the roughness $r$, it is also dependent on the intrinsic wettability of the surface as $\phi$ is dependent on the contact angle (see Equation 1.12). This allows a surface to be altered in multiple ways to give stable infusion.

However, as the geometric parameters used in Equation 1.19 are not easily measurable, the equation only gives a rough indication of whether a liquid will infuse or not. $\phi$ is estimated using the Cassie-Baxter equation which does give correct predictions on real surfaces due to chemical inhomogeneities. $r$ is difficult to calculate on real surfaces as the fractal nature of most structured surfaces means the value depends on how the true surface is area is either measured or defined. Additionally, the intrinsic uncertainty of contact angles means the value calculated using Equation 1.19 is an indication that liquids with static contact angle on a flat surface much below $\cos \theta_c$ will successfully infuse.

1.3.4.2 Environmental factors in lubricant choice

The most widely used lubricants, PFPE and silicone oil, are used in part for their chemical inertness. This inertness makes them ideal for broad application as they do not degrade due to reaction with foulants, or exposure to high temperatures (up to $300^\circ C$ in oxidative environments [151]). However, this inertness raises possible environmental concern as there are no natural pathways for degradation.

Although the first commercial antifouling paints based on LIS technology first went on sale in late 2019 (SLIPS N1x from Adaptive Surface Technology Pty Ltd using a fluorinated PDMS-based lubricant), silicone antifouling paints with added oils for lower foulant adhesion have been used for decades. [152–154] These antifouling paints are very similar to the 3D
LIS described in Section 1.3.2.3, with a PDMS (or similar) matrix swollen with up to 20 % w/w with an oil. [153] Although the presence of a lubricious overlayer was never confirmed in these studies, the antifouling behaviour of these surfaces is likely due to an immobilised and replenishing lubricant layer.

As a result of these existing antifouling technologies, there has been some concern surrounding silicone oil release into marine environments. [155] Silicone oil and other hydrophobic polymers are generally not bioactive owing to their hydrophobicity and high molecular weight. [156, 157] This means that they do not interact with biological systems and also do not bioaccumulate in marine organisms. [156–159] In addition, many researchers have shown that their lubricants are not biocidal. [50, 160–163] Instead, silicone oil released in the environment tends to coat particulate matter and end up in sediments. [156] While this is not a concern in low concentrations, in higher concentrations these oils have the potential to suffocate and damage marine organisms in a similar way to petroleum oil spills. Given the enormous volume of the ocean, this is unlikely to pose a threat in areas other than high traffic shipping lanes.[155] It is also believed that the potential damage from silicone oil in marine antifouling coating is far less than that from biocidal antifouling solutions, [155] such as the banned tributyltin (TBT) containing paints that bioaccumulate and were hugely damaging to shellfish populations. [164]

Although there is no clear data on the fate of PFPE in the environment, it is expected to be different from that of perfluorocarbons (PFCs) more generally. Most of the serious environmental concerns around the release of PFCs in the environment involve perfluorinated acids, which bioaccumulate in fish. [165] Bioaccumulation of perfluorinated acids is due to the presence of polar groups, which are not present in PFPEs. Due to their similar physicochemical properties, PFPEs likely face a similar fate as silicone oil, that is they are inert but could potentially lead to suffocation upon coating.

1.3.5 Performance of LIS as a function of lubricant thickness and distribution

The performance of liquid-infused surfaces, including their omniphobic character, icephobicity, anti-bacterial, anti-corrosive, antifouling properties and drag reduction, is closely related to the volume and distribution of lubricant on the surface. This phenomenon is similar to the failure of superhydrophobic surfaces due to plastron collapse, [19] and even though the lubricant layer is more robust than an air layer, LIS are still most likely to fail due to loss of lubricant. Relatively few publications have specifically addressed the relationship between
the performance of LIS and lubricant distribution, and the different mechanisms that lead to lubricant depletion.

The slippery properties (e.g. low roll-off angle and high interfacial slip length) of LIS likely depend on film thickness in a non-monotonic way. The limit at which the slippery properties start to degrade is likely to be of the order of tens of nm, and films thicker than this level are likely to be equally slippery, as long as they are homogeneous. Goodband et al. find little change in CAH as film thickness (estimated by change in mass) decreases from approx. 25 µm to 5 µm. [166] On a thick film (e.g. thicker than about 1 µm), the dynamic and static regimes of wetting are not affected by the exact lubricant film thickness. [60]

1.3.5.1 Performance of thin lubricant films in 1D LIS

In the absence of structural features, 1D LIS are unable to stabilise thick lubricant films. The films that remain are typically very thin (<5 nm) and stabilised via van der Waals or other intermolecular interaction. The ability of very thin films to effectively lubricate is still debated in 1D LIS research, with evidence pointing both to very low contact angle hysteresis and to more standard hydrophobic behaviour. The performance of 1D LIS is likely limited in time due to the low thickness of lubricant that can be stabilised compared to the structure of 2D LIS and the intrinsic reservoirs of 3D LIS. As there are relatively fewer publications concerning 1D LIS, it is difficult to make an accurate comparison of their performance.

Scarratt et al. found that the low amount of lubricant present in 1D LIS leads to distinct properties to those exhibited by surfaces with thicker lubricant layers. For example, a 2 nm thick silicone oil film stabilised by an octadecyltrichlorosilane (OTS) monolayer does not have strong drag-reducing properties, [60] which are only measured on thicker lubricant layers. [167, 168] Scarratt et al. found that low roll-off angle on flat infused self-assembled monolayers disappears once the lubricant layer is thinner than about 20 nm. [60] On the other hand, others have found 1D LIS exhibit many of the desirable properties associated with LIS. Zhang et al. show that a lubricant layer on a hydrophobic non-textured substrate exhibits low roll-off angles and delayed ice formation, but also that the layer thickness is drastically reduced after washing the sample with water. [84] Similarly, Eifert et al. show that lubricant is lost when a 1D LIS is held vertical, but that the surface is still slippery. [169] Wang et al. showed that silicone oil trapped using a molecular layer produces a slippery surface capable of repelling complex viscoelastic mixtures with impressive longevity that is extended with lubricant replenishment. [93]

Slippery Omniphobic Covalently Attached Liquid (SOCAL) surfaces and quasi-liquid surfaces (QLS) are an attractive method to produce low adhesion surfaces as they do not suffer from
depletion in the same way as the other types of LIS. Their performance relative to surfaces with mobile lubricant layers is difficult to gauge, however, as the main property that has been assessed on these surfaces is contact angle hysteresis. [90, 169–171] Wu et al. looked at how silicone brush tethered surfaces perform in regards to biofouling and have found that they perform well compared to hydrophilic controls and that they are much more robust than SLIPS against abrasion from sand and water. [172] There are recent reports suggesting that PDMS chains tethered to the surface produced a durable and slippery coating. [92, 94]

1.3.5.2 Methods to accelerate lubricant depletion

The common pathways by which lubricant is lost from 2D and 3D LIS are via spreading to surrounding surfaces, capillary effects, shear-induced by flow of air or other working fluids, drainage induced by gravity, and evaporation. Some of these mechanisms have been studied quantitatively, using conditions which mimic realistic operation conditions. Some common methods are shown in Figure 1.12. Spin coating is often used to demonstrate the robustness of a surface towards depletion. [173–177] However, spin-coating is not representative of the realistic depletion pathways that the surface would typically undergo during use, and does not induce the same degree of film depletion as other more aggressive methods. More effective tests of depletion involve dripping water droplets repeatedly on the surface (as lubricant is removed from the surface in the meniscus surrounding every drop, see Figure 1.12c), [168, 178–181] shearing with a jet of nitrogen gas (by aerodynamic stress [60] and evaporation), [146, 182] shearing with a water jet, [183–186] or even more effective, dipping the surface repeatedly across a water-air interface (see Figure 1.12d and Chapter 5). [105, 183] Other tests have attempted to characterise the slippery properties of a surface through expected use cases such as coming into contact with an unlubricated material, [111] icing/deicing cycles, [187] or in simulated underwater usage [162, 188, 189]. Comparison of different accelerated depletion methods is difficult as there is no standard metric to measure the performance of LIS. Most commonly, slippery properties are assessed through contact angle hysteresis or roll-off angle, or the performance is assessed in a given application such as through bacterial or ice adhesion tests.

1.3.5.3 Lubricant depletion induced by flow or shear

LIS are often tested in flow situations, as they offer potential for drag reduction in both laminar [55, 58, 190] and turbulent [191] flows. However, when exposed to high flow rates, LIS become depleted due to shear-induced drainage. [184, 192] The Stone group investigated the effect of viscosity ratio (the ratio of the viscosity of the working liquid over that of the infused liquid) on lubricant retention within streamwise grooves infused with lubricant and exposed
Figure 1.12. a) Gravimetric draining is the simplest depletion method, allowing excess lubricant to drain away under gravity. b) Spin coating partially removes lubricant due to rotation induced shear. c) Water dripping removes lubricant in the form of cloaking and wetting ridge around each droplet. Adapted with permission from [84] Copyright 2018 American Chemical Society. d) Dipping through an air/water interface removes lubricant due to shear at the interface. Adapted with permission from [105]. Copyright 2018 AIP Publishing.

to longitudinal flow within microfluidic devices. [193, 194] They found that a higher pressure gradient results in lower lubricant retention. Also, for a given shear stress, less viscous lubricants achieve higher retention because shear stress at the fluid-fluid interface decreases when the viscosity ratio increases. However, large viscosity ratios can cause instability at the liquid/liquid interface, which also triggers the failure of LIS. [195] The same group found that shear-induced drainage of the lubricant could be prevented by imposing a pattern of surface chemistry preferentially wetted by the working liquid rather than the lubricant on the
substrate. By interrupting the continuity of the infused lubricant, these patterns prevent the lubricant from draining from the infused roughness. [185]

An area that requires further study is the geometric surface parameters that enable most effective fluid retention under flow; limited work has been published both in regular and randomly patterned surfaces. [91, 104, 185] Numerical simulations suggest that there are multiple failure modes of LIS under flow. In a simple geometry of an infused groove, if the groove is deep enough the lubricant meniscus will de-pin from the front of the groove leading to failure. For a shallow groove, the meniscus will contact the bottom. [196]

### 1.3.6 Characterisation of lubricant thickness and distribution

Key to the rational development of LIS is the characterisation of the lubricant distribution on the macro-, micro- and nanoscale, including dynamic effects. Essential questions to be answered include: how much lubricant is trapped on the surface at time zero and as the lubricant depletes from the surface? How homogeneous is the layer thickness during ageing? How do droplets interact with the surface at different stages of depletion?

There are numerous challenges associated with the analysis of the lubricant layer. These layers are necessarily thin, making the volumes of lubricant present very small. Simple optical observation can help with the detection of the lubricant loss in the case of transparent 2D LIS (their roughness means they are only transparent when lubricated), the loss of transparency can be qualitatively correlated with a loss of infused layer. [59, 86, 119, 122, 197–199] For more detailed analysis on a wider variety of surfaces, more sensitive and general characterisation techniques are required.

Techniques reported for characterising lubricant layers fit into two broad categories: indirect and direct techniques. Indirect techniques rely on the measurement of the total lubricant present, while direct techniques attempt to spatially resolve lubricant thickness to understand how surface structure or interaction with droplets influence layer thickness. Techniques reported in the literature are summarised in Table 1.1.

### 1.3.6.1 Indirect methods

Indirect techniques measure the amount of lubricant on a surface with no spatial information on lubricant distribution. The most common of these is to measure the mass change of a test substrate before and after infusion or depletion. [104, 119, 166, 175, 200–202] The balance used for the measurement and the size of the sample limits the resolution of this technique which is problematic for heavily depleted lubricant films. For example, a liquid
Table 1.1. Comparison of techniques used to characterise liquid layer thickness on LIS.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Lateral Resolution</th>
<th>Vertical Resolution</th>
<th>Temporal Resolution$^a$</th>
<th>Possible Substrates</th>
<th>Used in Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indirect Methods</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass Change</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Any</td>
<td>[104, 119, 166, 175, 200–202]</td>
</tr>
<tr>
<td>UV Spectroscopy</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Any</td>
<td>[137, 203]</td>
</tr>
<tr>
<td>Direct Methods</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laser Scanning Confocal Microscopy</td>
<td>500 nm$^b$</td>
<td>200 nm</td>
<td>Seconds</td>
<td>Transparent</td>
<td>[71, 77, 111, 114, 183, 202, 204–212]</td>
</tr>
<tr>
<td>Scanning electron microscopy</td>
<td>10 nm</td>
<td>10 nm</td>
<td>Minutes</td>
<td>Any</td>
<td>[47, 63, 77, 128, 137, 141, 142, 145, 186, 213–220]</td>
</tr>
<tr>
<td>Ellipsometry</td>
<td>1 mm</td>
<td>&lt;1 nm</td>
<td>Minutes</td>
<td>Flat</td>
<td>[84, 171, 180, 207]</td>
</tr>
<tr>
<td>Interference Microscopy</td>
<td>500 nm$^b$</td>
<td>&lt;1 nm</td>
<td>Seconds</td>
<td>Any</td>
<td>[68, 221, 222]</td>
</tr>
<tr>
<td>Reflection Interference Contrast Microscopy</td>
<td>500 nm$^b$</td>
<td>10–30 nm</td>
<td>Milliseconds</td>
<td>Transparent</td>
<td>[68, 74, 223–225]</td>
</tr>
</tbody>
</table>

$^a$ timescales reported should only be interpreted as order of magnitude. Scan times for all techniques vary depending on scan size, resolution, sample etc.,

$^b$ based on the diffraction limit.

film of thickness 1 µm with density 2 g ml$^{-1}$ (typical of perfluorinated small molecules) has a mass of 0.2 mg cm$^{-2}$. Mass changes of this order approach the limit of typical analytical laboratory balances. This Thesis introduces another indirect method which uses fluorescence to measure the volume of lubricant present on the surface with the scope to have much higher sensitivity than mass change in Chapter 3. These approaches give a reasonable estimate of the volume of oil infused into the surface and can give an estimate into thickness, assuming a flat sample. [173]

### 1.3.6.2 Direct methods

Direct techniques map or measure the thickness of oil on the surface to provide much greater detail than indirect techniques. One of the most commonly used methods is laser scanning confocal microscopy. [71, 77, 111, 114, 183, 202, 204–212] This technique allows 3D imaging of substrate, lubricant and liquid drops on the surface simultaneously, and over time. In confocal microscopy, fluorescently dyed lubricant and working liquids are mapped in three dimensions, giving a stack of images that can be sliced arbitrarily. [226] For lubricated surfaces, the lubricant and liquid drops on the surface can be tagged with different dyes, allowing imaging of both, see Figure 1.13a. Although perfluorinated fluids are difficult to fluorescently tag owing to their unique chemistry, Howell et al. produced fluorescent nanoparticles that partition into the perfluorinated phase to image perfluorinated lubricants. [183] Due to the slow collection times, of the order of seconds to minutes per frame, this technique is useful for equilibrium systems or slow-paced dynamic processes. For example, it
has been used to image the condensation of a water drop on a lubricated surface. [210] There are a few drawbacks to using laser scanning confocal microscopy:

- To effectively image the lubricating layer, it is best to use the microscope in an inverted geometry, restricting analysis to transparent substrates.
- Films of thickness below 1 µm can be detected but not quantified.
- As the technique is based on visible light, interference at boundaries can occur.
- The resolution of the technique is diffraction-limited, giving a maximum lateral resolution of about 500 nm. [227]

Other light-based techniques used include ellipsometry, [84, 171, 180] and interferometric techniques. [68, 74, 221, 222] Keller et al. use a 3D optical profiler (based on white light interference) to image the surface of the lubricant layer, revealing depletion when the underlying surface structure begins to protrude, see Figure 1.13b. [222] This technique provides excellent precision in height measurements but limited lateral resolution and cannot quantify lubricant thickness. Ellipsometry was used to map the thickness of lubricant on a flat lubricated surface, see Figure 1.13c. [84] This technique gives very precise value of thickness (with error below 1 nm), but is limited in the $xy$-resolution by the spot size of the ellipsometer (approx. 1 mm on most instruments and down to approx. 10 µm on instruments with mapping capabilities) and is only suited to flat substrates. The accuracy of ellipsometry is dependent on the system studied, needing a contrast in optical properties between the lubricant and the substrate for successful model fitting. For example, a common substrate ($\text{SiO}_2$) and common lubricant (silicone oil) have very similar optical properties and so this system does not give accurate measurement. Additionally, although the precision of ellipsometry is below 1 nm, the technique struggles to measure thin films on the order of a few nm for systems in which the optical properties of the film are not known to high accuracy. Interference microscopy was used to map the lubricant thickness on a porous surface, showing areas where lubricant had dewetted. [221] Daniel et al. used reflective interferometric contrast microscopy (RICM), to capture a lubricant film thickness through a transparent substrate underneath a droplet, see Figure 1.13f [74] This technique uses the interference of monochromatic light as it reflects off the boundaries of an infused layer to measure the thickness of the lubricant with vertical resolution of 10–30 nm. [228] Daniel et al. also used white light interference (similar to the 3D optical profiler mentioned above) to measure micrometric film thickness as RICM tends to underestimate film thickness for thicker films. As all the techniques mentioned in this paragraph are based on light, their lateral resolution is diffraction-limited.

Another often-employed direct measurement technique is scanning electron microscopy (SEM). [47, 63, 77, 128, 137, 141, 142, 145, 186, 213–220] Environmental scanning electron
Figure 1.13. Direct lubricant characterisation methods. a) Laser scanning confocal microscopy allows for imaging the lubricant and droplets in 3D. The lubricant and water are dyed yellow and red respectively. Scale bar 40 µm. Adapted from [71] under Creative Commons 3.0. b) 3D Interference microscopy shows the structure of the lubricant surface, revealing the underlying structure when the lubricant depletes. Adapted with permission from [222]. Copyright 2019 American Chemical Society. c) Ellipsometry provides exceptional precision in lubricant thickness but has limited lateral resolution. Adapted with permission from [84]. Copyright 2018 American Chemical Society. d) Environmental SEM allows for the direct imaging of lubricant on the surface at high resolutions. Adapted from [128] under Creative Commons 3.0. e) Cryo SEM allows for direct imaging of cross sections of LIS. Copyright 2019 American Chemical Society. Adapted with permission from [47]. f) Reflection interference contrast microscopy allows for precise measurement of lubricant films under and around droplets with short collection times. Adapted with permission from [74]. Copyright 2017 Springer Nature
microscopy (ESEM) allows for higher chamber pressures, and so allows imaging of liquid systems including water. [229] This technique has been used to image lubricant in both randomly rough substrates and a regular array of micro-pillars, [77] see Figure 1.13d. This technique provides qualitative images of lubricant distribution but cannot measure lubricant thickness. On the other hand, cryo-SEM allows for direct imaging of a lubricant layer when used in conjunction with focused ion beam (FIB) lithography to produce a cross section of the surface showing the lubricant in depleted state, see Figure 1.13e. [128, 217] The surface can even be reconstructed in 3D using FIB tomography, but this process is slow and destructive. [217] One approach to investigating wetting at the nanoscale is to cure the liquid, making it solid, removing it from the surface and image it using SEM, although this has not been directly applied to LIS. [213]

In Chapter 4, this Thesis develops and validates a new technique based on AFM force mapping that maps lubricant thickness with much greater spatial resolution than confocal microscopy or SEM.

1.4 Biofouling

Biofouling is the tendency of any surface that is immersed in an aqueous environment for an extended period of time to have biological matter grow on it. [230] This is evident in our everyday life as oysters growing on jetty pylons or the moss that grows on wet rocks or the layer of plaque on our teeth. Biofouling is undesirable in most contexts as it modifies the surface chemistry and topography and allows for the proliferation of invasive or infectious species. This is particularly the case in the ocean where biofouling on the underside of ships (see Figure 1.14a) greatly increases the drag on their hull, increasing both the financial and environmental cost of shipping. A 1 mm biofilm on a ships hull can cause a 15% reduction in speed [230] and a thicker film can cause 14 % increase in emission of CO₂, NOₓ and SO₂. [231] Additionally, growth on ships can introduce invasive species to new areas. [232] Medically, biofouling of medical devices can cause secondary infection or rejection of implants with approximately 10% of patients receiving an implant contracting a related infection. [230]

Marine biofouling is a very old problem with ancient civilisations suffering from fouling in much the same way we do. The first evidence of antifouling coatings is from the early Phoenicians (1500–300 BCE) who lined the hulls of their ships in plates of copper and lead. [233] This technique was revisited in the 18th century by the British navy who lined the hull of their ships in copper. This is the origin of the phrase ‘copper bottomed’ meaning reliable
and unlikely to fail due to the superior function of British ships. [234] Transition metals (e.g. copper, lead, arsenic, mercury) were then incorporated into antifouling paints but needed costly dry docking for reapplication every 18 months or so. [233]

In the 20th century, biofouling was thought to be a solved problem with the introduction of self-polishing copolymers containing tributyltin (TBT). [232] TBT and other organotin compounds are powerful biocides that effectively stop all fouling. When they are incorporated into self-polishing copolymers (coatings which are constantly hydrolysed by seawater to expose new polymer surface) they allowed ships to stay in the water for over 5 years before needing reapplication or maintenance. [233] Unfortunately, TBT bioaccumulates and was responsible for a huge decrease in shellfish numbers in areas of high boat traffic. As a result, the International Maritime Organisation adopted the “AFS Convention” in November 2001, to ban the application of TBT on all vessels after 1 January 2003. By 2008, almost all jurisdictions had ratified or introduced their own bans on paint containing TBT and shellfish numbers have now returned to their previous levels. [233] This is considered by many to be one of the greatest global ecological victories ever. Unfortunately, no new shellfish-friendly antifouling paints have managed to match the effectiveness of TBT-containing paints.

The process of biofouling occurs in steps, shown in Figure 1.14b. First the surface is conditioned for attachment through reversible adsorption of biomolecules — generally proteins and polysaccharides. Bacteria then attach to the conditioned surface and excrete an extracellular polysaccharide matrix. From this point, the biofouling is now known as a biofilm and removal is very difficult and will not happen spontaneously. The biofilm is an ideal surface for larger organisms such as diatoms or barnacles to grow, but even in its absence the larval forms of larger foulers are still able to adhere. Efforts to reduce biofouling generally focus on stopping the early stages of adhesion of macro-organisms through reduction in biofilm growth and over reduction in the ability of organisms to adhere to the surface. To achieve this without using powerful biocides such as TBT, there are several approaches including using surface topography to disrupt bacterial adhesion [236, 237], using soft materials, [238] using bacterial chemical signaling to disrupt settlement, [165] or, as developed in Chapter 3, using LIS to stop settlement of bacteria.

The mechanism of anti-biofouling on LIS are not fully understood. While their ability to limit fouling has been demonstrated both in the lab and in the ocean (see Chapter 3), the underlying mechanism has not been studied in detail. The low adhesion of LIS suggests that their antifouling ability is, at least in part, due to adhered organisms being easily removed under applied shear. There is also some evidence that their antifouling ability is due an overall reduction in bio-molecule interaction with the surface. This is seen through anti-thrombotic

ability of LIS where thrombosis formation is heavily suppressed on LIS even after hours of blood flowing over them. [80] For some macro-organisms, such as mussels, the lubricant layer hinders their ability to sense a solid surface and so they choose not to settle on the LIS. [114, 239]
1.5 Atomic force microscopy

Analysis of the lubricant layer in LIS is faces many challenges due to the small volumes involved. Understanding the wetting of the lubricant at the nanoscale is necessary for a full understanding of LIS, but the layer cannot be visualised using using optical techniques when surface structure is on the nanoscale. Atomic force microscopy (AFM) is a technique that is commonly used for surface analysis below the diffraction limit and in Chapter 4 this Thesis expands the use of AFM to map the thickness and distribution of lubricant on the nanoscale.

AFM is a subset of the scanning probe microscopy (SPM), first introduced in 1986 by Binnig et al. [240]. Scanning probe microscopes scan a tip across a surface measuring an interaction at each point. The earliest of these to gain prominence in nanoscience is the scanning tunnelling microscope (STM) which was first introduced in 1982 also by Binnig. [241] The STM uses a sharp conductive tip to measure the tunnelling current between a single atom and the surface. Keeping this current constant allows for mapping of individual atoms in vacuo. Later, this concept, combined with concepts from the stylus profilometer, allowed for the invention of AFM.

AFM combines the precise scanning of the STM with the topography mapping of the stylus profilometer to produce nanoscale maps of surface topography. As the name suggests, this is achieved through mapping atomic forces — attractive and repulsive intermolecular interactions. The key development here is that micro-manufacture technology allowed for the production of cantilevers whose spring constant is on the order of the magnitude of intermolecular interactions, allowing controllers to use these interactions as a means of tracking the surface. Using optical methods to track the deflection of the cantilever (as opposed to tunnelling current) allowed AFM to operate in just about any conditions - even underwater and on non-conductive surfaces.

This basic design of a sharp tip attached to a soft cantilever with a laser tracking deflection has endured for three decades and is the basis of all modern AFM systems, see Figure 1.15. Deflection of the cantilever is measured using a laser reflected off the backside of the cantilever into a four-quadrant photodiode. By measuring the difference between the signal on each of the quadrants, deviation from the neutral position either parallel or lateral to the axis of the cantilever is quantified.

At its core, an AFM simply measures the interaction between the tip and a sample. Given the range of possible spring constants and the different ways the tip and sample can interact, AFM is used for a lot more than just mapping topography. Some common usage modes include:
1.5 ATOMIC FORCE MICROSCOPY

Figure 1.15. a) Contact mode AFM. The tip is dragged across the surface with constant force. The figure shows an alternative, less common contact mode where the tip is dragged across the sample at a constant height with all changes in topography seen as deflection of the cantilever. b) Tapping mode AFM. The cantilever is oscillated at its resonant frequency with constant amplitude. c) Force spectroscopy. The sample is moved towards the tip and the deflection of the tip measured.

- Contact mode - The tip is dragged along the surface with constant force (Figure 1.15a).
- Tapping mode - The tip is oscillated at its resonance frequency with damping of the oscillation used to maintain a height above the surface (Figure 1.15b).
- Force spectroscopy - The tip is moved normal to the surface and the forces on the cantilever recorded as a function of distance. The generated force curves can be used to calculate the sample’s materials properties (Figure 1.15c).
- Colloidal probe microscopy - A subset for force spectroscopy where a sphere replaces the sharp tip allowing AFM to measure colloidal interactions.
- Force mapping - Mapping force measurements across the surface.
- Magnetic force microscopy - Measure magnetic properties using an electrically charged tip.

1.6 Outline of Thesis

This Thesis examines the function and fundamental operation of LIS, with a particular focus on using them as a non-toxic coating for combating biofouling. Chapter 2 details the materials and methods used in this Thesis. Chapter 3 details the production of LIS using spontaneously wrinkled Teflon surfaces and their antifouling properties in marine environments. First, the Chapter examines the anti-biofouling properties of LIS against marine bacteria and develops a fluorescence-based lubricant quantification technique to link the level of lubricant depletion to antifouling performance. These surfaces are then tested in a real-world setting where their antifouling ability is assessed in the ocean. Chapter 4 develops a method of mapping lubricant thickness using atomic force microscopy. This technique gives much greater resolution compared to other characterisation methods described above. This method is then used to link the anti-biofouling results from Chapter 3 to the amount and distribution of lubricant on the surface. The nanoscale wettability of lubricants on rough surfaces is also examined using this mapping technique. Chapter 5 develops a method that, together with the method developed in Chapter 4, tracks the depletion of lubricant due to LIS passing through the air/water interface. This technique gives insight into how the wettability and capillarity influence the retention of lubricant on the surface. Finally, Chapter 6 provides a summary of the research presented in this Thesis and an outlook into future research directions.
CHAPTER 2

Materials & methods

2.1 General

2.1.1 List of chemicals

Table 2.1. List of chemicals used in this Thesis

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Supplier</th>
<th>Grade</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>MilliQ</td>
<td>18 MΩ</td>
<td>For dipping experiments</td>
</tr>
<tr>
<td>Water</td>
<td>MilliQ</td>
<td>Reverse Osmosis</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>Merck ACS reagent</td>
<td></td>
<td>For surface/polymer preparation</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Merck ACS reagent</td>
<td></td>
<td>Extracting crystal violet</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Merck Technical grade</td>
<td></td>
<td>For general glassware washing</td>
</tr>
<tr>
<td>Acetone</td>
<td>Merck ACS reagent</td>
<td></td>
<td>For surface/polymer preparation</td>
</tr>
<tr>
<td>Nile Red</td>
<td>Sigma Aldrich</td>
<td>technical grade</td>
<td></td>
</tr>
<tr>
<td>n-Heptane</td>
<td>Merck</td>
<td>Spectroscopic</td>
<td>For extraction of Nile Red tagged silicone oil</td>
</tr>
<tr>
<td>Toluene</td>
<td>Merck ACS reagent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Teflon AF</td>
<td>Chemours</td>
<td>1600</td>
<td></td>
</tr>
<tr>
<td>FC-40</td>
<td>Sigma</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(4-vinylpyridine) (P4VP)</td>
<td>Sigma</td>
<td>60 000 g mol⁻¹</td>
<td></td>
</tr>
<tr>
<td>Silicone oil (10 cSt)</td>
<td>Sigma-Aldrich</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Krytox GPL 100</td>
<td>Dupont</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mineral oil, white, light</td>
<td>Aldrich MQ200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal Violet</td>
<td>Sigma Aldrich</td>
<td>ACS Reagent</td>
<td></td>
</tr>
<tr>
<td>Sylgard 184</td>
<td>Dow Corning</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.1.2 List of instruments

- Laurell WS-400B-NPP-Lite Spin Coater
- Harrick Plasma Expanded PDC-002 Plasma Cleaner at 30 W
- KSV Cam200 Goniometer
- KSV Nima Dip Coater
- Nikon Eclipse LV150 Optical Microscope
- JA Woollam M-2000 Spectroscopic Ellipsometer
- Oxford Instruments Asylum MFP-3D Atomic Force Microscope
2.1.3 Work space and glassware

All surface preparation was performed in a laminar flow hood. All glassware used was washed using detergent, then rinsed with MilliQ® water, ethanol, and acetone before being blown dry with high purity nitrogen. Glassware used to mix and hold polymer solutions were also plasma cleaned (Harrick Plamsa, 30 W) for 3 minutes prior to use.

2.2 Polymer solution preparation

2.2.1 Teflon AF

Teflon AF solutions were prepared by dilution of commercially available 6% Teflon AF 1600 (Chemours) in FC-40. First, all glassware was scrupulously cleaned as described above. Then the 6% stock solution was diluted 1.5% w/w using FC-40. The solution was then filtered through a 0.2 µm PTFE syringe filter.

2.2.2 P4VP

All glassware was scrupulously cleaned as described above. Poly(4-vinylpyridine) (P4VP, 60.000 g mol⁻¹) was dissolved in absolute ethanol using a combination of sonication and vortex mixing. The mixture was then filtered through a 0.2 µm cellulose syringe filter.

2.2.3 Polystyrene

All glassware was scrupulously cleaned as described above. Polystyrene (50 000 g mol⁻¹) was dissolved in toluene using a combination of sonication and vortex mixing to make a 2.5 mg mL⁻¹ solution. The solution was then filtered through a 0.2 µm PTFE syringe filter.
2.3 Wrinkled surface fabrication

2.3.1 Teflon AF

All Teflon wrinkled surfaces are produced using the procedure defined in Scarratt et al. [19]. All samples used in this Thesis are produced in the same manner. A pre-stressed polystyrene substrate (Polyshrink®) is first cleaned via sonication in Ethanol (>99.9%, Sigma-Aldrich), then a layer of Teflon AF (1.5% in FC-40) is spin-coated onto the substrate. The substrate is then annealed at 130 °C so that the polystyrene substrate shrinks while the Teflon AF top layer stays rigid, spontaneously forming surface wrinkles. These spontaneously wrinkled surfaces generally consist of two length scales of roughness — nanoscale wrinkles on microscale folds. Both these scales of roughness are measured in terms of their wavelength, $\lambda$, and their height, $h$, see Figure 2.1.

The shrinking factor of Polyshrink is 2.3:1, meaning to produce a 1 cm$^2$ final substrate size (the size used in bacterial biofouling tests in Chapter 3) the Polyshrink must initially be 2.3×2.3 cm.

The size of the wrinkles formed is directly related to the thickness of the Teflon AF layer. [19] The optimal parameters to form a LIS using Teflon wrinkles was optimised by a previous student [242] based on how easily a surface sheds droplets and was determined to be 36 nm. This is produced using $\sim 30 \mu l$ of 1.5% Teflon AF for the 2.3×2.3 cm unshrunk samples mentioned above and 6000 rpm for 1 min spin coat parameters. This gives wrinkles with wavelength of 220±60 nm (measured peak to peak using SEM).

These parameters turn out to be not that important, however, with a sample prepared with spin speed 8000 rpm and annealed at 160 °C giving wrinkles with wavelength 230±50 nm. The volume of polymer solution and the duration of the spin coating need to be sufficient to cover the entire substrate and allow all the solvent to evaporate, respectively.

2.3.2 Poly(4-vinylpyridine)

P4VP wrinkled surfaces were fabricated analogously to the Teflon AF wrinkles above. As wrinkled P4VP films had not been manufactured prior, investigation of how film thickness influences the size of wrinkles was needed. For all tests in this Thesis, samples were produced using 12 mg mL$^{-1}$ P4VP.
2.3.2.1 Thickness of P4VP coating as a function of concentration

Three concentrations of P4VP solutions were tested to investigate the film thickness produced: 5 mg mL$^{-1}$, 12 mg mL$^{-1}$ and 25 mg mL$^{-1}$. These solutions were spin-coated onto two substrates: plain silicon wafer (Figure 2.2) and polystyrene coated silicon wafer (Figure 2.3). The latter of these was used to better simulate the wettability Polyshrink. All silicon wafer used was cleaned using the same procedure as glassware used for polymer solution preparation described above. Silicon wafers were coated in polystyrene by first spin coating 2.5 mg mL$^{-1}$ polystyrene solution at 6000 rpm for 1 minute, producing 270±5 nm films. All film thicknesses were measured using ellipsometry.

2.3.2.2 Wrinkle morphology as a function of P4VP concentration

All three concentrations created wrinkled surfaces when annealed. The size of the wrinkles is summarised in Table 2.2.

<table>
<thead>
<tr>
<th>P4VP concentration / mg mL$^{-1}$</th>
<th>Coating thickness / nm</th>
<th>$\lambda$ / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>19±1</td>
<td>$-$</td>
</tr>
<tr>
<td>12</td>
<td>47±1</td>
<td>400±100</td>
</tr>
<tr>
<td>25</td>
<td>113±2</td>
<td>500±200</td>
</tr>
</tbody>
</table>

$^a$ wrinkles too small to measure on SEM used
2.3 Wrinkled Surface Fabrication

Figure 2.2. Thickness of P4VP film spin-coated on silicon wafer at 6000 rpm, 1 minute.

Figure 2.3. Thickness of P4VP film spin-coated on $270 \pm 5$ nm thick polystyrene film on silicon wafer at 6000 rpm, 1 minute.

2.3.3 Polystyrene

Wrinkled polystyrene surfaces are produced by stripping the Teflon layer off the wrinkled surfaces by submerging them FC-40 for at least 45 min. The stripped surfaces retain the overall morphology of the Teflon wrinkles, but the features are generally taller and spaced
further apart, see Figure 2.4 and Table 2.3, quantified using tapping mode AFM (Bruker MultiMode 8).

Table 2.3. Comparison of the main features of Teflon wrinkles and polystyrene wrinkles. Measured from tapping mode AFM micrographs.

<table>
<thead>
<tr>
<th></th>
<th>Wrinkles</th>
<th>Folds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ / nm</td>
<td>h / nm</td>
</tr>
<tr>
<td>Teflon</td>
<td>240±60</td>
<td>190±60</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>380±120</td>
<td>270±90</td>
</tr>
</tbody>
</table>

Figure 2.4. AFM topography of Teflon wrinkles (a), with cross section in (c) and polystyrene wrinkles (b), with cross section in (d). Scale bars = 2 µm, colour scale = 1.3 µm. Polystyrene wrinkles are produced by stripping Teflon from the wrinkles in (a).

2.4 Infusion of substrates

All substrates were infused by simply pipetting a small volume of lubricant (typically 10–100 µL cm⁻²) onto the substrate. This is an excess of lubricant and so the lubricant is always
2.6 Standard measurement of interfacial properties

Depleted in some way before testing. Some typical depletion pathways include: draining vertically for 1 h, spin coating, underwater shear, or dipping through the air/water interface.

The surfaces used in Chapter 5 are intentionally produced with a large excess of lubricant.

See Table 2.4 for a summary of lubricant properties.

<table>
<thead>
<tr>
<th></th>
<th>Silicone Oil</th>
<th>PFPE</th>
<th>Mineral Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity / cSt</td>
<td>10</td>
<td>12.4</td>
<td>35.8&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Density / g cm&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>0.93&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.87</td>
<td>0.838</td>
</tr>
<tr>
<td>$\gamma_{la}$ / mN m&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>19</td>
<td>16&lt;sup&gt;b&lt;/sup&gt;</td>
<td>30&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>$\gamma_{lw}$ / mN m&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>35 [243]</td>
<td>53 [244]</td>
<td>59</td>
</tr>
</tbody>
</table>

<sup>a</sup> at 25 °C, <sup>b</sup> measured experimentally

2.5 Liquid-like PDMS coating fabrication (QLS)

Glass coated with tethered PDMS chains was produced as previously described. [94] Briefly, glass slides were sonicated in ethanol and acetone before being exposed to atmospheric plasma (30 W, Harrick Plasma) for 10 min. A thin layer of 350 cSt silicone oil was then applied to the surfaces before leaving them at room temperature for approximately 80 h. They were then sonicated in ethanol, acetone, and toluene for 1 minute each.

2.6 Standard measurement of interfacial properties

Throughout this this Thesis, interfacial properties including contact angles, contact angle hysteresis, roll-off angles, and surface tension were assessed using goniometry. These were all performed using a KSV Cam200 Goniometer.

Static contact angle measurements were performed by depositing a 10 μL droplet of water (MilliQ, 18 MΩ), or other liquid, onto the surface and capturing an image. Presented data is typically an average of 3 measurements.

Contact angle hysteresis was assessed in two ways: slowly adding and removing liquid from a droplet deposited on the surface (Chapter 3) or together with roll-off angle (Chapter 5). In the first method, a 5 μl droplet is placed on the surface and additional water pumped in and
then removed at a rate of $0.2 \mu L \text{ min}^{-1}$. In the second method, a $10 \mu L$ droplet is placed on
the surface and the surface is tilted until the droplet starts to move. CAH and roll-off angle
are measured just as the droplet begins to move. Presented data is typically an average of 3
measurements.

Surface tension was measured using the pendant drop method. A disposable syringe and blunt
needle were used to produce a droplet of liquid. Surface tension is calculated by fitting the
Young-Laplace equation to the droplet just before it falls from the needle using the in-built
software.

2.7 Artificial seawater

Artificial seawater was made for bacterial biofouling and simulated underwater shear tests and
the composition is summarised in Table 2.5. The pH was adjusted to 7 using HCl or NaOH.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Concentration / g L$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$Cl</td>
<td>$1.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>FeCL$_3$</td>
<td>$2.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>KH$_2$PO$_4$</td>
<td>$20 \times 10^{-3}$</td>
</tr>
<tr>
<td>TRIS Buffer</td>
<td>$76 \times 10^{-3}$</td>
</tr>
<tr>
<td>sodium glutamate</td>
<td>0.15</td>
</tr>
<tr>
<td>CaCl</td>
<td>0.3</td>
</tr>
<tr>
<td>KCl</td>
<td>0.6</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>8.0</td>
</tr>
<tr>
<td>NaCl</td>
<td>24</td>
</tr>
<tr>
<td>glycerol</td>
<td>0.46</td>
</tr>
</tbody>
</table>

2.8 Bacterial biofouling test

2.8.1 Bacterial growth and maintenance

Bacteria was cultured on agar plates (1:1 trypic soy agar:artificial seawater) at 4 °C. Single
cultures from the agar plates were used to inoculate the growth media for the bacterial fouling
assay. Bacteria cultures were stored in 15% glycerol at $-80$ °C.
2.8.2 Bacterial fouling assay

*Psuedoalteromonas spp.* was cultured in 3:1 tryptic soy broth:artificial seawater for 1 h before being diluted to an optical density of 0.25 (measured at 600 nm). Samples were placed in 12-well plates and covered in bacteria solution. They were left to settle for one hour before the supernatant was pipetted off and the samples were rinsed three times with artificial seawater. They were then topped up with fresh broth/seawater mixture and shaken at 150 rpm on an orbital shaker (Ratek) at ambient temperature for 24 hours. The supernatant was then pipetted off and the samples washed three times with MilliQ water before staining with aqueous crystal violet (0.1% w/w, Sigma Aldrich). Once dry, the crystal violet was extracted using 30% acetic acid and concentration measured using UV-Visible spectroscopy at 590 nm. Reported results are the average of five measurements.

2.8.3 Silicone oil toxicity

To test whether silicone oil itself is toxic to *Psuedoalteromonas spp.*, \( 2 \times 100 \text{ mL} \) of tryptic soy broth and artificial seawater (1:3) were inoculated with 100 \( \mu \text{L} \) of *Psuedoalteromonas spp.* (absorbance of 1.946 at 600 nm). One sample had 1 ml of silicone oil added and both were shaken at 150 rpm for 24 h. Samples were diluted by 50% with MilliQ water prior to measurement.

2.9 Marine fouling test

The marine fouling test was performed at Watsons Bay, NSW, Australia (33°50′37.7″ S, 151°16′53.4″ E). Wrinkled surfaces (5 cm \( \times \) 2.5 cm) were prepared as described above. Uninfused Teflon wrinkles were used as controls, whereas the test surfaces were Teflon wrinkles infused with silicone oil and drained vertically for 1 h. Two support Perspex plates (3 mm thick) were prepared: the first plate was a control, and seven uninfused wrinkled Teflon surfaces (entirely free of silicone oil) were attached on it (with marine epoxy, Selleys AQUAFIX). On the second Perspex support plate were attached seven control surfaces and seven test surfaces in an alternating pattern (see Figure 3.4). The plates were attached to a shark net using zip ties. The test was run for a total of seven weeks from June to August 2017. Although the test was run during the Australian winter, the water temperature never dropped below 19 °C during the test. The surfaces were removed from the ocean and stored in seawater before the analysis. Each surface was photographed without any treatment and then after rinsing (vigorous washing under the laboratory tap), and the images analyzed using ImageJ [245] and Photoshop (see Figure 2.5). Photoshop was used to crop the images, remove any
distortion, and flatten the lighting. The images were then converted to grayscale in ImageJ and a threshold applied to identify the percent area that had been fouled. Significance was assessed using two-way ANOVA.

Figure 2.5. Example of how a raw fouling image (L) is analysed by first processing in Photoshop to produce an image (M) that is suitable for a threshold to be applied (R).

2.10 Quantification of lubricant using fluorescence

A 1.0 μmol L⁻¹ stock solution of Nile red in silicone oil was prepared by adding 5.0 μL of 0.20 mmol L⁻¹ Nile red (Sigma) in ethanol to 1.0 mL 10 cSt silicone oil (Sigma-Aldrich) and then stirring until the ethanol had evaporated and the oil was pale yellow. The stock solution of Nile red was used to infuse surfaces for lubricant quantification. For the extraction of the oil, surfaces (1 cm²) infused with silicone oil containing 1.0 μmol Nile red were immersed in 2.5 mL n-heptane and sonicated for 30 s. Fluorescence was measured on a Cary Eclipse fluorimeter (Agilent) (excitation 484 nm, 20 nm slits). The amount of oil was determined by comparison to a standard curve prepared by diluting the aliquots of 1.0 μmol L⁻¹ Nile red in silicone oil with n-heptane. Raw fluorescence data is presented in Figure 2.6 showing that there are two peaks in the emission spectra. This is likely due to Nile Red’s emission being solvent dependent and there being some un-evaporated ethanol present. The peak at 525 nm was chosen as the calibration curve has a greater gradient, giving more sensitivity. The method was further validated by determining the recovery of Nile red after adding discrete aliquots of fluorescent lubricant to the test surfaces but not carrying out any treatments to remove lubricant before the analysis. The data is presented in Table 2.6.
2.11 Imaging topography using AFM

Standard imaging of surface topography was performed using tapping mode (Asylum MFP-3D & Bruker MultiMode 8) or PeakForce™ mapping (Bruker MultiMode 8). Typical imaging in tapping mode used Tap-300 probes (Budget Sensors, Sofia) which have spring constant $\sim 40 \text{N m}^{-1}$ and resonant frequency of 250–300 kHz. Tapping mode images of lubricated
Table 2.6. Recovery of lubricant from lubricant-infused surface.

<table>
<thead>
<tr>
<th>Silicone oil added / µL</th>
<th>Silicone oil measured / µL</th>
<th>Recovery / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.750</td>
<td>0.843</td>
<td>112</td>
</tr>
<tr>
<td>0.750</td>
<td>0.755</td>
<td>101</td>
</tr>
<tr>
<td>0.750</td>
<td>0.724</td>
<td>96.5</td>
</tr>
<tr>
<td>0.500</td>
<td>0.539</td>
<td>108</td>
</tr>
<tr>
<td>0.500</td>
<td>0.573</td>
<td>115</td>
</tr>
<tr>
<td>0.250</td>
<td>0.293</td>
<td>117</td>
</tr>
<tr>
<td>0.100</td>
<td>0.092</td>
<td>91.6</td>
</tr>
<tr>
<td>0.100</td>
<td>0.100</td>
<td>100.</td>
</tr>
<tr>
<td>0.100</td>
<td>0.100</td>
<td>100</td>
</tr>
<tr>
<td>0.075</td>
<td>0.057</td>
<td>75.5</td>
</tr>
<tr>
<td>0.075</td>
<td>0.074</td>
<td>99</td>
</tr>
<tr>
<td>0.050</td>
<td>0.043</td>
<td>85</td>
</tr>
<tr>
<td>0.050</td>
<td>0.047</td>
<td>93</td>
</tr>
<tr>
<td>0.050</td>
<td>0.050</td>
<td>101</td>
</tr>
<tr>
<td>0.025</td>
<td>0.032</td>
<td>129</td>
</tr>
<tr>
<td>0.025</td>
<td>0.024</td>
<td>96</td>
</tr>
</tbody>
</table>

Average recovery: 101±13 %

surfaces in Section 4.2.3 were captured using Multi-75 probes (Budget Sensors, Sofia) which have spring constant \( \sim 5 \text{ N m}^{-1} \) and resonant frequency of 60–80 kHz. Multi-75 probes were also used for PeakForce\(^\text{TM}\) imaging.

2.12 Quantification of lubricant using AFM meniscus force measurements

Lubricant quantification using meniscus force measurements is based on force-volume imaging. All measurements in this Thesis were performed using an Asylum MFP-3D and its native force mapping mode. All maps were collected using Multi-75 (Budget Sensors, Sofia) probes.

First, a 10 × 10 pixel map was collected on a clean silicon wafer to quantify the sensitivity of the probe. The sensitivity is calculated as the average gradient of the retraction slope for all 100 measurements. This is done automatically using a custom Python script (see Appendix Section C1 and Chapter 4 for more information) which ensures that the region of the slope used for fitting is linear by excluding points on either end until \( R^2 > 0.99 \). Analysis of \( \sim 3000 \) force curves from several probes taken on a hard surface finds the Multi-75 probes have typical sensitivity of 58±24 nm V\(^{-1}\), see Figure 2.8 for a distribution of sensitivities. The values
outside the main distribution are most likely due to force curves taken on a contaminated portion of the silicon wafer, hence why 100 curves are analysed for each tip.

![Histogram of calculated sensitivity for MULTI-75 AFM probes. Data is approximately 3000 force curves (from about 30 probes) recorded on silicon wafer.](image)

**Figure 2.8.** Histogram of calculated sensitivity for MULTI-75 AFM probes. Data is approximately 3000 force curves (from about 30 probes) recorded on silicon wafer.

For mapping lubricant on Teflon wrinkles, parameters are optimised for each scan, but generally scans are 2–10 μm in size and 48–128 pixels. The trigger point is 0.05 V which corresponds to a force of ∼5–10 nN and is soft enough not to cause plastic deformation to the substrate, but hard enough not to accidentally trigger during the scan (the exact spring constant of the cantilever is not measured as the technique does not require quantification of forces, see Chapter 4 for more information). The data is then exported to ASCII files which are analysed by a custom Python script (see Section C2 and Chapter 4 for more information).

### 2.12.1 Underwater measurements

The wettability difference between water and hydrophobic lubricants is sufficient to detect the lubricant/water interface in meniscus force measurements. Imaging samples using meniscus force mapping is much the same as in air, with the key exception that hydrophobised tips are used (modification described below). A custom built cell is used to flood sample *in situ* so that the same area can be imaged in air and water, see Figure 2.9. The cell consists of a superhydrophobic barrier (non-infused Teflon wrinkles) glued to a glass slide (using two-part...
epoxy) with a pipe built into one of the sides to allow water to be pumped in using a syringe pump.

As the superhydrophobic barrier is effectively an uninfused LIS, contamination from lubricant is a concern. One cell had to be discarded as it accidentally became infused and the increased slipperiness meant that it could not hold the water in effectively anymore.

![Figure 2.9. Custom made liquid cell for use with Asylum MFP-3D AFM. Samples can be flooded with water in situ allowing for direct comparison between samples in air and water.](image)

### 2.12.1.1 Modification of AFM tips

AFM tips are modified by PDMS chemical vapour deposition (CVD). First, Multi75 (Budget Sensors) AFM probes are cleaned in piranha solution (3:1 sulfuric acid:hydrogen peroxide) for 1 min before being rinsed with MilliQ water (18 MΩ) three times. They are then rinsed in toluene before blowing dry with a gentle stream of nitrogen. PDMS modification is carried out by placing the clean tips in a sealed glass vessel adjacent to a small amount (<1 g) uncured PDMS base (Sylgard 184, Dow Corning), see Figure 2.10, and placing in the oven for 4 h at 200 °C. Once cooled, the probes are then washed once more in toluene and dried with a gentle stream of nitrogen before use.

The PDMS CVD produced a 1.4±0.1 nm thick coating. The thickness is tracked by placing a clean silicon wafer in the chamber and measuring the film thickness using ellipsometry.

### 2.13 Calculation of Hamaker constants

For long-range interactions, the interface potential is dependent on the non-retarded van der Waals free energy interaction between two semi-finite layers 1 and 2 acting across a medium
2.13 Calculation of Hamaker Constants

Figure 2.10. Chemical vapour deposition chamber for coating AFM probes. Clean probes are placed in a staining jar with a small amount of uncured Sylgard 184 base and the whole chamber placed in an oven for 4 h at 200 °C.

3, as a function of layer separation $h$, is:

$$E_{vdW} = -\frac{A_{132}}{12\pi h^2}$$

(2.1)

Where $A_{123}$ is the Hamaker constant for the three-layer system. A negative van der Waal potential is an attractive force between layers 1 and 2, meaning that layer 3 is unstable. In the case of a thin film, this means that it will dewet. Conversely, a positive potential is a repulsive force and the thin film is stable. The system is modelled as a four-layer system where the bottom layer (1) is the shrinkable polystyrene substrate, the second layer (2) is the rigid polymer layer (Teflon or P4VP), the third layer (3) is silicone oil lubricant and the last layer (4) is air; see Figure 2.11 for a schematic of this stack. The overall expression for this is:

$$E_{vdW}(e) = -\frac{A_{234}}{12\pi e^2} + \frac{A_{234} - A_{132}}{12\pi (e + d)^2}$$

(2.2)

Where $A_{xyz}$ is the Hamaker constant for the three-layer system, $e$ is the thickness of the silicone oil layer and $d$ is the thickness of the Teflon coating.
The three-layer Hamaker constant can be calculated using the following expression:

$$A_{132} = \frac{3}{4} k_B T (\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}) (\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}) + \frac{3\hbar \nu_e}{8\sqrt{2}} \times \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{\sqrt{(n_1^2 + n_3^2)(n_2^2 + n_3^2)(\sqrt{(n_1^2 + n_3^2)} + \sqrt{n_2^2 + n_3^2})}}$$

where $\varepsilon_i$ and $n_i$ are the dielectric constant and the refractive index of material $i$, respectively, $k_B$ is the Boltzmann’s constant, $T$ is the absolute temperature, $h$ is Planck’s constant, and $\nu_e$ is the plasma frequency of free-electron gas.

The values used to calculate the Hamaker constants are detailed in Table 2.7.

There are several assumptions made in the calculation of Hamaker constants in this way. The first is that there are no retardation effects which is only valid if the separation between the two bodies is smaller than the characteristic wavelength of its absorption spectra. In reality, the Hamaker constant is not constant at all separation values, but only for low separations (e.g. $\sim 5$ nm). The final assumption is that all materials have the same value for $\nu_e$.

### 2.14 Measuring contact angle hysteresis through air/water interface

Contact angle hysteresis is measured as the sample passes through the air/water interface using an optical Wilhelmy plate tensiometer shown schematically in Figure 2.12. The set-up and analysis used in this Thesis is a modification of the one used in [4] to track the contact angle hysteresis of superhydrophobic surfaces as they are repeatedly passed through the air/water interface.
2.14 Measuring contact angle hysteresis through air/water interface

Table 2.7. Values used in Hamaker constant calculation

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>298 K</td>
</tr>
<tr>
<td>( \nu_c )</td>
<td>( 4 \times 10^{-14} ) s(^{-1} )</td>
</tr>
<tr>
<td>( n_{\text{Teflon}} )</td>
<td>1.31</td>
</tr>
<tr>
<td>( n_{\text{P4VP}} )</td>
<td>1.55</td>
</tr>
<tr>
<td>( n_{\text{PS}} )</td>
<td>1.557</td>
</tr>
<tr>
<td>( n_{\text{silicone oil}} )</td>
<td>1.41</td>
</tr>
<tr>
<td>( n_{\text{PFPE}} )</td>
<td>1.3</td>
</tr>
<tr>
<td>( n_{\text{mineral oil}} )</td>
<td>1.46</td>
</tr>
<tr>
<td>( n_{\text{air}} )</td>
<td>1</td>
</tr>
<tr>
<td>( n_{\text{water}} )</td>
<td>1.33</td>
</tr>
<tr>
<td>( \varepsilon_{\text{Teflon}} )</td>
<td>1.93</td>
</tr>
<tr>
<td>( \varepsilon_{\text{P4VP}} )</td>
<td>1.55</td>
</tr>
<tr>
<td>( \varepsilon_{\text{PS}} )</td>
<td>2.55</td>
</tr>
<tr>
<td>( \varepsilon_{\text{silicone oil}} )</td>
<td>2.60</td>
</tr>
<tr>
<td>( \varepsilon_{\text{PFPE}} )</td>
<td>2.10</td>
</tr>
<tr>
<td>( \varepsilon_{\text{mineral oil}} )</td>
<td>2.20</td>
</tr>
<tr>
<td>( \varepsilon_{\text{air}} )</td>
<td>1</td>
</tr>
<tr>
<td>( \varepsilon_{\text{water}} )</td>
<td>80.1</td>
</tr>
<tr>
<td>( d_{\text{Teflon}} )</td>
<td>40 nm</td>
</tr>
<tr>
<td>( d_{\text{P4VP}} )</td>
<td>50 nm</td>
</tr>
</tbody>
</table>

interface. The set-up and analysis used in this study are modified to increase experimental throughput.

Figure 2.12. Schematic of the set-up used in dipping experiments. A USB microscope captures the angle the air/water interface makes with the substrate as it enters an overflowing cuvette.

A camera (Techbrands USB Microscope) is used to capture the shadow cast from the shape of the air/water interface as the sample passes through the interface, see Figure 2.12. Samples
are driven vertically using a programmable dip coater (KSV Nima) which allows for precise control over speed and repetitions. Captured videos are first processed using ImageJ [245] to crop the region of interest and increase contrast, see Figure 2.13. Each frame is output individually for automatic analysis using a Python script.

The previous iteration of this technique used a high speed camera which increased temporal resolution, but made analysis more cumbersome, especially for longer experiments. The USB microscope has a frame rate of 20 fps which is low enough that it may miss some of the high speed contact line movement events, but is sufficient to capture the contact angle at most points on the surface. At 20 fps, a 20 mm long samples driven at 50 mm min$^{-1}$ gives approximately 400 frames for analysis, or one frame every $\sim$50 $\mu$m. In addition, in the previous version, analysis was done using Matlab using a semi-interactive script where the user regularly indicated the location of the air/water-sample triple line to ensure the fitting was correct. This point is not very clear for large contact angles (>150°), and so accuracy in the measurement of large contact angles comes at the cost of script efficiency. In fact, finding the location of the air/water-sample triple line remains the largest source of error in the fitting. In this iteration, accuracy at high contact angles is sacrificed for higher experimental throughput by removing the intermittent user input. Even with this sacrifice, the technique still clearly shows changes in contact angle.

Another change to accommodate use with LIS, is a specially made cuvette that has tubing built in to continually add new water from the bottom, see Figure 2.14, similar to the set-up described by Sotiri et al. [105]. Deionised water is pumped using a small water pump at a rate of 60 mL min$^{-1}$, so that the air/water interface is being continually refreshed and does not accumulate removed lubricant. The surface area of the cuvette is approximately 25 cm$^2$, meaning that the surface is fully refreshed every few seconds.

Figure 2.13. The raw image captured by the USB microscope is cropped and brightness/contrast adjusted to clearly show the interface. A Python script then finds the interface (red dots) before fitting a line to the substrate, finding where the air/water interface starts, fitting a line to the air/water interface and finding the angle between these two lines.
The Python script does the following:

(i) Find the interface between light and dark in the image (see Figure 2.13).
(ii) Fit a line to the vertical substrate.
(iii) Look for deviation from the substrate to find where the interface starts.
(iv) Fit a line to \( n \) points after the start of the interface.
(v) Find the angle between the two lines.

The Python script is reproduced in Section C4.

Fitting the interface with a parabola and finding the gradient of the tangent at the intersection with the substrate was also tested. However, this method turned out to be less reliable than fitting a line, as the parabola often did not follow the shape of the interface well. When it did fit properly, the calculated angles were not significantly different from the line.

![Image of the dipping set-up used in Chapter 5. Deionised water is pumped in the cuvette from an external reservoir. The lamp used for illumination is a desk lamp with an LED bulb and piece of printer paper used as a diffuser.](image)

**Figure 2.14.** Image of the dipping set-up used in Chapter 5. Deionised water is pumped in the cuvette from an external reservoir. The lamp used for illumination is a desk lamp with an LED bulb and piece of printer paper used as a diffuser.
2.14.1 Depletion of lubricant from LIS through the air/water interface

Samples (2 cm × 1 cm) are mounted on a small piece of glass slide using adhesive pads. The glass is cut so that it is narrower than the sample (~5 mm in width) to reduce any edge effects. The sample is then repeatedly driven through the air/water interface using a dip coater (KSV NIMA, Espoo, Finland) at 50 mm min⁻¹. Unless stated otherwise, the sample is held still for 30 s between each up and down motion to allow any lubricant on the surface of the water to clear.
CHAPTER 3

Antifouling lubricant-infused surfaces

LIS have attracted a lot of attention for their potential application as antifouling surfaces. This Chapter examines the antifouling behaviour of silicone oil infused Teflon wrinkled surfaces in both the lab and the ocean. The majority of this Chapter appears in: Ware, C. S., Smith-Palmer, T., Peppou-Chapman, S., Scarratt, L. R., Humphries, E. M., Balzer, D. & Neto, C. Marine Antifouling Behavior of Lubricant-Infused Nanowrinkled Polymeric Surfaces. ACS Applied Materials and Interfaces 10, 4173–4182 (2018).

Ware designed and characterised the wettability of the LIS; Smith-Palmer and myself designed the bacterial fouling tests; Smith-Palmer and myself performed the fouling tests; Smith-Palmer and myself designed the biofouling field test, I carried out the test and analysed the data; Smith-Palmer and myself designed the lubricant quantification test, measurements were taken by Balzer and myself; all remaining work was designed, performed and analysed by me; the manuscript was written by Ware, Smith-Palmer, Neto and myself. Work included in this Thesis: LIS design and optimisation in Section 3.1 was done by Ware, experimental design and execution in Section 3.2 was done in collaboration with Smith-Palmer and some experiments in Section 3.2.1 were carried out by Balzer.

3.1 Design of LIS

This Section describes some theory behind the manufacture of LIS and key findings from Ware’s Honours Thesis [242] that impact the work performed in this Chapter (and the rest of this Thesis).

The LIS used in this Chapter are all based on superhydrophobic Teflon wrinkled substrates developed previously in the Neto group. [33] These consist of randomly distributed wrinkles produced via a spontaneous process. A layer of Teflon AF is spin-coated onto a pre-stressed polystyrene substrate (Polyshrink) which is then annealed at a temperature between the polystyrene and the Teflon’s glass transition temperature, \( T_g \). This means that the Polyshrink
substrate shrinks while the top Teflon layer stays rigid, forming wrinkles. [33, 246] **Figure 3.1** shows an AFM micrograph of a large area of the wrinkled surface, showing its micro- and nanostructure. We term these two scales of roughness as *wrinkles* and *folds*. We characterise these surfaces in terms of wrinkle/fold wavelength, \( \lambda \), which is the average peak to peak distance measured either from SEM or AFM micrographs. Values of \( \lambda \) always have a large uncertainty due to the random nature of the surface. The size of the wrinkles is determined by the thickness of Teflon layer applied, with a thicker layer leading to larger wrinkles, see **Section 1.2.5**.

**Figure 3.1.** Tapping mode AFM micrograph of an as-prepared Teflon wrinkled surface with Teflon top layer \( \sim 40 \) nm. This is the main substrate used throughout this Thesis. Scale bar = 4 \( \mu \)m. Colour scale = 1.5 \( \mu \)m.

In terms of optimising wrinkles for making a LIS, the size of topography is vitally important as the roughness holds the lubricant via capillary action. Smaller pores are able to hold liquid more tightly compared to larger pores due to the inverse relationship of Laplace pressure to the radius of curvature (see **Equation 1.4**). A liquid which wets a pore has a negative curvature, and hence, a negative pressure (see **Figure 1.2b**). The smaller the pore, the smaller the curvature and larger the pressure difference. Therefore, there is a large negative pressure inside liquids held in small pores, making it very difficult to remove them. In the case of LIS,
this means that smaller roughness is more able to retain lubricant against depleting forces. For the case of the Teflon wrinkles used here, $\lambda \sim 400\text{ nm}$ giving a pressure difference on the order of $40\text{ kPa}$ across the silicone oil/air interface.

There is debate about what is the ideal length scale of roughness for LIS. There is evidence that microscale roughness cannot retain lubricant against applied shear while nanoscale can, and multiscale roughness loses lubricant out of the micropores but not the nanopores, leading to a non-slippery surface. [104] On the other hand, this depleted multiscale roughness can lead to a ‘slippery Wenzel state’ where the droplet impales the microscale roughness, but is still mobile due to the lubricant layer trapped in the nanoscale roughness. [62] There are many publications that manufacture LIS with only microscale roughness e.g. [71, 77] So while there is no consensus on the ideal length scales to manufacture LIS, our group takes the approach that smaller is better as it allows for greater retention of lubricant in the roughness.

The main criteria used by Ware [242] to optimise Teflon wrinkle-based LIS was their slippery properties as measured through roll-off angles. The as-prepared Teflon wrinkles are superhydrophobic with a roll-off angle of $9\pm1^\circ$ which reduces to $4\pm1^\circ$ when $\sim 10\mu\text{L}$ of silicone oil is spread on the surface. The reduction in roll-off angle is a result of the droplet being able to oleoplane on a layer of lubricant for the infused case while in the superhydrophobic case the droplet is only mostly suspended on an air cushion and so still interacts with the solid substrate. [223]

Table 3.1 shows the wettability and roll-off data for three values of thickness of Teflon for both the dry and infused case. All surfaces show small roll-off angle values in both their dry and infused state. Teflon wrinkles formed from a $34\text{ nm}$ thick layer of Teflon were selected for two reasons: they have lower roll-off angles than $13\text{ nm}$ when dry, suggesting less solid fraction in contact with the working fluid (water, in this case); and they uses less Teflon than the thicker layer. Having roughness on the nanoscale, these surfaces are expected to retain lubricant well.

Table 3.1. Wettability and dimensions of topographical features of LIS produced from Teflon Wrinkles.

<table>
<thead>
<tr>
<th>Teflon layer thickness / nm</th>
<th>Wrinkle wavelength / nm</th>
<th>Wrinkle height / nm</th>
<th>Dry Static CA / °</th>
<th>Dry Roll-off angle / °</th>
<th>Infused Static CA / °</th>
<th>Infused Roll-off angle / °</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>90±10</td>
<td>130±7</td>
<td>166±3</td>
<td>12±1</td>
<td>114±1</td>
<td>4±1</td>
</tr>
<tr>
<td>34</td>
<td>150±20</td>
<td>290±30</td>
<td>168±2</td>
<td>9±1</td>
<td>115±1</td>
<td>4±1</td>
</tr>
<tr>
<td>168</td>
<td>1190±100</td>
<td>1100±80</td>
<td>160±4</td>
<td>17±6</td>
<td>117±1</td>
<td>9±1</td>
</tr>
</tbody>
</table>
3.1.1 Lubricant infusion

Infusing the as-prepared wrinkles is as simple as spreading some silicone oil on them. Silicone oil is an ideal lubricant for the wrinkles as it does not damage the Teflon layer (like perfluorinated lubricants), its properties make it ideal for repelling aqueous foulants (see Section 1.3.4), and, even though it does not fully spread over Teflon, it can still be successfully infused into the structure.

This is seen by calculating the critical angle for infusion $\theta_c$:

$$\cos \theta_c = \frac{1 - \phi}{r - \phi}$$  \hspace{1cm} (1.19 revisited)

where $\phi$ corresponds to the fraction of the solid surface wet by the liquid, and $r$ is the roughness ratio. The $\phi$ factor for the wrinkles is estimated using the Cassie-Baxter equation:

$$\cos \theta^* = f_1(\cos \theta_1 + 1) - 1$$  \hspace{1cm} (1.13 revisited)

where $\theta_1$ is the static water contact angle on a flat substrate ($\theta = 121^\circ$ for Teflon) and $\theta^*$ is the static contact angle on the structured surface ($\theta^* = 164^\circ$ for wrinkled Teflon).

The roughness ratio $r$ is defined as the ratio of true surface area to apparent surface area. This ratio was approximated to the ratio of the original sample surface area to the final sample surface area after shrinking. Polyshrink shrinks to $\sim 20\%$ of its original surface area, giving an estimated roughness ratio of 5. As both $\phi$ and $r$ are estimates, only an approximation can be obtained for the critical contact angle, which is $\theta_c \approx 80^\circ$ for wrinkles on Polyshrink. The static contact angle of silicone oil on the flat Teflon surfaces in air is $44^\circ$ and completely spreads underwater ($0^\circ$ contact angle). In air, the silicone oil penetrates into the microstructure (as it is below the critical contact angle) and covers the structure fully underwater (as it completely spreads underwater) producing a stable lubricant-infused coating in both scenarios (see Section 1.3.3). [77, 150]

3.2 Inhibition of marine bacterial biofouling

Although LIS were shown to resist bacterial biofouling prior to this study, [40, 125, 188] most studies relied on clinically relevant bacteria and did not attempt to relate antifouling ability to the amount of lubricant present. In this Section, these issues are addressed by:
(i) Developing a method to quantify the volume of lubricant present to relate depletion of the surface to performance;
(ii) Assessing antifouling ability using a mixture of typical marine bacteria species, 
*Psuedoalteromonas* spp.

### 3.2.1 Quantification of lubricant

To understand how different treatments deplete lubricant from the surface, a method of quantifying the total volume of lubricant on the surface using fluorescence was developed.

This was achieved by first dissolving Nile Red in absolute ethanol and then adding this to silicone oil so that final concentration of Nile Red is $1.0 \mu$mol L$^{-1}$ after all the ethanol has evaporated. The volume of this fluorescently tagged oil was then quantified *via* extraction into *n*-heptane (as it is a good solvent for both silicone oil and Nile Red) and measurement of fluorescence intensity.

A volume/fluorescence intensity calibration curve was collected in the volume range expected for lubricant on $1 \times 1 \text{ cm}^2$ LIS (0.01–1 µL). The raw data is shown in Figure 2.6 and the calibration curve in Figure 2.7. The raw data shows two peaks in the emission spectra, probably due to Nile Red’s fluorescence being strongly influenced by the polarity of its solvent [247] and there being some ethanol that did not evaporate. The peak at 525 nm was chosen over the peak at 560 nm as it’s calibration curve has a steeper gradient and so gives more sensitivity. Although aggregation would affect the fluorescence intensity, there was no evidence that it did. If there was aggregation, it did not influence the measurement as the technique was validated before each measurement by checking known volumes of silicone oil containing Nile Red.

The calibration curve is linear with an $R^2$ value of 0.9972 (see Figure 2.7). Calibrated volumes of the tagged lubricant were infused onto Teflon wrinkled surfaces and then extracted into *n*-heptane to ensure that the procedure recovered all the lubricant on the surface (see Table 2.6). The average recovery is $101 \pm 13 \%$ meaning that although there is variability in the measurement, sufficient repetitions will produce an accurate value.

### 3.2.2 Antifouling properties of lubricant-infused surfaces

Superhydrophobic surfaces are known to be be ineffective antibacterial coatings. The air layer trapped in the roughness underwater is metastable and collapses over time due to shear or pressure, [19] allowing a biofilm to form on the rough surface. [248] For the infused Teflon
surfaces, the lubricant layer is thermodynamically stable, preventing the collapse of water into the roughness.

To test antifouling properties of Teflon wrinkled LIS, surfaces were exposed to marine bacteria, *Psuedoalteromonas spp.*, for one hour, rinsed, and then immersed for 24 h in fresh seawater medium rich in nutrients. Any adhered bacteria is stained with crystal violet which is then quantified using UV-visible spectroscopy.

Crystal violet stain also allows easy visualisation of the biofilm and shows that a biofilm is readily formed on dry Teflon wrinkles (Figure 3.2, left). The presence of infused silicone oil almost completely prevents the attachment of bacteria (Figure 3.2, center and right).

![Figure 3.2. Crystal violet stained samples exposed to bacteria. L-R Dry Teflon wrinkles; Infused Teflon wrinkles drained for one hour (center); infused Teflon wrinkles spun 1 min and exposed to vigorous shear in seawater for two weeks (right).](image)

The extent of inhibition is 99±1 % for the infused Teflon surfaces drained for one hour, which holds ~0.9 µL cm⁻² of silicone oil (Table 3.2). If the wrinkles are violently drained of oil by high rate spinning, or rotated in seawater for extended times (two weeks), the extent of inhibition is only slightly reduced, to 84±10 % and 76±16 %, respectively. The inhibition potential of the surfaces correlates with lower water roll-off angles and larger volumes of silicone oil. Bacterial attachment for several strains is known to be reduced on soft substrates, [238, 249] and liquid silicone oil offers a soft and mobile layer on which contact points between the bacteria and the solid surface are reduced. [119]

It is remarkable that the surfaces that have been treated to deplete the oil retain their antifouling abilities. These surfaces have tiny amounts of lubricant, down to 0.02 µL cm⁻² after two weeks of vigorous shear underwater, and yet are almost as effective as the the samples with
an order of magnitude more lubricant. These results suggest that the required amount of lubricant to impart antifouling properties is very small.

This study highlights two very important factors about LIS:

(i) The importance of being able to quantify the lubricant present to test the limits of surface performance; and

(ii) The amount of lubricant needed to impart antifouling behaviour is minuscule, but also that large excesses of lubricant are easily removed by external shear or even gravity.

Table 3.2. Quantification of silicone oil content on Teflon wrinkles with $\lambda = 147\, \text{nm}$, resulting water contact angle and roll off angles, and bacterial inhibition as tested by absorbance of crystal violet extracted from the surfaces exposed to bacteria. The bacterial inhibition is relative to non-infused Teflon wrinkled samples.

<table>
<thead>
<tr>
<th>Drainage treatment</th>
<th>Silicone oil volume / $\mu\text{L cm}^{-2}$</th>
<th>Water contact angle / $^\circ$</th>
<th>Roll-off angle / $^\circ$</th>
<th>% Inhibition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drained 1 h</td>
<td>0.9 ± 0.2</td>
<td>99±2</td>
<td>5±1</td>
<td>99±1</td>
</tr>
<tr>
<td>Spun at 8000 rpm, 1 min</td>
<td>0.4 ± 0.2</td>
<td>111±2</td>
<td>7±1</td>
<td>86±9</td>
</tr>
<tr>
<td>Spun at 8000 rpm, 5 min</td>
<td>0.3 ± 0.2</td>
<td>113±3</td>
<td>9±1</td>
<td>84±10</td>
</tr>
<tr>
<td>Drained 1 h, 2 weeks shear</td>
<td>0.04±0.01</td>
<td>113±1</td>
<td>6±3</td>
<td>73±13</td>
</tr>
<tr>
<td>Spun at 8000 rpm, 1 min, 2 weeks shear</td>
<td>0.02±0.01</td>
<td>122±6</td>
<td>8±4</td>
<td>76±16</td>
</tr>
</tbody>
</table>

3.2.3 Assessing potential toxicity of silicone oil

To test whether the presence of silicone oil, and not the properties it imparts, are responsible for the observed antifouling abilities, it’s toxicity to *Psuedoalteromonas spp.* was assessed. Two identical vessels containing 3:1 tryptic soy broth:artificial seawater were inoculated with *Psuedoalteromonas spp.* with one also having silicone oil added to it before being set to shake at ambient temperature at 150 rpm for 24 hours. Their absorbance (at 600 nm) were tested after 24h and the results summarised in Table 3.3. Silicone oil is not inherently toxic to *Psuedoalteromonas spp.* as there is no significant difference between the two samples.

Table 3.3. Toxicity of silicone oil to *Psuedoalteromonas spp.*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorbance at 600 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>1.1±0.1</td>
</tr>
<tr>
<td>1 % silicone oil</td>
<td>1.0±0.1</td>
</tr>
</tbody>
</table>
3.3 Inhibition of marine fouling in the open ocean

Although the results in Section 3.2.2 are very promising and show the remarkable antifouling behaviour of LIS, they do not represent a real-world use case. In particular, although they use a mixture of species, they are a single genus and do not represent the complex world of the marine environments which includes other foulants such as algae, molluscs and diatoms. There is evidence that testing a single species of bacteria is not sufficient to show the antifouling ability of a LIS as different species (and even different strains of a given species) show different interaction with the immobilised liquid layer. [204] In addition, the overall fouling of a surface cannot be predicted by single species. [250]

As a result, the infused Teflon wrinkled surfaces were tested in a real-world fouling test. This was the first experiment to test the fouling of 2D LIS in the ocean. The selected site was the shark net at Watsons Bay in NSW, Australia (33°50'37.7" S, 151°16'53.4" E) due to its proximity to the open ocean (close enough that the marine environment is indistinguishable), see Figure 3.3. Perspex support plates with samples attached were fixed to the shark net approx 1 m below the tide line, facing north to maximise growth through maximising sun exposure.

Two support Perspex plates are used: on the first, referred to as “Control Plate”, only Teflon wrinkled surfaces are attached (as controls). On the second plate, referred to as “Test Plate”, both infused Teflon wrinkles and uninfused Teflon wrinkles are attached. On the test plate, it was predicted that the silicone oil may creep from the infused surfaces to the uninfused surfaces while underwater, so the control plate acts as the real benchmark without any silicone oil. The infused and uninfused surfaces on the test plate are interspersed to mitigate any possible spatial effects in fouling. The control plate is placed approx. 1 m from the test plate at the same depth. Fouling was tracked qualitatively through in situ monitoring of the plates, as seen in Figure 3.4 and Figure 3.5, but due to the varied lighting conditions these images are not of high enough quality to analyse the surface coverage of the fouling.

The plates were removed from the ocean after seven weeks and the fouling analysed by photographing each sample individually (whilst the entire plate is submerged in a few centimetres of artificial seawater to ensure the thicker fouling does not cover additional area due to flattening out). An example image for each class of sample is given in Figure 3.6. To analyse the fouling quantitatively, images of each sample were processed in Photoshop to remove distortion and any lighting inconsistency. A threshold was then applied in ImageJ to quantify the fouling. Significance was tested using two-way ANOVA.
3.3 Inhibition of marine fouling in the open ocean

Figure 3.3. The field test was conducted at Watsons Bay in Sydney’s eastern suburbs. The shark net on the public baths (inset) was used to attach the samples. Map data copyright Google 2020.

After seven weeks of testing, the two Perspex support plates are heavily fouled, and completely covered with algae (Figure 3.6, Perspex (test plate) and Perspex (control plate)). There is no significant difference between the level of fouling on the Teflon wrinkles and the infused Teflon wrinkles mounted on the same test plate (p = 0.17). The Teflon wrinkles adjacent to infused Teflon wrinkles appear to have been infused with silicone oil spreading from the infused surfaces (labeled “Infused Teflon wrinkles (spontaneous spreading)” in Figure 3.7). This spreading, even underwater, is entirely expected, given the ultraspreading properties of silicone oil. [251] Silicone oil completely spreads underwater on Teflon (CA = 0°), but does not form a stable film on Perspex (CA = 120°), which is why the support Perspex plates are entirely fouled. The close proximity of the infused Teflon wrinkles to the initially uninfused surfaces on the test plate contributes to silicone oil spreading.

On the other hand, there is a significant difference between all of the surfaces on the test plate and those on the control plate (p < 0.05). Infused Teflon wrinkles have only about
Figure 3.4. *In situ* images of the test plate (infused and non-infused samples) during the marine fouling test. Images were taken underwater to ensure that the results were not influenced by removing them from the water. On this plate both infused Teflon wrinkles and uninfused Teflon wrinkles are attached in an alternating pattern: the first surface in the top left hand side was infused, and the one to the right and the one below it were non-infused, and so on.

23% of their surface fouled upon immersion in the ocean for seven weeks, much lower than the Perspex support sheets (99%), lower than the uninfused Teflon wrinkles (57%), and lower than the Teflon wrinkles that are infused by spontaneous underwater spreading (30%) (Figure 3.7). The difference between the test and control plates indicates that infusion with silicone oil was key in reducing fouling of the surfaces.

These surfaces have the additional benefit of being foul-release coatings, *i.e.*, coatings that reduce the adhesion of fouling species to the surface and make it easier to remove the fouling once it occurs. [252] Perfluorinated polymers are already used as foul-releasing materials (*e.g.*, Intersleek 900 produced by AkzoNobel), and the length scale of the wrinkles is smaller than that of fouling species, further reducing the adhesion. [252] This suggests that our control
3.3 Inhibition of Marine Fouling in the Open Ocean

Figure 3.5. *In situ* images of the control plate (non-infused samples) during the marine fouling test. Images were taken underwater to ensure that the results were not influenced by removing them from the water. The sample in the top left fell off whilst installing the plate to the net. This control plate acted as the real benchmark of Teflon wrinkles without any silicone oil.

Teflon samples already have a foul-releasing function. To test the foul-releasing properties, the fouled test and control surfaces are sprayed with water using a laboratory tap. Example results of this treatment are given in Figure 3.6 and Figure 3.7 (post wash). The infused surfaces have 65% of their fouling removed upon washing, as compared to only 30% for the uninfused control surfaces, indicating that the infused silicone oil aids in foul-releasing and that an approach to antifouling using infused surfaces is better than approaches based on low surface energy and structural elements alone.
3.4 Other favourable properties of wrinkled Teflon LIS

3.4.1 Transparency

Infusion of the surfaces has the additional benefit of making the surfaces more transparent when prepared using transparent substrates (Polyshrink comes in a number of varieties including transparent). The wrinkled surfaces scatter incident light, reducing the transparency of the substrate. By infusing the wrinkled substrates with silicone oil, the transparency is increased from 85% to 90% throughout the visible range in water and from around 60% to
85\% in air, see Figure 3.8 and Figure 3.9. This aspect makes these surfaces ideally suited to protect underwater sensors and cameras from fouling.

Figure 3.8. Optical image showing the transparency gained when a wrinkled substrate is infused. (L) uninfused; (R) infused

3.4.2 Ability to be molded

An advantage of using polymer substrates is that they can be easily molded to a shape during fabrication. After the polystyrene substrate has been annealed, it is still malleable and able to be molded to a desired shape. After infusion, a curved substrate is still very effective in resisting biofouling (Figure 3.10).
Figure 3.10. The substrate is able to molded without damaging its the wrinkle nanostructure or its antifouling ability as seen through crystal violet stain showing bacterial growth only on the uninfused substrate. (L) uninfused; (R) infused.

3.5 Conclusions

This Chapter assessed LIS based on spontaneously wrinkled Teflon surfaces previously developed in our group. These surfaces show exceptional biofouling resistance with exceedingly small amounts of lubricant present. A simple fluorescence protocol to quantify small volumes of lubricant present on LIS, regardless of the substrate was developed. The knowledge of the amount of lubricant present on a surface is crucial to understand the potential and limitations of these systems in application.

Remarkably, the Teflon wrinkled surfaces retain sufficient silicone oil after two weeks of vigorous shear in seawater (0.02–0.04 µL cm\(^{-2}\)) to have slippery properties and to inhibit marine bacteria attachment. Infused wrinkled Teflon surfaces are much more effective than Perspex and even uninfused wrinkled Teflon surfaces at reducing marine organism attachment.

The near-complete inhibition of bacterial fouling in the laboratory does not fully translate to real-world applications due to lubricant depletion. For the first time, fouling of 2D LIS was tested in the ocean. Marine organism attachment is reduced after seven weeks of depletion from tidal flow, again showing the small quantity of lubricant needed for antifouling properties.

The minimal volume of silicone oil needed for a surface to be effective was measured, and it was shown that not all of the oil is lost even under high shear for extended periods. In turn, the volume of silicone oil lost into the environment is correspondingly minimal. This constitutes a good premise for a sustainable and benign antifouling coating. The option of high transparency makes these surfaces suited to protect underwater sensors and cameras from
bacterial and microorganism fouling. Their high efficiency, robustness, and simple fabrication make these antifouling surfaces promising for a variety of applications.
CHAPTER 4

Analysis of lubricant layer using atomic force microscopy

Characterisation of the lubricant layer presents several challenges due to its thin nature and the scale of the roughness into which it is infused. Section 3.2.1 quantified the amount of lubricant present on a surface, but this technique gave no spatial information about the distribution of configuration of the lubricant. As described in Section 1.3.5, a detailed knowledge of lubricant distribution on LIS is key to establishing their function and depletion pathways.

This Chapter develops a method based on AFM force-distance curves to map lubricant thickness on 2D LIS with a high degree of precision and accuracy. This method is then used to examine how lubricant is removed from the surface as it depletes under different surface treatments.

The majority of this Chapter appears in:

I developed the mapping technique and designed all experiments together with Neto.

Section 4.9 appears in:

I carried out and analysed all data using the mapping technique developed in this Chapter.

4.1 Meniscus force measurements

4.1.1 AFM force curves

A force curve records the forces felt by the AFM tip as it moves normal to the surface. This is an alternative to traditional imaging modes that move the tip parallel to the surface to build up
a map of the topography, see Section 1.5. In force curves, the AFM records the deflection of the cantilever as a function of the $z$-displacement of the sample (see Figure A.1a). [253] It is necessary to convert this collected raw data into a more usable form using the sensitivity and spring constant of the cantilever. Appendix A gives a detailed explanation of how this is achieved. An example of a converted force curve is shown below in Figure 4.1 where the $x$-axis is the separation between the tip and the sample and the $y$-axis is the force felt by the cantilever. The approach curve is collected as the sample is driven towards the tip and the retract curve as the sample is withdrawn down.

A typical force curve is made up of several different regions that each contain a lot of information. The right-hand portion of the force curve at large separations is the non-contact region where the tip and sample do not interact. At zero separation, there is the contact region where the tip and the sample are in contact. The slope of the contact region gives the compliance of the sample. The example in Figure 4.1 is of a hard sample that cannot deform and so the contact region is a straight vertical line as all deformation is due to the tip and not the sample. The force curve in Figure 4.3a was collected on a Teflon wrinkled substrate and so shows some compliance due to the elastic deformation of the substrate. At a few nanometres of separation there is the jump-in where the tip snaps to the surface before hard contact is made, and is crucial to the measurement of liquid film thickness.

![Figure 4.1](image.png)

**Figure 4.1.** An example of an AFM force-distance curve on a hard substrate (silicon wafer) in air. Note the jump-in a few nanometres from zero separation due to a thin layer of water adsorbed onto the surface.
4.1.1.1 The jump-in

The jump-in, seen in Figure 4.1, is what makes meniscus force measurements possible as it originates from the formation of a meniscus around the tip. Solids in ambient conditions are coated in a thin water layer adsorbed onto the surface [254–258] that, when the tip makes contact, will wet it and form a meniscus that can draw the tip down, see Figure 4.2. For the jump-in to be pronounced, the spring constant of the cantilever must be on the same order as the capillary force due to meniscus formation in order to get large enough deflection to be seen in the force curve.

![Figure 4.2. A thin layer of water adsorbed onto the surface wets the AFM tip and is responsible for the jump-in seen in Figure 4.1.](image)

It is this phenomena that we exploit to measure the thickness of lubricant. When the tip contacts the lubricant layer, it is wet by the lubricant, and (given the correct spring constant) will show a large negative deflection at this point.

4.2 Development of meniscus force mapping technique

4.2.1 Anatomy of a force curve on a lubricated surface

For a lubricated surface, the features of the force curve are much the same as seen in Figure 4.1, but the jump-in is generally at much larger separations due to the thicker layer of lubricant. An example force curve taken on a lubricated surface is shown in Figure 4.3. At large separations, the tip and surface are not interacting and there is no deflection of the cantilever (region i in Figure 4.3). When the AFM tip contacts the surface of the lubricant layer, there is an abrupt negative deflection, the jump-in (point ii), due to an attractive capillary effect from a meniscus forming as the lubricant wets the tip, drawing it down. This negative
deflection continues as the tip continues moving through the lubricant layer (region iii) until the tip makes hard contact with the substrate (seen as a positive deflection, point iv). By mapping the z-piezo’s absolute position at the jump-in (point ii) and hard contact with the substrate (point iv) over the scan area, the surface of the lubricant and underlying substrate are mapped. By taking the difference in distance between these points, the thickness of the lubricant is mapped. When the tip is withdrawn from the surface, a capillary bridge is stretched away from the surface and the tip travels for a longer distance away from the surface compared to the jump-in point before the meniscus breaks and the tip snaps off the surface. This long snap-off distance is a signature of the presence of a liquid layer on the surface, [259] but analysis of the retraction curve here is not necessary as it does not contain any information about the thickness of the lubricant layer.

4.2.2 Automatic analysis of force curves

In order to build a map of lubricant thickness on a surface, each force curve is a pixel in the overall image. Appendix A details the general process of taking raw force curve data from the AFM and converting it to force-separation data for analysis. Even for a small map of 10×10 pixels, there are 100 force curves that need to be analysed, making this procedure much too labour intensive to do manually. Instead, I developed a Python script that automatically takes the raw force curve data and analyses it, allowing for quick and easy analysis of high resolution maps (tested up to 128×128 pixels with no issues). The script requires the sensitivity of the cantilever (determined prior to measurements from 100 force curves on silicon wafer, typical value is 58±24 nm V−1 determined from ∼3000 force curves, see Figure 2.8), but not the spring constant as the measurement only requires deflection data and not force data.

For each pixel, the script:

1. Loads the force curve from the ASCII file output by the AFM software.
2. Extract the extend portion of the curve.
3. Converts the x-axis to separation using the previously calibrated sensitivity for the cantilever (see Appendix A).
4. Finds the jump-in point (point ii on Figure 4.3) by looking for a large negative change in the derivative moving along the curve from the non-contact region.
5. Finds the hard contact point (point iv on Figure 4.3) by looking for a large positive change in derivative.
6. Calculates the distance between these two points.
The resulting multidimensional data \((x, y, z)\) (substrate surface), \(z\) (lubricant surface), lubricant thickness) are then output to a file for further analysis and visualisation.

The Python scripts used for analysis are reproduced in Appendix C.

![Figure 4.3. An example force curve taken on a lubricated surface showing schematically the forces felt by the cantilever at each stage.](image)

**4.2.3 Method validation**

Previous work has validated meniscus force measurement on thin films on flat substrates \((R_a < 20 \text{ Å})\) against film thicknesses measured using ellipsometry. [260–262] These studies showed that there is an overestimation of film thickness as measured using AFM of \(~3\ \text{nm}\) for film thicknesses in the range up to \(~30\ \text{nm}\). These studies attribute the overestimation to the presence of a thin film of lubricant on the AFM tip.

To validate this method on the scale of the roughness and lubricant film thicknesses found on the wrinkled substrates, a qualitative approach comparing the lubricant surface reconstructed from the force curves to lubricant surface imaged using tapping mode AFM was taken. To
validate that point ii and point iv are the bottom and the top of the lubricant layer, respectively, the mapping of these points was compared with AFM tapping mode images. Figure 4.4a shows the substrate surface as imaged using tapping mode AFM. By choosing a low set point (approx. 20\% of the free air amplitude, so-called “hard” tapping), the AFM tip taps below the surface of the lubricant layer and images the substrate surface. Figure 4.4c shows the topography of the same area of the sample as reconstructed using point iv on the force curves. Figure 4.4a,c displays qualitatively the same information, confirming the method reliably visualizes the surface of the substrate. Conversely, choosing a set point close to the free air amplitude (approx. 60\%) allows the tip to follow the surface of the lubricant layer and reveal the topography of the liquid surface, as seen in Figure 4.4b. Mapping point ii in the meniscus force curves produces the surface of the lubricant layer as shown in Figure 4.4d, showing qualitatively the same image as in tapping mode. The similarity between the data collected through the two techniques shows that the difference between point ii and point iv is indeed the thickness of the lubricating layer. Tapping mode micrographs cannot be used for quantitative analysis, as the tip does not always follow the surface of the lubricant layer well, especially in regions of thin lubricant. [263] Comparison of Figure 4.4b,d shows qualitative validation of the method: the surface reconstructed from force curves is qualitatively the same as the tapping mode image (with only a slight difference in location introduced by piezo drift).

4.2.4 Potential sources of error

Previous studies by Mate et al. showed that there is good agreement between the film thickness measured through AFM force-distance measurements and ellipsometry. [260–262] However, their results showed that the AFM force curve method gives a nonzero film thickness when there is no lubricant present on a surface. As this method cannot distinguish between different liquids, a thin adsorbed layer of water present on all surfaces, [258] including on the AFM tip, this leads to an overestimation of film thickness by 1–2 nm. [264] It is possible that film thickness could be overestimated if a large quantity of lubricant accumulated on the AFM tip. However, experimental tests suggest that this is not an issue. In particular, when a clean, dry, as-prepared Teflon wrinkled sample was mapped directly after one that was infused, a lubricant layer of constant measurable thickness was not observed, see Figure 4.11.

Even on a surface with no stable water film, a meniscus can spontaneously form around the AFM tip as it nears the surface. [265, 266] Small pores allow for condensation of vapours below their saturation partial pressures by giving greater spatial proximity to adsorbed layers and allowing coalescence. The junction between the AFM tip and the surface can act as a pore allowing a meniscus to form. It is unlikely that this phenomena would occur on the
Figure 4.4. Qualitative validation of meniscus force mapping as a method for measuring lubricant film thickness on a LIS. a) surface of Teflon wrinkles as imaged by tapping mode AFM; b) surface of the lubricant as imaged by tapping mode AFM; c) surface of Teflon wrinkles reconstructed from meniscus force curves, as described in the text; d) lubricant layer surface reconstructed from force mapping. The topography does not match up completely due to slight piezo drift. Panels (a,c) have a vertical range of 800 nm; panels (b,d) have a vertical range of 400 nm.

Another potential source of error is from the deformation of the liquid surface due to long-range intermolecular interactions. Long-range attraction between the AFM tip and the liquid layer could cause the liquid surface to deform and “jump-up” to meet the tip on approach, giving an overestimate of film thickness. Two experimental parameters influence this: cantilever spring constant and approach rate. Previously, it was reported that this error is
4.2 DEVELOPMENT OF MENISCUS FORCE MAPPING TECHNIQUE

a problem only for cantilevers with very high spring constant. [264] Cantilevers used in this Thesis have a relatively low spring constant (1–2 N m$^{-1}$), so should not introduce this error. To confirm this, several approach rates on the same spot of an infused sample were compared, varying from 1000–10 nm s$^{-1}$. **Figure 4.5** and **Table 4.1** show representative force curves and the resulting measured film thickness, respectively. These show that as the approach rate decreased, the measured lubricant thickness increased. For rates between 1000–100 nm s$^{-1}$, the change in thickness was within the error of the measurement, but for rates lower than 100 nm s$^{-1}$ the overestimation was significant. To avoid this overestimation, rates above 500 nm s$^{-1}$ were used for all data collection.

**Figure 4.5.** Representative force curves taken at the same location for different approach speeds of the AFM tip.

**Table 4.1.** Calculated silicone oil thicknesses for different approach speeds of the AFM tip. Reported values are the average of four measurements and the uncertainty is the standard error in the mean.

<table>
<thead>
<tr>
<th>Speed / nm s$^{-1}$</th>
<th>Calculated thickness / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>126.9±0.6</td>
</tr>
<tr>
<td>500</td>
<td>126.4±0.6</td>
</tr>
<tr>
<td>100</td>
<td>127.1±0.9</td>
</tr>
<tr>
<td>50</td>
<td>128.6±0.9</td>
</tr>
<tr>
<td>10</td>
<td>133.1±0.8</td>
</tr>
</tbody>
</table>
In regions of sheer topography or re-entrant geometry, the collected force curves have a consistent defect that may cause some error in the measurement of film thickness at that point. **Figure 4.6a** and **Figure 4.7a** show examples of such force curves, where there is a spike up before the tip makes hard contact with the substrate. As this defect only occurs in areas of sheer topography change, it is likely that it is due to hydrodynamic effects of confined lubricant in areas of re-entrant geometry. Of course, as AFM cannot detect or characterise re-entrant geometry, this cannot be confirmed. Another explanation is that the tip is drawn laterally towards the sheer face of the topography due to capillarity or intermolecular interaction between the tip and the substrate. If this phenomena were the sole cause of this artefact, a spike in the lateral deflection is expected at the same time. **Figure 4.6b** and **Figure 4.7b** show the lateral deflection of the cantilever and shows that a spike in lateral deflection is not consistently seen, suggesting that it cannot be the sole cause. In either case, only 1-2 force curves per line (there are usually 64 samples per line) are affected and so the overall measurement of lubricant distribution is not influenced heavily by this error.

In general, the topography imaged in this Thesis is much larger than the AFM tip, and so adjacent features do not influence the imaging of other features unless the tip is damaged or dirty — any surface with features able to be imaged effectively using tapping mode AFM will similarly be able to be imaged using this technique.

![Force curves](image)

**Figure 4.6.** Force curve taken in a region of sheer topography. a) deflection on the cantilever; b) lateral deflection of the cantilever. The presence of a change in lateral deflection suggests the tip may be attracted to the adjacent area of sheer topography.

The softness of the substrate is also not a concern (unless the substrate is very soft, such as an elastomer) as any deformation will still cause a reversal in the deflection of the cantilever, clearly marking the interface between lubricant and substrate. Effects due to plastic deformation of the substrate were minimized by ensuring the substrate only deformed elastically.
4.2 DEVELOPMENT OF MENISCUS FORCE MAPPING TECHNIQUE

Figure 4.7. Force curve taken in a region of sheer topography. a) deflection on the cantilever; b) lateral deflection of the cantilever. The absence of a change in lateral deflection suggests the artefact seen in areas of sheer topography is not entirely due to the tip being attracted to the adjacent sheer topography.

Plastic deformation is seen as a hysteresis between the approach and withdraw curves in the contact portion of the force-distance curve. [253] The trigger point was kept low enough so that no hysteresis (and hence, no plastic deformation) was seen.

4.2.5 Data presentation

Figure 4.8. 3D reconstruction of an infused surface with lubricant represented in yellow. The scale bar should be used as a guide only.
This meniscus force mapping technique provides a wealth of multidimensional data that is difficult to appreciate in 2D. As mentioned in Section 4.2.2, for each $x, y$-location, this technique gives the height of the substrate, the thickness of the lubricant, and by extension, the height of the lubricant surface. As a result, the thickness of the lubricant can be studied in direct relation to the local topography. An advantage of this is that the surface and lubricant can be reconstructed in 3D at the nanoscale (see Figure 4.8). This also allows for the substrate and lubricant to be 3D printed for a more hands-on approach to understanding the lubricant and nanoscale wetting.

Unfortunately, the 3D approach to data presentation is not well suited to conveying quantitative information in a Thesis as perspective in the visualisation means that any measured lengths are longer than they appear.

Instead, a visualisation method that conveys quantitative information about both the substrate and the lubricant effectively in 2D is needed. To achieve this, several visualisation techniques were explored before settling on a multi-panel visualisation using non-linear contours (linear between $0–20 \text{ nm}$ with a level at $150 \text{ nm}$ and $300 \text{ nm}$) to represent the lubricant thickness.

**Figure 4.9** details some of the visualisation styles tested:

a) The first style tested involved two panels where the left is the topography and the right is the lubricant thickness in the same, but opposite, color scale. This does not convey a lot of information about the lubricant thickness as most layers simply look like the inverse of the wrinkles due to the interface being mostly flat.

b) The next style tested presents the topography as 3D map with the colour scale being the lubricant thickness. This fails for the same reason as the previous style as it does not effectively show the difference between the topography and the lubricant.

c) The next style is similar to the first, but with the addition of two perpendicular cross sections to show representative lubricant configurations. Note that in this visualisation, the thin lubricant is quite clear in the right heat map. The idea of cross sections was not used routinely as it does not convey enough information about the surface as a whole, but is used sometimes to specifically show the wetting configuration of the lubricant around asperities.

d) This visualisation is similar to (b), but using the the lubricant surface as the 3D height with the lubricant thickness as the colour map. This does a better job of conveying the relationship between topography and lubricant thickness, but still not very intuitively.
e) Contours were used to help simplify the visualisation of the lubricant thickness by reducing the number of visual steps, but this still is not intuitive with most of the frame being white.

f) Filling in the contours makes it much clearer which areas are covered by thick lubricant and which are covered by thin lubricant.

g) Finally, presenting the filled contours (with extra levels added at 150 nm and 300 nm to give detail for some of the thicker lubricant areas) with the topography and an optional histogram of lubricant thickness gives an intuitive representation of how topography effects lubricant thickness and the general distribution of thicknesses. AFM meniscus force maps are presented this way throughout the rest of this Thesis.

4.3 Characterisation of dry substrates

Due to the presence of adsorbed water, a nanothin lubricant film, or other liquid on the AFM tip, the minimum measurable thickness as measured by meniscus force measurements on a dry substrate is non-zero. To quantify this, a number of experiments were performed on flat samples. A flat Teflon film (as a model hydrophobic surface, water CA: 120°) and a flat P4VP film (model hydrophilic surface, water CA: 50°) were scanned with a clean tip. Figure 4.10a shows a histogram of thicknesses measured on the substrates. The mean thickness of the water film measured was 2.25±0.02 nm on ‘dry’ Teflon and 3.17±0.02 nm on the ‘dry’ P4VP (uncertainty is the standard error in the mean). P4VP, being hydrophilic, showed a thicker water film, as expected. [258] These measured film thicknesses are greater than expected for a layer adsorbed in ambient conditions (~0.7 nm [258]), but is the same order of magnitude as the film measured on dry surfaces previously. [262] Possible reasons for the overestimation are that a film forms on both the substrate and the tip and that the experiment was carried out in January in Sydney which is a particularly humid time.

In separate experiments, a small drop of silicone oil was placed on each substrate and then drained from the surface. For the Teflon surface, where silicone oil has a non-zero contact angle, a similar procedure to Liu et al. [259] was used, wicking the lubricant drop into an adsorbing wipe. For P4VP, on which silicone oil completely spreads, a high-pressure stream of nitrogen (90 psi) was applied to the surface for one min. [60]

The mean film thickness of the remaining silicone oil layer on Teflon was 3.22±0.01 nm and 8.4±0.1 nm for P4VP (reported uncertainty is the standard error in the mean). This shows that there is a stable thin film of silicone oil remaining on both of these substrates. By considering the upper limits of the distribution of film thicknesses in each case, we can quantify what
Figure 4.9. Different visualisation options for presenting data collected using meniscus force mapping. The last option (g) was chosen as it clearly conveys the relationship between topography and lubricant thickness, it visualises lubricant thickness in both thick and thin regions and gives quantitative information on lubricant thickness in the form of histogram.
constitutes as a “dry” surface, see **Figure 4.10**. Any measurement of less than 5 nm for Teflon and 10 nm for P4VP are considered “dry” in further analysis.

To confirm that the surface topography has no effect on the measured lubricant thickness, a map was collected on a dry wrinkled Teflon substrate. The results are shown in **Figure 4.11**, showing that the topography has no effect on the measured film thickness for a dry Teflon surface, with an average measured film thickness of $1.85 \pm 0.03$ nm, close to the value for the dry flat Teflon film.

![Figure 4.10](image.png)

**Figure 4.10.** Histogram of film thickness collected on flat Teflon (a) and P4VP (b) before and after a drop of silicone oil was placed and onto and dewetted from the surface.

### 4.4 Lubricant layer depletion

As a LIS loses its lubricating layer, it loses its slipperiness and all favorable properties that come with it. This makes the depletion of lubricant from these surfaces of particular interest as this is their point of failure and an understanding here will lead to more robust surface design. To investigate LIS at their point of failure, the lubricant layer was investigated using meniscus force mapping on several surfaces that were depleted in different ways. **Figure 4.12** shows these results, presented as two panels for each sample. The first panel is topography,
Figure 4.11. Meniscus force measurements taken on an as-prepared Teflon wrinkled surface after measurement on an infused surface showing topography of the underlying substrate (a), the lubricant thickness as contours (b) and a histogram of lubricant thicknesses (c). The measured film thickness is similar to that of the flat Teflon film at $1.85 \pm 0.03$ nm.

reconstructed from point iv in the meniscus force curves (as identified in Figure 4.3), and the second is a contour map of lubricant thickness, highlighting depleted regions. The lubricant thickness is presented as a contour map, with levels spaced by 2 nm in the range 0–20 nm, and then in steps of <150 nm (yellow), <300 nm (light yellow), and >300 nm (white). The units of both scale bars are nm.

For all samples, the CAH, the volume of lubricant present, and the percentage of the surface that can be considered “dry” (as established in Section 4.3) are compared in Table 4.2. The total volume of lubricant present on the surface was estimated by taking the sum of the volume of lubricant at each point, found by multiplying the area of a pixel by the thickness of the lubricant in that spot. The substrate surface and the IL layer were very reproducible across several micrographs (typically of area 1–4 $\mu$m², $n = 3$), so although the surfaces are likely not homogeneous, the small scan sizes are likely very representative of the full surface.

The samples in Figure 4.12a,b were depleted by spinning them in a spin coater at 8000 rpm for one and five minutes, respectively, to shear down the lubricant layer. Chapter 3 showed that both of these surfaces have similar volume of lubricant (0.4 $\mu$L cm$^{-2}$ and 0.3 $\mu$L cm$^{-2}$, respectively, by fluorescence) and similar high levels of bacterial inhibition (86 % and 84 %, respectively). From the results presented in Figure 4.12 and Table 4.2, both samples have a similar, relatively thick lubricant layer, with few areas below 150 nm in thickness, and show very similar, low CAH (2°, Table 4.2). They also show very similar lubricant volumes as calculated from the force mapping. This confirms our previous result that spinning the Teflon wrinkled surfaces for one or five minutes results in similar lubricant film thickness.
Figure 4.12. Topography (left) and lubricant thickness (right) for a number of silicone oil infused Teflon wrinkled surfaces. (a,b) Wrinkled surfaces that had their lubricant layer sheared down by spinning on a spincoater at 8000 rpm for one and five minutes, respectively. (c) Surfaces that were exposed to shear in artificial seawater for two weeks. (d-f) Surfaces that were stored vertically for three, six, and nine weeks, respectively.

The difference in measured volume by fluorescence as opposed to lubricant film thickness mapping is likely due to the fluorescence protocol including lubricant that has erroneously spread onto the back or sides of the sample. On the other hand, the force mapping technique detects only lubricant trapped on the surface.
Table 4.2. Wetting and lubricant properties of Teflon wrinkled surfaces depleted in different ways. Reported uncertainties are the standard error in the mean.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CAH / °</th>
<th>Volume of Lubricant /µL cm⁻²</th>
<th>Area Exposed / %</th>
<th>Biofouling Inhibition / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>dry Teflon wrinkles</td>
<td>27±3</td>
<td>0ᵃ</td>
<td>100ᵃ</td>
<td>0</td>
</tr>
<tr>
<td>8000 rpm, 1 min</td>
<td>2±1</td>
<td>0.09 ±0.03</td>
<td>0ᵇ</td>
<td>86±9</td>
</tr>
<tr>
<td>8000 rpm, 5 min</td>
<td>2±1</td>
<td>0.09 ±0.02</td>
<td>0ᵇ</td>
<td>84±10</td>
</tr>
<tr>
<td>shear 2 weeks</td>
<td>23±2</td>
<td>0.020±0.002</td>
<td>1±1ᵇ</td>
<td>76±16</td>
</tr>
<tr>
<td>drain 3 weeks</td>
<td>7±2</td>
<td>0.02 ±0.01</td>
<td>4±2ᵇ</td>
<td>N/Aᶜ</td>
</tr>
<tr>
<td>drain 6 weeks</td>
<td>13±2</td>
<td>0.02 ±0.01</td>
<td>4±2ᵇ</td>
<td>N/Aᶜ</td>
</tr>
<tr>
<td>drain 9 weeks</td>
<td>9±2</td>
<td>0.02 ±0.01</td>
<td>4±2ᵇ</td>
<td>N/Aᶜ</td>
</tr>
<tr>
<td>P4VP</td>
<td>N/Aᵈ</td>
<td>0.037±0.004</td>
<td>0ᶜ</td>
<td>N/Aᶜ</td>
</tr>
</tbody>
</table>

ᵃ This surface was not infused.
b Exposed is defined as measured lubricant thickness <5 nm.
c Exposed is defined as measured lubricant thickness <10 nm.
d Water pins on P4VP so CAH cannot be measured.
e Bacterial adhesion testes were not performed on these surfaces.
f Water displaces silicone oil on P4VP, making it unsuitable for biofouling tests.

Of particular interest are LIS that have undergone two weeks of shear in artificial seawater, seen in Figure 4.12c. In Chapter 3, infused wrinkled surfaces sheared in the same way showed 76% bacterial inhibition and had only 0.02±0.01 µL cm⁻² of lubricant on their surface (as measured through fluorescence). Remarkably, the volume calculated by force mapping is the same, 0.020±0.002 µL cm⁻². The greater similarity between the two techniques, in this case, is likely due to the underwater shear removing any lubricant not trapped in the surface, reducing the overestimation made by the fluorescence technique.

As an alternative method of depleting the lubricant from wrinkled surfaces, infused surfaces were stored vertically for several weeks to observe depletion due to gravity. The lubricating layer thickness was measured at three, six, and nine weeks, seen in Figure 4.12d-f, respectively. Interestingly, the lubricant depleted to the thickness seen after three weeks and then remained at the same thickness for up to nine weeks (and is similar to the level seen in the samples that were depleted under shear). This level of depletion is very stable, with the same samples that were held vertical for nine weeks showing a similar lubricant level after more than a year of storage as shown in Section 5.8.2. At this level, only lubricant held between the wrinkles by capillary action remains and lubricant not stabilized by capillary forces flowed away relatively quickly, leaving high points depleted.
There is no clear relation between CAH and either the volume of lubricant or amount of surface exposed, as seen in Table 4.2. Once enough lubricant has been sheared from the surface to expose some of the topography, there is an increase in the CAH, but changes in the macroscale wettability do not relate to differences in the lubricating layer past this point. This highlights a shortcoming in the use of macroscale observables to account for micro- and nanoscale differences. This also highlights the binary nature of slippery properties with lubricant depletion. When the lubricant layer is thick, the surfaces are very slippery, displaying very low CAH; when the layer is thinned down, a number of pinning sites for the droplet contact line become available and CAH increases drastically. However, despite local depletion, overall the surface is still effective at inhibiting bacterial attachment.

A histogram of film thicknesses clearly shows differences in lubricant configuration for different depletion states. Figure 4.13a,b shows that for the Teflon surfaces that were depleted only slightly, using a spin-coater, there is a thick layer of lubricant over the whole wrinkled surface (approx. 600–800 nm), and there is one wide population of film thickness. For the more depleted samples (Figure 4.13c-f), depleted through underwater shear and vertical drainage, there are two distinct regions of lubricant film thickness: areas on the top of the wrinkles have around \(\sim\)5 nm and thicker areas with thickness around 150–500 nm. The insets in Figure 4.13 show the 0–20 nm region in more detail and show that there is a clear peak in lubricant film thickness around \(\sim\)5 nm for all of these cases.

### 4.5 Effect of surface chemistry on lubricant configuration

As silicone oil does not fully spread on flat Teflon, the model presented by Smith et al. predicts that the lubricant adopts a “tops exposed” configuration in air, where there is lubricant between the wrinkles, but not over their tops. [77] This is not exactly what our nanoscale measurements show. In our results, the silicone oil does not fully dewet from the tops of the wrinkles, with the majority of these regions having a film thickness of around 5 nm, close to, but greater than the minimum measurable thickness of 3 nm.

To contrast the Teflon/silicone oil system, a system where silicone oil completely spreads on the substrate was also studied: a wrinkled P4VP surface. Water displaces the silicone oil on P4VP, so this system is not suitable as a slippery surface. However, it is a good system to study in air, as the silicone oil should adopt a “tops covered” configuration over the wrinkles, as it completely spreads over P4VP. [77] Infused wrinkled P4VP was prepared in the same way as the Teflon samples but sheared down using a stream of high-pressure nitrogen (90 psi), a method that has been adopted by our group before to effectively deplete smooth polymer
Figure 4.13. Histograms of the measured silicon oil film thickness for the Teflon wrinkled surfaces shown in Figure 4.12.

The thin film of lubricant is significantly thicker than the minimum measurable film thickness stated before (∼8 nm). The film thickness on the top of the P4VP wrinkles is thicker than the Teflon wrinkled samples in Figure 4.13, as expected.

4.6 Nanoscale wettability

Different forces are responsible for the immobilization of lubricant in different regions of topography. Between the wrinkles, in both cases, capillary forces dominate and the majority of the lubricant in the depleted state is held there. In a thick layer, however, most of the lubricant is not be held by capillary forces and can easily flow away or be removed through external forces, as seen in the previous section. This depletion continues until capillary action balances the depleting force and immobilizes the layer. This point must be below
4.6 Nanoscale Wettability

Figure 4.14. (a) Representative topography and lubricant thickness for a P4VP wrinkled sample. (b) Histogram showing the distribution of silicone oil film thickness for the P4VP sample in (a). Cross sections of infused (c) Teflon and (d) P4VP wrinkles showing the different lubricant configurations for each. As silicone oil does not spread on Teflon, the bulk liquid dewets from the surface, leaving a measured film of $\sim 5 \text{ nm}$ and forming a contact angle of $60\pm2^\circ$ with the wrinkles. Silicone oil does spread on P4VP and so forms a continuous layer over the topography. Note that the vertical and horizontal scales are different in (c) and (d). Schematic representation of a depleted state for silicone oil in (e) Teflon wrinkles and (f) P4VP.

the maximum height of the wrinkles to ensure a negative curvature and hence a stabilizing capillary force. At this point, the nanoscale wettability of the surface will determine whether the tops of the wrinkles are covered or not.

Although both substrates have the majority of the surface covered in lubricant, they show different behavior in terms of wettability. Teflon shows a discontinuous layer thickness, with the lubricant meeting the surface with a finite contact angle ($60\pm2^\circ$, Figure 4.14c) and as a
schematic in Figure 4.14e). On the other hand, P4VP shows a continuous layer indicating that silicone oil spreads fully on the surface (Figure 4.14d and as a schematic in Figure 4.14f). These results are in agreement with what is expected from their macroscale wettability: silicone oil does not fully spread on a Teflon surface ($S < 0$), whereas silicone oil fully spreads on P4VP ($S > 0$) and continuously cover the substrate.

Both substrates show a nonzero film thickness on the tops of the wrinkles, and although this is expected for P4VP, it is not expected for Teflon. To investigate if the lubricant on the tops of the wrinkles is due intermolecular forces, the van der Waals interaction [122] portion of the interface potential was calculated for both systems (see Section 2.13 for details of calculation). The P4VP-silicone oil-air system has a positive van der Waals interaction for all film thicknesses (see Figure 4.15), indicating a stable film. As such, the equilibrium film thickness ($\sim 5 \text{ nm}$) is a result of the balancing of the cohesive surface tension drawing the lubricant away from the top of the wrinkles and intermolecular forces stabilizing a larger film thickness. Contrasting this, the approximate estimate for the van der Waals interaction for the Teflon-silicone oil-air system is negative for all film thicknesses and so no stable film is expected (see Figure 4.15). As the meniscus force measurement cannot distinguish between liquid on a surface and liquid on the AFM tip, it cannot be excluded that our measurements overestimate the film thickness by 2–3 nm because of a residual film on the AFM tip.

When the samples are placed underwater, the opposite trends are expected. Figure 4.16 shows the van der Waal potential as function of silicone oil film thickness on both Teflon and P4VP calculated when the surfaces are underwater. In this case, silicone oil forms a stable film on Teflon, but an unstable film on P4VP. This again highlights the unsuitability of P4VP as a material to manufacture LIS due to its inability to stabilise silicone oil underwater.

### 4.7 Stages of depletion

An advantage of mapping lubricant thickness across a sample is that it gives insights into the mechanism of depletion of lubricant from the surface. Sloped regions of the wrinkled topography capture a snapshot of film depletion. By taking cross sections at different heights of the sloped region, we see the system at a range of film thicknesses for a consistent feature shape. Figure 4.17 shows a range of cross sections at different lubricant film thicknesses, from a thick layer between the wrinkles to a thin layer on top of the wrinkles for both Teflon and P4VP.

There is a stark difference between Teflon and P4VP in terms of lubricant depletion. For Teflon, the height of the lubricant is independent of the underlying substrate staying at roughly
4.7 Stages of Depletion

Figure 4.15. Van der Waal potentials for both Teflon and P4VP as a function of silicone oil thickness in air.

Figure 4.16. Van der Waal potentials for both Teflon and P4VP as a function of silicone oil thickness underwater.

the same level while the substrate rises up. As the surfaces of the substrate and the lubricant become closer, the surface of the lubricant deforms down toward the surface of the substrate, until the film reaches its minimum thickness and dewets from the surface (Figure 4.14c and Figure 4.17). For P4VP, the height of the lubricant follows the height of the substrate, being deformed by the underlying substrate (Figure 4.14d and Figure 4.17). The lubricant forms a tangent to the surface of the asperity, an indication that there is no contact angle. These results give us insights into how a thick lubricating layer not immobilized through capillary action will deplete from the surface. For Teflon, the layer will be flat and not follow the topography
of the surface until the film thickness is reduced to the point where the thinnest areas will begin to dewet from the top of the wrinkles. In contrast, a lubricant layer over P4VP will follow the topography of the underlying substrate as it thins.

4.8 Wettability and biofouling of LIS in a depleted state

The nanometric film of lubricant that remains on the tops of the wrinkles is unlikely to provide a lubricating effect. The Neto group has shown on smooth surfaces that lubricant film thicknesses less than about 20 nm no longer provide a lubricating effect in terms of droplet mobility and in terms of increasing interfacial slip. [60] This gives a new perspective on how we view LIS. For our wrinkles and other 2D LIS, a thick layer of lubricant will not be immobilized on the surface for very long and will easily flow away, leaving the depleted state described above. Once this thick layer is removed, the residual liquid is immobilized within the surface structure, held by a combination of capillary and van der Waals forces, having a minimum thickness of the order of a few tens of nanometres. For both complete and partial spreading cases, the film thickness on the top of the highest regions is too thin to provide lubrication. This means that the surface is heterogeneous where most of the surface is covered with a thick lubricating layer (95%, see Table 4.2), and the remainder is the top of the wrinkles which are non-lubricating. This heterogeneity is reflected in the CAH of the various depleted substrates. Table 4.2 shows that the volume of oil or the amount of surface exposed does not correlate with the CAH. Once any amount of surface is exposed, there is an increase in CAH, indicating a heterogeneous surface.

Although there is no thick lubricating layer, the infused Teflon-wrinkled surfaces are still very effective in stopping biofouling. Chapter 3 showed that a sample in this depleted state was still effective against biofouling. This indicates that a thick lubricating layer and “slippery” properties, usually characterized by low CAH, are not needed for LIS to be effective in stopping biofouling. As most LIS will quickly adopt this depleted state, they should be thought of as heterogeneous as opposed to a continuous thick layer of lubricant.

It has previously been assumed that the anti-biofouling ability of LIS is due to a continuous liquid overlayer that provides a fully mobile interface. [267] Our results show that this is not entirely necessary. While the samples depleted using the spin coater show very good anti-biofouling performance and a consistently thick lubricant overlayer, the sample sheared under seawater for two weeks shows similar performance without a continuous lubricant overlayer, see Table 4.2. Although the value of bacterial inhibition is lower for the depleted samples than for the samples with a continuous thick layer, it is still very good compared with
Figure 4.17. Wrinkle topography and cross sections of lubricant on Teflon and P4VP as lubricant thickness is reduced. As thickness of the lubricant layer is reduced, the lubricant dewets off the Teflon and a contact angle of $60\pm2^\circ$ is seen. In contrast, as the film thickness reduces on P4VP, the lubricant layer remains stable and a continuous layer covers the top of the wrinkle.
the control samples. The likely reason for this is the scale of exposed regions (on the order of $\sim500 \text{ nm}$) is smaller than the scale of a bacterium ($\sim1 \mu \text{m} \times 3 \mu \text{m}$), meaning that each bacterium does not see enough solid surface to be able to adhere. This shows that bacterial adhesion is significantly lowered by the surface being mostly liquid and hence LIS are still functional without a thick lubricant layer.

### 4.9 Application of meniscus force mapping to cement-based LIS

The meniscus force mapping technique developed in this Chapter is very versatile as it easily extends to a range of substrates and lubricants. As an example, the technique was used to visualise the depletion of lubricant through the pores of cement-based LIS. [3] Briefly, portland cement surfaces were first silanised to make them hydrophobic before infusing with silicone oil (10, 350, 1000, 10 000 and 20 000 cSt). The three dimensional porous network of cement provides an avenue for the lubricant to drain. This makes meniscus force mapping an ideal tool to track the depletion of lubricant through this drainage. Figure 4.18 shows how the mapping tracks the loss of lubricant with the sample 11 days after preparation already showing depleted areas. By 17 days there are areas showing different levels of depletion and by 40 days most of the lubricant has left the sample.

### 4.10 Conclusions

Chapter 3 showed that Teflon wrinkled LIS are effective against biofouling from marine bacteria with as little lubricant as $0.02 \mu \text{L cm}^{-2}$. Depletion of LIS is a universal phenomenon and so most LIS will be in a depleted state without a thick lubricating layer. As a result, a nanoscale understanding of the lubricant in this state is necessary.

This Chapter introduced a new technique to directly map lubricant film thickness on opaque, irregular substrates, down to nanoscale resolution using AFM force–distance measurements. By studying different depletion routes, this technique shows a thick lubricating layer quickly depletes from the tops of surface structures, leaving thicker pockets of lubricant only in locations where they are stabilized through capillary force. Any further lubricant is held through intermolecular interactions. In this state, LIS are not surfaces coated by a thick layer with an uninterrupted lubricating liquid surface. Instead, they are heterogeneous surfaces consisting mostly of thick lubricant with patches of non-lubricating nanothin film of lubricant. For non-wettable Teflon wrinkles, a nanothin layer ($5 \text{ nm}$) of silicone oil was found to remain
Figure 4.18. (a1–d1) Topography of cement samples; (a2–d2) map of lubricant (10 000 cSt silicone oil) film thickness over the same areas, measured by AFM meniscus force measurements; (a3–d3) distribution of lubricant film thickness. (A) 11, (B,C) 17, 17 (different areas), and (D) 40 days.

on the tops of the wrinkles in the depleted state in air, and a finite contact angle of the oil on the surface could be observed locally of around 60°. For wettable P4VP wrinkles, a slightly
thicker layer (15 nm) of silicone oil was found to remain on the tops of the wrinkles in the depleted state in air, with a continuous film following the surface.
Measuring lubricant depletion due to an air/water interface

LIS cannot function without their lubricant layer, making lubricant depletion their greatest challenge. Chapter 3 showed that only a small volume of lubricant is needed to reduce bacterial biofouling (0.02 µL cm⁻²) and Chapter 4 showed that this volume corresponds to a lubricant layer where only lubricant stabilised by capillarity remains. These results indicated that a thick lubricant layer is not needed for LIS to be effective against biofouling and that depletion of lubricant is inevitable. What is not clear from these results is how easily the remaining lubricant is depleted from the surface, or how lubricant wettability influences depletion.

For LIS deployed in marine antifouling applications, there is a significant depletion pathway that has not been widely studied in the literature: depletion due to an air/water interface. This is a particularly important pathway as it is an unavoidable phenomenon whenever LIS are deployed in the ocean.

1D LIS, manufactured through immobilisation of polymer brushes on a surface, have been gaining increasing attention due to their ease of manufacture and their lack of lubricant depletion. These polymer brushes claim to create a liquid-like surface which, like the liquid layer of LIS, provides a mobile interface to reduce adhesion. [90, 93, 94, 98, 170, 172, 268, 269] This functionalisation is also sometimes used as a platform to stabilise lubricant. [60, 93, 169, 270, 271] Manufacture of these layers can be simple: plasma activation of glass then coating with silicone oil for at least 24 hours to form a bond between the siloxane backbone of the oil and the glass. [94] Effectiveness of these surfaces in applications is not widely studied, and their lubricant retention not well characterised.

This Chapter investigates lubricant depletion for different types of 2D LIS as they pass through a clean air/water interface. Changes in the dynamic contact angle are tracked in situ as the sample passes through the air/water interface, and gradual depletion of lubricant is inferred from the changes in contact angle hysteresis (CAH). Depletion is visualised by mapping the volume and distribution of the lubricant using the technique developed in Chapter 4.
5.1 Substrates studied in this Chapter

This Chapter examines multiple model LIS comprising different structured surfaces and lubricant combinations to understand the role of the air/water interface on lubricant retention. The systems are chosen to represent the major lubricants used in the literature and the different wetting configurations they can adopt. The first system is Teflon wrinkles infused with 10 cSt silicone oil (TW/SO), which Chapter 3 showed were effective against marine biofouling. The other systems investigated are the same wrinkles infused with mineral oil (TW/0) and typographically similar polystyrene wrinkles (produced by dissolving the Teflon top layer of the aforementioned surfaces using FC-40) infused with either 10 cSt silicone oil (PSW/SO), Krytox GPL 100 (perfluoropolyether, PFPE) (PSW/PFPE), or mineral oil (PSW/MO). Table 5.1 summarises the properties of the lubricants tested.

Table 5.1. Physical properties of lubricants used in this study. All values at 20°C unless specified. Values taken from manufacturer data sheet unless referenced. \(\gamma_{la}\) and \(\gamma_{lw}\) are the lubricant/air and the lubricant/water interfacial tension, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Viscosity / cSt</th>
<th>Density / g cm(^{-3})</th>
<th>(\gamma_{la} / \text{mN m}^{-1})</th>
<th>(\gamma_{lw} / \text{mN m}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicone Oil</td>
<td>10</td>
<td>0.93(^a)</td>
<td>19</td>
<td>35[243]</td>
</tr>
<tr>
<td>PFPE</td>
<td>12.4</td>
<td>1.87</td>
<td>16(^b)</td>
<td>53[244]</td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>35.8(^b)</td>
<td>0.838</td>
<td>30(^b)</td>
<td>59(^b)</td>
</tr>
</tbody>
</table>

\(^a\) at 25°C, \(^b\) measured experimentally

The vast majority of LIS publications opt for either silicone oil or PFPE as lubricant (see Appendix B). These lubricant classes are chosen for their immiscibility with most common solvents, their thermal and chemical stability, and their super spreading properties which allow for successful infusion into most substrates.

The Teflon and polystyrene wrinkles, which have a similar topography, allow for the study of different lubricant wettability without significantly changing the effect of capillarity. Silicone oil does not entirely spread on Teflon in air (spreading parameter \(S_{ls(A)} < 0\), with a contact angle of 44°), and therefore, capillarity is the main force leading to retention within the wrinkles. In contrast, silicone oil fully spreads on polystyrene in air (\(S_{ls(A)} > 0\)) so capillarity, favourable spreading, and favourable van der Waals interactions stabilise the oil layer, as shown in Table 5.2. Similarly, PFPE on polystyrene is stabilised by capillarity, favourable spreading and favourable van der Waals interactions, see Table 5.2. Due to the very low surface tension of PFPE (16 mN m\(^{-1}\)), a surface on which it does not spread could not be found, and it could not be tested on Teflon as it dissolves the Teflon AF layer. Mineral oil has a key difference compared to the other lubricants tested: it does not spread over the surface of
water ($S_{\text{ld}} < 0$). This allows examination of the relative effect of spontaneous spreading of lubricant over the air/water interface on the depletion of lubricant.

For all systems investigated, the Bond Number ($Bo = \Delta \rho g \lambda^2 / \gamma_{lw}$) and the Weber Number ($We = \rho V^2 \lambda / \gamma_{lw}$) are on the order of $10^{-6}$ and $10^{-11}$, respectively. Consequently, surface tension forces dominate over both buoyancy and inertial forces in these experiments.

At the end of this Chapter, the effect of repeated dipping on the contact angle hysteresis of 1D LIS is examined. These surfaces consist of a liquid-like layer of PDMS on a glass surface (quasi-liquid surface, QLS) manufactured from a simple reaction between PDMS and the oxide of the glass surface. This 1D LIS is also studied after infusion with 10 cSt silicone oil.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lubricant CA / °</th>
<th>Hamaker constant / J</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>air</td>
<td>water</td>
</tr>
<tr>
<td>TW/Si Oil</td>
<td>44</td>
<td>0</td>
</tr>
<tr>
<td>PSW/Si Oil</td>
<td>0</td>
<td>54</td>
</tr>
<tr>
<td>PSW/PFPE</td>
<td>0</td>
<td>77</td>
</tr>
<tr>
<td>TW/MO</td>
<td>35</td>
<td>48</td>
</tr>
<tr>
<td>PSW/MO</td>
<td>0</td>
<td>59</td>
</tr>
</tbody>
</table>

### 5.2 Tracking depletion of lubricant due to the air/water interface

The depleting effect of a mobile air/water interface across a LIS was studied by repeatedly driving the LIS in and out of a water-filled custom-made cuvette. In situ measurement of the contact angle was achieved through imaging the shape of the air/water interface as the sample is driven through it. These contact angle measurements are combined with ex situ measurements of lubricant thickness using the technique described in Chapter 4 to correlate changes in contact angle with the quantifiable loss of lubricant. This technique is also expanded to image LIS underwater, visualising the lubricant/water interface and tracking changes in wettability as when the sample is submerged.

**Figure 5.1a** schematically shows the optical Wilhelmy plate tensiometer set-up used in this Chapter to track the water contact angle as the sample is driven through the interface. This
set-up and technique is adapted from the work of visiting PhD student, F. Vüllers, to track changes in contact angle as superhydrophobic surfaces pass through the air/water interface. A USB microscope is placed in-line with a lamp so that the air/water interface casts a clear shadow in the captured image. The cuvette is specially designed so that the interface continuously refreshes as water is pumped in from the bottom. Figure 5.1b shows an example of the data collected and how it is processed. Data processing is performed automatically using a Python script (reproduced in Appendix C) and limitations of this technique are discussed in more detail below. See Section 2.14 for more information on data collection.

**Figure 5.1.** a) Schematic of the set-up used in dipping experiments. A USB microscope captures the angle the air/water interface makes with the substrate as it enters an overflowing cuvette. b) The raw image captured by the USB microscope is cropped and brightness/contrast adjusted to show the interface clearly. A Python script then finds the interface (red dots) before fitting a line to the substrate, finding where the air/water interface starts, fitting a line to the air/water interface and finding the angle between these two lines.

### 5.2.1 Visualising LIS underwater

An advantage of meniscus force measurements is that the key feature needed for them to work is a contrast in wetting between the lubricant and the continuum fluid. In other words, as
long as there is a contrast in wettability on the AFM tip between the two fluids, the AFM tip deflects and the interface is clearly visible in the force curve. This is the case with silicone oil and water, with the silicone oil spreading more readily on the AFM tip than the water, causing a jump-in at the interface, just like in air. Figure 5.2 shows a typical force curve of a LIS taken underwater, and although the shape is slightly different, the lubricant thickness is still easily calculated.

![Figure 5.2](image)

**Figure 5.2.** An example of a force curve taken underwater with a hydrophobised AFM tip.

Although the native silicon nitride of the tip allows for contrast between the water and the silicone oil, hydrophibisation increases the contrast and gives better data. Hydrophibisation is achieved through chemical vapour deposition (CVD) of PDMS. Briefly, AFM tips are first cleaned using piranha solution before being placed in sealed glass vessel with a small amount of Sylgard 184 base and heated at 200 °C for four hours. This procedure deposits a thin layer (∼1.4 nm by ellipsometry, see Section 2.12.1.1) of PDMS on the surface. For in situ flooding, the samples are mounted in a custom-made liquid cell consisting of a superhydrophobic border to hold a droplet of water over the sample, see Figure 2.9.

Analysis of force curves collected underwater is much the same as for surfaces in air. The magnitude of the jump-in is reduced underwater and some artifacts can sometimes be seen in the region between the jump-in and hard contact point. As a result, analysis of curves is done using slightly altered algorithms to detect the top and bottom of the lubricant layer designed to minimise noise due to these effects. The standard algorithm finds the jump-in and hard-contact points by moving along the extend portion of the force curve from the
non-contact region, looking at the instantaneous gradient between adjacent points and check to see if this is above a pre-calculated threshold. For analysis underwater, the algorithm finds the jump-in point by first smoothing the data to make the change in gradient due to the jump-in the most prominent feature in the derivative. It then uses the same algorithm as in air. For the hard contact point, the underwater algorithm starts at the turn around point in the contact region and moves in the opposite direction looking for a change in gradient.

5.2.2 Accuracy of in situ measurement of contact angle

There is reasonable agreement between the contact angle measured in situ from the optical Wilhelmy plate tensiometer and the contact angle measured using a sessile drop. Table 5.3 compares values collected using each of the samples tested in this Chapter and shows good agreement for all, except polystyrene wrinkles infused with PFPE, whose contact angle is higher when measured using a sessile drop. Several factors influence the contact angle collected using the optical Wilhelmy plate tensiometer, but most of their effects are masked by the large uncertainties which are a result of the contact angle being an average over the whole surface.

As the contact angle is measured in situ while the surface is in motion, the measured contact angle is dependent on the capillary number of the fluid generating the interface. Table 5.3 shows that this is not an issue for samples moving at \( 50 \text{ mm min}^{-1} \), but for faster moving samples, a correction factor is needed to compare results with sessile drop measurements. [273]

As this is an optical technique, small variations in the way the data is captured and processed can have a significant impact in the measured angles, especially at high contact angles. These errors are also present in sessile drop measurements. [274, 275] The main consequence of this is a large error when fitting high contact angles (close to and above 150°). For high contact angles, it is difficult to find where the air/water interface and the substrate meet. Any error in fitting here has a large impact on the calculated contact angle values. This work only fits contact angles up to 150° to increase analysis throughput. The Neto Group’s previous use of the optical Wilhelmy plate tensiometer [4] method used a semi-interactive method to find the substrate which allowed analysis of larger contact angle values on superhydrophobic surfaces but was much slower. This work sacrifices that accuracy for the ability to fit orders of magnitude more images. As a result, contact angles close to 150° are underestimated. For example in the present work, the measured contact angle values for superhydrophobic Teflon Wrinkles (\( \theta_A = 131° \), and \( \theta_R = 127° \), see horizontal lines in Figure 5.5) are significantly lower than the values measured with the sessile drop method (\( \theta_A = 169° \), \( \theta_R = 150° \)) [33] due to
5.3 Effect of dipping rate on lubricant film thickness for structured surfaces

Multiple effects contribute to the thickness of lubricant on a sample after driving the sample through the air/water interface. Figure 5.3a shows the average thickness of lubricant as quantified from AFM meniscus force maps (10 µm × 10 µm) after one dip at different insertion/withdrawal speeds. Figure 5.3b, c, d show representative force maps after one dip for 5 mm min⁻¹, 50 mm min⁻¹ and 200 mm min⁻¹, respectively. The data is presented in the same way as in Chapter 4. The trend observed in Figure 5.3a is that a thicker lubricant film remains on the Teflon wrinkle surface after dipping at high immersion rate compared to that at low rates. For 200 mm min⁻¹, most of the film is of thickness of the order of several hundreds of nanometres (white portions), and smaller portions have thickness of the order of tens of nanometres (yellow portions). For the surface immersed at 50 mm min⁻¹, the majority of the lubricant layer has thickness on the order of hundreds of nanometres, but a larger portion of the surface is covered with lubricant of thickness on the order of tens of nanometres. For the surface immersed at 5 mm min⁻¹, the film is much thinner, with much of the surface only covered in a thin film on the order of a few nanometres (purple portions) and a small portion covered by a layer on the order hundreds of nanometres.

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**Table 5.3.** Comparison between dynamic contact angle values measured using a sessile drop and measured in situ using an optical Wilhelmy plate tensiometer as the sample passes through the air/water interface. All values are collected after the sample has passed through the interface (up and down) once at 50 mm min⁻¹. Sessile drop measurements are measured via roll-off and are an average of three measurements. Optical Wilhelmy plate measurements are the average across a single surface.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sessile Drop</th>
<th>Optical Wilhelmy Plate</th>
<th>Roll-Off</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>θA/°</td>
<td>θR/°</td>
<td>CAH/°</td>
</tr>
<tr>
<td>TW/SO</td>
<td>114±2</td>
<td>103±2</td>
<td>11±2</td>
</tr>
<tr>
<td>PSW/SO</td>
<td>112±2</td>
<td>106±3</td>
<td>5±3</td>
</tr>
<tr>
<td>PSW/PFPE</td>
<td>121±1</td>
<td>114±2</td>
<td>7±2</td>
</tr>
<tr>
<td>TW/MO</td>
<td>114±3</td>
<td>99±2</td>
<td>16±4</td>
</tr>
<tr>
<td>PSW/MO</td>
<td>99±3</td>
<td>95±2</td>
<td>5±4</td>
</tr>
<tr>
<td>QLS</td>
<td>109±2</td>
<td>100±2</td>
<td>9±2</td>
</tr>
</tbody>
</table>

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the above reasons. Although the absolute contact angle value may not always be accurate, changes in contact angle values as the lubricant is lost are still clear.
Figure 5.3. a) Average thickness of silicone oil film on Teflon wrinkles after one dip at different speeds. Data is the average of all points from 10 µm × 10 µm maps (64 × 64 pixels) on three samples. Error bars are standard deviation. The line is for a scaling law from Equation 5.1. The black dotted line is the average wrinkle height, with the grey region representing the standard deviation of this value. b), c), d) Representative AFM maps of Teflon wrinkles, lubricant distribution, and histogram of lubricant thickness after one dip at different speeds for 5 mm min⁻¹, 50 mm min⁻¹, and 200 mm min⁻¹, respectively.
Although there are parallels between this experiment and dip coating, the thickness of the lubricant cannot be predicted using the Landau-Levich-Derjaguan scaling (LLD) typically observed in dip-coating processes.\[11\]

Although there are many parallels between this experiment and dip-coating, there are some differences which means that the average lubricant thickness cannot be predicted using dip-coating theory. In Figure 5.3a the line is a fit of experimental data to the Landau-Levich-Derjaguan (LLD) scaling law:

\[ h \sim Ca^{2/3} \]  \hspace{1cm} (5.1)

Where the thickness of lubricant, \( h \), depends on the capillary number 

\[ Ca = \frac{\mu V}{\gamma} \]  \hspace{1cm} (5.2)

where \( \mu \) is the viscosity of the lubricant, \( V \) is the velocity and \( \gamma \) is the water/lubricant interfacial tension. This equation has previously been used to predict the thickness of lubricant deposited by a droplet moving on a LIS, [68] but cannot explain the data presented in this Chapter. Lubricant that is removed from the surface forms a film on the top of the reservoir and is available to re-coat the surface. The thickness of liquid coating a textured solid only follows the LLD scaling above a critical withdrawal speed, with the thickness matching the height of the topography below this speed\[276\]. At dipping speed of 50–200 mm min\(^{-1}\) the thickness is close to the average height of the wrinkles (black dotted line in Figure 5.3a with grey area representing the standard deviation). When the surface is withdrawn more slowly at 5 mm min\(^{-1}\), the surface of the reservoir has time to fully refresh within a single insertion/withdrawal cycle, leading to stronger depletion of the lubricant layer. In the rest of the manuscript, only one removal speed (50 mm min\(^{-1}\)) is used.

### 5.4 Instability of a thick lubricant layer as it passes through the air/water interface

When a LIS with excess lubricant passes through the air/water interface, the large excess is removed. For all experiments, the samples are initially infused with a large excess of lubricant to see how depletion occurs from the best case where there is ample lubricant present. In all instances, this large excess of lubricant is removed in the first dip.

This is true for all surface/lubricant combinations studied in this Thesis. After the first dip, the thickness of the lubricant film is reduced to a value that is measurable by AFM meniscus force measurements, see Figure 5.5c, Figure 5.12c, Figure 5.14c, Figure 5.17c, and Figure 5.18c. The maximum measurable thickness of this technique depends on the maximum travel of the
z-piezo, the topography of the surface and how close the AFM head is to the sample. For these systems, this is generally on the order of a few micrometres, but less than 10 µm.

A lubricant film that is not stabilised by capillarity is removed after it passes through the air/water interface. Figure 5.4 shows AFM meniscus force maps collected on flat polystyrene coated in silicone oil and PFPE after passing through the air/water interface. Little to no lubricant is retained on the featureless surface. The remaining film thickness of 5–10 nm is the same thickness that is measured on the tops of the wrinkles in Figure 5.3b and corresponds to a film stabilised by van der Waals forces or adsorbed water. [256, 277] Smooth Teflon surfaces were not tested as silicone oil forms droplets with a contact angle of 44° in air and cannot be stabilised in the absence of structure. PFPE was also not tested on smooth Teflon as it dissolves the Teflon layer.

The distributions in Figure 5.4 show two distinct distribution of lubricant thickness which is surprising. A possible reason for this is that the two distributions are actually from the thin liquid film on the surface of the polystyrene dewetting — the thinner population is the “exposed” surface while the thicker population is the dewetted droplets of liquid on the surface. At such a thin film thickness, dewetting can easily occur due to either spinodal or heterogenous dewetting. Another possible explanation is that the liquid being imaged is not lubricant and is instead water from the dipping. Water would be expected to dewet on either polystyrene or on a thin layer of lubricant. As this technique cannot identify the chemistry of the liquid it images, it is impossible to say with certainty what is happening.

### 5.5 Lubricant retention for lubricants that do not spread over the substrate

When the lubricant does not fully spread on a structured LIS (\(S_{ls(A)} < 0\)), as is the case for the LIS studied previously in this Thesis (i.e. silicone oil on Teflon wrinkles in air), the lubricant is kept in place within the structure by capillarity. LIS based on Teflon wrinkles are particularly well suited for tracking depletion through CAH as the underlying substrate is superhydrophobic, so lubricant loss is revealed by a substantial increase in both the advancing and receding contact angle.

Figure 5.5a shows the advancing and receding contact angle of infused Teflon wrinkles as a function of the number of dips. The first measurements (\(\theta_A = 113°\), and \(\theta_R = 103°\)) correspond to the contact angle values expected on a well-infused surface coated by excess silicone oil with low CAH (see the case TW/SO in Table 5.3 for comparison to sessile drop
Figure 5.4. Lubricant thickness maps for flat polystyrene films after one dip through the air/water interface for (a) silicone oil and (b) PFPE. The insets in the histograms show film thickness in the range 0–20 nm.

measurements). After the first dip, the large excess of silicone oil is removed and a continuous layer is left with most of the lubricant thickness thicker than 300 nm (Figure 5.5c) and the CAH remains small. As more silicone oil is removed (dips 3-13), portions of the underlying topography are exposed (see Figure 5.5d for a snapshot of lubricant depletion at dip ten), producing a surface with heterogeneous wetting properties. This causes an increase in CAH, with the maximum hysteresis reached after nine dips ($\theta_A = 130^\circ$, and $\theta_R = 105^\circ$). Finally, at around dip fourteen, almost the entirety of the silicone oil layer has been removed, and the contact angle values are higher than before, with reduced CAH, similar to the values for the superhydrophobic Teflon surface before infusion (horizontal lines, $\theta_A = 131^\circ$, and $\theta_R = 127^\circ$). At dip twenty, the surface is devoid of almost all lubricant (Figure 5.5e) and the CAH remains small.
Figure 5.5. Advancing and receding contact angle values as a function of the number of dips for Teflon wrinkles infused with silicone oil with (a) 30 seconds between dips; and (b) 300 seconds between dips. Error bars are standard deviation in contact angle values across the surface. The horizontal lines represent the average measured dynamic angles on a non-infused surface. AFM meniscus force maps (c-f) collected after the corresponding coloured markers in parts (a) and (b).

This change in CAH as the surface is repeatedly dipped is only seen when water is flowing into the cuvette to continuously refresh the top layer. If there is no flow, no significant change in CAH is seen over twenty dips, see Figure 5.6.
For silicone oil on Teflon wrinkles, the time between dips determines the rate of lubricant depletion. Figure 5.5b shows representative dynamic contact angle values as a function of the number of dips when the surface was kept out of the water for 300 s between dips (in all experiments the samples are underwater for 30 s). Comparing Figure 5.5a and Figure 5.5b, samples held out of the water for 300 s between dips deplete more quickly than those held for 30 s, with the sample held for 300 s between dips being completely depleted by about six dips (as opposed to fourteen dips for 30 s between dips). As described in the next Section, the longer wait time allows the lubricant to collect into large droplets on the surface, and these are removed more easily by the air/water interface.

**Figure 5.6.** Advancing and receding contact angle values of Teflon wrinkles infused with silicone oil when there is no flow in the immersion cell. In this case, removed lubricant is re-applied onto the surface with each crossing of the interface. Error bars are standard deviation in contact angle values across the surface.

### 5.5.1 Movement of lubricant after a LIS emerges from underwater

To understand the different behaviour of the lubricant layer after the sample is removed from the water, the layer was tracked using optical microscopy and AFM meniscus force measurements. Figure 5.7 shows optical micrographs of horizontal Teflon wrinkled substrates infused with silicone oil after an air/water interface has retreated across the surface. The water was removed by drawing it into a syringe, meaning that silicone oil spread over the air/water interface is redeposited onto the surface in this case. Immediately after the surface emerges from underwater, there is a continuous layer of silicone oil which retreats into droplets, with
the speed of retreat depending on the overall thickness of lubricant. A very thick layer of lubricant quickly breaks up into droplets within seconds, see Figure 5.7a-c. A thinner layer (produced after one dip at 50 mm min$^{-1}$) breaks up more slowly, on the order of minutes to hours, see Figure 5.7d-f. Once this breakup has taken place, smaller droplets disappear as larger droplets increase in size. Figure 5.7g-i shows this ripening process over the course of an hour. The red arrows indicate the location of smaller droplets that disappear while the remaining larger droplets increase in size.

The observed dependence on the time between dips is a consequence of the silicone oil not spreading on Teflon (CA = 44°). The silicone oil film breaks up into droplets, with some lubricant held by capillarity in the topography and the rest as droplets on the surface. The droplets are typically very small and the full dewetting of the lubricant happens on a relatively long timescale of hours. There are three phases to lubricant dewetting from the LIS once the surface is extracted from the water:

(i) When the sample is removed from the water, there is a continuous layer of lubricant due to the lubricant spreading underwater and the interface acting like a wiper, homogenising the layer.

(ii) This continuous lubricant layer is unstable and immediately begins to break up into droplets.

(iii) The droplets ripen into larger droplets through flow of lubricant from the higher curvature droplets to the lower curvature droplets, directed by Laplace pressure difference.

The process of droplet ripening occurs because the lubricant layer interconnects droplets. Laplace pressure is much higher in smaller droplets [11] and so lubricant is driven from them into the overall layer and ultimately into larger droplets. This process was tracked using AFM meniscus force measurements. Figure 5.8 shows the percentage of surface exposed (defined here as areas of thickness <5 nm) for a time series of meniscus force maps taken after an air/water interface has just passed over the surface. The insets show images captured by the AFM’s optical microscope before the indicated data points. Immediately after the air/water interface passes over the surface, the thick silicone oil layer retreats into droplets, and the first map records a thick film of silicone oil with little exposed surface. By the next map, more silicone oil has retreated into droplets, revealing more surface. Over the next hour or so, the amount of exposed surface decreases as silicone oil begins to flow from the small droplets to the larger ones. As this process approaches equilibrium, the film thickness begins to reduce once more as a balance is reached between the capillary force holding lubricant in the topography and the drive to dewet into droplets. During all of this, droplets of lubricant
5.5 Lubricant retention for lubricants that do not spread over the substrate

Figure 5.7. Optical micrographs of Teflon wrinkles infused with silicone oil after an air/water interface has passed over it. For a thick layer of excess lubricant (a-c, scale bar = 400 µm), the lubricant very quickly dewets into droplets. For a thinner layer (d-f, scale bar = 200 µm) the retreat is slower and the droplets smaller. Smaller droplets disappear as larger ones increase in size (g-i, scale bar = 50 µm) as the lubricant flows driven by Laplace pressure differences. Note that the time scale in (a-f) is relative to the LIS emerging from the water and (g-i) is relative to the appearance of droplets and not relative to time since the interface passed over the LIS.

on the surface either retreat as they reduce their surface area or disappear entirely as they flow to larger droplets, see insets in Figure 5.8.
Figure 5.8. Percentage of the surface exposed (defined as regions with film thickness <5 nm) for a series of 4 µm × 4 µm meniscus force maps taken in air on a Teflon wrinkled surface infused with silicone oil, after an air/water interface passes over it, as measured using AFM meniscus force mapping. Insets are optical micrographs taken in situ using the AFM optics. Scale bar = 100 µm.

5.5.2 Movement of lubricant after the sample is submerged

Looking at the reverse process, when the sample is submerged in water by flooding a custom-made AFM liquid cell, an increase in lubricant thickness is seen as the droplets redistribute into a continuous layer. The same area of a Teflon wrinkled surface was mapped after in situ flooding to see any changes in lubricant distribution (Figure 5.9).

Surprisingly, when the sample is underwater, there is a much greater volume of lubricant present. This increase in the lubricant is due to a large scale redistribution of dewetted droplets of lubricant into a continuous homogeneous layer. When the contact line moves across the surface, it collects any lubricant that has retracted into droplets and redistributes it across the surface. This effect combines with the increased spreading of silicone oil on Teflon underwater to give the dramatic increase in lubricant thickness seen in Figure 5.9.
Figure 5.9. Meniscus force maps of a Teflon wrinkled surface before (L) and after (R) it has been submersed in water. This map was collected by flooding the surface with water *in situ*.

The dynamic position of the lubricant/air interface on top of and within the wrinkles was imaged *in situ* in real time by performing repeated meniscus force maps on the same area of sample. Figure 5.10 shows cross sections of a surface which has recently emerged from underwater with an initially thick layer of lubricant that thins down over the course 105 minutes until the once continuous layer becomes discontinuous at regions of high topography.

Figure 5.11 shows the converse, after a sample it is placed underwater. Initially, the layer is like the one in air, but over time the lubricant spreads over regions of high topography until the tops are covered by a film of thickness around 10 nm (see inset in Figure 5.11). The rearrangement occurs on the order of minutes and can be seen within a single map. For example, the underwater map in Figure 5.9 shows the lubricant rearrangement occurring over the course of data collection with more regions of thin lubricant (purple) seen at the bottom of the map than the top. The map was collected from bottom to top, with each line taking approximately 30 seconds.

As a result of the long timescale to come to equilibrium, all AFM meniscus force maps presented were taken immediately after dipping (unless stated otherwise) to ensure the data is comparable. Maps are generally started approximately within five minutes after dipping and each map takes approximately 35 minutes to complete.
Figure 5.10. A series of cross sections showing the lubricant/air interface after Teflon wrinkles infused with silicone oil emerges from underwater. The substrate is represented by the black line and is filled in with grey for visual clarity.

The observed lubricant redistribution means that any exposed areas in air are no longer exposed underwater and the lubricant layer is now continuous (after sufficient time underwater). This confirms the postulations in Chapter 4 and Smith et al. [77] based on macroscopic wettability that although the lubricant is not expected to be a continuous layer over Teflon wrinkles in air, it is expected to be continuous underwater. The appearance of a lubricant film on the top of the wrinkles is supported by the estimation of favourable long-range van der Waals interactions of the substrate and lubricant underwater, see Table 2.7.

5.6 Lubricant retention for lubricants that spread over the substrate

Polystyrene wrinkles infused with silicone oil and PFPE were used to investigate the case of the lubricant fully wetting the substrate ($S_{ls(A)} > 0$). These wrinkles are obtained via dissolution of the Teflon top layer on Teflon wrinkles using FC-40. This method minimises topographic changes while modifying the surface chemistry, however, removal of the Teflon top layer does modify the topography slightly (the features are slightly taller and skinnier, see
Figure 5.11. A series of cross sections showing the lubricant/water interface after Teflon wrinkles infused with silicone oil is submerged with inset showing a detailed view of the highlighted region. The substrate is represented by the black line and is filled in with grey for visual clarity. Slight drift of the piezos meant that these maps needed alignment (by hand) and this may have introduced some artifacts such as the lubricant/water interface crossing into the substrate.

Figure 2.4 and Table 2.3), but not enough to significantly change the scale of the topography, and, by extension, the effect of capillarity.

5.6.1 Silicone oil on polystyrene wrinkles

Like Teflon wrinkles infused with silicone oil, an increase in CAH is seen on polystyrene wrinkles infused with silicone oil as the lubricant is lost. However, as the underlying wrinkled polystyrene substrate is not a low hysteresis surface, there is no reduction in hysteresis when the majority of lubricant is removed. Figure 5.12a shows the change in advancing and receding contact angle with increasing dips for polystyrene wrinkles infused with excess silicone oil. Again, after a single dip, the large excess is removed, see Figure 5.12c, with only a thin layer left on highest areas of topography. Further dipping removes more lubricant producing a heterogeneous surface by dip five (see Figure 5.12d), coinciding with an increase in CAH. After eight dips, the CAH equilibrates to a roughly steady value, similar to that of the uninfused surface (solid lines in Figure 5.12a/b, measured before infusion). At this stage,
most of the lubricant is removed from the surface, with lubricant only held in the deepest regions of the topography, where capillarity is strongest.

Figure 5.12. Advancing and receding contact angle values as a function of the number of dips for polystyrene wrinkles infused with silicone oil with (a) 30 s between dips; and (b) 300 s. Error bars are standard deviation in contact angle values across the surface. The horizontal lines represent the average measured dynamic angles on a non-infused surface. AFM meniscus force maps (c-f) collected after the corresponding colored markers in parts (a) and (b).

Figure 5.13 shows this more clearly with 1 µm × 1 µm AFM meniscus force maps taken after eight and twenty dips highlighting that lubricant is only held at the very bottom of topographic
features. This lubricant is very difficult to remove, with the amount of lubricant only slightly decreasing between eight and twenty dips. The last volume of remaining lubricant is much more difficult to remove than on Teflon due to the lower contact angle of the lubricant on the polystyrene, increasing the capillary pressure of the system.

5.6.2 PFPE on polystyrene wrinkles

The behaviour of polystyrene wrinkles infused with PFPE (Krytox GPL 100) is different to the same wrinkles infused with silicone oil, showing that the nature of the lubricant is also important in determining depletion due to the air/water interface. Figure 5.14a shows the change in advancing and receding contact angle with increasing dips for polystyrene wrinkles infused with excess PFPE. Like silicone oil on both Teflon and polystyrene, the thick layer of excess PFPE is removed with the very first dip, see Figure 5.14c, with a very thin layer covering the highest areas of topography. Unlike silicone oil, the dynamic contact angle values do not approach the values of the uninfused surface within twenty dips, see Figure 5.14a. Instead, the samples retain lubricant across twenty dips. PFPE is still gradually removed

Figure 5.13. AFM meniscus force maps for wrinkled polystyrene surface infused with silicone oil and dipped eight and twenty times at 50 mm min$^{-1}$ with (a/c) 30 s between dips; and (b/d) 300 s between dips.
from the surface with successive dips, as revealed by an overall reduction in regions with thickness greater than 300 nm (white regions) from the first dip (Figure 5.14c) to the tenth dip (Figure 5.14d) to the twentieth dip (Figure 5.14e), but much more lubricant remains after the twentieth dip than for silicone oil.

**Figure 5.14.** Advancing and receding contact angle values as a function of the number of dips for polystyrene wrinkles infused with PFPE with (a) 30 s between dips; and (b) 300 s. Error bars are standard deviation in contact angle values across the surface. The horizontal lines represent the average measured dynamic angles on a non-infused surface. AFM meniscus force maps (c-f) collected after the corresponding coloured markers in parts (a) and (b).
This different behaviour is surprising given the similarity between the silicone oil and PFPE. The lubricants were chosen to be as similar as possible while representing the two main classes of lubricant used in LIS research (see Appendix B). The physical properties of the lubricants are very similar except for density, as outlined in Table 5.1. As a result, the capillary number of the lubricant is very similar for both systems with \( Ca = 2.2 \times 10^{-4} \) and \( Ca = 3.6 \times 10^{-4} \) for silicone oil and PFPE, respectively. This suggests that the drag between the water and lubricant is not responsible for the differences seen, with viscous effects far outweighed by capillary effects. In addition, intermolecular interactions do not explain the difference, with similar estimates of Hamaker constants (see Table 5.2).

This is also reinforced by the fact that both lubricants are completely removed from an unstructured piece of polystyrene after just one dip (see Figure 5.4). A similar effect is also seen on the structured surfaces with both systems having all lubricant above the tops of the wrinkles removed after one dip and the sample having similar lubricant configuration at this point, see Figure 5.15. These results suggest that the difference in depletion is instead related to how lubricant held within the surface structure interacts with the air/water interface. The next Section shows that the different behaviour is explained by the relative energies involved with the lubricant spreading over the air/water interface.

![Figure 5.15. AFM force maps, lubricant distribution maps and cross sections of wrinkled polystyrene infused with (a) silicone oil and (b) PFPE after one dip.](image)
5.7 Significance of a cloaking layer to lubricant depletion

As described in Section 1.3.1.2, the choice of lubricant and working fluid can produce a cloaking layer due to the spreading of lubricant over the working fluid. This Section shows this can be a major depletion pathway as a LIS passes through the air/water interface. The cloaking layer is usually discussed in the context of a droplet on a LIS being spontaneously covered by the lubricant, but the same principle applies to a LIS passing through the air/water interface where the surface of the reservoir is cloaked with a thin lubricant film. The spreading of lubricant over the working fluid is due to the reduction in overall energy due to a thin film spreading over the working fluid and is described using the spreading parameter $S_{lw}$ for the lubricant over the working fluid (see Equation 1.2). This Section examines the significance of this spreading as a depletion pathway by comparing the previous results obtained with silicone oil and PFPE (both have $S_{lw} > 0$) with a lubricant with a negative spreading parameter over water ($S_{lw} < 0$).

Mineral oil is an ideal choice due to its previous use as a lubricant (see Appendix B) and it having negative spreading parameter over water:

$$S_{lw} = \gamma_{wa} - \gamma_{la} - \gamma_{lw} = 72 - 30 - 59 \text{ mN m}^{-1} = -17 \text{ mN m}^{-1}$$

Mineral oil is also very similar to silicone oil in its behaviour on the different wrinkled substrates. On Teflon wrinkles, the non-zero contact angle of mineral oil (35°) means that it also retreats into droplets and capillarity is the only stabilising force ($S_{ls(A)} < 0$). On polystyrene wrinkles, the mineral oil fully spreads and both capillarity and favourable spreading are stabilising forces ($S_{ls(A)} > 0$), and a favourable intermolecular interaction. This means that changes in depletion due to the lack of spreading over the water reservoir are easily identified. The mineral oil used in this Chapter is slightly more viscous than the silicone oil and PFPE used (see Table 5.1) meaning that it has a larger lubricant capillary number at $Ca = 4.1 \times 10^{-4}$, but as it is on the same order of magnitude, changes in depletion are unlikely to be due to this difference.
5.7.1 Lubricant that does not spread over the substrate

As mentioned above, mineral oil on Teflon wrinkles behaves very similarly to silicone oil with the continuous film retreating into droplets upon removal from water. The details of this retraction were not studied as they are expected to be very similar to the dynamics of silicone oil described in Section 5.5. It is important to note, however, that all AFM meniscus force maps were collected between dewetted droplets. Figure 5.16 shows two optical micrographs collected during AFM meniscus force mapping after one (Figure 5.16a) and ten (Figure 5.16b) dips. After one dip, the droplets are very large, but are much smaller after ten dips due to more lubricant being removed.

The behaviour of Teflon wrinkles infused with mineral oil is very different from the behaviour of the same wrinkles infused with silicone oil. Figure 5.17a shows the change in advancing and receding contact angle with increasing dips for Teflon wrinkles infused with excess mineral oil. After the first dip, a large amount of the excess is removed and the remainder retreats into droplets as described for Teflon wrinkles infused with silicone oil. The meniscus force map in Figure 5.17c, taken after one dip and between the lubricant droplets, shows large portions of exposed wrinkled surface (purple areas) and lubricant is only held between the wrinkles by capillarity. This regime remains for further dips, with the lubricant level staying roughly the same after ten dips (Figure 5.17d) and twenty dips (Figure 5.17e). This
stable lubricant level is accompanied by very little change in CAH with neither the advancing or receding angle approaching the values for the uninfused surface. This is very different behaviour compared to Teflon wrinkles which see the lubricant all removed within twenty dips. This suggests the main driver for removing lubricant from between the wrinkles is the spreading of lubricant onto the fresh air/water interface.

Figure 5.17. Advancing and receding contact angle values as a function of the number of dips for Teflon wrinkles infused with mineral oil with (a) 30 s between dips; and (b) 300 s. Error bars are standard deviation in contact angle values across the surface. The horizontal lines represent the average measured dynamic angles on a non-infused surface. AFM meniscus force maps (c-f) collected after the corresponding coloured markers in parts (a) and (b).
Increasing the time between dips to 300 s does not have much of an effect on the lubricant depletion. Figure 5.17b shows that the CAH remains similar across the experiment and Figure 5.17f shows that a similar amount of lubricant is left after twenty dips. This again reaffirms that the driving force for depletion from this substrate is the spreading of the lubricant over the water surface and not the removal of lubricant from the topography and into the dewetted droplets.

### 5.7.2 Lubricants that spreads over the substrate

Mineral oil fully spreads on polystyrene wrinkles and shows a very similar evolution in dynamic contact angles as PFPE on polystyrene wrinkles. Figure 5.18a shows the change in advancing and receding contact angle with increasing dips for polystyrene wrinkles infused with excess mineral oil.

There is very little change in CAH across twenty dips with both advancing and receding contact angles staying stable across the experiment. The higher contact angles for the first dip are an artifact from the script misfitting the contact angle due to the large excess of lubricant present at the start of the experiment. At this point, the surface is covered by a thick, continuous lubricant layer as seen in Figure 5.18c where the majority of the surface has a layer with thickness greater than 300 nm. As the dipping proceeds, lubricant is removed from the surface, but there is very little effect on the dynamic contact angle values. At the tenth dip, more regions of lubricant are thinned down, seen as the appearance of yellow regions (less than 300 nm) in Figure 5.18d. At dip twenty, much more lubricant has been removed with Figure 5.18e showing a film with the majority of regions now <300 nm, but this is not enough depletion to have an impact on the dynamic contact angle values. As there is no lubricant movement after the LIS is withdrawn from the reservoir, the amount of time between the dips does not influence depletion with the evolution of dynamic contact angles in Figure 5.18b closely following those in Figure 5.18a and showing a similar amount of depletion (Figure 5.18f).

While these results resemble the results for polystyrene wrinkles infused with PFPE, the lack of spontaneous spreading of the lubricant over the surface of the water reservoir means less depletion is expected for mineral oil. This is indeed the case, with Figure 5.19 showing a histogram of film thickness for the maps presented in Figure 5.14f and Figure 5.18f. The mineral oil sample overall has a thicker layer with average thickness 240±120 nm compared to the PFPE sample with 160±100 nm.
Figure 5.18. Advancing and receding contact angle values as a function of the number of dips for polystyrene wrinkles infused with mineral oil with (a) 30 s between dips; and (b) 300 s. Error bars are standard deviation in contact angle values across the surface. The horizontal lines represent the average measured dynamic angles on a non-infused surface. AFM meniscus force maps (c-f) collected after the corresponding coloured markers in parts (a) and (b).

5.7.3 Energetic explanation of depletion due to spreading

To validate the hypothesis that spreading of the lubricant across the air/water interface is a depleting force for lubricant held within the surface topography, a simple model of the
5.7 Significance of a Cloaking Layer to Lubricant Depletion

Figure 5.19. Histogram showing the relative distribution of lubricant on the polystyrene wrinkles after twenty dips for both PFPE and mineral oil.

wrinkles was developed to compare the amount of energy needed to remove the lubricant from within a pore with the energy gained from the spreading. This process models a Teflon wrinkled surface which has been depleted of all lubricant except that which is held within the topography so that any further depletion requires removal of this lubricant and not lubricant held in dewetted droplets.

The energy gained from the lubricant spreading over the water reservoir is equal to the spreading parameter multiplied by the surface area of water:

\[ E_{\text{spreading}} = S_{lw} \times A_{\text{reservoir}} \]  

(5.3)

Where \( S_{lw} \) is the spreading parameter for the lubricant over water and \( A_{\text{reservoir}} \) is the surface area of the water.

For silicone oil spreading over the surface of the cuvette used in this Chapter with \( A_{\text{reservoir}} \sim 25 \text{ cm}^2 \):

\[
S_{lw} = \gamma_{wa} - \gamma_{la} - \gamma_{lw} \\
= 72 - 19 - 35 = 18 \text{ mN m}^{-1} \\
S_{lw} \times A_{\text{reservoir}} = 18 \text{ mN m}^{-1} \times 25 \text{ cm}^2 \\
\approx 4.5 \times 10^{-5} \text{ J}
\]

To estimate the energy required to remove lubricant from within the surface topography of Teflon wrinkles, the wrinkles are modelled as a single two-dimensional triangular pore
with height and width equal to the average wrinkle wavelength and height (200 nm and 250 nm, respectively, see Table 2.3). The Laplace pressure across the lubricant/air interface for different levels of depletion was then calculated. The radius of curvature is found by fixing the angle of intersection of a circle and the pore to the contact angle of silicone oil on Teflon (44°). Four depletion levels are shown in Figure 5.20a together with the curvature of the interface and the resultant Laplace pressure (assuming the pore is infinitely long so that it only as a single radius of curvature contributes to the Laplace pressure).

To deplete the lubricant from the pore a pressure equal to the Laplace pressure must be applied. From Figure 5.20a, we see that the change in Laplace pressure due to lubricant depletion in the early stages of depletion is on the order 30–50 kPa and at later stages, it is on the order 70–150 kPa. The total energy required to remove lubricant is equal to the Laplace pressure times the change in volume:

$$E_{\text{removal}} = \Delta P \times \Delta V$$  \hspace{1cm} (5.4)

$\Delta V$ can be estimated by looking at the change in lubricant volume as measured using AFM meniscus force maps for different levels of depletion and is on the order of $\sim 1 \times 10^{-9}$ m$^3$ cm$^{-2}$. This gives the energy for depleting lubricant from the tops of pores across the entire surface as

$$E_{\text{removal}} \approx 40 \text{ kPa} \times 1 \times 10^{-9} \text{ m}^3$$

$$\approx 4 \times 10^{-5} \text{ J}$$

Which is on the same order of magnitude as the energy change from the lubricant spreading, showing that it is likely that silicone oil is depleted from within Teflon wrinkles via the spreading of lubricant onto the surface of the reservoir.

Table 5.4 summarises $E_{\text{removal}}$ (for two levels of depletion at the top and bottom of the pore, see Figure 5.20) and $E_{\text{spreading}}$ for all wrinkled LIS studied in this Chapter. The difference in depletion observed for PSW infused with SO and PFPE is also explained by their relative spreading over the air/water interface. $E_{\text{spreading}}$ for PSW/PFPE is two orders of magnitude smaller than $E_{\text{removal}}$ while it is only one order of magnitude smaller for PSW/SO, meaning that SO is expected to be depleted from PSW due to spreading over the air/water interface while PFPE is not. However, as shown in Table 5.4, it is unlikely the SO held in the bottom of PSW topography is able to removed due to spreading across the air/water interface (as was observed, see Figure 5.13).

However, as the energy gained from spreading depends on the surface area of the water onto which the lubricant spreads, this may be a significant depletion pathway if the LIS is deployed in a reservoir with large surface area.
Figure 5.20. Expected radius of curvature and resulting Laplace pressure for
(a) silicone oil on Teflon wrinkles; (b) mineral oil on Teflon wrinkles; (c)
silicone oil on polystyrene wrinkles; (d) PFPE on polystyrene wrinkles; (e)
mineral oil on polystyrene wrinkles. Each subfigure shows a triangular pore
depleted to four different levels.
Table 5.4. Summary of the approximate energies related to the spreading of lubricant from within an idealised pore to the air/water interface. $E_{\text{removal}}$ is the energy required to remove lubricant from the pore with top and bottom corresponding to lubricant level within the pore (see Figure 5.20). $E_{\text{spreading}}$ is the energy gained from the lubricant spreading across the air/water interface. Lubricant is expected to deplete from within the surface structure if $|E_{\text{removal}}| < |E_{\text{spreading}}|$.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{removal}}$ / J</th>
<th>$E_{\text{spreading}}$ / J</th>
</tr>
</thead>
<tbody>
<tr>
<td>TW/So</td>
<td>$-7 \times 10^{-5}$</td>
<td>$3 \times 10^{-4}$</td>
</tr>
<tr>
<td>PSW/So</td>
<td>$-3 \times 10^{-4}$</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>PSW/PFPE</td>
<td>$-2 \times 10^{-4}$</td>
<td>$9 \times 10^{-4}$</td>
</tr>
<tr>
<td>TW/MO</td>
<td>$-4 \times 10^{-2}$</td>
<td>$2 \times 10^{-3}$</td>
</tr>
<tr>
<td>PSW/MO</td>
<td>$-2 \times 10^{-4}$</td>
<td>$8 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

*does not spread across the air/water interface

5.8 Depletion due to spreading onto adjacent surfaces

Depletion of lubricant via spreading onto adjacent surfaces is a consideration for the long term application of LIS. While a lubricant that fully spreads over topography is beneficial in terms of resisting depletion from a mobile air/water interface, this regime leads to a more passive depletion of lubricant over time. This was tested by observing changes in the amount of silicone oil and PFPE in infused wrinkles over time.

5.8.1 Spreading of PFPE onto adjacent surfaces

PFPE-infused polystyrene wrinkles significantly deplete through spreading onto adjacent surfaces. Although the samples were not depleted due to spreading onto the surface of the reservoir, over the course of tens of hours, lubricant in PFPE-infused polystyrene wrinkles spreads out of the wrinkles, approaching complete depletion. Figure 5.21a shows the percentage of a PFPE-infused polystyrene wrinkled surface exposed (defined here as regions with film thickness $<5 \text{ nm}$ measured using meniscus force measurements) as a function of time. Initially, most of the surface is covered with lubricant (approx. 30% exposed), but after twenty hours the layer depletes and much more of the underlying topography is exposed (approx. 80% exposed).

To ascertain whether the lubricant is spreading out of the surface and not depleting through another pathway such as evaporation, a similar experiment was performed on a non-infused
5.8 Depletion due to spreading onto adjacent surfaces

The mapping was performed on an area adjacent to where the infused surface was placed so that any lubricant thickness measured is a result of it spreading from the infused surface. Figure 5.21b shows the percentage of exposed surface as a function of time. Initially, almost the entirety of the surface is exposed, but after twenty hours less than 40% of the surface is exposed, indicating that the lubricant spread out of the infused surface and onto the previously dry surface.

Figure 5.21. Percentage of the surface exposed (defined as regions with film thickness <10 nm) for a series of 4 µm × 4 µm meniscus force maps of a) polystyrene wrinkles initially infused with PFPE; b) initially dry polystyrene wrinkles, which become infused through spreading of PFPE from infused polystyrene wrinkles (similar to the surface in (a)) placed on top of it.

5.8.2 Limited spreading of silicone oil onto adjacent surfaces

The lubricant in silicone oil-infused Teflon wrinkles is very stable when the sample is stored in air. A similar amount of lubricant is retained in a silicone oil-infused Teflon wrinkles after vertical storage in air for one year. Figure 5.22a shows a sample after nine weeks of vertical storage (the same data as Figure 4.12) and Figure 5.22b shows the same sample after one year of vertical storage, showing very little loss of lubricant over this time period. This remarkable longevity is a result of silicone oil not fully spreading on Teflon. Once an equilibrium is reached between the dewetting of the lubricant into droplets and the lubricant held within the topography, there is unlikely to be any lubricant in contact with sides of the sample and, as a result, adjacent surfaces. This means that lubricant held by capillarity has no pathway for spreading out of the surface. The only pathway for depletion of this sample is via evaporation, which is a very slow process for silicone oil and accounts for the decrease in areas with lubricant thickness greater than 300 nm (white regions).
This is not the case for polystyrene wrinkles infused with silicone oil. Figure 5.22c and Figure 5.22d show silicone oil-infused polystyrene wrinkles after one dip and the same sample after one month, respectively. There is a much greater reduction in lubricant level compared to the Teflon wrinkles, but the majority of lubricant is retained after a month. In this case, the lubricant has depleted due to the combined effects evaporation and spreading onto adjacent surfaces, but at a much slower rate than PFPE, likely due to the slightly higher surface tension of silicone oil compared to PFPE (see Table 5.1).

Figure 5.22. AFM meniscus force maps for silicone oil infused into Teflon wrinkles and stored vertically (a) nine weeks and (b) the same sample stored vertically for one year; silicone oil infused in polystyrene wrinkles (c) after one dip and (d) the same sample after one month stored vertically.

5.9 Lubricating effects of a molecular layer (QLS)

Molecular layers represent an attractive avenue to both create an inherently non-adhesive surface and as a platform for infusion due to their simplicity of manufacture and the fact they do not require a structured surface. To investigate these surfaces, PDMS chains were grafted to glass as outlined by Teisala et al. [94] Briefly, plasma activated glass is coated with silicone oil (350 cSt) and left to react with the surface for an extended time at room temperature (approximately 80 h in this study) before being sonicated in toluene.
The as-prepared surface is hydrophobic (CA = 105±1°) with a roll-off angle of 17±3°. This surface coating is very stable, with no change in dynamic contact angles seen through repeated immersion into a constantly refreshing reservoir, see Figure 5.23a, suggesting that the lubrication effect is long-lasting and not due to unbound polymer. The CAH recorded here (approx. 13°) is similar to the value reported by Tiesala et al. for a similar grafting time (approx. 10°). [94] AFM meniscus force measurements reveal that there is no appreciable liquid film on the surface, see Figure 5.23c, recording a film thickness of 7±2 nm. The non-zero film thickness measurement is a limitation of the technique due to a thin layer of adsorbed water present on all surfaces in ambient conditions [256–258] and is similar to the value previously observed on a ‘dry’ flat Teflon surface in Section 4.3. After forty dips, the film thickness increases slightly to 11±3 nm, likely due to deposited water from the repeated dipping, see Figure 5.23d.

There are multiple claims that these layers aid the stabilisation of lubricant. [60, 93, 169, 270, 271] To test this, the PDMS-tethered surface was lubricated with an excess of silicone oil (10 cSt, 100 µL cm⁻²) and dipped repeatedly. Figure 5.23b shows the dynamic contact angles on this surface as function of dips and shows that the PDMS coating is not able to stabilise a lubricant layer, with the CAH returning to the value for the non-infused surface after a few dips. In fact, after just one dip, there is no appreciable film of lubricant on the surface, with an average measured film thickness of 11±2 nm, similar to the surface that was dipped 40 times, see Figure 5.23e.

These results show that PDMS-grafted surfaces are robust against the depleting forces that reduce the efficacy of LIS, but that these coatings cannot stabilise a mobile lubricant layer against depletion. This gives physical insight into their method of action and shows the low hysteresis of these surfaces is not due to unbound polymer or any other material that would be removed through repeated immersion.

5.10 Conclusions

This Chapter takes the method developed in Chapter 4 and combines it with in situ measurement of dynamic contact angles to track the depletion of lubricant from various LIS as they pass through the air/water interface. This depletion pathway is a significant one for any LIS that are deployed in marine applications or anywhere with periodic immersion.

The results presented in this Chapter reaffirm the observations from Chapter 4 that a 2D LIS cannot effectively stabilise lubricant not held in place by capillarity. In every test, LIS infused with excess lubricant deplete in just one dip to a level where the highest regions
Measuring lubricant depletion due to an air/water interface

Figure 5.23. Dynamic contact angle values for PDMS-grafted glass (QLS) (a) as prepared according to Teisala et al. [94]; (b) infused with 10 cSt silicone oil. Histograms of film thickness as measured using meniscus force measurements on (c) the as-prepared PDMS-grafted glass, (d) the same sample after forty dips and (e) PDMS-grafted glass lubricated with 10 cSt silicone oil after a one dip at 50 mm min\(^{-1}\). Insets show the distribution of film thickness in the range 0–20 nm.

Of topography are covered in a film on the order of tens of nanometres or less. This again reiterates the need for LIS research to analyse surface properties at this level of depletion and not an unrealistically thick lubricant layer soon after infusion.

The results reported in this Chapter are summarised in Table 5.5.

Through examination of the effects of various lubricant/substrate combinations, this Chapter shows that a lubricant that does not spread fully over the surface topography (\(S_{ls(A)} < 0\), e.g. silicone oil on Teflon wrinkles) is more rapidly depleted by a mobile air/water interface as a result of the lubricant retreating into droplets as the LIS emerges from underwater. These droplets ripen with time as lubricant is driven from smaller droplets to larger ones via the
lubricant layer due to an imbalance in Laplace pressure, with this accelerating depletion as larger droplets are more easily removed.

**Table 5.5.** Summary of the wetting and behaviour of the various substrates/lubricant combinations studied in this Chapter. $S_{ls(A)}$ and $S_{ls(W)}$ are the spreading parameter of the lubricant over the substrate in air and underwater, respectively. $S_{lw}$ is the spreading parameter of the lubricant over the air/water interface. $\rho_l/\rho_w$ is the ratio of lubricant density to water density.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{ls(A)}$</th>
<th>$S_{ls(W)}$</th>
<th>$S_{lw}$</th>
<th>$\rho_l/\rho_w$</th>
<th>% exposed 10 dips</th>
<th>% exposed 20 dips</th>
<th>No. dips</th>
</tr>
</thead>
<tbody>
<tr>
<td>TW/Si Oil</td>
<td>−5</td>
<td>&gt; 0$^b$</td>
<td>18</td>
<td>&lt;1</td>
<td>70±7</td>
<td>92±2</td>
<td>13</td>
</tr>
<tr>
<td>PSW/Si Oil</td>
<td>&gt; 0$^b$</td>
<td>−14</td>
<td>18</td>
<td>&lt;1</td>
<td>34±17$^c$</td>
<td>64±8</td>
<td>8</td>
</tr>
<tr>
<td>PSW/PFPE</td>
<td>&gt; 0$^b$</td>
<td>−41</td>
<td>3</td>
<td>&gt;1</td>
<td>1±1</td>
<td>4±3</td>
<td>&gt;20</td>
</tr>
<tr>
<td>TW/MO</td>
<td>−5</td>
<td>−20</td>
<td>−17</td>
<td>&lt;1</td>
<td>0</td>
<td>67±6</td>
<td>&gt;20</td>
</tr>
<tr>
<td>PSW/MO</td>
<td>&gt; 0$^b$</td>
<td>−30</td>
<td>−17</td>
<td>&lt;1</td>
<td>2±2</td>
<td>60±4</td>
<td>&gt;20</td>
</tr>
</tbody>
</table>

$^a$ 30 s in, 30 s out, $^b$ not enough data to quantify positive $S$, $^c$ at eight dips

Lubricants that do spread fully over the surface topography are more resistant to depletion due to a mobile air/water interface ($S_{ls(A)} > 0$, e.g. silicone oil or PFPE on polystyrene wrinkles). These surfaces do not deplete as readily as Teflon wrinkles across twenty dips due to the lubricant remaining in a continuous layer. For these surfaces, the effect of lubricant spreading over the air/water interface is much more pronounced and is a primary driver of depletion. Both silicone oil and PFPE spread over the air/water interface and, as a result, will deplete more readily due to a film spreading mechanism onto the water surface (depending on reservoir size). The significance of lubricant spreading over the working fluid is debated in the literature. For applications where a LIS only encounter droplets, the volume of lubricant in the wetting ridge is a much greater volume than the lubricant in the cloaking layer, [68] and so the presence of a cloaking layer is not considered detrimental in terms of depletion. However, for applications in heat exchangers, the presence of a cloaking layer negatively affects performance [79]. This work suggests that, for LIS that pass through the interface of large reservoirs of fluid, a cloaking layer accelerates depletion and is undesirable.

Lubricants with $S_{ls(A)} > 0$ also face an additional depletion pathway of the lubricant spreading onto adjacent surfaces during storage. The rate of this depletion is dependent on the lubricant, the substrate and the adjacent surfaces, but can be quite rapid. PFPE on polystyrene wrinkles spreads out of the surface topography within hours, while silicone oil on polystyrene wrinkles remains after a month. Surfaces with $S_{ls(A)} < 0$ are much more robust, with silicone oil on Teflon wrinkles remaining after a full year of vertical storage.
Finally, this Chapter shows that a molecular layer of PDMS grafted to glass is resistant against degradation after repeated immersions, but cannot stabilise a lubricant layer. These surface represent an exciting new avenue for low-adhesion surfaces free from depletion.
Lubricant-infused surfaces (LIS) are a paradigm shift in the study of functional surfaces. Before their popularisation, the main tools for tuning surface functionality were modification of surface chemistry using a molecular coating or modification of surface structure. LIS present another method to modify functionality: a thin layer of liquid held on the surface. This layer allows the surface to combine the mobility of a liquid surface, with the applicability of a solid surface.

There are many applications for LIS that take advantage of their low-adhesion nature with one of the most prominent and exciting being their ability to resist biofouling. Bacteria and other fouling organisms cannot settle on the low-adhesion LIS and, as a result, further fouling is suppressed.

Unfortunately, the mobility of the liquid layer means that all LIS suffer from an inevitable degradation in properties due to depletion of the lubricant layer. Being a liquid, it is not possible to fully immobilise the lubricant, and it will deplete over time due to a variety of depleting forces including spreading onto adjacent surfaces, evaporation, shear from air or water, or movement of an air/water interface.

This Thesis examined the functionality and depletion of antifouling LIS, not only to measure their antifouling capabilities, but to also understand how different types of depletion remove lubricant from the surface. This was achieved through the development of several new characterisation methods that quantify the thickness and distribution of the lubricant present and changes in dynamic contact angles as LIS pass through the air/water interface.

Prior to this Thesis, LIS had been shown to be effective against bacterial biofouling in vitro from various marine bacteria and algae but had not been shown to be effective in a field test. Chapter 3 tests LIS (manufactured via the infusion of superhydrophobic Teflon wrinkles with silicone oil) against biofouling from a genus of common marine bacteria _Psuedoalteromanas spp._ and in a field test in the open ocean. Both of these tests showed that these surfaces are effective at resisting fouling, but that the fouling correlated with how much lubricant
was depleted from the surface. To quantify this relationship, fluorescent molecules were dispersed throughout the lubricant so that its volume could be quantified using a fluorescence intensity/volume calibration curve. This showed that these surfaces were effective against biofouling with just $0.02 \mu \text{L cm}^{-2}$ of lubricant on the surface.

The small amount of lubricant detected raised the question of just how much lubricant is needed for LIS to be effective, and how the lubricant is configured on the surface in this state. To answer this, Chapter 4 developed a method using AFM meniscus force measurements to map the lubricant thickness and distribution on the nanoscale. This allows for the local wetting of the nanostructure in the Teflon wrinkles to be imaged and understood. With this method, the thickness of the lubricant layer after shearing underwater or vertical storage is easily measured and it was found that lubricant that is not held within the surface structure quickly depletes.

This power of the algorithmic analysis of AFM force curves motivated the work in Chapter 5 where automated image analysis was used to track the dynamic contact angles that the air/water interface makes with a LIS as it is repeatedly immersed. This work is an extension of work previously undertaken in the Neto group looking at the effect of repeated immersion on superhydrophobic surfaces. The work presented in this Thesis recreated the analysis from scratch to ensure that it was suitable for LIS.

Combining in situ measurement of dynamic contact angle values with mapping of the lubricant on the nanoscale, Chapter 5 examined how lubricant is removed during passage through an air/water interface. This is particularly pertinent to LIS designed for marine antifouling applications as this is an unavoidable situation in marine settings. Chapter 5 again showed that a thick lubricant layer is not stabilised, with all samples seeing a thick layer of excess lubricant thinned to a layer which, at most, extends tens of nanometres above the highest regions of topography. This reinforces the observation that capillarity is the main force which immobilises lubricant on the surface. Retention is enhanced for lubricants with $S_{ls} > 0$ (i.e. the lubricant spreads over the substrate) as the lubricant does not dewet into droplets which are more easily removed. In the case of $S_{ls} < 0$, the spreading parameter of the lubricant over the water reservoir ($S_{lw}$) is important – lubricants with $S_{lw} > 0$ will easily deplete as the drive for spreading over the water reservoir may be sufficient to remove the lubricant from within the topography.
6.1 Future outlook

The work presented in this Thesis shows that LIS cannot sustain a thick lubricant layer. A LIS with an initially thick layer will quickly deplete down to the level where the lubricant is only held within the surface topography due to various depleting forces. Although this is unavoidable, it does not necessarily mean the LIS is unusable. Even in this depleted state, LIS can resist biofouling and have low CAH. This Thesis emphasises the argument for studying LIS under more realistic conditions and quantifying the amount of lubricant present so that results relate to expected use cases and not to an unstable configuration that exists only soon after infusion.

The work presented in this Thesis and throughout the literature has shown unequivocally that LIS have superior antifouling abilities to any other class of non-toxic surface. In this regard, the focus of research related to antifouling LIS can move past simple lab-scale proof of concepts to optimisation of specific manufacturing parameters to limit depletion and scale up production. Indeed, the first commercial product based on LIS was released in 2019 (SLIPS N1x from Adaptive Surface Technology Pty Ltd [278]). There is still a wealth of fundamental research questions related to LIS and biofouling, however, with the biological interactions of microbes and the infused layer not well understood. There is evidence of a complex interaction between LIS and microbes with the fouling level of infused surfaces depending on the species of bacteria fouling. [204] A deeper understanding of this interaction may reveal not only insight into the biofouling process but also into biology itself. Similarly, interaction of LIS with mammalian cells presents a fascinating avenue for research with cells being able to grow, but not adhere. [279]

There are still many depletion forces that require full characterisation in a similar manner to that used for the air/water interface in Chapter 5. Many forces, such as spreading from the LIS onto adjacent surfaces or evaporation are taken for granted but have been relatively neglected in favour of studying other depleting forces. Although these phenomena are not unique to LIS, the fact they are competing against a stabilising force (capillarity in the case of 2D LIS) means that the system and its behaviour is distinct to the well-understood cases. Investigation of these mechanisms will also provide insight into the inverse problem of removing liquid from 2D porous structures such as oil extraction from rock surfaces.

LIS are a unique class of material combining both liquid and solid and, as a result, existing techniques cannot fully characterise them. While this Thesis introduced new characterisation methods that allow specific aspects of LIS to be studied for the first time, they do not allow for complete characterisation of the surface. Ideally, the lubricant thickness and distribution
on 2D LIS would be able to be measured in situ at all length scales to fully characterise how lubricant depletes from the surface. For example, the dynamics of depletion events could be compared and contrasted with the order of events taken into consideration e.g. the effect of an air/water interface compared to a turbulent water flow. Such a technique would also allow for micro- and nanoscale study of foulants interacting with the lubricant layer enabling further optimisation of LIS and insights into the interactions mentioned in the previous paragraph.

Meniscus force mapping has limitations that restrict the scope of LIS that it can investigate. Two phenomena stifled study of the lubricant layer on 3D LIS. Firstly, the soft nature of the substrate means that the point between AFM tip and the substrate is not clear. Secondly, if the 3D LIS is manufactured from PDMS, the surface easily gains electrostatic charge, making it impossible to image using AFM. Additional research into sample preparation and AFM probe choice may minimise these effects and enable imaging of these substrates. This would allow answering of several key questions surrounding iPDMS such as how quickly the lubricant layer is replenished and how does overall depletion level of lubricant from the bulk effect the lubricant layer on the surface.

Finally, a lubricant layer may not be the best method to create a low-adhesion surface. Recent literature has been increasingly focused on 1D LIS, which consist of polymer chains tethered to a surface to create a liquid-like coating. [90, 93, 94, 98, 170, 172, 268, 269] These are particularly attractive as they do not suffer depletion while still having the low hysteresis seen in LIS. Chapter 5 briefly examined this class of surface and found that they cannot stabilise an additional lubricant layer, but that their low CAH is robust against repeated immersion. Due to their simple manufacture and outstanding longevity compared to a lubricant layer that can be removed, these surfaces present an exciting avenue for any application where low CAH is the goal.
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APPENDIX A

Conversion of raw force curve data

Raw force curve data must be converted from its raw form (usually \( z \)-sensor position for the \( x \)-axis and deflection in Volts for the \( y \)-axis) to separation for the \( x \)-axis and force for the \( y \)-axis. Although the analysis in Chapter 4 does not require the conversion of the \( y \)-axis to force, this Appendix describes the full process.

A1 Theory

An AFM, at its core, is a device that measures small voltage changes due to very small movements. In the case of a force curve, where the \( x \)-axis is tip-sample separation and the \( y \)-axis is force on the cantilever, these are the voltage signal from the \( z \)-displacement sensor and from the photodiode, respectively. These signals must then be converted using conversion factors (usually termed sensitivity) to their desired quantities.

Sensitivity is just a calibration between one quantity and another determined experimentally. The sensitivity that converts the voltage read by the \( z \)-sensor to displacement in nm is determined by the AFM manufacturer and is automatically applied so that \( z \)-sensor reading is already in nm. It is easy to check this conversion factor in the parameter list of an AFM file. The sensitivity of the cantilever is determined experimentally with each cantilever. It is simply the conversion factor between how much the cantilever bends for each unit Volt read by the photodiode and is simply the gradient of the the contact region when a force curve is collected on a non-deformable substrate. For a force curve collected on a non-deformable substrate, each nm of deflection in the contact region is a nm of bend on the cantilever, meaning that any change in the signal on the photodiode is due to bending of the cantilever (see Figure A.1b). This gives you a conversion factor in \( V \text{ nm}^{-1} \) that allows any deflection of the cantilever to be interpreted as the distance the cantilever has moved either up or down. This is usually termed \( \delta \).
Conversion of this deflection to a force is simply by multiplying the deflection by the cantilevers spring constant using Hook’s Law: \( F = kx \), where \( k \) is the spring constant and \( x \) is the displacement of the spring from its resting position. The spring constant is able to be determined in a number of ways, most commonly using Sader’s method. [280]

**A2 Measuring sensitivity**

As mentioned above, sensitivity is the slope of the contact region of a force curve collected on a non-deformable sample, usually sapphire or silicon wafer (see Figure A.1b). It is best to collect many force curves and take the sensitivity as an average of those as the exact gradient of the contact region tends to change slightly with each measurement. Generally, all measurements in this Thesis use a sensitivity calculated as the average of gradient of 100 measurements (10x10 map) on a clean silicon wafer. The script SensitivityCalc.py (Section C1) automatically takes this data and returns the average sensitivity, ensuring the fit region is linear.

**A3 Measuring spring constant**

There are many ways to measure spring constant. Most AFM software include a module to calculate spring constant. These usually require the sensitivity of the cantilever, its resonant frequency (measured using a thermal tune) and the dimensions of the cantilever. Refer to the AFM software manual for more information.

**A4 Conversion to force-separation**

Converting from the raw units output by the AFM, deflection (V) - position (nm) to force (N) - Separation (nm):

(i) Offset the data in the \( y \)-axis so that zero deflection (the flat portion in the non-contact region) is on the \( x \)-axis (see Figure A.1b);
(ii) Offset the data in the \( x \)-axis so that hard contact with the surface is on the \( y \)-axis;
(iii) Convert the \( y \)-axis to deflection, \( \delta \), by multiplying by the inverse of sensitivity (e.g. if sensitivity has units \( V \text{ nm}^{-1} \) and the \( y \)-axis has units of \( V \), multiply by the inverse of sensitivity to end up with nm) (see Figure A.1c);
(iv) Subtract \( \delta \) from each x-axis point. Separation (nm) = z-position - \( \delta \);
(v) Convert $y$-axis to force by multiplying by the spring constant. $F = \delta \times k$ (see Figure A.1d).

The force curve is now in Force-Separation and ready for analysis.

**Figure A.1.** a) Raw force curve data as captured by the AFM (Asylum MFP-3D). b) The same data, offset so that the hard contact point is at zero on the $x$-axis, with the baseline (over all gradient on the non-contact region) removed, zoomed in to show the contact region where the sensitivity is calculated. c) The same data as (b) with the $y$-axis converted to deflection of the cantilever in nm. d) The same data as (c) fully processed with the $x$-axis as tip-sample separation and the $y$-axis as force.
APPENDIX B

Lubricants reported in the literature
### Table B.1. Properties of the different Krytox and silicone oil lubricants used in LIS research. Properties are taken from manufacturer data sheets, MSDS or reporting reference.

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>$\rho$ / g cm$^{-3}$</th>
<th>$\gamma_{la}$ / mN m$^{-1}$</th>
<th>$\mu$ / cSt</th>
<th>Vapour Pressure / Pa</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Krytox Series</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Krytox 100</td>
<td>1.87</td>
<td>16-20</td>
<td>12.4</td>
<td>$\ldots$</td>
<td>[39, 43, 45, 52, 54, 59, 66, 68, 76, 119, 126, 135, 161, 162, 181, 182, 221, 281–291]</td>
</tr>
<tr>
<td>Krytox 101</td>
<td>1.89</td>
<td>16-20</td>
<td>17.4</td>
<td>$\ldots$</td>
<td>[74, 176, 214, 292, 293]</td>
</tr>
<tr>
<td>Krytox 102</td>
<td>1.91</td>
<td>16-20</td>
<td>38</td>
<td>$\ldots$</td>
<td>[68, 225, 294, 295]</td>
</tr>
<tr>
<td>Krytox 103</td>
<td>1.92</td>
<td>16-20</td>
<td>82</td>
<td>$\ldots$</td>
<td>[67, 72, 168, 183, 190, 215, 269, 287, 296–307]</td>
</tr>
<tr>
<td>Krytox 104</td>
<td>1.93</td>
<td>16-20</td>
<td>177</td>
<td>$\ldots$</td>
<td>[162, 197, 225, 282]</td>
</tr>
<tr>
<td>Krytox 105</td>
<td>1.94</td>
<td>16-20</td>
<td>522</td>
<td>$\ldots$</td>
<td>[72, 113, 162, 225, 287, 298, 308, 309]</td>
</tr>
<tr>
<td>Krytox 106</td>
<td>1.95</td>
<td>16-20</td>
<td>822</td>
<td>$\ldots$</td>
<td>[135, 162, 225]</td>
</tr>
<tr>
<td>Krytox 143 AZ</td>
<td>1.91</td>
<td>16-20</td>
<td>40</td>
<td>500</td>
<td>[162]</td>
</tr>
<tr>
<td>Krytox 1506</td>
<td>1.88</td>
<td>$\ldots$</td>
<td>60</td>
<td>$5 \times 10^{-5}$</td>
<td>[54, 128, 141, 217]</td>
</tr>
<tr>
<td>Krytox 1514</td>
<td>1.89</td>
<td>18</td>
<td>140</td>
<td>$2 \times 10^{-5}$</td>
<td>[135]</td>
</tr>
<tr>
<td>Krytox 16256</td>
<td>1.92</td>
<td>19</td>
<td>2560</td>
<td>$5 \times 10^{-12}$</td>
<td>[135]</td>
</tr>
<tr>
<td><strong>Silicone Oil</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 cSt</td>
<td>0.90$^b$</td>
<td>19</td>
<td>3</td>
<td>&lt;700</td>
<td>[105, 310]</td>
</tr>
<tr>
<td>5 cSt</td>
<td>0.91$^b$</td>
<td>20</td>
<td>5</td>
<td>&lt;700</td>
<td>[115, 169, 208, 286, 290, 311–314]</td>
</tr>
<tr>
<td>10 cSt</td>
<td>0.93$^b$</td>
<td>20</td>
<td>10</td>
<td>&lt;700</td>
<td>[1–3, 60, 65, 68, 75, 105, 160, 163, 169, 173, 202, 239, 315–319]</td>
</tr>
<tr>
<td>20 cSt</td>
<td>0.94$^b$</td>
<td>21</td>
<td>20</td>
<td>&lt;700</td>
<td>[68, 148, 166, 173, 192, 304, 311, 320–324]</td>
</tr>
<tr>
<td>40 cSt</td>
<td>0.95$^b$</td>
<td>21</td>
<td>40</td>
<td>&lt;700</td>
<td>[68, 84, 325]</td>
</tr>
<tr>
<td>50 cSt</td>
<td>0.96$^b$</td>
<td>21</td>
<td>50</td>
<td>&lt;700</td>
<td>[68, 169, 180, 207, 311, 326–328]</td>
</tr>
<tr>
<td>100 cSt</td>
<td>0.97$^b$</td>
<td>21</td>
<td>100</td>
<td>&lt;700</td>
<td>[109, 148, 174, 186, 286, 290, 311, 321, 324, 326, 329–334]</td>
</tr>
<tr>
<td>350 cSt</td>
<td>0.97$^b$</td>
<td>21</td>
<td>350</td>
<td>&lt;700</td>
<td>[3, 120, 178, 187, 318, 335–340]</td>
</tr>
<tr>
<td>500 cSt</td>
<td>0.97$^b$</td>
<td>21</td>
<td>500</td>
<td>&lt;700</td>
<td>[173, 318, 326, 333, 334, 341, 342]</td>
</tr>
<tr>
<td>1,000 cSt</td>
<td>0.97$^b$</td>
<td>21</td>
<td>100</td>
<td>&lt;700</td>
<td>[75, 201, 286, 290, 324, 333, 334]</td>
</tr>
<tr>
<td>10,000 cSt</td>
<td>0.97$^b$</td>
<td>22</td>
<td>10,000</td>
<td>&lt;700</td>
<td>[3, 324]</td>
</tr>
<tr>
<td>20,000 cSt</td>
<td>0.97$^b$</td>
<td>22</td>
<td>20,000</td>
<td>&lt;700</td>
<td>[3]</td>
</tr>
</tbody>
</table>

$^a$ at 20 °C, unless specified otherwise, $^b$ 25 °C, $^c$ unavailable
Table B.2. Reported lubricants used in LIS research and their properties (other than Krytox and silicone oil lubricants). Properties are taken from manufacturer data sheets, MSDS or reporting reference.

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>$\rho$ / $g \cdot cm^{-3}$</th>
<th>$\gamma_{la}$ / $mN \cdot m^{-1}$</th>
<th>$\mu$ / cSt</th>
<th>Vapour Pressure / Pa</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Perfluorinated Compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FC-43</td>
<td>1.86</td>
<td>16</td>
<td>2.5</td>
<td>192</td>
<td>[293, 343]</td>
</tr>
<tr>
<td>FC-70</td>
<td>1.84</td>
<td>18</td>
<td>12</td>
<td>15</td>
<td>[71, 120, 143, 179, 282, 344, 345]</td>
</tr>
<tr>
<td>Fomblin Y</td>
<td>1.88-1.90</td>
<td>21-22</td>
<td>38-470</td>
<td>$8 \times 10^{-6}$</td>
<td>[121, 198, 199, 216, 346–348]</td>
</tr>
<tr>
<td>Fomblin YR</td>
<td>1.91</td>
<td>24</td>
<td>1200</td>
<td>$2 \times 10^{-4}$</td>
<td>[44, 349, 350]</td>
</tr>
<tr>
<td>Perfluorodecalin</td>
<td>1.92</td>
<td>17.6</td>
<td>5.1</td>
<td>880</td>
<td>[80, 183, 203, 318]</td>
</tr>
<tr>
<td>Perfluorooctylsiloxane (Vitrex)</td>
<td>203</td>
<td>19</td>
<td>28.2</td>
<td>&lt;100</td>
<td>[81, 203, 318, 351, 352]</td>
</tr>
<tr>
<td>Unspecified PFPE</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[49, 50, 223, 353–357]</td>
</tr>
<tr>
<td><strong>Silicone compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetramethyldiphenyletrisiloxane (DC-704)</td>
<td>1.07</td>
<td>37</td>
<td>38</td>
<td>&lt;0.1</td>
<td>[47]</td>
</tr>
<tr>
<td>Decamethylocyclopentasiloxane (D5)</td>
<td>0.96</td>
<td>19$^b$</td>
<td>4</td>
<td>20$^b$</td>
<td>[120]</td>
</tr>
<tr>
<td>Unspecified Silicone Oil</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td><strong>Ionic liquids</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>1.44</td>
<td>33</td>
<td>50</td>
<td>&lt;0.01</td>
<td>[63, 71, 142–144, 147]</td>
</tr>
<tr>
<td>1-octyl-3-methylimidazolium hexafluorophosphate</td>
<td>1.30</td>
<td>33</td>
<td>34</td>
<td>&lt;0.006</td>
<td>[147]</td>
</tr>
<tr>
<td>1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>1.53</td>
<td>35</td>
<td>35</td>
<td>-</td>
<td>[144, 145]</td>
</tr>
<tr>
<td>1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
<td>1.37</td>
<td>55</td>
<td>31</td>
<td>-</td>
<td>[144]</td>
</tr>
<tr>
<td><strong>Plant Oils</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Canola Oil</td>
<td>0.91</td>
<td>32</td>
<td>78</td>
<td>&lt;13</td>
<td>[136, 366]</td>
</tr>
<tr>
<td>Coconut Oil</td>
<td>0.92</td>
<td>18</td>
<td>23</td>
<td>-</td>
<td>[136]</td>
</tr>
<tr>
<td>Olive Oil</td>
<td>0.91</td>
<td>32</td>
<td>75</td>
<td>-</td>
<td>[119, 366]</td>
</tr>
<tr>
<td>Almond Oil</td>
<td>0.92</td>
<td>-$^f$</td>
<td>-$^f$</td>
<td>-$^f$</td>
<td></td>
</tr>
<tr>
<td>Carnation Oil</td>
<td>0.92</td>
<td>-$^f$</td>
<td>-$^f$</td>
<td>-$^f$</td>
<td>[135]</td>
</tr>
<tr>
<td>Cocoa Oil</td>
<td>0.92</td>
<td>-$^f$</td>
<td>-$^f$</td>
<td>-$^f$</td>
<td>[219]</td>
</tr>
<tr>
<td>Cottonseed Oil</td>
<td>0.92</td>
<td>35</td>
<td>73</td>
<td>-</td>
<td>[111]</td>
</tr>
<tr>
<td>Soybean Oil</td>
<td>0.92</td>
<td>34</td>
<td>59</td>
<td>-</td>
<td>[202]</td>
</tr>
<tr>
<td><strong>Other lubricants</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>0.85</td>
<td>30</td>
<td>10, 68</td>
<td>&lt;1</td>
<td>[67, 137, 163, 176, 202, 218, 304]</td>
</tr>
<tr>
<td>Decanol</td>
<td>0.83</td>
<td>29</td>
<td>12$^b$</td>
<td>1</td>
<td>[71]</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>1.12</td>
<td>48</td>
<td>16.9$^b$</td>
<td>8</td>
<td>[48, 120, 139]</td>
</tr>
<tr>
<td>Triethylene Glycol</td>
<td>1.13</td>
<td>46</td>
<td>49$^b$</td>
<td>&lt;1</td>
<td>[139]</td>
</tr>
<tr>
<td>85% Glycerol</td>
<td>1.23</td>
<td>65</td>
<td>1300</td>
<td>900</td>
<td>[120]</td>
</tr>
<tr>
<td>Kerosene</td>
<td>0.80</td>
<td>23-32</td>
<td>1.64$^b$</td>
<td>282</td>
<td>[179]</td>
</tr>
<tr>
<td>Motor Oil</td>
<td>-$^e$</td>
<td>-$^e$</td>
<td>-$^e$</td>
<td>-$^e$</td>
<td></td>
</tr>
<tr>
<td>Oleic Acid</td>
<td>0.90</td>
<td>33</td>
<td>27.64$^b$</td>
<td>8</td>
<td>[87, 114, 139, 367]</td>
</tr>
<tr>
<td>Methyl Oleate</td>
<td>0.87</td>
<td>29$^b$</td>
<td>6.39</td>
<td>$5.4 \times 10^{-16}$</td>
<td>[114]</td>
</tr>
<tr>
<td>Ethyl Oleate</td>
<td>0.87</td>
<td>28</td>
<td>6.9</td>
<td>$4 \times 10^{-16}$</td>
<td>[140, 200, 305]</td>
</tr>
<tr>
<td>Ferrofluid</td>
<td>-$^e$</td>
<td>-$^e$</td>
<td>-$^e$</td>
<td>-$^e$</td>
<td>[368–371]</td>
</tr>
<tr>
<td>Paraffin Wax</td>
<td>0.90</td>
<td>30</td>
<td>-$^d$</td>
<td>-$^d$</td>
<td>[220, 305, 362, 372–376]</td>
</tr>
<tr>
<td>Thermotropic Liquid Crystal</td>
<td>-$^f$</td>
<td>-$^f$</td>
<td>-$^f$</td>
<td>-$^f$</td>
<td>[136]</td>
</tr>
<tr>
<td>Water</td>
<td>1</td>
<td>72</td>
<td>1</td>
<td>2339</td>
<td>[36, 74, 100, 119–121, 123, 225]</td>
</tr>
</tbody>
</table>

$^a$ at 20 °C, unless specified otherwise, $^b$ at 25 °C, $^c$ properties vary with sample as plant oils are variable mixtures, $^d$ solid at 20 °C, $^e$ varies, $^f$ unavailable
APPENDIX C

Python scripts

C1 - SensitivityCalc.py
C2 - MeniscusForceMapProcessing.py
C3 - RemoveNANModule.py
C4 - DipCoatCA.py
C1 SensitivityCalc.py

```python
# coding: utf-8

Created on Thu Jan 24 09:50:36 2019
@author: Sam Peppou-Chapman

#Script to automatically calculate sensitivity from force curves on
#some incompressible substrate
#force curves must be in their own folder
#Takes in deflection data (in volts) and zsensor data (in nm) to give sensitivity in nm/V

import numpy as np
import scipy.stats
import os.path
import glob
import csv

def main():

    #Variables that need to be changed ######

    DataPath = r'F:\Temp for export\BareSi01'
    #DataPath is the folder that contains the Ascii
    #force curves (from Asylum)
    #Don't remove the 'r' at the front

    #End variables that need to be changed ######

    DataPath.replace(\\, '/')  #sanatise path if it is on windows
    DataPath = DataPath + '/'

    SavePath = DataPath + 'Sensitivity.csv'

    InitialiseSaveFile(SavePath)
    ExtendSens = []
    RetractSens = []

    for Xfilename in glob.glob(os.path.join(DataPath, '*ZSnsr.txt')):
        #load the x-data for the first file
        currentFileName = os.path.basename(Xfilename)
        currentFileName = currentFileName.replace('ZSnsr.txt','')
```
print(currentFileName)

# build the file path for the Y data
Yfilename = DataPath + currentFileName + ‘DeflV.txt’

# load the data
currentFileX = np.loadtxt(Xfilename)
currentFileY = np.loadtxt(Yfilename)

# find the contact region for both extend and retract by first separating
# extend and retract and then deleting everything that isn't contact region
maxIndex = np.argmax(currentFileY)
retractDeleteArray = np.arange(maxIndex, len(currentFileY))  # all indexes after the max
extendDeleteArray = np.arange(0, maxIndex)  # all indexes before the max

# separate out extend and retract
ExtendX = np.delete(currentFileX, extendDeleteArray)
ExtendY = np.delete(currentFileY, extendDeleteArray)
RetractX = np.delete(currentFileX, retractDeleteArray)
RetractY = np.delete(currentFileY, retractDeleteArray)

ExtendMin = np.argmin(ExtendY)
RetractMin = np.argmin(RetractY)

# generate the array to delete everything that isn't the contact region
ContactExtendDeleteArray = np.arange(ExtendMin, len(ExtendY))
ContactRetractDeleteArray = np.arange(0, RetractMin)

# extract the contact region
ContactExtendX = np.delete(ExtendX, ContactExtendDeleteArray)
ContactExtendY = np.delete(ExtendY, ContactExtendDeleteArray)
ContactRetractX = np.delete(RetractX, ContactRetractDeleteArray)
ContactRetractY = np.delete(RetractY, ContactRetractDeleteArray)

# fit a line to the contact regions, moving closer and closer to the middle
# until the residual is small enough
ExtendCoeffs = scipy.stats.linregress(ContactExtendX, ContactExtendY)
RetractCoeffs = scipy.stats.linregress(ContactRetractX, ContactRetractY)

while ExtendCoeffs[2]**2 < 0.99:
    # 20190227 Commented out these deletions so that all deletions are from
    # turnaround point toward the contact point to get rid of non-linear effects
    # ContactExtendX = np.delete(ContactExtendX, [len(ContactExtendX) - 1])
    ContactExtendX = np.delete(ContactExtendX, [0])
    # ContactExtendY = np.delete(ContactExtendY, [len(ContactExtendY) - 1])
    ContactExtendY = np.delete(ContactExtendY, [0])

    ExtendCoeffs = scipy.stats.linregress(ContactExtendX, ContactExtendY)
while RetractCoeffs[2]**2 < 0.9:
    ContactRetractX = np.delete(ContactRetractX, [len(ContactRetractX)-1])
    ContactRetractY = np.delete(ContactRetractY, [len(ContactRetractY)-1])
    RetractCoeffs = scipy.stats.linregress(ContactRetractX, ContactRetractY)

    ExtendSens.append(1/ExtendCoeffs[0])
    RetractSens.append(1/RetractCoeffs[0])

    WriteFile(SavePath, currentFileName, 1/ExtendCoeffs[0], 1/RetractCoeffs[0])

    AvExSens = np.mean(ExtendSens)
    AvRetSens = np.mean(RetractSens)

    WriteFile(SavePath, '', '', '')
    WriteFile(SavePath, 'Average:', AvExSens, AvRetSens)

    print("""
    print("Extend Sensitivity: " + str(AvExSens) + " m/V")
    print("Retract Sensitivity: " + str(AvRetSens) + " m/V")

    def InitialiseSaveFile(path):
        #initialises the save file so that there is somewhere to save
        with open(path, 'w') as csvfile:
            savewriter = csv.writer(csvfile, delimiter=','
                                   quotechar='|', quoting=csv.QUOTE_MINIMAL, lineterminator='
')
            savewriter.writerow(['File', 'Extend Sensitivity (m/V)', 'Retract Sensitivity (m/V)'])

        return()

    def WriteFile(path, filename, ExtendSens, RetractSens):
        #adds a row to the .csv save file
        with open(path, 'a') as csvfile:
            savewriter = csv.writer(csvfile, delimiter=' ',
                                     quoting=csv.QUOTE_MINIMAL, lineterminator='
')
            savewriter.writerow([filename, ExtendSens, RetractSens])

        return()

main()
This script is used calculate the thickness of oil from raw force map data obtained on an Asylum AFM. The script needs a folder with the data output by the Asylum software using AsciiExportForce() (I suggest looping through your forcemap using RunSHOandPFM() and then running AsciiExportForce("*","*","*"). Be careful though, this will export all force curves in memory so make sure you only load the forcemap you are interested in exporting; UPDATE: Asylum have implemented AsciiExportARDF() which will export the ARDF automatically and quickly.)

It will then output to a .csv in the same directory. You set the name of the file in the variable declaration below. The script also needs the sensitivity of your probe (ie the deflection due to the deformation of the cantilever). I usually calculate it from some force curves on Si Wafer before I do my force map. The units don’t really matter, just as long as they are consistent.

The basic idea of the script is it looks for the point where the curve goes down at the start of the oil layer and the point where it goes up when it makes contact with the substrate. It does this by looking at the difference between adjacent points and then defining the jump in and hard contact as the points that are above a certain threshold. It is pretty much looking for changes in the derivative. The threshold is defined as the average difference between the first 100 points + n standard deviations (n can be changed depending on the data, I usually use 7–15). If you are having trouble with the script, I would change this first— the amount of inherent noise in your signal will influence the threshold and hence how well the script works. The script should spit out ‘NAN’ whenever something goes wrong, but I haven’t tested it exhaustively.

```

import numpy as np
import csv
import matplotlib.pyplot as plt
import os.path
from scipy import stats
import datetime
from scipy.signal import savgol_filter
import RemoveNAN_module as RemoveNAN

##### Variables that need to be changed #####

DataPath = [  
    'F:\Temp for export\File1',  
    'F:\Temp for export\File2',  
    'F:\Temp for export\File3'  
]
```
#DataPath is the folder that contains the Ascii force curves (from Asylum)
#Don't remove the 'r' at the front

ExportDir = r"F:\Temp for export\AFM output"
#path for the summaries to be saved

Sensitivity = 2.53E-07 #m/V

Resolution = [64,64,64,64,64,64,64,64,64,64,64]
#Resolution is the number of pixels in the image
#(has to be less than 1000 or script wont work)

SideLength = [10,4,2,1,0.5]
#scan size in micrometers

iPDMS_bottom_algorithm = False
#If true, script will use minimum point as bottom of lubricant layer,
#else will use change in derivative

Water_top_algorithm = False

Water_bottom_algorithm = True
#if true will use algorithm that works better for samples underwater

KeepN = 1
#delete all but every Nth data point.
#Useful if your force data is too high resolution.
#Set to 1 if you dont want to delete anything

Plot = False
#If true will plot every force curve

SavePlot = False
#if true will save every plot force curve

##### End varaibles that need to be changed ######

def main(DataPath, Sensitivity, Resolution, SideLength):

nThresh = 7

BaseName = os.path.basename(DataPath)

DataPath.replace('\\', '/') #sanatise path if it is on windows

DataPath = DataPath + '/'

date = datetime.datetime.today().strftime('%Y-%m-%d')

#build the save name
SavePath = ExportDir + '/'+ BaseName + "_summary_" + date + "_.csv"

print(SavePath)
InitialiseSaveFile(SavePath)
NumNAN = 0

x_ind_save = [] #initialise variables that will store the data before the save
y_ind_save = []
x_loc_save = []
y_loc_save = []
thick_save = []
btm_out_save =[]
tic = datetime.datetime.now() #start a timer

for i in range(0, Resolution):
    for j in range(0, Resolution):
        CurrentFileX = ImportDataX(i,j,DataPath) # import data
        CurrentFileY = ImportDataY(i,j,DataPath)

        if KeepN > 1:
            CurrentFileX = KeepEveryN(CurrentFileX ,KeepN)
            CurrentFileY = KeepEveryN(CurrentFileY ,KeepN)

        #CurrentFileY = RemoveBaseline(CurrentFileX ,CurrentFileY)

        ExtendXNoOff , ExtendYNoOff = ExtractExtend(CurrentFileX ,CurrentFileY)

        #offset y-axis
        ExtendY = RemoveBaseline(ExtendXNoOff ,ExtendYNoOff)

        #offset x-axis
        XOffset = np.full(len(ExtendXNoOff), ExtendXNoOff[np.argmin(ExtendYNoOff)])[0]
        ExtendX = ExtendXNoOff — XOffset
        #ExtendY = ExtendYNoOff

        XSep = ConvertToSep(ExtendX, ExtendY, Sensitivity) #convert x to separation

        #offset x-axis
        XOffset = np.full(len(XSep), XSep[np.argmin(ExtendYNoOff)])[0]
        XSep = XSep — XOffset

        ExtendY = ExtendY*Sensitivity #convert y axis to m

        ### Find thickness ###
Threshold = FindThreshold(ExtendY, nThresh, 8)

if Water_top_algorithm == True:
    TopIndex = FindTopUnderwater(ExtendY)
else:
    TopIndex = FindTop(ExtendY, Threshold)

if iPDMS_bottom_algorithm == True:
    BottomIndex = FindBottomiPDMS(ExtendY, TopIndex)
elif Water_bottom_algorithm == True:
    BottomIndex = FindBottomUnderwater(ExtendY)
else:
    BottomIndex = FindBottom(ExtendY, TopIndex, Threshold)

XSep = ConvertToSep(ExtendX, ExtendY, Sensitivity)  # convert x to separation

# offset x-axis
if BottomIndex == 'NAN':
    XOffset = np.full(np.count_nonzero(XSep), XSep[np.argmin(ExtendYNoOff)])
else:
    XOffset = np.full(np.count_nonzero(XSep), XSep[BottomIndex])

XSep = XSep - XOffset

# make sure the program found the top and bottom
if TopIndex != str('NAN') and BottomIndex != str('NAN'):
    Top = XSep[TopIndex]
    Bottom = XSep[BottomIndex]
    BottomOut = ExtendXNoOff[BottomIndex]
    if BottomIndex < TopIndex:  # make sure that the bottom is below the top
        Thickness = 'NAN'
    else:
        Thickness = Bottom - Top  # calculate the thickness

elif TopIndex == str('NAN'):
    if BottomIndex == str('NAN'):  # check so see if there is a bottom index
        Thickness = 'NAN'
        Top = 'NAN'
        Bottom = 'NAN'
        BottomOut = 'NAN'
    else:
        Thickness = 'NAN'
        Top = 'NAN'
        Bottom = XSep[BottomIndex]
        BottomOut = ExtendXNoOff[BottomIndex]
else:
    Thickness = 'NAN'
    Top = 'NAN'
    Bottom = 'NAN'
BottomOut = 'NAN'

### Plot ###

PlotThisOne = False

if i*resolution+j%100 == 0:
    PlotThisOne=True
if Thickness == 'NAN':
    PlotThisOne = True

if Plot == True or SavePlot == True or PlotThisOne == True:
    plt.scatter(XSep−1e9,ExtendY*1e9)

    #plt.plot(RetraXXo−1e9,RetraXX*1e9)
    plt.xlabel('Separation (nm)')
    plt.ylabel('Deflection (nm)')
    #plt.xlim((−20,20))
    #plt.ylim((−1,0.5))
    plt.autoscale(enable=True)

if TopIndex != 'NAN':
    plt.axvline(XSep[TopIndex]*−1e9)
if BottomIndex != 'NAN':
    plt.axvline(XSep[BottomIndex]*−1e9, color = 'r')
    #plt.axvline(XSep[FindBottom(ExtendY,TopIndex,Threshold)]*−1e9, color = 'y')

SavePathPlot = DataPath + "Line" + GenNum(i) + "Point" + GenNum(j) + ".png"

if SavePlot == True:
    SaveFolder = ExportDir + '/' + BaseName + "ForceCurves" + date + '/'
    try:
        os.mkdir(SaveFolder)
    except OSError:
        pass
    SavePathPlot = SaveFolder + "Line" + GenNum(i) + "Point" + GenNum(j) + ".png"
    plt.savefig(SavePathPlot)
plt.close()

if Plot == True or PlotThisOne == True:
    plt.show()
plt.close()

if Thickness == 'NAN':
    NumNAN += 1
    print(" NaNs: " + str(NumNAN) + " out of " + str(i*resolution+j), end='')
elif int((i/Resolution)*100)%10 == 0 and j == 0:
    print("% done ", end='')
    if i != 0:
        toc = datetime.datetime.now()
elapsed = toc - tic  # seconds
FinishTime = tic + elapsed/Resolution/i
print("'Estimated completion time: ' + str(FinishTime.strftime('%H:%M'))

if i == 2 and j == 0:
toc = datetime.datetime.now()
elapsed = toc - tic  # seconds
FinishTime = tic + elapsed/Resolution/2

print("n' + 'Estimated completion time: ' + str(FinishTime.strftime('%H:%M')))  

#calculate where you are in the image
xLocation = (SideLength/(Resolution-1))*i
yLocation = (SideLength/(Resolution-1))*j

x_ind_save.append(i)
y_ind_save.append(j)
x_loc_save.append(xLocation)
y_loc_save.append(yLocation)
thick_save.append(Thickness)
btm_out_save.append(BottomOut)

#save the data
print('Starting save')
WriteFile(SavePath,x_ind_save,y_ind_save,thick_save,btm_out_save,x_loc_save,y_loc_save)
print('Done!')

if NumNAN > 0:  # remove NaNs if they are there
    print("nRemoving NaNs")
    RemoveNAN.Remove_NAN(SavePath)

return()

def KeepEveryN(data,N):
    newLen = int(round(len(data)/N))
    trimmedData = np.zeros(newLen)
    for i in range(0,newLen*N):
        if i%N == 0:
            trimmedData[int(i/N)] = data[i]
    return(trimmedData)

def RemoveBaseline(X,Y):
    Partition = int(0.2*len(X))
    m, c, r_value, p_value, std_err = stats.linregress(X[:Partition],Y[:Partition])
    baseline = X*m+c
    OffsetY = Y - baseline
def ImportDataX(Line, Point, Path): # imports x data (z-sensor)
    LineNum = GenNum(Line)  # Needs to give num in the format '000X' or '00XX' etc.
    PointNum = GenNum(Point)  # Needs to give num in the format '000X' or '00XX' etc.
    # import Zsnr data
    FileNameZsnr = Path + "Line" + str(LineNum) + "Point" + str(PointNum) + "ZSnsr" + ".txt"
    CurrentFileX = np.loadtxt(FileNameZsnr)  # read the data into file
    return(CurrentFileX)

def ImportDataY(Line, Point, Path): # imports y data (deflection)
    LineNum = GenNum(Line)  # Needs to give num in the format '000X' or '00XX' etc.
    PointNum = GenNum(Point)  # Needs to give num in the format '000X' or '00XX' etc.
    # import Defl data
    FileNameDefl = Path + "Line" + str(LineNum) + "Point" + str(PointNum) + "DeflV" + ".txt"
    CurrentFileY = np.loadtxt(FileNameDefl)  # read the data into file
    return(CurrentFileY)

def GenNum(Number):
    # make a string that is the right number to be used with the file name
    # only works for force maps resolution less than 1000x1000
    OutNum = 0
    if Number < 10:
        OutNum = "000" + str(Number)
    elif Number < 100:
        OutNum = "00" + str(Number)
    elif Number < 1000:
        OutNum = "0" + str(Number)
    return(OutNum)

def ExtractExtend(XData, YData): # delete the retraction portion of the curve
    index = FindDeleteArray(YData)  # find what needs to be deleted
    OutputX = np.delete(XData, index)
    OutputY = np.delete(YData, index)
    return(OutputX, OutputY)

def ExtractRetract(XData, YData): # delete the retraction portion of the curve
    index = FindDeleteArrayRet(YData)  # find what needs to be deleted
    OutputX = np.delete(XData, index)
    OutputY = np.delete(YData, index)
```python
return(OutputX, OutputY)

def FindDeleteArrayRet(Data):
    MaxIndex = np.argmax(Data)  # find index of maximum number (i.e the turnaround point)
    index = np.arange(0, MaxIndex)
    return(index)

def FindDeleteArray(Data):
    # returns an array of all the positions to delete (all numbers that aren't extension)
    MaxIndex = np.argmax(Data)  # find index of maximum number (i.e the turnaround point)
    MaxNum = np.count_nonzero(Data)
    index = np.arange(MaxIndex, MaxNum)
    return(index)

def ConvertToSep(CurrentFileX, CurrentFileY, sensitivity):
    # converts the data to separation
    MaxNum = np.count_nonzero(CurrentFileX)
    delta = np.empty(MaxNum)  # make empty arrays ready to calculate delta and output
    output = np.empty(MaxNum)
    delta = CurrentFileY * (sensitivity)  # calculate the delta
    output = CurrentFileX - delta
    return(output)

def FindTop(data, threshold):
    # find the index of the point the corresponds to the start of the jump in
    MaxNum = np.count_nonzero(data) - 5
    diff = 0
    counter = 10
    counter1 = 0
    output = 'NAN'
    while diff < threshold:
        # loop through data until a difference is larger than the threshold
        counter1 = counter + 1
        diff = data[counter] - data[counter1]  # find a negative difference
        if counter < MaxNum:
            counter += 1
            output = counter - 1
        else:
            diff = 10  # make diff large to exit loop
            output = 'NAN'
    return(output)

def FindTopUnderwater(data):
    # find the index of the point the corresponds to the start of the jump in
```
# smooth the data
```
data = savgol_filter(data, 131, 2)
data = savgol_filter(data, 71, 2)
data = savgol_filter(data, 51, 2)
data = np.diff(data)
data = savgol_filter(data, 101, 2)
```

```python
# plt.plot(np.flip(data))
# plt.show()
```

threshold = FindThreshold(data, 15, 15)

MaxNum = np.count_nonzero(data) - 10
diff = 0

```
counter = 10
counter1 = 0
output = 'NAN'
```

```python
while diff < threshold:
    # loop through data until a difference is larger than the threshold
    counter1 = counter + 1
diff = abs(data[counter] - data[counter1])  # find a negative difference
    if counter < MaxNum:
        counter += 1
        output = counter - 1
    else:
        diff = 10  # make diff large to exit loop
        output = 'NAN'
```

```
return(output)
```

```python
def FindBottomUnderwater(data):
    # returns the index of the bottom for underwater (goes backwards from the turnaround point)
    # assumes that the data is extend only
    Threshold = FindThreshold(data, 2, 5)
data = np.flip(data)
```

```python
for i in range(5, len(data) - 5):
diff = abs(data[i] - data[i + 1])
if diff < Threshold:
    BottomIndex = len(data) - i + 2
    break
if i == len(data) - 10:
    BottomIndex = 'NAN'
```

```
return(BottomIndex)
```

```python
def FindBottomiPDMS(data, TopIndex):
    # returns the index of the bottom of the lubricant layer for PDMS (the minimum value)
```
AvY = savgol_filter(data, 51, 5)

if TopIndex != 'NAN':
    AvYDelArray = np.arange(0, TopIndex)  # delete everything before the top index
    AvY = np.delete(AvY, AvYDelArray)
    BottomIndex = TopIndex + np.argmin(AvY)
else:
    BottomIndex = np.argmin(AvY)

return(BottomIndex)

def FindBottom(data, TopIndex, threshold):
    # finds the index of the point that corresponds to the hard contact with the substrate surface
    MaxNum = np.count_nonzero(data) - 3
    diff = 0
    if TopIndex == 'NAN':
        counter = 1
    else:
        counter = TopIndex
    while diff < threshold:
        # loop through data until a difference is larger than the threshold
        if counter < MaxNum:
            diff = data[counter + 1] - data[counter]  # find a positive difference
            counter += 1
            output = counter
        else:
            diff = 10  # make diff large to exit loop
            output = 'NAN'
    return(output)

def FindThreshold(data, nThresh, percent):
    # finds a relevant threshold based on the first 100 data points
    counter = 0
    diff = []
    if np.count_nonzero(data) <= 100:  # ensure there is enough data to find a threshold
        threshold = 1e-6  # if not, set it to something large to ensure that the output is NAN
    else:
        for counter in range(0, int(percent * 0.01 * len(data))):
            # populate an array with the difference between adjacent data points
            counter1 = counter + 1
            diff.append(abs(data[counter1] - data[counter]))
        average = np.mean(diff)
        std = np.std(diff)
        threshold = abs(average + nThresh * std)
    return(threshold)
def InitialiseSaveFile(path):
    #initialises the save file so that there is somewhere to save
    with open(path, 'w') as csvfile:
        savewriter = csv.writer(csvfile, delimiter=',',
        quotechar='|', quoting=csv.QUOTE_MINIMAL, lineterminator='
')
        savewriter.writerow(['x', 'y', 'x (um)', 'y (um)',
            'height (nm)', 'thickness (nm)',
            'sum (nm)', 'thickness (m)', 'sum (m)'])

    return()

def WriteFile(path, x, y, z, Bottom, xLoc, yLoc):
    #adds a row to the .csv save file
    with open(path, 'a') as csvfile:
        savewriter = csv.writer(csvfile, delimiter=',',
        quotechar='|', quoting=csv.QUOTE_MINIMAL, lineterminator='
')
        for i in range(0, len(x)):
            # do some conversions so that the output has both nm an m
            if Bottom[i] == 'NAN' or z[i] == 'NAN':  #make sure you only add numbers
                if Bottom[i] == 'NAN':
                    BottomOut = 'NAN'
                else:
                    BottomOut = -Bottom[i]*1E9
                    Sum = 'NAN'
                    Znm = 'NAN'
            else:
                BottomOut = -Bottom[i]*1E9  #multiply by -1 to flip over
                Sum = (-Bottom[i] + z[i])
                Znm = z[i]*1E9

            savewriter.writerow([x[i], y[i], xLoc[i], yLoc[i],
                BottomOut, Znm, Sum, z[i], Sum])

    return()

for path, resolution, side in zip(DataPath, Resolution, SideLength):
    #loop through all the files
    main(path, Sensitivity, resolution, side)

C2 MENISCUSFORCEMAPPROCESSING.py
Module that will remove any NANS from the output of the meniscus force mapping analysis script. This module will first interpolate any NANS that have 8 non-NAN neighbours, then 7, then 6 etc. until all are gone.

This file needs to be in the same directory as the analysis script for the analysis script to work properly.

```python
import numpy as np
import os.path
import math
import csv

def Remove_NAN(path):
    path.replace('\\', '/')
    print('path: ' + str(path))
    basepath, basename = os.path.split(path)
    savename = basename
    savename = savename.replace('.csv', '_No_NAN.csv')
    savepath = basepath + '/' + savename
    print(savepath)
    if os.path.isfile(path) == True:
        # Import Data
        dataForSave = np.genfromtxt(path, delimiter=',', skip_header=1, usecols=(0, 1, 2, 3, 4, 4, 6, 7, 8))
        dataHeight = np.genfromtxt(path, delimiter=',', skip_header=1, usecols=(0, 1, 4))
        dataThickness = np.genfromtxt(path, delimiter=',', skip_header=1, usecols=(0, 1, 5))
        ThicknesNoNAN = RemoveNAN(dataThickness)
        HeightNoNAN = RemoveNAN(dataHeight)
        InitialiseSaveFile(savepath)
```
```python
print("Starting Save")

with open(savepath , 'a') as csvfile:
    savewriter = csv.writer(csvfile, delimiter=',', quotechar='|',
    quoting=csv.QUOTE_MINIMAL, lineterminator='\n')
    for k in range(0, len(dataForSave)):
        Sum = (HeightNoNAN[:,2][k] + ThicknesNoNAN[:,2][k])
        Sumnm = Sum * 1e-9
        Znm = ThicknesNoNAN[:,2][k] * 1e-9
        savewriter.writerow([dataForSave[:,0][k],dataForSave[:,1][k],
                             dataForSave[:,2][k],dataForSave[:,3][k],
                             HeightNoNAN[:,2][k],ThicknesNoNAN[:,2][k],
                             Sum, Znm, Sumnm])

print("Done!")

# Functions

def FindNAN(data):
    NANx = []
    NANy = []
    NAN_ind = []
    for i in range(0,len(data[:,2])):
        if math.isnan(data[:,2][i]) == True:
            NANx.append(data[:,0][i])
            NANy.append(data[:,1][i])
            NAN_ind.append(i)
    return(NANx,NANy,NAN_ind)

def AdjNAN(data,x,y): #function to calculate the number of adjoining NANS
    NumNAN = 0
    for i in range(int(x)-1,int(x)+2):
        for j in range(int(y)-1,int(y)+2):
            if not(i == x and j == y):
                ifInRange(i,j,data):
                    #print("NumNAN: " + str(NumNAN) + " i: " +str(i)+" j: " + str(j))
                    if math.isnan(get_z(data,i,j)) == True:
                        NumNAN += 1
    return(NumNAN)

def AverageNAN(data,x,y): #function to average NAN to adjacent values
```
values = []
for i in range(int(x)−1,int(x)+2):
    for j in range(int(y)−1,int(y)+2):
        if not(i == x and j == y):
            if InRange(i,j,data):
                if math.isnan(get_z(data,i,j)) == False:
                    values.append(get_z(data,i,j))

return(np.mean(values))

def InRange(i,j,data): #Check to see if index in range of data
    length = len(np.unique(data[:,1]))−1
    if i < 0 or j < 0:
        return False
    elif i > length or j > length:
        return False
    else:
        return True

    # I'm fairly sure there's a more efficient way of doing this...
def get_z(mat, x, y):
    ind = (mat[:,0,1] == (x,y)).all(axis=1)
    row = mat[ind,:]  
    return row[0,2]

def RemoveNAN(data):
    NANx, NANy, NAN_ind = FindNAN(data)
    NumNAN = len(NANx)
    print("# of NANs: " + str(NumNAN))
    MaxAdj = 0
    while NumNAN > 0:
        for i in range(0,MaxAdj+1):
            for j in range(0,NumNAN):
                if AdjNAN(data,NANx[j],NANy[j]) <= MaxAdj:
                    data[:,2][NAN_ind[j]] = AverageNAN(data,NANx[j],NANy[j])
                    #print("fixed " + str(NANx[j]) +" +str(NANy[j]))
                    #print(data[NAN_ind[j]])
                    MaxAdj += 1
        NANx, NANy, NAN_ind = FindNAN(data)
        NumNAN = len(NANx)
        print("# of NANs: " + str(NumNAN))

    return(data)
def InitialiseSaveFile(path):
    # initialises the save file so that there is somewhere to save
    with open(path, 'w') as csvfile:
        savewriter = csv.writer(csvfile, delimiter=',', quotechar='|',
                                quoting=csv.QUOTE_MINIMAL, lineterminator='
')
        savewriter.writerow(['x', 'y', 'x (um)', 'y (um)', 'height (nm)',
                             'thickness (nm)', 'sum (nm)', 'thickness (m)', 'sum (m)'])

def WriteFile(path, x, y, z, Bottom, xLoc, yLoc):
    # adds a row to the .csv save file
    # do some conversions so that the output has both nm an m
    Sum = Bottom + z
    Sumnm = Sum * 1e-9
    BottomOut = Bottom
    Znm = z * 1e-9

    with open(path, 'a') as csvfile:
        savewriter = csv.writer(csvfile, delimiter=',', quotechar='|',
                                quoting=csv.QUOTE_MINIMAL, lineterminator='
')
        savewriter.writerow([x, y, xLoc, yLoc, BottomOut, z, Sum, Znm, Sumnm])
        return()
# User variables
/filepath = r'F:\Temp for export\20200522 — PSW K100 50 mm min 30i300o 20d'

# path to folder containing cropped images of interface

overwrite = False

# process all images if True
# process unprocessed images only if False

plot = True

# plots and saves all the fitted images

# End user variables

savepath = os.path.join(filepath, 'fitted_images')

try:
    os.mkdir(savepath)
except OSError:
    print('Folder Exists')
else:
    print(savepath)

savename = os.path.join(os.path.dirname(filepath),
                       str(os.path.basename(filepath)) + '_summary.csv')

if os.path.isfile(savename) == False or overwrite == True:
    InitialiseSaveFile(savename)

filepaths = sorted(glob.glob(os.path.join(filepath, '*.png')))

if overwrite == False:
    alreadyProcessed = sorted(glob.glob(os.path.join(savepath, '*.png')))  
    if len(alreadyProcessed) > 0:
        lastProcessed = os.path.basename(alreadyProcessed[-1])
        lastProcessed = os.path.join(filepath, lastProcessed)
        filepaths = filepaths[filepaths.index(lastProcessed)+1:len(filepaths)]

counter = 0
for path in filepaths:
    print(path)

    # load image
    image = imageio.imread(path)
    vertRes = len(image[:,0])
    horiRes = len(image[0,:])
# find the edge (contrast between water/substrate and water/air)
edgeX, edgeY = FindEdge(image)

# find the substrate bottom
substrateBottom = 0
for i in range(0, vertRes):
    if edgeX[i] > 10:
        substrateBottom = i
        break

if substrateBottom < 20:
    substrateBottom = 20

# fit a line to the substrate
fit_points = 120
cleanFitRegionX = edgeX[substrateBottom:substrateBottom + fit_points]
m1, b1 = np.polyfit(edgeY[substrateBottom:substrateBottom + fit_points],
                    cleanFitRegionX, 1)
x = np.arange(0, vertRes)
Substrate_Fit = m1 * x + b1

# find the start of the air water interface
water_start = FindWaterStart(edgeX, Substrate_Fit, substrateBottom, vertRes)
# water_start = FindWaterStartDeriv(edgeX, substrateBottom, vertRes)

# check if the points we are about to fit are on the edge of the image
# e.g. because the CA is close to 90
N_edge = 0
for e in edgeX[water_start:water_start + 30]:
    if e > horiRes - 5:
        # if the point is within 5 pixels of the edge of the image
        N_edge += 1
if N_edge < 5:
    # do the old fitting algorithm
    m2_line, b2_line = np.polyfit(edgeY[water_start:water_start + 30],
                                  edgeX[water_start:water_start + 30], 1)
    Water_Fit_line = m2_line * x + b2_line
    angle_line = 180 - np.degrees(abs(math.atan((m2_line - m1) / (1 + m1 * m2_line))))

elif N_edge < 15:
    m2_line, b2_line = np.polyfit(edgeY[water_start:water_start + 29 - N_edge],
                                  edgeX[water_start:water_start + 29 - N_edge], 1)
    Water_Fit_line = m2_line * x + b2_line
    angle_line = 180 - np.degrees(abs(math.atan((m2_line - m1) / (1 + m1 * m2_line))))
else:  # fit the angle by finding the interface in the other direction
    print("EDGE")
    fitStart=0
    edgeXwater, edgeYwater = FindEdgeWater(image)
    edgeXwater = np.flip(edgeXwater)
    edgeYwater = np.flip(edgeYwater)
    # fit a line to the data points that are to the right of the substrate
    # find the first point of the edge that is to the right of the substrate fit
    for i in range(len(edgeXwater)):
        if edgeXwater[i] > Substrate_Fit[len(Substrate_Fit) - 1]:
            fitStart = i
            break
    if len(edgeYwater[fitStart+30:len(edgeXwater) -1]) == 0:
        angle_line = 90
    else:
        m2_line, b2_line = np.polyfit(edgeYwater[fitStart+30:len(edgeXwater) -1],
                                      edgeXwater[fitStart+30:len(edgeXwater) -1], 1)
        Water_Fit_line = m2_line * x + b2_line
        angle_line = 180 - np.degrees(abs(math.atan((m2_line - m1)/(1+m1 * m2_line))))

    # build name to save image
    basename = os.path.basename(path)
    basename = basename.replace('.png','')
    ImSave = os.path.join(savepath,basename)

    if plot == True:
        plt.imshow(image,cmap='gray')
        plt.scatter(edgeX,edgeY,color='r',s=5)
        plt.scatter(edgeXwater,edgeYwater,color='',s=5)
        plt.plot(Substrate_Fit,x)
        plt.scatter(edgeX[water_start],edgeY[water_start],color='b')
        plt.plot(Water_Fit_line,x,color='y')
        plt.xlim(0,horiRes)
        plt.ylim(vertRes,0)
        plt.savefig(ImSave)
        plt.clf()
        plt.close('all')

    print(str(angle_line), int(counter/len(filepaths)*100), "%")
    writeFile(savename,basename,angle_line)
    del image
    counter += 1
```python
def FindWaterStartDeriv(edgeX, substrateBottom, vertRes):
    # find the threshold
    diff = []
    for i in range(substrateBottom, substrateBottom + 60):
        diff.append(abs(edgeX[i + 1] - edgeX[i]))
    threshold = np.mean(diff) + 0.5 * np.std(diff)

    water_start = 'NAN'
    counter = 0
    LastTriggered = False
    for i in range(substrateBottom + 60, vertRes - 5):
        if abs(edgeX[i + 1] - edgeX[i]) > threshold:
            if LastTriggered == True:
                counter += 1
            LastTriggered = True
            if counter == 10:
                return(i - 11)
        else:
            LastTriggered = False
            counter = 0
    return(water_start)

def FindWaterStart(edgeX, Substrate_Fit, substrateBottom, vertRes, offset=60, window=60):
    water_start = FindWaterStartDeriv(edgeX, substrateBottom, vertRes)
    if water_start != 'NAN':
        # print(water_start)
        return(water_start)
    thresh_region = abs(edgeX[substrateBottom+offset:substrateBottom+offset+window] - Substrate_Fit[substrateBottom+offset:substrateBottom+offset+window])
    threshold2 = np.mean(thresh_region) + 10 * np.std(thresh_region)
    threshold2 = 50
    threshold_vis = Substrate_Fit + np.full(len(Substrate_Fit), threshold2)

    # find the start of the air/water interface
    counter = 0
    lastTriggered = False
    water_start = substrateBottom+offset
    for i in range(substrateBottom+offset, vertRes-5):
        if edgeX[i] > threshold_vis[i]:
            # first_triggered = i
            if lastTriggered == True:
                counter += 1
            lastTriggered = True
            if counter == 30:
                water_start = i - 31
```
```python
break
else:
    lastTriggered = False
counter = 0

# count back to find out the distance between the threshold and the substrate
counter = 0
for i in range(water_start, substrateBottom, -1):
counter += 1
    if edgeX[i] <= Substrate_Fit[i] + 10:
        break
    if i == substrateBottom:
        counter = 10
        break

water_start = water_start - counter
return(water_start)

def FindEdge(image):
    # find the edge (contrast between water/substrate and water/air)
    vertRes = len(image[:,0])
horiRes = len(image[0, :])

    edgeX = []
    edgeY = []

    threshold = 50
    for i in range(0, vertRes):
        for j in range(horiRes - 1, -1, -1):
            if image[vertRes - i - 1][j] < threshold:
                edgeX.append(j)
                edgeY.append(vertRes - i - 1)
                break
            if j == 0:
                edgeX.append(j)
                edgeY.append(vertRes - i - 1)
    return(edgeX, edgeY)

def FindEdgeWater(image):
    # find the edge (contrast between water/substrate and water/air)
    vertRes = len(image[:,0])
horiRes = len(image[0, :])

    edgeX = []
    edgeY = []
```

threshold = 50

for j in range(horiRes-1,-1,-1):
    for i in range(0,horiRes):
        if image[vertRes-i-1][j] < threshold:
            edgeX.append(j)
            edgeY.append(vertRes-i-1)
            break
        if j == 0:
            edgeX.append(j)
            edgeY.append(vertRes-i-1)

return(edgeX,edgeY)

def InitialiseSaveFile(path):
    #initialises the save file so that there is somewhere to save
    with open(path , 'w') as csvfile:
        savewriter = csv.writer(csvfile , delimiter=',', quotechar='|',
                          quoting=csv.QUOTE_MINIMAL , lineterminator='
')
        savewriter.writerow(['File', 'Contact Angle (line) (deg)'])

    return()

def WriteFile(path ,filename ,CA_line): #adds a row to the .csv save file
    with open(path ,'a') as csvfile:
        savewriter = csv.writer(csvfile , delimiter=',', quotechar=' ',
                          quoting=csv.QUOTE_MINIMAL , lineterminator='
')
        savewriter.writerow([filename ,CA_line])

    return()

def reject_outliers(data , n=2):
    for i in range(0,len(data)):
        if abs(data[i] - np.mean(data)) > n*np.std(data):
            data[i] = np.mean(data)

    return(data)

main()