Depletion of lubricant from lubricant-infused surfaces due to the air/water interface

Sam Peppou-Chapman†‡ and Chiara Neto*,†‡

†School of Chemistry, The University of Sydney, NSW 2006 Australia
‡University of Sydney Nano Institute, The University of Sydney, NSW 2006 Australia

E-mail: chiara.neto@sydney.edu.au
Phone: +61 2 9351 2752. Fax: +61 2 9351 3329

Abstract

Lubricant-infused surfaces (LIS) have emerged as an innovative way to combat several modern challenges such as biofouling, ice formation and surface drag. The favourable properties of LIS are dependent on the presence and distribution of a lubricant layer coating the underlying substrate. Unfortunately, this layer is not stable indefinitely and will deplete due to external forces. Here, we study how an air/water interface depletes lubricant from LIS as a function of lubricant wettability on the substrate by varying the chemistry of both the lubricant and the substrate. The lubricants were chosen to represent some of those most commonly used in the literature (silicone oil, perfluoropolyethers, and mineral oil). We use an optical Wilhelmy plate tensiometer to measure the contact angle of the air/water interface on the LIS in situ as the sample is driven through the interface and use contact angle hysteresis as a qualitative measure of lubricant depletion. This data is augmented with ex situ quantitative mapping of lubricant thickness using atomic force microscopy (AFM) meniscus force measurements. We find that a thick layer of excess lubricant is always removed in just one dip, regardless of wettability, and that lubricants which do not spread fully
on the substrate deplete faster due to their dewetting into droplets. We also find that lubricants which spread onto the air/water interface are more susceptible to depletion. Finally, we investigate the effect of repeated immersions on the properties of liquid-like PDMS chains tethered to glass and find that dynamic contact angles on these surfaces remain constant over several dips and therefore their low hysteresis is unlikely due to unbound polymer.

**Introduction**

Lubricant-infused surfaces (LIS), introduced in 2011, have emerged as the leading innovation in functional surfaces. Inspired by the *Nepenthes* pitcher plant, these low adhesive surfaces have attracted interest from many fields including anti-biofouling, anti-icing, anti-drag, and condensation (for both refrigeration and water collection). Crucial to the function of these surfaces is the immobilised lubricant layer which affords them their desirable properties.

Lubricant may be held on a LIS through capillarity, favourable spreading and intermolecular interactions for micro-/nanostructured LIS, the lubricant is retained within the surface structure by Laplace pressure. Secondly, the lubricant should spread on the substrate as quantified by the spreading parameter (approximated using the Young-Dupré equation):

\[
S_{ls} = \gamma_{SG} - (\gamma_{SL} + \gamma_{LG}) \approx \gamma_{LG} (\cos \theta_E - 1)
\]

Where \( \gamma_{LG} \), \( \gamma_{SL} \), and \( \gamma_{SG} \) are the interfacial tension terms (solid (S), liquid (L), and gas (G)) and \( \theta_E \) is the equilibrium contact angle of the lubricant on the solid. The condition of \( S > 0 \) is not necessary for successful infusion. Even a partially wetting lubricant is held within the surface texture as long as its contact angle is below the critical contact angle. Finally, van der Waals forces can stabilise nano-thin films. In the presence of an air/water interface (e.g. bubbles in a microfluidic device or a surface immersed in the ocean near the
tide line), the spreading parameter for the lubricant over water, $S_{lw}$, becomes significant as the lubricant can be depleted by spreading across the air/water interface. In addition to using structure to trap lubricant, several studies have reported successful manufacture of LIS without the aid of topography. \cite{20, 34–36}

Regardless of LIS design, the lubricant layer is not fully immobilised and will deplete over time. Our recent review of the literature\cite{3} showed that the mechanisms of lubricant depletion from LIS are not fully understood; in particular the volume and distribution of lubricant remaining on the surface following a given depletion event, and how this affects performance, is not known for common classes of LIS. Instead, the majority of LIS research focuses on the properties of these surfaces in a freshly lubricated state, even though a thick lubricant layer is not likely to persist during use, and surface properties will degrade in a depleted state.\cite{3} This knowledge gap impedes meaningful comparisons between different LIS designs and optimisation of surface design for improved retention.

Lubricant can deplete from LIS in many ways such as spreading onto adjacent surfaces, gravity-induced flow, removal due to drag-induced shear, removal as droplets are shed from the surface, and evaporation. Our previous work found that a thick layer of silicone oil lubricant on nanowrinkled Teflon surfaces depletes due to gravity-induced flow and underwater shear.\cite{37} However, even with only 0.2 ml m$^{-2}$ of silicone oil, the surfaces remained effective against bacterial adhesion and delayed marine biofouling.\cite{10, 37}

Another significant pathway for lubricant depletion, particularly for marine antifouling applications, is the passing of an air/water interface over the surface. This remains a rarely studied phenomenon but there is some evidence that a significant amount of lubricant is removed when an air/water interface crosses a LIS. Howell et al. observed that little lubricant is lost as water is continually pumped through a lubricant-infused microfluidic channel but that almost all of the lubricant is lost when an air/water interface passes through the channel (as observed through the fluorescence of the lubricant).\cite{38} Sotiri et al. found an increase in contact angle hysteresis (CAH) as iPDMS (PDMS elastomer swelled with silicone oil) was
repeatedly driven through a fresh air/water interface. Zhang & Yao found that the droplet shedding velocity and slip velocity (measured using particle imaging velocimetry (PIV)) of a droplet on a LIS decreases after the surface was rinsed with water. From these results, it is clear that the air/water interface is effective at removing lubricant. What is not clear is the dynamics of lubricant depletion by an air/water interface and the amount and distribution of lubricant that remains after a certain number of immersions or if any design choices may reduce the effect.

Recently, non-textured anti-adhesive surfaces that rely on a thin layer of grafted polymer brushes have appeared in the literature. These polymer brushes claim to create a liquid-like surface which, similar to the liquid layer of LIS, provide a mobile interface to reduce adhesion. This functionalisation is also used as a platform to stabilise lubricant. 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 and the glass. Effectiveness of these surfaces in applications is not widely studied, and their lubricant retention not well characterised.

In this study, we investigate lubricant depletion on polymeric nanowrinkled surfaces in five different wetting scenarios, as summarised in Figure 1 as the LIS pass through a clean air/water interface. Smooth surfaces grafted with molecular layer of PDMS, known as quasi-liquid surfaces (QLS), were also assessed. In all cases, gradual depletion of lubricant is inferred from the changes in contact angle hysteresis (CAH), measured in situ as the sample passes through the air/water interface. Depletion is quantified by mapping the volume and distribution of the lubricant both in air and underwater using atomic force microscopy (AFM) meniscus force measurements. Thermodynamic considerations allow us to estimate the principal failure modes in each case.
Figure 1: Overview for wetting of lubricant (orange) over the wrinkled substrate (grey) in the presence of air and water (blue) for the different systems examined in this study: Teflon wrinkles (TW) and polystyrene wrinkles (PSW) infused with silicone oil (SO), or perfluoropolyether (PFPE) or mineral oil (MO). The spreading parameter $S$ is calculated from values in Table S4 and is in units of mN m$^{-1}$.

Materials and Methods

Sample Preparation

Wrinkled Teflon surfaces were prepared as previously described. Briefly, shrinkable polystyrene substrate (Polyshrink™) was spin-coated with a thin layer (40 nm) of Teflon AF (Chemours, 1.5% in FC-40), and then annealed in an oven (France Etuves XFM020) at 130 °C, inducing shrinking and spontaneously forming Teflon wrinkles.

Wrinkled polystyrene surfaces are produced by stripping the Teflon layer off the wrinkled surfaces by submerging them in FC-40 (Sigma) for at least 45 min. The removal of the Teflon was confirmed by the disappearance of the C-F band at 1400–1000 cm$^{-1}$ from the FTIR spectrum after 30 min immersion in FC-40 (see Figure S4). The stripped polystyrene
surfaces retain the overall morphology of the Teflon wrinkles, but the features are generally
taller and spaced further apart, see Figure S3 and Table S2, quantified using tapping mode
AFM (Bruker MultiMode 8). Height and width of the wrinkles are defined in Figure S2. The
slightly larger spacing of PSW relative to TW is expected to slightly reduce their ability to
retain lubricant but we show that this effect is negligible compared to the effect of surface
and lubricant chemistry.

The as-produced wrinkles are infused by pipetting an excess of the lubricant (approx. 200 µl cm\(^{-2}\)), either silicone oil (10 cSt, Aldrich), mineral oil (white, Aldrich) or Krytox GPL
100 (DuPont), spreading it, and then holding vertical for 1 min to drain some of the excess
lubricant. The samples are intentionally prepared with a large excess of lubricant present,
so are used immediately after lubrication.

Glass coated with tethered PDMS chains was produced as previously described. Briefly,
glass slides were sonicated in ethanol (Merck, ACS reagent) and acetone (Merck, ACS
reagent) 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 hours, which is sufficient to enable chemical binding to the
surface. They were then sonicated in ethanol, acetone, and toluene (Merck, ACS reagent)
for 1 minute each to remove unbound silicone oil.

**Optical Wilhelmy plate tensiometer**

An optical Wilhelmy plate tensiometer was used to track advancing contact angle (receding)
as the sample is immersed (withdrawn) vertically through the air/water interface. Briefly,
a camera (Techbrands USB Microscope) was used to capture the shadow cast from the
shape of the air/water interface as the sample passes through the interface, see Figure 2a/b.
Captured videos are first processed using ImageJ to crop the region of interest and increase
contrast. Each frame is then output individually for automatic analysis using a Python script
(reproduced in SI).
Figure 2: 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 and exits an overflowing cuvette. b) 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. c) Representative force-distance curve from an AFM meniscus force measurement to measure lubricant thickness with schematic of the AFM tip at different portions of the force-distance curve. d) 3D reconstruction of a LIS from meniscus force measurements. Scale bar = 200 nm
Using a dip coater (KSV NIMA, Espoo, Finland), the surfaces are repeatedly immersed and withdrawn at 50 mm min\(^{-1}\) from a custom-made cuvette (5 cm x 5 cm) that has tubing built-in to continually add new water from the bottom, similar to the set-up described by Sotiri \textit{et al.} Milli-Q water was pumped in at a rate of 60 ml min\(^{-1}\), so that the air/water interface is being continually refreshed every few seconds. The sample is held still for 30 s between each up and down motion (unless stated otherwise) to allow lubricant on the surface of the water to clear. Samples (2 cm x 1 cm) are mounted on a support glass slide that is narrower than the sample (approx. 5 mm in width) to reduce edge effects.

As the samples used in this study are infused with excess lubricant, the contact angle measurements in the first few dips have increased error due to the contact line being obscured by the large amount of lubricant being removed. As a result, the script may fit higher contact angle values to the receding angle (measured while withdrawing the surface from the cuvette) than the advancing (measured while immersing the surface, \textit{e.g.} in Figure S12). When this is the case, the advancing and receding angles should be considered indistinguishable by this technique.

\textbf{Lubricant thickness and distribution}

Lubricant thickness and distribution are mapped at the nanoscale using AFM meniscus force measurements. Briefly, the surface is mapped using force-distance curves with a custom Python analysis script to extract lubricant thickness. Figure 2c shows an example force-distance curve collected on a LIS with schematics showing the effect of a meniscus on the tip. When the AFM tip contacts the top of the lubricant, a meniscus forms which pulls the tip down due to capillary action, visible in the force curve (point ii). When the tip makes hard contact with the solid surface underneath, the tip deflects in the opposite direction, also visible in the force curve (point iv). The distance between these two points is the lubricant thickness. These maps allow us to reconstruct the infused LIS in 2-dimensions (Figure S7) and in 3-dimensions (Figure 2d). Deflection of the cantilever is accounted for by converting
the raw z-height into tip-sample separation during analysis. All experiments use Multi75 probes (Budget Sensors, Sofia, Bulgaria) with an MFP-3D AFM (Asylum, Santa Barbra) as previously described.

**Underwater measurements**

The interfacial tension of water and hydrophobic lubricants is sufficiently high that lubricant thickness can be measured underwater. To increase the magnitude of the jump-in, the AFM probes were hydrophobised using PDMS. The AFM probes are first cleaned using piranha solution, 3:1 sulfuric acid (98%, Ajax):hydrogen peroxide (30%, Merck) for 5 minutes before being rinsed twice in MilliQ water, once in toluene and dried under a gentle nitrogen flow. They are then placed in a glass staining jar with a small amount of uncured PDMS (Sylgard 184, Dow Corning) and placed in an oven at 200 °C for 4 hours. After cooling, they are rinsed once more with toluene and dried under a gentle nitrogen flow. The procedure deposits 1–2 nm of PDMS (by ellipsometry). For underwater AFM measurements, a custom-made sample holder is used to flood the samples with water in situ, allowing imaging of the same area in air and underwater. Figure S6 shows a typical force curve of a LIS taken underwater, and although the shape is slightly different than one collected in air, the lubricant thickness is still easily calculated. The magnitude of the jump-in is reduced underwater and some artefacts 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. Redistribution of the lubricant under water was observed also by optical microscopy (Nikon Eclipse LV150) using the same custom cell as used for the underwater AFM measurements.

**Sessile drop measurements and roll-off angles**

Sessile drop measurements were performed using a goniometer (KSV CAM200). Advancing and receding contact angle values were measured at the same time as roll-off angles. A 10 μl
droplet of Milli-Q water was deposited onto the surface and the surface slowly tilted until
the drop started moving. The first frame recorded after the drop began to move was used
to measure the advancing (front of the droplet) and receding (rear of the droplet) contact
angle. The tilt angle of the surface at this point is the roll-off angle. Reported data is the
average of 5 independent measurements.

Results and discussion

This study examines model LIS comprising different structured surface/lubricant combina-
tions to understand the role of the air/water interface on lubricant depletion. The structured
surfaces used in this study consist of a hierarchical structure of wrinkles (about 200–400 nm in
width and 200–300 nm in height) superimposed on larger folds (∼2 µm in width and ∼600 nm
in height), as described in Figure S3 and Table S2.

Teflon wrinkles (TW) and polystyrene wrinkles (PSW) were infused with common lubri-
cants used in the literature: 10 cSt silicone oil (SO), Krytox GPL 100 (perfluoropolyether,
PFPE) and mineral oil (MO). Prior to infusion, TW are superhydrophobic (CA = 163±4°)
while PSW are simply hydrophobic (CA = 136±2°). The valleys formed between Teflon
wrinkles are very effective at retaining silicone oil[37] and the TW/SO surfaces reduces ma-
rine fouling over periods of more than seven weeks[10]. As shown in Figure 1, the employed
surface/lubricant combinations lead to different wetting scenarios in air or underwater, as
quantified by the spreading coefficient $S$, and to the presence of a cloaking layer or not (MO
does not spread fully on the water/air interface).

Table S5 details the spreading parameter of the lubricant over the substrate in air ($S_{ls(A)}$)
and underwater ($S_{ls(W)}$) and of the lubricant over the water reservoir ($S_{lw}$) as well as an
estimation of the non-retarded Hamaker constant for all structured LIS systems studied (see
Table S1 and Figure S1 for more information). Negative values of the Hamaker constant
indicate that van der Waals interactions stabilise a nano-thin lubricant film. Finally, a
substrate without topography was studied, a quasi-liquid surface (QLS) which consists of PDMS chains tethered to a non-textured glass substrate.

For all systems investigated, the Bond Number ($Bo = \Delta \rho g \lambda^2 / \gamma l_w$) and the Weber Number ($We = \rho^2 \lambda / \gamma l_w$) 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.

**Accuracy of in situ measurement of contact angle**

The depletion of lubricant from a LIS was studied by repeatedly driving the LIS in and out of a water-filled custom-made cuvette, which continuously refreshes as water is pumped in from the bottom. Figure 2 schematically shows the optical Wilhelmy plate tensiometer set-up used to track contact angle hysteresis in situ as the sample is driven through the interface. Figure 2 shows an example of the data collected and how it is processed. As shown in Table S6, all the systems studied show the wettability typical of LIS, with low contact angle hysteresis ($5^\circ$-$15^\circ$), and with advancing contact angle value around $110$-$120^\circ$, characteristic of the lubricants used for infusion. These values of contact angle are taken as indicative of the starting properties of LIS prior to extensive depletion. The contact angle values obtained with the Wilhelmy plate agree with those obtained with the sessile droplet method, except for PSW/PFPE, where the sessile drop contact angle is higher. Several factors influence the contact angle collected using the optical Wilhelmy plate tensiometer, but most of these effects are small compared the large uncertainties which result from the contact angle being an average over the whole surface. In the Wilhelmy plate method, the contact angle value measured is affected by the rate of motion across the interface, but Table S6 shows that this is not an issue for samples moving at $50$ mm min$^{-1}$. For faster moving samples, a correction factor would be needed to accurately compare results with sessile drop measurements. Here, contact angles values only up to $150^\circ$ were fitted to increase analysis throughput and eliminate large errors that affect optical measurements of larger angles. In the present work, the contact angle values measured using the Wilhelmy plate for superhydrophobic
TW ($\theta_A = 131^\circ$, $\theta_R = 127^\circ$, see horizontal lines in Figure 4) are significantly lower than the values measured with the sessile drop method ($\theta_A = 169^\circ$, $\theta_R = 150^\circ$). Although the absolute contact angle value may not always match the sessile drop value, changes in contact angle values as the lubricant is lost are clear.

**Effect of dipping rate on lubricant film thickness for structured surfaces**

Multiple effects contribute to the thickness of the lubricant layer remaining on a sample after it has crossed the air/water interface. Figure 3a shows the average thickness of silicone oil remaining on TW as quantified from AFM meniscus force maps after one dip at different insertion/withdrawal speeds. Figures 3b,c,d show representative maps after one dip for $5 \text{ mm min}^{-1}$, $50 \text{ mm min}^{-1}$ and $200 \text{ mm min}^{-1}$, respectively. Surface topography is presented in the left panel, with the colour scale representing the height in nm. The central panel shows lubricant thickness as a series of non-linear contours with equal spacing between 0–20 nm (purple to yellow) and then contours at 150 nm (light yellow) and 300 nm (beige). White areas represent regions with more than 300 nm of lubricant. The trend observed in Figure 3a is that a thicker lubricant film remains on the TW surface after dipping at high immersion rate compared to that at low rates. For $50$–$200 \text{ mm min}^{-1}$, most of the film is of thickness of the order of several hundreds of nm (white portions), and smaller portions have thickness of the order of tens of nm (yellow portions). On the other hand, for the surface immersed at $5 \text{ mm min}^{-1}$, the film is much thinner, with much of the surface only covered in a thin film on the order of a few nm (purple portions) and a small portion covered by a layer on the order hundreds of nm.

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. 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
Figure 3: a) Average thickness of SO film on TW 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 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 TW topography (left), lubricant distribution (centre), and histogram of lubricant thickness (right) after one dip at different speeds for 5 mm min⁻¹, 50 mm min⁻¹ and 200 mm min⁻¹, respectively.
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. 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 3a, with grey area representing the standard deviation). Only when the surface is withdrawn more slowly, at 5 mm min\(^{-1}\), the surface of the reservoir is fully refreshed and cleared within the 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.

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

For all surface/lubricant combinations studied here, on first crossing of the air/water interface, the large excess of lubricant present on the LIS is removed. After the first dip, the thickness of the lubricant film is reduced to a value that is measurable by AFM meniscus force measurements (less than 10 µm), see Figure 4c, Figure 6c, Figure S10c, Figure S12c and Figure S13c.

A lubricant film that is not stabilised by capillarity is removed after it passes through the air/water interface. Figure S8 shows AFM meniscus force maps collected on flat polystyrene coated in SO 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 3b and corresponds to a film stabilised by van der Waals forces or adsorbed water. Smooth Teflon surfaces were not tested as SO and MO form droplets and cannot be stabilised in the absence of structure. PFPE was also not tested on Teflon as it dissolves the Teflon layer.
Lubricant retention for lubricants that do not spread over the substrate

The first substrate/lubricant combination studied is Teflon wrinkles infused with silicone oil (TW/SO), which is representative of a LIS in which the lubricant does not spread completely over the substrate in air ($S_{ls(A)} < 0$), but is still antifouling and slippery as the lubricant is kept in place by capillarity.\textsuperscript{10,17} Figure 4a shows the advancing and receding contact angle on TW/SO as a function of the number of dips. The first measurements ($\theta_A \approx 113^\circ$, $\theta_R \approx 105^\circ$) correspond to the contact angle values expected on a well-infused surface coated by excess SO with low CAH (see Table S6 for comparison to sessile drop measurements). After the first dip, the large excess of SO is removed and a continuous layer is left with most of the lubricant thickness greater than 300 nm (Figure 4c) and the CAH remains small. As more SO is removed (dips 3-13), portions of the underlying topography are exposed (see Figure 4d for a snapshot of lubricant depletion at dip ten, where 77% of the surface is coated with a film less than 10 nm thick), producing a surface with heterogeneous wetting properties. This causes an increase in CAH, with the maximum hysteresis reached after nine dips ($\theta_A \approx 130^\circ$, $\theta_R \approx 105^\circ$). Finally, at around dip fourteen, almost the entirety of the SO layer has been removed, and the contact angle values are higher than before, with reduced CAH, similar to the values for the underlying superhydrophobic TW surface before infusion (horizontal lines, $\theta_A \approx 131^\circ$, $\theta_R \approx 127^\circ$). At dip twenty, most of the lubricant is removed, with 95% of the surface coated with a film less than 10 nm thick (Figure 4e) and the CAH remains small, matching that of the underlying superhydrophobic TW (horizontal lines). This transition from liquid-infused to superhydrophobic behaviour upon loss of lubricant has been observed before.\textsuperscript{62}

The change in CAH upon repeated immersions is only seen when water is flowing into the cuvette to continuously remove the top lubricant layer. If there is no flow, no significant change in CAH is seen over twenty dips, as shown in Figure S9 because the lubricant which has collected on the surface of the reservoir continually recoats the surface.
Figure 4: Advancing (black) and receding (orange) contact angle values as a function of the number of dips for TW/SO with (a) 30 seconds between dips; and (b) 300 seconds between dips. Error bars are standard deviation in contact angle values across the whole surface. The horizontal lines represent the average measured dynamic angles on a non-infused surface (only the average value is presented for visual clarity, but these measurements have a similar uncertainty of 5-10°). AFM meniscus force maps (c-f) collected after the corresponding coloured markers in parts (a) and (b); the numbers in the bottom right quantify the portion of the surface exposed (i.e. with lubricant thickness <10 nm).
For TW/SO, the time between dips determines the rate of lubricant depletion. Figure 4b 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 4a and Figure 4b, samples held out of the water for 300 s between dips deplete more quickly (completely depleted by about six dips) than those held for 30 s (depleted in fourteen dips). As described below, the longer wait time in air allows the lubricant to collect into large droplets on the surface, and these are removed more easily by the air/water interface.

Dewetting of lubricant after the LIS emerges from underwater

To understand how the SO layer rearranges on the TW after the sample is removed from the water, the layer was tracked using optical microscopy and AFM meniscus force measurements (Figure 5) after an air/water interface has passed across the surface. The water was removed by drawing it into a syringe, meaning that some of the SO which had spread over the air/water interface was redeposited on the surface. Immediately after the surface emerges from underwater, there is a continuous layer of SO which dewets into droplets as SO has a negative spreading parameter on Teflon in air. The speed of dewetting depends on the overall thickness of lubricant: a thick layer of lubricant breaks up into droplets within seconds (Figure 5a-c) while a thinner layer (produced after one dip at 50 mm min$^{-1}$) breaks up more slowly, on the order of minutes to hours (Figure 5d-f). Once this breakup has taken place, the droplets ripen, with smaller droplets disappearing as larger droplets increase in size (Figure 5g-i, red arrows indicate the location of droplets that disappear).

The process of droplet ripening occurs because the lubricant layer interconnects droplets. Laplace pressure is much higher in smaller droplets and so, during dewetting, lubricant is driven from them into the overall layer and ultimately into larger droplets. Figure 5j shows sequential cross-sectional profiles of a lubricant film thinning in air, after an air/water interface has crossed it. Tracking the lubricant film thickness in an area away from large
Figure 5: Optical micrographs of TW/SO after an air/water interface has crossed over it. For a thick layer of excess lubricant (a-c), the lubricant very quickly dewets into droplets. For a thinner layer (d-f) the dewetting is slower and the droplets smaller. Smaller droplets disappear as larger ones increase in size (g-i) as the lubricant flows driven by Laplace pressure differences. The time scale in (a-f) is relative to the LIS emerging from the water and in (g-i) is relative to the first appearance of droplets (approx. 5 min after the interface passed over). (j-k) Time series of cross sections taken from AFM meniscus force maps showing (j) the lubricant/air interface after TW/SO emerges from underwater and (k) after the sample is submerged with inset showing a detailed view of the highlighted region. Cross sections were taken from successive maps in the same area and aligned by hand, introducing some artefacts in the process (such as the lubricant/water interface crossing into the substrate).
droplets by AFM meniscus force measurements reveals a gradual reduction of the layer thickness until portions of the air/lubricant interface are touching the underlying substrate. In similar timeframes other portions of the surface will become covered by large droplets. The observed dependence of depletion on the time between dips (Figure 4a and b) is a consequence of the SO dewetting on the Teflon substrate. The appearance and growth of these droplets correlates with a faster depletion rate of lubricant from the surface, relative to the other systems studied here. As a result, the hypothesis is that as the air/water interface passes over the TW, it carries away numerous SO droplets, which increases the rate of lubricant depletion relative to a lubricant that spreads fully on the substrate.

Re-wetting of lubricant after the LIS is submerged

Looking at the reverse process, when TW/SO is submerged in water, there are two stages of lubricant redistribution that happen on different time scales: the first is an overall increase in lubricant thickness as the dewetted droplets quickly spread into a continuous layer. Figure S7 shows the same area of a TW/SO surface mapped using meniscus force measurements before and after in situ flooding with water and shows that there is an increase in the local lubricant thickness after the surface is submerged. Once this process has occurred, there is a slower redistribution (on the order of minutes, see Figure S7b) in which the tops of the wrinkles are covered with lubricant until there is ∼10 nm film of lubricant. This slower redistribution is seen in Figure 5k which shows sequential cross-sectional profiles of a TW/SO surface that has just been submerged. After thirty five minutes, the film thickness on the tops of the wrinkles has increased from ∼0 nm to ∼10 nm (see inset in Figure 5k).

The exact shape of the lubricant interface is determined by the balancing of the spreading of the lubricant on the top of the wrinkles and the Laplace pressure difference across the valleys between the wrinkles. Fitting circles to the profiles in Figure 5k gives a decrease in the radius of curvature from $R = \sim 9.6 \mu m$ at zero minutes to $R = \sim 6.6 \mu m$ after thirty five minutes, corresponding to an increase in Laplace pressure difference of $\sim 3 kPa$. 

19
This lubricant redistribution means that areas that are exposed in air are no longer exposed underwater and the lubricant layer is now continuous (after sufficient time underwater). All AFM meniscus force maps presented were taken immediately after dipping (unless stated otherwise). Maps are generally started approximately within five minutes after dipping and each map takes approximately 35 minutes to complete.

**Lubricant retention for lubricants that spread over the substrate**

The results presented up to this point have concerned a lubricant which does not spread over the substrate. While we have previously shown this lubricant/substrate combination to be effective against biofouling,\textsuperscript{10} it is not the only wetting scenario for LIS.\textsuperscript{3} Polystyrene wrinkles (PSW) infused with SO and PFPE were used to investigate the case of the lubricant fully wetting the substrate in air ($S_{ls(A)} > 0$) but not spreading on the substrate underwater ($S_{ls(A)} < 0$).

**Silicone oil on polystyrene wrinkles (PSW/SO)**

Like TW/SO, an increase in CAH is seen on PSW/SO as the lubricant is lost. However, as the underlying PSW substrate is not a low hysteresis surface, there is no reduction in hysteresis when the majority of lubricant is removed at later dips (Figure S10a). Again, after a single dip, the large excess of SO is removed, with only a thin layer left on the tops of the wrinkles (Figure S10c). Further dipping removes more lubricant producing a heterogeneous surface by dip five (Figure S10d), 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 S10a/b). At this stage, most of the lubricant is removed from the surface, with lubricant only held in the deep areas of the topography, where capillarity is strongest.

This state remains largely unchanged up to dip twenty (see Figure S11). The remaining lubricant held deep in the topography is very difficult to remove, with the amount of lubri-
cant only slightly decreasing between eight and twenty dips. The last volume of remaining lubricant is much more difficult to remove than on the Teflon due to the lower contact angle of SO on the polystyrene, increasing the capillary pressure of the system (Table 1). For PSW/SO, a longer wait time between dips (300 s, Figure S10b and Figure S11b) does not change the rate of depletion relative to the shorter wait time (30 s, Figure S10a). This is due to the fact that SO does not dewet into droplets on PSW after it emerges from the water.

**PFPE on polystyrene wrinkles (PSW/PFPE)**

PSW infused with PFPE (Krytox GPL 100) maintain a lower CAH compared to the same wrinkles infused with SO (Figure S12), showing that the nature of the lubricant is important in determining depletion due to the air/water interface. Similar to the other LIS studied, a thick layer of excess PFPE is removed with the very first dip (see Figure S12c) with a very thin layer covering the tops of the wrinkles. Unlike SO, the dynamic contact angle values do not approach the values of the uninfused surface within twenty dips (Figure S12a). Instead, the contact angle hysteresis remains stable as the samples retain lubricant across twenty dips. The regions of PFPE film with thickness greater than 300 nm (white regions) decrease from the first dip (Figure S12c) to the tenth dip (Figure S12d) to the twentieth dip (Figure S12e), but still 99% of the surface is not exposed after the twentieth dip (compared to 68% for SO.)

This different depletion behaviour is surprising given that SO and PFPE are very similar in many respects: physical properties (Table S3); capillary number \( Ca = 2.2 \times 10^{-4} \) for SO and \( Ca = 3.6 \times 10^{-4} \) for PFPE; Hamaker constants (Table S5); complete removal from unstructured polystyrene after just one dip (Figure S8); tops of wrinkles exposed after one dip for both systems and similar lubricant configuration at this point (Figure S14). The difference in depletion must be due to the fact that the energy of gained in the spreading of PFPE over the air/water interface is lower than that of SO. This aspect is explained later in Table 1.
Significance of a cloaking layer for lubricant depletion

Both lubricants studied so far (SO and PFPE) spontaneously spread across the air/water interface, producing a cloaking layer. Here, we examine MO, a lubricant that does not spread over the air/water interface ($S_{lw} = -17 \text{ mN m}^{-1}$) but that behaves otherwise similarly to SO on the wrinkled surfaces.

MO on a non-wetted substrate (TW/MO)

The behaviour of TW infused with mineral oil is very different from the behaviour of the same wrinkles infused with SO. The TW/MO system is a relatively poor LIS as prepared (roll-off angle of 32°, Table S6), but retains its performance steadily throughout twenty dips. For TW/MO, after most of the mineral oil is removed in the first dip, the lubricant level does not change much in the following dips (see Figure S13a and compare to TW/SO in Figure 4a). After one dip, 75% of the surface is exposed (Figure S13c, 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 (within error) after ten (Figure S13d) and twenty (Figure S13e) dips. 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.

Increasing the time between dips to 300 s does not have much of an effect on the lubricant depletion (Figure S13b and f). Because MO does not spread across the air/water interface, the main mechanism of depletion is the removal of dewetted MO droplets.

MO on a wetted substrate (PSW/MO)

Mineral oil fully spreads on PSW in air, and shows a very similar evolution in dynamic contact angles as PSW/PFPE (compare Figure 6a and Figure S12a). In Figure 6a, there is very little change in CAH across twenty dips, with both advancing and receding contact angles values staying stable across the experiment. After the first dip, the surface is covered
by a thick, continuous lubricant layer as seen in Figure 6c, where \( \sim 99\% \) of the surface is covered by an MO thickness greater than 300 nm. As the dipping proceeds, some lubricant is removed from the surface, as seen by the appearance of yellow regions (less than 300 nm), but there is very little effect on the dynamic contact angle values. At dip twenty, more lubricant has been removed, with Figure 6e showing a film with the majority of regions now <300 nm, but the MO thickness is still sufficient to maintain a low contact angle hysteresis. As there is no lubricant dewetting after the LIS is withdrawn from the reservoir, the amount of time between the dips does not influence depletion (Figure 6b and Figure 6f).

While these results resemble the results for PSW infused with PFPE, the lack of spontaneous spreading of mineral oil over the air/water interface means lower depletion is expected for mineral oil. This is indeed the case, as shown in Figure S15: the MO layer is thicker (average thickness 240±120 nm) compared to the PFPE layer (160±100 nm).

**Energetic explanation of depletion due to spreading**

A simple model of the wrinkles was developed to compare the energy needed to remove the lubricant from within a pore \((E_{\text{removal}})\) with the energy gained from the lubricant spreading over the air/water interface \((E_{\text{spreading}})\). The space between the wrinkles was modelled as a triangular pore the same size as the average wrinkle width (Figure S16 and Table S2). Lubricant is expected to deplete from within the surface structure if \(|E_{\text{removal}}| < |E_{\text{spreading}}|\), or rather, given the simplicity of the model, if \(E_{\text{removal}}\) and \(E_{\text{spreading}}\) are within an order of magnitude of each other. The volume removed is estimated by measuring the typical volume change between dips (\(\sim 1 \times 10^{-9} \text{ m}^3 \text{ cm}^{-2}\)). See SI for a detailed explanation of this calculation.

Table 1 summarises \(E_{\text{removal}}\) (for two levels of depletion at the top and bottom of the pore, see Figure S16) and \(E_{\text{spreading}}\) for all wrinkled LIS studied. For lubricant located at the top of the pore for TW/SO, \(E_{\text{removal}} \sim E_{\text{spreading}}\) indicating that spreading over the air/water interface is a key depletion mechanism for this system. Due to the similarity in
Figure 6: Advancing and receding contact angle values as a function of the number of dips for PSW/MO 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 (only the average value is presented for visual clarity, but these measurements have a similar uncertainty of $5-10^\circ$). AFM meniscus force maps (c-f) collected after the corresponding coloured markers in parts (a) and (b) with the number in the bottom right quantifying the proportion of the surface exposed (i.e. with thickness <10 nm).
physical properties of SO and MO, this suggests that the difference in their depletion is due to their different spreading over the air/water interface.

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 1, it is unlikely the SO held in the bottom of PSW topography is able to be removed due to spreading across the air/water interface (as was observed, see Figure S11).

Table 1: 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. $E_{\text{spreading}}$ is the energy gained from the lubricant spreading across the air/water interface. Lubricant is expected to deplete from within the surface structure if $|E_{\text{removal}}| < |E_{\text{spreading}}|$. See SI for more information on the calculation of these values.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{removal}} / J$</th>
<th>$E_{\text{spreading}} / J$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>top</td>
<td>bottom</td>
</tr>
<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>

*a*does not spread across the air/water interface

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.*

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.

Figure 7: Dynamic contact angle values for PDMS-grafted glass (QLS) (a) as prepared according to the recipe by Teisala et al. (b) infused with 10 cSt silicone oil. Histograms of film thickness as measured using AFM 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 one dip at 50 mm min$^{-1}$.

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 7a, suggesting that the lubrication effect is long-lasting and unlikely to be due to unbound polymer (which would be carried away with each dip). The CAH recorded here (approx. 13°) is similar to the value reported by Tiesala et al. for a similar grafting time (approx. 10°) AFM meniscus force measurements reveal that there is no appreciable liquid film on the surface, see Figure 7c, 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 and is similar to the value previously observed on a ‘dry’ flat Teflon surface. After forty dips, the film thickness increases slightly to 11±3 nm, likely due to deposited water from the repeated dipping, see Figure 7d.

There are multiple claims that these layers aid the stabilisation of lubricant. To test this, the QLS was lubricated with an excess of silicone oil (10 cSt, 100 µL cm⁻²) and dipped repeatedly. Figure 7b shows the dynamic contact angles on this surface as a 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 non-infused surface that was dipped 40 times, see Figure 7e.

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 unlikely to be due to unbound polymer or any other material that would be removed through repeated immersion.

**Conclusions**

Depletion of lubricant due to an air/water interface is significant for any LIS that is deployed in marine applications or anywhere with mobile interfaces. Using *in situ* measurement of dynamic water contact angles as a LIS passes through the air/water interface and *ex situ* mapping of lubricant thickness, we examined the effect of twenty repeated immersions through the air/water interface on LIS.

This study reinforces our previous observation that LIS cannot effectively stabilise lubricant not held in place by capillarity. In most tests, LIS infused with excess lubricant
deplete to a level where the highest regions of topography are covered in a film on the order of tens-hundreds nm in just one dip. This highlights the need for LIS research to analyse surface properties at this level of depletion and not coated with an unrealistically thick lubricant layer soon after infusion. Additionally, the initial slippery properties of a lubricant/substrate system are not a predictor on how well lubricant is retained as it passes through the air/water interface, and we observed no correlation between lower initial roll of angles and longevity of lubricant retention (Table S6). Instead the opposite was true: a relatively poor LIS, such as the TW/MO system, retained its performance unchanged over the full twenty dips.

For the Teflon wrinkles, which are initially superhydrophobic as prepared, as the SO is gradually removed, we observed a transition from the behaviour on a LIS back to that of a superhydrophobic surface. On TW/SO the contact angle hysteresis reached a maximum value in the intermediate stage between the infused and well-depleted state. The results of this study are summarised in Table 2 and in the last column of Figure 1. Through examination of the effects of various lubricant/substrate combinations, we show that a lubricant that does not spread fully over the surface topography in air ($S_{ls}(A) < 0$, e.g. TW/SO) is more rapidly depleted by a mobile air/water interface than a completely wetting lubricant, because dewetted lubricant droplets, formed when the LIS emerges from underwater, deplete the lubricant more rapidly than smaller droplets or a continuous lubricant film.

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. SO or PFPE on polystyrene wrinkles). These surfaces do not deplete as readily as the same lubricants on Teflon wrinkles across twenty dips due to the lubricant remaining in a continuous layer in air. For these surfaces, the effect of lubricant spreading over the air/water interface is more pronounced and is a main driver of depletion. Both SO and PFPE spread over the air/water interface and, as a result, deplete due to a film spreading mechanism onto the water surface (depending on reservoir size). SO is more readily depleted from Teflon wrinkles than from polystyrene
Table 2: Summary of the wetting and depletion behaviour of the various substrates/lubricant combinations studied. \( S_{ls(A)} \) 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. \( \frac{\rho_l}{\rho_w} \) is the ratio of lubricant density to water density.

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

\(^a\) 30 s in, 30 s out, \(^b\) calculated using the Young-Dupré equation \( S \)

wrinkles because the capillary force holding it in place on TW is closer to the driving force for spreading on the air/water interface. Mineral oil, a lubricant that does not spread on water, is removed through droplets floating away in the first dip but does not further deplete. Lubricants that spread over the substrate, but not over water (e.g. PSW/MO), provide more robust and long-lasting lubrication without any perfluorination, which is beneficial for the environment.

The significance of lubricant spreading over the working fluid is debated in the literature. For applications where a LIS only encounters droplets, the volume of lubricant in the wetting ridge is much greater than the lubricant in the cloaking layer,\(^{15}\) and so the presence of a cloaking layer is generally not considered detrimental in terms of depletion. However, the presence of a cloaking layer negatively effects performance for LIS applied in condensers in heat exchangers.\(^{16}\) This work suggests that the presence of a cloaking layer can significantly contribute to depletion and is undesirable when a LIS is deployed in intermittent contact with a large water reservoir.

Finally, we show 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.
Acknowledgement

The authors thank Jun Ki Hong for development of polystyrene wrinkles manufacturing. SPC acknowledges the Australian Government Research Training Program (RTP) for support. CN acknowledges funding from the Australian Research Council through the Future Fellowship scheme (FT180100214).

Supporting Information Available

The Supporting Information is available free of charge on the ACS Publications website. Additional data includes: calculation of Hamaker constant for systems used; calculation of energy of spreading; dimensions and AFM micrographs of wrinkles substrates used; viscosity, density and interfacial tension for lubricants used; ATR FTIR spectra of PSW; contact angle values of lubricants on substrates used in air and water; photo of custom AFM/optical cell; spreading parameter and Hamaker constant for systems used; example force curve on a LIS taken underwater; water contact angle values on infused systems used; force maps of TW upon flooding with water; maps of lubricant thickness on flat polystyrene; contact angle values on infused substrates in absence of flow in the immersion cell; dynamic contact angle values, AFM maps and higher resolution maps for wrinkled polystyrene surface infused with SO upon immersion; dynamic contact angle values and distribution of lubricant on PSW/PFPE and TW/MO; AFM force maps of PSW/SO and PSW/PFPE systems after one dip; histogram of lubricant distribution for PSW/PFPE and PSW/MO after twenty dips; radius of curvature and resulting Laplace pressure in model wrinkles; Python script used for automatic analysis of contact angle while dipping.

References


(43) Khatir, B.; Shabanian, S.; Golovin, K. Design and High-Resolution Characterization of


