Engineered Interfaces Controlling the Nucleation and Flowability of Complex Fluids

by

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Abstract

In recent years, surface engineering has enabled remarkable advances in various fields of fluid mechanics. High mobility of water and even low surface tension fluids was demonstrated using surfaces with engineered chemistry and textures, with driving forces ranging from electrical, magnetic, gravitational, as well as Marangoni forces. Engineered surfaces were also shown to control and improve processes that involve nucleation phenomena such as boiling, condensation, and water collection from moist air. However, when the working fluid contains dissolved media such as salts or an additional fluid, or when it has non-Newtonian properties such as yield stress, the performance of these surfaces may change drastically. This thesis explores how the introduction of complex fluids changes the performance of engineered surfaces, and how these surfaces may be altered to regain their capabilities and expand their range of applicability.

We start with yield stress fluids which are ubiquitous in our daily lives (examples ranging from lotions, condiments, grease, etc.) and show how even superhydrophobic surfaces fail to allow these fluids the high mobility they enable water. We show how the special combination of yield stress fluids and Lubricant-Impregnated Surfaces can yield dramatic results allowing these fluids to flow as a plug without shearing. We study the underlying principles that govern this type of mobility, and its limiting cases. We apply these principles to non-aqueous flow batteries and demonstrate how Lubricant-Impregnated Surfaces can increase the capacity of these batteries by up to fourfold by retaining the integrity of their suspended conductive media.

We then focus on nucleation and show how the performance of heat transfer surfaces during pool boiling deteriorates when hard salts such as calcium sulfate are dissolved in the liquid. We demonstrate how nucleation of salt crystals from even an undersaturated solution can cause the critical heat flux to decrease by up to threefold. We analyze the cause of this decrease and propose a passive method for restoring the performance of the surface so that the effect of dissolved salts on the critical heat flux is negligible.

Apart from salts, the interfacial properties of liquids can also change when other
liquids are dissolved in them. By monitoring the motion of bubbles under large thermal gradients, we demonstrate how the liquid-vapor surface tension of a binary mixture of alkanes differ substantially from the corresponding property of its constituents. Furthermore, we show how the liquid-vapor surface tension of these mixtures is non monotonic with respect to temperature and has a maximum (as opposed to self-rewetting fluids) for any mixture ratio.

Finally, we use engineered surfaces to capture bubbles. By studying the drainage dynamics of the thin liquid film separating a bubble and a hydrophobic surface, we learn how the textures of a surface affect its ability to capture bubbles. We leverage this understanding to create surfaces with three levels of textures that reduce the capture time of a bubble by two orders of magnitude compared to a flat surface. We then apply this design to create a device that captures bubbles in a foaming solution and prevents foam from forming in a passive and additive-free manner.

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Chapter 1

Introduction

Engineered interfaces have been in the focus of academic and industrial attention in recent years due to their ability to fundamentally change the behavior of pure fluids in various applications. From creating self-cleaning surfaces by minimizing the contact angle hysteresis of a water droplet, to improving evaporative cooling by reducing the nucleation time of vapor bubbles during pool boiling. These interfaces have shown the potential to impact various industries by using innovative manufacturing and fabrication techniques that allow to precisely tailor the mechanical, chemical, and electrical properties of these interfaces to the application of interest. However, new challenges arise when these interfaces are put into practice and used with industrial fluids which in many cases are complex. The complexities of these fluids can evoke interfacial phenomena which are different than those demonstrated with pure fluids.

For example, a common problem which we encounter on a daily basis is dispensing of fluids such as condiments, lotions, toothpaste, etc. from containers. Beyond consumer products, assuring the flow of fluids such as crude oil, mud, blood, paint, pharmaceutical products, etc., is essential for the respective industries. All of these fluids are complex as they have a yield stress which can render them immobile on engineered surfaces which otherwise allow for high mobility of Newtonian fluids. Consequently, mobility solutions for Newtonian fluids will perform differently when the working fluid is complex.

Bubble nucleation is another example of a process that is changed by complexities
of the working fluid. In pool boiling, the thermal performance of a heat transfer surface can be adversely affected by the presence of dissolved salts whose solubility decreases with temperature. Scaling due to the precipitation of such salts poses serious operational and safety challenges in several practical applications including heat exchangers, pipelines, and desalination. In other industrial processes the presence of surfactants in a liquid can give rise to foam formation driven by ebullition which can introduce process inefficiencies and decrease productivity.

This thesis explores the fundamental changes in flow and nucleation of complex fluids on engineered interfaces compared to flow and nucleation of pure fluids on these interfaces. We show how interfaces engineered for pure fluids perform differently on complex fluids and we provide fundamental understanding as to the reasons behind this change. We then leverage this understanding to design interfaces specifically for the complex fluid of interest.

In chapter 2 we study the mobility of yield stress fluids on Lubricant Impregnated Surfaces (LIS), explain the relationship between their macroscale flow behavior and the microscale properties of LIS, and elucidate the fundamental physics governing the flow of yield stress fluids on LIS. We show that LIS can induce mobility of yield stress fluids even below their yield stress by eliminating wall-induced friction and allowing for complete drag reduction with infinite slip length. We identify different mobility mechanisms, and establish a regime map for drag reduction in terms of the shear stress to yield stress ratio and the microscopic properties of the LIS, and we demonstrate these regimes in a practical application of pipe flow. We then apply these principles to viscous flow batteries which are a promising technology for large-scale grid storage needs. Today, most redox flow batteries are based on low viscosity, low concentration aqueous solutions with low cell voltage, as well as low energy density. Higher voltage and more energy dense non-aqueous flow batteries can reduce costs but can also exhibit yield stress. We incorporate LIS to promote flow in these systems and show a fourfold increase in specific charge capacity relative to conventional slippery surfaces.

In chapter 3 we explore the effect of engineered surfaces on nucleation by examin-
ing the special case of salt crystals nucleation during pool boiling in undersaturated solutions. In particular, we study the effect of dissolved salts on the dynamics of pool boiling and its impact on the heat transfer coefficient and critical heat flux (CHF). We find that even undersaturated conditions can lead to crystallization and scale buildup on boiling surface and dramatically reduce heat transfer performance. For example, the CHF for a salt solution that is 75% of the saturation concentration is found to be at least two times lower than that for deionized water. Using simultaneous high-speed optical and infrared imaging, we determine the interdependence between crystallization-induced scale formation and bubble evolution dynamics, including, bubble nucleation, growth, and departure. Based on the role of the microlayer and triple contact line on scale formation, we propose manipulating surface wettability as a means to avoid scale formation and associated reduction in heat transfer coefficient. Surfaces with hybrid wettability are demonstrated as a means to mitigate the reduction in heat transfer coefficient and CHF in the presence of dissolved salts.

In chapter 4 we explore how surface forces give rise to unique mobility regimes in complex fluids. We use a thermally pulsed wire to create a cloud of bubbles in a binary ethane-n-octane mixture and observe how the bubbles nucleate and flow under a large temperature gradient in different environment temperatures. We show that the mobility of these bubbles is non-monotonic with respect to the environment temperature and is dictated by thermocapillary forces. Specifically at low temperatures the surface tension of the vapor-liquid mixture increases with increasing temperature which causes the bubbles to eject away from the heated wire. At high temperatures the sign of the thermocapillary force is inverted such that the nucleated bubbles are attracted to the wire. As opposed to water-alcohol mixtures that have a surface tension minimum, we show that this mixture which we refer to as an equilibrated vapor-liquid mixture exhibits a surface tension maximum, creating a unique set of behaviors which have not yet been fully examined in the literature.

Finally, in chapter 5 we examine the rule of surface engineering in capturing bubbles in the context of foam prevention. Bubble capture is ubiquitous in nature and critical in many industrial applications. When a rising bubble approaches a
horizontal surface the thin liquid film separating the bubble and the surface drains. If the surface is sufficiently non-wetting, the film will break at a critical thickness and the bubble will attach itself to the surface. If the surface is sufficiently wetting, the bubble will stay detached from the surface as in the case of a spirit level. Here, we focus on aerophilic surfaces that can entrap a gaseous layer between their textures when submerged, and we show how their ability to catch bubbles relates to their texture parameters. We propose simple guidelines, based on surface slip length and liquid properties, to determine when the film would drain. We then use these findings to design a hierarchical surface that enable a reduction of two order of magnitude in capture time relative to a flat surface. Finally, we leverage these principles to create an easily scalable device that passively captures a rising flow of bubbles. This capability is applicable to a broad range of processes such as antifoaming and methane collection.
Chapter 2

Mobility of Yield Stress Fluids on Lubricant Impregnated Surfaces with Application to Energy Storage

Yield stress fluids are ubiquitous across different industries ranging from cosmetics and food products to building materials and energy.[1] These fluids exhibit solid-like properties when the applied shear stress is lower than the yield stress $\tau_y$. Once the applied stress exceeds this value, flow is initiated. The fluid behavior can be described by the Herschel-Bulkely model, which relates the shear stress $\tau$ and strain rate $\dot{\gamma}$:

$$\tau = \tau_y + \eta \dot{\gamma}^n$$  \hspace{1cm} (2.1)

where $\eta$ and $n$ are the consistency and flow indices. Because of these properties, a key challenge with yield stress fluids is that they are difficult to flow and stick to surfaces resulting in significant additional energy required for flow as well as associated product loss and cleaning costs. For example, up to 25% of a product per container is wasted because it cannot be dispensed, resulting in an overall product loss that is estimated in the order of millions of tons. Hence reducing wall friction, improving flowability, and eliminating stiction of these fluids is of significant interest. Despite the vast existing knowledge on the drag reduction of Newtonian fluids,[2–8] rheology
of yield stress fluids,[9–11] and the flow of yield stress fluids in various geometries,[12–15] drag reduction of yield stress fluids remains a developing field as slip mechanisms differ depending on the type of fluid in question.[16] Surfaces that reduce drag for Newtonian fluids do not necessarily have the same performance for yield stress fluids. Hence, there is a need to develop slippery surfaces that can increase the mobility of these fluids in a repeatable, controlled, and robust manner.

Here we show how Lubricant-Impregnated Surfaces[17] can be designed to enhance mobility of yield stress fluids. These surface were shown to reduce drag of water,[18] alter the dynamic behavior of water droplets,[19] and render a yield stress fluid to flow as plug and improve the performance of a suspension-based flow battery.[20] An LIS consists of a textured solid impregnated with a lubricating fluid.[19, 21–26] A droplet on such a surface can exist in one of twelve thermodynamic states which depend on the properties of the solid, the impregnated lubricant, the working fluid, and the environment.[19] For stable lubricant impregnation, the contact angle of the lubricant (subscript o) on the smooth surface (subscript s) in the surrounding environment (here air, subscript a) as well as the contact angle of the lubricant on the smooth surface in the presence of the working fluid (subscript w) need to be smaller than the critical angle defined as:

$$\cos \theta_{cr} = \frac{1 - \varphi}{r - \varphi}$$

where \( r \) is the total surface area divided by the projected area, and \( \varphi \) is solid fraction defined as the emerged surface area divided by the projected surface area. Two specific LIS configurations are of interest here and they are determined by the spreading coefficient of the lubricant on the solid in the presence of the working fluid (\( S_{os(w)} = \gamma_{wa} - \gamma_{oa} - \gamma_{ow} \)). When this spreading coefficient is positive \( S_{os(w)} \geq 0 \), the case of spreading LIS, the tops of the micro-posts are covered by a thin van der Waals film of the impregnated lubricant. When the spreading coefficient is negative \( S_{os(w)} < 0 \), the case of non-spreading LIS, the tops of the micro-posts remain exposed. Commercial applications[27] on the flow of yield stress fluids such as ketchup,
mayonnaise, waxy crude oil, toothpaste, etc. on LIS have demonstrated its performance but have not explained the physical mechanism that govern the remarkable slip phenomenon. Herein we study the dynamic behavior of yield stress fluids on LIS, elucidate the key physical mechanisms that control slip, and establish mobility regimes.

2.1 Mobility of Yield Stress Fluids on Lubricant Impregnated Surfaces

A common example of a yield stress fluid is a suspension of particles in a solvent; these fluids exhibit a yield stress when the volume fraction of the particles is above a critical value.[28–30] One example is Carbopol which is considered an ideal yield stress fluid whose slip mechanisms have been extensively studied.[31–36] We use 1% wt Carbopol ($\tau_y = 66.7 Pa$) as a model fluid in our study.

For example, a water droplet exhibits low contact angle hysteresis on flat polytetrafluoroethylene (PTFE), which allows it to rapidly roll when the surface is tilted as shown in Figure 2-1A. However, a similar volume of Carbopol placed on the same surface sticks and stays immobile as shown in Figure 2-1B. Surprisingly, this is also the case for a superhydrophic surface (static contact angle $165.3^\circ$) on which water droplets exhibit high mobility while Carbopol stays immobile. A similar behavior is observed when Carbopol is placed on a non-spreading LIS with a large enough $\varphi$ as shown in Figure 2-1F (the LIS consists of an array of square micro-posts of size $a$ and depth $h$ with varying posts pitch $b$, see Materials and Methods section). However, on a spreading LIS Carbopol moves readily along the surface as shown in Figure 2-1H. To understand this peculiar behavior, systematic experiments were conducted under a stress-controlled cone and plate rheometer on both spreading and a non-spreading LIS with different texture geometries.
Figure 2-1: Performance of drag reduction solutions. A 187 μL water droplet moving down a tilted PTFE tape. B 723 μL 1%wt Carbopol sticking to a tilted Teflon tape. C 65 μL water droplet moving down a tilted superhydrophobic surface. D 57 μL 1%wt Carbopol sticking to a tilted superhydrophobic surface. E Illustration of a non-spreading LIS where \( h \) is the height of the post, \( b \) is the pitch, and \( a \) is the width of a post with a square profile. F 165 μL 1%wt Carbopol sticking to a tilted non-spreading LIS. G Illustration of a spreading LIS. H 118 μL 1%wt Carbopol sliding on a tilted spreading LIS. 30° tilt for all panels. All scale bars are 5 mm.

2.1.1 Spreading LIS

Figure 2-2A illustrates the experimental set up with a spreading LIS sample in which Carbopol is placed between a rotating stainless steel cone (20 mm diameter) and the surface of interest and sheared under a prescribed shear stress (see Materials and Methods section). The control surface was the stationary plate of the rheometer (stainless steel) on which the Carbopol did not slip and its behavior is well described by a Herschel-Bulkely model as presented in Figure 2-2B. In contrast on a spreading LIS, the Carbopol is mobile even when the applied shear stress is below the yield stress for all samples. Moreover, for a given shear stress, the apparent strain rate grows with increasing values of texture pitch \( b \). In fact, at high enough shear stresses, drag reduction was so high that Carbopol flew off the samples with the highest pitch.
(b = 25, 50μm) due to centrifugal forces; hence measurements were restricted to lower shear stresses values for these samples. Drag reduction DR is quantified in terms of the ratio of the apparent strain rate, \( \dot{\gamma}_c \), measured on the control sample to that measured on an LIS, \( \dot{\gamma}_{LIS} \). Since the measurements are performed in a stress-controlled regime, the drag reduction is a function of the applied shear stress and is given by:

\[
DR(\tau) = 1 - \frac{\dot{\gamma}_c}{\dot{\gamma}_{LIS}}
\]  

(2.3)

As can be seen in Figure 2-2C, drag reduction grows inversely with the ratio of shear stress to yield stress. When this ratio is smaller than unity, complete drag reduction is attained since the fluid is immobile on the control surface. To understand the underlying phenomenon we focus on the regime in which the Carbopol does not undergo any shear, \( \tau < \tau_y \). Normally, in a cone and plate rheometer the angular velocity of the rotating cone, \( \Omega \), will be used to calculate the apparent strain rate \( \dot{\gamma}_{app} = \Omega / \alpha \), where \( \alpha \) is the cone angle. However, in this regime the Carbopol does not shear and the measured velocity is exclusively due to slip which is caused by flow of the lubricant between the micro-posts. For this case we approximate the system as a plate-plate rheometer in which the bottom face of the undeformed Carbopol is acting as the rotating top plate and the base of the LIS sample is acting as the stationary bottom plate. The relevant dimensions are shown in the inset of Figure 2-2A. Hence, the measured angular velocity is entirely due to the shearing of the impregnating lubricant so that the strain rate of the lubricant is given by:

\[
\dot{\gamma}_{out} = \frac{r \Omega}{h}
\]  

(2.4)

where \( r \) is the cone radius. Plotting the strain rate \( \dot{\gamma}_{out} \) in the lubricating layer against the shear stress \( \tau_r \) for a plate-plate rheometer shows that the relation between the two is linear for all values of pitch. Thus, LIS act as a Newtonian lubricating layer with effective viscosity that increases as the pitch of the textures decreases. The ratio of this effective viscosity to the lubricant viscosity depends on the ratio of post height to post pitch as \( \mu_{eff}/\mu \approx 1 + \beta h^2/(a + b)^2 \) where \( \beta \) is a constant as shown
in Figure 2-3. This scaling was shown previously in experiments studying wicking of fluids through textured samples.[37, 38]

Figure 2-2: Mobility on spreading LIS. A Illustration of experiment set up. Cone is 20 mm in diameter and has an angle of 4°. B Results for the control substrate and spreading LIS with varying post pitch. Solid line represents a Herschel Bulkely model with $\tau_y = 66.7 Pa$ $\eta = 55.6 Pa s^{-n}$ $n = 0.40$. C Drag reduction on LIS samples. D Stress vs. strain rate in the lubricating layer. Solid lines represent linear fits. E Slip-dominated regime and the transition regime. Slope of the solid line is 0.75. F Transition regime and shear-dominated regime. Solid line represents the Herschel-Bulkley model in A.

Thus, in the regime of low shear stress, the stress versus strain rate is linear and given by:

$$\frac{\tau}{\tau_y} \approx \frac{\mu \dot{\gamma}_{oil}}{\tau_y} \left(1 + \beta \frac{h^2}{(a + b)^2}\right)$$  \hspace{1cm} (2.5)

By plotting the measurements according to this relation we see in Figure 2-2E that the data collapses on a linear master curve with a slope of 0.75. When the applied shear stress is larger than the yield stress of the material, the apparent strain rate has contributions from both shearing of the lubricant and Carbopol. Strain
rate due to the shearing of Carbopol can be expressed by \( \dot{\gamma}_{YS} = (\Omega - \Omega_s)/\alpha \), where \( \Omega_s \) is the angular velocity at the lubricant- Carbopol interface. When \( \tau \gg \tau_y \), the angular velocity at the lubricant- Carbopol interface becomes negligible compared to that measured by the rheometer (\( \Omega \gg \Omega_s \)) and we can approximate the strain rate of Carbopol by the apparent strain rate, \( \dot{\gamma}_{YS} \approx \dot{\gamma}_{app} \). As a result, when \( \tau \gg \tau_y \) using 2.1 we write the following relation between the applied shear stress and the apparent strain rate,

\[
\frac{\tau}{\tau_y} = \frac{\eta \dot{\gamma}_{YS}}{\tau_y} + 1 \approx \frac{\eta \dot{\gamma}_{app}}{\tau_y} + 1 \quad (2.6)
\]

The above model is in good agreement with the experiments as shown in Figure 2-2F. In between the slip dominated and shear dominated regimes (\( \tau < \tau_y, \tau \gg \tau_y \)), the contribution of slip to the measured strain rate is comparable to that of Carbopol shearing since \( \Omega_s \) is no longer negligible compared to \( \Omega \).
2.1.2 Non-spreading LIS

On non-spreading LIS (Figure 2-4A), we find that the behavior of Carbopol for $\tau < \tau_y$ is no longer linear but follows a Herschel-Bulkely model with parameters that depend on the pitch as shown in Figure 2-4B. Furthermore, we measure an effective yield stress which is lower than the actual yield stress because of the contact area is limited to the post tops.

Hence, by minimizing the solid fraction of a non-spreading LIS we can induce high mobility similar to that of a spreading LIS. We demonstrate this effect by creating vanishingly small solid fraction surfaces ($\varphi \sim 0$) comprising an array of close packed pyramidal structures with hierarchical features as shown in Figure 2-4C. For these structures the critical angle $\theta_{cr} = 63.4^\circ$ is large enough so that the lubricant will be stably impregnated within the texture. As shown in Figure 2-4D and E, the mobility of Carbopol on the non-spreading LIS with low $\varphi$ is similar to that of the spreading LIS. Indeed, rheometer experiments for both spreading and non-spreading LIS show the dependence between stress and strain rate collapses onto each other as can be seen in Figure 2-4F. Note that this is in contrast to the immobility of Carbopol on both superhydrophobic surface (Figure 2-1D) and non-spreading LIS with high $\varphi$ (Figure 2-1F).

2.2 Application to Enclosed Conduits

Here we demonstrate the performance of an LIS in a practically relevant configuration of pipe flow. A spreading LIS is created on the inner surface of a glass tube (see Materials and Methods section), and the LIS tube is then compared to an unmodified tube by imaging the behavior of Carbopol under a constant pressure difference. On the unmodified glass tube Carbopol is immobile when the applied pressure induces a wall shear stress below the yield stress of the material (here $\tau_{wall} = 0.6\tau_y$). However, on a spreading LIS, the Carbopol moves without shearing as the system is in the slip dominated regime ($\tau_{wall} < \tau_y$). Consequently, Carbopol moves as a plug throughout the entire length of the coated tube as shown in Figure 2-5A. Increasing the pressure so
Figure 2-4: Mobility on non-spreading LIS. A Illustration of non-spreading LIS on the experiment set up. View Z emphasizes the bare post-tops and the regions in which they pin the Carbopol. B Results of non-spreading LIS with different pitch values. Solid lines represent Herschel-Bulkley of the Carbopol and the samples in the region below yield stress. C A low solid fraction pyramid surface with inset focusing on the small features on the face of the pyramid. Scales bar are 50 μm in the panel and 1 μm in the inset. D Carbopol sliding down a spreading low-phi LIS. E Carbopol sliding down a non-spreading low-phi LIS. F Stress versus strain rate for Carbopol on spreading and low φ non-spreading LIS. Solid line represents a Herschel-Bulkley model for a 1%wt Carbopol.

that the wall stress exceeds the yield stress ($\tau_{wall} = 2\tau_y$) causes the Carbopol to shear as well as slip within the LIS coated tube. In Figure 2-5B, this flow behavior can be seen by the displacement of the free surface on which the pressure is applied as well as deformation of the Carbopol. When the wall stress is increased further ($\tau_{wall} = 4.5\tau_y$), displacement due to slip is small compared to deformation due to shear. as the system is in the shear dominated regime. This effect is represented in Figure 2-5D, where the Carbopol deforms in the LIS coated tube and the displacement of the free surface
due to slip is relatively small such that the Carbopol smears on the tube walls. We quantify the mobility induced by LIS by introducing a parameter which compares translation due to slip with deformation due to shear \( \xi = L_t/[(L_f + L_t) - L_t] \) where \( L_t \) and \( L_f \) are the initial and final lengths of the Carbopol, and \( L_t \) is the translation length as shown in Figure 2-5A. In the slip dominated regime (\( \tau_{wall} = 0.6\tau_y \)), \( \xi = 1 \), indicating pure translation with negligible deformation whereas in the shear dominated regime (\( \tau_{wall} = 4.5\tau_y \)) \( \xi = 0.13 \) indicating high deformation and low mobility. On an unmodified tube Carbopol displacement is exclusively due to shear (\( \xi = 0 \)) as the Carbopol deforms without slipping until it ruptures and smears on the wall as shown in Figure 2-5D.

![Figure 2-5: Flow regimes in an enclosed geometry. Flow of Carbopol in a 0.25" outer diameter, 0.16" inner diameter borosilicate glass tube. Carbopol was dyed using a water soluble dye at a 0.2%wt concentration. A Slip dominated regime on a spreading LIS. B Transition regime on a spreading LIS. C Shear dominated regime on a spreading LIS. D Unmodified glass tube.](image)

### 2.3 Designing LIS for Viscous Flow Batteries

Flow batteries are a promising technology for large-scale energy storage due to their potential for meeting costs of $100 per kWh at a system level and their scalability.[49, 50] Today, most redox flow batteries are based on dissolved redox molecules (e.g. vanadium ions) in an aqueous solution. However, expensive ion-selective membranes, low solubility of active materials (<2 M), and low cell voltages limited by
the electrolysis of water challenge widespread commercialization. On the other hand, flow electrodes based on semi-solid suspensions that have a yield stress[50–64] can increase the energy density by an order of magnitude using solid lithium storage compounds.[51] A continuous percolating network of nano-scale carbon (such as Ketjenblack ECP600JD) provides electronic conductivity to the suspended active materials in the electrolyte. Higher loadings of carbon in the flow electrode allow for higher current densities and lower polarization but drastically increase the yield stress of the flow electrode.[50] For example, increasing the carbon content from 0.50 to 0.75 vol% can increase the capacity threefold from ~250 to ~750 mAh/g. However, this effective increase in capacity has the adverse effect of increasing the yield stress, increasing the yield stress from 1.3 to 4 Pa (see Table 2.1).

Table 2.1: Herschel-Bulkley model parameters for the rheology of Li-PS flow electrodes as a function of KB loading.

<table>
<thead>
<tr>
<th>vol % KB</th>
<th>( \tau_y ) Pa</th>
<th>( \eta ) Pa ( \cdot ) s(^n)</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>9.34</td>
<td>3.54</td>
<td>0.40</td>
</tr>
<tr>
<td>0.75</td>
<td>3.87</td>
<td>1.13</td>
<td>0.51</td>
</tr>
<tr>
<td>0.50</td>
<td>1.33</td>
<td>0.49</td>
<td>0.59</td>
</tr>
<tr>
<td>0.25</td>
<td>0.20</td>
<td>0.12</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Here we demonstrate that LIS can be applied to the design of flow batteries with electrodes comprising a wide variety of solvents. In particular, we explore using LIS to enable the flow of a lithium polysulfide flow electrode (Li-PS)[50,59] comprising 2.5 M sulfur in triglyme solvent, with electronic conductivity imparted by 0.75 vol% of dispersed Ketjenblack (KB). We demonstrate a specific capacity of ~800 mAh/g – S in a model gravity-induced flow cell (GIFcell) of half-cell configuration (i.e. one electrode flows and the other is stationary), which is a fourfold increase compared to previous work.

In order to design LIS for use in an electrochemical system: (1) the lubricant should be immiscible with the working fluid, (2) the lubricant must be electrochemically inactive, and (3) the lubricant must preferentially wet the porous walls in the presence of the working fluid. In order to function as designed, the lubricant and
the working fluid (in this case the flow electrode) should be immiscible; otherwise, no interface would exist. Flow electrode solvents demonstrated in the literature are diverse[49] and an ideal lubricant should be immiscible with a number of common solvents. Both silicone oils and fluorinated liquids are appropriate choices for the lubricant due to their stability and widespread availability. These oils have been screened for miscibility with nine common solvents. Whereas the fluorinated liquids are immiscible with all solvents, silicone oil was found to be miscible with several including dichloromethane, diglyme, and THF. The results for all solvents are presented in Table 2.2.

Table 2.2: Solubility of fluorinated lubricants and silicone oil with common flow electrode solvents. Miscibility is determined by vigorously shaking a vial of 5 mL of the lubricant and 5 mL of the solvent and visually determining if an interface exists after 24 hours. The fluorinated lubricants tested are FC70, Fomblin, Krytox, and perfluorodecalin.

<table>
<thead>
<tr>
<th></th>
<th>Fluorinated</th>
<th>Silicone Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>immiscible</td>
<td>immiscible</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>immiscible</td>
<td>miscible</td>
</tr>
<tr>
<td>Diglyme</td>
<td>immiscible</td>
<td>miscible</td>
</tr>
<tr>
<td>DMSO</td>
<td>immiscible</td>
<td>immiscible</td>
</tr>
<tr>
<td>PC</td>
<td>immiscible</td>
<td>immiscible</td>
</tr>
<tr>
<td>TEG-DME</td>
<td>immiscible</td>
<td>immiscible</td>
</tr>
<tr>
<td>THF</td>
<td>immiscible</td>
<td>miscible</td>
</tr>
<tr>
<td>Triglyme</td>
<td>immiscible</td>
<td>immiscible</td>
</tr>
<tr>
<td>Water</td>
<td>immiscible</td>
<td>immiscible</td>
</tr>
</tbody>
</table>

Additionally the lubricant must be electrochemically stable. Consistent with the electrochemical cycling described later in this paper, lubricants were screened for electrochemical activity in a voltage window of 1.6 to 2.8 V with respect to Li/Li+. Figure 2-6b,c shows the cyclic voltammograms of several fluorinated liquids and silicone oil as well as a reference solvent, triglyme, used in the polysulfide flow electrodes. The current densities (<1.5 \( \mu A/cm^2 \)) over the 1.6-2.8 V window are significantly less than that encountered during operation of typical electrochemical cells (>0.1 mA/cm\(^2\)). Although Krytox lubricant had the lowest current density, all of the fluorinated liq-
uids as well as silicone oil appear to be free of parasitic side reactions over the relevant voltage window. Finally, the morphology adopted by the lubricant phase needs to be thermodynamically stable in order to form an LIS as described in the previous subsections.

Figure 2-6: (a) Cyclic voltammogram of several candidate lubricants and triglyme solvent conducted at a scan rate of 10 mV/s. Lithium is used as the counter and reference electrodes. A Tonen separator wetted with the electrolyte is used in all the tests. (b) Zoomed region depicted in (a) showing a current density of 0.1-0.2 μA/cm² over the relevant voltage range for lithium-sulfur chemistry for the lubricants and solvent. The current density in the model electrochemical cell during operation is more than two orders of magnitude greater.

To create an LIS suitable for the current flow battery, a fluorinated liquid (Krytox) was chosen as the lubricant and a porous Teflon was chosen as the textured solid due to its chemical similarity to fluorinated liquids. The Krytox/Teflon LIS was validated against nine common solvents with surface tensions $\gamma_w = 25 - 72 \text{ mN/m}$ by submerging in each solvent for five days. The sample was then removed and a 5μL drop of solvent was placed on the surface. In all cases, the solvent drop rolls from the sample when it is tilted to $< 5^\circ$ indicating that the Krytox/Teflon LIS retain their slippery properties and are stable in the solvents tested.

Figure 2-7 visually demonstrates the ability of LIS to promote slip. In Figure 2-7a a drop of Li-PS suspension (yield stress $\tau_y = 4Pa$) placed on a gold surface flows under gravity but shortly thereafter stops flowing and the trailing edge remains pinned on the substrate. The same drop, however, slides on the LIS (Figure 2-7b). This experiment also highlights the difficulty of overcoming contact line pinning in
such a flow. Although low energy materials such as Teflon have been shown to provide slip for yield stress fluids,[16] any surface roughness can eliminate that slip.[33, 36]

![Gold (no-slip)](image)

**Figure 2-7:** Time-lapse comparing the flow behavior of a 2.5 M Li-PS suspension with 0.75vol% KB on (a) flat gold surface tilted to 60° and (c) an LIS tilted to 60°. The flow electrode drop yields under gravity on gold but shortly thereafter stops flowing, and the trailing edge remains pinned on the substrate. The same drop, however, slides on the LIS. Both drops are 25 μL.

### 2.4 LIS Demonstrated in a Gravity-Induced Flow Cell

In order to demonstrate the impact of LIS surfaces in a flow battery system, we conducted experiments on a novel device referred to as the gravity-induced flow cell (GIFcell).[50] This type of flow battery has a simple construction with no moving parts, and uses energy-dense electrodes that flow under the force of gravity through a centrally positioned electrochemical stack. The LIS used here could also be integrated into other redox flow battery configurations and chemistries. Following earlier work,[50] lithium-sulfur chemistry was utilized, with the positive flowing electrode being a suspension comprising a solution of lithium polysulfide (Li-PS) containing dissolved Li₂S₈ at 2.5 M concentration with respect to S, in triglyme solvent, to which 0.75vol% KB as a solid phase is added for electronic conductivity. In the liquid
electrolyte, 0.5 M LiTFS (lithium bis(trifluoromethanesulfonyl)imide) was added to provide ionic conductivity, and 1wt% LiNO3 was added as a solid-electrolyte inter-phase (SEI) stabilizer. The stationary negative electrode is a lithium metal foil. A microporous separator (Tonen Chemical Corporation, Japan), with pore size smaller than the KB particle aggregates was used to prevent electrical shorting between the positive and negative electrodes. An exploded view of the device is shown in Figure 2-8. The LIS lines the flow channel except at the surfaces of the current collectors which must remain in electronic contact with the KB in suspension. Figure 2-9b show that the Li-PS promotes flow in the GIFCell.

![Image](image.png)

Figure 2-8: Exploded view of the gravity-induced flow cell (GIFcell) used to demonstrate the benefits of LIS. The flow electrode flows under the action of gravity in a 100 x 16 mm flow channel that is lined with LIS. In the electrochemical stack region, the Li-PS electrode flows between a stainless steel current collector sputtered with gold and a separator beneath which the Lithium anode sits.

The GIFcell was tested in an intermittent-flow mode, wherein an aliquot of Li-PS filling the cell remains stationary during electrochemical cycling. Upon completion of the electrochemical cycle, the next aliquot flows into the electrochemical active region by tilting the GIFcell as depicted in Figure 2-9a. The electrochemical energy efficiency for each cycle is calculated as:

\[
\text{Energy efficiency} = \frac{V_d I_d t_d}{V_c I_c t_c} \tag{2.7}
\]

where \(V\) is the potentiostatic voltage, and \(I t\) is the total charge delivered. The subscripts D and C represent discharging and charging respectively. Figure 2-9c shows the potentiostatic cycling performance and Figure 2-9d shows the discharged capacity.
and energy efficiency for various aliquots and cycle numbers of the GIFcell with LIS. An energy efficiency of 93% is achieved for the first cycle, which shows that energy can be effectively transferred in and out of the GIFcell. The current density of 0.65-0.7 mA/cm² for the first 6 min corresponds to a theoretical C-rate of 1/20 h⁻¹. The current density then decays to 0.2 mA/cm², giving a discharge specific density of 777 mAh/g - S over the duration of 20 hours. The second aliquot is then moved into the active region by tilting the GIFcell, after which about 770 mAh/g - S of capacity is extracted.

2.5 Discussion and Outlook

We show that that LIS can be designed to achieve drag reduction of up to 100% for the flow of yield stress fluids. This dramatic reduction is in contrast with only 16% for Newtonian fluids[18] and highlights the potential of LIS for applications involving yield stress fluids. Essentially, LIS acts as a stable Newtonian lubricating layer with an effective viscosity that depends on the viscosity of the lubricating fluid and the post height to pitch ratio. When the shear stress is lower than the yield stress, the system is in the slip dominated regime, where the yield stress fluid moves without shearing. When the shear stress is sufficiently larger than the yield stress, the apparent strain rate is mainly due to shearing of the yield stress fluid, and the drag reduction due to LIS is negligible. In the transition regime, the contribution of slip to the apparent strain rate is comparable to that of shearing of the yield stress fluid. When the applied shear stress is much larger than the yield stress, an LIS will not be as efficient in reducing drag as in applications where the applied shear stress is smaller than the yield stress. For the latter case LIS can induce mobility without shear (plug flow) which is of high importance in applications where the integrity of the fluid, and more specifically the suspended media, is crucial. Furthermore, LIS can avoid smearing of the product on the substrate, which is essential to eliminate product loss, cleaning costs, and assure flowability. Most often, designing a thermodynamically stable spreading LIS is extremely challenging for many practical applications due to material
Figure 2-9: (a) Schematic of the GIFcell half-flow configuration with lithium metal as the anode and the Li-PS suspension as the flowable cathode. The GIFcell operates in intermittent flow mode where one aliquot moves into the electroactive zone (between the two current collectors) and remains to undergo electrochemical cycling. Then, the GIFcell is tilted to move the next aliquot into the zone to undergo the same cycling. The Li-PS suspension consists of 2.5 M (with respect to sulfur) of Li₂S₈, 0.75vol% KB, 0.5 M LiTFSI, and 1wt% LiNO₃. (b) Time-lapse photos of the Li-PS suspension flowing over the electrochemical stack in the GIFcell demonstrate that the Li-PS suspension can repeatedly flow on the LIS in the GIFcell. The first frame shows the GIFcell immediately after being flipped, and the second frame shows 60 seconds later after the flow electrode has passed through the current collector. (c) Current density against time for the GIFcell during electrochemical cycling for four aliquots. Each aliquot was subjected to two potentiostatic cycles of discharging at 1.7 V for 20 hr and charging at 2.7 V for 20 hr. (d) The specific capacity of the GIFcell during discharge (black squares) and the round-trip efficiency (blue triangles) of the GIFcell with LIS for the four aliquots where each aliquot is subjected to two electrochemical cycles.

constraints. Using an excess layer of lubricant to submerge the texture will only have a temporary effect as the excess lubricant will drain due to external forces. However, stable non-spreading LIS can be more readily achieved and expands the materials set. In this case mobility is dictated by the solid fraction of the exposed features as they induce pinning. We demonstrate that high mobility can be attained even for non-
spreading LIS by developing surfaces with minimal solid fraction, thereby opening the
door to many practical applications. We incorporate LIS into viscous flow batteries
with yield stress, which expand the material design space for flow batteries and allow
the use of more energy-dense solid materials. However, such suspensions are con-
sequently challenging to flow, and low surface energy solid materials, such as Teflon
appear to be insufficient for enabling repeatable flow as they do not eliminate pinning
forces. Furthermore, low surface energy solids are limited to a few specific polymers
that may not be widely usable in electrochemical systems.[16] By contrast, LIS has
a set of well-defined design rules,[17–19] which we exploit to create LIS that is sta-
ble chemically, electrochemically, and thermodynamically. In future work, additional
benefits from incorporating LIS into flow batteries may be explored, including the
boosting of energetic efficiencies from velocity profiles that are controllably modified
due to slip[65] and mitigating electronic conductivity losses associated with shearing
of the carbon network.[56,66] In addition, the design rules laid out here for incorpo-
rating LIS into batteries, combined with previous work demonstrating inhibition of
mineral scale formation in aqueous systems,[67] could be used to mitigate precipitate
formation in both flowing and non-flowing battery configurations.

2.6 Materials and Methods

The textured silicon substrates used in this study were prepared by a standard pho-
tolithography process. The resulting micro-posts had a square geometry with width
$a = 10 \mu m$, height $h = 12 \mu m$, and varying pitch $b = 5, 10, 25$ and $50 \mu m$. The
samples were then cleaned in an oxygen plasma chamber (PDC-32G-2 by Harrick
Plasma) at 200 mTorr for 20 minutes and then treated with a low-energy silane
Octadecyltrichlorosilane (denoted here as OTS, advancing and receding contact an-
gle of water on a flat surface in the presence of air are $\theta_{ws(a),adv} = 109.4^{\circ} \pm 0.5$
and $\theta_{ws(a),rec} = 100.1^{\circ} \pm 1.1$), or Perfluorooctyltrichlorosilane (denoted here as FS,
$\theta_{ws(a),adv} = 112.4^{\circ} \pm 0.7$ and $\theta_{ws(a),rec} = 93.4^{\circ} \pm 3.3$, respectively). Both were pur-
chased from Sigma Aldrich and used without modification. To create a stable layer
of lubricant the samples were lowered perpendicularly into a bath of silicone oil using a controlled dip coater (Multi Vessel Small by KSV Nima) at a speed of 10 mm/min to prevent entrapment of air bubbles on the surface. To avoid entraining excess films and ensure a thermodynamically stable impregnation, the sample was withdrawn at a speed such that the critical capillary number $C_{ac} = \mu V_{cr}/\sigma = 10^{-4}$, is attained,[37] where $\mu$ is the viscosity of the lubricant, $\sigma$ is its surface tension, and $V_{cr}$ is the resulting critical withdrawal speed. LIS in the glass tube was prepared by baking a 5 cSt silicone layer on the inner surface of a 0.25" outer diameter, 0.16" inner diameter borosilicate glass tube and impregnating this layer by dipping the tube in a 100 cSt silicone oil.[25] To create the LIS for the flow battery, a Teflon membrane (PTFE Unlaminated Membrane Filters, Sterlitech Corporation, United States) with an effective pore size of either 200 nm pores was impregnated with Krytox 1506 (DuPont) using the method above and the resulting LIS were then lightly rinsed with isopropyl alcohol. Contact angles of silicone oil were measured on the FS coated silicon surfaces in the presence of air and deionized (DI) water using a Contact Angle Goniomètre (Ramé-Hart Model 500). The advancing and receding angles were taken as an average of at least three measurements on different location on the surface. The advancing angle was measured by adding silicone oil to a 5 $\mu$L oil droplet at a rate of 4.2 nL/s while measuring the diameter of the triple contact line. When the diameter started to increase, the measured contact angle was taken as the advancing contact angle. Similarly for the receding contact angle, oil was extracted from the droplet at a rate of 6.7 nL/s and the receding contact angle was taken as the contact angle when the triple contact diameter has started to decrease. The measured contact angles are reported in Table 2.3.

Table 2.3: Contact Angle of Silicon Oil on FS Functionalized Flat Wafer in Water and in Air

<table>
<thead>
<tr>
<th></th>
<th>Advancing</th>
<th>Receding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>58.3 ± 2.7</td>
<td>31.3 ± 0.3</td>
</tr>
<tr>
<td>Air</td>
<td>62.6 ± 0.3</td>
<td>42.4 ± 0.6</td>
</tr>
</tbody>
</table>
Carbopol was prepared by slowly adding crosslinked polyacrylic acid polymer (Carbopol 940 by Lubrizol) into DI water that was agitated at a rate of 800 rpm by a mixing impeller (Cole-Parmer Compact Digital Mixer System, 50 to 2500 rpm by Cole Parmer). Before adding the dry polymer, any lumps were broken apart. Agitation continued for an hour, after which a solution of 18% NaOH in water (prepared by diluting a 50% NaOH solution by Sigma Aldrich) was added in order to neutralize the pH. The base solution was introduced at a weight ratio of 2.3 in a dropwise manner. Rheology experiments were performed using a torsional rheometer (AR-G2 by TA Instruments). A cone and plate geometry (20 mm diameter, 4° cone angle) was used in all experiments with silicon samples attached to the bottom flat plate using a double sided tape. Carbopol was then placed on the silicon samples and the cone was lowered until it was 30 μm above its truncation gap. Then, any excess of Carbopol was cleaned from the perimeter of the geometry before the cone was lowered further to the truncation gap. All tests were performed at atmospheric pressure and at 25 °C, which was regulated with a Peltier plate system. All samples were pre-sheared at 100 s⁻¹ prior to measurement and left to equilibrate for 4 minutes. The tests were performed by decreasing the applied shear rates to avoid possible transient shear banding.[68] The constant pressure set up consists from a syringe pump connected to a pressure transducer and a signal amplifier (PHD ULTRA syringe pump with an APT300 pressure transducer and a TAM-D amplifier, all by Harvard Apparatus). The behavior of the Carbopol was recorded with an optical camera (D800 with a 70-180mm lens, both by Nikon).

Electrochemical and rheological testing for the flow battery sections were conducted in an Argon-filled glove box (MBRAUN, Newburyport, MA, US) with oxygen and moisture levels maintained below 5 and 1 ppm, respectively. The lithium polysulfide flow electrode was formulated by adding 1 wt% of lithium nitrate (LiNO₃, Sigma-Aldrich) and 0.5 M of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Sigma-Aldrich) to triglyme (Sigma-Aldrich). Lithium sulfide (Li₂S, Alfa) and sulfur (Sigma-Aldrich) was then added to the solution to a total sulfur concentration of 2.5 M. The mixture was stirred mechanically at a temperature of 60 °C for 12
h to obtain a dark brown lithium polysulfide (Li₂S₈) solution. Conductive carbon black (Ketjenblack ECP600JD, Azko Nobel Polymer Chemicals LLC, Chicago, Illinois, US) was combined with half of the Li₂S₈ solution in a 20 mL glass vial and then the rest of the Li₂S₈ solution was added. This method of mixing was found to yield a more reproducible suspension compared to directly adding the KB to the solution. The resulting suspension was then sealed in a vial by black insulating tape and removed from the glove box. The vial was sonicated in an ultrasonic bath for 60 min to obtain homogeneity before testing. For cyclic voltammetry tests to measure the electrochemical stability of lubricants, Swagelok type cells with 0.56 mm deep and 0.55 mm diameter circular wells were used. Lithium was used as the counter and reference electrode. A Tonen separator (Tonen Chemical Corporation, Japan) soaked with the electrolyte (0.5 M LiTFSI, 1wt% LiNO₃ in triglyme) separated the lithium from the cathode. The cathode consisted of 5 μL of the solution of interest. The voltage was swept between 1.6 and 2.8 V with respect to Li/Li⁺, at a 10 mV/s scan rate. All cell assembly was performed inside an argon-filled glovebox. The cells were tested on a Solartron potentiostat operating a 1400 Cell Test System. Prior to assembly of the GIFcell, the following procedures were carried out. The stainless steel current collector that would be in contact with the cathode material was sputtered with gold to reduce interfacial impedance. The LIS were placed on the flow channels. The GIFcell parts were then assembled in the glove box. A thin foil of lithium was placed on a current collector and wrapped with a Tonen separator soaked with the electrolyte (0.5 M LiTFSI, 1wt% LiNO₃ in triglyme) separated the lithium from the cathode. The wrapped current collector was then secured in place. The two plates of the GIFcell were secured using bolts and nuts. The flow electrode (Li₂S₈ suspension) was introduced into one side of the channel by injection with a syringe through a port. The GIFcell was tested on a Solartron potentiostat operating a 1400 Cell Test System.
Boiling is important in various processes ranging from power generation, oil and gas, chemical processes, and desalination.[69, 70] There has been an intense effort towards enhancing boiling performance by engineering surfaces.[6, 71–76] These studies have almost always used deionized water or pure working fluids such as fluorinated liquids to characterize boiling behavior. However, the presence of even small amount of salts (minerals) can have a significant negative impact on the overall performance of heat exchangers, and boiling curves obtained using idealized working liquid are no longer applicable.[77] Crystallization of dissolved minerals in water often leads to scaling (fouling) of heat exchanger surfaces, which adversely affects the thermal performance and power efficiency in industrial applications.[77, 78] The formation of scale in combustion steam generators can lead to rapid increase in wall temperature and pose safety and operational issues in boilers.[79] The efficiency losses associated with fouling of heat exchanger surfaces have been estimated be about 2% of the total world
energy production per year.\[80,81\] The issue of scaling is pronounced in the presence of salts such as calcium sulfate, barium sulfate and calcium carbonate that have an inverse solubility (the solubility decreases with increase in temperature).\[82\] Owing to the low thermal conductivity, the precipitated scale layer acts as a thermal barrier and causes severe deterioration in heat transfer, which results in the loss in energy efficiency, overheating of boiler tube material, and even tube failure.\[83\] Due to the detrimental effects of scale, the quality of feed water into the boilers is stringently controlled. Even with the controlled water chemistry, scaling almost always occurs. Existing solutions for scale mitigation rely on mechanical or chemical techniques.\[79\] The mechanical techniques are based on physical removal while the chemical techniques rely on additives that can shift the precipitation equilibrium curve or act as inhibitors that slow down the kinetics of scaling. These approaches are expensive, energy intensive or environmentally unfriendly, and are often insufficient to remove the scale layer.\[83\] Furthermore, these approaches require a shut down of the equipment to either treat or to replace the fouled components.\[83\] In order to devise solutions for efficient scale mitigation under boiling, it is important to understand how scale forms during boiling. Most studies on the mechanism of scale formation have focused on slow evaporation, where precipitation occurs as the bulk fluid becomes supersaturated.\[67,84\] However, in the case of boiling, precipitation occurs even when the bulk fluid is undersaturated. There are limited studies on scale formation during boiling and its impact on heat transfer.\[77,78,80\] The reduction in the heat transfer coefficient in the presence of salts has been primarily attributed to the reduction in bubble nucleation as a result of change in surface tension due to dissolved salts.\[78\] A few studies have proposed a reduction in adhesion of scale by means of altering the surface energy of the boiling surface using ion-implantation and hydrophobic coatings.\[85,86\] While some of these results are promising, a fundamental understanding of incipience of crystallization under boiling remains elusive.\[78\] We believe that such insights can lead to better anti-scaling approaches for boiling applications. Here, we study how coupled microscale phenomena of bubble evolution and salt precipitation impacts the macroscale heat transfer performance. We use calcium sulfate solution...
as a model system since it is one of the commonly found salts in feed water. By using simultaneous high-speed visualization and infrared imaging, we study the coupled dynamics of bubble evolution and precipitation, and explain the precipitation mechanism in terms of the transport phenomena in the liquid microlayer associated with bubble formation. Based on this understanding, we propose tailoring the surface wettability to alter the morphology of the liquid microlayer, to reduce scale formation and enhance boiling performance.

3.1 Experimental Setup

The boiling test chamber consists of a double walled jacket through which a 1:1 mixture of propylene glycol and water is circulated to maintain the test solution inside the main chamber at saturated boiling conditions of 100 °C and 1 atm. A schematic of the experimental setup is shown in Figure 3-1a. The test substrate comprises of an IR transparent grade silicon wafer. A layer of titanium (150 nm) is evaporated on top of the wafer, which ensures accurate measurement of the substrate temperature by eliminating the difference in the IR signal due to the difference in the emissivity of water and water vapor.[87] The titanium layer is coated with a layer of silicon nitride (100 nm) for chemical resistance and a layer of silicon dioxide (200 nm) for electrical insulation. A 1 cm x 2 cm indium tin oxide (ITO) layer that is 120 nm in thickness, sputtered on the electrically insulated backside of the 5 cm x 5 cm silicon test substrate, serves as the heater and defines the boiling area (Figure 3-1a). The sputtering parameters of the ITO layer are selected to ensure semi-transparency of the layer to IR radiation. The ITO heater is resistively heated via silver contact pads using a DC power source. The test solution comprises of an undersaturated solution of calcium sulfate to avoid precipitation in the bulk and on the chamber walls and to restrict crystallization exclusively to the heated area. The solution is degassed by boiling in a microwave for ~15 minutes, and subsequently left inside the test chamber maintained at 100 °C for an hour, prior to experiments to ensure temperature equilibration. Consistent with previous studies, two different
salt concentrations, $0.94C_{\text{sat}}$ (8.70 mM) and $0.75C_{\text{sat}}$ (6.97 mM), where $C_{\text{sat}}$ is the saturation concentration at 100 °C, are used for the experiments. A high-speed optical camera is used to visualize the boiling behavior at 1000-2500 fps from the top of the substrate and a high-speed infrared camera is used to image the temperature profile of the boiling area at 1250 fps from the bottom (Figure 3-1a). An in-situ calibration of the IR camera is used to correlate the infrared counts with the absolute temperature. The calibration relates the infrared counts to the absolute temperature at the top of the surface. The 150 nm Ti coating at the top of the substrate ensures that the difference in the IR count is solely due to the difference in temperature and the effect of difference in emissivity of liquid and vapor on IR count is eliminated. During calibration the chamber is maintained at saturated conditions and is filled with water till the level of the mounted sample. A thermocouple is attached to the top of the sample at the center of the heated area. The substrate temperature is increased in steps of 2-5 °C by resistively heating the ITO heater using the DC power source. The corresponding IR images are recorded. The calibration curve is subsequently obtained through a quadratic fit between the IR count and the absolute temperature. During the experiments, the first data point using the calibration curve corresponds to $100 \pm 1 °C$. Figure 3-1b and Figure 3-1c show representative optical and infrared images, with the temperature contour lines superimposed on the latter, of boiling DI water and salt solution, respectively, at a heat flux of 25 W/cm².

### 3.2 Results and Discussion

For the CHF studies, the applied heat flux is increased in steps of 5 W/cm² every 5 minutes (defining ramp rate) till a sudden increase in substrate temperature that is often accompanied with burnout of the sample. For DI water, CHF conditions are reached when the vapor film, which acts as an insulating layer, covers the entire heat transfer surface and leads to a sudden increase in the temperature of the substrate. In the case of the salt solution, the crystalized scale layer on the substrate acts as insulation and has a similar effect to that of a vapor film leading to CHF conditions.
Figure 3-1: (a) Boiling experimental setup showing schematic of the specifically fabricated test substrate and arrangement of the high-speed camera and IR camera. Representative images of high speed images and infrared image of bubble dynamics during pool boiling of (b) DI water (c) 0.94 Csat salt solution at heat flux of 25 W/cm². The scale bar represents 5 mm.

It should be noted that for salt solution, the ramp rate of applied heat flux determines the extent of salt crystallization on the substrate, which in turn affects the CHF. Figure 3-2 shows the plot of heat flux versus wall superheat corresponding to DI water and salt solutions. The data points are an average of two to three independent experiments and error bars denote standard error. The CHF for DI water was measured to be 115±9 W/cm², consistent with previous studies.[73] In the presence of dissolved salts, the boiling performance deteriorates, resulting in a significant increase in substrate temperature with increasing heat flux. For instance, at a heat flux of 15 W/cm², the heat transfer coefficient, given by the ratio of surface heat flux to wall superheat, reduces from ~0.83 W/cm²K for DI water to ~0.64 W/cm²K and ~0.48 W/cm²K for 0.75C_sat and 0.94C_sat salt solution, respectively. At the salt concentration of 0.94C_sat, the CHF reduces drastically by three folds to 32±2 W/cm². Even at a lower salt concentration of 0.75C_sat, the CHF still remains low at 43±3 W/cm². These results indicate the adverse effects of the presence of dissolved salts on boiling performance.

The reduction in the boiling heat transfer coefficient in the presence of dissolved salts can be explained by considering the bubble dynamics and evolution of the
crystallization-induced scale layer. The number of bubble nucleation sites reduces drastically in the presence of salts (Figure 3-1b,c). Since the heat transfer coefficient is directly related to the number of nucleation sites, the boiling performance significantly reduces and there is a steep increase in the substrate temperature. Owing to the inverse solubility of calcium sulfate with temperature, salt precipitates on the hot substrate. These crystal deposits pin the contact line and delay bubble departure, reducing the bubble departure frequency by a factor of ten and increasing the bubble size by a factor of two (Figure 3-3a). The reduced bubble departure frequency leads to further increase in substrate temperature compared to that of DI water (Figure 3-3a). In addition to influencing the bubble dynamics, the calcium sulfate scale deposit increases the thermal resistance of the substrate due to its low thermal conductivity (~1 W/mK). For example, at a heat flux of 20 W/cm², a 100 μm thick scale layer can result in a temperature drop of 20 °C/mm across its thickness. The lower temperature atop the fouling layer restricts boiling, causing the substrate to signifi-
cantly overheat (Figure 3-3a). The scale layer also increases the thermal mass of the substrate resulting in longer heating timescale (\(\sim 400 \text{ ms} \)) before a bubble nucleates when compared to that of DI water (\(\sim 40 \text{ ms} \)) as shown in Figure 3-3a. Figure 3-3b shows the spatial evolution of temperature along the centerline of the bubble basal area for salt solution and DI water. The locations of the lowest temperature, denoted by arrows, along each temperature curve correspond to the triple contact line where maximum evaporation occurs. The presence of scale in the case of the salt solution restricts the lateral spreading of the bubble-formation-induced evaporative cooling on the substrate because the heat has to be transferred along the thickness of the scale layer. This localization of cooling at the triple contact line results in insufficient cooling at the center of the bubble leading to large temperature gradients along the centerline. For example, the temperature differential between the center of the bubble and the triple contact line is 2 °C/mm for salt solution as opposed to 0.7 °C/mm for DI water at a time instant corresponding to one-fourth the bubble residence time (Figure 3-3b).

Figure 3-3: (a) Frequency of bubble formation represented by the variation of the local temperature at substrate underneath an individual bubble, and (b) Temperature along the contact diameter of the bubble for DI water (blue) and 0.94 \(C_{sat}\) salt solution (black dashed) at time instants corresponding to \(t = 0 \text{ ms} \), \(1/4\)th and \(3/4\)th the bubble residence time at a surface heat flux of 20 W/cm². The arrows denote the location of the triple contact line.

To address the issue of scale buildup during boiling, it is important to understand
its incipience mechanism. The driving force for crystallization is the increase in supersaturation at the heated substrate due to the reduced solubility of calcium sulfate with increasing temperatures. At low heat flux, as the bubble grows and departs from the surface, salt crystallizes in a “coffee-ring” pattern under the bubble (Figure 3-4a).[88] The ring shaped scale can be rationalized in terms of the transport mechanism in the liquid microlayer beneath the bubble as it grows. The microlayer beneath a growing bubble is well established on a hydrophilic surface and is attributed to the lubrication layer attached to the surface.[87, 89] The maximum heat transfer during boiling occurs due to the evaporation of the liquid microlayer associated with bubble nucleation.[90] The thickness of this microlayer has been experimentally shown to be on the order a few microns.[87, 90] Assuming that the mass transfer to form the vapor bubble is only from the microlayer, the volume \( V_\mu \) of microlayer that has evaporated to form a bubble of volume \( V_b \) is given as \( V_\mu = V_b (\rho V / \rho L) \), where \( \rho L \) and \( \rho V \) are the density of liquid and vapor, respectively. The evaporation or the bubble formation timescale \( (\tau_e) \), given by \( \tau_e \sim \frac{\rho V R h_{fg}}{q^*} \), is on the order of tens of milliseconds [6]. Here, \( R \) is the radius of the bubble prior to departure, \( h_{fg} \) is the latent heat of vaporization, and \( q \) is the applied heat flux. The diffusion timescale of the \( SO_4^{2-} \) ions in the microlayer \( L^2 / D \sim 300s \), where \( D \) is the diffusion coefficient of the ion in water \( (=3 \times 10^{-9} m^2/s) \), and \( L \) is the length of the microlayer beneath the bubble \( (~1 \ mm) \) [20] (Figure 3-4a), is significantly larger than the bubble departure timescale \( (~100 ms, \ see \ Figure \ 3-3a) \). Thus, it can be assumed that the ions in the microlayer remain trapped during bubble growth and the evaporation of water causes the microlayer to become increasingly supersaturated (Figure 3-4a). The local ion concentration in the microlayer \( (C_\mu) \), therefore, increases as \( C_\mu = (1 - (1 / V_{\mu_0}) (dV_\mu / dt) \Delta t)^{-1} C_b \), where \( C_b \) is the bulk salt concentration, \( V_{\mu_0} \) is the initial volume of the microlayer, \( dV_\mu dt \sim (\pi R^2 q^*) (\rho L h_{fg}) \) is the rate of evaporation, and \( \Delta t \) denotes the instantaneous time difference from the instant of formation of the initial microlayer. When the supersaturation \( C_\mu / C_s(T) \) in the microlayer \( (C_s(T) \) is the saturation concentration corresponding to the substrate temperature) exceeds critical supersaturation crystallization occurs at the contact line resulting in a ring-shaped scale deposit. With
increase in heat flux, the surface temperature increases leading to a reduction in $C_s(T)$, which in turn leads to faster supersaturation of the microlayer which causes early precipitation leading to a thicker deposit (Figure 3-4b). At even higher heat fluxes (>25 W/cm$^2$ for 0.75$C_{sat}$ concentration), a uniform scale covers the entire bubble basal area.

![Schematic of factors affecting scale formation during bubble evolution](image)

Figure 3-4: (a) Schematic of factors affecting scale formation during bubble evolution. The inset on the right shows the transport mechanism in the liquid microlayer. (b) Representative images of bubble departure as the heat flux is increased for the salt solution of 0.75$C_{sat}$ concentration; the thickness of the scale ring increases with increasing heat flux.

One way to avoid scale formation is to eliminate the ionic supersaturation caused by the evaporation in the microlayer. To achieve this, we fundamentally alter the microlayer and bubble geometry by rendering the surface hydrophobic. Hydrophobicity is incorporated by coating the boiling surface with Octadecyltrichlorosilane (OTS). The advancing contact angle of a water drop on the surface is $\sim110^\circ$ while the receding contact angle is $\sim100^\circ$. As shown in Figure 3-5a, the bubble geometry on the hydrophobic surface is different than a conventional hydrophilic surface: the vapor-liquid interface at the contact line is concave on the hydrophobic surface in contrast to the convex shape on a hydrophilic surface (Figure 3-5a).[91] The high
receding contact angle ensures an absence of the liquid microlayer in the case of the hydrophobic surface as shown in Figure 3-5a. As a result, bubble formation on a hydrophobic surface is not accompanied by scale formation further confirming the absence of microlayer. Recent studies using Lattice Boltzmann simulations have also shown the absence of microlayer during boiling on a hydrophobic surface. The maximum evaporation occurs via heat transfer in the thermal boundary layer of the heated surface and subsequent growth is aided by the coalescence of multiple bubbles. The geometry of the triple contact line leads to an absence of evaporation-induced supersaturation near the contact line, thus preventing crystallization. The absence of scale during boiling on a hydrophobic surface results in a sustained near-uniform boiling performance at a given surface heat flux over the experimental test duration (90 mins). At a constant heat flux of 20 W/cm², the initial heat transfer coefficient of the hydrophobic surface is higher than that of the unscaled hydrophilic surface due to higher bubble nucleation density. While boiling heat transfer on a hydrophilic surface decreases by 50% within 60 minutes due to scale formation, the heat transfer coefficient on hydrophobic surface remains relatively unchanged over the same duration (Figure 3-5b). At higher heat fluxes the surface temperature can exceed a critical value leading to supersaturation conditions near the surface, which can result in crystallization at the contact line. Here we find that crystallization is initiated when heat flux exceeds 40 W/cm², and the surface temperature is greater than 130 °C. The corresponding supersaturation \( C_b / C_s(T) \) near the surface exceeds 1.5 leading to crystallization on the heat transfer surface independent of the bubble evolution. While hydrophobic surfaces are known to increase the energy barrier for crystallization,[67,80,86] we believe that the antiscaling property of hydrophobic surfaces in boiling can be attributed to the absence of microlayer. Unlike hydrophilic surfaces, the CHF on hydrophobic surface remains relatively unaltered (~40-55 W/cm², see Figure 3-6) going from DI water to salt solutions. This is because the CHF limitation on hydrophobic surfaces arises from the affinity of vapor films rather than scaling as in the case of hydrophilic surfaces.

While hydrophobic surfaces provide sustained heat transfer performance at lower
Figure 3-5: (a) Dependence of bubble morphology on wettability of surface. (b) Temporal evolution of heat transfer coefficient on a hydrophilic and hydrophobic surface for an 0.94$C_{sat}$ salt solution at constant heat flux of 20 W/cm$^2$; insets show scaling on the different wettability surfaces.

heat fluxes due to higher nucleation sites and ability to resist scale formation, the CHF remains low due to vapor coverage (Figure 3-7). To enhance CHF while controlling the extent of vapor affinity and scaling we propose to pattern the hydrophilic surface with disconnected hydrophobic regions as shown in the inset of Figure 3-7. The hybrid sample was prepared by coating a silicon sample with a photoresist (AZ 5214). The photoresist is removed selectively from square patterns (size = 100 $\mu$m and pitch = 400 $\mu$m). Subsequently, the sample is plasma cleaned to further remove traces of photoresist, if any, from the exposed areas and generate OH- bonds for silanization. The exposed areas are silanized by means of vapor deposition of fluorosilane (tridecafluoro-1,1,2,2 tetrahydrooctyl-trichlorosilane). Then the photoresist is removed via soaking in acetone and IPA. The resulting substrate possesses hybrid wettability with hydrophobic square patterns separated by the continuous hydrophilic areas. This hybrid surface aids bubble nucleation, avoids vapor film coverage, and restricts scaling to the hydrophilic regions. The CHF experiments are conducted using a 0.75$C_{sat}$ salt solution. We find that the hybrid surface outperforms the hydrophilic and hydrophobic surfaces both in terms of heat transfer coefficient and CHF (Fig-
Figure 3-6: Comparison of boiling curves for DI water and salt solutions on the hydrophobic boiling surface. The CHF on the hydrophobic surface remains relatively unaltered in the presence of dissolved salts.

The higher heat transfer coefficient results from the hydrophobic islands contributing to an increased number of bubble nucleation sites that lead to smaller bubbles and higher departure frequency (inset of Figure 3-7). The lower extent of scale formation that is restricted to the hydrophilic areas in conjunction with the aforementioned bubble dynamics results in higher CHF. The CHF on the hybrid surface is ~100 W/cm$^2$ as opposed to ~43 W/cm$^2$ on a hydrophilic surface, and ~50 W/cm$^2$ on a hydrophobic surface under identical experimental conditions. Thus, we are able to mitigate the adverse effect of dissolved salts through hybrid surfaces.

### 3.3 Conclusions

In summary, we show that the heat transfer performance during pool boiling is severely degraded by the presence of dissolved salts as crystallized scale increases the thermal resistance and dramatically alters the bubble evolution. We explain the mechanism of scale formation by considering the transport in the liquid microlayer
Figure 3-7: Comparison of boiling curves for a smooth hydrophilic surface, hydrophobic surface, and a hybrid surface for a 0.75 $C_{sat}$ salt solution. The insets show the representative visual and IR images of boiling corresponding to a surface heat flux of 20 $W/cm^2$. The contour line plot on the IR images represents absolute surface temperature. The inset in the top right corner shows the hybrid surface, which comprises square hydrophobic islands with a width of 100 $\mu m$ and pitch of 400 $\mu m$ on a hydrophilic surface.

underneath the bubble. Tailoring surface wettability is proposed as a means to manipulate the microlayer and avoid scale formation for sustained thermal performance. We demonstrate that hybrid hydrophilic-hydrophobic surfaces can mitigate the heat transfer deterioration caused by dissolved salts. Further studies on the optimization of the hydrophobic-hydrophilic patterns to minimize scale formation can maximize boiling performance in many industrial applications.

### 3.4 Materials and Methods

An in-situ infrared calibration is conducted to relate the infrared counts to the absolute temperature at the top of the surface. The 150 $nm$ Ti coating at the top of the substrate (refer main text for the substrate configuration) ensures that the diff-
ference in the IR count is solely due to the difference in temperature and the effect of difference in emissivity of liquid and vapor on IR count is eliminated. During calibration the chamber is maintained at saturated conditions and is filled with water till the level of the mounted sample. A thermocouple is attached to the top of the sample at the center of the heated area. The substrate temperature is increased in steps of 2-5 °C by resistively heating the ITO heater using the DC power source. The corresponding IR images are recorded. The calibration curve is subsequently obtained through a quadratic fit between the IR count and the absolute temperature. During the experiments, the first data point using the calibration curve corresponds to 100 ± 1°C.

Experimental values for surface tension of DI water and saturated solution of calcium sulfate solution at different temperatures are shown in Table 3.1.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>DI Water mN/m</th>
<th>Salt Solution mN/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>72.70</td>
<td>72.63</td>
</tr>
<tr>
<td>40</td>
<td>69.60</td>
<td>69.86</td>
</tr>
<tr>
<td>60</td>
<td>66.24</td>
<td>66.23</td>
</tr>
</tbody>
</table>
Chapter 4

Radially Ejected Bubbles Driven by Thermocapillarity in Equilibrated Vapor-Liquid Mixtures

Thermocapillary forces arising from surface tension play a significant role in the dynamics of small bubbles in the presence of large temperature gradients.\cite{119-126} This work uses the set up utilized in previous works that were interested in the nucleation of bubbles in alkane mixtures with a novel method that generates huge (up to $10^8 K/m$) but short-lived (millisecond) temperature gradients with a thermally pulsed wire in a high pressure cell.\cite{127,128} This nucleation process, which takes the system locally and temporarily far from equilibrium, has been demonstrated to nucleate bubbles at pressures and temperatures where the equilibrated fluid mixture would be single phase.\cite{127} In this work we show how a rapid heat pulse applied to an alkane mixture of ethane - n-octane generates bubbles with short-time trajectories controlled by the magnitude and direction of the thermocapillary force. We also show that the bubble behavior confirms that the fluid mixture has a surface tension maximum for all molar fractions studied.

Since the temperature-dependence of the surface tension discussed in this manuscript is atypical of those experienced in everyday life, we start by reviewing standard surface tension behavior and contrast it to that discussed here. We propose to classify
the behavior of surface tension into three categories, designated as: standard, self-rewetting, and equilibrated vapor-liquid mixtures, the last being the type of fluid discussed in this manuscript. Here we provide only a brief introduction to this classification scheme and a broader commentary can be found in the discussion section.

Fluids with what is generally considered to be a standard surface tension, such as water or alkane mixtures, display a monotonic decrease with increasing temperature when measured open to the atmosphere. This conventional measurement defines what is generally considered to be standard fluid behavior, but does not take place with equilibrium between the pure vapor and liquid phases. Under similar measurement conditions self-rewetting fluids exhibit a surface tension minimum above which the surface tension increases with temperature, creating much scientific interest and leading to more efficient heat transfer.[129-136] Similarly, many multi-component alloys exhibit a surface tension that increases with temperature, significantly affecting their weldability due to strong thermocapillary forces. Finally, equilibrated vapor-liquid mixtures exhibit a maximum in surface tension, meaning a surface tension that increases with temperature at low temperatures and fixed pressure.[137, 138] Equilibration requires that the vapor and the liquid phases be at the same temperature and pressure, free to exchange molecules between the two phases (in fluidic communication) and with equal chemical potentials. Equilibration is typically carried out in a temperature-controlled closed system that includes an agitation device as well as a piston that can control the pressure. In spite of being studied for decades by researchers, very little work has taken place on the thermocapillary forces generated in equilibrated vapor-liquid mixtures, which are particularly challenging to investigate due to the necessity of working with high pressures. In this manuscript, we demonstrate that the magnitude and the sign of the thermocapillary force generated by a thermal pulse controls the trajectories of nucleated bubbles in such mixtures.
4.1 Experimental

4.1.1 Sample Preparation

Samples of ethane and n-octane mixtures were prepared in a customized high pressure piston reactor (High Pressure, Incorporated), with ethane molar percentages of 35.1%, 42.7%, 53.1%, 59.7%, 67.7%, and 78.3%. The piston reactor consists of a high-pressure cylindrical container with a sealed piston free to move in its bore with integrated valves. The piston divides the cylinder into two isolated chambers, one containing the sample and the other a hydraulic fluid (usually water) whose pressure is controlled using a high pressure syringe pump (65HP by Teledyne Isco). The total internal volume, shared between the hydraulic and sample sides, is approximately 30 mL.

A sample is prepared by first cleaning and evacuating the piston reactor under house vacuum. The reactor is weighed (MS12002TS by Mettler Toledo) before and after it is filled with a controlled amount of n-octane (anhydrous, ≥99% from Sigma Aldrich). While its weight is being monitored, the sample is filled with high pressure ethane gas (American Gas Products, 99.0%) until the desired mixture ratio is reached. Finally, the sample is left to equilibrate by rocking for an hour at 5,000 psi and at ambient temperature while the volume of hydraulic fluid is monitored.

4.1.2 Bubble Nucleation in a Phase Transition Cell (PTC)

After the sample is prepared, fluid from the piston reactor is charged into a custom phase transition cell (PTC) which operates at elevated pressure and temperature (Figure 4-1A). The PTC has an internal volume of 5 μL and contains a 25 μm diameter platinum-iridium alloy wire of length approximately 2 mm that is briefly heated with an electrical pulse. Fluid adjacent to the wire surface is heated more rapidly than the time scales for diffusion or convection, nucleating bubbles. Thermal nucleation of bubbles with this cell has been discussed previously.[127] The wire is heated by applying a 5 V electric pulse (between \(V_+\) and \(V_{GND}\)) from a high power voltage supply (E3631A by Keysight Technologies) while measuring the current that passes
through the wire. The pulse duration is controlled with a function generator (3320A by Keysight Technologies), ranging from 9 $\mu$s to 20 $\mu$s which corresponds to a 50 $^\circ$C and 100 $^\circ$C increase in the wire temperature, respectively. The combination of a low pulse energy (millijoules) and a low duty cycle (0.002% when operated at 1 Hz), results in a maximum temperature increase of the PTC housing of no more than 4 milliKelvin. No pressure increase is observed when bubbles are nucleated due to their small volume compared to that of the entire system. The PTC contains two spherical sapphire lenses positioned perpendicular to the suspended wire through which the response of the mixture to the applied pulse is recorded. One window is illuminated by a red LED via an optical fiber (M660F1 fiber-coupled LED, 660 nm, by Thorlabs) and the wire and bubbles are imaged through the other window with a high speed camera (Fastcam Mini by Photron with a 12X lens by Navitar). In order to control the temperature of the mixture, the PTC is positioned in a temperature-controlled oven (M33M by Sigma Systems) while the pressure is measured by a quartz pressure transducer (QMB102-16-177 by Quartzdyne). The thermal pulse increases the temperature of the fluid adjacent to the wire relative to that of the ambient oven temperature. A custom micropiston external to the phase transition cell is used to control the pressure and the depressurization rate of the system. The micropiston consists of a sapphire piston, similar to that used in high pressure liquid chromatography, along with electronics and a motor that uses pressure feedback to control the volumetric rate of the piston. An illustration of the system (without micropiston) can be seen in Figure 4-1A. The PTC contains inlet and outlet ports used to charge new fluid into the system and to dispose of the used fluid after completion of the experiment.

In order to generate bubbles we use a method that was presented recently.[127] An aliquot is loaded into the PTC and is initially maintained in single-phase at lower temperatures (by the oven) than the phase envelope and higher pressures (by the Isco pump) than the cricondenbar, dictating that no thermodynamically stable vapor bubbles can be generated. At this pressure, the heat pulse originating from the wire does not generate bubbles since the temperature increase near the wire does not cause
Figure 4-1: A) Schematic of the experimental setup used in this study. Bubbles (circles) are nucleated in the pressurized ethane - n-octane mixture (yellow). The spherical sapphire lenses are indicated by the purple circles. The volume of bubbles created by each thermal pulse is far smaller than shown in this schematic. Inset - the applied electric pulse sequence. B) Illustration of the procedure to find the bubble point pressure of the system at an oven temperature of 55 °C. The phase envelope (black line) was generated by a phase modeling software for a 42.7% ethane molar fraction mixture. While the pulse energy is identical for each pulse, the maximum temperature of the fluid is determined by the kinetic limit of superheat (not shown), just inside of the phase envelope. The results of experiments performed in the region indicated by the dashed lines are presented in Figure 4-3B.

The mixture to cross the phase envelope of the sample (line 1-2 in Figure 4-1B). The pressure is lowered and the mixture enters the unstable nucleation region where the heat pulse causes bubbles to nucleate, however they collapse as the system returns to the single phase region after the heat is dissipated (line 3-4). Pressure is lowered further until the bubble point pressure - where the vapor phase can coexist with the liquid phase in a stable manner - is reached (point 5). At this point phase separation does not occur spontaneously (for pressures and oven temperatures sufficiently far from the critical point) due to the energy barrier associated with bubble nucleation, [139] but the barrier is crossed after the heat pulse is applied and the generated bubbles remain stable (point 6). This heat pulse enables the nucleation barrier to be overcome, facilitating measurement of the phase envelope. The maximum temperature of the fluid just after extinction of the pulse is determined by the kinetic limit.
of superheat, beyond which bubbles spontaneously nucleate. While this limit has not been directly measured in our experiments, for simple alkane mixtures it will be within the phase envelope, as indicated in the figure.

4.1.3 Calculation of Surface Tension

This section provides a brief description of the method by which the surface tension of the ethane - n-octane mixture is calculated using a standard software package. Surface tension arises from unbalanced molecular interactions near the vapor-liquid interface. In the bulk, cohesive molecular forces are uniformly balanced around a given molecule, but near an interface cohesive forces are larger in the higher-density liquid phase than in the lower density vapor phase. The magnitude of surface tension can be roughly understood as the product of the magnitude of the long-range intermolecular forces (such as van der Waals) and the density difference between the phases. A number of theoretical and heuristic models have been developed to quantify this idea. Building on the Macleod-Sugden method for single component fluids,[140, 141] Weinaug and Katz[142] extended this model for hydrocarbon mixtures with surface tension $\sigma$ to be:

$$\sigma = \left[ \sum_{i=1}^{N} P_i \left( \frac{x_i}{V_L} - \frac{y_i}{V_V} \right) \right]^4 \quad (4.1)$$

In the above equation $P_i$ is a temperature and pressure independent quantity (not a pressure) called the parachor which approximates the effect of intermolecular cohesive forces, $i$ is the component index, $x$ the liquid molar fraction, $y$ the vapor molar fraction, $V_L$ the liquid molar volume, $V_V$ the vapor molar volume, and $N$ the number of components. This simple model is particularly applicable to non-polar hydrocarbon systems. Given a multi-component hydrocarbon mixture, the Weinaug-Katz equation provides a simple method to calculate the mixture surface tension provided that the equilibrium liquid and vapor properties can be calculated. This can be found using an equation of state (EOS) such as Peng-Robinson (PR), Soave-Redlich-Kwong (SRK), or Groupe Europeen de Recherches Gazieres (GERG)
along with the appropriate thermodynamic relationships to allow calculation of phase equilibria given the EOS.\cite{143} We use commercially available EOS software (GERG-2008) to calculate the phase envelope and coexisting phase properties (liquid and vapor composition and density) for the mixtures of interest.

![Graph of Surface Tension vs Temperature](image)

**Figure 4-2:** Surface tension vs temperature for an equilibrated binary fluid (ethane - n-octane) consisting of 42.7\% (mol) ethane for several pressures, where the maximum in surface tension can most easily be identified on the 50 psi curve. The grey region qualitatively displays the two-phase region; outside of this temperature and pressure range the mixture is single-phase.

Equilibrated vapor-liquid mixtures that exhibit a surface tension maximum appear to be ubiquitous; one example is studied in this manuscript, consisting of ethane and n-octane. In Figure 4-2 the surface tension of ethane - n-octane is calculated using the above technique at several fixed pressures; the ends of each curve corresponds to the two temperatures of the phase envelope outside of which the fluid is single phase for each specific pressure. The lowest pressure trace of 50 psi (topmost on graph) of the ethane - n-octane mixture shown in Figure 4-2 most clearly displays a maximum in surface tension, distinguishing it from standard surface tension behavior. The surface tension displays a positive slope at low temperature and a negative slope at high temperature. The sign of the slope of the surface tension at the lowest temperature on each isobaric curve is indicated by + or -. The isobaric curve at 650 psi with
approximately zero slope at the lowest temperature is indicated by a 0.

4.2 Results

4.2.1 Phase Boundary

The nucleation method discussed earlier was used to map the bubble point pressure of each ethane - n-octane mixture over the maximum temperature range for the PTC by nucleating bubbles. Examples of nucleated bubbles are shown in Figure 4-3A. The bubble point pressure measurements were then compared to a phase envelope curve produced by the GERG EOS modeling software. GERG EOS covers a wide range of temperatures and pressures for both pure substances as well as mixtures. Six mixtures with different molar ratios (see experimental section) were examined and the experimental results agree reasonably with the predictions of the software. The measurements on which the binary interaction parameters for the GERG model are based are limited to 100 °C; there is generally good agreement at and below this temperature but poorer agreement above.[144, 145] The measured bubble point pressures are all within ±25 psi of the theoretical phase envelope curve for all measured temperature values; results for the sample of ethane fraction 42.7% are shown in panel B of Figure 4-3.

4.2.2 Bubble Trajectories

For measurement of bubble trajectories, the pressure was typically set to be 50 psi above the phase envelope so as to avoid the possibility of nucleating stable bubbles. For the 42.7% ethane sample, bubbles that were nucleated by the thermal pulse were ejected (shooting) from the wire surface at low oven temperatures (Figure 4-3A, left photos). In contrast, similarly nucleated bubbles at high oven temperatures adhered (sticking) to the wire for the entire length of the observation period (~20 ms) (Figure 4-3A, right photos). In all experiments buoyant forces eventually dominated the motion after the temperature gradient introduced by the wire’s short thermal pulse.
wire had dissipated. Data points corresponding to the measured phase envelope are color-coded to indicate the direction of the bubble trajectory on Figure 4-3B. These data indicate that bubbles shoot away from the wire at oven temperatures below around 65 °C and stick to the wire at higher temperatures.

The surface tension of simple binary fluids can be calculated using the densities of the liquid and vapor phases as described earlier.[140] In Figure 4-3B, we have superimposed the surface tension of the vapor-liquid mixture as a color-coded map. The most noticeable trend is the decrease in surface tension (from red to blue) with increasing pressure and temperature; this is the expected trend as one approaches the critical point for this fluid composition (the critical point is at a higher pressure and temperature than shown here). Restricting our observations to the surface tension derivative with respect to temperature situated on the phase envelope, we note that at low temperatures, the surface tension derivative with respect to temperature is positive, but for high temperatures, it is negative. The thermocapillary forces created by the positive and negative surface tension derivatives explain the two bubble trajectories described in the previous paragraph. Calculation of the surface tension maximum for each pressure yields a locus of maxima (more clearly shown in Figure 4-5B) that passes near the measured transition from shooting to sticking shown on the phase envelope at 65 °C. However, there is some uncertainty in the proximity due to the lines of the surface tension maximum and the phase envelope intersecting acutely in this pressure and temperature range. We believe that this uncertainty is the origin of the discrepancy between the transition between shooting and sticking (65 °C, 400 psi) and the point at which the surface tension derivative is zero (40 °C, 280 psi).

As an illustration of the bubble motion below and above the pressure-dependent surface tension maximum, Panel C of Figure 4-3 shows the instantaneous temperature and surface tension distribution about the wire shortly after extinction of the thermal pulse for low oven temperatures where the surface tension increases with temperature. In this case, the two curves of instantaneous temperature and surface tension track one another qualitatively. The gradient in temperature causes a surface tension that is
Figure 4-3: Bubble trajectories of nucleated bubbles and phase envelope of a 42.7% ethane (mole) mixture consisting of ethane – n-octane. A) Bubbles nucleated by pulsed wire within milliseconds of extinction of pulse. Bubbles shoot away from the wire at low oven temperatures (left images) and stick to the wire at high oven temperatures (right images). B) Bubble point pressure measurements (blue and orange squares) and the theoretical phase envelope (solid line) predicted by the EOS software. This phase envelope corresponds to the small region indicated by the dashed box in Figure 4-1B. The calculated surface tension has been color-coded in the two-phase region. On the phase boundary, the derivative of the surface tension with respect to temperature is positive at lower temperatures (plus symbols) and bubbles shoot away (blue squares). At higher temperatures, the derivative is negative (negative symbols) and bubbles stick to the wire (orange squares). The transition between these two behaviors occurs where the surface tension is maximum and hence the derivative of the surface tension is zero. Panels C and D show that the thermal pulse of the wire briefly increases the temperature T of the adjacent fluid with the maximum temperature always at the wire surface. At low oven temperature (panel C), this thermal pulse creates an elevated surface tension σ near the wire (plotted vs radial distance r) surface resulting in a thermocapillary force F that repels the bubbles from the wire, but at high oven temperature (panel D), the thermal pulse reduces the surface tension at the same location, resulting in a force that attracts the bubbles to the wire.
highest on the wire surface, generating a thermocapillary force that pushes the bubbles out radially. Panel D shows the same configuration, but at high oven temperatures where the surface tension behavior is more typical. In this case the surface tension decreases with increasing temperature and the two curves of temperature and surface tension show opposing trends. The higher surface tension far away from the wire pushes the bubbles inwards by thermocapillarity.

4.2.3 Timescales and Forces of Bubble Motion

A simple calculation of the timescale associated with viscous drag demonstrates that a continuously applied force must be present during the bubble's radial motion. If bubbles of diameter $d$ had been ejected from the wire solely by an instantaneous event, such as volumetric expansion due to boiling, then we should expect to see the bubbles decelerate due to viscous drag. The inertial term corresponding to the bubble motion, $m \cdot dU/dt$, includes the bubble mass $m$, velocity $U$, and time $t$, and in the viscous limit will be balanced with the viscous drag on a bubble, $2\pi \mu dU$, where $\mu$ is the liquid viscosity. Such motion leads to a velocity that decays exponentially with a time constant given by $m/(2\pi \mu d)$. Using typical values for the liquid viscosity of 0.1 mPa·s, bubble diameter of 10 μm and added mass of $(1/12)\rho L \pi d^3$ (a factor of 1/2 is included that originates from the added mass of liquid), we calculate a characteristic decay time of approximately 25 $\mu$s. While we generally do see bubbles decelerate rapidly as they travel away from the wire, the motion is visible over a duration of tens of milliseconds, many orders of magnitude more than would be expected from purely inertial motion, suggesting that the motion (at least initially) is driven by an applied force (e.g. thermocapillarity).

Given the temperature gradient created by the thermal pulse and the large density difference between the liquid and the vapor, the two forces that should play a role are those of thermocapillarity ($F_{Th}$) and buoyancy ($F_b$). A simple calculation illustrates that the thermocapillary force dominates over the buoyancy force when the temperature gradient is the strongest, i.e. just after extinction of the thermal pulse. The thermocapillary force will depend on the surface tension ($\sigma$) derivative
with respect to temperature $T$, the temperature gradient with respect to the radial coordinate $r$, and the bubble diameter $d$, which can be written as:

$$F_{Th} \sim \pi d \frac{d}{dT} \frac{dT}{dr}$$

(4.2)

The buoyancy force can be calculated as a function of the vapor-liquid density difference $\Delta \rho$ and the standard acceleration due to gravity $g$ as:

$$F_g \sim \frac{\pi}{6} \Delta \rho gd^3$$

(4.3)

Using typical values for the bubble diameter ($10 \mu m$), thermal diffusivity ($8 \cdot 10^{-8} m^2/s$), density contrast ($500 kg/m^3$), a surface tension derivative with respect to temperature of $0.01 mN/m - K$ (though maximum values can be much higher), and maximum temperature gradient (conservatively estimated $10^6 K/m$ just after extinction of pulse), then $F_{Th}/F_g$ is about $10^3$.

$$\frac{F_{Th}}{F_g} \sim \frac{6 \frac{d}{dT} \frac{dT}{dr}}{\Delta \rho gd^3} \sim 10^3$$

(4.4)

We note that the surface tension derivative can be far greater than our conservative estimate here, especially far from the surface tension maxima, rendering the ratio of forces above even more extreme. As the system cools the thermal gradient will relax to zero and buoyancy will eventually dominate any thermocapillary forces.

The bubbles being studied are far from equilibrium, being produced by a non-equilibrium nucleation process, but locally the vapor - liquid interface is thought to be in equilibrium at the timescale of investigation because of the rapidity by which the interface equilibrates at the molecular lengthscale. Assuming a conservative lengthscale of $10 nm$ for the interface, and a mass diffusivity of $10^{-7} m/s$, we would expect an equilibration timescale of nanoseconds. Hence our equilibrium calculations of surface tension would then be applicable to calculate the thermocapillary forces.
4.2.4 Bubble Velocity Analysis

To further test whether thermocapillary forces create the observed bubble trajectories, we next measured the velocities of individual bubbles nucleated by the pulsed wire as the oven temperature was varied. For experiments performed near the phase envelope and at temperatures below that of the temperature of the cricondenbar, the color map of Figure 4-3B indicates that there is a region where the derivative of the surface tension with respect to temperature is positive, but decreasing in magnitude as the temperature is increased. The literature on thermocapillarity indicates that the bubble velocity, in steady state, should be proportional to the thermocapillary force, as indicated in 4.2. While the bubble trajectories that we measure never reach steady state, their instantaneous bubble velocity can give us insight into the magnitude and relative values of the thermocapillary force. For each experiment, the temperature increase due to the thermally pulsed wire was maintained at a fixed value (120 °C) by setting the thermal pulse duration to 9 μs, as determined by prior calibration. The magnitude of undersaturation was maintained at 50 psi for all experiments by setting the measurement pressure to be higher than the bubble point pressure by 50 psi. The bubbles were tracked using ImageJ software (National Institutes of Health) and the bubble velocity was calculated by taking the average velocity of the first four bubbles that shot away from the wire. Bubbles were chosen such that they were reasonably separated from other bubbles so as to minimize multi-bubble interactions and hydrodynamics. No effort was made to separate in-plane and out-of-plane motion so that the measured velocity was only that of in-plane motion. The results can be seen in Figure 4-4 where the bubble velocity and surface tension derivative with respect to temperature are simultaneously plotted with respect to the oven temperature. The bubble velocity is proportional to the surface tension derivative; both decrease as the oven temperature is increased, consistent with motion driven by thermocapillarity. It is interesting to note that the decrease in velocity with increasing temperature is contrary to the effect of viscosity alone; the viscosity of this mixture decreases with increasing temperature which would allow the bubble to move faster.
Figure 4-4: Sample of 59.7% ethane molar percentage. A) Snapshot of the bubble near the wire taken 0.5 ms after extinction of pulse for three different oven temperatures arranged from low to high. Note that the bubble is ejected at a faster speed at an oven temperature of 80 °C as compared to 99 °C. B) The maximum bubble velocity plotted vs oven temperature (blue circles, left axis, error bars of one standard deviation). As a comparison, the derivative of the surface tension with respect to temperature (black line, right axis) is superimposed, where both decrease proportionally as the oven temperature is increased.
4.2.5 Surface Tension Maxima for Several Mixtures

The bubble point measurements along the phase envelope presented in Figure 4-3 were next undertaken with six samples that ranged from ethane-poor to ethane-rich (Figure 4-5A). For each sample there is a transition for bubble trajectories between shooting (blue symbols, low temperature) and sticking (orange symbols, high temperature) which coincides reasonably with the maximum in surface tension (dashed red line). The measured transition between shooting and sticking (we identify this as the lowest temperature at which bubbles "stick") occurs at the temperature and pressures shown in the table below for each sample. The uncertainty of these measurements corresponds to the pressure and temperature steps of approximately 5 °C and 25 psi which were used when searching for the transition points. The derivative of the surface tension with respect to temperature is zero along the surface tension maximum (dashed red line), such that at lower temperatures the surface tension derivative with respect to temperature is positive, and at higher temperatures, negative. The uncertainty in the surface tension maximum ranges from ±5 °C at low temperature to ±10 °C at high temperature, primarily based on uncertainty as to vapor-liquid equilibrium properties, such as density, composition, and the parachor. The good agreement between the transition between the bubble trajectory directions (symbol color change from blue to orange) and the transition between positive and negative surface tension derivatives (delineated by dashed red line) for all six samples strongly suggests that bubble motion is driven by thermocapillarity.

Table 4.1: Lowest temperature and pressure for each sample at which bubbles stick to the wire. Each sample is identified by the ethane molar percentage.

<table>
<thead>
<tr>
<th>Ethane mol%</th>
<th>Temperature °C</th>
<th>Pressure psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.1</td>
<td>30.1</td>
<td>213</td>
</tr>
<tr>
<td>42.7</td>
<td>65.2</td>
<td>415</td>
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<td>95.1</td>
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<td>1231</td>
</tr>
<tr>
<td>78.3</td>
<td>148.8</td>
<td>1408</td>
</tr>
</tbody>
</table>
Figure 4-5: For both panels, the solid magenta line is referred to as the “critical line” and defines the largest pressure and temperature of the two phase region for ethane-n-octane binary mixtures. The black and green lines correspond to the boiling lines for ethane and n-octane, respectively. For each pressure, there is a temperature at which the surface tension in the two phase region is maximum, and the locus of these points is marked by the red dashed line. A) Combined data set from six fluid mixtures, each represented by a different symbol, for which the trajectories of nucleated bubbles have been color-coded blue (shooting) and orange (sticking). The pressure-dependent surface tension maximum (dashed red line) coincides with the transition between shooting and sticking bubble trajectories. B) Same pressure and temperature range as panel A, but here we have superimposed the calculated phase envelopes (35.1%, 42.7%, 53.1%, 59.7%, 67.7%, and 78.3%) and color-coded the surface tension. The black-outlined orange symbols indicate the lowest temperature at which bubbles stick to the wire, corresponding to the lowest temperature orange symbols in panel A.

To further demonstrate the relationship between surface tension, bubble trajectories, and the phase envelope, we plot the calculated phase envelopes of all six ethane-n-octane fluid mixtures between the boiling lines of ethane and n-octane, mapping out a critical line in magenta which corresponds to the maximum temperature and pressure at which two phases can coexist in equilibrium (Figure 4-5B). Gibbs’ phase rule dictates that the densities and hence the surface tensions are completely determined (for a binary fluid with two phases present) by the pressure and temperature, regardless of the initial molar fraction of the sample. Hence the color-coded surface tension under the magenta critical line in Figure 4-5B applies to all two-phase samples.
made with ethane-n-octane, regardless of the overall system molar fraction. The locus of these calculated surface tension maxima is indicated by the dashed red line under the magenta critical line in both panels of Figure 4-5. The intersection of this dashed red line and the calculated phase envelope for a particular ethane-n-octane sample coincides with the temperature at which the temperature derivative of the surface tension switches sign from positive (low temperatures) to negative (high temperatures). At these points the temperature derivative of the surface tension is zero and we should expect that the thermocapillary forces at lower and higher temperatures to be of opposite sign, giving rise to the measured transition between shooting and sticking. For low temperatures, the calculated surface tension maxima (red) and the measured transition points (orange, from table above) both lie on the calculated phase envelope (yellow-white). However, at temperatures greater than 100 °C, we begin to see the transition points moving away from the calculated phase envelope (particularly for the 78.3% sample). At these temperatures there is a paucity of measurements in the literature, suggesting that the calculated phase envelope is of limited accuracy. The overall good agreement serves as additional evidence to support the claim that the dynamic behavior of bubbles is controlled by thermocapillary forces and that for any molar ratio of these two components there will be a temperature below which the surface tension increases with increasing temperature.

4.3 Discussion

This section further elaborates on the measurement of surface tension in single and multi-component fluid mixtures to motivate our classification scheme and the use of the term equilibrated vapor-liquid mixture (alternatively as surface tension maximum mixtures). For a multi-phase fluid consisting of liquid and vapor, equilibrium requires that the vapor pressure of the liquid (also known as equilibrium vapor pressure, an intrinsic property) be identical to the system pressure. Consequentially, the liquid and vapor compositions change with pressure and temperature, resulting in a surface tension that can increase or decrease with temperature. For single component
two phase systems, Gibbs’ phase rule allows just one free parameter such that the temperature determines the pressure, or vice versa. If the temperature is increased, the vapor pressure and system pressure both increase (increasing the density of the vapor), while at the same time the liquid density decreases due to thermal expansion. The net effect is a lower density contrast between the liquid and vapor, resulting in a lower surface tension, as is observed in equilibrated vapor-liquid boiling experiments in closed systems. The only single-component fluid that these authors are aware of that exhibits a surface tension that increases with temperature is that of liquid $^3$He at extremely low temperatures.[146] Surprisingly, similar behavior is observed in a typical benchtop experiment where the liquid being measured is open to the atmosphere, hence not equilibrated. However, the key distinction with an open system is that although the vapor pressure of the liquid increases in an identical fashion as with the closed system, the system pressure is held fixed by the atmosphere, meaning that the density of the vapor will never increase above a pressure-defined limit (maximum density would require displacing all air locally). In both equilibrated and non-equilibrated (open) systems with single component fluids, the liquid density decreases due to thermal expansion, moving towards the vapor density, such that the surface tension’s temperature dependence will also be similar.

For a multicomponent equilibrated two phase system, Gibbs’ phase rule is less constraining, allowing the temperature to be varied independently of the system pressure. For such closed systems pressure is typically controlled by an expansion piston and temperature by an oven. An increase in temperature at constant pressure results in an increase of the vapor pressure of the components such that the liquid and vapor phases adopt pressure and temperature dependent compositions. In a non-equilibrated system open to the atmosphere, however, the system pressure is maintained by the atmosphere while the vapor pressures of the liquid components increase with increasing temperature, with little effect on the liquid composition, assuming the measurement is done quickly enough that the liquid composition does not change by preferential volatility of one component. The two situations are quite different, with largely constant composition in the open (non-equilibrated) system,
but with varying composition in the closed (equilibrated) system. As an example, we present measurements and calculations of the surface tension of an n-heptane-n-decane mixture in Figure 4-6. The open system (panel A) shows the typical surface tension decrease with increasing temperature seen in single and multi-component fluids, while the varying composition in the liquid phase (as well as vapor phase) of the closed system held at atmospheric pressure (panel B) leads to a surface tension that increases with temperature (over a limited range). Panel C shows the consequences of fixing the liquid molar fraction in the equilibrated vapor-liquid system, namely that the surface tension's temperature dependence is similar to that of panel A and what we refer to as "standard". For this example and for the experiments presented in this manuscript we have focused exclusively on binary systems for simplicity, but similar results would be obtained for tertiary (or even more complicated) compositions, though the calculations of surface tension would become more complicated.

As mentioned above, both the pressure and the temperature can be varied independently for fluid mixtures with two or more components and two phases present; the surface tension can be measured as a function of temperature while holding pressure to be constant. At sufficiently high pressures, the critical line will intersect a given pressure at a low and a high temperature for many binary mixtures (e.g. at 1000 psi, the magenta critical line in Figure 4-5 passes through 1000 psi at 50 °C and 275 °C, each of them being a critical point). As the surface tension is zero at each critical point and positive in coexisting regions, continuity requires that there will be at least one surface tension maximum between these two critical points. Even at pressures well below the critical line, a surface tension maximum can be observed. At high temperatures, surface tension behaves similar to single-component fluids where increasing the temperature causes a decrease in the liquid density and an increase in the vapor density (for both molar and mass density), leading to an overall decrease in the system surface tension. At low temperatures, however, different behaviors are observed. As temperature is decreased near the boiling line of the more volatile component, it condenses into the liquid phase and lowers the molar density of the less volatile component (in the liquid phase), as well as lowering the mass density

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Figure 4-6: A) Surface tension of a liquid with equal molar fractions of n-heptane and n-decane measured in an open container as measured by Rolo and coworkers. In this typical open-vessel measurement, the liquid is not in equilibrium with the vapor and it results in standard surface tension behavior where the surface tension decreases with temperature. B) In contrast, a closed and equilibrated vapor-liquid mixture of the same components at the same pressure but at a higher temperature (to push the system into the two phase region) displays a surface tension that increases with temperature. For a binary system, Gibbs’ phase rule dictates that the composition of the liquid (molar fraction shown on right axis) and the vapor phases are directly determined by the pressure and temperature. The n-heptane (being more volatile than n-decane) liquid fraction drops quickly with increasing temperature. C) Similar to panel B, but in this case the two components of the liquid fraction are held at equal molar fractions for each temperature requiring an increase in system pressure. As with panel A where the liquid molar fraction was held fixed, the surface tension decreases with temperature.
of the entire liquid phase. As the parachor of the more volatile component is much smaller (the parachor of ethane is about one third that of octane), the surface tension decreases with decreasing temperature even when the overall molar density contrast of the liquid and vapor does not. The decrease in surface tension with decreasing temperature at low temperatures and the decrease in surface tension with increasing temperature at high temperatures dictates that there is a surface tension maximum in such systems. Calculations with other binary and multi-component mixtures show more complicated phase diagrams but with similar trends for surface tension. Conventional crude oils at reservoir conditions, often referred to in oilfield parlance as “black oils”, can also be classified as equilibrated vapor-liquid mixtures on the basis of their surface tension. Such oils are referred to as live when at elevated and original (reservoir) pressures and contain large quantities of dissolved gas, such as methane and ethane. When measuring the surface tension of such systems (typically with pendant-drop method), a pressure and temperature is chosen to create an equilibrium between the black oil liquid, primarily the heavier molecules, and its vapor, primarily made of methane and other light molecules. Interestingly enough, many technologists working on oilfield projects over 75 years ago noticed that the surface tension of equilibrated and pressurized hydrocarbon mixtures displays a maximum with respect to temperature, but little research appears to have been undertaken that focuses on exploiting this phenomenon. By introducing the concept of an equilibrated vapor-liquid system to those studying thermocapillarity as well as those working on microfluidics, we hope to spur interest in studying and using this phenomenon.

4.4 Conclusions

We have used a method of rapidly heating a thin wire to nucleate bubbles in an equilibrated ethane-n-octane fluid mixture in order to study the driving forces on the bubble trajectories. At low temperatures the bubbles shoot away from the wire radially while at high temperatures the bubbles stay attached (stick) to the wire for the duration of the temperature gradient. The observed behavior can be explained
by thermocapillary forces driving the bubbles from regions of high to low surface tension. We have found that the transition temperature at which the behavior of the bubbles switches from shooting to sticking increases with the ethane content of the fluid mixture. The transition temperature for each mixture occurs at the intersection of the phase envelope and the line consisting of the surface tension maximum for each pressure. For the temperature range in which bubbles shoot away from the wire, we measured that the maximum bubble velocity decreased with increasing temperature, consistent with the calculated decrease in thermocapillary forces. There are very few experiments with thermocapillary forces on fluids with a maximum in surface tension reported in the literature, suggesting that these equilibrated vapor-liquid mixtures provide a rich avenue of investigation.
Chapter 5

Capturing Bubbles and Preventing Foam using Aerophilic Surfaces

Capturing bubbles is an essential part of many industrial processes and a key challenge in several technological advances. Methane for example is the second largest contributor to global warming and has 25 times the global warming potential of carbon dioxide.[93, 94] Its release rate from wetlands and freshwater sources due to ebullition was shown correlate to temperature rise in various places across the world.[95, 96] Capturing methane bubbles before they are released to the environment could have a significant environmental impact and could potentially serve as an additional source of energy. Another example is foam buildup, which is a common challenge across a wide range of industries such as paper, coatings, water treatment, food and beverage, agrochemical, biochemical, and others. Capturing gas bubbles as they rise through the bulk of a bioreactor for example could passively prevent foam from forming and mitigate associated adverse effects such as cell death[97, 98] and reduced product yield.[99] Controlled bubble capturing can also improve pool boiling by allowing for faster replenishment of bubbles on the heat transfer surface and thereby improving the performance of heat exchangers and desalination plants.[69, 70]

In order to capture bubble we use aerophilic surfaces, which are able to sustain a gaseous layer between their textures called plastron. Plastron is used by insects and spiders for underwater respiration,[100–102] and can be utilized to introduce slip[103]
and reduce drag in various applications.\cite{7,104,105} Plastron stability depends on the geometrical and chemical properties of the surface.\cite{106–108} Capturing bubbles by aerophilic surfaces have been observed on natural and artificial surfaces,\cite{109–111} yet the relationship between surface parameters and the dynamics of bubble capturing remains elusive.

In this study we systematically show how the properties of aerophilic surfaces control their ability to capture bubbles. We explain the underlying dynamics behind this process and use these findings to create hierarchical surfaces with an enhanced bubble capturing ability. We then use these design guidelines to create a foam preventing device that can be submerged into a foaming solution to capture bubbles in the bulk and prevent foam from forming.

5.1 Results

5.1.1 Capturing Bubbles

To analyze the effect of surface parameters on bubble capture we use a submerged needle to release bubbles onto a leveled surface at varying distances as shown in Figure 5-1a. The bubble diameter is chosen to maximize its terminal velocity.\cite{112} We record the impact using a high speed camera and reconstruct the bubble trajectory by tracking its centroid as can be seen in Figure 5-1b (see Materials and Methods). As the bubble approaches a flat surface its velocity reduces from its terminal value due to the presence of the surface. When the velocity reaches negative values the bubble starts to move away from the surface and regains its spherical shape to complete a single bounce. With each bounce the energy of the bubble is dissipated until it rests on the thin liquid film separating it from the surface. This film drains until it reaches a critical value at which it ruptures and the surface captures the bubble.\cite{113–115}

We examine the influence of surface parameters on the capture time by performing bubble impact experiments on hydrophobic surfaces with different texture morphologies (see Materials and Methods). Specifically, we compare a flat hydrophobic surface
to hydrophobic surfaces with micro and nano textures as shown in Figure 5-1c-e. After the bubble is captured by a flat hydrophobic surface its shape corresponds to the contact angle of water on the surface. The final shape of the captured bubble will resemble a flat film as the surface coverage of the plastron increases (Figure 5-1f-h). Plastron surface coverage also influences the bubble capture time as can be seen from Figure 5-1i,j. Specifically, capture time on a nano textured surface is a fraction of the corresponding value on a flat hydrophobic surface as the nano textured surface captures the bubble during its second bounce. To understand the fundamental principles governing bubble capturing and the dependence of capture time on plastron coverage, we examine the drainage dynamics of the thin liquid film separating the bubble and the plastron.

5.1.2 Dynamics of Film Drainage

To analyze the drainage dynamics we model the film as a cylinder with diameter \( D_b \), the basal diameter of the bubble, and thickness \( h \). We use a hydrodynamic drainage model to receive an expression for the time it takes the film to drain to the critical thickness at which the film breaks \( h_{cr} \). Assuming steady state and axisymmetric conditions, the Navier-Stokes for the thin liquid film yields:

\[
\frac{\partial^2 u}{\partial z^2} = \frac{1}{\mu} \frac{\partial P}{\partial r}
\]  
(5.1)

The interface between the film and the bubble at \( z = h \) is assumed to be planar so that the boundary condition is that of a free surface, while a slip length boundary condition is used for the interface between the liquid and the surface at \( z = 0 \):

\[
\frac{\partial u}{\partial z} \bigg|_{z=h} = 0 \quad u(0) = \beta \frac{\partial u}{\partial z} \bigg|_{z=0}
\]  
(5.2)

Where the slip length \( \beta \) is given by:[103]

\[
\beta \approx \frac{1}{\pi} \frac{(a + b)}{\sqrt{\phi}}
\]  
(5.3)
Figure 5-1: (a) Schematic of the experimental setup and data acquisition system for bubble impacts. (b) Typical sequence of bubble motion during an impact. The dashed line represents the distance between the bubble centroid and the surface as a function of time. (c) (d) (e) Illustrations of the immersed samples. A plastron layer remains between the textures of the micro-textured and the nano-textured sample. (f) (g) (h) Bubble position prior to film rupture and after the triple contact line has been established. The nano-textured surface captures the bubble during the second bounce while it still has residual velocity so that the shape of the bubble prior to capture is flatter than on the other surfaces. Each of the scale bars is 0.5mm. (i) Velocity profiles of bubble centroid during impact. At $t = 0$ bubble velocity starts decreasing and at $t_{capt}$ the film breaks and the bubble is captured. The last peak in velocity is caused by the rupture of the thin film separating the bubble and the surface and the establishment of the triple contact line. (j) Capture times on the three different surfaces. Capture time is approximately three times smaller on a nano-textured surface compared to the flat and micro-textured ones.
Where $a$ and $b$ are the size and wall-to-wall pitch of the microposts, while $\varphi$ is the solid fraction of the surface which is defined as the ratio of the emerged area to the total projected area of the surface. For a square microposts sample it is given by:

$$\varphi = \frac{a^2}{(a + b)^2} \quad (5.4)$$

Combining 5.1 and 5.2 we can derive an expression for the velocity profile and the mass flow rate:

$$u(z) = \frac{2h^2 P_{film}}{\mu D_b} \left[ \frac{z}{H} - \frac{1}{2} \left( \frac{z}{H} \right)^2 + \frac{\beta}{h} \right]$$

$$Q = 2\pi R_b \int_0^h u(z) dz = \frac{2\pi P_{film} h^3}{\mu} \left[ \frac{1}{3} + \frac{\beta}{h} \right] \quad (5.5)$$

We write the mass balance on the film and get a differential equation for the film thickness:

$$\frac{\pi D_b^2}{4} \left( -\frac{d h}{d t} \right) = Q$$

$$\left( -\frac{d h}{d t} \right) = \frac{8h^3 P_{film}}{\mu D_b} \left[ \frac{1}{3} + \frac{\beta}{h} \right] \quad (5.6)$$

For a hydrophobic surface that does not sustain a plastron, we assume a no-slip boundary condition so that $\beta = 0$ and equation 5.6 can be solved to relate the critical film thickness and drainage time:

$$\frac{1}{h_{cr}^2} - \frac{1}{h_0^2} = \frac{16l_d P_{film}}{3\mu D_b^2} \quad (5.7)$$

Choosing an initial film thickness $h_0$ such that $h_0 \gg h_{cr}$ we get a scaling for the drainage time:

$$t_d \sim \frac{\mu}{P_{film}} \frac{D_b^2}{h_{cr}^2} \quad (5.8)$$

Similarly for surfaces with large slip length $\beta \gg h_{cr}$ we can solve equation 5.6:

$$\frac{1}{h_{cr}^2} - \frac{1}{h_0^2} = \frac{16l_d P_{film}}{3\mu D_b^2} \quad (5.9)$$

Again we get the scaling for the drainage time after assuming $h_0 \gg h_{cr}$:
Note that the difference between 5.8 and 5.10 is the replacement of $h_{cr}$ by $\beta$ in the denominator. This means that a plastron containing surface will substantially reduce relative to the capture time of a hydrophobic surface only when $\beta \gg h_{cr}$. We can summarize these equations by writing:

$$t_d \sim \frac{\mu}{P_{film}} \frac{D_b^2}{\beta h_{cr}}$$

$$\tilde{h}^2 = \begin{cases} h_{cr}^2 & \beta = 0 \\ \beta \cdot h_{cr} & \beta > h_{cr} \end{cases}$$

Where $\mu$ is the viscosity, $P_{film}$ is the equivalent pressure in the film, and $\beta$ is the slip length (the case of $0 < \beta < h_{cr}$ can be solved numerically and is not discussed here as $h_{cr} < \beta$ for all plastron sustaining samples used in this work). If the bubble is sufficiently slow so that $U < \sqrt{\Delta \rho g}$ the equivalent pressure in the film is the result of buoyancy and the deceleration of the bubble:

$$P_{film} = \frac{2\Delta \rho g D}{3} \left(1 - C_m \frac{dU}{dt} / g\right) \left(\frac{D}{D_b}\right)^2$$

Where $D$ is the bubble diameter, $\Delta \rho$ is the density difference, and $C_m$ is the coefficient of added mass. The force dominating pressure buildup in the film as well as its drainage is dictated by the ratio $(-C_m dU/dt) / g$. When this ratio is greater than unity film drainage is governed by the bubble’s deceleration and the system is in the inertial drainage regime. When this ratio is smaller than unity film drainage is governed by buoyancy and the system is in the buoyant drainage regime.

In order to calculate this ratio we perform bubble impact experiments on samples with varying plastron coverage. Specifically we use samples decorated with square microposts of size $a = 10 \mu m$ and varying wall-to-wall pitch $b = 5, 10 \mu m$, and a sample with 50 $\mu m$ pyramidal structures with sub-micron textures on their walls which we denote as a low $\varphi$ surface. We also use a flat hydrophobic sample that does not sustain a plastron. We extract the bubble velocity profile for impacts on each of the
samples and calculate the deceleration to gravity ratio for each bounce on each of the surfaces. As shown in Figure 5-2a, this ratio does not change between samples as the bubble deceleration is similar for all surfaces. We then use these values to get the ratio \((-C_m dU/dt)/g\) shown in Figure 5-2b and find that in the first couple of bounces the deceleration of the bubble dominates buoyancy so that the system is in the inertial drainage regime. However, as the bubble’s energy is dissipated with each bounce the deceleration to buoyancy ratio decreases and from the fifth bounce the system transitions into a buoyant drainage regime. Note that except for the low \(\varphi\) surface, the system always enters the buoyant drainage. In the case of a low \(\varphi\) surface, the bubble is captured in the inertial regime during its second bounce on the surface.

For both the inertial and the buoyant drainage regimes, bubble capturing is governed by drainage of the liquid film separating the bubble and the surface as illustrated in Figure 5-2c. In the inertial drainage regime, film drainage is limited by the bubble residence time on the surface during an impact. If during this time the film reaches the critical film thickness, then the bubble will be captured by the surface. If during this time the film does not reached the critical film thickness, then the bubble will bounce away. In the buoyant drainage regime on the other hand (after the fifth bounce) the bubble resides on the thin liquid film until it is captured.

To understand the relationship between surface properties and capture regime we first need to find the critical thickness \(h_{cr}\) at which the liquid film separating the bubble and the surface drains. To fulfill that purpose we perform buoyant drainage experiments in which we release a bubble close to a surface and measure the time until the bubble is captured and the triple contact line is established. In these experiments we vary bubble diameter, liquid viscosity, and surface parameters and measure the capture time \(t_b\) as shown in Figure 5-2d (the subscript \(b\) is to emphasize that during each of these experiments the system is in the buoyant drainage regime). We apply the drainage time analysis presented in 5.11 and 5.12 to derive an expression for the capture time \(t_b \sim \mu/\Delta \rho g (D_b/D)^3 D_b/\tilde{h}^2\) and use linear regression to find an equivalent critical film thickness of \(h_{cr} = 5\mu m\) as shown in Figure 5-2e.
We then use this value to assess whether the bubble can be captured during one of its bounces in the inertial drainage regime. Specifically, we compare the critical film thickness to the minimal film thickness achieved in each of the bubble's bounces in the inertial drainage regime. As can be seen in Figure 5-2f, on the micro textured surfaces as well as for a flat hydrophobic surface, the minimal film thickness to which the film drains in each of the bounces is larger than the critical film thickness and the bubble is not captured in the inertial drainage regime. However, while during the first bounce on the low $\varphi$ surface the minimal thickness is still larger than the critical thickness, on the second bounce the bubble manages to drain the film past the critical value and it is captured as shown in Figure 5-2b. Respectively, the capture time on the low $\varphi$ surface is substantially shorter than on the other surfaces as it is reduced from hundreds of milliseconds on the flat surface to tens of milliseconds.

### 5.1.3 Enhanced Capturing

To reduce the capture time even further we aim to drain the film during the first impact of the bubble and before it bounces away from the surface. To achieve this we erect localized protrusions in the plastron of a high slip length surface as shown in Figure 5-3a,b. The size of these protrusions is chosen to be an order of magnitude greater than the minimal equivalent film thickness achieved during the bubble's first bounce. As shown in Figure 5-3c, the bubble is captured by the surface upon initial impact without bouncing away from the surface. As can be seen in Figure 5-3d, the corresponding capture time is a mere few milliseconds, which is an order of magnitude reduction relative to other areas of the sample. Interestingly, as long as the bubble impacts the protrusion the capture time of a bubble is agnostic to its lateral location relative to the protrusion, as shown in Figure 5-3e.

To conclude, we were able to reduce the capture time of a bubble by a hydrophobic surface by two orders of magnitude from hundreds of milliseconds to a mere few milliseconds. A first order of magnitude reduction (hundreds of milliseconds to tens of milliseconds) was achieved by changing the textures of the sample so that its slip length is be substantially larger than the critical film thickness. An additional
reduction in order of magnitude (tens of milliseconds to a few milliseconds) was achieved by preventing the bubble from bouncing away from the surface using plastron protrusions as shown in Fig. 3f.

5.1.4 Foam Prevention

We use the principles developed in the previous sections to prevent foam from forming by catching bubbles as they rise through the bulk of the solution as illustrated in Figure 5-4a. We construct a device that contains a stainless steel porous plate and a stainless steel mesh that are rendered superhydrophobic so that the contact angle of a water droplet on these surfaces is greater than 160° (see Materials and Methods). The stainless steel porous plate effectively acts as a high slip length surface while the mesh is chosen so that the wire diameter is similar to the size of the protrusion shown in the previous section. Furthermore, the distance between two adjacent wires in the mesh is on the order of a typical bubble diameter to ensure impact of incoming bubbles on at least one of the protruded elements. As shown in Figure 5-4b the porous plate and the mesh are sandwiched between two 3D printed parts, an enclosure and a cover, as well as an o-ring seal to create a sealed device. The device is connected to a tube which provides a continuous gaseous pathway between the environment and the porous mesh when the device is submerged.

We use this device in a foaming solution (see Materials and Methods) after a stable foam layer has been formed. After the device is submerged into the solution it disrupts the balance between bubbles rising into the foamy layer and foam breakage by continuously collecting gas from bubbles that would otherwise add to the foamy layer. Consequently the foam layer decreases until it is finally reduced to a fraction of its initial size. In contrast when a control surface (see Materials and Methods) is used instead of the porous stainless steel plate and the mesh it does not reduce the foam thickness as shown in Figure 5-4e-g.
5.2 Summary and Discussion

In this work, we have shown how the ability of aerophilic surfaces to captures impacting bubbles depends on the structure of their micro and nano textures. A bubble is captured after the thin liquid film separating it from the plastron is drained to a critical value. The thin film's spatiotemporal evolution can be described more accurately by the Stokes-Reynolds model.[116,117] However, using the flat film model we can derive a simple scaling law describing the attachment dynamics and achieve a value for the equivalent critical thickness of the film, $h_{cr}$. The value of $h_{cr}$ obtained by this method is on the order of values that have been achieved using the Stokes-Reynolds model.[114]

The drainage of this film is due to pressure buildup which is driven by two forces: the deceleration of the bubble and buoyancy. When the deceleration of the bubble is smaller than the gravitational acceleration $g$, the system is in the buoyant drainage regime. In this regime, the pressure in the film is due to buoyancy and it drains the film until the critical film thickness is reached and the bubble is captured. When the deceleration of the bubble is larger than the gravitational acceleration $g$, the system is in the inertial drainage regime. In this regime, the pressure in the film is due to bubble deceleration and it is larger than the pressure in the buoyant drainage regime. However, this pressure acts for a limited time which is the residence time of the bubble on the surface during a bounce. If during this time film thickness reaches the critical value, the bubble will be captured by the surface. Otherwise, the bubble will bounce away.

In both cases film drainage can be enhanced by increasing the slip length of the sample. Specifically, when the slip length is much greater than the critical film thickness, drainage time can be reduced by an order of magnitude and a bubble can be captured during the inertial drainage regime. However, even on samples with slip length greater than $150 \mu m$, the liquid film may not reach the critical thickness during the first bounce. In order to minimize capture time, we create local protrusions in the plastron of a high slip length surface. These protrusions are much larger than the
thickness to which the film drains during the bubble's first bounce. On the protrusion, capture time is lower by an order of magnitude relative to the rest of the sample as bubbles are captured upon initial impact. In total, by increasing slip length and creating plastron protrusions we were able to reduce the capture time by two orders of magnitude from hundreds of milliseconds to only a few milliseconds.

Finally, we use these principles and design guidelines to create a submerged bubble-catching device, which is based upon an aerophilic surface with sub milimetric protrusions. This device is the embodiment of a passive, retrofittable, one-fits-all method to prevent foam by capturing bubbles as they rise through the bulk. Furthermore, this method is environmentally friendly as it can replace the use of antifoaming agents which are a popular method for foam mitigation. As the performance of the device is dependent only on the existence and stability of a plastron, this design can be extended to other applications such as capturing methane bubbles from wetlands, and removing vapor from heat transfer surfaces in boiling applications.

5.3 Materials and Methods

5.3.1 Experiment setup

Single bubbles are generated using a syringe pump (Pump 11 Elite by Harvard Apparatus) with a 3mL syringe (by BD) connected to a j-shaped needle of various gauges to generate bubbles of different diameters (gauges 20, 25, 26, and 30 by McMaster) under a constant flow rate of 20 $\mu m/s$. The sample is placed on a colorimeter cell (by Starna Cell) which is placed onto a two-axis goniometer stage (by Thorlabs) levelled to 0.0° on roll and yaw. To allow for impact on predetermined locations on the sample, the needle is connected to a 3-axis stage (XYZ stage by Thorlabs). For impacts in the buoyant regime, the needle's tip is placed at the minimal distance ensuring bubble detachment without touching the sample. For impacts at terminal velocity, the needle's tip is approximately 25 mm away from the sample. We verify the bubble's terminal velocity by comparing to known values. [114]
5.3.2 Samples

The textured silicon surfaces used in this study were prepared by a standard photolithography process. The resulting micro-posts had a square geometry with width $a = 10 \mu m$ and varying pitch $b = 5, 10 \mu m$. The low $\phi$ surface was prepared using a 1064 nm Nd:YAG laser (TYMKA Electrox) which we used to ablate a flat silicon surface in a controlled pattern. The resulting texture consists of closely packed and reproducible pyramidal features spaced approximately 50 $\mu m$ apart and 50 $\mu m$ deep that are covered with sub-micron features. The samples were then cleaned in an oxygen plasma chamber (PDC-32G-2 by Harrick Plasma) at 200 mTorr for 20 minutes and treated with a low-energy silane Octadecyltrichlorosilane (advancing and receding contact angle of water on a flat surface in the presence of air are $\theta_{\text{ws(a),adv}} = 109.4^{\circ} \pm 0.5$ and $\theta_{\text{ws(a),rec}} = 100.1^{\circ} \pm 1.1$), or Perfluoroctyltrichlorosilane ($\theta_{\text{ws(a),adv}} = 112.4^{\circ} \pm 0.7$ and $\theta_{\text{ws(a),rec}} = 93.4^{\circ} \pm 3.3$). Both were purchased from Sigma Aldrich and used without modification. The Nano-textured samples were obtained by spraying hydrophobic nanometric silica particles (Glaco by Soft 99) onto flat silicon wafers. The foam prevention device was prepared by sandwiching a porous stainless steel plate (20 $\mu m$ grade by Wald Krause Engineering) and a mesh (0.7 mm opening, 0.16 mm wire diameter by McMaster) between two custom 3D printed parts and an o-ring seal (McMaster). The surface were rendered superhydrophobic by functionalization with fluorophosphoric acid (Sigma Aldrich) and by adding a layer of hydrophobic nano particles by spray coating (Neverwet by Rust-Oleum).

5.3.3 Fluids

Mixtures of DI water (18.2 $\Omega \cdot cm$ from Milli-Q Integral System by Millipore) and Glycerol (Sigma Aldrich) of different viscosities were obtained by mixing the appropriated quantities during 12 hours with a magnet stirrer at 220 rpm.

The device was placed in a foaming solution of Tween 80 (by Sigma Aldrich) in water at a concentration of 0.012 mM (twice the CMC, surface tension 45 $mN/m$) into which bubbles were introduced using a sparger (5 $\mu m$ grade media by Wald...
Krause Engineering) connected to house air.

5.3.4 Dynamic Analysis

The dynamics of single bubble impact is recorded using high-speed photography (Fast-cam SA1.1 and SA5 by Photron) and a high magnification lens (x12 by Navitar) at up to 40,000 frames per second. Image analysis is performed using ImageJ. The performance of the foam preventing device was recorded with an optical camera (D800 with a 70-180 mm lens, both by Nikon).

5.3.5 Procedures

Contact angles and surface tension were measured using a Goniometer (Model 500 by Ramé-Hart). The advancing and receding angles were taken as an average of at least three measurement on different location on the surface. The advancing angle was measured by adding water to a 5 μL water droplet at a rate of 4.2 nL/s while measuring the diameter of the triple contact line. When the diameter started to increase, the measured contact angle was taken as the advancing contact angle. Similarly for the receding contact angle, water was extracted from the droplet at a rate of 6.7 nL/s and the receding contact angle was taken as the contact angle when the triple contact diameter started to decrease. Surface tension was measured using a pendant droplet method in which water was added to water droplet of 3 μL suspended from a 30 gauge needle at a rate of 6.7 nL/s while the surface tension is recorded. When the measured surface tension no longer changed with the addition of water and hovered over a constant value, this value was recorded as the surface tension of the liquid with respect to air.

To produce images of the plastron on the low φ sample we used an upright laser scanning confocal microscope (LSM 880 by Carl Zeiss) with a x20 water-immersion lens. The sample was immersed in a 0.05 mg/L solution of Rhodamine B (by Sigma Aldrich) in water. We used a 514 nm wavelength laser to excite the Rhodamine B to receive an image for the wetted part of the sample together with a 488 nm wavelength
laser to receive the reflection images of the submerged part of the sample.[118] The two signals were superimposed and analyzed using a 3D image processing software (Imaris by Bitplane).
Figure 5-2: (a) Bubble centroid position normalized by bubble radius (solid line) and bubble velocity normalized by its terminal velocity (dashed line) as a function of time during an impact on a surface. We consider drainage to occur when the bubble centroid is less than one radius away from the surface, and a bounce as a finite period of time during which the film is draining. The five bounces of the bubble are highlighted and numbered. We approximate the deceleration of the bubble during a bounce by a constant shown here in red. (b) Bubble deceleration to buoyancy ratio for four different surfaces. The drainage is dominated by inertia during the three first bounces and by buoyancy for the later ones. On the low $\varphi$ surface, the film ruptures at the second bounce in the inertial regime. (c) Illustration of film drainage. The film is considered to be flat with an equivalent thickness $h$ and a basal area. A no-slip boundary condition is used for a flat hydrophobic surface, while a slip length boundary condition is used for the plastron containing surfaces. (d) Capture time $t_b$ of bubbles with different diameters released close to the surface in solutions of different viscosities. The capture time increases with liquid viscosity, and decreases substantially when the bubble is impacting the low $\varphi$ surface regardless of bubble size or liquid viscosity. (e) Scaled data for capture time using the flat film model. The solid line is obtained by linear regression with a fitting parameter $h_{cr} = 5\mu m$. The slope of the linear regression is 0.73. The legend was changed so that the surfaces are represented by the associated value of slip length $\beta$. (f) Ratio of the minimum equivalent thickness $h_{min}$ reached during each bounce and $h_{cr}$. The minimal thickness is lower than the critical thickness only for low $\varphi$ surface and it is the only surface that is able to capture bubbles in the inertial regime. Furthermore, the model predicts that the capture occurs at the second bounce as observed. The minimum film thickness reached during the first bounce on the other samples is in the order of $50 \mu m$. 

105
Figure 5-3: (a) Illustration of a bubble with horizontal radius $R$ approaching a protrusion at a lateral distance to bubble centroid $W$. (b) SEM image of the protrusion. Scale bar is 100 $\mu$m. (c) Frame sequence of a bubble impacting a protrusion. Film breakage and establishment of the triple contact line occurs on top of the protrusion. Scale bar is 1 mm. (d) Velocity profile of an impact on (solid line) and off (dashed line) the protrusion normalized by the terminal velocity. When the bubble impacts the protrusion, the capture occurs during the initial impact. (e) Normalized capture time as a function of the normalized lateral distance $W/R$. The capture time is normalized by the average value away from the protrusion. The capture time on the protrusion is independent of the lateral distance and is an order of magnitude lower than the capture time away from the protrusion. (f) Capture time for impacts at terminal velocity on a flat hydrophobic surface (left), low $\varphi$ surface (middle), and on a protrusion (right). By combining high slip length and plastron protrusion, a two orders of magnitude reduction of the contact time is achieved.
Figure 5-4: (a) Illustration of the experimental setup where bubbles are generated using a sparger. The detail shows the aerophilic porous stainless steel plate which enables a continuous gaseous pathway from the surface on which the bubbles impact to the outer environment. (b) Exploded view of the device components. (c) An image of the operational parts of the device which include the porous plate and the mesh. Scale bar is 1 mm. (d) SEM image of the porous mesh. Scale bar is 50 μm. (e) Foam thickness as a function of time. At $t = 0$, the device is immersed into the solution where bubbles are rising. The foam thickness then decreases to reach a plateau in 10 minutes. A control experiment is performed using a flat hydrophilic surface instead of the porous plate and the mesh. The control has no effect on the foam thickness over time. (f) After 10 minutes the foamy layer reduced to a residual thickness of 1 cm.
Appendix A

Mechanical Design of Set Up for Pool Boiling Experiments

A.1 Overview

The purpose of the pool boiling experiment set up is to allow controlled generation of bubbles on a sample while simultaneously recording the temperature at the surface of the sample as well as the behavior of the bubbles as they nucleate and depart. The chamber maintains the fluid at constant temperature for which its vapor phase is in equilibrium with its liquid phase (100°C for water). The bubbles are then generated by locally heating the liquid in the vicinity of the sample using an ohmic heater embedded in the sample. This heater generates the additional energy required to generate the bubbles on the surface of the sample. The temperature on the surface of the sample is recorded using a high speed infrared (IR) camera which images the sample through an IR window in the bottom plate assembly. For this measurement to be accurate the path from the window to the sample needs to be clear of IR obstruction such foreign objects or liquids. The high speed visual imaging and illumination is performed through side windows which allows the camera to be positioned at a horizontal angle of up to 16°. The set up is comprised of four sub-assemblies: top plate assembly, chamber body, heater holder assembly, and bottom plate assembly as shown in Figure A-1. The sample is nested in the heater holder assembly where
it is pressed against spring loaded electrical contacts as well as a sealing gasket. Note that in order to allow quick sample replacement, the electrical contacts between the heater holder and the external power supply (through the voltage feedthrough on the bottom plate) are not irreversible but rather pressed against each other with springs. The features of each assembly as well as the parts needed to build them are described in details in the following subsections while the drawings for the custom parts machined for this set up are shown in Appendix B.

A.2 Top Plate

The top plate assembly contains eight slots that allow fast connection of the assembly the chamber body using eight pairs of hex nuts and bolts as shown in Figure A-2. The assembly also contains two plastic carrying handles which allow comfortable grip even after experiments when the temperature of the top plate can get up to \( \sim 100 \, ^\circ C \). The assembly has connections to an external pressure gauge, thermocouples, a high voltage feedthrough, as well as a window assembly that allows to heat the sample externally using a laser (not used in the experiments presented in Chapter 3). In experiments where the fluid in the chamber is a salt solution, a reflux condenser can be connected to a the top plate in order to maintain the salt concentration constant by condensing the evaporating liquid back to the chamber (this feature can be also used when the level of the liquid in the chamber needs to be kept constant).

A.3 Bottom Plate

The bottom plate assembly has eight through holes that are used to connect it to the chamber assembly. In the center of the bottom plate a Germanium window sandwiched between two gasket is connected to the bottom plate using window cover. The horse-shoe shape of the window cover allows for easy evacuation of water droplets from vapor that might condense on the window through the venting port at the open section of the window cover as shown in Figure A-3. The other venting port on the
other side of the window cover and in between the two o-ring grooves is used to evacuate the chamber from the fluid while the heater holder is still connected to the
Table A.1: Top Plate Bill of Materials

<table>
<thead>
<tr>
<th>Name</th>
<th>Quantity</th>
<th>Supplier</th>
<th>Part Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflux Condenser</td>
<td>1</td>
<td>Chemglass</td>
<td>CG-1213-14</td>
</tr>
<tr>
<td>Voltage Feedthrough Flange</td>
<td>1</td>
<td>Kurt Lesker</td>
<td>4464K5611</td>
</tr>
<tr>
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<td>GA-0133V</td>
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<td>Voltage Feedthrough</td>
<td>1</td>
<td>Kurt Lesker</td>
<td>F0133X075NW</td>
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<td>Condenser Adapter</td>
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<td>Machined</td>
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<td>Top Plate</td>
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<tr>
<td>Top Window Flange</td>
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<td>Machined</td>
<td></td>
</tr>
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<td>1</td>
<td>Machined</td>
<td></td>
</tr>
<tr>
<td>Top Window Plate</td>
<td>1</td>
<td>Machined</td>
<td></td>
</tr>
<tr>
<td>Top Window Gasket 1</td>
<td>1</td>
<td>Machined</td>
<td></td>
</tr>
<tr>
<td>Top Window Gasket 2</td>
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<td>Pressure Gauge Adapter</td>
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<td>Pull Handle</td>
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<td>Condenser Base Adapter</td>
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<td>McMaster</td>
<td>8477K48</td>
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</table>

bottom plate assembly. The outer o-ring is used as a sealant between the bottom plate assembly and the chamber body, while the inner o-ring is used as a sealant between the bottom plate and the heater holder. As the heater holder assembly is lowered into the chamber, the two power feedthrough connectors located in the inner
part of the assembly come into contact with spring loaded electrical contacts in the heater holder assembly to provide continuous electrical pathway from the power source located outside the chamber to the ohmic heater on the sample. Note that there are two additional slots for power feedthrough which allow flexibility in the assembly. Furthermore in order to position the heater holder correctly during assembly, the bottom plate contains three assembly pins (and three corresponding through holes are located in the heater holder assembly) positioned so that only one orientation of the bottom plate relative to the heater holder is possible. Finally, the space bounded between the bottom plate and the heater holder assembly is sealed and kept free of liquids to allow clear IR imaging of the sample as well as prevent direct electrical contact between the two voltage feedthrough connectors.

Figure A-3: Bottom Plate Assembly. All dimensions are in inches.
Table A.2: Bottom Plate Bill of Materials

<table>
<thead>
<tr>
<th>Name</th>
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<th>Supplier</th>
<th>Part Number</th>
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<td>Power Feedthrough</td>
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<td>ETF0513095</td>
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<td>Window Cover</td>
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</tr>
<tr>
<td>Bottom Plate</td>
<td>1</td>
<td>Machined</td>
<td></td>
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<tr>
<td>Power Feedthrough Cap</td>
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<tr>
<td>Cut Gasket 2</td>
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<tr>
<td>Bottom Outer O-Ring</td>
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<td>McMaster</td>
<td>9396K246</td>
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A.4 Chamber Body Assembly

The chamber is comprised from two concentric schedule 40 stainless steel pipes as shown in Figure A-4. The inner and the outer pipes have nominal diameters of 5" and 8" respectively. The inner pipe contains the fluid that comes in contact with the sample, this fluid is maintained at a prescribed temperature by an additional fluid circulating in the gap between the inner and the outer pipe. In the experiments presented in Chapter 3 the circulating liquid was a 1:1 mixture of propylene glycol and water which was kept at 100 °C by an external temperature bath connected to the outer pipe through two 3/8" NPT connections. The inner pipe and outer pipe have each four concentric holes that allow positioning and welding of four 2.5" nominal diameter schedule 40 stainless steel pipes in a cross formation. A flange is welded to each of those pipes and onto each flange a window assembly that contains a window sandwiched between two gaskets and an outer flange is assembled. These four glass windows allow imaging and illumination of the sample and the fluid in the inner pipe. The flat faces of the inner and outer pipes are welded to two stainless steel circular plates that connect the chamber to the top and bottom covers of the boiling set up. The upper plate contains an o-ring groove that allows for sealing against the top cover of the boiling set up, whereas the sealing of the bottom plate is done using an o-ring in the bottom cover.
Figure A-4: Left - Chamber Body Assembly, Right - Assembly Cross Section. All dimensions are in inches.

Table A.3: Chamber Body Bill of Materials

<table>
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<th>Name</th>
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<td>Outer Tube</td>
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<td>Machined</td>
<td></td>
</tr>
<tr>
<td>Inner Tube</td>
<td>1</td>
<td>Machined</td>
<td></td>
</tr>
<tr>
<td>Bottom Plate</td>
<td>1</td>
<td>Machined</td>
<td></td>
</tr>
<tr>
<td>Window Pipe</td>
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<td>Machined</td>
<td></td>
</tr>
<tr>
<td>Window Flange</td>
<td>4</td>
<td>Machined</td>
<td></td>
</tr>
<tr>
<td>Window Cover</td>
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<td>Machined</td>
<td></td>
</tr>
<tr>
<td>Inner Window Gasket</td>
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<td>9473K61</td>
</tr>
<tr>
<td>Outer Window Gasket</td>
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<td>McMaster</td>
<td>9473K61</td>
</tr>
<tr>
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<td>1283N215</td>
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<td>Window 0.25&quot; Thickness</td>
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<td>McMaster</td>
<td>8477K88</td>
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A.5 Heater Holder

The heater holder assembly holds the silicon sample between its top and bottom sub-assemblies. The sample is pressed against two electrical contacts as well as a square gasket (shown in pink in Figure A-5) that keeps the inner area of the heater holder free of liquids. This is specifically important as this area is used both for IR imaging
through the viewing port shown in the figure as well as electrical connection between the bottom plate assembly and the heater holder assembly. This electrical connection is made possible by two spring loaded voltage feedthrough contacts that come into contact with the power feedthrough connectors shown in Figure A-3. To finalize the continuous electrical pathway between the external power source and the sample, the voltage feedthrough contacts are connected to the sample with high temperature electrical wires that are not shown here. The sample needs also to be electrically insulated from the environment and apart from the spring loaded sample contacts it does not come into contact with any metal parts. This, it is kept in place between two polyether ether ketone (PEEK) parts shown in white in the figure. The top plate sub-assembly of the heater holder (shown in orange in the figure) has four slots in a cross formation which allow to image the sample directly from all four sides without any obstructions. This plate has also a thread which allows connection of an external rod as shown in the assembly drawing in Appendix B. This rod is used to lower the heater holder assembly into the chamber and connect it to the bottom plate assembly using six captive screws located on the base plate of the bottom sub-assembly of the heater holder.

Figure A-5: Heater Holder Assembly. All dimensions are in inches.
Table A.4: Heater Holder Bill of Materials

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<td>Bottom Plate</td>
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<td>Bottom Plate Flange</td>
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Appendix B

Drawings of Machined Parts for Pool Boiling Set Up

B.1 Top Plate
1. All dimensions are in inch
2. Please purchase ITEM 4 from www.lesker.com
   Part # HN-0133

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<td>Top cell plate</td>
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<td>2</td>
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<td>SST 316L</td>
<td>Top window tube</td>
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<tr>
<td>3</td>
<td>1</td>
<td>SST 316L</td>
<td>Top window plate</td>
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<tr>
<td>4</td>
<td>1</td>
<td>SST 316L</td>
<td>Voltage lead through flange <a href="http://www.lesker.com">www.lesker.com</a> (HN-0133)</td>
</tr>
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1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004x45°

2. Material: PEEK
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004X45°

2. Material: Stainless steel 316L

D -- + 1.050

M6x1 - 6H F .160 (+4)

1/8 - 27 NPT (X4) Tap from this side

M6x1 - 6H F .160 (+4)

0.031 x 45° Chamfer

0.180 (X8)

0.031 F

0.011 x 45° Chamfer

SECTION D-D
SCALE 1 / 2

VIEW 3
SCALE 1 / 2

Leonid Rapoport 3/30/2015
CHECKED
APPROVED
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004X45°
2. Material: Stainless steel 316L.
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004X45°
2. Material: Stainless steel 316L

NPS - 2" SCH.40
Ø2.375

VIEW1
SCALE 2 : 1

SECTION A-A
SCALE 2 : 1

DETAIL B
SCALE 5 : 1

DETAIL C
SCALE 5 : 1

VIEW3
SCALE 1 : 1

VIEW D-D
SCALE 1 : 1

Material: Stainless steel 316L
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004X45°
2. Material: Stainless steel 316L
B.2 Bottom Plate
1. Unless stated otherwise:
All dimensions are in inch
Linear tolerances ±0.005
Angular tolerances ±0.5°
Deburr sharp edges up to 0.004°/45°
Material: Stainless steel 316L
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up
to 0.004X45°
2. Material: Stainless steel 316L
3. Quantity: 4
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004X45°
2. Material: Stainless steel 316L
B.3 Chamber Body Assembly
Ensure correct orientation between top plate and side windows.

Drill holes for 2.5" pipe in Inner Tube and Outer Tube only after parts are assembled with the bottom plate.

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</table>

David Rapport 5/29/2015

Drawn

Check

MFG

Approved

Size

BOS YF

REV

Scale 1/2

VIEW2

SECTION A-A

SCALE 1/2

VIEW6

SCALE 1/4

PARTS LIST
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004X45°

2 Material: Stainless steel 316L
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004×45°
2. Material: Stainless steel 316L
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004X45°
2. Material: Stainless steel 316L
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004X45°
2. Material: Stainless steel 316L
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004X45°
2. Material: Stainless steel 316L
1. Unless stated otherwise:
All dimensions are in inch
Linear tolerances ±0.005
Angular tolerances ±0.5°
Deburr sharp edges up to 0.004x45°
2 Material: Stainless steel 316L
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004X45°
2. Material: Stainless steel 316L
B.4 Heater Holder
1. All dimensions are in inch

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**SECTION A-A**

**SECTION B-B**

**VIEW1**

**VIEW2**

**VIEW4**
1. This is the entire heater holder assembly showing how all the components will be assembled by the users.

SECTION A-A
SCALE 1:1

SECTION B-B
SCALE 1:1

Top VIEW1
SCALE 1:1

Bottom VIEW3
SCALE 1:1

VIEW2
SCALE 2:3

VIEW3
SCALE 2:3
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004X45°
2. Material: PEEK

- Make the smallest possible semi-circular cut on one side to yield a 90 degree inside corner

DETAIL B
SCALE 10 : 1

SECTION A-A
SCALE 3 : 1
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004X45°

2. Material: Stainless steel 316L
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004X45°
2 Material: Stainless steel 316L
This 82 degree cone surface will interface with the part "lower_through_cap" and so the angle on the two surfaces should be kept the same. Both surfaces should also be made smooth for good electrical contact.

1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004X45°
   2. Material: Stainless steel 316L
   3. Quantity: 4
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004X45°
2. Material: Stainless steel 316L
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004 x 45°
2. Material: Stainless steel 316L
   Raw tube is available from McMaster
1. Unless stated otherwise:
   - All dimensions are in inch
   - Linear tolerances ±0.005
   - Angular tolerances ±0.5°
   - Deburr sharp edges up to 0.004×45°
2. Material: PEEK
3. Quantity: 4
As you can see, these are actually two similar parts (mirror images); heed all of these (4 of what is shown in drawing).

VIEW1
SCALE 10 : 1

VIEW3
SCALE 10 : 1

SECTION A-A
SCALE 10 : 1

1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004X45°

2. Material: PEEK

3. Quantity: 4
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004X45°
2. Material: PEEK
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004x45°
2. Material: PEEK
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004×45°
2. Material: PEEK
3. Quantity: 2
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°
   Deburr sharp edges up to 0.004x45°
2. Material: PEEK
3. Quantity: 2
1. Unless stated otherwise:
   All dimensions are in inch
   Linear tolerances ±0.005
   Angular tolerances ±0.5°

2. Material: Stainless steel 316L
Bibliography


