Modeling Time-Dependent Performance of Submerged Superhydrophobic or Slippery Surfaces

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Modeling Time-Dependent Performance of Submerged Superhydrophobic or Slippery Surfaces

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Virginia Commonwealth University.

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Dedication

I would like to dedicate this work to my family. Their sincere prayers have always paved (and still pave) the roughness of all my scientific endeavors. I would like to express my gratitude to my wife and because of her this work has been done while she is taking care of our children. My mother, father, brothers, children and all of my family, the near and the far, thank you for your contribution to this work through supporting me emotionally and materialistically.
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Abstract

Modeling Time-Dependent Performance of Submerged Superhydrophobic or Slippery Surfaces

By: Ahmed A. Hemeda, Ph.D.

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Virginia Commonwealth University, 2016

Major Director: Hooman V. Tafreshi, Professor, Department of Mechanical and Nuclear Engineering Department

The goal of this study is to quantify the transient performance of microfabricated superhydrophobic surfaces when used in underwater applications. A mathematical framework is developed and used to predict the stability, longevity, and drag reduction benefits of submerged superhydrophobic surfaces with two- or three-dimensional micro-textures. In addition, a novel design is proposed to improve the drag-reduction benefits of lubricant-infused surfaces, by placing a layer of trapped air underneath the lubricant layer. The new design is referred to as lubricant–infused surfaces with trapped air, and it is designed to eliminate the long-lasting longevity problem of submerged superhydrophobic surfaces. The effectiveness of liquid-infused surface with trapped air design was examined via numerical simulation, and it was found to outperform its liquid-infused surface counterpart by about 37%.
Chapter 1. Introduction

1.1 Background

Different contact angles of a water droplet (or for any other fluid) can be obtained using different chemical treatments. For example, there are three basic surfaces made of different materials as shown in Fig. 1.1a-c for superhydrophilic, hydrophilic and hydrophobic materials, respectively (1,15). This classification was based on the contact angle value as can be seen in the figure. Similarly, for an oil droplet on substrate, the contact angle would be greater than 90 degrees in case of having substrate made of oleophobic material. In addition, superhydrophobicity is resulted from adding micro- or nanoscale roughness to a hydrophobic material in such a way that air can be entrapped when the surface is submerged as can be seen in Fig. 1.1d (16) (i.e., bio-inspired techniques). These roughnesses can be comprised of 2-D or 3-D textures (e.g., parallel ridges or posts). The contact angle for a droplet on such surfaces exceeds 150 degrees (see Fig. 1.1d). This is because of the entrapped air layer between the solid and liquid which prevents the water from penetrating into the surface. This is due to the surface tension of water (or other working fluid). There are several applications for these bio-inspired surfaces such as anti-fouling, anti-corrosion, drag reduction and so many others (15,17–19).
Fig. 1.1: Schematic views of superhydrophilic (a), hydrophilic (b), hydrophobic (c), and superhydrophobic surfaces (d).

Such surfaces are however plagued with some problems as will be discussed in this chapter, e.g., mechanical stability of the meniscus. However, there are some suggestions in order to stabilize these surfaces. For example, when hierarchical structure is added to the superhydrophobic (SHP) surfaces, the system will be more stable (e.g., adding nanoscale hierarchical structure to microscale patterns (20).

The roughness patterns of the SHP surfaces can be ordered textures, e.g., polygon pores or posts (microfabrication in Ref. (8,10,21)), or these patterns can be a random textures, e.g., by depositing hydrophobic fibers or particles on a substrate (22,23). There is also another suggestion for entrapping other fluid, e.g., lubricant as given in the work of Ref. (1), and this surface is named as Liquid–Infused Surface. The discussions about these surfaces are in the following section.
1.2 Slippery Surfaces Needs and Challenges

As mentioned before, SHP surfaces or liquid-infused surfaces are bio-inspiration techniques. For instance, self-cleaning on a Lotus leaf, underwater breathing for some insects (plastron gel), and drag reduction provided by sharkskin are the famous known examples of SHP surfaces in nature (see Fig. 1.2, see Ref. (24)). In fluid mechanics, there are many potential applications for superhydrophobic surfaces. This, again, is because of the entrapped air layer, which can be used for drag reduction (18,19). In the last two decades, there are enormous efforts to produce a manmade SHP surface to gain the benefits, e.g., drag reduction, anti-fouling, self-cleaning, anti-corrosion, anti-icing, and anti-clotting.

![Fig. 1.2: An example of superhydrophobic surfaces in nature: lotus leaf. There is an SEM for this surface.](image)

The SHP surfaces are still plagued with problems: air dissolved in ambient water under moderate pressure (2,21,23,25,26) and collapsing under high pressure (10,27,28). Moreover, there are other problems under investigation for SHP surfaces, e.g., failure under mechanical vibration (or droplet impact), droplet evaporation, limited repellency to oils, and they can be expensive to produce (29,30).

On the other hand, in liquid-infused surface other entrapped fluid will take the place of the air layer in the SHP surfaces (1). The new design is named as Slippery Liquid infused Porous Surface
Several problems (e.g., stability of the entrapped fluid) have been solved using the new design, while others have not been solved. In the following section, the literature review for the stability issues are addressed and discussed for the two known surfaces: SHP surfaces and SLIPS (or liquid-infused surface).

1.3 Literature Review

Several experimental and numerical models to quantify the performance (critical pressure, longevity, and drag reduction or slip length) of the SHP surfaces are discussed in this section. In addition, there are other works for the liquid-infused surface applications and these works are reviewed in this section.

1.3.1 Superhydrophobic Surfaces

As mentioned before, water may penetrate into the pores of the SHP surfaces and replace the entrapped air at high hydrostatic pressure, i.e., critical pressure (16,33). This critical hydrostatic pressure—the pressure at which a superhydrophobic surface starts departing from the Cassie state—is often reported as a measure for the quality or wetting stability of the surface (22,34). It is worth mentioning that a similar phenomenon takes place during the evaporation of a droplet placed on an SHP surface: pressure inside the droplet increases due to evaporation and forces the air–water interface into the air-filled pores underneath the droplet (30).

Generally speaking, there are two ways to determine the critical pressure: experimentally and numerically. In the experimental work, the light reflection or diffraction are the most common
methods to measure the critical pressure (10,23,35). In the numerical work, there are two approaches; force balance (9,12,27); and minimization of the energy of the system (36,37). In the present work, we propose an analytical model using the force balance approach to determine the critical pressure for different SHP surfaces (2-D and 3-D features, e.g., polygon pores and posts in ordered or random distribution).

While critical pressure can be used to judge if the Cassie state is mechanically stable under elevated pressures, it is the surface longevity that matters the most for a submerged SHP surface. Longevity is the time that it takes for an SHP surface to transition to the Wenzel state (or wetting state). In other words, a submerged superhydrophobic surface loses its air content in ambient water, or because of excessive hydrostatic pressures, e.g., in some cases few hours (21,23,38). This effect is believed to be caused by the dissolution of air in water. It is also expected to accelerate when the hydrostatic pressure is increased, as the solubility of air in water increases with pressure (39). Therefore, because of the air dissolution, the surface gradually transitions from the Cassie state to the Wenzel state. The term longevity is used in this work to refer to the time it takes for the surface to lose its air content underwater.

There have been few experimental studies on the longevity of submerged superhydrophobic surfaces. The authors of Ref. (21) used an optical technique to measure longevity of microfabricated superhydrophobic surfaces, by measuring the number of shiny spots that indicate an interface between air and water. Similar studies were performed using a laser beam to investigate the importance of surface microstructure on longevity (7,25,38). The measurements by the authors of Ref. (21) and (38) indicated that the longevity of a superhydrophobic surface
decreases with increasing hydrostatic pressure. The authors of Ref. (28) developed an optical technique to study the effects of different environmental conditions on the longevity of submerged superhydrophobic coatings. They used an optical spectroscopy system to quantify the intensity of reflected light in the visible range scattered from the surface. Using the above technique, the authors of Refs. (23,40) also measured the effects of water flow and hydrostatic pressure on the longevity of superhydrophobic coatings. Recently, the longevity was measured using optical techniques for an SHP surface comprised of: circular pore by the authors of Ref. (26); and rectangular trench by the authors of Ref. (2).

Superhydrophobic (SHP) surfaces can be used to reduce the skin-friction drag in a microchannel. There are several works for the drag reduction using SHP surfaces. For example, the authors of Ref. (18) showed a drag reduction of about 25% in an SHP microchannel. This is due to the peculiar ability of these surfaces to entrap air in their pores and thereby reduce the contact area between water and the solid surface (see Fig. 1.3). The favorable drag-reduction effect, however, can quickly deteriorate if the surface geometry is not designed properly. The deterioration can be sudden, caused by exposure to excessive pressures, or gradual, due to the dissolution of the entrapped air into the ambient water.

Fig. 1.3: Slip length in SHP microchannel.
1.3.2 Liquid-Infused Surfaces

In 2011, a new bio-inspired surface is suggested to solve some of the SHP surface issues (1). In the new surface, the entrapped air is replaced by another lubricant fluid; therefore, this design is named Slippery Liquid–infused Porous Surface (SLIPS) (Ref. (1) see Fig. 1.4). With this design, the lifespan of the entrapped fluid may be extended indefinitely. Note that this surface is also known as Liquid–infused Surface (31,41,42) or Lubricant-impregnated Surface (32). Such surface is still plagued with other problems and it will be discussed in this section.

![Fig. 1.4: An example of Slippery liquid infused surface (SLIPS) (1).](image)

Initially, liquid-infused surface was first used in applications such as anti-fouling and anti-coagulation (43,44). The water or other fluids show beading angle greater than 150° and highly slippery of the droplet was obtained using SLIPS or liquid-infused surface. Recently, liquid-infused surface was used for drag reduction application in the work of Ref. (32). In the work of Solomon et al., the working fluid was a water-glycerol mixture with a viscosity of about 2000 times the viscosity of the infused lubricant, and a 16 % drag reduction was achieved. There was no further work regarding the drag reduction using liquid-infused surface.

Unlike SHP surfaces, liquid-infused surface suffers from different stability problems due to shear or gravitational forces as examined in the recent liquid-infused surface literatures (31,41,42). There is also recent suggestion to avoid this issue by splitting the longitudinal grooves into
rectangular trenches using chemical treatment so that there will be no more drainage of the lubricant from the surface (41).

### 1.4 Overall Objectives of This Thesis

This thesis primarily focuses on predicting the performance of SHP surfaces and liquid-infused surface. For this reason, several mathematical models for predicating the critical (transition) pressure, longevity of the entrapped air and slip length (or drag reduction) are given in this work for two- and three-dimensional featured surfaces. There are seven chapters in this work and the objectives of these chapters are given below.

The time-dependent drag-reduction in a microchannel enhanced with transverse or longitudinal SHP grooves of varying wall profiles or wettabilities are to be studied in Chapter 2. Therefore, different approaches are to be discussed and distinguished the performance of a sharp-edged groove from that of a groove with round entrance. The instantaneous slip length are needed to be then calculated by solving the Navier–Stokes equations for flow in microchannels with SHP grooves. Our results are finally are needed to be compared with the studies in the literature.

The effects of adding hierarchical features to side walls of SHP surface on the longevity of superhydrophobic surfaces are to be discussed in Chapter 3. For the sake of simplicity, our study is limited to superhydrophobic surfaces comprised of parallel grooves with side fins. The effects of fins on the critical pressure and longevity are to be predicted using a mathematical approach based on the balance of forces across the air–water interface. The mathematical framework
presented in this chapter may be used to custom-design superhydrophobic surfaces for different applications.

To extend the work of Chapter 2 and 3, a comprehensive mathematical framework is needed to be developed in Chapter 4 to predict the mechanical stability and the longevity of submerged SHP surfaces with arbitrary pore or post geometries. The effects of geometrical parameters and hydrostatic conditions on surface stability and longevity will be discussed in detail in this chapter. A mathematical framework is also needed to be developed to describe some of the important intermediate wetting states of a superhydrophobic surface between the two extreme states of Cassie and Wenzel. This are to be discussed in Chapter 5. The superhydrophobic surfaces considered in Chapter 5 are comprised of sharp-edged polygonal pores or posts. Two different critical pressures need to be defined in this chapter, and they are used to distinguish pinned, partially-pinned, and de-pinned air–water interfaces from one another. In the the work presented in this chapter, comparisons between the pressure-dependent performances of superhydrophobic surfaces having different pore or post designs from one another are to be discussed in Chapter 5.

As discussed before in Sec. 1.3.2, while an liquid-infused surface surface has been shown to reduce drag for flow of water–glycerol mixture (32), no significant drag reduction has yet been reported for the flow of water (a lower viscosity fluid), over liquid-infused surface . In this concern, we have designed a new surface in which a layer of air is trapped underneath the infused lubricant to reduce the frictional forces preventing the liquid-infused surface to provide drag reduction for water or any fluid with a viscosity less than that of the lubricant as will be seen in Chapter 6. Drag
reduction performance of such surfaces, referred to here as liquid-infused surfaces with trapped air, are to be predicted by solving the Naiver–Stokes equations for the water–oil–air three-phase system in transverse grooves with enhanced meniscus stability using double-reentry designs (45). Finally, the overall thesis conclusions are presented in Chapter 7.
Chapter 2. Instantaneous Slip Length in Superhydrophobic Microchannels Having Grooves With Curved or Dissimilar Walls

2.1 Introduction

Concerned with the excessive pressures required to pump aqueous solutions through a microchannel, superhydrophobic (SHP) surfaces have been suggested as a wall treatment to potentially reduce the skin-friction drag in the channels. An SHP surface is generally comprised of a micro- or nanoscale texture made of (or coated with) a hydrophobic material. A peculiar property of an SHP surface is that it can entrap air in its pores and thereby reduce the contact area between the solid surface and water. The reduced solid–water contact area may then result in a reduction in the friction between the wall and the flow. Studies reporting on the use of SHP micro-posts and micro-grooves in channels include, but are not limited to, the experimental and theoretical work of refs. (3–5,18,19,48,49).

Depending on the geometry and operating conditions, the Cassie state (fully-dry), the Wenzel state (fully-wetted), or a series of transition states in between the Cassie and Wenzel states can exist for an SHP surface in a microchannel. Departure from the Cassie state under elevated pressures is often characterized in terms of a critical pressure, as will be discussed later in this chapter. In fact, there are two paths by which a submerged SHP surface may transition from the Cassie state to the Wenzel state: a gradual transition over a certain period of time, or a sudden transition due to exposure to elevated pressures. The former takes place due to the dissolution of the entrapped air in the ambient water, whereas the latter occurs because of the imbalance of the mechanical forces
acting on the air–water interface.\(13,26,50–59\) The drag-reduction effect generated by an SHP surface therefore depends on both the operating pressure and the time in service. It is also important to note that even at a given transition state, the drag-reduction gain may vary with the flow regime (see e.g., Ref.\(60\)) and may also be delayed by adding hierarchical structures to an SHP surface.\(56,61\) Interestingly, the entrapped air bubble can also protrude into the flow if the pressure outside the pore is less than that inside the pore. This may occur, for instance, at low operating pressures when there is a moving flow over the surface.\(6,62\) Similar studies have also been reported in ref.\(63\), where an optimum protrusion angle at which the drag-reduction gain reaches a maximum (dependent on the surface properties) was discovered. While the sudden termination of the slip effect under high pressures has been the subject of numerous studies, there are only a few studies in which the gradual demise of the slip effect generated by a submerged SHP surface has been reported.\(2,7,40,64,65\) More specifically, no study has yet been conducted to predict the unsteady slip effect in a microchannel while considering an accurate air–water interface shape and position beyond the Cassie state (i.e., when the air–water interface is partially or completely de-pinned). The current study aims at providing a mathematical framework to predict the longevity of the slip effect in an SHP microchannel. More importantly, this work provides a means for optimizing the geometry of an SHP microchannel to achieve the best performance in terms of both the magnitude and durability of the slip effect.

Our formulations for critical pressure and longevity predictions developed for SHP surfaces consisting of grooves with asymmetric straight walls with dissimilar wettabilities are given in Sec. 2.2. A modified form of these equations tailored for grooves with symmetric walls having arbitrary curvatures is presented in Sec. 2.3. In Sec. 2.4, a brief parameter study is presented to demonstrate how our equations can be used to custom-design the geometry of an SHP groove for a specific
application. Examples of unsteady-state slip length calculation are presented in Sec. 2.5 for microchannels with transverse and longitudinal SHP grooves. The conclusions drawn from our study are outlined in Sec. 2.6.

### 2.2 Grooves with Dissimilar Straight Walls

Consider the flow of water in a channel formed between two parallel walls each comprised of transverse or longitudinal SHP grooves as shown in Fig. 2.1 driven by an operating pressure of $p_{op}$. For the case shown in Fig. 2.1a (transverse grooves), the grooves with different positions along the length of the channel experience different local pressures $p_{op} - (\Delta P / L_{ch}) x_i$, where $\Delta P$, $L_{ch}$, and $x_i$ are the pressure drop across the microchannel, length of the channel, and the local center point of the $i$th groove (or the origin of the groove at $y=0$), respectively. For our formulations to be both conservative and simple, we assume all grooves are exposed to a pressure equal to that experienced by the first groove, i.e., the maximum pressure. For the case shown in Fig. 2.1b (longitudinal grooves), the grooves experience different pressures along their length. For the sake of simplicity, we again assumed that the pressure acting on a longitudinal groove is a constant value equal to the pressure near the channel entrance, i.e., the maximum pressure.
2.2.1 Critical Pressures and The Corresponding Air–Water Interfaces

In this section, we first derive our mathematical formulations for channels with transverse SHP grooves and then modify these equations for channels with longitudinal grooves. Using the balance of forces across the air–water interface, we previously developed an Integro-Partial Differential Equation for the shape of the meniscus in a submerged groove or pore with vertical walls, and between the fibers of a thin fibrous coating.(13,55,56,59) A novel approach is undertaken in the current chapter to decouple the time and space variables, and thereby reduce the above integro-partial differential equation to a set of first-order Ordinary Differential Equations (ODEs) that can easily be solved using a conventional 4th order Runge–Kutta (RK4) method.

\[
P_{cap} = \sigma \nabla \cdot \hat{n} = \sigma \frac{\partial^2 f_{\phi}}{\partial x^2} \left( 1 + \left[ \frac{\partial f_{\phi}}{\partial x} \right]^2 \right)^{-3/2} \tag{2.1}
\]
Fig. 2.2: An example air–water interface inside a groove with dissimilar walls is shown in (a). The first and second critical air–water interfaces as well as a detached air–water interface are shown in (b). The area of the two dark grey triangles shown in (b) is subtracted from the area above the air–water interface in deriving Eq. 2.18a (see the Appendix). An example of our air–water interface tracking performed for an arbitrarily chosen groove with walls having sinusoidal profiles \( y = \frac{\pi y}{2h} / 2 - \frac{w_1}{2} \) is shown in (b). The area of the blue triangles in (d) is subtracted from the area above the air–water interface (see Eq. 2.31 in the case of \( \theta_{app} \)).

Consider a groove consisting of two straight walls with different angles \( \beta_L \) and \( \beta_R \) measured with respect to horizon, as shown in Fig. 2.2a. The walls on the left and right are allowed to have their own Young–Laplace contact angles \( \theta_{YL}^{L} \) and \( \theta_{YL}^{R} \), i.e., they can be made of different materials. The apparent contact angle for the air–water interface in a groove is considered to be the angle between the air–water interface and the vertical direction at the wall. These angles at the left and right walls are shown in Fig. 2.2b (\( \theta_{app}^{L} = \theta_{YL}^{L} - \beta_L + \pi / 2 \), and \( \theta_{app}^{R} = \theta_{YL}^{R} - \beta_R + \pi / 2 \)). For simplicity, we assumed that \( \theta_{app}^{L} > \theta_{app}^{R} \) in our derivations; however, one can alternate the subscripts \( L \) and \( R \) if needed. Also, the distance between the groove’s axis and the left and right walls is given as \( w_L = \frac{w_1}{2} / \tan \beta_L \), and \( w_R = \frac{w_1}{2} / \tan \beta_R \), respectively. These distances are calculated at the location where the interface is in contact with the walls (see Fig. 2.2b). Here \( w_1 \) represents the
width at the top of the groove, i.e., at \( y=0 \). Note that \( w_2 \) is the width of the groove at \( y=-h \), where \( h \) is the groove height. The air–water interface is initially pinned to the sharp edges of the grooves when the operating pressure is below the critical pressure of the surface.\(^{(13,55,56)}\) In fact, when the two walls have different inclination and/or contact angles, the groove will have two critical pressures each corresponding to a critical air–water interface (see Fig. 2.2b). The pressure at which the slope of the air–water interface at one of the walls reaches an apparent contact angle is considered to be the first critical pressure and is denoted by \( p_{cr}^{(1)} \). To obtain the shape of the air–water interface corresponding to this critical pressure \( f_{cr}^{(1)} \), we use the Young–Laplace equation

\[
P_{cap} = \sigma \nabla \cdot \vec{n} = \sigma \frac{\partial^2 f_{cr}}{\partial x^2} \left( 1 + \left[ \frac{\partial f_{cr}}{\partial x} \right]^2 \right)^{-3/2}
\]

(2.1)

At the moment of interface detachment from one of the sharp corners (point \( A_R \) in Fig. 2.2a), the capillary pressure can be taken as \( P_{cap} = 2\sigma \left| \cos \theta_{R}^{app} \right| / w_i \). Since the air–water interface in a groove conforms to the shape of a circular arc, the first or second critical interface can be defined as,

\[
f_{cr} = \sqrt{\left[ R_{cr} \right]^2 - \left( w_L + \left[ R_{cr} \cos \theta_{R}^{app} \right] - w_R \right) x} - \sqrt{\left[ R_{cr} \right]^2 - \left( x + \left[ R_{cr} \cos \theta_{R}^{app} \right] - w_R \right) x}^2
\]

(2.2)

where \( R_{cr} \) is the critical radius of curvature of the air–water interface, and \( x = 0 \) and \( x = 1 \) correspond to the first and second critical air–water interfaces \( (R_{cr}^{(1)}) \) and \( (R_{cr}^{(2)}) \), respectively. Note that the boundary conditions for a pinned interface, \( f_{cr}^{(1)}(x=-w_L=-w_i/2)=0 \) and \( f_{cr}^{(1)}(x=w_R=w_i/2)=0 \), are automatically satisfied in this equation when \( x = 0 \). The first critical radius can be calculated by substituting Eq. 2.2 in Eq. 2.1 when \( P_{cap} = 2\sigma \left| \cos \theta_{R}^{app} \right| / w_i \), i.e.,
\[ R_{cr}^{(i)} = \frac{w_1}{2} \left| \sec \theta_R^{app} \right| \tag{2.3} \]

Now the slope at the right boundary becomes \(-\cot \theta_R^{app}\), and this is the maximum slope that the air–water interface can maintain at the right boundary \(A_R\). The first critical air–water interface can be obtained by substituting Eq. 2.3 in Eq. 2.2. The first critical pressure at \(t=0\) can be obtained using the balance of forces (see Fig. 2.2a),

\[ P_{cap} - P_{cr}^{(1)} + P_{hub} = 0 \tag{2.4} \]

where \(P_{hub}\) is the pressure of the air entrapped in the groove. The entrapped air (bubble) is assumed to undergo an isothermal compression during the deflection of the interface, i.e., \(P_{hub} = P_{\infty} v_\infty\) with the volume of the bubble per unit length of the groove at the atmospheric and instantaneous pressures being \(v_\infty = h w_1 + 0.5 h^2 \left(\frac{1}{\tan \beta_R} + 1/ \tan \beta_L\right)\) and \(v_{hub} = v_\infty + \int_{-w_1/2}^{w_1/2} f_{cr}^{(1)}(x) \, dx\), respectively. As mentioned before, the first critical air–water interface can be obtained from Eq. 2.2 if \(R_{cr} = R_{cr}^{(i)}\) and \(\chi = 0\) (and hence the bubble volume). Also, by using the capillary pressure from Eq. 1 (\(P_{cap} = 2 \sigma \left|\cos \theta_R^{app}/w_1\right|\)), the first critical pressure can be obtained from Eq. 2.4 as,

\[ P_{cr}^{(1)} = \frac{\sigma}{R_{cr}^{(1)} v_\infty} + \frac{P_{\infty} v_\infty}{w_1^2 \left|\tan \theta_R^{app}\right|\left[4 - \left(R_{cr}^{(1)}\right)^2 \sin^{-1}\left(\left|\cos \theta_R^{app}\right|\right)\right]} \tag{2.5} \]

For operating pressures larger than \(P_{cr}^{(1)}\), the air–water interface will detach from the right corner but remains pinned to the left corner at \(A_L\). There will be a higher operating pressure at which the air–water interface will also detach from the left corner. We refer to this pressure as the second critical pressure \(P_{cr}^{(2)}\). At this pressure the slope of the air–water interface at the left boundary
reaches its apparent contact angle \( \frac{\partial f_{cr}^{(2)}}{\partial x} \left( x = -\frac{w_L}{2}, t = 0 \right) = \cot \theta_L^{app} \). The air–water interface profile \( f_{cr}^{(2)} \) can then be obtained from Eq. 2.2 by setting \( \chi = 1 \) and \( R_{cr} = R_{cr}^{(2)} \). Note again that the interface is represented by a circular arc with the boundary conditions of \( f_{cr}^{(2)}(x = -w_L = -w_i / 2) = 0 \) and \( \frac{\partial f_{cr}^{(2)}}{\partial x}(x = w_R, t = 0) = -\cot \theta_R^{app} \). Unlike the first critical interface, this equation is the equation of a circle with its center shifted from the original axis. Also, \( w_R \) can be obtained from Eq. 2.2 at \( x = w_R \) with \( w_R = w_i / 2 - y / \tan \beta_R \) and \( \chi = 1 \). Using the equation of the air–water interface when the slope at the left boundary (point \( A_L \)) reaches \( \cot \theta_L^{app} \), the second critical radius \( R_{cr}^{(2)} \) can be then obtained as

\[
R_{cr}^{(2)} = \frac{w_l \tan \beta_R}{\tan \beta_R \left( |\cos \theta_L^{app}| + |\cos \theta_R^{app}| + |\sin \theta_L^{app}| - |\sin \theta_R^{app}| \right)}
\]

(2.6)

Note that Eq. 2.6 can be written in many different forms; for example, using the concept of capillary pressure like in Eq. 2.3 but with a new boundary condition at \( A_L \). It is worth mentioning that Eq. 2.6 reduces to \( R_{cr}^{(1)} \) when both walls are identical (\( \beta_L = \beta_R \)).

The second critical pressure \( p_{cr}^{(2)} \) can be calculated using the balance of forces (Eq. 2.4). Let the ordinate value of the second critical air–water interface \( f_{cr}^{(2)} \) at the point \( B_R \) along the right wall be \( y^*_R \) (see Fig. 2.2b). Therefore, we obtain \( y^*_R = R_{cr}^{(2)} \left( |\sin \theta_L^{app}| - |\sin \theta_R^{app}| \right) \) from Eq. 2.2 with \( \chi = 1 \). Note that \( y^*_R \) becomes zero when the left and right apparent contact angles are equal (denoted with the superscript \(*\)). An expression for the second critical pressure \( p_{cr}^{(2)} \) can be obtained following the steps outlined previously for calculating the first critical pressure.
\begin{equation}
\frac{p^{(2)}_{cr}}{R^{(2)}_{cr}} = \frac{\sigma}{v^{(2)}_{sc}} + \frac{P_{sc}v_{sc}}{\left(\frac{y_R^*}{(2\tan\beta_R)} + R^{(2)}_{cr}\sin\theta_{LPP}\left|w_i - \frac{y_R^*}{\tan\beta_R}\right|\right) - \epsilon_0}
\end{equation}

(2.7)

where \( \epsilon_0 \) is the area directly above the air–water interface inside the groove (see Appendix A).

Note that, the volume of the two grey-shaded triangles shown in Fig. 2.2b should be removed from the bubble volume calculation \( v_{hub} = v_\infty + \int_{-w_2}^{w_2} fdx - \left(\frac{y_R^*}{2\tan\beta_R}\right)^2 \). With \( p^{(1)}_{cr} \) and \( p^{(2)}_{cr} \) obtained from Eqs. 2.5 and 2.7, one can define three different regimes of interface tracking depending on whether the operating pressure is lower than \( p^{(1)}_{cr} \) (Regime I), between \( p^{(1)}_{cr} \) and \( p^{(2)}_{cr} \) (Regime II), or greater than \( p^{(2)}_{cr} \) (Regime III) as shown in Fig. 2.2b. The formulations for these regimes are derived in the next subsections.

2.2.2 Longevity in Regime I

In Regime I, the operating pressure is less than the first critical pressure, i.e., \( P_{op} < p^{(1)}_{cr} \). In this regime, the air–water interface is initially pinned to both corners of the groove (points \( A_R \) and \( A_L \)), but it detaches from them over time and moves down into the groove as the entrapped air continues to dissolve into the ambient water. The mathematical representation of this process is given in the following subsections.

2.2.2.1 Interface Pinned to both Corners

By applying the balance of forces across an air–water interface represented with a circular arc, we obtain for \( t=0 \),
\[ P_{\text{sub}i=0} + \sigma \nabla \cdot \hat{n}_{t=0} - P_{\text{op}} \frac{\Delta P_{\text{ch}}}{L_{\text{ch}}} x_i \approx 0 \]  \hspace{1cm} (2.8)

where \( x_i \) is the \( x \)-coordinate of the middle point of the \( i \)th groove (approximately zero for the first groove). The air–water interface profile can be expressed at any moment of time using the following equation.

\[ f = \sqrt{R^2 - \left( -w_L + \left[ R \cos \theta_{R}^{\text{app}} \right] - w_R \right) \chi} - \sqrt{R^2 - \left( x + \left[ R \cos \theta_{R}^{\text{app}} \right] - w_R \right) \chi} + \tau \]  \hspace{1cm} (2.9)

where \( R \) is the radius of curvature of the air–water interface, and the parameters \( \chi \) and \( \tau \) are used to generalize the equation such that it can be used to describe the air–water interface profile in different regimes and at different times. For example, one can set \( R = R_0 \), \( \chi = 0 \), and \( \tau = 0 \) to obtain the initial air–water interface profile in Regime I (i.e., \( f_0 \)). By substituting Eq. 2.9 in Eq. 2.8 and following the same steps as discussed earlier, the following equation can be produced for the balance of forces across the initial air–water interface.

\[ \sigma / R_0 - P_{\text{op}} + \left[ P_{\text{v}} v_\infty \right] / \left[ v_\infty + \frac{w_1}{2} \sqrt{R_0^2 - w_1^2} / 4 - R_0^2 \sin^{-1} \left( w_1 / 2 R_0 \right) \right] = 0 \]  \hspace{1cm} (2.10)

This equation can be solved numerically to obtain \( R_0 \) and consequently the initial air–water interface profile.

In order to obtain the instantaneous shape of the air–water interface over time, we again consider the balance of forces across the interface. This time however, the formulation is time-dependent.

\[ \sigma \nabla \cdot \hat{n} - P_{\text{op}} + P_{\text{sub}} \approx 0 \]  \hspace{1cm} (2.11)
The bubble pressure varies over time as the entrapped air (20% Oxygen and 80% Nitrogen on a molar basis) dissolves into the ambient water. According to Henry’s law, the volume flow rate of air dissolving into water can be calculated as

\[ \dot{v} = \bar{\xi} A (kC - P_{\text{sub}}) \]  

(2.12)

where \( \bar{\xi} \) is the weighted-average invasion coefficient of air. In this equation, \( A \) is the surface area of the air–water interface (i.e., \( A = \int_{-w_2}^{w_2} \left( 1 + \left[ \frac{\partial f}{\partial x} \right]^2 \right)^{1/2} dx \)), \( k \) is Henry’s constant and \( C \) is the concentration of dissolved air in water. Note that when water is saturated with air under atmospheric pressure, \( kC \approx P_a \). Equation 2.12 is used here to represent the bubble pressure in Eq. 2.11. The invasion coefficient can be written as,

\[ \bar{\xi} = \frac{D_{\text{air}} R_{\text{air}} T}{kP_{\text{sub}}} \]  

(2.13)

where \( l \) is the characteristic length (or diffusion length), \( D_{\text{air}} \) is the diffusion coefficient for air in water, and \( R_{\text{air}} \) is the gas constant. \( P_{\text{sub}} \) and \( T \) are the pressure and temperature (here room temperature) of entrapped air, respectively. For simplicity, the bubble pressure in Eq. 2.13 is assumed to be the channel’s operating pressure. It is important to note that this assumption becomes inaccurate if the pores or grooves are extremely small (e.g., for the SHP surfaces of ref.(57)), as the contribution of the capillary pressure becomes very important causing the bubble pressure to vary significantly with time. Here we assume a characteristic length of 0.1 mm for the first 1000 sec of the system’s operation under water, resulting in \( \bar{\xi} = 2.5 \times 10^{-12} \text{ m}^2 \text{.sec/kg} \) for when \( P_{\text{sub}} \approx P_a \). Note that at high operating pressures the bubble pressure cannot be assumed...
equal to the atmospheric pressure, and hence we consider \( \xi = \left( P_\infty / P_{\text{op}} \right) \xi_0 (P_\infty) \) where 
\[
\xi_0 (P_\infty) = 2.5 \times 10^{-12} \text{m}^2/\text{s}/\text{kg}.
\]

Using the rate of change of bubble volume with time 
\[
\dot{V} = \int_{-w}^{w} f(t, x) \, dx \quad \text{for } 0 < t < t_{\text{cr}}^{(1)},
\]
where \( t_{\text{cr}}^{(1)} \) is the first critical time) in Eq. 2.11 and using Eq. 2.9 with \( \chi = 0 \) and \( \tau = 0 \), the instantaneous radius of curvature can be obtained as,
\[
\frac{\sigma}{R} - \frac{1}{\xi A} \left( \frac{R w_1}{\sqrt{R^2 - w_1^2 / 4}} - A \right) \frac{dR}{dt} + \Pi \approx 0
\]
where \( \Pi = P_e - P_{\text{op}} \). Note that the semi widths \( w_k \) and \( w_L \) are equal to \( w_1 / 2 \) for \( 0 < t < t_{\text{cr}}^{(1)} \). The air–water interface surface area can also be reduced to 
\[
A = 2R \sin^{-1} \left( \frac{w_1}{2R} \right).
\]
This simple 1st ODE can now be solved using a conventional RK4 method with the initial condition of \( R(t = 0) = R_0 \). The air–water interface sagging continues during this time period until the radius of curvature of the interface reaches the first critical radius 
\[
R \left( t = t_{\text{cr}}^{(1)} \right) = R_{\text{cr}}^{(1)}.
\]

### 2.2.2.2 Interface Detached from One Corner

The air–water interface conforms to the aforementioned first critical interface at the moment of detaching from one of the sharp corners (point \( A_k \) here). When the interface detaches from the right corner, it retains a slope of \( -\cot \theta_k^{\text{op}} \). The new air–water interface is a profile that can be described as a circular arc using Eq. 2.9 with \( \chi = 1 \) and \( \tau = 0 \). The boundary conditions force the air–water interface to stay pinned at point \( A_L \) and hold an angle equal to \( \theta_k^{\text{op}} \) at the right wall. In Eq.
2.9, \( w_R \) changes as a function of time (i.e., \( w_R = w_i / 2 - y / \tan \beta_R \)), while \( w_L \) remains equal to \( w_i / 2 \). The ordinate value along the right boundary (from \( A_R \) to \( B_R \)) can be written as

\[
y_R = \sqrt{R^2 - \delta^2} - R \sin \theta_R^{opp} \]

where \( \delta = -w_L - w_R + R \cos \theta_R^{opp} \) and \( y_R \) is calculated using Eq. 2.9 with \( \chi = 1 \) and \( \tau = 0 \) at \( x = w_R \).

To obtain the transient air–water interface profile, the balance of forces (Eq. 2.11) is used again along with Eq. 2.12 for the bubble pressure. However, one should account for the change in the span of the interface as it moves down, i.e.,

\[
y = y_c + \int_{-w_i/2}^{w_i} f(x) dx - (w_R - w_i/2) y_R/2 \]

The last term in this equation is the area of the right triangle formed between the right wall and the abscissa (see Fig. 2.2b). Using the Leibnitz formula the rate of change of bubble volume can be obtained as

\[
\dot{v} = \left[ \left( R \{ w_L + w_R \} \right) / \sqrt{R^2 - \delta^2} - A + \varepsilon_1 + \varepsilon_2 \right] \dot{R}
\]

(2.15)

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are mathematical terms defined in Appendix A, and

\[
A = R \left( \sin^{-1} \cos \theta_R^{opp} - \sin^{-1} \frac{\delta}{R} \right)
\]

is the surface area of the air–water interface. The balance of forces can now be simplified as

\[
\frac{\sigma}{R} - \frac{1}{\xi} A \left( \frac{R \{ w_L + w_R \}}{\sqrt{R^2 - \delta^2}} - A + \varepsilon_1 + \varepsilon_2 \right) \frac{dR}{dt} + \Pi \approx 0
\]

(2.16)

where \( \Pi = p_a - p_{opp} \). The 1st order ODE given in Eq. 2.16 can be solved using an RK4 method to obtain the transient radius of curvature of the air–water interface using the first critical air–water interface (at \( t = t_{crit}^{(1)} \)) as the initial condition, i.e., \( w_R = w_i / 2 \), \( y_R = 0 \), and \( R = R_{crit}^{(1)} \) (see Appendix 2.A).
This calculation can be continued until the air–water interface slope at the left boundary reaches \(-\cot \theta_{app}^L\) at the second critical time \(t = t_{ crt2}^L\) where \(R(t = t_{ crt2}^L) = R_{L2}^{(2)}\).

### 2.2.2.3 Interface Detached from Both Corners

The air–water interface detaches from the left and right sharp corners of the groove, when the slope of the air–water interface at these walls reach \(-\cot \theta_{app}^L\) and \(-\cot \theta_{app}^R\), respectively. The air–water interface profile can then be obtained at any time during its descent using Eq. 2.9 with \(\chi = 1\). The parameter \(\tau\) in this case is the vertical position of the air–water interface as shown in Fig. 2.2b. The radius of curvature of the interface remains the second critical radius of curvature but at different \(w_R\) and \(w_L\) values. This radius of curvature can then be calculated as

\[
R = \left[ w_L + w_R \right] / \left[ \cos \theta_{app}^L + \cos \theta_{app}^R \right]
\]

Following the steps discussed in Sec. 2.2.2.1, the volume flow rate of the air escaping the groove can become

\[
\dot{v} = \int_{w_L}^{w_R} \dot{f}(t, x) dx + \varepsilon_3 \ddot{\tau}.
\]

Note that there are now two triangular areas to be considered in the volume calculation (see Fig. 2.2b). The equation for the balance of forces, Eq. 2.11, can then be reduced to

\[
\frac{\sigma}{R} - \frac{1}{\varepsilon A} \left( \frac{\dot{R}}{\dot{\tau}} \left( w_L + w_R \right) \sin \theta_{app}^L \right) - A = w_L + w_R + \varepsilon_3 + \varepsilon_4 \frac{d\tau}{dt} + \Pi \approx 0
\]

with \(\varepsilon_3\) and \(\varepsilon_4\) are given in Appendix A. Equation 2.17 is then used to calculate the rate of change of air–water interface radius of curvature.
Knowing the surface area of the air–water interface \( A = R \left( \sin^{-1} \left| \cos \theta_{\text{app}}^{\text{app}} \right| + \sin^{-1} \left| \cos \theta_{\text{app}}^{\text{app}} \right| \right) \), the transient shape and position of the air–water interface can be obtained by solving Eqs. 2.18a–2.18b until the interface touches the bottom of the groove. The initial conditions for these equations (i.e., at \( t = t_f^{(2)} \)) were previously obtained in Sec. 2.2.2.2. When the failure occurs in this regime, the time is referred to as \( t = t_f \).

### 2.2.3 Longevity in Regime II

In Regime II, the operating pressure is between the first and the second critical pressures, i.e., \( P_{\text{cr}}^{(1)} < P_{\text{op}} < P_{\text{cr}}^{(2)} \). In this regime, the initial air–water interface starts from a position in between the two critical air–water interfaces and moves down as the entrapped air continues to dissolve into water. The mathematical formulations in this regime are similar to the last two stages of Regime I, except for the initial condition. The vertical position of the air–water interface contact point at the right wall at \( t = 0 \), \( y_{R0} \) (between points \( A_R \) and \( B_R \) in Fig. 2.2b) can be derived to be

\[
y_{R0} = \sqrt{R_0^2 - \left( -w_L - w_{R0} + R_0 \left| \cos \theta_{\text{app}}^{\text{app}} \right| \right)^2} - R_0 \left| \sin \theta_{\text{app}}^{\text{app}} \right|
\]  

(2.19a)

This value is calculated using Eq. 2.9 by setting \( \chi = 1 \) and \( \tau = 0 \) when \( x = w_{R0} \). Following the steps described in Sec. 2.2.2.1, Eq. 2.8 can be modified to obtain the initial radius of curvature of the interface \( R_0 \) using the balance of forces at \( t = 0 \) using Eq. 2.9 with \( f_0 = f \), \( \chi = 1 \), and \( \tau = 0 \).

\[
\frac{\sigma}{R_0} - P_{\text{op}} + \left[ P_{\text{op}} v_{\text{op}} \right] / \left[ v_{\text{op}} + \varepsilon_5 + \varepsilon_6 + y_{R0}^2 / (2 \tan \beta_R) \right] = 0
\]  

(2.19b)

In this equation, \( y_{R0}^2 / (2 \tan \beta_R) \) represents the area of the grey-shaded triangle on the right side of the groove as shown in Fig. 2.2b (see Appendix A for \( \varepsilon_5 \) and \( \varepsilon_6 \)). Equations 2.19a and 2.19b are
solved simultaneously to obtain the required initial conditions for \( y_R \) and \( w_R \). Equation 2.16 is then solved to obtain the radius of curvature of the air–water interface at different times until the air–water interface slope reaches \(-\cot \theta_L^{app}\) at point \( A_L\). The interface will then continue to move down into the groove as described in Sec. 2.2.2.3. The time that it takes for the interface to touch the bottom of the groove in this regime is referred to as \( t = t_{f_2} \).

### 2.2.4 Longevity in Regime III

In this regime, operating pressure is greater than the second critical pressure \( (P_{op} > P_{cr}^{(2)} )\) and the interface tracking procedure is exactly the same as the one used in the last stage of air–water interface tracking in Regime I, except that here the initial air–water interface is different. In this regime, Eq. 2.9 with \( \chi = 1 \) and \( \tau = \tau_0 \) can be used to represent the initial air–water interface, and Eq. 2.8 can be used to represent the balance of forces at \( t = 0 \) with

\[
y_R^* = R_{Lr}^{(2)} \left( |\sin \theta_L^{app}| - |\sin \theta_R^{app}| \right).
\]

Assuming the initial air–water interface to be located at a distance \( \tau_0 \) below the groove’s entrance, Eq. 2.17 can be modified as

\[
R_0 = \left[ w_{L0} + w_{R0} \right] / \left[ \left| \cos \theta_L^{app} \right| + \left| \cos \theta_R^{app} \right| \right] \quad (2.20a)
\]

Also, the initial width of the groove can be determined as

\[
w_{R0} = w_i / 2 - \left( y_R^* + \tau_0 \right) / \tan \beta_R , \quad \text{and} \quad w_{L0} = w_i / 2 - \tau_0 / \tan \beta_R .
\]

Unlike Regime II, \( w_{L0} \) is now an unknown in this regime. Therefore, Eq. 2.8 should be written as

\[
\frac{\sigma}{R_0} - P_{op} \left[ x_n x_e \right] / \left[ v_n + \varepsilon_s + \varepsilon_o + \tau_0^2 / (2 \tan \beta_L) + \left( y_R^* + \tau_0 \right)^2 / (2 \tan \beta_R) \right] \quad (2.20b)
\]

Equations 2.20a–2.20b are solved numerically to obtain the initial radius of curvature of the interface \( R_0 \) and its location inside the groove \( \tau_0 \), as well as \( w_{R0} \) and \( w_{L0} \). Equations 2.18a and
2.18b are then used for the remainder of the interface tracking procedure until the air–water interface comes in contact with the bottom of the groove, i.e., failure time $t_f$.

2.2.5 Test Case

The mathematical framework developed in this chapter allows one to isolate and study the effects of each individual parameter affecting the performance of an SHP microchannel with transverse or longitudinal grooves. For instance, consider a groove characterized by six geometric parameters: width and height of $w_l = 30 \mu m$ and $h = 10 \mu m$, right and left wall angles of $\beta_R = 80^\circ$ and $\beta_L = 60^\circ$, and right and left Young–Laplace contact angles of $\theta_{RL} = 110^\circ$ and $\theta_{LL} = 100^\circ$, respectively. For such a groove, the first and second critical pressures can be obtained using Eq. 2.5 and Eq. 2.7 to be (1) $136 \text{ kPa}$ and (2) $176 \text{ kPa}$, respectively. Figure 2.3 shows examples of air–water interfaces obtained for this groove in Regimes I, II, and III, respectively. Note that the exit pressure of the microchannel is assumed to be the atmospheric pressure here. Our calculations resulted in longevity values of about 5 hr, 1 min, and 25 sec, for operating pressures of 104 kPa (Regime I), 150 kPa (Regime II), and 200 kPa (Regimes III), respectively. The pressure-dependence of the invasion coefficient becomes more noticeable in Regimes II and III (see Eq. 2.13); we obtained $1.667 \times 10^{-12} \text{ m}^2 \text{ sec} / \text{ kg}$ and $1.25 \times 10^{-12} \text{ m}^2 \text{ sec} / \text{ kg}$ for the invasion coefficient in the former and latter regimes, respectively.
Regime I, $P_{op} = 104$ kPa, $t_{f1} = 5.0$ hr

Regime II, $P_{op} = 150$ kPa, $t_{f2} = 62.2$ sec

Regime III, $P_{op} = 200$ kPa, $t_{f3} = 24.7$ sec

Fig. 2.3: The air–water interfaces in a groove with dissimilar walls at different times under an operating pressure of $P_{op} = 104$ kPa in (a), $P_{op} = 150$ in (b), and $P_{op} = 200$ kPa in (c), representing Regimes I, II, and III, respectively.

Note again that the first transverse groove in a microchannel is the one experiencing the highest pressure; the subsequent grooves along the length of the channel are expected to have better longevity values. The results of our calculations are in good qualitative agreement with the experimental measurements of refs. (64,65) reporting longevity values ranging from a few minutes to a few seconds, under operating pressures higher than the first critical pressure of the surface.

2.2.6 Special Case: Grooves with Vertical Straight Walls

The equations describing the shape and position of an air–water interface in a groove with vertical walls are a special case of the formulations presented in Secs. 2.2.2.1–2.2.2.4. Therefore, we only list these equations in a table here for the sake of brevity (see Table 2.1).

For grooves with vertical walls made of the same materials ($\theta_l^r = \theta_l^v = \theta_r^v$ and $\beta_L = \beta_R = \pi / 2$), an analytical method is developed in this subsection which circumvents the need for solving the ODEs presented in the previous sections (i.e., Eqs. 2.14, 2.16, and 2.18). When the two walls of a
groove and their Young–Laplace contact angles are similar, there is only one critical profile for
the air–water interface. The critical air–water interface is the one described by Eq. 2.2 with \( \chi = 0 \),
and the critical radius of curvature \( R_c \) is similar to \( R_c^{(1)} \) in Eq. 2.3. The critical pressure here can be
obtained using Eq. 2.5 following the steps given Sec. 2.2.2.1.

Since the grooves are symmetric, there are only two stages of interface tracking in Regime I. The
initial air–water interface is calculated using Eq. 2.9 with \( \chi = 0 \) and \( \tau = 0 \), and Eq. 2.10. To
calculate the air–water interface at different times, we assume a solution in the form of Eq. 2.21,
i.e., we assume the instantaneous air–water interface to be presented by its initial profile \( f_0(x) \)
scaled with a time-dependent function \( T(t) \).

Table 2.1: Analytical formulations for grooves with vertical walls

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.21) ( f(x,t) = f_0(x) T(t) )</td>
<td>( f(x,t) ) is the instantaneous air–water interface, ( f_0(x) ) is the initial profile, and ( T(t) ) is the time-dependent function.</td>
</tr>
<tr>
<td>(2.22) ( \alpha \dot{T} + \beta T + (P_{op} - P_v)w_1 = 0 )</td>
<td>( \alpha ) and ( \beta ) are constants, ( P_{op} ) is the atmospheric pressure, and ( P_v ) is the contact pressure.</td>
</tr>
<tr>
<td>(2.23) ( T(t) = \left(1 + \frac{P_{op} - P_\infty}{\beta w_1}\right)e^{-\beta t / \alpha} - \frac{P_{op} - P_\infty}{\beta w_1} )</td>
<td>( T(t) ) is the time-dependent function, ( P_\infty ) is the pressure far from the interface, and ( \alpha ) and ( \beta ) are constants.</td>
</tr>
<tr>
<td>(2.24) ( t_{cr} = \alpha R_0 / (\sigma w_i) \ln \left[ (P_{op} - P_\infty) R_0 w_i + 2\sigma \sqrt{R_0^2 - w_i^2 / 4 \cot \theta^{YL}} \right] / \left[ w_i [(P_{op} - P_\infty) R_0 - \sigma] \right] )</td>
<td>( t_{cr} ) is the time at which the interface reaches the grooves, ( \sigma ) is the surface tension coefficient, and ( \theta^{YL} ) is the Young-Laplace contact angle.</td>
</tr>
<tr>
<td>(2.25) ( t_{f1} = t_{cr} + w_i^2 \left[ h + \frac{w_i}{2} \left( \left</td>
<td>\tan \theta^{YL} \right</td>
</tr>
<tr>
<td>(2.26) ( \tau_0 = h \left( 1 - \frac{P_\infty}{P_{op} - P_\infty + 2\sigma \cos \theta^{YL} / w_i} \right) + \frac{w_i}{4} \left</td>
<td>\tan \theta^{YL} \right</td>
</tr>
<tr>
<td>(2.27) ( t_{f2} = w_i^2 \left[ h - \tau_0 + \frac{w_i}{2} \left( \left</td>
<td>\tan \theta^{YL} \right</td>
</tr>
</tbody>
</table>
Equation 2.11 can now be simplified to read as Eq. 2.22 where
\[ \alpha = \left[ \xi A(t) \right]^{w_i/2} \int_{-w_i/2}^{w_i/2} f_0(x) \, dx, \]
and
\[ \beta = -\sigma \int_{-w_i/2}^{w_i/2} \frac{\partial^2 f_0}{\partial x^2} \left( 1 + T^2 \left( t, \frac{\partial f_0}{\partial x} \right) \right)^{-3/2} \, dx. \]
For simplicity, these terms are calculated at \( t = 0 \). Because the initial air–water interface can be calculated from Eq. 2.9 (with \( \chi = 0 \) and \( \tau = 0 \)) and Eq. 2.10, one can assume
\[ \alpha = \frac{w_i}{\xi A_0}, \]
where
\[ A_0 = 2R_0 \sin^{-1} \left( w_i / 2(2R_0) \right) \]
representing the surface area of the initial air–water interface. Solving the first order ODE given in Eq. 2.22, an analytical expression (Eq. 2.23) can be obtained for \( T(t) \). The critical time can then be calculated in the form of an explicit function in terms of \( R_0 \) (Eq. 2.24). The first failure time can then be obtained as given in Eq. 2.25 with
\[ A_{cr} = 2R_{cr} \sin^{-1} \left( w_i / [2R_{cr}] \right). \]

In Regime II, the interface tracking process starts with a critical air–water interface initially located inside the groove with a distance \( \tau_0 \) from the entrance. The distance \( \tau_0 \) can be derived from the balance of forces to read as Eq. 2.26. Finally, an expression for the longevity of the entrapped bubble can be obtained as shown in Eq. 2.27.

The predictions of our formulations are compared with the experimental data of ref. (2) for validation. The results shown in Fig. 2.4a are obtained for a submerged groove made of vertical walls with a width of \( w_i = 147 \mu m \), a height of \( h = 85 \mu m \), and a Young–Laplace contact angle of \( \theta^{\ell} = 130^\circ \). The operating pressure in our equations is replaced by \( P_{\infty} + \rho g H \) where \( H = 165 \text{ mm} \).
was the depth of water in the experiment of ref.(2). For such a symmetric groove, the lowest point on the air–water interface profile \( y_{\text{min}} = f(x = 0) \) can be calculated using Eq. 2.9 (with \( \chi = 0 \) and \( \tau = 0 \)), Eq. 2.21, and Eq. 2.23, of our proposed analytical model, or Eq. 2.12, and Eq. 2.18, from our numerical model. Excellent agreement can be seen between the analytical, numerical, and experimental data. These results are also in qualitative agreement with the work of ref. (26) in which the longevity of an SHP circular pore was estimated via confocal microscopy. Our results also agree with the longevity measurements of the self-regulating grooves reported in ref. (64) as well as the measurements of ref. (65).

![Fig. 2.4](image)

**Fig. 2.4**: Time evolution of the air–water interface’s minimum height \( y_{\text{min}} \) for a submerged SHP groove with vertical walls. A comparison is made between our analytical and numerical results, as well as the experimental data of ref. (2) in (a). The effect of characteristic length on the time evolution of \( y_{\text{min}} \) in (b).

The effects of characteristic length \( l \) on longevity predictions is demonstrated in Fig. 2.4b, where the middle point of the air–water interface in the above-mentioned groove is monitored over time for three different characteristic lengths of \( l = 0.05, 0.1, \) and \( 0.15 \) mm. It can be seen that the choice of characteristic length can significantly impact the longevity prediction, as mentioned earlier.
2.3. Symmetric Grooves with Arbitrary Wall Profiles

2.3.1 Sharp-Edged Grooves

In this section, we consider grooves with arbitrary wall curvature, e.g., grooves with bell-shaped cross-sections. For simplicity, we assumed the grooves to be symmetric both in terms of geometry and wall wetting properties.

2.3.1.1 Critical Pressure and its Corresponding Profile

Our strategy is to first predict the critical pressure of the surface and then predict the longevity of surface in each pressure regime. Figure 2.5a shows a curved-wall groove with its half-width represented with an arbitrary function \( w_L = w_R = -g(y) \) (see Sec. 2.2). The groove width at the top and bottom are denoted by \( w_1 \) and \( w_2 \), respectively. The slope of the wall at any point \( \beta_L = \beta_R = \pi/2 - \tan^{-1} \left( \frac{\partial g}{\partial y} \right) \) can be obtained by differentiating \( g(y) \) with respect to \( y \). In the case of low operating pressures, the air–water interface is assumed to be pinned initially (see Sec. 2.2), and the critical pressure is obtained using the slope of the air–water interface near the wall at \( y = 0 \) (i.e., \( \beta_L^{0} = \pi/2 - \tan^{-1} \left( \frac{\partial g}{\partial y} \right) \)). The first critical air–water interface can be calculated from Eq. 2.2 with \( \chi = 0 \), with a groove half-width of \( w_L = w_R = w_1 / 2 \), an apparent contact angle of \( \theta_L^{app} = \theta_R^{app} = \theta_L^{cr} + \pi / 2 \), and a groove volume of \( v_g = 2 \int_0^h g(y) dy \).

It is worth mentioning that one could also use Eq. 2.2 to obtain the instantaneous shape of air–water interface by replacing the critical radius of curvature \( R_{cr} \) with the instantaneous radius of...
curvature $R(t)$. Following the same steps as described in Sec. 2.2.1, the critical pressure can be calculated using Eq. 2.5 (using the critical radius of curvature at the top of the groove $R_{cr} = w_i / \left[2 \cos \theta_{app}^{L} \right]$). In the next subsections, we discuss the two operating regimes of submerged SHP surfaces with symmetric curved-wall grooves.

### 2.3.1.2 Longevity in Regime I

Because of the groove’s symmetry, there are only two stages of air–water interface tracking in Regime I: 1) the air–water interface is pinned at both ends, and 2) the air–water interface is detached from both walls. For a pinned air–water interface, the initial radius of curvature $R_0$ can be obtained from Eq. 2.10 using e.g., the Newton–Raphson method. The initial profile $f_0$ can then be obtained using Eq. 2.9 with $\chi = 0$ and $\tau = 0$. Following the steps described in Sec. 2.2.2.1, the bubble pressure can be obtained from Eqs. 2.11 and 2.12 (2,13,26,66,67) with the rate air dissolution $\dot{v} = \left(\frac{RW_i}{\sqrt{R^2 - w_i^2 / 4 - A}}\right) \frac{dR}{dt}$ written in terms of the rate of change of radius of curvature of the air–water interface. The invasion coefficient is assumed to be $\xi = 2.5 \times 10^{-12}$ m$^2$/s/kg for when the operating pressure is low, and $\bar{\xi} = \frac{\xi(P)}{P_{op}}$, it is high (2,13,26,66–68).
Fig. 2.5: An example of our air–water interface tracking performed for an arbitrarily chosen groove with walls having sinusoidal profiles \( g(y) = (w_2 - w_1) \sin(\pi y / [2h]) / 2 - w_1 / 2 \) is shown in (b). The area of the blue triangles in (d) is subtracted from the area above the air–water interface (see Eq. 2.31 in the case of \( t > t_c \)).

The balance of forces in Eq. 2.11 can then be simplified as Eq. 2.14 to be solved using the RK4 method for a pinned air–water interface \((y = 0 \text{ at the boundaries})\). After reaching the critical profile, the air–water interface detaches from the groove’s edges (see Fig. 2.5b), and the air–water interface can be expressed using Eq. 2.9 with \( \chi = 0 \). Here \( \tau \) is again the distance from the top of the groove (see Sec. 2.2.2.3) and \( R \) is the radius of curvature of the air–water interface given as

\[
R = w_L / \left[ \cos \theta_L^{app} \right] \quad (2.28)
\]

The capillary and bubble pressures in the balance of forces can be determined in terms of the geometrical and wetting parameters of the grooves. Note that only one half of the groove is considered in the equations due to symmetry. The rate of change of radius of curvature for the air–water interface, can be obtained as

\[
\frac{\dot{R}}{\dot{\tau}} = \left[ \frac{w_L}{\dot{\tau}} \cos \theta_L^{app} - \frac{w_L}{\dot{\tau}} \cos \theta_L^{app} \sin \theta_L^{app} \right] / \left( \cos \theta_L^{app} \right)^2 \quad (2.29)
\]
where, using the definitions of $\theta^\text{app}$ and $w_L$ (see Fig. 2.5b), one can obtain

$$\frac{\dot{\theta}^\text{app}}{\dot{t}} = -\frac{\dot{\beta}_L}{\dot{t}} = \frac{\partial^2 g}{\partial y^2} \left[ 1 + \left( \frac{\partial g}{\partial y} \right)^2 \right]$$  \hspace{1cm} (2.30a)

$$\frac{\dot{w}_L}{\dot{t}} = -\frac{\partial g}{\partial y}$$  \hspace{1cm} (2.30b)

The volume flow rate of air dissolving into water can be calculated as function of the wall profile $g(y)$,

$$\dot{\nu} = 2 \frac{\partial}{\partial t} \left[ \int_{-w_L}^{\tau} g(y) dy + \int_{-w_L}^{0} \{ f - \tau \} dy \right]$$  \hspace{1cm} (2.31)

Equation 2.31 can be used to calculate $\tau$ at any time in terms of $g(y)$. Likewise, the balance of forces across the air–water interface can be written as

$$\frac{\sigma}{R} - \frac{2}{\zeta A} w_L \left( \frac{\dot{R}}{\dot{t}} - \frac{\dot{w}_L}{\dot{t}} \right) / \sqrt{R^2 - w_L^2} - \frac{A}{2} \frac{\dot{R}}{\dot{t}} - g(\tau) \frac{d\tau}{dt} + \Pi \approx 0$$  \hspace{1cm} (2.32)

For a given wall profile, the instantaneous air–water interface can be tracked by solving Eqs. 2.29, 2.30a, 2.30b, and 2.32 for $R$, $\theta^\text{app}$, $w_L$, and $\tau$, respectively, via the RK4 method. Note that, while $g(y)$ is explicitly included in Eq. 2.32, it is only incorporated in Eq. 2.14 through $R_0$ and $R_e$, which are the initial and final solutions of Eq. 2.32. Note that the air–water interface may touch the bottom of the groove before reaching the critical air–water interface. This is the case when the groove’s height is less than a minimum height, $h_{\text{min}}$. The minimum height is a function of the groove’s width $w_1$ and the apparent contact angle $\theta^\text{app}$, and can be obtained using Eq. 2.9 with $\chi = 0$ and $\tau = 0$ at $x = 0$. 

35
\[ h_{\text{min}} / w_1 = \left[ 1 - \sin \theta_L^{\text{upp}} \right] / \left[ 2 \cos \theta_L^{\text{upp}} \right] \] (33)

The above formulations can, for instance, be used to predict the experimental data of ref. (2) as discussed in Sec. 2.2.6 for the special case of parallel ridges (i.e., \( g(y) = -w_1 / 2 \)).

### 2.3.1.3 Longevity in Regime II

The air–water interface tracking follows only one stage in Regime II, which is the same as the last stage of interface tracking in Regime I, except for the initial condition. Equation 2.9 with \( \chi = 0 \) can represent the initial air–water interface in terms of \( \tau_0 \). To calculate \( \tau_0 \), the balance of forces are used at \( t=0 \),

\[
\frac{\sigma}{R_0} - P_{op} + 2P_0 \int_0^{-h} g(y)dy \left[ 2 \int_{\tau_0}^{-h} g(y)dy + w_{L,0} \sqrt{R_0^2 - w_{L,0}^2} - R_0^2 \sin^{-1} \left( \frac{w_{L,0}}{R_0} \right) \right] = 0 \quad (2.34)
\]

where \( R_0 \) is the initial radius of curvature in Eq. 2.35 (or the critical radius of curvature).

\[
R_0 = w_{L,0} / \left| \cos \left( \theta_L^{\text{up}} + \tan^{-1} \frac{\partial g}{\partial y}_{y=y_0} \right) \right| \quad (2.35)
\]

Here \( w_{L,0} \) is the half-width of the groove at which the air–water interface was initially in contact with the wall. Equations 2.34, 2.35 and the wall function \( g(y) \) for \( y = \tau_0 \) are simultaneously solved to obtain the initial air–water interface \( \tau_0, R_0, \) and \( w_{L,0} \), respectively. With these initial conditions, the formulation of the last stage of interface tracking in Regime I is then repeated here (i.e., Eqs. 2.29–2.32) to predict the location of the air–water interface as function of time until it comes into contact with the bottom of the groove at \( t = t_{f2} \).
2.3.1.4 Test Case

In this section, an example is given to demonstrate how the formulations given in this chapter can be used to study and optimize the geometry of an SHP groove to improve its performance in terms of stability (critical pressure), durability (longevity), or drag reduction (Sec. 2.2.5). To do so, a symmetric groove is considered to illustrate the applications of the formulations derived in the above subsections for sharp-edged symmetric grooves with arbitrary wall profiles given with a sinusoidal profile having top and bottom widths of $w_1 = 30 \, \mu m$ and $w_2 = 36 \, \mu m$, respectively, and a groove height of $h = 10 \, \mu m$ and a Young–Laplace contact angle of $\theta = 105^\circ$.

\[
g(y) = \left[\frac{w_2}{2} - \frac{w_1}{2}\right] \sin\left(\frac{\pi y}{2h}\right) - \frac{w_1}{2}
\] (2.36)

Using the equations given in previous sections, one can obtain a critical pressure of 155.2 kPa for this groove. To predict the longevity of this groove in Regime I and Regime II, we consider two arbitrary operating pressures of $P_{op} = 104.7 \, kPa$ and 160 kPa, respectively (see Fig. 2.6). It is worth mentioning that the capillary pressure (the first term in Eq. 2.5) for this groove equals 104.25 kPa, indicating that for lower operating pressures the surface can remain superhydrophobic indefinitely, as also suggested in Refs. (2,64,65).

Regime I, $P_{op} = 104.7 \, kPa$, $t_{f1} = 16 \, hr$

Regime II, $P_{op} = 160 \, kPa$, $t_{f2} = 46 \, s$
Fig. 2.6: The time-evolution of the air–water interface in a groove made of sinusoidal walls under an operating pressure of $P_{op} = 104.7$ kPa (a) and $P_{op} = 160$ kPa (b) with $w_1 = 30 \mu$m, $w_2 = 36 \mu$m, $h = 10 \mu$m, and $\theta_{yl} = 105^\circ$.

2.3.2 Round-Edged Grooves

The formulation presented in Sec. 2.3.1 needs to be modified before it can be applied to grooves with round edges. However, as the equations are somewhat similar, we only list them in a table here for the sake of brevity (see Table 2.2). A air–water interface in touch with a round surface maintains an angle with the wall equal to the Young–Laplace contact angle regardless of the pressure applied over the interface. Therefore, the air–water interface freely moves up or down along the wall in response to operating pressure. In the case of no pressure difference across the air–water interface, for instance, a flat profile $f_\omega = 0$ as shown in Fig. 2.7a is expected. The concept of critical hydrostatic pressure is not well defined for submerged round-edge grooves. One can adopt a critical hydrostatic pressure definition on the basis of maximizing the capillary pressure as opposed to the de-pinning pressure.(24,27,59,69–72) A transition to the Wenzel state can also occur if the air–water interface touches the bottom of the pore (either with sharp or round entrance) before reaching a position at which the capillary pressure is maximum. This has been identified in the literature as failure due to air–water interface sagging, and has also been observed in the current study to be the dominant cause of air–water interface failure.(73)

Table 2.2: Model for air–water interface in circular groove

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v = \frac{L_d}{2}(1 + \cos \alpha) - \frac{d^2}{8}[2\pi - 2\alpha - \sin(2\pi - 2\alpha)] - R^2 \sin^{-1}\left(\frac{w_L}{R}\right) + w_L \sqrt{R^2 - w_L^2}$</td>
<td>(2.37)</td>
</tr>
<tr>
<td>$\frac{\sigma}{R_0} - P_{op} + \frac{2P_v v_{\infty}}{v} = 0$</td>
<td>(2.38)</td>
</tr>
<tr>
<td>$\frac{\dot{w}_L}{\dot{\alpha}} = \frac{-d \cos \alpha}{2}$</td>
<td>(2.39a)</td>
</tr>
</tbody>
</table>
\[
\frac{\dot{R}}{\alpha} = \left\{ \cos\left(\frac{3\pi}{2} - \theta^{nl} - \alpha\right) \frac{\dot{w}_L}{\alpha} - w_L \sin\left(\frac{3\pi}{2} - \theta^{nl} - \alpha\right) \right\} \left[ \cos\left(\frac{3\pi}{2} - \theta^{nl} - \alpha\right) \right]^2
\] (2.39b)

\[
\frac{\dot{Y}}{\alpha} = -\frac{Ld}{2} \sin\alpha - \frac{d^2}{8} \left[ -2 + 2\cos(2\pi - 2\alpha) \right] - \frac{\dot{v}_{cr}}{\alpha}
\] (2.40a)

\[
\frac{\dot{v}_{cr}}{\alpha} = 2R\frac{\dot{R}}{\alpha} \sin^{-1}\left(\frac{w_L}{R}\right) - \frac{\dot{w}_L}{\alpha} \sqrt{R^2 - w^2_L} - \frac{\dot{w}_L}{\alpha} \left[ R^2 + w^2_L \right] - 2Rw_L \frac{\dot{R}}{\alpha} \right]/\sqrt{R^2 - w^2_L}
\] (2.40b)

\[
\frac{\sigma}{R} - \frac{1}{A} \left( \frac{\dot{v}}{\alpha} \right) \frac{d\alpha}{dt} + \Pi \approx 0
\] (2.41)

\[
\frac{d}{2} (1 + \sin \alpha_f) = (L - d \sin \alpha_f) \left\{ 1 - \sin\left( \theta^{nl} + \alpha_f - \frac{\pi}{2} \right) \right\} / \left\{ 2 \cos\left( \theta^{nl} + \alpha_f - \frac{\pi}{2} \right) \right\}
\] (2.42)

Fig. 2.7: An example of our air–water interface tracking inside a general round-edge groove is shown in (a). The case of a round-edge groove made of two parallel cylinders with a diameter \( d \) and spacing \( L \) is shown in (b). The volumes and parameters used in calculating bubble pressure are shown in (c).

The formulations presented in this section are derived with the coordinate system placed in the middle of a flat air–water interface (when there is no pressure difference). Such an air–water interface satisfies the condition of \( \beta_L = \beta_R = \frac{\pi}{2} - \tan^{-1}\left( \frac{\partial g}{\partial y} \right) = \theta^{nl} \) (see Fig. 2.7a). The air–water interface tracking procedure for grooves with round inlets is somewhat similar to that presented in Sec. 2.3.1. An example of grooves with round entrance is the one formed between two parallel cylinders as shown in Figs. 2.7b–2.7c. For such a groove, the air–water interface can be obtained from Eq. 2.9 by setting \( \chi = 0 \). For this case, \( R \), \( w_L \), and \( \tau \) are the radius of curvature of the air–
water interface, the groove’s half-width, and the vertical distance of the air–water interface from
the flat air–water interface, \( f_{\infty} \) (Fig. 2.7b–2.7c), respectively. Note that these variables are time-
dependent, and they can be related to the immersion angle, \( \alpha \), as shown in Fig 2.7b. The
parameters \( w_{L} = [L - d \sin \alpha] / 2 \), \( R = w_{L} / \cos \left(3\pi / 2 - \theta^{in} - \alpha\right) \), \( \tau = d \left[\cos \alpha - \cos \alpha_{\infty}\right] / 2 \) are shown in
Fig. 2.7 where \( \alpha_{\infty} = \pi - \theta^{inc} \). The volume of the entrapped air in the absence of pressure can now
be written as \( v_{e} = 2\int_{0}^{h} g(y)dy = Ld(1 + \cos \alpha_{\infty}) / 2 - d^{2}\left[2\pi - 2\alpha_{\infty} - \sin(2\pi - 2\alpha_{\infty})\right] / 8 \). Also, the
instantaneous volume of the entrapped air can be calculated the same way as expressed in Eq. 2.37
(Table 2.2). The first term in Eq. 2.37 is the shaded rectangular area in Fig. 2.7c. The second and
third terms in Eq. 2.37 represent the areas marked as \( v_{sec} \) and \( v_{cr} \) in Fig. 2.7c, respectively (the
dark-grey area represents the volume of the entrapped air \( V_e \). As mentioned earlier in Sec. 2.2, the
initial air–water interface for a given operating pressure is calculated using Eqs. 2.34 and 2.35
(condensed into Eq. 2.38 in this section). The initial values \( w_{L,0} \), \( R_{0} \), \( \tau_{0} \), and \( \alpha_{0} \) can be obtained
by simultaneously solving Eqs. 2.37–2.38, and the initial air–water interface can be determined
using Eq. 2.9 with \( \chi = 0 \), \( R = R_{0} \) and \( \tau = \tau_{0} \) for the given operating pressure (see Fig. 2.7). The
instantaneous air–water interface can be obtained from the force balance equation (Eq. 2.11) with
the capillary pressure defined as \( \sigma / \rho \), and the bubble pressure determined using the steps described
in Sec. 2.2.2.1. The volume flow rate of air escaping from the groove can be determined using Eqs.
2.39–2.41 with \( \alpha_{0} \) from Eq. 2.38. As mentioned earlier, the sagging failure takes place when the
air–water interface comes into contact with the bottom of the groove and it can be determined from
Eq. 2.42.
In summary, for grooves with round inlets, we numerically solve Eq. 2.38 to obtain the initial air–water interface under the given operating conditions (i.e., \( w_{L0} \), \( R_0 \), \( \tau_0 \), and \( \alpha_0 \)). Equations 2.39–2.41 are then integrated to track the shape and position of the air–water interface over time until the failure happens at \( t = t_f \) when \( \alpha = \alpha_f \) from Eq. 2.42.

### 2.4. Groove Design

In order to quantify the effects of wall profile on the performance of an SHP groove, two sets of grooves are considered as shown in Table 2.3. In each set, three different wall profiles are considered: vertical walls (Sec. 2.2.6); inclined walls (Sec. 2.2.1-2.2.2); and sinusoidal walls (Eq. 2.36 in Sec. 2.3.1). The grooves in the first set have identical heights whereas the grooves in the second set have identical volumes. An entrance width of \( w_i = 30 \, \mu\text{m} \) and an arbitrary Young–Laplace contact angle of \( \theta_{L}^{\text{Y}} = \theta_{A}^{\text{Y}} = 105^\circ \) are assigned to each groove. Also, an arbitrary width ratio of \( w_2 / w_1 = 1.2 \) is considered for the grooves with the inclined and sinusoidal walls. Note that the volume of the grooves in the constant-volume set is less than that of their counterpart in the constant-height set (except for the groove with vertical walls). The critical pressure and longevity of these grooves are obtained using symmetric groove equations of Sec. 2.3.1. As can be seen in the results shown in Table 2.3, the longevity and critical pressure values are strongly dependent on the shape of the wall profile. For instance, critical pressure is higher for grooves that promote a higher apparent contact angle for the critical air–water interface (Eqs. 2.3 and 2.5). Note also that the apparent contact angles for the grooves in the constant-volume set are larger than their corresponding grooves in the constant-height set. Longevity also increases with the initial volume of the entrapped air. However, increasing the initial volume of the entrapped air decreases the critical pressure.\(^{56}\) As can be seen for both sets in Table 2.3, the critical pressure and longevity increase as we move from grooves with vertical walls on the left to grooves with sinusoidal walls.
on the right. It is also interesting to note that, while the groove in the constant-volume group has a critical pressure higher than that of its counterpart in the constant-height set, its longevity is slightly shorter. This is due to the interplay between the opposing effects of varying the apparent contact angle and the initial volume of the groove on critical pressure and longevity.

Table 2.3: Longevity (min) and critical pressure (kPa) for constant height and constant volume grooves with $\theta_{LY} = \theta_{H} = 105^\circ$.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Vertical walls</th>
<th>Inclined walls</th>
<th>Sinusoidal walls</th>
</tr>
</thead>
<tbody>
<tr>
<td>constant groove height</td>
<td>$t_f = 3.41$</td>
<td>$t_f = 5.96$</td>
<td>$t_f = 11.89$</td>
</tr>
<tr>
<td>$P_{cr} = 16.68$</td>
<td>$P_{cr} = 38.56$</td>
<td>$P_{cr} = 53.8$</td>
<td>$P_{cr} = 72.5$</td>
</tr>
<tr>
<td>$v_\infty = 300 \mu m^3$</td>
<td>$v_\infty = 330 \mu m^3$</td>
<td>$v_\infty = 338 \mu m^3$</td>
<td>$v_\infty = 300 \mu m^3$</td>
</tr>
<tr>
<td>$w_1 = 30 \mu m$</td>
<td>$w_1 = 30 \mu m$</td>
<td>$w_1 = 30 \mu m$</td>
<td>$w_1 = 30 \mu m$</td>
</tr>
<tr>
<td>$\theta_{LY} = 105^\circ$</td>
<td>$\theta_{LY} = 121.7^\circ$</td>
<td>$\theta_{LY} = 123.1^\circ$</td>
<td>$\theta_{LY} = 131.2^\circ$</td>
</tr>
<tr>
<td>$h = 10 \mu m$</td>
<td>$h = 10 \mu m$</td>
<td>$h = 9.16 \mu m$</td>
<td>$h = 8.87 \mu m$</td>
</tr>
</tbody>
</table>

To better demonstrate the applications of the mathematical formulations presented in this work, a brief parameter study is presented here. Consider a groove with a constant entrance width of, a height of $h = 10 \mu m$, and a right wall angle of $\beta_R = 75^\circ$ placed in a microchannel (see the inset in Fig. 2.8a). Also, assume that both walls are made of the same material having an arbitrary Young–Laplace contact angle of $\theta_{LY} = \theta_{H} = 100^\circ$. The effects of the left wall’s angle $\beta_L$ on the critical pressure of the groove is isolated and studied quantitatively in Fig. 2.8. For $\beta_L < 75^\circ$, the interface detaches from the right corner (point $A_R$) for different operating pressures (see Fig. 2.8a). The first critical pressure $P_{cr}^{(1)}$ is obtained from Eq. 2.5 with the only term varying with $\beta_L$ being the groove’s volume $v_\infty$. Since the volume of the groove decreases with increasing $\beta_L$, the compression pressure caused by the interface ingress into the groove increases slightly resulting in a small
increase in $P_{cr}^{(1)}$. On the other hand, the second critical pressure $P_{cr}^{(2)}$ sharply decreases with increasing $\beta_L$. This is because increasing the left wall angle decreases the left apparent contact angle according to $\theta_L^{app} = \theta_L^{\text{YL}} - \beta_L + \pi / 2$, which decreases both the capillary and compression terms in Eq. 2.7. In other words, increasing $\beta_L$ increases the curvature of the second critical air–water interface, as described by Eq. 2.6 (the two terms in Eq. 2.7 are inversely related to the second critical radius of curvature of the interface).

For $\beta_R = \beta_L = 75^\circ$, the interface detaches from both corners and hence $P_{cr}^{(1)} = P_{cr}^{(2)}$. Note that at this point the critical pressure reaches its minimum value (when $\theta_L^{app} = \theta_R^{app}$). For $\beta_L > 75^\circ$, the same exact equations can be used to predict the critical pressure by only exchanging the subscripts “L”
and “$R$”. For this case, de-pinning takes place at the left corner. It can be seen in Fig. 2.8a that the first critical pressure decreases with increasing $\beta_L$. Unlike the case of $\beta_L < 75^\circ$, here the first critical pressure decreases with the left apparent contact angle (see Eq. 2.5). Critical pressure values for the same groove but with symmetric walls having $\beta_R = \beta_L$ are also shown in Fig. 2.8a in the inset. In this case, there is only one critical pressure, $p^{(1)}_{cr} = p^{(2)}_{cr}$, and $\theta_{lp}^\infty = \theta_{rp}^\infty$. The critical pressure in this figure is an intermediate value between the two critical pressures of Fig. 2.8a. However, the amount of air entrapped in the groove as well as the critical radius of curvature decrease with increasing $\beta_L$. Note that while the capillary pressure plays some role in resisting the channel’s operating pressure, the major contribution in this case is made by the air compression pressure which is strongly dependent on groove’s volume.

Figure 2.8b shows the effects of the left wall angle $\beta_L$ on the groove’s longevity for three different Young–Laplace contact angles of $\theta_{L}^{\text{YL}} = \theta_{R}^{\text{YL}} = 100^\circ, 105^\circ,$ and $110^\circ$ with $\beta_R = 75^\circ$ under an operating pressure of $p_{op} = 104.5$ kPa. Since the failure can happen in any regime, the $y$-axis can be $t_{f1}$, $t_{f2}$, or $t_{f3}$ depending on the operating pressure and the groove geometry (i.e., $p^{(1)}_{cr}$, and $p^{(2)}_{cr}$ for the case of $\theta_{L}^{\text{YL}} = \theta_{R}^{\text{YL}} = 100^\circ$, see Fig. 2.8a). The results shown in Fig. 2.8b reveal that increasing the wall angle $\beta_L$ decreases the longevity of the air entrapped. This is because increasing $\beta_L$ decreases the amount of air that can be trapped in the groove. Also, the apparent contact angle, and so the capillary pressure, decrease with increasing $\beta_L$. In other words, the pressure difference across the air–water interface increases with increasing $\beta_L$, and consequently the longevity decreases. The effects of wall angle on longevity are shown in Fig. 2.8b as an inset for the symmetric groove having $\beta_R = \beta_L$ and $\theta_{L}^{\text{YL}} = \theta_{R}^{\text{YL}} = 100^\circ$. It is expected that decreasing the wall angles (while keeping
the entrance width constant) improves the grooves’ longevity at low operating pressures (i.e., \( P_{op} < P_{cr}^{(1)} \) or \( P_{cr}^{(2)} \)) for the above-mentioned reason.

Considering three sharp-edged symmetric grooves with different sinusoidal wall profiles (Eq. 2.36), Fig. 2.9a shows the effects of the groove’s entrance width \( w_1 \) on critical pressure. More specifically, we considered three different grooves, referred to here as Groove A, Groove B, and Groove C with a height of \( h = 20 \mu m \) and width ratios of as \( w_2 / w_1 = 0.8, 1.0, \) and \( 1.2, \) respectively. Note that Groove B is a special case when \( w_2 / w_1 = 1.0 \) (i.e., \( g(y) = -w_1 / 2 \)). The critical air–water interface and critical pressure values are also shown in Fig. 2.9a for each groove when \( w_1 = 100 \mu m \).

It can be seen that Groove C exhibits the highest critical pressure for the range of entrance widths considered. This is because the apparent contact angle in this groove is the highest. Generally speaking, there are three parameters that can affect the critical pressure of a groove: groove entrance width \( w_1 \), apparent contact angle \( \theta^{app} \), and groove height \( h \). The entrance width and height are same for these grooves, while the apparent contact angle \( \theta^{app}_L = \theta^{app}_R = \theta_L - \beta_L + \frac{\pi}{2} \) changes depending on \( w_2 / w_1 \) (\( \beta_L^{app} \) is the smallest in case of Groove C resulting in a higher air compression and capillary pressure acc. to Eq. 2.5). Critical pressure for Groove C reaches a peak value at \( w_1 = 87 \mu m \). This is because the height of this groove is less than the aforementioned minimum height for a groove with an entrance width of \( w_1 > 87 \mu m \) (Eq. 2.33). For such cases, we considered critical pressure the pressure at which the air–water interface touched the groove’s bottom (\( \theta < \theta_{cr} \) when \( w_1 > 87 \mu m \)).
Comparing Grooves A and B, it can be seen that critical pressure is higher for Groove A when $w_1 > 68 \ \mu m$. This is because the volume of the entrapped air is smaller in this groove and hence the air compression term plays a significant role when $w_1 > 68 \ \mu m$. It is also interesting to mention that when $w_1 = 34 \ \mu m$ the apparent contact angle in Groove A becomes almost equal to $90^\circ$ and hence the two terms in Eq. 2.5 vanish. This is the reason for the critical pressure of Groove A reaching zero at $w_1 = 34 \ \mu m$.

Fig. 2.9: The effects of $w_1$ on critical pressure (a) and longevity (b) for SHP grooves with sinusoidal walls (Groove A, Groove B, and Groove C), respectively.

Effects of operating pressure on the longevity of Grooves A, B, and C is shown in Fig. 2.9b. As expected, the best and worst longevity values were obtained for Groove C and Groove A, respectively. This is because the bubble pressure (proportional to the rate of air escaping from the groove) is the highest in Groove A and lowest in Groove C. The results shown in Fig. 2.9b are in qualitative agreement with the experimental work of refs. (40,64,65) which reported accelerated
collapse of air–water interface in grooves with wide inlet entrances. Interestingly, the recent experimental results of ref. (2) indicate that a submerged SHP surface can achieve infinite longevity at pressures below the groove’s capillary pressure, which is in agreement with the trends shown in Fig. 2.9b as well as the predictions of ref. (55). The experimental data of refs. (2,50) also confirm that longevity is inversely dependent on the operating pressure.

To study grooves with round entrance, we consider the groove formed between two parallel circular cylinders placed horizontally on a flat surface. Figure 2.10a shows the failure pressure of such grooves (the pressure at which the initial air–water interface reaches the bottom of the groove) when the diameter and the spacing of the cylinders are varied. It can be seen that the failure pressure curves reach a peak value when the spacing between the cylinders increases for each diameter. Although it is not shown for the sake of brevity, the peak values also depend on the Young–Laplace contact angle. As mentioned earlier, both the capillary pressure and air compression pressure contribute in balancing the pressure acting over a air–water interface. Increasing the spacing between the walls does not affect these contributions equally. The relationship between failure pressure and spacing between the cylinders is shown with a combination of solid and dashed lines for each diameter. The solid part of the curve represents the failure pressures at which the immersion angle is less than the critical immersion angle (the angle at which the capillary forces are maximal). The dashed part of the curves, on the other hand, shows the failure pressures for which the immersion angle has passed the above-mentioned critical immersion angle, i.e., \( \alpha > \alpha_{cr} \). The recent experimental work of ref. (73) revealed that a stable air–water interface cannot be maintained for \( \alpha > \alpha_{cr} \) even when there is a cushion of entrapped air underneath the air–water interface.
The longevity of the entrapped air is calculated for such an SHP groove and is shown in Fig. 2.10b for two different spacing values of 50 and 60 µm, with a cylinder diameter of \( d = 12 \) µm and an Young–Laplace contact angle of \( \theta^\text{yl} = 100^\circ \). It can again be seen that longevity decreases with increasing the operating pressure. Obviously, one can optimize the geometry of the grooves to improve the longevity of the surface for a given operating pressure. Longevity also varies with varying other dimensions of the groove e.g., width or depth. However, conducting a complete parameter study is beyond the scope of this chapter. Interested readers can use the formulations presented here to custom-design the geometry of a SHP groove according to the needs of a specific application.

2.5. Time-Dependent Slip Length

The time-dependent interface tracking formulations presented in this work can be used to estimate the slip velocity generated by an SHP surface as a function of time. Stokes’ equation is solved
using the Fluent CFD code for the laminar flow of water inside a microchannel with SHP bottom walls. For SHP surfaces with transverse grooves, \( u \), and \( v \) are used as the components of the velocity in the \( x \) and \( y \) directions, respectively. The computational domain for the transverse grooves is shown in the insets of Figs. 2.11a–2.11b. No-slip (i.e., \( u=0 \) and \( v=0 \)) and no-shear (i.e., \( \hat{n} \cdot \nabla u = 0 \)) boundary conditions are considered for water in contact with the solid walls and the air–water interface, respectively. (5,14,74) Periodic boundary conditions (PBC) are considered for the boundaries normal to the flow.

For the case of longitudinal grooves, the computational domain is shown in Figs. 2.11c-2.11d (the flow is normal to the plane). The Poisson equation \( \frac{\partial p}{\partial z} = \frac{\omega u}{\mu} \) is solved with \( u \) being the flow velocity in the \( z \)-direction, \( \mu \) denoting water viscosity, and \( \frac{\partial p}{\partial z} = (P_{op} - P_{sa}) / L_{ch} \) representing the pressure drop across the microchannel. For these calculations, we have used the FlexPDE software for its speed and accuracy.

Equation 2.43 (see Table 2.4) was proposed in ref. (16,75) for effective slip length in a microchannel with SHP bottom comprised of transverse grooves. In this equation \( Q_{T1} \) is the volume flow rate in the microchannel, \( Q_{T2} \) is the volume flow rate between two parallel plate with no-slip boundaries, i.e., \( Q_{T2} = -(dP/dx)(H^{3/2}/12 \mu) \), and \( b_{eff}(t) \) is the overall effective slip length (for the longitudinal grooves, the subscripts “T” will be replaced by “L”). The slip length can also be obtained using the shear stress and velocity magnitude along the lower boundary of the channel including the air–water interface as mentioned in Eq. 2.44, where \( \langle \mathbf{u} \rangle \), and \( \langle \hat{n} \cdot \nabla u \rangle \) are the
average velocity and velocity gradient along the solid–water boundary and the air–water interface on the lower wall, respectively.\(^{16,75}\)

**Table 2.4**: Slip length equations and previous analytical slip length models

\[
b_{\text{eff}} = \left[ \frac{Q_{r1} - Q_{r2}}{4Q_{r2} - Q_{r1}} \right] H_{0x} \tag{2.43}
\]

\[
b_{\text{eff}} = \frac{< u >}{< n \cdot \nabla u >} \tag{2.44}
\]

\[
\frac{b_{\text{eff}}}{w_i} = \frac{1}{2\pi\phi} \ln \left( \sec \left( \frac{\pi\phi}{2} \right) \right) \tag{2.45}
\]

\[
\frac{b_{\text{eff}}}{w_i} = \frac{\pi\phi \times \int B(s) ds}{2} \tag{2.46a}
\]

\[
B(s) = \frac{s}{\sinh 2s(\pi - \phi) + \sin 2\phi} \times \left[ \cos 2\phi + \frac{s \sin 2\phi \cosh s\pi + \sinh s(\pi - 2\phi)}{\sinh s\pi} \right] \tag{2.46b}
\]

\[
\frac{b_{\text{eff}}}{w_i} = \frac{1}{\pi\phi} \ln \left( \sec \left( \frac{\pi\phi}{2} \right) \right) \tag{2.47}
\]

\[
\frac{b_{\text{eff}}}{w_i} = \frac{\pi\phi}{24} \left[ \frac{3\pi^2 - 4\pi\phi + 2\phi^2}{(\pi - \phi)^2} \right] \tag{2.48}
\]

\[
\frac{b_{\text{eff}}}{w_i} = \phi \sum_{i=1}^{s} a_i \phi \tag{2.49}
\]

For our finite volume (Fluent) and finite element (FlexPDE) calculations, we used about 60,000 and 20,000 computational cells (obtained from a grid-independence study not reported here for the sake of brevity), respectively. Most of the previous studies reporting slip length in microchannels assumed a flat air–water interface over the SHP surface. There are only a few studies in which a curvature was considered for the air–water interface. For transverse grooves containing a flat air–water interface, we used Eq. 2.45 from the analytical work of ref. (4) for comparison. In this equation \( \phi = \frac{w_i}{L} \) is the gas area fraction (GAF) of the surface and \( L \) is the spacing between the
grooves. For the case of air–water interface having a negative protrusion angle, a comparison is made with the slip length values obtained from Eq. 2.46 given in ref. (3) (see Table 2.4).

For SHP surfaces with longitudinal grooves, the analytical expression of ref. (4) for flow over a flat air–water interface is considered (Eq. 2.47). With some assumptions similar to those made in deriving Eqs. 2.46a–2.46b, an expression is given in ref. (6) for the effective slip length in microchannels with longitudinal grooves when the air–water interface has a negative protrusion angle $\theta$ (see Eq. 2.48). The slip length has also been calculated numerically in a microchannel with longitudinal grooves in ref. (5), and the results were used to produce a fifth-order polynomial curve fit as shown in Eq. 2.49. In this equation, $a_0 = 0.39479$, $a_1 = 0.08545\theta$, $a_2 = 0.03359$, $a_3 = 0.01415$, $a_4 = 0.01234$, and $a_5 = 0.00496$. Note that in the theoretical models given in refs. (3,4,6), the slip length was predicted for a Couette flow geometry, where the velocity profile is linear. We therefore, considered microchannels with a relatively high aspect ratio of $H_{ch}/L = 10$ to establish a linear velocity profile near the wall.

Figures 2.11a and 2.11b show the non-dimensional slip length as a function of GAF and protrusion angle for flow through SHP microchannels with transverse grooves. Figures 2.11c and 2.11d show similar results for when the grooves are longitudinal. In Fig. 2.11d, we have compared our results with the numerical work reported in ref. (5) as well as the theoretical studies of ref. (6). Good agreement between our simulation results and previous studies is evident in Fig. 2.11 for all cases.
Fig. 2.11: Comparison between slip length values obtained from our study and those reported in the literature in refs. (3–6) for microchannels with $L/H_{ch} = 0.1$. Effects of GAF on slip length for channels with $w_1/L = 0.3$ are shown in (a) and (b) for flat and protruded air–water interfaces, respectively, in the case of transverse grooves. Similar results for the case of longitudinal grooves are shown in (c) and (d).

It is worth mentioning that, in the case of a protrusion angle of $\vartheta = 0$ for transverse grooves, the agreement between the method of ref. (3) and that of ref. (4) depends on the surface GAF. The mismatch between these two formulations ranges from about 0.4% at $\varphi = 0.1$ to about 85% at
\( \phi = 0.9 \). In our numerical calculations here, we considered a GAF of \( \phi = 0.3 \), where the mismatch between the abovementioned methods is about 5%.

To demonstrate how our formulations can be used to estimate the transient effective slip length over time, a rectangular microchannel is considered with arbitrary height and length of \( H_{\text{ch}} = 200 \, \mu\text{m} \) and \( L_{\text{ch}} = 100 \, \text{mm} \), respectively (Fig. 2.12). The SHP grooves are placed on both the top and bottom walls. The grooves are considered to be similar to the one shown in Fig. 2.3 and they are separated from one another with a distance \( L \). A pressure drop of \( \Delta P / L_{\text{ch}} = \left[ P_{\text{op}} - P_{\text{ba}} \right] / L_{\text{ch}} = 27.75 \, \text{kPa/m} \) is assumed across the length of the channel with the pressure at the outlet being the atmospheric pressure. For comparison, we have also considered two reference channels as shown in Fig. 2.12. The channels, from left to right, are referred to as Channel ST1 (grooves in the Cassie state), Channel ST2 (no grooves), and Channel ST3 (grooves in the Wenzel state), respectively. Similarly, their volume flow rates are denoted as \( Q_{\text{ST1}} \), \( Q_{\text{ST2}} \), and \( Q_{\text{ST3}} \), respectively. The subscripts “S” and “R” are used here to distinguish between grooves with “sharp” and “round” edges (round-edge grooves will be discussed later in this section), respectively. Similarly, the subscript “T” or “L” is used to denote whether the groove is oriented in the “transverse” or “longitudinal” direction in the channel. Transient volume flow rate and slip length for SHP surfaces with transverse and longitudinal grooves are shown in Fig. 2.12. It can be seen that both the flow rate and slip length decrease with time. This is because the solid–water contact area increases with time as the entrapped air dissolves into water. Note that the volume flow rate ratio does not reach one, as we have assumed that failure happens when the lowest point of the air–water interface touches the bottom of the groove.
Fig. 2.12: Non-dimensionalized volume flow rate through Channels ST1 and SL1 are shown in (a) and (b) for the case of transverse and longitudinal grooves, respectively. Transient slip lengths obtained from Eqs. 2.43 and 2.44 for transverse and longitudinal grooves are shown in (c) and (d), respectively. Here $\phi = 0.68$, $H_{ch} = 200\mu m$ and $L_{ch} = 100\,mm$. An exponential curve-fit is presented for each case (7).
Note in Fig. 2.12 that, for \( t > t_{cr1} = 0.25 \) hr, the air–water interface detaches from the right top corner of the groove as shown in the inset figures. To the knowledge of the authors no expression (analytical, numerical, or empirical) has yet been suggested for slip length prediction in such a condition, and so the numerical simulation presented here is the first attempt in quantifying the effective slip length for flow over partially de-pinned air–water interfaces.

It is interesting to note that adding longitudinal SHP grooves to the microchannel discussed in Fig. 2.12b can increase the water volume flow rate through its by about 30%. However, this favorable effect may decrease to less than 18% after about 5 hr. This is in somewhat good qualitative agreement with the 15% time-averaged reduction in the pressure drop (proportional to volume flow rate) reported in ref. (18) for an SHP microchannel with \( H_{ch} \phi / w_i \approx 4.5 \) enhanced with longitudinal grooves. Rearranging the grooves into a transverse position (Fig. 2.12a) leads to an initial 15% increase in water volume flow rate through the microchannel, which drops to about 5% after 5 hr.

Equations 2.43 and 2.44 are also used for the slip length predictions given in Figs. 2.12c and 2.12d. The predictions of Eq. 2.44 (from shear stress calculation) seem to be lower than those obtained based on volume flow rate in the channel (Eq. 2.43). As mentioned earlier, these slip length values can only be identical if the flow is in a Couette geometry.

The results shown in Fig. 2.12 are also in qualitative agreement with the experimental data of ref. (7) where an exponential decay was observed for the volume flow rate and effective slip length in an SHP microchannel. Therefore for comparison, exponential functions are fitted to our simulation results, and the coefficients are given for each case in Fig. 2.12.
For further comparison with experimental data, we simulated the experiment of ref. (76) in which longitudinal grooves with trapezoidal cross-sections having a wall angle of $\beta_L = \beta_R = 92^\circ$, a Young–Laplace contact angle of $120^\circ$, and an entrance width of 0.18 $\mu$m were placed on the top and bottom walls of three microchannels with different heights of 6, 10, and 22 $\mu$m. Formulations given in Sec. 2.2 or Sec. 2.3 can be used to obtain a capillary pressure of about 3.8 atm for these trapezoidal grooves. Therefore, for a operating gauge pressure range of 0.1 to 1 atm considered in the experiments, one expects the grooves to remain SHP indefinitely. With a GAF of 0.783 for the channels’ SHP walls, the authors in Ref. (76) reported average volume flow rate ratios of $Q_{SL1} / Q_{SL2}$ equal to 1.111, 1.0793, and 1.0361 for channels with a height of 6, 10, and 22 $\mu$m, respectively. Using an arbitrarily chosen operating gauge pressure of 1 atm ($p_{op} = 2$ atm in our formulations) and producing the expected steady state air–water interface profile in the above grooves, we computed $Q_{SL1} / Q_{SL2}$ ratio to be 1.0768, 1.0461, and 1.0209 for the above microchannels, respectively (an average mismatch of about 37%).

Figure 2.13 shows the dimensionless transient volume flow rate and effective slip length for the above-mentioned microchannel when enhanced with transverse and longitudinal grooves with circular walls. The results of Fig. 2.13a and 2.13b clearly show that SHP grooves, whether in the transverse or longitudinal direction, help to increase the flow rate in a channel. However, this effect decreases with time as the air–water interface moves further down into the grooves. Note that water flow rate through Channel RL3 is considerably higher than that in Channel RL2 when the grooves are in the longitudinal direction (Channel RL3 provides a larger passage for water to flow). However, for the case of transverse grooves, these flow rates are close to one another. Figures 2.13c and 2.13d compare the transient slip length for the transverse and longitudinal grooves using Eqs. 2.43 and 2.44, respectively.
Fig. 2.13: Non-dimensionalized volume flow rate through Channels RT1 and RL1 are shown in (a) and (b) for the case of transverse and longitudinal grooves, respectively. Transient slip lengths obtained from Eqs. 2.43 and 2.44 for transverse and longitudinal grooves are shown in (c) and (d), respectively. For these calculations, $d = 12 \, \mu\text{m}$, $L = 50 \, \mu\text{m}$, and $\theta^{\text{TG}} = 100^\circ$. The height and length of the microchannel are $H_{\text{ch}} = 200 \, \mu\text{m}$ and $L_{\text{ch}} = 100 \, \text{mm}$, respectively. The operating pressure is considered to be $p_{\text{op}} = 103.5 \, \text{kPa}$.
Note that, depending on the hydrophobicity of the groove’s bottom surface, some small pockets of air may remain inside the groove even after the air–water interface comes into contact with the groove’s bottom. (2) For simplicity, we have assumed hydrophilic bottom surface for the grooves, to enforce a complete transition to the Wenzel state when the air–water interface reaches the groove’s bottom.

As can be seen from the results of Fig. 2.12 or Fig. 2.13, longitudinal grooves seem to perform better than their transverse counterparts in terms of reducing the friction in a microchannel. With regards to grooves’ longevity, we reported identical performance for microchannels having longitudinal and transverse grooves. However, this is only because the channel’s inlet pressure was taken as the operating pressure for both cases in our calculations. In reality, as the pressure decreases along the length of a microchannel, transverse grooves experience different local pressures, and thus will have different longevity values depending on their positions along the length of the channel (unless pressure drop across the length of a channel is negligible in comparison to its operating pressure). The situation with the longitudinal grooves is more complicated. The longitudinal grooves in a channel experience the same pressure field and will therefore have identical longevity values. (77,78) However, the shape and position of the air–water interface along the length of a longitudinal groove may vary in response to the decreasing local pressure along the length of the microchannel. For instance, it may be possible for the air–water interface to become detached near the channel inlet but stay attached near the outlet, i.e., formation of a partially-detached air–water interface along the length of the groove. Therefore, if the groove’s bottom is hydrophobic, the groove may maintain some of its entrapped air even when the air–water interface reaches the bottom surface, and so continue generating slip effect.
2.6. Conclusions

A mathematical framework to study the time-dependent drag-reduction effect achievable by using SHP grooves inside a microchannel is presented in this chapter. Our formulations allow for the grooves to have asymmetric straight walls with dissimilar wettabilities or symmetric walls with different curvatures. Different approaches are presented for predicting the performance of an SHP groove based on the ability of the groove to pin the air–water interface at its entrance. More specifically, three different pressure regimes are defined for asymmetric grooves, depending on whether the air–water interface is pinned to both walls (Regime I), one of the walls (Regime II), or none of the walls (Regime III). For grooves with symmetric walls, two pressure regimes (for sharp-edged grooves) and one single regime (for grooves with round entrance) has been identified and formulated.

For demonstration purposes, a brief parameter study is presented for an SHP microchannel with arbitrary dimensions and properties. For instance, it is shown that increasing the wall angles, groove height, or Young–Laplace contact angle improves the durability of the drag-reduction effect. On the contrary, increasing the operating pressure or the width-to-height ratio of the groove accelerates the failure of the SHP surface.

Comparing for instance the performance of sharp-edged grooves with vertical walls, inclined walls, and sinusoidal walls having identical heights or groove volumes, increasing the apparent contact angle or initial volume of the groove enhances the longevity of the entrapped air. On the other hand, the critical pressure decreases as the initial volume increases while this pressure increases with increasing the apparent contact angle. Also, the pinned effect in sharp-edged-groove
enhances the performance (longevity or critical pressure) of the SHP surfaces. More specifically, the interplay between the opposing effects of varying the apparent contact angle and the initial volume of the sharp or round-edged grooves judge the performance of the SHP surfaces. For these reasons in sharp-edged grooves, critical pressure and longevity were found to be the highest for sinusoidal grooves and on other hand the performance for inclined grooves is higher than the vertical walls. Moreover, the performance for round-edged grooves is lower than those with sharp-edged grooves having the same geometric parameters and environmental condition of sharp edged grooves.

The effective slip length in the microchannels is calculated with two different methods (Eq. 2.43 and Eq. 2.44) for both the transverse and longitudinal groove configurations. While the two slip length calculation methods do not perfectly agree with one another, they both indicated that a greater slip length is achievable with the longitudinal grooves. The demise of slip length with time was found to follow an exponential decay in agreement with the experimental studies reported in the literature. Our slip length calculations are compared with the analytical, experimental, and numerical studies in the literature whenever available (i.e., grooves with a flat air–water interface or with a curved but pinned air–water interface) and perfect agreement was observed. Our study is the first to obtain quantitative slip length results for partially or completely pinned air–water interfaces. The present work is the first to present quantitative predictions for the transient effective slip length in an SHP microchannel with grooves having curved walls and/or grooves with round-edge entrance.

In summary, our results indicate that an SHP surface made of longitudinal grooves can produce greater slip than a similar surface with identical grooves arranged in a transverse configuration. We also conjecture that the longevity of the entrapped bubble is higher in the case of longitudinal
grooves, but this can only be quantitatively proved in the future studies. The present work is the first to present quantitative predictions for the transient effective slip length in an SHP microchannel with grooves having curved walls and/or grooves with round-edge entrance.

This work is expected to be valuable in custom-designing SHP microchannels for different applications.
Chapter 3. Effects of Hierarchical Features on Longevity of Submerged Superhydrophobic Surfaces with Parallel Grooves

3.1 Introduction

For superhydrophobic surfaces, the critical hydrostatic pressure—the pressure at which a superhydrophobic surface starts departing from the Cassie state—is often reported as a measure for the quality or wetting stability of the surface (79–81). To calculate the critical pressure, the balance of forces acting on the air–water interface has been considered in many studies in the past (9,12,24,29,33,34,72). The same approach has also been used to obtain an integro-differential equation for the shape of the interface over superhydrophobic surfaces with complicated geometries (82–84).

The air–water interface that forms an angle equal to the Young–Laplace contact angle with the walls of the groove is considered to be the critical profile, and its corresponding pressure is taken as the critical pressure. Critical pressure can be a good criterion to judge whether the Cassie state is mechanically stable when a superhydrophobic surface is exposed to elevated pressures (e.g., when a droplet falls on a superhydrophobic surface or when the surface is submerged for a short period of time). However, for extended underwater operations, the surface longevity is extremely important. Longevity is the time that it takes for a superhydrophobic surface to transition to the Wenzel state. Unfortunately, surfaces with high critical pressures do not always possess good longevity, and vice versa. In a previous study, we developed a mathematical model to predict the longevity of submerged superhydrophobic smooth-walled grooves under different hydrostatic
pressures (8). Our computational method can potentially be used to design and optimize—in terms of critical pressure and/or longevity—the microstructure of superhydrophobic surfaces for their specific applications. In the present work, the effects of adding side fins to the above-mentioned smooth-walled superhydrophobic grooves—often referred to as hierarchical features—will be studied theoretically. Hierarchical superhydrophobic surfaces have been shown to exhibit improved stability, i.e., attaining higher critical pressures, in comparison to surfaces without the hierarchical features (8,20,27,66). The present study is the first to investigate effects of hierarchical features on the longevity of superhydrophobic surfaces. To simplify the complicated mathematical calculations, our study is limited to parallel grooves.

As mentioned earlier, we recently developed a mathematical framework to predict the longevity of the entrapped air in submerged superhydrophobic grooves with flat smooth walls, i.e., without side fins (8). We used a balance of forces to derive an integro-differential equation for the shape of the air–water interface inside the grooves over time. This information was then used to predict the critical pressure and the longevity of the surface under different hydrostatic pressures. Our longevity calculations were conducted in two different regimes depending on whether the hydrostatic pressure $P_g$ was smaller or greater than the critical pressure $P_{cr}$ of the surface. In regime I, $P_g < P_{cr}$, the interface was initially assumed to be pinned to the sharp edges of the grooves at $t = 0$, and was allowed to deflect (sag) as the air escaped by diffusion from the groove. The interface was allowed to reach a critical profile at $t = t_{cr}$, when it is detached from the groove edges and move downward into the groove without any additional deflection until it reached the bottom of the groove. In regime II, $P_g > P_{cr}$, the interface was allowed to instantly reach the critical air–water interface profile inside the groove at a distance $h_0$ from the grooves top surface.
at \( t = 0 \), where \( h_0 \) depends on the hydrostatic pressure. In this regime, the air–water interface could only translate downward with a constant speed as the entrapped air dissolved in water.

The above procedure needs to be significantly revised before it can be used to predict the longevity of grooves with hierarchical side fins. The undercut space under a fin, the space bounded by two fins on the same wall, may allow the air–water interface to reach advancing contact angles much greater than the Young–Laplace contact angle \( \theta_y \). This will help the surface reach higher mechanical stability under elevated pressures, i.e., attaining higher critical pressures. Longevity calculation for grooves enhanced with side fins involves additional complications as will be discussed later.

In the remainder of this chapter, we first present our mathematical formulations for predicting the critical pressure and longevity of a submerged superhydrophobic groove in Section 3.2. This is followed by our algorithm for solving these equations for the evolution of the air–water interface in a groove enhanced with hierarchical fins. A parametric study is given in Section 3.4 where the effects of fins with different dimensions and counts on critical pressure and longevity are investigated. To demonstrate the versatility of our mathematical approach, the critical pressure and longevity of a superhydrophobic groove when enhanced with four arbitrary fin configurations is studied in Section 3.5. Our conclusions are given in Section 3.6.
3.2 Formulation

There are only four forces applied across an air–water interface: hydrostatic pressure $P_g$, ambient pressure $P_\infty$, bubble pressure $P_{bub}$, and finally capillary pressure $P_{cap}$ (see Fig. 3.1). Balance of static forces requires that

$$P_{cap} + P_{bub} - P_\infty - P_g = 0 \quad (3.1)$$

where $P_{cap}$, $P_{bub}$, and $P_\infty$ are, respectively, capillary pressure, entrapped bubble pressure, and atmospheric pressure. The critical air–water interface in a 2-D groove with a width of $w$ and a height of $h$ can be obtained by solving

$$f''(1 + f'^2)^{-3/2} + \frac{2 \cos \theta}{w} = 0 \quad (3.2)$$

The boundary conditions are $f_{cr} \left( x = \pm \frac{w}{2} \right) = 0$ and $f'_{cr} \left( x = \pm \frac{w}{2} \right) = \mp \cot \theta$, where $\theta \geq 90^\circ$ is the contact angle, and $f_{cr}$ is the critical profile. Because the interface profile between parallel walls of a groove is always an arc of a circle, the air–water interface profile $f(x, t)$ can be represented as

$$f = \sqrt{R^2 - x^2} - \frac{R^2}{4} - \sqrt{R^2 - x^2} \quad (3.3)$$

where the radius is a function of time, i.e., $R = R(t)$. Using Eqs. 3.2 and 3.3, one can obtain the critical radius of curvature for the interface

$$R_{cr} = \frac{w}{2} |\sec(\theta)| \quad (3.4)$$

Assuming that the entrapped air undergoes an isothermal compression due to the interface deflection, we obtain the bubble pressure
\[
P_{\text{bub}} = P_{\infty} v_0 / \left( v_0 + \int_{-w/2}^{w/2} f_{cr}(x) \, dx \right) \tag{3.5}
\]

where \(v_0\) is the initial volume of the groove, \(v_0 = hw\). An expression for the critical pressure can now be obtained by combining Eqs. 3.5 and 3.1:

\[
P_{cr} = -\frac{2\sigma \cos \theta}{w} - P_{\infty} \left[ 1 - \frac{v_0}{v_0 + \frac{w}{2} \sqrt{R_{cr}^2 - w^2/4 - R_{cr}^2 \sin^{-1} \left( \frac{w}{2R_{cr}} \right)}} \right] \tag{3.6}
\]

where \(\sigma\) is the liquid surface tension. Note that according to Eq. 3.6, there are only two parameters \(w\) and \(\theta\) that determine the shape of the critical air–water interface in a simple groove (the groove’s depth \(h\) and the other two parameters only affect the critical pressure).

To predict the initial interface, the entrapped bubble is assumed to undergo an isothermal compression. The initial air–water interface profile (i.e., at \(t = 0\)) in a simple groove \(f_0(x)\), using Eq. 3.1, corresponding to a circular profile with a radius of \(R = R_0\), can be calculated from the equation

\[
\sigma f_0'' (1 + f_0'^2)^{-3/2} - P_g - P_{\infty} \left[ 1 - \frac{v_0}{v_0 + \int_{-w/2}^{w/2} f_0(x) \, dx} \right] = 0 \tag{3.7}
\]

Following the same procedure described for the critical pressure expression in Eq. 3.6, one can derive the following equation for the initial air–water profile with a radius of curvature of \(R_0\):

\[
\frac{\sigma}{R_0} - P_g - P_{\infty} \left[ 1 - \frac{v_0}{v_0 + \frac{w}{2} \sqrt{R_0^2 - w^2/4 - R_0^2 \sin^{-1} \left( \frac{w}{2R_0} \right)}} \right] = 0 \tag{3.8}
\]
Equation 3.8 is a nonlinear algebraic equation for $R_0$, which can readily be solved numerically and used to obtain the initial interface profile $f_0$ utilizing Eq. 3.3. Given that the air–water interface moves very slowly with negligible inertial forces, one can apply the balance of forces across a deflecting interface to obtain the time evolution of the air–water interface from Eq. 3.9:

$$\sigma \nabla \cdot \vec{n} + P_{\text{bub}}(t) - P_\infty - P_g = 0 \quad (3.9)$$

where $\vec{n}$ is the unit normal to the air–water interface. Using the method advanced in Ref. (86) one can calculate the rate of air dissolution in water as
\[ P_{\text{bub}}(t) = P_v - \frac{\dot{v}(t)}{\xi A(t)} \] (3.10)

where \( P_{\text{bub}} \) is the bubble pressure, \( \xi = \sum n_i \xi_i \) is the weighted-average invasion coefficient for each gaseous species \( i \) in the air, \( n_i \) is the molar concentration of gas \( i \) in air, \( A(t) = \int_{-w/2}^{w/2} (1 + f'^2)^{1/2} dx \) is the surface area of the air–water interface, and \( P_v = P_\infty \) is the vapor pressure of the air bubble. The entrapped air volume is \( v = v_0 + \int_{-w/2}^{w/2} f(x)dx \); hence the volume flow rate \( \dot{v} \) is calculated from

\[ \dot{v}(t) = \int_{-w/2}^{w/2} \dot{f}(x,t)dx \] (3.11)

After substituting Eqs. 3.10, and 3.11 into Eq. 3.9, the transient air–water interface can be calculated from

\[ \sigma \int_{-w/2}^{w/2} f''(1 + f'^2)^{-3/2} dx - \frac{w}{\xi A(t)} \int_{-w/2}^{w/2} \dot{f}(x,t)dx + \Pi w = 0 \] (3.12)

where \( f' = \frac{\partial f}{\partial x}, \dot{f} = \frac{\partial f}{\partial t} \), and \( \Pi \equiv P_v - P_\infty - P_g = -P_g \). With the air–water interface in a groove being a circular arc, Eq. 3.3, the partial differential Eq. 3.12 can be reduced to a nonlinear ordinary differential, which can be solved via conventional numerical methods such as the fourth-order Runge–Kutta method. For any contact angle \( 90^\circ \leq \theta \leq 180^\circ \), we obtain

\[ \frac{\sigma}{R(t)} - \frac{1}{\xi A(t)} \left( \frac{R(t)w}{\sqrt{R(t)^2 - w^2/4}} - A(t) \right) \frac{dR}{dt} + \Pi \approx 0 \] (3.13)

Previous studies have indicated that hierarchical structures help to increase the advancing contact angle of a surface (8,27,29,66,87). This is because the undercut space below a fin allows the air–water interface to reach advancing contact angles much greater than the Young–Laplace contact
angle. Previous studies suggested an advancing contact angle $\theta_{adv}$ of about 180 degrees for surfaces with hierarchical nanostructures \((67,85,88)\). In the absence of more detailed information, we assumed an advancing contact angle of 180 degrees for the air–water interface inside a groove anchored to a fin (see Fig. 3.2).

![Diagram of air–water interface profiles](image)

**Fig. 3.2:** Graphical presentation of the air–water interface profiles in different regions inside a submerged superhydrophobic groove enhanced with hierarchical side fins (a). The entrapped air bubble is shown with blue color for different positions of the air–water interface inside the groove in (b) through (e). The air shown with grey color in the magnified sub-figure will escape to the ambient water as the interface moves from position (d) to position (e).

We start by solving Eq. 3.8 for $R_0$. This value is then used as an initial condition to solve Eq. 3.13 over time until the slope of the interface at the boundaries reaches $\mp \cot \theta_{YL} (R = R_{cr})$, or 180 degrees if the interface is pinned to the bottom edge of a fin, above an undercut. This will be the
critical profile at \( t = t_{cr} \), as shown in Fig. 3.2. With additional air dissolution from the groove, the critical profile \( f_{cr} \) will detach from the groove’s edges and move downward with a constant speed. The profile can be described as

\[
f(x, t) = f(x, t = t_{cr}) + \tau(t) \tag{3.14}
\]

where \( \tau \) is defined as

\[
\tau(t) = \frac{\xi}{w} A(t = t_{cr}) \left( \Pi - \frac{2\sigma \cos \theta}{w} \right) (t - t_{cr}) \tag{3.15}
\]

These equations can be used to simulate the longevity of an entrapped bubble in a groove enhanced with side fins. The instantaneous shape and position of the air–water interface is calculated until it touches the bottom of the groove. In the next section, we present our procedure for conducting such calculations.

### 3.3 Algorithm

A groove with \( M \) number of fins on its walls is subjected to a hydrostatic pressure equal to a column of water with a height of \( H \) (see Fig. 3.1). We assume that the first fin is placed at the groove’s entrance. The fins have a thickness of \( d \), a length of \( l \), and a fin-to-fin spacing of \( s \)

\[
s = \frac{h - Md}{M} \tag{3.16}
\]

Obviously, there is a maximum number of fins that a groove can accommodate, \( M_{max} = h/d \). Similarly, there is a maximum length that can be considered for a fin \( l_{max} = w/2 \). For clarity of presentation, the fins and the vertical distance between them are given identification numbers: \( N = 2M - 1 \) for the fins, and \( N = 2M \) for the space between the fins on the same wall. For the interface
calculations, we used a span (width) equal to \( w - 2l \) in regions labeled as \( N = 2M - 1 \) and \( w \) in regions labeled as \( N = 2M \) (see Fig. 3.2). Also note that with the addition of the side fins, the groove volume is reduced to \( v_0 = (h - Md)w - Md(w - 2l) \).

The air–water interface calculations start at the region denoted by \( N = 1 \). At \( t = 0 \), the initial interface profile \( f_{0}^{N=1} \) is calculated using Eq. 3.8 for \( R_0 \), and Eq. 3.3 with the boundary points \( A_1^L \) and \( A_1^R \), the left and right sharp upper corners of the fins at \( N = 1 \). The evolution of the air–water interface can be simulated by numerically solving Eq. 3.13 with the initial condition of \( R = R_0 \), and Eq. 3.3 until the slope at the wall reaches the Young–Laplace contact angle (here \( \theta_{YL} = 115^\circ \)) or \( R = R_{cr} \), in the time interval \( 0 < t < t_{cr,A}^{N=1} \). The interface has now reached the critical profile \( f_{cr,A}^{N=1} \) (see Fig. 3.2a). The critical interface then detaches from the points \( A_1^L \) and \( A_1^R \) and moves downward with a constant speed. The interface location in this region can be calculated at any time by substituting the solution of Eq. 3.15 in Eq. 3.14 until the interface comes in contact with the new boundary points \( B_1^L \) and \( B_1^R \), the end of the first fin. This profile is then named \( f_{cr,B}^{N=1} \), and the time is labeled as \( t_{cr,B}^{N=1} \). At this instant, the air–water interface is allowed to further expand in the undercut area below the fins to reach an advancing contact angle of \( \theta_{adv} = 180^\circ \) (67,85,88). The interface is then named \( f_{adv}^{N=1} \), \( R_{adv} \) at the new apparent angle, and the time is labeled as \( t_{adv}^{N=1} \).

At this point, we assume that the air–water interface spreads outward instantly in the undercut region below the fin, \( N = 2 \), to reach the new corner points \( C_1^L \) and \( C_1^R \), or the groove walls, depending on the geometric and hydrostatic conditions. For the latter calculation, the volume of the entrapped air under the last profile, \( f_{adv}^{N=1} \), is used to produce a new initial profile \( f_0^{N=2} \) in the region \( N = 2 \). To obtain \( f_0^{N=2} \), we use Eqs. 3.8 and 3.13, and substitute the results in Eq. 3.3 until the entrapped air volume shown with red color in Figs. 3.2b and 3.2c are equal. In this calculation,
the time is still $t_{adv}^{N=1}$. With the initial profile in $N = 2$ region, Eq. 3.13 is integrated in time until the slope of the air–water interface reaches the Young–Laplace contact angle at time $t_{cr}^{N=2}$.

Depending on the geometric and hydrostatic conditions, it is very probable that $f_0^{N=2}$ becomes the critical profile in the region $N = 2$, as shown in Fig. 3.2a. Maintaining a slope equal to the Young–Laplace contact angle, this interface moves down until it comes in contact with the next fin, points $A_2^L$ and $A_2^R$, at time $t_{cr,A}^{N=2}$. This concludes our interface tracking algorithm for $m = 1$.

When the interface reaches another set of fins, the initial profile in the new region $f_0^{N=3}$ is instantly formed. This new interface should entrap the same amount of air as was entrapped by the previous interface, the last interface from the region $N = 2$, except for a small amount of air entrapped between the interface and the upper part of the fins, as shown with grey color in Fig. 3.2d. To obtain $f_0^{N=3}$, we use Eq. 3.8 and Eq. 3.13 and substitute the results in Eq. 3.3 until the entrapped air volume shown with orange color in Figs. 3.2d and 3.2e are equal. After that, the interface will continue to first deform and then translate downward until it comes in contact with the points $B_2^L$ and $B_2^R$, using the same algorithm discussed earlier.
Fig. 3.3: A flowchart describing the MATLAB implementation of the formulations presented in Section 3.2. The main flowchart is shown in (a). The flowchart shown in (b) is a smooth-walled groove algorithm used when the interface is in contact with the front faces of a set of fins. The flowchart in (c) is for producing a new air–water interface for when the volume of the entrapped air is kept constant.

When the number of fins increases, careful attention should be paid to the special case where an initial interface $f_0^{N=2}$ comes in contact with the next set of fins, points $A_2^L$ and $A_2^R$. In such case, we
assume that a new interface is instantly generated in the next region and that the difference between
the entrapped air volumes under the two interfaces has escaped. In other words, the air volume
under the interface $f_{a}^{N=3}$ is equal to the volume of the air under the interface $f_{adv}^{N=1}$ minus the
volume of the air between the fins $2sl$.

The above procedure is repeated $m$ times for a groove with $m$ fins, until the interface touches the
bottom of the groove (see the flowchart in Fig. 3.3). The algorithm presented here can be used to
calculate the critical pressure and longevity of superhydrophobic surfaces comprised of parallel
grooves with side fins, and to optimize the number of fins and their dimensions.

### 3.4 Results and Discussion

#### 3.4.1 Failure in Regime I

We start our parametric study by simulating the case of parallel simple grooves (no side fins) to
examine the accuracy of our present formulation in comparison to that of Ref. (8). We consider a
Young–Laplace contact angle of $\theta_{YL} = 115^\circ$ for all the simulations reported here. Fig. 3.4 shows
the critical pressure and longevity as obtained from the formulation given here and those reported
in Ref. (8). There are two mechanisms that affect the critical pressure: capillary force and air
compression. The capillary force and the force generated by the compressed air against interface
sagging act with opposite trends when increasing the groove’s width. This results in a minimum
critical pressure at a certain groove width. For the case considered in Fig. 3.4, this minimum occurs
for grooves with a width of about 35$\mu$m. Generally speaking, when the pore is wider, interface
deflection causes more volume reduction leading to higher air compression. Obviously, if the
groove is open from the ends, i.e., if the air can escape from the groove ends, one should expect
an opposite effect. The decrease in the critical pressure values in Fig. 3.4 is because when the groove’s height is large in comparison to its width, the air compression caused by the interface’s deflection is insignificant.

![Graph](image)

**Fig. 3.4:** Effects of a groove’s width on its critical pressure and longevity for $h = 150 \mu m$ and $\theta_{yu} = 115^\circ$. Predictions of the method reported in Ref. (8) for smooth-walled grooves are added for comparison.

Figure 3.4 also depicts the longevity of the entrapped air in grooves with different widths along with the critical pressure of the surface. Unlike the critical pressure, the longevity always decreases as the width of the groove increases. Agreement with the simulation method developed in Ref. (8) is evident.

To study the influence of fins on critical pressure, a groove with a width of $w = 100 \mu m$ and a height of $h = 150 \mu m$ is considered. Simulations are conducted to predict the critical pressure of this groove when enhanced with different numbers of fins ranging from $M = 0$ to $M = 15$ with two different heights of 5 and 10 $\mu m$ and two different fin thickness of 2 and 4 $\mu m$. Note that the contact angle will increase from the Young–Laplace contact angle (here 115 degrees) to an
advancing contact angle (here 180 degrees) when fins are added. Addition of fins decreases the width of a groove, which adversely affects the critical pressure. However, because of the advancing contact angle applied when the interface is anchored to a fin, the net result is a significant increase in the critical pressure (see Fig. 3.5). It is also interesting to note that critical pressure slowly increases with increasing $M$. This is because the volume of the groove (i.e., entrapped air) decreases as more fins are added. Of course, excessive increase in the number of fins or their thickness leads to a critical pressure that is expected from a groove with smooth walls (no fins) but with a reduced width of $w - 2l$. Note also that the thickness of a fin has only a small influence on the critical pressure.

![Fig. 3.5: Effects of the number of fins on critical pressure for a groove with $w = 100 \mu m, h = 150 \mu m, H = 0.4 m, \theta_{yl} = 115^\circ$ and $\theta_{adv} = 180^\circ$. Two different fin lengths of $l = 5$ and $10 \mu m$ and two different fin thicknesses of $d = 2 \mu m, 4 \mu m$ are considered.](image-url)
To study the effects of fins on longevity, we considered a groove with a width of $w = 100 \mu m$ and a depth of $h = 150 \mu m$, enhanced with fins having length and thickness of, respectively, 10 and 5 micrometers. A hydrostatic pressure of $H = 0.4 m$ along with our default Young–Laplace contact angle of $\theta_{\gamma L} = 115^\circ$ is considered for these simulations.

Figure 3.6 shows the air–water interface at different moments of time inside a groove enhanced with 3, 5 and 8 side fins. Note that for $M = 3$, the interface comes in contact with the side walls, the front face of the fins, and the lower sharp corner of the fins (where it reaches an advancing contact angle of 180 degrees). For $M = 5$, the interface is only in contact with the front face of the fins or anchored to their lower sharp corner. Interestingly, with $M = 8$ the air–water interface is only in contact with the fins lower sharp corner (we will return to this figure later when we discuss Fig. 3.8). These results indicate that longevity is improved with the addition of longer fins. This is mainly because the air–water interface area available for the entrapped air to diffuse out of the pore is smaller with the longer fins.
Fig. 3.6: The time evolution of the air–water interface inside a groove with \( w = 100 \, \mu m, \, h = 150 \, \mu m, \, H = 0.4 \, m, \, \theta_{YL} = 115^\circ \) and \( \theta_{adv} = 180^\circ \) enhanced with side fins having lengths of \( l = 5 \) and \( 10 \, \mu m \), and thicknesses of \( d = 2 \) and \( 4 \, \mu m \). Number of fins are \( M = 3, 5, \) and \( 8 \) for (a)–(c), (d)–(f), and (g)–(i), respectively. The longevity values for the entrapped air bubble are reported in the figure for each case.
It is worth mentioning that one can derive an equation to obtain the minimum number of fins \( M_{\text{min}} \) (or \( s_{\text{max}} \)) needed for the interface to jump from the lower sharp corner of one set of fins to the next, i.e., instantaneous transition from \( f_{ab}^{N=1} \) profile to \( f_{cr,B}^{N=3} \) profile without forming an intermediate interface profile like \( f_0^{N=2} \) as shown in Fig. 3.7a. For this derivation one can assume that the volume of the air below the advancing interface \( f_{ab}^{N=1} \) is the same as that under \( f_{cr,B}^{N=3} \) i.e., conservation of mass for the entrapped air (see Figs. 3.7b and 3.7c). Therefore, \( s_{\text{max}} \) can be calculated as

\[
(w - 2l)(d + s_{\text{max}}) + (R_{cr}^{N=1})^2 \sin^{-1}\left(\frac{w - 2l}{2R_{cr}^{N=1}}\right) - \frac{w - 2l}{2} \sqrt{(R_{cr}^{N=1})^2 - (w - 2l)^2/4} \leq \frac{\pi}{8} (w - 2l)^2
\]

(3.17)

where \( R_{cr}^{N=1} = \frac{w - 2l}{2} \sec(\theta_{YL}) \). For a given fin thickness \( d \), the minimum number of fins \( M_{\text{min}} \) can be calculated using Eq. 3.16 at \( s = s_{\text{max}} \). Note that for with \( M \geq M_{\text{min}} \) the air–water interface always anchor to the lower sharp corner the fins, i.e., the edge points at \( B_m^L \) and \( B_m^R \). Note also that when an interface jumps from a set of fins to the next, the air trapped in the between the two consecutive fins in the vertical direction (shown with grey color in Fig. 3.7c) will be lost to the ambient water.
Fig. 3.7: Graphical presentation of the air–water interface profiles inside a groove for when the interface jumps from the lower sharp corners of a set of fins to those of the next set without going through the intermediate stages shown for instance with the dashed-line in (a). The schematic profiles drawn in (b) and (c) represent air–water interfaces at $t = t_{adv}^{N=1}$ and $t = t_{cr,B}$, respectively. Figures (a) through (c) illustrate the underlying hypothesis of the expression derived for $M_{min}$. Note that the air shown with grey color escapes to the ambient water as the interface moves from (b) to (c).

The effects of number of fins on longevity are shown in Fig. 3.8 for a groove with a width of 100 μm equipped with fins with 10 and 5 μm lengths and 2 and 4 μm thickness. For comparison, we have also included the longevity values obtained for three smooth-walled grooves with widths of 100, 90, and 80 μm. Despite the local fluctuations (will be discussed in this section), longevity of the entrapped air generally increases with increasing the number of fins $M$(see Fig. 3.8). Also, longevity for grooves having fins with a length of $l$ is better than that in grooves with smooth walls, with either the original width $w$ or a new width of $w - 2l$. As mentioned before, our calculations are based on two stages of interface tracking: sagging while pinned, and translating with a fixed profile. The addition of fins, allows the interface to undergo an extended sagging process as an advancing contact angle of $\theta_{adv} = 180^\circ$ needs to be reached before the interface can
leave the fin to which it is pinned. During the sagging process, the contribution of the interfacial forces in resisting the hydrostatic pressure is greater than that during the interface translating with a fixed profile. This allows the bubble pressure remain lower during the sagging process which consequently slows the rate of air dissolution in water.

![Graph](image1)

**Fig. 3.8:** The effect of the number of fins on the longevity of the entrapped air bubble for a groove with $w = 100 \mu m$, $h = 150 \mu m$, $H = 0.4 m$, $\theta_{vl} = 115^\circ$, and $\theta_{adv} = 180^\circ$. Two different fin lengths of $l = 5 \mu m$ and $l = 10 \mu m$, and two fin thicknesses of $d = 2 \mu m$ and $d = 4 \mu m$ are considered. Longevity predictions are also reported for smooth-walled grooves with $w = 80$, $90$, and $100 \mu m$ for comparison.

Figure 3.9 shows the air–water interface in a groove with two different fin counts of $M = M_{min} = 7$, and $M = 15$. Note that the interface does not touch the groove side walls in either case as $M \geq M_{min}$. The corresponding entrapped air pressures and mass flow rates for these cases are shown in Figs. 3.9c and 3.9d. We have also included the case of grooves with smooth walls having widths of $w = 100 \mu m$ and $w - 2l = 80 \mu m$ for comparison. It can be seen that, on average, the bubble
pressure is lowest for the groove with $M = 15$. This is followed by the groove with $M = 7$, the groove with a width of 80 µm, and finally the groove with of 100 µm. Consequently, the air mass transfer rate into water is the lowest for the groove with $M = 15$ and highest for the smooth-walled groove with $w = 100$ µm (see Fig. 3.9d).

**Fig. 3.9:** The time evolution of the air–water interface inside a groove with $w = 100$ µm, $h = 150$ µm, $H = 0.4$ m, $\theta_{yL} = 115^\circ$, $\theta_{adv} = 180^\circ$ enhanced with two different fin counts of $M = 7 = M_{\text{min}}$ and $M = 15 > M_{\text{min}}$ are shown in (a) and (b), respectively, along with their corresponding longevity values. The fins have a length and thickness of $l = 10$ µm, and $d = 2$ µm. Figures (c) and (d) show the bubble pressure and the rate of air dissolution into water across the interface over time for the grooves shown in (a) and (b) as well as smooth-walled grooves with $w = 80$ and 100 µm.
To explain the aforementioned fluctuations the longevity predictions reported in Fig. 3.8, we recall that when an interface touches the bottom of the groove, the remainder of the air left in the groove is assumed to escape into the ambient water. Depending on the number of fins in a groove, the air–water interface that reaches the groove’s bottom may have different profiles. In other words, the amount of air escaped into the ambient water at the moment when the last interface touches the bottom depends on the number of fins. Note also that the aforementioned loss of air due to interface jumping from one set of fins to the one below it should be considered in interpreting the results in Fig. 3.8 (the amount of air escaped to the ambient water is less when interface moves from a contact with the walls to contact with the fins). More specifically, for $0 \leq M \leq 3$, the last air–water interface that touches the bottom is in contact with groove walls, and as expected, longevity increases linearly with increasing the fin count and the fin thickness has minimal importance (see Figs. 3.6a-3.6c). For $M = 4$, there is a slight reduction in longevity for both cases. This is because now the last air–water interface that touches the bottom was pinned to the last pair of fins, and so the volume of the air escaped to the ambient was slightly more than that with $M = 3$. For $4 < M < 6$, while the last air–water interface touching the bottom is still pinned to the last pair of fins, its radius of curvature increases with increasing $M$. Therefore, the volume of the air released to the ambient at the last moment of operation decreases with $M$, i.e., longevity increases with $M$ (see Figs. 3.6d–3.6f). At $M = 7$, there is a sudden drop in longevity for the grooves with $l = 10.0 \, \mu m$. This is because the air–water interface touching the bottom is now pinned to the second-to-last set of fins and so there is a relatively large volume of air that escapes from the groove in the last stage of interface tracking (sees Figs. 3.6g–3.6i). Note that the same happens for the grooves with $l = 5.0 \, \mu m$, but the effects is less pronounced. One can generally conclude that longevity is more sensitive to the number of fins, when the fins are longer.
It is interesting to note that, for the grooves considered here, fin thickness starts to play a role at $M > 5$ for $l = 5 \mu m$ and $M > 7$ for $l = 10 \mu m$. The reason is that when the fins are thicker, the amount of air that escapes the groove when an interface jumps from one set of fins to the next is smaller. Therefore, the longevity tends to be longer for thicker fins (see Fig. 3.7 and the accompanied discussion).

Figure 3.10 shows the effects of hydrostatic pressure on longevity for two of the grooves previously discussed in Fig. 3.8. The first is a groove with $M = 14$ and $d = 2 \mu m$ and the other is with $M = 7$ and $d = 4 \mu m$. The fin length is $l = 4 \mu m$ for both. For both grooves the initial volume of the entrapped air is the same (i.e., $Md = \text{constant}$). The longevity values are also computed for two smooth-walled grooves with widths of $w = 100 \mu m$ and $w = 80 \mu m$ and added to the figure for comparison.
It can be seen that longevity decreases with increasing the hydrostatic pressure, which is in agreement with the experimental studies reported in Ref. (38) and Ref. (54) as well as the computational work presented in Ref. (8). Also note that fins with identical $Md$ have almost identical longevity under different hydrostatic pressures. The results shown in Fig. 3.10 indicate that while side fins can help to improve the longevity of the entrapped air in superhydrophobic grooves, the effect is limited to surfaces under relatively low hydrostatic pressures (hydrostatic pressure below 0.5 m of water for the set of parameters considered here).

### 3.4.2 Failure in Regime II

As mentioned earlier, the critical pressure increases when fins are added to a groove with smooth walls. In regime II, the hydrostatic pressure is greater than the critical pressure of the groove (i.e., $P_g > P_{cr}$). The solution algorithm described in Section 3.3 should slightly be modified for grooves operating under hydrostatic pressures greater than their critical pressure, as the initial air–water interface in this regime starts at a location below the groove’s inlet. Our algorithm therefore, starts by calculating the radius of curvature and the location of the initial air–water interface inside the groove before following the procedure described in Section 3.3.

Calculating the initial interface for grooves with side fins is not a trivial task. In the case of $M < M_{min}$ and depending on the hydrostatic pressure, the initial interface may happen to fall in the region between two vertical fins, or reach a position that is pinned to the second or third … pair of fins (see Figs. 3.11a and 3.11b). In our analysis here, we assume the fins to be very thin for the sake of simplicity (with the thick fins, it is also possible that the initial interface comes in contact
with the tip the fins but not yet at a pinning position at the lower edge). For the case where the initial interface is located between the two consecutive fins (Fig. 3.11a), the distance \( s_0 \), can be calculated by considering an isothermal compression process for the air entrapped in the groove. By using Eq. 3.5, the bubble pressure can be obtained as

\[
P_{\text{bub}} \left( v_0 - w s_0 - \left( \frac{R_{cr}^{N=2}}{2R_{cr}^{N=2}} \right)^2 \sin^{-1} \left( \frac{w}{2R_{cr}^{N=2}} \right) + \frac{w}{2} \sqrt{\left( \frac{R_{cr}^{N=2}}{2R_{cr}^{N=2}} \right)^2 - \frac{w^2}{4}} \right) = P_\infty v_0 \tag{3.18}
\]

where \( R_{cr}^{N=2} = \frac{w}{2} \sec(\theta_{rL}) \). Then, using Eq. 3.1 the distance \( s_0 \) is obtained as

\[
s_0 = \frac{1}{w} \left[ v_0 - (m - 1) s - \left( \frac{R_{cr}^{N=2}}{2R_{cr}^{N=2}} \right)^2 \sin^{-1} \left( \frac{w}{2R_{cr}^{N=2}} \right) + \frac{w}{2} \sqrt{\left( \frac{R_{cr}^{N=2}}{2R_{cr}^{N=2}} \right)^2 - \frac{w^2}{4}} \right. \\
- v_0 \left/ \left\{ 1 - \frac{P_\infty}{\sigma} \frac{R_{cr}^{N=2}}{P_g} \right\} \right. \tag{3.19} \]

where \( m \) is the number of fins above the interface ( \( m = 1 \) for the case shown in Fig. 3.11a). With this information, one can now calculate the new initial air–water interface using Eqs. 3.3 and 3.4. Note that this will not be the case if \( M \geq M_{\text{min}} \). For \( M \geq M_{\text{min}} \) or the hydrostatic pressures that are high enough to force the interface to reach the next row of fins, the new initial interface will be pinned to the lower edge of the fin’s tip with an undetermined radius of curvature \( R_0 \), in the range of \( R_{cr} < R_0 \leq R_{adv} \). With the same isothermal compression process, one can calculate the initial radius of curvature \( R_0 \) (or the initial slope at boundaries) which makes Eq. 3.1 now a nonlinear algebraic equation in \( R_0 \) for a given hydrostatic pressure \( P_g \):

\[
\frac{\sigma}{R_0} - P_g - P_\infty \left[ \frac{1}{v_0} \left( v_0 - (m - 1) s \right) + \frac{w}{2} \sqrt{R_0^2} - \frac{w^2}{4} - R_0^2 \sin^{-1} \left( \frac{w}{2R_0} \right) \right] = 0 \tag{3.20}
\]
where $m$ again represents the number of fins which are before the current fin ($m = 1$ for the case shown in Fig. 3.11b). With this initial profile one can then use the algorithm described in Section 3.3 to predict the longevity of superhydrophobic surfaces in regime II.

To demonstrate the application of the above formulations, longevity of the air bubble in a groove with $M = 3, l = 5 \, \mu m$, and $d = 2 \, \mu m$ is simulated under three different hydrostatic pressures of 0.4, 3.0, and 6.0 m of water (see Table 3.1). The air–water interface for simulations with hydrostatic pressures of 3.0 and 6.0 m of water are shown over time in Figs. 3.11c and 3.11d, as they represent failure mechanisms in regime II. For comparison in Table 3.1, we have also included the corresponding longevity values obtained for smooth-walled grooves with widths of $w = 90 \, \mu m$ and $w = 100 \, \mu m$. The data presented in Table 3.1, indicate that the addition of fins have no practical values at elevated pressures.
Fig. 3.11: The two scenarios considered for the initial air–water interface in Regime II: (a) the initial interface is located at an unknown distance $s_0$ below the surface and is in contact with the groove walls, and (b) the initial interface is pinned to a set of fins inside the groove with an unknown radius of curvature $R_0$. The time evolution of the air–water interface in Regime II is calculated for hydrostatic pressures of $H = 3.0$ and 6.0 m of water in (c) and (d), respectively, along with their corresponding longevity values. The geometric and hydrostatic parameters used for (c) and (d) are $w = 100 \mu m$, $h = 150 \mu m$, $l = 5 \mu m$, $d = 2 \mu m$, $\theta_{yL} = 115^\circ$, and $\theta_{adv} = 180^\circ$.

Table 3.1: Longevity predictions for the entrapped air in a groove with $w = 100 \mu m$, $h = 150 \mu m$, $M = 3$, $d = 2 \mu m$, $l = 5 \mu m$, $\theta_{yL} = 115^\circ$ and $\theta_{adv} = 180^\circ$ under three different hydrostatic pressures of $H = 0.4$, 3.0, and 6.0 m of water. The cells filled with grey color represent performance in regime I.
3.5 Groove Design

In this section, we study the performance of a groove enhanced with four different configurations of fins of unequal lengths hereon, referred to as groove A, B, C, and D (see Fig. 3.12). For simplicity, we arbitrarily consider four fins for the study and assume them to be placed inside the grooves in a symmetric manner. The fin thickness is 2 \( \mu m \). The objective of this study is to demonstrate the application of our theoretical method for designing hierarchical grooves. As mentioned before, the important parameters in designing hierarchical grooves for underwater applications are the width of the entrance \( w \), the groove volume \( v_0 \), and the advancing contact angle \( \theta_{adv} \). In the absence of more accurate empirical values, an advancing contact angle of 180° has been assumed for the calculations presented here. We vary the length of the fins linearly from 20 \( \mu m \) to 5 \( \mu m \) in groove A, and from 5 \( \mu m \) to 20 \( \mu m \) in groove B. We also use two different alternations of staggered distribution of fins with 5 and 20 \( \mu m \) lengths in groove C and D. Note that grooves A through D all have an identical volume of \( v_0 \). Because of this, grooves with identical entrance widths have identical critical pressures (12.97 kPa for grooves A and D and 28.31 kPa for grooves B and C).

The simulations shown in Fig. 3.12 are conducted at three different pressures of 0.4, 2.0, and 4.0 kPa. At a pressure of 0.4 kPa, all grooves operate in regime I (Figs. 3.12a–3.12d). At a pressure of 2.0 kPa, groove A and D fall into regime II while groove B and C are still in regime I (Figs. 3.12e–3.12f). Finally, at a pressure of 4.0 kPa, all four grooves are in regime II (Figs. 3.12g–3.12i). The longevity values obtained for the entrapped air in grooves A through D are shown in Table 3.2, and are also compared with those of the smooth-walled grooves having widths of 100 and 60 \( \mu m \). Note that the longevity of air in any other smooth-walled groove with 60 < \( w < 100 \) falls in
between those of the 100-µm and 60-µm grooves (see Fig. 3.4). The results shown in Table 3.2 and Fig. 3.12, once again show that fins can only help to improve the longevity of the entrapped air at low hydrostatic pressures.
Fig. 3.12: The time evolution of the air–water interface in four arbitrarily chosen fin configurations (groove A through groove D) are shown in (a)–(d), (e)–(h), and (i)–(l) for hydrostatic pressures of $H = 0.4$, $2.0$, and $4.0$ m of water, respectively. In groove A the fin length is linearly decreased from 20 to 5 µm. In groove C fins with lengths of only 5 and 20 µm are used. The fins in grooves B and D are the other alternative configuration of the fins in grooves A and C, respectively. For all the four grooves $w = 100$ µm, $h = 150$ µm, $d = 2$ µm, $\theta_{YL} = 115^\circ$ and $\theta_{adv} = 180^\circ$. At $H = 0.4$ m of water all grooves are in regime I. At $H = 2.0$ m of water grooves A and D operate in regime II while grooves B and C are still regime I. At $H = 4.0$ m of water all grooves are in regime II.

Table 3.2: Longevity predictions for the entrapped air in grooves A through D. The cells filled with grey color represent performance in regime I.

<table>
<thead>
<tr>
<th>hydrostatic pressure (m of water)</th>
<th>$t_f$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>groove A, $P_{cr} = 12.97$ kPa</td>
<td>43.70</td>
</tr>
<tr>
<td>groove B, $P_{cr} = 28.31$ kPa</td>
<td>43.50</td>
</tr>
<tr>
<td>groove C, $P_{cr} = 28.31$ kPa</td>
<td>45.10</td>
</tr>
<tr>
<td>groove D, $P_{cr} = 12.97$ kPa</td>
<td>43.80</td>
</tr>
<tr>
<td>smooth groove, $w = 100$ µm, $P_{cr} = 5.90$ kPa</td>
<td>34.96</td>
</tr>
<tr>
<td>smooth groove, $w = 60$ µm, $P_{cr} = 4.15$ kPa</td>
<td>40.50</td>
</tr>
</tbody>
</table>

3.6 Conclusions

In this chapter, the longevity of entrapped air bubbles in submersed superhydrophobic surfaces comprised of grooves with hierarchical fins is studied for the first time. Our simulations quantitatively demonstrate that addition of the hierarchical fins significantly improves the mechanical stability of the air–water interface inside a superhydrophobic groove (i.e., increases the groove’s critical pressure). This is thanks to the high advancing contact angles that can be achieved when an interface comes in contact with the sharp corner of a fin. For the longevity on the contrary, the hierarchical fins are only effective at pressures below the critical pressure of the original smooth-walled groove (about 50% improvement for the parameters considered here). When the hydrostatic pressure is raised above the critical pressure of the original surface, the improvement in longevity of is marginal (below 15% for the parameters considered here).
The critical pressure of a smooth-walled groove was found to significantly improve by addition of only one set of fins at its inlet. While additional fins continued to improve the critical pressure, the improvement was incremental. Longevity also improved with the addition of fins, although not monotonically. It was shown that for $M \geq M_{min}$ the air–water interface will never come in contact with the walls of the groove. An analytical expression is developed for predicting $M_{min}$ in terms of the groove’s geometric and hydrostatic parameters. Our results indicate that increasing the length of the fins decreases the critical pressure of a submerged superhydrophobic groove but increases its longevity. Increasing the thickness of the fins improved both the critical pressure and longevity of the groove.

The mathematical framework presented in this chapter can be used to custom-design superhydrophobic surfaces for different applications. An example of such studies is shown in Fig. 3.12.
Chapter 4. General Formulations for Predicting Longevity of Submerged Superhydrophobic Surfaces Comprised of Pores or Posts

4.1 Introduction

As mentioned before in Chapter 2, superhydrophobic surfaces are characterized by water droplets beading on them with contact angles exceeding $150^\circ$. This is thanks to the peculiar ability of such surfaces in trapping air in their pores, thereby reducing the contact between water and the solid surface (the Cassie state) (15). The reduced solid–water contact area can result in a reduction in the skin-friction drag, if the surface is exposed to a moving body of water (16). For such applications, the stability of the air–water interface under pressure is critically important. An elevated pressure can force the water into the air-filled pores of the surface and lead to a partial or complete wetting of the surface (the Wenzel state). A similar phenomenon also takes place during the evaporation of a droplet on a SHP surface: pressure inside the droplet increases due to evaporation and forces the air–water interface into the air-filled pores beneath the droplet (89).

The method of balance of forces has been used to predict the pressure at which the surface starts transitioning from the Cassie state to the Wenzel state, the critical pressure, for surfaces made up of grooves, posts, and particles (9,12,24,29,36,80,90,91). Critical pressure has also been measured experimentally in many pioneering studies (8,10,54,82,92). While critical pressure can be used to judge if the Cassie state is mechanically stable under elevated pressures, it is the surface longevity that matters the most for a submerged SHP surface. Longevity is the time that it takes for a SHP surface to transition to the Wenzel state. Optical techniques have been used to experimentally estimate the longevity of SHP surfaces with different microstructures under elevated pressures.
These studies have shown that longevity decreases with increasing hydrostatic pressure. No theory however, has yet been developed to establish a quantitative relationship between the longevity of a SHP surface and its microstructural parameters (e.g., diameter and height of posts or pores). Our group was the first to propose a mathematical framework to quantify the longevity of a SHP surface (52). Our previous study however, was only applicable to surfaces made of parallel grooves as the equations were derived in a 2-D space. In the current work, new formulations are derived in a generalized 3-D form such that predicting the critical pressure and longevity of surfaces comprised of dissimilar pores and posts with arbitrary round cross-sections (not necessity circular) with ordered or random arrangements is made possible. The formulation presented in this chapter can directly be used to design and optimize the microstructure of a SHP surface for different applications ranging from self-cleaning to underwater drag reduction.

Our generalized formulations for critical pressure and longevity predictions are presented in Sec. 4.2 for surfaces made of arbitrary pores and posts. Specific solution methods and closed-form analytical expressions are derived for surfaces with circular pores and circular posts in Secs. 4.3 and 4.4, respectively. Proposing new equivalent pore diameter definitions for SHP surface made of ordered and/or random posts, we have developed easy-to-use analytical expressions for predicting critical pressure and longevity of such surfaces in Sec. 4.5. This is followed by our conclusions in Sec. 4.6.

### 4.2 General Formulations

The air–water interface in a pore (or between vertical posts) is considered to be at equilibrium, when the hydrostatic $P_g$ and ambient pressures $P_{ao}$ are balanced by the capillary pressure $P_{cap}$ and the pressure caused by the air entrapped in the pore $P_{bub}$ (see Fig. 4.1). The angle between the
solid walls and the air–water interface increases with increasing the hydrostatic pressure. At a certain hydrostatic pressure, i.e., the critical pressure $P_{cr}$, this angle reaches the Young–Laplace Contact Angle Young–Laplace contact angle $\theta$. Our study on the time evolution of the air–water interface is divided into two major categories in terms of the hydrostatic pressure. We define Regimes I and Regime II for systems operating under hydrostatic pressures smaller or greater than the critical pressure of the surface, respectively. At a given hydrostatic pressure in Regime I, the air–water interface first deforms (sags) over time, as the pressure of the entrapped air $P_{bub}$ decreases due to air dissolution in water, and then translates downward with further air dissolution. In the deforming stage, the air–water interface remains pinned to the sharp edges of the wall, but the angle between the interface and the wall increases with time until it reaches the Young–Laplace contact angle. This interface profile is referred to as the critical profile, and the time required for the interface to reach this profile is called the critical time $t_{cr}$ in this work. Once the air–water interface reaches the critical profile, it translates downward at a constant speed (due to the constant rate of air dissolution from the bubble). The time needed for the interface to touch the bottom of the pore in Regime I is referred to as the failure time $t_{f1}$ here. Unlike Regime I, the air–water interface in Regime II conforms to its critical profile instantly (at time $t = 0$) but at a depth $h_0$ inside the pore, depending on the difference between the hydrostatic pressure and critical pressure. This interface then moves down further into the pore (similar to the case of Regime I) until it touches the bottom of the pore in a time period denoted here as $t_{f2}$. 
In the next sections, we first derive our general formulations for the calculation of the critical pressure, and its corresponding air–water interface profile (Sec. 4.2.1), and then present a method for calculating the failure times (Sec. 4.2.2).

### 4.2.1 Critical Pressure and Critical Air–Water Interface

For a given pore (or a post), the hydrostatic pressure that makes the angle between the air–water interface and the solid walls equal to the Young–Laplace contact angle \( \theta \) is the critical pressure \((38,66,93)\). Consider capillary pressure defined as \( P_{\text{cap}} = \sigma \nabla \cdot \hat{n} \) where \( \sigma \) is the surface tension and \( \hat{n} \) is the unit vector normal to the interface. Assuming \( z = F(x, y, t) \) to be the profile of the interface, the unit normal becomes \( \hat{n} = \left( F_x, F_y, -1 \right) / \sqrt{1 + F_x^2 + F_y^2} \). The capillary pressure or the divergence term therefore become,

\[
P_{\text{cap}} = \sigma \nabla \cdot \hat{n} = \sigma \left[ \left( 1 + F_y^2 \right) F_{xx} + \left( 1 + F_x^2 \right) F_{yy} - 2F_x F_y F_{xy} \right] \left( 1 + F_x^2 + F_y^2 \right)^{-3/2}
\]

Let the critical profile at \( t = 0 \) be \( z = F(x, y, 0) = G(x, y) \). From the balance of forces,

\[
P_{\text{cap}} - P_g - P_{\infty} + P_{\text{bub}} \approx 0
\]
In order to calculate the pressure of the entrapped bubble, an isothermal compression \( P_{\text{bub}} \nu_{\text{bub}} = P_\alpha \nu_0 \) is assumed, with the bubble volume represented as \( \nu_{\text{bub}} = \nu_0 + \iiint_S F dS \). Rearranging these two equations yields,

\[
P_{\text{bub}} = P_\alpha \frac{\nu_0}{\nu_{\text{bub}}} = \frac{P_\alpha \nu_0}{\nu_0 + \iiint_S G dS}
\]

where \( \nu_0 \) is the pore volume (\( \nu_0 = \text{S. h} \)). Eq. 4.2 then becomes

\[
P_{cr} = \sigma \left[ (1 + G^2_y)G_{xx} + (1 + G^2_x)G_{yy} - 2G_xG_yG_{xy} \right] \left( 1 + G^2_x + G^2_y \right)^{-3/2}
\]

\[- P_\alpha \left[ 1 - \frac{\nu_0}{\nu_0 + \iiint_S G dS} \right]\]

Eq. 4.4 is solved using an iterative interpolation method (68). The Integro-Partial Differential Equation given in Eq. 4.4 is solved in each iteration using the finite element engine of a commercial PDE solver (PDE Solutions Inc) controlled by an in-house MATLAB code.

### 4.2.2 Failure Time in Regime I

In Regime I, the hydrostatic pressure is less than the critical pressure. Here the transition from the Cassie state to the Wenzel state takes place in two steps. The interface first deforms (sags) while being pinned (\( t \leq t_{cr} \)) and then detaches from the edges and moves deeper into the pore (\( t_{cr} < t < t_{f1} \)). For a pinned interface, one should first calculate the initial interface profile, i.e., the shape of the interface at \( t = 0 \) by applying the balance of forces across the interface (Eq. 4.2). Let \( z = F(x, y, 0) = f(x, y) \) be the interface shape at \( t = 0 \). By following a procedure similar to the one discussed in the previous section, Eq. 4.2 can be written as

\[
\sigma \left[ (1 + f^2_y) f_{xx} + (1 + f^2_x) f_{yy} - 2f_x f_y f_{xy} \right] \left( 1 + f^2_x + f^2_y \right)^{-3/2}
\]

\[- P_\alpha \left( 1 - \frac{\nu_0}{\nu_0 + \iiint G dS} \right) - P_g = 0
\]
The above integro-partial differential equation is subjected to the “pinned interface” boundary condition at the wall $f = 0$. The shape of the initial interface can then be calculated by numerically integrating Eq. 4.5 using an integro-partial differential equation solver. The transient interface is calculated using Eq. 4.2, where the pressure of the entrapped air changes as air dissolves in water $P_{bub} = P_{bub}(t)$. The rate of dissolution of a gas from a bubble into water is proportional to the difference between the partial pressure of the gas in the bubble and its mole fraction in water (94).

$$v_i = \xi_i A(k_i c_i - p_{bub,i})$$ \hspace{2cm} (4.6)

where $v_i$, $k_i$, $c_i$, and $\xi_i$ are volume flow rate, Henry’s constant, mole fraction in water, and the invasion coefficient of gas $i$, respectively. The surface area $A$ can be obtained as $A = \iint_S (1 + F_x^2 + F_y^2)^{1/2} dS$ \hspace{0.5cm} (dS = dx \times dy).$ Following Ref. (94), the bubble pressure can be obtained as

$$P_{bub} = P_v - v' / (\bar{\xi} A)$$ \hspace{2cm} (4.7)

where $\bar{\xi} = \sum n_i \xi_i$, $P_v = \frac{1}{\bar{\xi}} \sum k_i c_i \xi_i = P_\infty$ because $p_\infty_i = k_i c_i$. As mentioned in Sec. 4.2.1, the volume of the bubble is $v(t) = v_0 + \iint_S FdS$ where $v_0 = (h)(S)$ is a constant, and therefore,

$v' = \iint_S F_t dS.$ Substituting Eq. 4.7 into Eq. 4.2 and integrating over the area $S$ we obtain,

$$-\sigma \left[ (1 + F_y^2)F_{xx} + (1 + F_x^2)F_{yy} - 2F_x F_y F_{xy} \right] (1 + F_x^2 + F_y^2)^{-3/2} dS - \Pi S$$ \hspace{2cm} (4.8)

$$+ \frac{S}{\bar{\xi} A} \iint F_t dS \approx 0$$

where $\Pi = P_v - P_g - P_\infty$. Eq. 4.8 can directly be solved with a generic integro-partial differential equation solver. Alternatively, one can assume that the air–water interface profile at each moment
during its evolution is similar the initial interface profile but scaled with a factor that is a function of time, i.e.,

$$F(x, y, t) = T(t)f(x, y)$$  \hspace{1cm} (4.9)$$

where $f(x, y)$ is the initial profile obtained from Eq. 4.5. The time evolution of the interface can be obtained by calculating the scale function $T(t)$. Using Eqs. 4.8 and 4.9, one obtains

$$\alpha T_t + \beta T + \gamma = 0$$  \hspace{1cm} (4.10)$$

where $\gamma = -:\Pi S$ and

$$\alpha = \frac{S}{\xi A(t)} \int f dS \hspace{1cm} (4.11a)$$

$$\beta = -\sigma \int \left[ (1 + T^2 f_x^2) f_{xx} + (1 + T^2 f_y^2) f_{yy} - 2T^2 f_x f_y f_{xy} \right] (1 + T^2 f_x^2 + T^2 f_y^2)^{-3/2} dS \hspace{1cm} (4.11b)$$

Eq. 4.10 is a nonlinear PDE in time as $\alpha = \alpha(t)$, and $\beta = \beta(t)$. In order to find an analytical solution for this equation, we assume that $\alpha = \alpha(t = 0)$, and $\beta = \beta(t = 0)$ with an initial condition of $T(t = 0) = 1$,

$$T = (1 + \gamma/\beta)e^{-\beta t/\alpha} - \gamma/\beta$$  \hspace{1cm} (4.12)$$

This equation is valid until the Young–Laplace contact angle is reached at the boundaries, i.e., $|\nabla F|_{max} = |\cot \theta|$. Finally, the critical time $t = t_{cr}$, can be analytically calculated using

$$t_{cr} = -\frac{\alpha}{\beta} \ln \left( \frac{\gamma |\nabla f|_{max} - \beta \cot \theta}{(\beta + \gamma) |\nabla f|_{max}} \right) \hspace{1cm} (4.13)$$

For times greater than the critical time ($t_{cr} \leq t$), the air–water interface is detached from the edges of the pore and slowly moves down as the entrapped air continues to dissolve. Substituting Eqs. 4.1 and 4.7 in Eq. 4.2 and integrating over the cross-section of the air–water interface, one obtains
\[ \frac{1}{\xi A} \iint F_t dS - \sigma \left[ (1 + F_y^2)F_{xx} + (1 + F_x^2)F_{yy} - 2F_x F_y F_{xy} \right] (1 + F_x^2 + F_y^2)^{-3/2} \quad (4.14) \]

\[ - \Pi \approx 0 \]

Since the shape of a detached interface remains invariant, we assume a solution for Eq. 4.14 in the form of

\[ F(x, y, t) = G(x, y) + \tau(t) \quad (4.15) \]

where \( G(x, y) \) is the critical profile as defined in Eq. 4.4. After substituting in Eq. 4.14 and integrating the result over the cross-sectional area, we obtain

\[ S \tau_t / (\xi A) \approx \kappa + \Pi \quad (4.16) \]

where \( \kappa \) is

\[ \kappa = \frac{\sigma}{S} \iint \left[ (1 + G_y^2)G_{xx} + (1 + G_x^2)g_{yy} - 2G_x G_y G_{xy} \right] (1 + G_x^2 + G_y^2)^{-3/2} dS \quad (4.17) \]

The initial condition for this equation is \( \tau(t = t_{cr}) = 0 \). Therefore \( \tau \) can easily be calculated as shown in Eq. 4.18 in the interval \( t_{cr} < t < t_{f1} \).

In summary, the transient shape of the air–water interface in Regime I can be obtained as

\[ F(x, y, t) = \begin{cases} \left[ (1 + \gamma / \beta) e^{-\beta t / \alpha} - \gamma / \beta \right] f(x, y) & 0 < t < t_{cr} \\ G(x, y) + (\kappa + \Pi) \xi A (t - t_{cr}) / S & t_{cr} < t < t_{f1} \end{cases} \quad (4.18) \]

The failure time \( t_{f1} \) is reached when \( F(x^*, y^*, t_{f1}) = -h \), where \( (x^*, y^*) \) is the location of the minimum height of the critical profile \( G(x, y) \). From Eq. 4.18, the failure time can be calculated as

\[ t_{f1} = t_{cr} - S[h + G(x^*, y^*)] / (\kappa + \Pi) \xi A \quad (4.19) \]

where \( (x^*, y^*) \) is the coordinates of the minimum height of the critical interface and it is the center point of the critical profile in the case of axi-symmetric (or symmetric) cross-sections.
4.2.3 Failure Time in Regime II

In Regime II, the hydrostatic pressure is greater than the critical pressure \( P_g > P_{cr} \) and the interface at \( t = 0 \) is detached from the edges. With an appropriate coordinate systems, the initial interface can be described by \( F = G(x, y) \), which can be calculated from Eq. 4.4 (the balance of forces over the interface at a distance \( h_0 \) from the edges at \( t = 0 \)). Eq. 4.2 indicates that the pressure of the entrapped air remains constant during air dissolution in Regime II, \( P_{bub} = P_{bub}\vert_{t=0} \). Assuming the entrapped air (ideal-gas) to be in thermal equilibrium with water,

\[
h_0 = \left(1 - P_\infty / (P_g + P_\infty - \kappa)\right)h + \frac{1}{S}\int GdS \tag{4.20}
\]

Substituting Eqs. 4.1, and 4.7 into Eq. 4.2, we obtain

\[
\frac{1}{\bar{\xi}A}\int F_t dS - \sigma \left[ (1 + F_y^2)F_{xx} + (1 + F_x^2)F_{yy} - 2F_xF_yF_{xy} \right] (1 + F_x^2 + F_y^2)^{-3/2} - \Pi \approx 0 \tag{4.21}
\]

With the procedure described in Sec. 4.2.2, the transient interface profile becomes

\[
F(x, y, t) = G(x, y) - h_0 + \Im(t) \tag{4.22}
\]

Substituting into Eq. 4.21, with \( \Im(t = 0) = 0 \), the air–water interface equation is

\[
F(x, y, t) = G(x, y) - h_0 + (\kappa + \Pi)\bar{\xi}At / S \tag{4.23}
\]

The failure time \( t_{f2} \) is reached when \( F(x^*, y^*, t_{f2}) = -h \) and can be calculated using

\[
t_{f2} = S[h_0 - h - G(x^*, y^*)] / ((\kappa + \Pi)\bar{\xi}A) \tag{4.24}
\]

With the critical pressure (and its corresponding profile \( G(x, y) \)) numerically obtained from Eq. 4.4, one can use Eq. 4.24 to predict the lifetime of the entrapped air. The general formulations derived here in Sec. 4.2 can predict the critical pressure and longevity of SHP surfaces comprised of pores or posts with arbitrary round cross-sections (not necessarily circular). For the special case
of circular pores, we obtain easy-to-use analytical expressions for critical pressure and longevity calculations, as will be discussed in the next section.

4.3 Superhydrophobic Surfaces Made of Circular Pores

For the special case of circular pores, the air–water interface conforms to the shape of a spherical cap. Therefore, the general PDE given for critical pressure calculation in Sec. 4.2, Eq. 4.4, can significantly be simplified to yield an analytical solution (Sec. 4.3.1). Also the PDE presented in Eq. 4.8, for the transient air–water interface (needed for longevity calculation), can be reduced to an easy-to-solve Ordinary Differential Equation (ODE) (Sec. 4.3.2). Unless otherwise specified, default parameters considered in this chapter are \( h = 30 \mu m \), \( \theta = 115^\circ \), and \( D = 112.8 \mu m \). Hydrostatic pressures corresponding to 0.4 and 3.0 m of water are considered for the calculations conducted in Regime I and Regime II, respectively. Note that these parameters are chosen arbitrarily.

4.3.1 Critical Pressure and Critical Air–Water Interface for Circular Pores

The air–water interface takes the shape of a spherical cap inside a circular pore. Therefore, the critical interface can be described as

\[
G = \sqrt{R_{cr}^2 - D^2/4} - \sqrt{R_{cr}^2 - x^2 - y^2} 
\]

(4.25)

where \( R_{cr} \) is the critical radius of curvature of the interface. For a circular pore, capillary pressure can be defined as \( P_{cap} = -2\sigma \cos \theta / D \), and so the critical radius can be obtained from Eq. 4.1 as

\[
R_{cr} = -D/(2 \cos \theta) 
\]

(4.26)
Using Eqs. 4.25 and 4.26, the critical air–water interface, and its corresponding pressure, can explicitly be determined using Eq. 4.4.

\[
P_{cr} = \frac{2\sigma}{R_{cr}} - P_{\infty} \left( 1 - \sqrt{\frac{v_0}{\frac{\pi D^2}{4} - \frac{D^2}{4} + \frac{2\pi}{3} \left[ (\frac{R_{cr}^2}{D^2/4})^{3/2} - R_{cr}^3 \right]}} \right)
\]

(4.27)

Fig. 4.2 shows the effects of pore diameter \(D\) on the critical pressure of a SHP surface calculated using the above analytical equation. For comparison, critical pressure is also calculated numerically by solving Eq. 4.4. This figure also presents the effects of pore depth on the critical pressure. It can be seen that shallow pores exhibit better resistance against elevated pressures. This is because the ratio of the volume of the air displaced by the sagging interface to the volume of the pore is greater when the pores are shallow causing higher compression pressures. We have also calculated the minimum pore depth \(h_{min}\)—the depth below which failure occurs before the interface reaches the critical profile—for circular pores with different diameters (the inset in Fig. 4.2).

**Fig. 4.2:** A compression between the critical pressure predictions obtained from a numerical solution of the PDE in Eq. 4.4 and the analytical calculation using Eq. 4.27 for different diameter pore diameters with \(\theta = 115^\circ\). The minimum pore height \(h_{min}\) is shown in the inset.
It is interesting to note that for longer pores critical pressure becomes almost independent of the pore diameter (determined mostly from the balance between the capillary pressure and hydrostatic pressure). This can easily be seen in Eq. 4.27 where the contribution of the second term becomes almost negligible for long pores. Note in Fig. 4.2 that $h_{\text{min}}$ is independent of the pore depth as it only depends on the shape of the critical profile.

4.3.2 Failure Time

For longevity calculations, the air–water interface for both regimes can generally be written as

$$F(x, y, t) = \sqrt{R^2 - D^2/4} - \sqrt{R^2 - x^2 - y^2} + h_0$$  \hspace{1cm} (4.28)

where $R = R(t)$ and $h_0$ is the depth at which the initial interface reaches an equilibrium with the hydrostatic pressure at $t = 0$. This depth can be calculated using Eq. 4.20, and is zero in Regime I. Eq. 4.28 can be used to convert the PDE given in Eq. 4.5 for the initial air–water interface ($f$ at $t = 0$), to a simple algebraic equation,

$$\frac{2\sigma}{R_0} - p_g - P_\infty \left( 1 - v_0 / \left[ v_0 + S \sqrt{R_0^2 - D^2 / 4} + \frac{2\pi}{3} \left[ \left( R_0^2 - D^2 / 4 \right)^{3/2} - R_0^3 \right] \right] \right) = 0$$  \hspace{1cm} (4.29)

where $R(t = 0) = R_0$. Moreover, using Eq. 4.28, one can reduce the PDE in Eq. 4.8 to a simpler equation in which the space and time dependence are decoupled,

$$\frac{2\sigma}{R} - \frac{1}{\xi A} \left( R S / \sqrt{R^2 - D^2 / 4} - A \right) \frac{dR}{dt} + \Pi \approx 0$$  \hspace{1cm} (4.30)

Eq. 4.30 is an ODE which can easily be solved via a simple Runge–Kutta method for the radius of curvature of the interface from $R(0) = R_0$ until the critical time $R(t_{cr}) = R_{cr}$. For times greater than the critical time, one can simplify Eq. 4.14 with the critical interface profile known from Eqs. 4.25–4.26, where $\kappa$ is $\frac{2\sigma}{R_{cr}}$. Therefore, the interface profile and longevity can easily be calculated in
Regime I using Eq. 4.18 and Eqs. 4.25–4.26. In Regime II, the critical interface is the same as that represented by Eqs. 4.25–4.26. The equation for $h_0$, (Eq. 4.20) can now be simplified to

$$
h_0 = \left(1 - \frac{P_\infty}{P_g + P_\infty - \kappa}\right) h + \sqrt{R_{cr}^2 - D^2/4} + \frac{2\pi}{3S} \left[ (R_{cr}^2 - D^2/4)^{3/2} - R_{cr}^3 \right] \quad (4.31)
$$

With $\kappa = \frac{2\sigma}{R_{cr}}$ the interface and longevity can be obtained using the method of Sec. 4.2.3.

The air–water interface inside a circular pore having a diameter of $D = 112.8 \mu m$, a depth of $h = 30 \mu m$, and a contact angle of $\theta = 115^\circ$ is studied in Fig. 4.3. For these calculations, our interface tracking process started by solving Eq. 4.29 for the initial profile $R(t = 0) = R_0$. Then, the transient air–water interface was obtained by solving Eq. 4.30 until the interface slope at the wall reached the Young–Laplace Slope (YLS). Note that in deriving the formulations presented in this section, we did not use the method of Separation of Variables as described in Eq. 4.9. Now Eq. 4.12 can now be used with

$$
\alpha = \frac{S}{\xi A(t = 0)} \left( S \sqrt{R_0^2 - \frac{D^2}{4}} + \frac{2\pi}{3} \left[ \left( R_0^2 - \frac{D^2}{4} \right)^{3/2} - R_0^3 \right] \right) \quad (4.32a)
$$

$$
\beta = -\frac{2S\sigma}{R_0} \quad (4.32b)
$$
Fig. 4.3: A compression between the longevity predictions obtained from a numerical solution of the ODE in Eq. 4.30 and the analytical calculation using Eq. 4.32 for SHP surfaces made up of pores with different diameters is given in (a) and under different hydrostatic pressures in (b) in Regime I ($t_{f1}$) and Regime II ($t_{f2}$). The air–water interface under a hydrostatic pressure of 0.4 m of water is shown in the inset of (b) for $t = 0$, $t = 3.9$ min, $t = 10$ min, and $t = 19.4$ min from top-left to bottom-right, respectively. The instantaneous pressure of the air entrapped in the pore $P_{pub}$ is shown for two different depths of water in (c) and two different pore diameters in (d).

With this information, the critical and failure times in Regime I can be calculated using Eqs. 4.13 and 4.19, with the maximum slope at the boundary $|\nabla f|_{\text{max}} = \frac{D}{2\sqrt{R_0^2-D^2/4}}$. Longevity of the entrapped air in Regime I $t_{f1}$ and Regime II $t_{f2}$ are shown for circular pores with different diameters in Fig. 4.3a under two hydrostatic pressures of $H = 0.4$ m and $H = 3.0$ m, respectively.
(the longevity calculations in Regime II follow the same analytical procedure as described earlier using Eq. 4.32). It can be seen that longevity decreases with increasing the pore diameter. In this figure, the longevity predictions obtained from analytical solution using Eq. 4.32 are compared with those obtained from the ODE of Eq. 4.30, showing excellent agreement. Fig. 4.3b shows that longevity decreases with increasing the hydrostatic pressure. This is in agreement with the experimental observation reported for square pores (35). It again can be seen that longevity predictions obtained from analytical solution in Eq. 4.32 are in excellent agreement with those obtained from the simple ODE given in Eq. 4.30. For this reason, we use Eq. 4.30 later in Sec. 4.5 when presenting our equivalent pore diameter method for a SHP surface made of ordered or random posts. The inset in this figure shows the air–water interface at four different moments of time under a hydrostatic pressure of 0.4 m of water. The effects of hydrostatic pressure and pore diameter on longevity (Figs. 4.3a and 4.3b), can be explained by monitoring the pressure inside the entrapped bubble $P_{bub}$ over time. We therefore considered the air bubbles inside two pores with diameters of 112.8 µm and 56.4 µm at a depth 0.4 m in Fig. 4.3c, and inside a pore with a diameter of 112.8 µm but under two different hydrostatic pressures of 0.4 and 3.0 m in Fig. 4.3d. It can be seen that $P_{bub}$ decreases with time until $t = t_{cr}$ (e.g., 2 min for the pore with $D = 112.8$ µm at $H=0.4$ m). Beyond the critical time, the bubble pressure remains constant equal to the sum of the ambient and hydrostatic pressures minus the capillary pressure at the critical condition, if the surface is in Regime I. If the surface is in Regime II (e.g., at $H = 3.0$ m), the bubble pressure remains constant over time (see Fig. 4.3d when $H = 3.0$ m). Note that the rate of air dissolution in water (absolute value) is proportional to the bubble pressure. Therefore, one can expect that increasing the hydrostatic pressure from 0.4 m to 3.0 m to reduce the longevity of the surface.
Similarly, increasing the pore diameter increases the bubble pressure and so reduces the surface longevity.

4.4 Superhydrophobic Surfaces Made of Circular Posts

The formulations developed in Sec. 4.2 are used here to predict the critical pressure and longevity of SHP surfaces comprised of circular micro-posts arranged in ordered and random configurations. Note that the work presented in this chapter is the first to include the effects of air compression in calculating the critical pressure of SHP surface made of randomly distributed dissimilar posts. More importantly, the current chapter is the first to present a mathematical framework for predicting the longevity of such surfaces.

4.4.1 Surfaces with Ordered Posts

We characterize surfaces made of micro-posts with their solid area fraction defined as \( \varphi = S/L^2 \) where \( L \) is the length of the unit cell when posts are placed in ordered configurations. The solution domain is only a unit cell with symmetric boundary conditions not shown for the sake of brevity. Eq. 4.4 is numerically solved to obtain critical pressure values for SHP surfaces comprised of ordered posts with different solid area fractions (careful attention has been paid to ensure grid-independence). Here we considered posts with \( h = 9.5 \, \mu m \), diameter, \( d = 6.0 \, \mu m \), and two different contact angles of \( \theta = 103.5^\circ \) and \( 122.1^\circ \). These particular dimensions are chosen so that our results can be compared with the experimental data of Ref. (82). These authors have also reported theoretical predictions for the critical pressure of their surfaces using the equations of Ref. (29). Perfect agreement between our numerical results and those reported in Ref. (82) can be seen in Fig. 4.4a. When compared to the experimental data, our theoretical predictions (and obviously
those of Ref. (29)) show good agreement for solid area fractions between 0.2 and 0.3. Outside this range however, the theoretical predictions and experimental data deviate from one another by up to about 35%. To better understand the reason for the mismatch, one should note that our computational method is expected to slightly under-predict the true critical pressure. This is because critical pressure in our work is defined as the pressure at which the local slope of the air–water interface at some point along the contact-line reaches the YLS (the pressure needed for a local interface detachment). It is not impossible for a partially-detached interface to withstand hydrostatic pressures somewhat greater than this pressure until all the other points along the contact-line reach the critical slope. However, in the absence of more detailed quantitative information regarding partially-detached interfaces in the literature, we proceed with the conservative assumption that the entire interface detaches from the post once a local detachment takes place. We conjecture that the mismatch between the theoretical predictions and experimental data at solid area fractions less than 0.2 (see Fig. 4.4a) is probably due to experimental errors. Nevertheless, given the complexity of the problem from both the computational and experimental viewpoints, the general agreement shown in Fig. 4.4a is appreciable. It is also interesting to note the interplay between the contribution of air compression (dominant at low solid area fractions) and capillary pressure (dominant at high solid area fractions) in balancing the hydrostatic pressure in Fig. 4.4a (see also Fig. 4.2). The minimum post height required to avoid premature $h_{min}$ is calculated and shown in Fig. 4.4b for two different Young–Laplace contact angles. As expected, $h_{min}$ is greater for more hydrophobic posts. In other words, when the posts are more hydrophobic they should be taller to take full advantage of the hydrophobicity of the surface. It is also interesting to note that posts which are closely packed can be shorter than those farther away from each other.
Our critical pressure predictions obtained from a numerical solution of Eq. 4.4 for SHP surfaces comprised of circular posts with ordered arrangements are compared with those of Lobaton and Salamon (9) and the experimental data of Forsberg et al. (10) in (a). The minimum post height is shown in (b) for different solid area fractions.

The evolution of the air–water interface between posts is studied in Fig. 4.5. The inset in this figure shows the air–water interface for a when $\varphi = 0.08$ at $t = 0$, $t = 0.24$ min (critical time), $t = 1.30$ min, and $t = 2.66$ min (failure time) under a hydrostatic pressure of 0.6 m of water. It is interesting to note the similarity between the instantaneous shape of the air–water interface shown in this figure and those imaged during the evaporation of a droplet placed on a SHP surface made of ordered posts (the sagging and impalement of the air–water interface underneath an evaporating droplet follows the same physics—the Laplace pressure increases as the droplet evaporates and forces the interface into the open space between the posts) (80). Effects of posts’ packing fraction...
and the hydrostatic pressure on longevity are shown in Fig. 4.5b. It can be seen that longevity increases with $\varphi$ but decreases as hydrostatic pressure increases. The reason for this is that bubble pressure increases with hydrostatic pressure or when the posts are placed far from one another (due to a decrease in the total capillary force per unit area). Note that surfaces with $\varphi = 0.08$ and $\varphi = 0.3$ shown here have almost identical critical pressure (about 16 kPa, from Fig. 4.4a) although their longevity values are different.

![Fig. 4.5: Effects of hydrostatic pressure and solid area fraction on longevity of the entrapped air on a SHP surface made of ordered posts are shown in (a) and (b), respectively. The inset in (a) shows the air–water interface in the space between circular posts with $\varphi = 0.08$ under a hydrostatic pressure of 0.6 m of water at $t = 0$, $t = t_{cr} = 0.24$ min (critical time $t_{cr}$), $t = 1.3$ min, and $t = t_f = 2.66$ min.](image)

4.4.2 Surfaces with Randomly Distributed Posts

With the random arrangement not having a unit-cell, our computational domain should now encompass a group of posts. These posts are randomly distributed in a square domain with periodic
boundary conditions and dimensions much larger than the average spacing between the posts. To reduce statistical uncertainty, the results were averaged over an ensemble of five statistically identical surfaces. As mentioned earlier, in the absence of more detailed information on the stability of a partially-detached interface, we have assumed that the entire air–water interface detaches from all the posts once a local detachment on one of the posts is occurred. The detached interface will then move downward as the entrapped air dissolves in water (Regime I) or if more penetration is needed to balance the hydrostatic pressure (Regime II). Grid-independence for the critical pressure calculations was guaranteed by using 30 grid-points per post perimeter (the analysis is eliminated for brevity). Note that grid-independence for the longevity predictions is automatically guaranteed once the critical pressure predictions are grid-independent. This is because the accuracy of the longevity calculations depends only on the accuracy of the interface profile calculations (see Eq. 4.10), which is obtained from solving Eq. 4.4 for critical pressure. Fig. 4.6 compares the critical pressure values obtained for SHP surfaces with random and ordered post arrangements at different solid area fractions ranging from $\varphi = 0.15$ to $\varphi = 0.4$. As expected, critical pressure is lower when the posts are arranged randomly. Note again that the critical pressures in this chapter are obtained by including the compression forces generated by the entrapped air in the balance of forces acting on the meniscus, and is therefore different from those presented in Ref. (8) in which the hydrostatic pressure was solely balanced by the capillary pressure under the assumption that the posts are so tall that air compression is negligible. When capillary forces are the only forces balancing the hydrostatic pressure, critical pressure monotonically increases with increasing solid area fraction.
Fig. 4.6: Critical pressure vs. solid area fraction obtained for SHP surfaces with ordered and random post distributions.

Figs. 4.7a and 4.7b show the effects of solid area fraction and pressure on the longevity of a SHP surface comprised of randomly distributed posts, respectively. The inset in this Fig. 4.7a shows the air–water interface between the posts with a solid area fraction of $\phi = 0.15$ at $t = 0$, $t = 0.04$ min (critical time), $t = 0.60$ min, and $t = 1.19$ min (failure time) under a hydrostatic pressure of 1.0 m of water. As expected, longevity increases with solid area fraction but decreases with increasing the hydrostatic pressure. A comparison between longevity values obtained for SHP surfaces with ordered and random posts at different hydrostatic pressures is given in Fig. 4.8 for a solid area fraction of $\phi = 0.15$. It can be seen that random post arrangement can affect the longevity of a SHP surface. Note that the surface with random posts operates in the Regime II for the entire range of hydrostatic pressures considered in this figure (i.e., from 1 to 2 m of water). However, the surface with ordered posts operates in Regime II only when the hydrostatic pressure is above 1.5 m of water.
Fig. 4.7: Effects of hydrostatic pressure and solid area fraction on longevity of the entrapped air on a SHP surface comprised of random posts is given in (a) and (b), respectively. The inset in (a) shows the air–water interface in the space between randomly distributed circular posts with $\varphi = 0.15$ under a hydrostatic pressure of 1.0 m of water in at $t = 0$, $t = t_{cr} = 0.02$ min (critical time $t_{cr}$), $t = 0.6$ min, and $t = t_f = 1.19$ min.

Fig. 4.8: A comparison between the longevity values obtained for SHP surfaces with order and random post distributions.
4.5 Equivalent Pore Diameters for Surface Made of Posts

As discussed earlier, predicting the critical pressure and longevity of a SHP surface requires a complicated integro-partial differential equation to be solved numerically. This equation however, can significantly be simplified if the surface is made of circular pores (see analytical formulations in Sec. 4.3). Therefore, it is highly desirable to define an equivalent circular pore that can resemble the porous structure of a SHP surface made of posts with arbitrary arrangements. The first study to define equivalent pore diameters for estimating the critical pressure of SHP surfaces comprised of ordered posts is reported in Ref. (86). In the current chapter, we define equivalent pore diameters for both the critical pressure and longevity predictions and for both the ordered and random post arrangements. As mentioned before, capillary pressure and air compression are the two forces balancing the hydrostatic pressure acting on an air–water interface. A geometry-based equivalent pore diameter representing the contribution of gas compression in the balance of forces can be defined using the maximum distance between the posts in a unit cell (see Fig. 4.9a),

\[ D_{g}^{eq} = \left( \sqrt{\frac{\pi}{2\varphi}} - 1 \right)d \]  (4.33)

The concept of hydraulic diameter was used in Ref. (86) to define a second pore diameter to represent the capillary forces acting on the air–water interface,

\[ D_{cap}^{eq} = (1 - \varphi)d/\varphi \]  (4.34)

The definition for \( D_{g}^{eq} \) was then modified in Ref. (86) to read as

\[ D_{g}^{eq*} = \frac{\varphi}{1 - \varphi} \frac{(D_{g}^{eq})^3}{2d^2} = \frac{D_{cap}^{eq}}{2} \left( \frac{D_{g}^{eq}}{d} \right)^3 \]  (4.35)

The authors in Ref. (86) neither discussed how they arrived at Eq. 4.35 nor presented a reason as to why such modifications were justified. We therefore, use only \( D_{g}^{eq} \) and \( D_{cap}^{eq} \) in the formulations...
given here. With the above equivalent diameters representing the capillary and air compression, the critical pressure (Eq. 4.27) can be written as

$$P_{cr} = -4\sigma \cos \theta / D_{cap}^{eq} - P_\infty (1 - 1/(1 + D_g^{eq} [2 - 3 \sin \theta + \sin^3 \theta]) / (6h\cos^3 \theta))$$  \hspace{1cm} (4.36)
given for geometric equivalent pore $D_g^{eq}$ (current study) and $D_g^{eq*}$ (Ref. (86)). Note that both equivalent pore diameter formulations provide reasonable predictions. For longevity calculations, we have developed an approximate method that does not require solving a PDE. In this method, we treat the initial air–water interface between the posts in a unit cell as the initial interface in a circular pore. We then calculate the angle $\theta_0$ between the interface and the walls of the pore (instead of calculating the initial radius of curvature $R_0$ as in Secs. 4.2 and 4.3). Eq. 4.29 can therefore be modified as

$$-4\sigma \cos \theta_0 / D_{cap}^{eq} - P_g$$

$$- P_w[1 - 1/(1 + D_g^{eq}[2 - 3 \sin \theta_0 + \sin^3 \theta_0])/(6 \cos^3 \theta_0)] = 0$$

(4.37)

From Sec. 4.2, parameters $\beta^{eq} = -4\sigma \cos \theta_0 / D_{cap}^{eq}$, $\kappa^{eq} = -4\sigma \cos \theta / D_{cap}^{eq}$ and $R_{cr}^{eq} = -D_{cap}^{eq} / (2 \cos \theta)$ and $\alpha^{eq}$ can now be written as

$$\alpha^{eq} = S^2(h + D_g^{eq}[2 - 3 \sin \theta_0 + \sin^3 \theta_0])/(6 \cos^3 \theta_0))/(\xi A_0)$$

(4.38)

With the maximum initial slope of the interface at the wall given as $|\nabla f|_{max} = |\cot \theta_0|$. In this method, we do not obtain an explicit equation for the shape of the air–water interface. Therefore, we used the projected area of interface surface (i.e., $A_0$, or $A_{cr}$) in our calculations as the deflection of the initial air–water interface is not generally significant,

$$A_0 = (1/\varphi - 1)\pi d^2/4$$

(4.39a)

To predict the surface area of the critical air–water interface, we assumed that the critical-to-initial surface area ratio for the interface between posts is the same as the critical-to-initial surface area ratio for the interface inside its equivalent pore (with a diameter $D_g^{eq}$). Hence,
\[ A_{cr} = 8A_0 R_{cr}^{eq} \left[ R_{cr}^{eq} - \sqrt{\left[ R_{cr}^{eq} \right]^2 - \left[ D_g^{eq} / 2 \right]^2} / \left[ D_g^{eq} \right]^2 \right] \] (4.39b)

Note that the critical radius \( R_{cr}^{eq} \) is also used to estimate the coordinate of the lowest point on the interface (the point that makes the first contact with the bottom). The critical and failure times can now be calculated as

\[ t_{cr} = -\frac{\alpha^{eq}}{\beta^{eq}} \ln \left( \frac{\gamma |\nabla f|_{max} - \beta^{eq} \cot \theta}{(\beta^{eq} + \gamma) |\nabla f|_{max}} \right) \] (4.40a)

\[ t_{f1} = t_{cr} - S \left[ h + \sqrt{\left( R_{cr}^{eq} \right)^2 - \left[ D_g^{eq} / 2 \right]^2 - R_{cr}^{eq}} / \left[ (\kappa^{eq} + \Pi) \xi A_{cr} \right] \right. \] (4.40b)

Fig. 4.9b shows a comparison between the longevity values obtained for SHP surfaces made of ordered posts with different solid area fractions and under different hydrostatic pressures using the equivalent pore diameter method (Eq. 4.40) and the numerical solution of the PDE given in Eq. 4.10 (see Fig. 4.5). It can be seen that the equivalent pore diameter method produces reasonable predictions while being significantly less complicated mathematically. Note that, the predictions of the equivalent pore diameter method tend to become less accurate when the solid area fraction of the surface is high especially at low hydrostatic pressures. This is due perhaps to the increasing mismatch between the shape of a air–water interface inside a pore and that formed between four closely packed posts. Nonetheless, with the equivalent pore diameter method one can easily estimate the longevity of a SHP surface without actually solving a PDE.

The equivalent pore diameters discussed here can also be utilized for critical pressure and longevity estimation when the posts are distributed randomly. For such calculations, we produced the so-called Voronoi diagram for each surface (see the inset in Fig 4.10a). In a Voronoi diagram, each post is placed in a cell with its boundaries defined as the locations of the points on the surface that
are equidistant from the two nearest posts \(11\). Voronoi diagram is used here to determine the local minimum solid area fraction, i.e., \(\varphi_{\text{min}}\), for calculating the capillary pore diameter, i.e.,

\[
D_{\text{cap}}^{eq} = (1 - \varphi_{\text{min}})d / \varphi_{\text{min}}
\]

(4.41)

For the geometric pore diameter \(D_{g}^{eq}\) we used Eq. 4.33. The remainder of the procedure is similar to that described earlier for surfaces with ordered posts. Figs. 4.10a and 10b show a comparison between critical pressure and longevity values obtained from solving the PDEs given in Sec. 4.4 (Eq. 4.4 for critical pressure and Eq. 4.10 for longevity) and those from the simple equivalent pore diameter calculations of this section. As mentioned before, the equivalent pore diameter method becomes less accurate in the case of large solid area fractions under low pressures.

Fig. 4.10: Critical pressure predictions obtained from our equivalent pore diameter method (Eq. 4.41) are compared in (a) with those obtained from solving the PDE in Eq. 4.4. An example Voronoi diagram with \(\varphi = 0.25\) is given in
the inset in (a). Longevity values obtained from solving PDEs in Eq. 4.5 and Eq. 4.10 for a SHP surface with \( \phi = 0.15 \) are compared with those of our equivalent diameter method (Eq. 4.41) in (b).

4.6 Conclusions

The work presented here is a generalized theory that allows one to predict the mechanical stability and the service life (longevity) of SHP surfaces when used for underwater applications. The formulations presented are general enough to handle surfaces comprised of pores or posts of any arbitrary cross-sections, as long as they are round (i.e., do not have sharp corners). Moreover, our formulations can significantly be simplified to algebraic equations or ODEs if the surface is comprised of circular pores. On this basis, an equivalent pore diameter method is developed to predict the stability and longevity of surfaces with ordered or random posts.

Our work quantifies the contributions of the capillary forces and the forces generated by the entrapped air in balancing the hydrostatic pressure. It is shown that the air compression forces are more significant when the pores are shallow and wide whereas the capillary forces are dominant for long and narrow pores (or posts). This leads to a U-shaped behavior for the mechanical stability of a SHP surface in terms of pore diameter (for surfaces with pores) or solid area fraction (for surfaces with posts). Surface longevity is found to drastically decrease with increasing the hydrostatic pressure. Increasing the pore diameter or decreasing the solid area fraction is found to also decrease the longevity of the surface. Comparing surfaces with ordered and random posts, it was found that randomness in the posts’ spatial position decreases both the mechanical stability and the longevity of the surface.
Chapter 5. Wetting States of Superhydrophobic Surfaces Made of Polygonal Pores or Posts

5.1 Introduction

When a superhydrophobic (SHP) surface comes into contact with water (e.g., when it is submerged), it may entrap some air in its pores, resulting in the formation of the so-called Cassie state, in which the contact area between the solid material and water is reduced. A surface in the Cassie state may exhibit a reduced skin-friction drag if exposed to a moving body of water (7). However, the Cassie state may become unstable under elevated pressures, causing the surface to transition to the so-called Wenzel (fully-wetted) state. The pressure at which such a transition takes place is generally referred to as the critical pressure, and it has been investigated in many previous studies (9,10,12,35,57,92,95). In fact, an SHP surface may experience a series of transition states in between the Cassie and Wenzel states, depending on the hydrostatic/hydrodynamic pressure applied to the surface and its microscale geometry (17,69,77,80,86,96). Therefore, the solid–water contact area (and so the skin-friction drag) may depend on the shape and position of the air–water interface between the peaks and valleys of the surface at each transition state (see for instance Refs. (7,97)). An example of how skin-friction drag over an SHP surface comprised of round asperities may vary with hydrostatic pressure is given in the work of Refs. (37,98,99). Conducting a similar study for surfaces that have sharp asperities is more challenging, as the air–water interface tends to pin itself to the sharp corners of these asperities. A pinned air–water interface often experiences a partial de-depinning process when the hydrostatic pressure is increasing. The de-pinning process can be difficult to predict accurately as it depends strongly on the surface
microscale geometry. This, in turn, makes it challenging to predict the solid–water contact area (wetted area) and the skin-friction drag of the surface. The current research is devised to shed some light on the behavior of SHP surfaces that promote partial de-pinning. For the sake of simplicity, the study is limited to SHP surfaces comprised of polygonal posts or pores (sharp asperities with ordered spatial distributions). Similar to many previous studies, a force balance method, as it applies to an air–water interface in equilibrium, is considered in the present work, but the boundary conditions are modified here to simulate additional critical pressures and air–water interfaces as will be discussed later (68,86,92,97,100).

As will be discussed later, critical hydrostatic pressure and wetted area will be calculated in this chapter for SHP surfaces made of polygonal pores or posts, and the results will be discussed with respect to those reported for surfaces comprised of circular posts or pores with comparable geometric properties. The remainder of this chapter is organized as follows. Section 5.2 presents our force balance formulations for surfaces comprised of polygonal asperities. These equations are then solved for surfaces with different pore (Sec. 5.3.1) and post (Sec. 5.3.2) shapes to produce predictive correlations for the surface critical pressures and wetted area. Detailed comparison between the predictions of the above correlations and previously-reported data from literature and our capillary rise experiment is given in Sec. 5.4. This is followed by our conclusions in Sec. 5.5.

5.2 Formulations

As previously stated, critical pressure is generally assumed to be the pressure at which an SHP surface starts transitioning from the Cassie state to the fully-wetted state. However, depending on
the hydrostatic pressure and surface geometry, an SHP surface may experience a series of transition states in between these two extreme states. To better formulate this problem, we start by defining the critical capillary pressure as the highest capillary pressure that an air–water interface can withstand before losing its mechanical equilibrium. If the air entrapped below the air–water interface becomes pressurized due to air–water interface deflection, then the air compression and capillary forces work together to balance the hydrostatic pressure above the air–water interface. In this case, we use critical hydrostatic pressure in describing the air–water interface stability. We define the first critical hydrostatic pressure as the hydrostatic pressure at which at least one point along the air–water–solid contact line reaches the Young–Laplace contact angle, and denote this pressure with $P_{cr}^{(1)}$ in this work. Similarly, the hydrostatic pressure at which all points along the air–water–solid contact line reach Young–Laplace contact angle is referred to as the second critical hydrostatic pressure and is denoted with $P_{cr}^{(2)}$ (see Ref. (97) for additional information). The transition states corresponding to hydrostatic pressures between $P_{cr}^{(1)}$ and $P_{cr}^{(2)}$ are those for which the air–water interface is partially de-pinned (for axi-symmetric geometries e.g., a circular pore, the two critical hydrostatic pressures are identical). It is worth mentioning that wetting transition may have different meanings in different applications. In the context of drag reduction, the onset of transition from the Cassie state is the moment when additional frictional areas start to come into contact with water. Therefore, the first critical pressure is considered to be the pressure at which de-pinning starts to occur at some point along the contact line. Pressures greater than the first critical pressure bring additional frictional walls into contact with water as the air–water interface continues to deform and de-pin from the sharp corners of the pores/posts. The air–water interface is completely de-pinned and is about to move downward as a rigid surface at the second critical pressure. Note that predicting the shape of the air–water interface at pressures between $P_{cr}^{(1)}$ and
is mathematically difficult and so is not included in the current study. Also, note that the
dissolution of the entrapped air into the ambient water is not included in the current work. This is
because the air dissolution problem (the surface longevity problem) has been formulated and
discussed in our previous studies, and it can easily be combined to the findings of the present
chapter to provide time-dependent predictions for the wetted area a surface composed on polygonal
pores or posts (13).

The volume of the air entrapped under a flat air–water interface (at the ambient pressure $P_\infty$) inside
a pore with a cross-sectional area of $A$ can be written as $v_\infty = Ah$ where $h$ is the pore height. Note
that the same equation can be used to describe the volume of the air entrapped under the air–water
interface formed between four posts as shown in Fig. 5.1. Generally, the balance of forces can be
written as (13)

$$P = \Psi - P_\infty \left[1 - v_\infty/(v_\infty + v)\right]$$

(5.1)

where $\Psi = \sigma \nabla \cdot \hat{n}$ is the capillary pressure, and $v = \iint f dA$ is the volume above the air–water
interface displaced by water. In this equation, $f = z$ is a function describing the 3-D shape of the
air–water interface, $\hat{n} = (f_x, f_y, -1)/\sqrt{1 + f_x^2 + f_y^2}$ is the unit normal to the air–water interface
pointing outward of the bulk of the fluid, and $\sigma$ is the surface tension. Eq. 5.1 combines the two
pressures that counter the hydrostatic pressure over the air–water interface: the capillary
pressure $\Psi$ and the gage pressure of the entrapped air ($P_\infty [1 - v_\infty/(v_\infty + v)]$). This equation can
be used to determine $P_{cr}^{(1)}$ (or $P_{cr}^{(2)}$), provided that the first critical air–water interface profile $f_{cr}^{(1)}$
(or the second critical air–water interface profile $f_{cr}^{(2)}$) is available. To find $f_{cr}^{(1)}$, we pin the air–
water interface to the solid boundaries $f_{SB} = 0$, and monitor the slope of the air–water interface as we increase the hydrostatic pressure. The first critical air–water interface profile will be the interface for which the slope of the air–water interface at one point along the air–water–solid contact line satisfies the condition

$$\cos \theta^{YL} = \hat{n} \cdot \hat{m}|_{max}$$

(5.2)

In this equation, $\hat{m}$ is the unit normal vector to the side of the pore (or post), which is directed towards the center of the void (see Fig. 5.1), and $\theta^{YL}$ is the Young–Laplace contact angle (8). The computational domain for an SHP surface comprised of polygonal posts is shown in Fig. 5.1b. We have considered periodic boundary conditions (PBCs) and symmetry boundary conditions ($\frac{\partial f}{\partial y} = 0$) along $x = \pm L/2$ (where $L$ is the center-to-center spacing between the posts) and $y = \pm L/2$, respectively. To find $f_{cr}^{(2)}$, we use Eq. 5.2 as the boundary condition at all points and monitor the position of the air–water–solid contact line along the length of the pore (or post). The second critical air–water interface will be the interface for which the condition $f_{SB} = 0$ is satisfied at least at one point along the air–water–solid contact line. Our results shows that, as pressure increases the de-pining process starts from the mid-points of the pore edges (i.e., the last points to de-pin are the corners). Note that this second critical air–water interface profile $f_{cr}^{(2)}$ has the same mathematical representation as the equilibrium air–water interface profile resulted from water rising vertically in a hydrophilic pore with an identical shape but an Young–Laplace contact angle supplementary to the Young–Laplace contact angle used here. In the absence of a universally applicable advancing contact angle, we have used the Young–Laplace contact angle in our calculations; advancing contact angle is not a material property (unlike the Young–Laplace contact
angle), and it varies depending on many factors that may not all be known ahead of time. Obviously, one can use an advancing contact angle in the equations presented here, if available.

The FlexPDE finite element code from PDE Solutions is used to solve Eq. 5.1. Careful attention has been paid to the grid-independence of the simulation results presented in the chapter. In particular, the number of computational cells near the sharp corners was found to be very important. To achieve grid convergence, the mesh size near the corners was reduced by a factor of 10 or greater. A grid-independent study is performed for the first critical capillary pressure for an SHP surface comprised of square posts with a width of \( w = 50 \mu m \), a height of \( h = 300 \mu m \), and a Young–Laplace contact angle of \( \theta^{YL} = 114^\circ \). The surface solid area fraction \( \varphi = \frac{S_w}{L^2} \) (where \( S_w \) is the post’s cross-sectional area) is taken to be \( \varphi = \frac{1}{9} \) so that the results of our critical capillary pressure calculation can be compared to those of Ref. (12). The sharp corners of the square posts are assumed to be round with a fillet having a very small radius of curvature of \( r_c/w = 0.02 \). Figure 5.2 shows how the first critical capillary pressure varies with the number of grid

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**Fig. 5.1:** Schematic of a superhydrophobic surface made of sharp-edged pentagonal posts packed in a square arrangement.
points $n$ used across the length of the fillet shown in the inset figure. The blue dotted line represents the first critical capillary pressure reported in Ref. (12) for this surface.

![Image](image_url)

**Fig. 5.2:** The effects of the number of grid points across the fillet arc length on the first critical capillary pressure of SHP surface comprised of square posts. The critical capillary pressure value reported in Ref. (12) is added to the figure (blue dashed line) for comparison.

Figures 5.3a and 5.3b show the first and second critical air–water interfaces, respectively, over a SHP surface comprised of square pores with the abovementioned dimensions and material properties. As can be seen in Fig. 5.3a, the first critical air–water interface is pinned to the pore edges at every point along the contact line. However, for the second critical air–water interface (Fig. 5.3b), the four corner points of the square pore are the last ones to satisfy Eq. 5.2. Likewise, the first and second critical air–water interfaces for square posts are shown in Figs. 5.3c and 5.3d, respectively. Again, it can be seen that the first critical air–water interface is pinned at every point, while the second critical air–water interface is only pinned at four points (the mid-point of each edge of the square posts). For these surfaces, the first and second critical capillary pressures were found to be $\psi_{cr}^{(1)} = 94.3$ and $\psi_{cr}^{(2)} = 296$ Pa, which are in good agreement with 93 and 296 Pa reported in Ref. (12). We also calculated the first and second critical hydrostatic pressures for each surface shown in Fig. 5.3 and added those results to the figure.
Fig. 5.3: The first and second critical air–water interfaces are shown for a surface comprised of square pores in (a) and (b), and for a surface comprised of square posts in (c) and (d), respectively. The calculations are performed for \( \omega = 50 \mu m \), \( h = 300 \mu m \), \( \theta^{yl} = 114^\circ \) and \( L = 150 \mu m \).

### 5.3 New Correlations for Critical Pressures

In the following subsections (Secs. 5.3.1, and 5.3.2), predictive correlations will be developed for the first and second critical hydrostatic pressures for an SHP surface in terms of its microscale geometry as well as the properties of the fluid over the surface in the form of

\[
P_{cr} = P_{cr}(\sigma, N, l, h, \varphi, \theta^{yl})
\]  

where \( N \) is the number of sides of the polygonal pore or post, \( l \) is a reference length (e.g., diameter of a circular pore), and \( \varphi \) is the solid area fraction of the surface (surfaces comprised of vertical posts). It should be noted that the study conducted in this work can only be used when the water flow over the surface is very slow as the effects of turbulence and/or flow fluctuations are not included in our equations (quasi-static equations). We used a Weber number of \( \text{We} = \frac{\rho v^2 d}{\sigma} < 1 \).
where $V$ is the creeping flow velocity along the air–water interface, $d$ is reference length, and $\rho$ is the fluid density and a Capillary number of $Ca = \frac{\tau}{\sigma/d} < 1$ (where $\tau$ is the shear stress along the air–water interface) to justify that the surfaces considered in our study can in fact accommodate a stable air–water interface (101,102).

5.3.1 Polygonal Pores

In this section, we introduce an analytical method to estimate the first and second critical hydrostatic pressures for SHP surfaces comprised of polygonal pores. To calculate $P_{cr}^{(1)}$, Eq. 5.1 should be solved. The air compression term in that equation can be determined by calculating the volume above the air–water interface as it penetrates into the pore (i.e., the double-integral term).

This volume is referred to here as the critical displaced volume and will hereafter be denoted as $\nu_{cr}$. The reason we use the displaced volume in our formulations is so that the pore height from the parameters listed in Eq. 5.3 is omitted. Using Eq. 5.1, the first critical hydrostatic pressure $P_{cr}^{(1)}$ can be expressed as

$$P_{cr}^{(1)} = \psi_{cr}^{(1)} - P_{\infty} \left[1 - \frac{\nu_{\infty}}{\psi_{\infty} + \nu_{cr}^{(1)}}\right]$$

(5.4)

where $\psi_{cr}^{(1)}$ and $\nu_{cr}^{(1)}$ are the first critical capillary pressure and critical displaced volume, respectively. The second critical capillary pressure can be obtained by simply changing the superscript (1) to (2) in Eq. 5.4. In our previous work, the critical capillary pressure and critical displaced volume were formulated for an SHP surface comprised of circular pores in terms of the parameters given in Eq. 5.3:
where $R_{cr} = -d/(2 \cos \theta^{YL})$ and $d$ is the diameter of the circular pore. As mentioned before, the two critical hydrostatic pressures are the same for a circular pore (i.e., $\Psi_{cr}^{(1),c|ir} = \Psi_{cr}^{(2),c|ir}$, and $\nu_{cr}^{(1)} = \nu_{cr}^{(2)}$). For an SHP surface comprised of cylindrical pores having a diameter of 50 µm, a height of 40 µm, and a Young–Laplace contact angle of 120°, Ref. (26) reported critical hydrostatic pressures ranging from 12 to 15 kPa obtained via confocal microscopy. Using Eqs. 5.4 and 5.5, we obtain a critical hydrostatic pressure of $P_{cr}^{(1),c|ir} = P_{cr}^{(2),c|ir} = 12.5$ kPa for this surface which is in good agreement with the results of the experiment conducted in Ref. (26).

The first critical capillary pressure and critical displaced volume for polygonal pores, $\Psi_{cr}^{(1)}$ and $\nu_{cr}^{(1)}$, are non-dimensionalized here using their corresponding values obtained for a circular pore with identical cross-sectional areas, $\Psi_{cr}^{(1),c|ir}$ and $\nu_{cr}^{(1),c|ir}$. Additionally, the diameter of the circular pores $d$ is taken here as a reference dimension in Eq. 5.3. For a circular pore, it can be seen from Eq. 5.5 that critical capillary pressure is linearly dependent on surface tension (not the case with the critical displaced volume). Therefore, there are only three parameters ($N$, $d$ and $\theta^{YL}$) that can affect the capillary pressure and displaced volume in a polygon pore (see Eq. 5.3). In the present study, these parameters are varied while their effects on critical capillary pressure and critical displaced volume are monitored. Our parameter study conducted for SHP pores with different properties ($40 \mu m < d < 100 \mu m$, $110^\circ \leq \theta^{YL} \leq 130^\circ$, and $4 \leq N \leq 8$) indicated that the first
critical capillary pressure ratio \( \Psi_{cr}^{(1)}/\Psi_{cr}^{(1),cir} \) and the first critical displaced volume ratio \( v_{cr}^{(1)}/v_{cr}^{(1),cir} \) do not depend on the above reference dimension \( d \). Unlike the critical capillary pressure, the critical displaced volume is only weakly dependent on Young–Laplace contact angle. Therefore, we considered both \( N \) and \( \theta^{\text{YL}} \) as the independent variables in developing a correlation for \( \Psi_{cr}^{(1)}/\Psi_{cr}^{(1),cir} \) but used only \( N \) for the \( v_{cr}^{(1)}/v_{cr}^{(1),cir} \) correlation, i.e.,

\[
\frac{\Psi_{cr}^{(1)}}{\Psi_{cr}^{(1),cir}} = \alpha_0 + \alpha_1 N + \alpha_2 \cos \theta^{\text{YL}} \tag{5.6a}
\]
\[
\frac{v_{cr}^{(1)}}{v_{cr}^{(1),cir}} = \beta_0 + \beta_1 N + \beta_2 N^2 \tag{5.6b}
\]

Parameters \( \alpha_i \) and \( \beta_i \) (where \( i = 0, 1, \) and \( 2 \)) are curve fitting coefficients (see Fig. 5.4a and 5.4b) and are found to be \( \alpha_0 = 0.7965, \alpha_1 = 0.0095, \alpha_2 = -0.0998, \beta_0 = 0.4767, \beta_1 = 0.0796, \) and \( \beta_2 = -0.0040 \). Note that using a higher order curve fitting polynomial does not improve the results significantly, but it adds unnecessary complexity to the equations. Note also that triangular pores are not considered in our study as they behave differently from other polygonal pores with \( N > 3 \) (see Ref. (92)).

For the second critical hydrostatic pressure, the capillary pressure and displaced volume are estimated in a way similar to how it was done for the first critical hydrostatic pressure. To predict the second critical capillary pressure, we use the concept of fluid rise in a vertical capillary tube. For a capillary tube with an arbitrary cross-sectional shape, the capillary pressure is given as \( \Psi = \rho g \bar{z} = \cos \theta \frac{p_t}{A_t} \), where \( \bar{z} \) represents the average height of the fluid column in the tube, \( p_t \) is
the perimeter of the tube, and $A_c$ is the tube's cross-sectional area. Therefore, the second critical capillary pressure ratio can be estimated from the ratio of the perimeter of the polygonal pore to that of the circular pore $\frac{p_{cr}^{(2)}}{p_{cr}^{(1), cir}} = \frac{p_{cr}^{(2)}}{p_{cr}^{(1), cir}}$ \[6, 24-25\] In other words, for identical cross-sectional areas and Young–Laplace contact angles, the second critical capillary pressure ratio simply becomes the ratio of the pores perimeters.

**Fig. 5.4:** The first critical capillary pressure ratio and the critical displacement volume ratio are shown in (a) and (b) versus the number of sides of the polygonal pores $N$, respectively. The second critical capillary pressure and critical displaced volume ratios are given in (c) and (d), respectively. The symbols are from numerical simulations and the lines are curve fit (Eqs. 5.6 and 5.7).
As critical displaced volume cannot be obtained from the above capillary rise model, we obtain $v_{cr}^{(2)}$ from solving Eq. 5.1 for a hydrostatic pressure equal to the abovementioned second critical hydrostatic pressure. We, therefore, propose the following expressions for the second critical capillary pressure and critical displaced volume ratios:

$$\frac{\psi_{cr}^{(2)}}{\psi_{cr}^{(2),cir}} = \sqrt{\frac{N}{\pi}} tan\left(\frac{\pi}{N}\right)$$  \hspace{1cm} (5.7a)$$

$$\frac{v_{cr}^{(2)}}{v_{cr}^{(2),cir}} = (\tau_2 N^2 + \tau_1 N + \tau_0) - (\xi_3 N^3 + \xi_2 N^2 + \xi_1 N + \xi_0) \cos^3 \theta^{YL}$$  \hspace{1cm} (5.7b)$$

where $\tau_2 = 0.0835, \tau_1 = -1.2640, \tau_0 = 6.0451, \xi_3 = -0.1028, \xi_2 = 2.0971, \xi_1 = -14.2520$, and $\xi_0 = 32.4927$. As will be discussed later in this section, one can also use the Laplace equation $\psi = \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$ for $\psi_{cr}^{(2)}$ and $v_{cr}^{(2)}$ at the second critical hydrostatic pressure to solve this problem. Note that $R_1 = R_2$ at the second critical hydrostatic pressure and these radii of curvature can be determined from the boundary condition given in Eq. 5.2.

Similar to the first critical capillary pressure and critical displaced volume ratios in Eq. 5.6, it can also be observed in Figs. 5.4c and 5.4d that the ratios $\frac{\psi_{cr}^{(2)}}{\psi_{cr}^{(2),cir}}$ and $\frac{v_{cr}^{(2)}}{v_{cr}^{(2),cir}}$ are independent of the abovementioned reference dimension $d$. Unlike $\psi_{cr}^{(1),c} (\text{see Eq. 5.5a})$, $\psi_{cr}^{(1)}$ is a nonlinear function of $\cos \theta^{YL}$ (see Eq. 5.6a). In addition, the ratio of the second critical displaced volumes (i.e., $\frac{v_{cr}^{(2)}}{v_{cr}^{(2),c}^{(2)}}$) is a function of Young–Laplace contact angle. This is because at the second critical hydrostatic pressure, all points on the air–water–solid contact line along the walls have already reached a slope
equal to \( \cot \theta^{YL} \). Note that the second critical displaced volume for polygonal pores is not a linear function of Young–Laplace contact angle (see Eq. 5.5b and Eq. 5.7b) because \( v_{cr}^{(2),cir} \) is not a linear function of the Young–Laplace contact angle. Good agreement can be observed in Fig. 5.4 between the results of our numerical simulations and an expression with a cubic relationship to \( \cos \theta^{YL} \) (Eq. 5.7b).

The ratios \( \frac{v_{cr}^{(2)}}{v_{cr}^{(2),cir}} \) and \( \frac{v_{cr}^{(2)}}{v_{cr}^{(2),cir}} \) are calculated in Figs. 5.4c and 5.4d, respectively, for polygonal pores with different number of sides. The results in Fig. 5.4a show that the first critical capillary pressure ratio increases with \( N \). This is because the air–water interface slope at more number of points along the air–water–solid contact line reaches \( \cot \theta^{YL} \) as \( N \) increases (one point on each side of the polygon). Conversely, the second critical capillary pressure ratio decreases with \( N \), as the perimeter of a polygonal pore with a constant cross-sectional area decreases when \( N \) increases. Note that the slope at all points on the air–water–solid contact line has already reached \( \cot \theta^{YL} \) in this case. For the first critical displaced volume, the ratio \( \frac{v_{cr}^{(1)}}{v_{cr}^{(2),cir}} \) increases with \( N \) as the slope of air–water interface at more number of points along the air–water–solid contact line reaches \( \cot \theta^{YL} \). This also means that the curvature of the first critical air–water interface increases with \( N \). The second critical displaced volume \( \frac{v_{cr}^{(2)}}{v_{cr}^{(2),cir}} \) decreasing with \( N \) results from the air–water interface radius of curvature \( R_1 = R_2 \) tending to its minimum value as \( N \to \infty \) (i.e., a circular pore) as will be discussed later in this section. Note that the ratios \( \frac{v_{cr}^{(1)}}{v_{cr}^{(1),cir}} \) and \( \frac{v_{cr}^{(1)}}{v_{cr}^{(1),cir}} \) or \( \frac{v_{cr}^{(2)}}{v_{cr}^{(2),cir}} \) and \( \frac{v_{cr}^{(2)}}{v_{cr}^{(2),cir}} \) converge to 1 (the value for a circular pore) as \( N \) increases (see Fig. 5.4). It is also worth
mentioning that, one can neglect the second term in Eq. 5.7b at the second critical hydrostatic pressure to further simplify the equation but accepting a relative error of about 18% for $4 < N < 8$.

In the remainder of this section, we will develop analytical equations for the second critical air–water interface profile and its corresponding capillary pressure in polygonal pores. These equations can then be used as an alternative method to circumvent the need for conducting numerical calculations to solve Eq. 5.1. Considering a polygon defined by its side length $w$ and the radius of its circumscribed circle $\alpha$, we obtain

$$w = 2 \sqrt{\tan \left( \frac{\pi}{N} \right)} \frac{\pi d^2}{4N} \quad (5.8a)$$

$$a = \frac{w}{2 \sin \left( \frac{\pi}{N} \right)} \quad (5.8b)$$

The second critical air–water interface over a polygonal pore can generally be considered as a spherical cap pinned to the $N$ corners of the polygon, i.e., (103),

$$f_{cr}^{(2)} = \sqrt{\left( R_{cr}^{(2)} \right)^2 - a^2} - \sqrt{\left( R_{cr}^{(2)} \right)^2 - x^2 - y^2} \quad (5.9)$$

where $R_{cr}^{(2)}$ is the radius of curvature of the air–water interface at $P_{cr}^{(2)}$. In addition, the slope of the air–water interface is equal to $\cot \theta^{yl}$ at all points along the air–water–solid contact line with the vertical wall. Therefore, $R_{cr}^{(2)}$ can be written as
\[ R_{cr}^{(2)} = a \frac{\sin \left( \frac{N - 2}{2N} \pi \right)}{|\cos \theta^{yl}|} \tag{5.10} \]

Note that Eq. 5.10 reduces to \( R_{cr}^{(2)} = \frac{d}{2|\cos \theta^{yl}|} \) when \( N \to \infty \) (a circular pore) and \( a \to d/2 \) (see Eq. 5.5). It is worth mentioning that the assumption of a spherical cap profile in Eq. 5.9 is only accurate for small Young–Laplace contact angles, especially when \( N \) is a small number. More specifically, \( R_{cr}^{(2)} \) should be larger than one half of the polygon’s side length, i.e., \( R_{cr}^{(2)} \geq w/2 \). An upper limit for the range of acceptable Young–Laplace contact angles in Eq. 5.10 can therefore be derived as

\[ |\cos \theta^{yl}| \leq \frac{\sin \left( \frac{N - 2}{2N} \pi \right)}{2 \sin \left( \frac{\pi}{N} \right)} \tag{5.11} \]

For instance, when \( N > 6 \), the maximum allowable Young–Laplace contact angle becomes 150° which covers most hydrophobic materials that can be used to produce an SHP surface. One can substitute Eq. 5.9 into Eq. 5.1 to determine the second critical hydrostatic pressure. As mentioned before, the second critical capillary pressure ratio \( \frac{w_{cr}^{(2)}}{w_{cr}^{(2),cr}} \) can also be calculated using the ratio of the perimeters of these pores or simply \( Nw/(d\pi) \) (see Eqs. 5.5a and 5.7a).

Note that the pore’s minimum height \( h_{min} \) is another constraint for the applicability of Eq. 5.9. The pore should be deep enough to prevent the air–water interface from touching the bottom of the substrate at pressures lower than the critical hydrostatic pressures. The minimum pore height \( \left| f_{cr}^{(2)} \right|_{\text{max}} \) can be written as
\[ h_{\text{min}} = R^{(2)}_{cr} - \sqrt{R^{(2)}_{cr}^2 - a^2} \tag{5.12} \]

which should be smaller than the pore height in order to obtain the second critical air–water interface using Eq. 5.9.

With the second critical air–water interface profile available (Eq. 5.9), one can derive an expression for the surface area of the vertical side walls wetted by the penetrating water \( S_{vw} \) at the second critical hydrostatic pressure, i.e.,

\[ S_{vw} = N \left( w \sqrt{R_{cr}^{(2)}} - a^2 - \frac{w^2}{2} \left( C^2 - \frac{w^2}{4} - C^2 \sin^{-1} \frac{w}{2C} \right) \right) \tag{5.13} \]

where \( C = \sqrt{R_{cr}^{(2)}} - a^2 + \frac{w^2}{4} \). Note that the walls’ vertical wetted area is zero at the first critical hydrostatic pressure.

Figure 5.5a shows a comparison between the predictions of our numerical calculations (Eq. 5.1) for the first critical hydrostatic pressure of polygonal pores and those of Eq. 5.7. The cross-sectional area of the polygonal pores shown in this figure is equal to that of a circular pore with a diameter of 60 \( \mu \text{m} \). By comparing Fig. 5.4a and 5.5a, one can see that the first critical hydrostatic pressure ratios (Fig. 5.5a) approach the first critical capillary pressure ratios (Fig. 5.4a) when the pores are very long (e.g., 3000 \( \mu \text{m} \)). In other words, the contribution of air compression (or the critical displaced volume) decreases as the pore height increases (see Eq. 5.4). Figure 5.5b shows the ratio of the second critical hydrostatic pressure of the polygonal pores to that of their circular
counterpart obtained from a numerical solution of Eq. 5.1, and the exact solution given in Eq. 5.9. Similar to Fig. 5.5a, the second critical hydrostatic pressure ratios approach the second critical capillary pressure ratios of Fig. 5.4c as the pore height increases. Also note that the pressure ratios in Figs. 5.5a and 5b converge to 1 (circular pore) as $N$ increases. Good agreement can be seen between the results of our proposed expressions (Eq. 5.6 and 5.7) and the numerical solution of Eq. 5.1 for the first or second critical hydrostatic pressures (5% margin of error for $4 < N < 8$). Neglecting the second term in Eq. 5.7b causes 15–20% error for $N = 4$ or 5. Figure 5.5c shows the ratio of the vertical walls’ wetted area to the cross-sectional area of the pore ($S_{vw}/A$) for different $N$ and Young–Laplace contact angle at the second critical hydrostatic pressure (Eq. 5.13). This area ratio is only a function of $N$ and Young–Laplace contact angle, and it tends to zero as $N$ approaches infinity (i.e., circular pore). As shown in Fig. 5.5b, the second critical hydrostatic pressure of a square pore is always greater than that of its circular counterpart area, but this comes with an additional wetted area (see Fig. 5.5c).
Fig. 5.5: The first and second critical hydrostatic pressure ratios are shown in (a) and (b) for polygonal pores with different heights $h$ but a Young–Laplace contact angle of $\theta^{\text{YL}} = 120^\circ$. These pores have an identical cross-sectional area equal to that of a circular pore with diameter of 60 $\mu$m. The pores’ dimensionless vertical wetted area at the second critical hydrostatic pressure are calculated using Eq. 5.12 and are shown in (c) for $100^\circ \leq \theta^{\text{YL}} \leq 130^\circ$.

5.3.2 Polygon Posts

In this subsection, we discuss SHP surfaces comprised of polygonal posts arranged in square configurations. Similar to the case with the pores, the first and second critical capillary pressure and critical displaced volume are used to determine the first and second critical hydrostatic pressures of the surface. Unlike the case of circular pores, there is no analytical solution for either the first or second critical hydrostatic pressure of a surface made of circular posts. Also, the first
and second critical hydrostatic pressures are not equal to one another \((P_{cr}^{(1),cir} \neq P_{cr}^{(2),cir})\) for such a surface.

In this section, we propose a new method to obtain the first and second critical capillary pressures and critical displaced volumes of an SHP surface comprised of circular posts. The proposed approach is then used to develop first (or second) critical capillary pressure and critical displaced volume ratios for SHP surfaces with polygonal posts. We start by first studying the second critical hydrostatic pressure as it is mathematically easier to formulate than the first critical hydrostatic pressure (the slope of the air–water interface at all points along the air–water–solid contact line is fixed at \(\cot \theta^{YL}\)). Similar to what was discussed for circular pores, the second critical capillary pressure for a circular post \(\psi_{cr}^{(2),cir}\) is directly proportional to the surface tension, and the \(\cos \theta^{YL}\) (see Eq. 5.5a). This pressure is also proportional to the ratio of the post perimeter to the projected area of the air–water interface.\(\)\(^{(12,13,104)}\). The second critical displaced volume for circular posts \(v_{cr}^{(2),cir}\) is proportional to \(D^3\) and to \(\cos \theta^{YL}\), but inversely proportional to \(\varphi\) (see Eq. 5.5b) where \(D\) is the diameter of the post. Based on these assumptions and our analysis of the numerical data, the following relationships are proposed for the second critical capillary pressure and critical displaced volume.

\[
\psi_{cr}^{(2),cir} = s_1 \eta 
\]

\[
v_{cr}^{(2),cir} = s_2 \zeta
\]
Here $s_1$ and $s_2$ are the proportionality constants and parameters $\eta = -\sigma \frac{\varphi}{D(1-\varphi)} \cos \theta^{YL}$ and $\zeta = \frac{D^3}{\varphi^2} \cos \theta^{YL}$ are functions that describe the geometric and wetting properties of the surface. In order to normalize the second critical capillary pressure and critical displaced volume, an arbitrary surface with a square arrangement of circular posts having a diameter of $D_{ref} = 40 \mu m$, a solid area fraction of $\varphi_{ref} = 0.2$, and a Young–Laplace contact angle of $\theta^{YL}_{ref} = 120^\circ$ is considered. For this surface, one can obtain $\eta_{ref} = 227.34$ Pa and $\zeta_{ref} = -8 \times 10^{-13}$ m$^3$. Figure 5.6a shows $\psi_{cr}^{(2),cjr}/\eta_{ref}$ and $v_{cr}^{(2),cjr}/\zeta_{ref}$ versus $\eta/\eta_{ref}$ and $\zeta/\zeta_{ref}$, respectively, for SHP surfaces comprised of circular posts with different diameters ($D = 40 \mu m$), Young–Laplace contact angles ($110^\circ \leq \theta^{YL} \leq 130^\circ$), and solid area fractions ($0.2 \leq \varphi \leq 0.4$). The linear relationships given in Eq. 5.14 are fitted into the numerical data in this figure to obtain $s_1 = 4.0$ and $s_2 = 0.0526$. The second critical capillary pressure predictions from Eq. 5.14a for a surface comprised of circular posts are in perfect agreement with the previous studies reported in Ref.(12) and Ref. (94) (Eq. 5.14a was previously obtained in Ref. (12) and Ref. (94) using the force balance and energy methods, respectively). Once the second critical capillary pressure and critical displaced volume are known, the corresponding critical hydrostatic pressure can be calculated using Eq. 5.4. The linear relationships given in Eq. 5.14a and 5.14b are fitted into the numerical data in this figure to obtain $s_1 = 4.0$ and $s_2 = 0.0526$. Note that Eq. 5.14a was also produced in Ref. (12) (using a force balance method that included only the capillary and hydrostatic forces) and Ref. (94)(via an energy minimization approach) with the same slope of $s_1 = 4.0$. Neither Ref. (12) nor Ref. (94) reported an expression for the second critical hydrostatic pressure in presence of entrapped air (e.g., a submerged SHP surface).
As mentioned before, the first and second critical capillary pressures (or critical hydrostatic pressures) are not identical for a surface with circular posts as the air–water interface is not axi-symmetric around a post (unless the solid area fraction approaches zero). Therefore, we use the second critical capillary pressure and critical displaced volume as reference values to obtain the first critical hydrostatic pressure. Figure 5.6b shows the ratio of the first critical capillary pressure to the second critical capillary pressure for surfaces with circular posts having different diameters,

\[
\frac{\psi_{cr}^{(1),cir}}{\psi_{cr}^{(2),cir}} = 1 + \varepsilon_2 \varphi^2 + \varepsilon_4 \varphi^4
\]

\[
\frac{v_{cr}^{(1),cir}}{v_{cr}^{(2),cir}} = 1 + \kappa_2 \varphi^2 + \kappa_4 \varphi^4
\]
Young–Laplace contact angles, and solid area fractions. It can be seen that the results are mainly
dependent on the solid area fraction of the surface. We, therefore, developed the following
expressions for the first-to-second critical capillary pressure and critical displaced volume ratios
in terms of the surface solid area fraction.

\[
\frac{\psi_{cr}^{(1),cir}}{\psi_{cr}^{(2),cir}} = 1 + \varepsilon_2 \varphi^2 + \varepsilon_4 \varphi^4 \tag{5.15a}
\]

\[
\frac{\nu_{cr}^{(1),cir}}{\nu_{cr}^{(2),cir}} = 1 + \kappa_2 \varphi^2 + \kappa_4 \varphi^4 \tag{5.15b}
\]

In these equations, \( \varepsilon_2 = -0.2197 \), \( \varepsilon_4 = -2.8846 \), \( \kappa_2 = -0.6906 \), and \( \kappa_4 = -6.2306 \). The
maximum relative error between the predictions of Eq. 5.15a (or 5.15b) and our numerical data
was found to be less than 4\%. The proposed values for the critical capillary pressures (i.e., \( \psi_{cr}^{(1),cir} \)
and \( \psi_{cr}^{(2),cir} \)) and the critical displaced volumes (i.e., \( \nu_{cr}^{(1),cir} \) and \( \nu_{cr}^{(2),cir} \)) of an SHP surface with
circular posts in Eqs. 5.14 and 5.15 will be used to non-dimensionalize the corresponding values
obtained for surfaces made of polygonal posts with identical cross-sectional areas and solid area
fractions.

As discussed earlier in this section, the second critical capillary pressure for a surface comprised
of polygon posts in square arrangement is proportional to the ratio of the perimeter of the posts to
the projected area of the air–water interface between the posts, i.e., \( \frac{Nw}{L^2 - \pi D^2 / 4} \) where \( w \) is given in
Eq. 5.8a (12,94). Thus, \( \frac{\psi_{cr}^{(2)}}{\psi_{cr}^{(2),cir}} \), as given in Eq. 5.7a can still be used to calculate the second critical
capillary pressure for an SHP surface comprised of polygonal posts. Note that the denominator of this equation is the second critical capillary pressure of an SHP surface made of circular posts with the same cross-section areas as the polygonal posts ($\psi_{cr}^{(2),cir}$, Eq. 5.14a). Figure 5.7a and 5.7b show $\frac{\psi_{cr}^{(2)}}{\psi_{cr}^{(2),cir}}$ and $\frac{v_{cr}^{(2)}}{v_{cr}^{(2),cir}}$ for polygonal posts with different $N$, respectively. Analyzing our numerical data indicated that the second critical displaced volume can be obtained from Eq. 5.7b but with new coefficients $\tau_2 = 0.0047$, $\tau_1 = -0.0887$, $\tau_0 = 1.4473$, $\xi_3 = 0.0$, $\xi_2 = -0.0014$, $\xi_1 = -0.0049$, and $\xi_0 = 0.6914$. Note that for simplicity a solid area fraction of $\varphi = 0.2$ is used as a reference value in determining the abovementioned coefficients, as the solid area fraction effect on $\frac{\psi_{cr}^{(2)}}{\psi_{cr}^{(2),cir}}$ and $\frac{v_{cr}^{(2)}}{v_{cr}^{(2),cir}}$ seems to be negligible according to the results in Figs. 5.7a and 5.7b. It can be seen that the second critical capillary pressure and critical displaced volume ratios from Eq. 5.7 are in good agreement with the results obtained from numerically solving Eq. 5.1 numerically.
Fig. 5.7: Effects of $N$ on the second critical capillary pressure ratio and the second critical displaced volume ratio are shown in (a) and (b), respectively, for $4 < N < 8$. Similar results for the first critical capillary pressure and critical displaced volume ratios are shown in (c) and (d), respectively. The symbols are from numerical simulations; the lines are curve fit (Eqs. 5.7 and 5.16).

The predictions of the first critical capillary pressure and critical displaced volume for a surface made of circular posts from Eq. 5.15 are used as reference values to normalize their corresponding values obtained for surfaces with polygonal posts. Analyzing our numerical results indicated that the first critical capillary pressure and critical displaced volume ratios are somewhat dependent on Young–Laplace contact angle and solid area fraction. We therefore propose Eq. 5.16a and 16b for $4 \leq N \leq 8$,

$$\frac{\psi_{cr}^{(1)}}{\psi_{cr}^{(1), cr}} = (\gamma_1 \phi + \gamma_2) N^2 + (\gamma_3 \cos \theta_{YL} + \gamma_4 \phi + \gamma_5) N + \gamma_6 \cos \theta_{YL} + \gamma_7 \phi + \gamma_8$$  \hspace{1cm} (5.16a)
\[ \frac{\nu_{cr}^{(1)}}{\nu_{cr}^{(1)}, cir} = (\delta_1 \cos \theta^Y + \delta_2 \varphi + \delta_3) N + \delta_4 \cos \theta^Y + \delta_5 \varphi + \delta_6 \]  \hspace{1cm} (5.16b)

where \( \gamma_1 = 0.0255, \; \gamma_2 = -0.0031, \; \gamma_3 = -0.0099, \; \gamma_4 = -0.3104, \; \gamma_5 = 0.0558, \; \gamma_6 = -0.0785, \; \gamma_7 = 1.1735, \; \gamma_8 = 0.0728, \delta_1 = -0.013, \; \delta_2 = 0.0695, \; \delta_3 = 0.011, \; \delta_4 = -0.0658, \; \delta_5 = -0.2675, \; \text{and} \; \delta_6 = 0.2275. \) The first critical hydrostatic pressure can be calculated using Eq. 5.4 after obtaining the first critical capillary pressure and first critical displaced volume values from Eqs. 5.16a and 5.16b. Figures 5.7c and 5.7d show the effects of \( \nu \) on the ratio of the first critical capillary pressure and the first critical displaced volume ratios of surfaces with polygonal posts to their circular counterparts, respectively. It can also be seen that the first critical capillary pressure and first critical displaced volume ratios depend strongly on \( \nu \). The maximum relative error between the predictions of Eq. 5.16 and their corresponding numerical values from Eq. 5.1 was found to be about 8\% for \( 4 \leq N \leq 8 \).

As discussed earlier in Sec. 5.3.1, posts should also be tall enough to accommodate a second critical air–water interface (i.e., \( h > h_{\text{min}} \)). The minimum post height \( h_{\text{min}} \) can only be determined by numerically solving Eq. 5.1 at the second critical hydrostatic pressure. From the analysis of our numerical data at this pressure, we propose the following expressions for \( h_{\text{min}} \) are for SHP surfaces comprised of circular posts and polygon posts,

\[ \frac{h_{\text{min}}}{D} = s_3 (\varphi^{-2/3} + \pi/2) \cos \theta^Y \]  \hspace{1cm} (5.17a)
\[
\frac{h_{\text{min}}}{D} = -(\varepsilon_2 N^2 + \varepsilon_1 N + \varepsilon_0) \varphi^{-1/2} \cos \theta^{\text{YL}}
\]  

(5.17b)

respectively, where \( s_3 = 0.074, \varepsilon_2 = 0.0007, \varepsilon_1 = -0.0122, \) and \( \varepsilon_0 = 0.2164. \)

Figure 5.8a shows the dimensionless minimum height for circular posts obtained from Eq. 5.1 (symbols) and Eq. 5.17a (line) for surfaces with different solid area fractions and Young–Laplace contact angles. Figure 5.8a shows the effect of different values of \( \varphi, \theta^{\text{YL}}, \) and \( N \) on the dimensionless minimum height. Good agreement between the predictions of our proposed equations and the numerical data is evident.
Fig. 5.8: Non-dimensionalized minimum post height for an SHP surface comprised of (a) circular posts and (b) polygonal posts. The symbols are from numerical simulation (Eq. 5.1) and the lines are predictions of our proposed expression (Eq. 5.17).

The vertical wetted area of polygonal posts can only be obtained from the numerical calculations of Eq. 5.1 at the second critical hydrostatic pressure (unlike the case with polygonal pores). Figure 5.9 shows the dimensionless vertical wetted area for circular ($S_{vw}^{c\text{ir}}/\cos\theta^L L^2$) and polygonal ($S_{vw}/\cos\theta^L L^2$) posts. In this figure, different symbols represent the results of our numerical calculations for posts with different $N$. Neglecting the effects of $N$ for simplicity (leading to an error of less than 8%), we developed expressions given in Eqs. 5.18a and 5.18b for dimensionless vertical wetted area of posts as a function of solid area fraction.

\[
\frac{S_{vw}^{c\text{ir}}}{L^2 \cos \theta^L} = -(\omega_2 \varphi^2 + \omega_4 \varphi^4) \tag{5.18a}
\]

\[
\frac{S_{vw}}{L^2 \cos \theta^L} = -(\lambda_0 + \lambda_2 \varphi^2 + \lambda_4 \varphi^4) \tag{5.18b}
\]

Equations 5.18a and 5.18b are proposed for circular and polygonal posts, respectively. In these equations, $\omega_2 = 0.0138$, $\omega_4 = 1.3449$, $\lambda_0 = 0.0074$, $\lambda_2 = 0.2450$, and $\lambda_4 = 0.6538$. As discussed earlier, the vertical wetted area $S_{vw}$ or $S_{vw}^{c\text{ir}}$ can be used to estimate an effective slip length for the surface as reported previously (7,97,105).
In summary, the first and second critical hydrostatic pressures for polygonal posts can be calculated numerically by using Eq. 5.1, or analytically, with Eqs. 5.14 and 5.15. In addition, Eqs. 5.17a and 5.17b can be used to predict the minimum height for posts with circular and polygonal cross-sections, respectively. Finally, the vertical wetted area can be estimated using Eqs. 5.18a and 5.18b for surfaces with circular and polygon posts, respectively.

5.3.3 Posts vs. Pores: Wetted Area

The information provided in Eqs. 5.13, 5.18a and 5.18b (Figs. 5.5c and 5.8) allows one to compare the vertical wetted areas of an SHP surface comprised of polygonal pores (see Fig. 5.5c) to its counterpart surface having polygonal posts (see Fig. 5.9) under the same operating conditions. For the ease of comparison, a reference surface is considered here. The reference surface is comprised of circular pores with an arbitrary diameter of \(d = 10 \mu m\) and an Young–Laplace contact angle of 120°. Three different solid area fractions of \(\varphi = 0.3, 0.5\) and 0.7 are considered for this comparison. Figure 5.10a shows the effect of \(P_g, N, \varphi\) on the ratio of the vertical wetted area of the polygonal posts to the projected area of the air–water interface \(\frac{S_{we}}{A}\), where \(A = \frac{\pi}{4}d^2 = \)
$L^2 - \frac{\pi}{4}D^2$, $d$ is the diameter of the pores, and $D$ is the diameter of the posts). Note that at pressures higher than the second critical hydrostatic pressure, the vertical wetted area of the pores or posts is calculated using the air–water interface profile obtained from solving Eq. 5.1 (13). As expected, the vertical wetted area of polygonal posts is smaller at lower hydrostatic pressures or at lower solid area fractions. Increasing $N$ is also shown to decrease the vertical wetted area of the surface at a given hydrostatic pressure or solid area fraction.

**Fig. 5.10:** Effects of hydrostatic pressure $P_g$ on the dimensionless vertical wetted area of superhydrophobic surfaces comprised of polygonal posts in shown in (a) for surfaces with different solid area fractions of $\varphi = 0.3$ (red), $\varphi = 0.5$ (blue), and $\varphi = 0.7$ (green). The polygons’ number of sides $N$ is varied from $N = 4$ to infinity for each solid area fraction. Dimensionless vertical wetted area of a surface made of polygonal pores is compared to that of its counterpart surface comprised of polygonal posts in (b) for $N = 4$, $N = 6$, and $N \rightarrow \infty$ (circle) at a solid area fraction of $\varphi = 0.5$. 
Figure 5.10b compares the effects of $N$ on the vertical wetted areas of polygonal pores and posts for $N=4, 6$ and $N \to \infty$ (circle) at $\varphi = 0.5$. It can be seen that the vertical wetted areas for both surfaces are almost identical especially as $N \to \infty$. Given the fact that solid area fraction has no effect on the vertical wetted area of an SHP surface comprised of polygonal pores, one can conclude from Figs. 5.10a and 5.10b that circular posts are the best choice for a surface with $\varphi < 0.5$ in terms of vertical wetted area. Obviously, for a surface with $\varphi > 0.5$, circular pores provide the minimal vertical wetted area.

### 5.4 Comparison with Experiment

In this section, we compare the predictions of our proposed equations to the experimental or computational data available in the literature. Reference (10) reports experimental data for critical hydrostatic pressure of two SHP surfaces, one comprised of square posts with a width of $5.4 \mu\text{m}$, and the other made of circular posts with a diameter of $D = 6.0 \mu\text{m}$. The posts were measured to be $9.5 \mu\text{m}$ tall and were coated with a fluoropolymer. Reference (10) reports only the advancing ($122.1^\circ$) and receding ($84.7^\circ$) contact angles of the surface. In the absence of a value for the surface Young–Laplace contact angle, we used the reported advancing contact angle in our calculations, as it may be closer to the Young–Laplace contact angle of the surface. Figure 5.11a and 5.11b show these experimental data along with our predictions of the surface first and second critical hydrostatic pressures. Note that detecting the first critical hydrostatic pressure experimentally is quite difficult. Therefore, the data reported in Ref. (10) are most probably the second critical hydrostatic pressures (or close to second critical hydrostatic pressures in nature). While the agreement between the numerical predictions and the experimental data is excellent at $\varphi \approx 0.25$ and within an acceptable margin of error for most SVFs considered here, there is an increased
mismatch at $\varphi \cong 0.1$ (about 50% error for circular posts and about 100% for square posts). We believe the mismatch at $\varphi \cong 0.1$ must be due to experimental error as the experimental critical hydrostatic pressures do not appear to form a V-shape profile as expected for submerged SHP surfaces (increasing solid area fraction has opposing effects on capillary pressure and the pressure of the entrapped air (12,13,37)).

Fig. 5.11: The first and the second critical hydrostatic pressures obtained from solving Eq. 5.1 for surfaces with different solid area fractions are compared to the experimental data from Ref. (10) in (a) and (b). The first and the second critical hydrostatic pressures obtained from our proposed expressions (Eqs. 5.7, 5.14–5.16) for SHP surfaces comprised circular posts (c) or square posts (d) are compared to those from numerical simulations (Eq. 5.1), predictions of the equivalent pore diameters method of Ref. (13), and the mean curvature method of Ref. (9).

Comparing the critical hydrostatic pressures obtained for the square and circular posts, it can be seen that the surface with square posts has a higher second critical hydrostatic pressure for all solid
area fractions, which is in agreement with the experimental data. This seems to be due to the fact that square posts have greater perimeters and also because their sharp corners promote partially de-pinned air–water interfaces (longer air–water–solid contact line). The first critical hydrostatic pressure of the surface with square posts is quite smaller than that of its counterpart surface with circular posts as expected. Also note that first and second critical hydrostatic pressures are identical for a surface with circular posts at small solid area fractions. This is because at such low solid area fractions, the effects of partial de-pinning can be quite negligible (the air–water interface around a circular post is almost axi-symmetric at low solid area fractions).

Figures 5.11c and 5.11d show a comparison between the results of our numerical solution of Eq. 5.1 and the predictions obtained from the equivalent pore diameter method of Ref. (13) as well as the numerical calculations of Ref. (9) for the same SHP surfaces (see Figs. 5.11a and 5.11b). In these figures, we also added the predictions of our analytical expressions given in Eq. 5.14 and Eq. 5.15. It should be noted that the numerical data reported in Ref. (9) are obtained using an approximate method in which the air–water interface mean curvature was obtained from an analysis similar to the one presented here for the second critical hydrostatic pressure, but with an enforced pinned boundary condition. In fact the calculation method presented in Ref. (9) is a simplified approach combining the two methods that we presented here for the first and second critical hydrostatic pressure calculations. Figs. 5.11c and 5.11d, also include the predictions of the equivalent diameter method. It can be seen that the equivalent diameter method is more accurate in predicting the second critical hydrostatic pressures. This is because of the inherent assumption considered in development of this model where the slope at all points on the air–water–solid contact line is equal to \( \cot \theta^L \) (the slope of the second critical air–water interface). Finally, and
most importantly, Figs. 5.11c and 5.11d show very good agreement between the predictions of our new analytical expressions (Eqs. 5.7, 5.14–5.16) with those of other methods.

To further examine the accuracy of the predictive expressions developed in Sec. 5.3.1, the second critical capillary pressure obtained from Eq. 5.9 for a surface comprised of polygonal pores was compared with the results from a water capillary rise experiment in a square tube with a width of 400 \(\mu\text{m}\) and a height of 100 mm (purchased from Wale Apparatus Co. 8320-100). We used the PMI Silwick solution (C13-C16 Isoalkanes) having a near zero contact angle with glass surface to measure the contact angle of water with the tubes. Equilibrium height rise values of \(z_w = 34 \pm 0.7\) mm and \(z_o = 26 \pm 0.4\) mm were measured for water and Silwick in the square tubes, respectively. The equilibrium height rise ratio between water and Silwick can be obtained as from the balance of forces as,

\[
\frac{\rho_w z_w}{\rho_0 z_0} = \frac{\sigma_w \cos \theta_w}{\sigma_0}
\]

where the subscripts ‘w’ and ‘o’ represent water and Silwick, respectively. Knowing the density and surface tension of Silwick as \(\rho_0 = 798 \text{ kg/m}^3\) and \(\sigma_0 = 0.021 \text{ N/m}\), respectively, one can obtain an approximate contact angle of 60.3° for water inside the tubes. Equation 5.9 can be used to predict the second critical air–water interface inside the square tubes but with a contact angle of \(\theta_{cr} = 180 - 60.3 = 119.7°\). In excellent agreement with our measurements, the fluid height was calculated to be 36.8 mm. Figure 5.12 compares the computed air–water interface profile (i.e., \(f_{cr}^{(2)}\) from Eq. 5.9) with the profile obtained by imaging the water front in the square tubes. The solid line and square symbols show the contact line between the air–water interface and the side walls.
of the tube. The solid line and square symbols represent the air–water interface in the middle of the tube as shown also with red lines in the inset 3-D figure. Good agreement between the spherical cap equation (Eq. 5.9) and experimental measurements is evident in Fig. 5.12 (the symbols are the average values over three measurements).

**Fig. 5.12:** The 3-D equilibrium air–water interface $f_{cr}^{(2)}$ is shown in the inset. The air–water–solid contact line with the side walls and the air–water interface 2-D profile in the middle of the tube are shown with blue and black colors, respectively. The lines are obtained from Eq. 5.9 whereas the symbols are from experiment.

### 5.5 Conclusions

Two critical hydrostatic pressures are mathematically defined for submerged superhydrophobic surfaces comprised of sharp-edged polygonal pores or posts in this work. These definitions are used to show how the wetted area inside or between the surface asperities varies with elevated pressure or surface morphology. Grouping the dominant independent variables affecting the critical pressure or wetted area, we developed new predictive expressions are via curve fitting into numerical data. The accuracy of our expressions is benchmarked against available experimental or numerical data. These expressions allow one to compare the pressure-dependent performance of superhydrophobic surfaces comprised pores or posts with one another. Detailed comparison is presented for the performance of superhydrophobic surfaces made of polygonal posts or pores with
their counterpart surfaces comprised of circular posts or pores. Our results are discussed in relation to those from the literature. This chapter can be used to custom-design SHP surfaces with pores or post for different applications.
Chapter 6. Liquid–Infused Surfaces with Trapped Air for Drag Force Reduction

6.1 Introduction

The superhydrophobic (SHP) surfaces designed for underwater drag reduction applications are often affected adversely by the water hydrostatic pressure or the time in service (10,33,37,66,96,106). Excessive hydrostatic pressures can imbalance the stability of the mechanical forces acting on the air–water interface that forms over an SHP surface as discussed before in Chapter 4. In addition, the dissolution of the trapped air into the surrounding water can also lead to the collapse of an air–water interface over time (2,13,21,26,66,107,108). In this concern, investigators in Ref. (32) used a lubricant to impregnate the pores of their drag-reducing surface and thereby extended its lifespan almost indefinitely. Such surfaces have been referred to as Slippery Liquid-Infused Porous Surfaces (SLIPS) or Lubricant-Infused Surfaces and were first used in applications such as anti-fouling and anti-coagulation (1,31,41,43,44). Despite the success of liquid-infused surface surfaces in providing slippery contacts with viscous fluids like crude oil, such surfaces are not likely to show a measurable drag reduction when the working fluid is a low-viscosity fluid like water (32). Liquid-infused surface may also suffer from additional problems such as fluid drainage from the pores due to shear or gravitational forces as examined in the recent liquid-infused surface literature (31,41,42). In the current chapter, we present a new design for liquid-infused surface in which an air layer is placed underneath the infused lubricant to improve the drag-reduction benefits of the surface when used with low-viscosity fluids like water. The entrapped air layer is expected to reduce the frictional forces against the formation of a vortical
flow in the lubricant layer, and therefore allow the surface to provide a slip velocity at the lubricant–water (working fluid) interface. Inspired by a recent study reported in Ref. (45), a double-reentry geometry is considered in our design to enhance the mechanical stability of the lubricant layer (Fig. 6.1) (see also Ref. (22). For the sake of brevity, a lubricant-infused surface with trapped air is referred to here as liquid-infused surface with trapped air. The drag reduction performance of liquid-infused surface with trapped air is examined in the current chapter by solving the biharmonic equation, and the advantages of this new design over its liquid-infused surface counterpart are discussed in detail. Our numerical calculations are conducted for a Couette flow formed between a moving upper plate and a stationary bottom plate. The bottom plate is comprised of transverse parallel grooves impregnated with lubricant or lubricant and air layers.

The remainder of the chapter is organized as follows. Design and stability of liquid-infused surface with trapped air are discussed in Sec. 6.2. Problem formulations, boundary conditions, and comparison between the present and previous studies conducted for SHP transverse grooves are presented in Sec. 6.3. Detailed comparison between the slip effects of the liquid-infused surface and liquid-infused surface with trapped air surfaces are discussed in Sec. 6.4 for a Couette flow with arbitrary dimensions. This is followed by our conclusions in Sec. 6.5.

5.2 Liquid-Infused Surface with Trapped Air Design and its Mechanical Stability

In a recent study reported in Ref. (32), a drag reduction benefit of 16% was reported for glycerol-water mixture flowing over a liquid-infused surface with Silicon oil as the lubricant (a viscosity ratio of 261 between the working fluid and the lubricant). The liquid-infused surface with
trapped air design is aimed at decreasing the skin-friction drag of the liquid-infused surface surfaces and so to potentially expand their applications to working fluids with viscosities less than that of the infused lubricant (see Fig. 6.1a–1e). In addition to the low drag-reduction benefits, liquid-infused surface surfaces may suffer from problems involving lubricant stability. A stable liquid-infused surface surface is generally designed by targeting the configuration that minimize the total interfacial energy per unit area of the four phases in contact, i.e., air, working fluid, lubricant, and solid, in comparison to all other possible configurations (see Ref. (109)). We conjecture that the entrapped air in liquid-infused surface with trapped air helps to stabilize the lubricant in the grooves. The compressibility of the air layer can potentially dampen the pressure fluctuations in the flow field and relax some of the shear forces acting on the lubricant layer (see Refs. (31,41,42) for problems with lubricant stability in liquid-infused surface, and Ref. (110) for the effects of pressure fluctuations on stability of submerged SHP grooves). In fact, thinner the air layers better resist the elevated pressures (13,66).

Generally speaking, SHP surfaces are made of hydrophobic materials. However, as shown in Ref. (22), superomniphobicity can be achieved with a so-called single-reentry design even with “philic” solid materials. The study reported in Ref. (45) shows that a surface with doubly-reentry features can exhibit superomniphobic (or superrepellent) behavior regardless of the Young–Laplace contact angle between the solid material and the working fluid. This concept can be used here to better enhance the mechanical stability of the lubricant layer in our liquid-infused surface with trapped air design. For instance, a single or double reentry design can help to stabilize the air–lubricant interface in a liquid-infused surface with trapped air made of preferably an oleophobic material, except for the interior walls of the lubricant groove as shown with red color (and marked
with an “s”) in Fig. 6.1, which should be oleophilic. Depending on the wettability of the groove’s surfaces, the lubricant–water interface and air–lubricant interface may become pinned to different points at different walls. For instance, the lubricant–water interface and air–lubricant interface will probably anchor themselves to points A and B, respectively, if all walls are “phobic” except the s-labeled walls (see Fig. 6.1b). However, the air–lubricant interface may move along the BC wall and pin itself to point C if the BC wall is not oleophobic as shown in Fig. 6.1c.
Fig. 6.1: Schematic illustration of a unit cell of a liquid-infused surface with trapped air comprised of transverse grooves with a double reentry inlet is given in (a). All walls are oleophobic except for the AB wall (shown in red) which must be oleophilic. The air–lubricant interface and lubricant–water interface are shown in (b) and (c) for oleophobic and oleophilic BC walls, respectively. Schematic illustration of a liquid-infused surface is shown in (d). A liquid-infused surface with trapped air with an additional double reentry design is shown in (e) as a means of further enhancing lubricant stability in the groove under a negative pressure.
To better stabilize the lubricant inside a liquid-infused surface with trapped air design exposed to negative pressures (or fluctuating pressures), one can use another double reentry design for the surface in contact with water (or working fluid) as shown in Fig. 6.1e. This new design can promote the lubricant–water interface to become pinned to points D or A (depending on the wettability of DA surface) when the surface is exposed a negative pressures (111–113). Note that the menisci curvatures (air–lubricant interface and lubricant–water interface) shown in Fig. 6.1e are calculated from the force balance equations discussed in our previous work (111). For the sake of simplicity, in the numerical calculations presented in the next sections, we assume the air–lubricant interface and lubricant–water interface to be flat as shown in Fig. 6.1a. In order to obtain a stable rigid flat interface (lubricant–water interface and air–lubricant interface), the Weber ($We$) and capillary ($Ca$) numbers should be much smaller than 1 with almost no pressure difference across the interface (101,102) (i.e., $We \ll 1$ and $Ca \ll 1$). Generally, the $We$ and $Ca$ numbers are defined as $\frac{\rho V^2_w w_1}{\sigma}$ and $\frac{\tau_1}{\sigma/w_1}$, respectively, where $V_1$ and $\tau_1$ are the average velocity and shear stress along the lubricant–water interface, $\rho$ is the density of working fluid, $w_1$ is the width of the rectangular groove (contact length between the fluids), and $\sigma$ is the surface tension between water and lubricant. Similarly, the calculations can be easily repeated along the air–lubricant interface. Again, the values of $We$ and $Ca$ need to be as small as possible to validate the assumption of flat lubricant–water interface and air–lubricant interface.

It should be noted that, the effects of surfactants or impurities on lubricant–water interface or air–lubricant interface are not included in the study presented here. Such contaminations are
known to rigidify a fluid–fluid interface and prevent momentum transfer between different phases (114,115). This can obviously affect the performance of a liquid-infused surface with trapped air design.

The mole fraction of dissolved air in the lubricant layer adjacent to the air–lubricant interface in a liquid-infused surface with trapped air can be found according to Henry’s law,

$$X_{al}^a = \frac{P_a}{H^{al}}$$  \hspace{1cm} (6.1)

where the superscript “l” refers to lubricant, the letter “a” (either subscript or superscript) refers to air, $H^{al}$ is Henry’s constant for air transport across an air–lubricant interface, and $P_a$ is the air pressure in the entrapped bubble (39,116). Neglecting capillary forces for simplicity, one can assume that $P_l = P_a$, and hence the air partial pressure in the lubricant becomes $\frac{P_a^2}{H^{al}}$. Likewise, the mole fraction of the dissolved air in the working fluid next to lubricant–water interface can be written in terms of the pressure of the entrapped air bubble as,

$$X_{af}^{lf} = \frac{P_a^2}{H^{af}} \frac{1}{H^{al}}$$  \hspace{1cm} (6.2)

where the superscript “f” refers to the working fluid (water), and $H^{af}$ is Henry’s constant for air transport across an lubricant–water interface. Note that in the absence of the lubricant layer (i.e., a SHP surface simple with air-filled grooves), the mole fraction of dissolved air in the working fluid can be estimated as $\frac{P_a}{H^{af}}$. In other words, the lubricant layer in liquid-infused surface with trapped
air can reduce the rate of air dissolution into the working fluid (e.g., water) by a factor of $\frac{P_a}{H^{af}}$ (about 2 to 4 orders of magnitude since $H^{af}$ is about $10^2$ to $10^4$ bar for most fluids) (117).

6.3 Mathematical Formulations and Validation

In this section, we present the governing equations for the flow of water (working fluid) between a moving upper plate and a stationary hydrophobic bottom surface comprised of transverse grooves (Fig. 6.1). The Naiver–Stokes equations for this problem can be written as,

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0$$  \hspace{1cm} (6.3a)

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} = \frac{1}{\mu} \frac{\partial P}{\partial x}$$  \hspace{1cm} (6.3b)

$$\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} = \frac{1}{\mu} \frac{\partial P}{\partial y}$$  \hspace{1cm} (6.3c)

where $u$ and $v$ are the velocities in the $x$ and $y$-directions, respectively, $P$ is pressure, and $\mu$ is the dynamic viscosity. Using the stream function definition for the velocity field $u = \frac{\partial \psi}{\partial y}$ and $v = -\frac{\partial \psi}{\partial x}$, and by multiplying Eqs. 6.3b and 6.3c by their complementary partial derivatives and adding them together, we obtain

$$\nabla^4 \psi = 0$$  \hspace{1cm} (6.4)

where $\psi$ is the stream function, and $\nabla$ is the gradient operator. The flow is driven by a given shear stress at the upper wall $\tau_\infty$ at $y = H$, where $H$ is the gap between the plates. For simplicity, a flat profile is considered for the interface between water and the trapped fluid as mentioned earlier (see
Ref. (97) for more information about the importance of interface curvature in slip length calculation). The no-slip boundary condition (i.e., \( u = v = 0 \)) is considered for flow along the solid boundaries, i.e.,

\[
\begin{align*}
    u_f &= \frac{\partial \psi_f}{\partial y} = u_l = \frac{\partial \psi_l}{\partial y} = 0 \\
    v_f &= -\frac{\partial \psi_f}{\partial x} = v_l = -\frac{\partial \psi_l}{\partial x} = 0
\end{align*}
\]  
(6.5a, 6.5b)

Periodic boundary conditions (PBCs) are considered for the inlet and outlet boundaries at \( x = -L/2 \) and \( x = L/2 \), i.e.,

\[
\begin{align*}
    \frac{\partial \psi_f}{\partial x} &= 0 \\
    \frac{\partial^3 \psi_f}{\partial x^3} &= 0
\end{align*}
\]  
(6.6a, 6.6b)

Constant shear stress \( \tau_\infty \) and no-pressure-gradient boundary conditions are used for the upper boundary at \( y = H \), i.e., (118)

\[
\begin{align*}
    \frac{\partial^2 \psi_f}{\partial y^2} &= \frac{\tau_\infty}{\mu_f} \\
    \frac{\partial^3 \psi_f}{\partial y^3} &= 0
\end{align*}
\]  
(6.7a, 6.7b)

At \( y = 0 \) along the air–water interface, or the lubricant–water interface, the velocity and shear stress are assumed to be identical for the fluids in contact, i.e., (14,119)
where $N_{lf} = \mu_l/\mu_f$ is the viscosity ratio between the lubricant and the working fluid. A constant stream function is considered along the fluids’ interface line (e.g., $\psi = 0$). It is worth mentioning that the shear stress along the fluid–fluid interface can often be neglected if the trapped fluid is air, and this can been accomplished by simply assuming a zero-shear boundary condition for the air–water interface (4,118,120). For liquid-infused surface with trapped air, the abovementioned boundary conditions in Eqs. 6.8a and 6.8b at the air–lubricant interface (or $y = -h_1$), are changed to $u_l = \frac{\partial \psi_l}{\partial y} = u_a = \frac{\partial \psi_a}{\partial y}$ and $\frac{\partial u_l}{\partial y} = \frac{\partial^2 \psi_l}{\partial y^2} = \frac{1}{N_{la}} \frac{\partial u_a}{\partial y} = \frac{1}{N_{la}} \frac{\partial^2 \psi_a}{\partial y^2}$ where $N_{la} = \mu_l/\mu_a$ is viscosity ratio between the lubricant (subscript or superscript “$l$”) and air (subscript or superscript “$a$”).

Equation 6.4 is discretized using a central finite difference (five-point) scheme and is solved via a successive over-relaxation Gauss-Seidel (iterative) algorithm, i.e.,

$$
\psi_{l,j}^{n+1} = \omega \psi_{l,j}^n + (1 - \omega) \psi_{l,j}^*
$$

(6.9a)

where

$$
\psi_{l,j}^* = \frac{1}{20} \left\{ 8 \left( \psi_{l+1,j}^n + \psi_{l-1,j}^n + \psi_{l,j+1}^n + \psi_{l,j-1}^n \right) \\
- 2 \left( \psi_{l+1,j+1}^n + \psi_{l-1,j-1}^n + \psi_{l-1,j+1}^n + \psi_{l+1,j-1}^n \right) \\
- \left( \psi_{l+2,j}^n + \psi_{l-2,j}^n + \psi_{l,j+2}^n + \psi_{l,j-2}^n \right) \right\}
$$

(6.9b)
where the indices $i$ and $j$ represent the spatial steps in the $x$ and $y$ directions, respectively, and $n$ denotes the iteration level. The over-relaxation factor is taken to be $\omega = 0.8$ for convenience. In order to quantify the effective slip length, the Navier slip condition is used at $y = 0$, i.e.,

$$
\bar{b} = \frac{\langle \frac{\partial \psi_f}{\partial y} \rangle}{\langle \frac{\partial^2 \psi_f}{\partial y^2} \rangle}
$$

(6.10)

where $\langle \rangle$ represents average value (4).

The governing equations and boundary conditions used for liquid-infused surface are also considered for liquid-infused surface with trapped air. We benchmarked our work using the results reported in the fluid dynamics literature. We start by solving Eq. 6.4 for the classical lid-driven cavity problem (Fig. 6.2a) and then move on to the case of a Couette flow with liquid-infused surface with transverse grooves as the bottom surface. Figures 6.2b–6.2c show the solution of the classical lid-driven cavity problem for cavities with two different aspect ratios $a_r = h_1/w_1$ where $w_1$ and $h_1$ are the width and height of the rectangular groove, respectively. The position of the center of the main vortex from the upper plate $d_e$ is obtained from our numerical simulations and is compared to the predictions obtained from the equation given in Ref. (121), i.e.,

$$
\frac{d_e}{w_1} = c_0 \text{erf}(c_1 a_r)
$$

(6.11)

where $c_0 = 0.251$ and $c_1 = 1.319$. In the work of Ref. (121), the $d_e/w_1$ ratios were chosen to be 0.088, 0.160, 0.240, and 0.250 for cavities with $a_r$ of 0.25, 0.5, 1.0, and 2.0, respectively. With excellent agreement with the aforementioned results (or Eq. 6.11), the $d_e/w_1$ ratios are obtained.
from our calculations to be 0.084, 0.163, 0.240, and 0.244 for \( a_r \) values of 0.25, 0.5, 1.0 and 2.0, respectively.

Fig. 6.2: The classical lid-driven cavity problem is considered for benchmarking our numerical calculations (a). Stream function contour plots are shown for cavities with aspect ratios of \( a_r = 1 \) and 2 in (b) and (c), respectively. Comparison between the results of present calculations (dotted line) and those from the analytical solution of Ref. (14) (solid line) are given in (d).
To further benchmark our numerical calculations, we considered a Couette flow geometry similar to the one shown in Fig. 6.1d but with air as the trapped fluid, and compared our resulting flow field with that from the analytical solution given in Ref. (14), i.e.,

\[
\psi_{ex} = \frac{\tau_\infty w_1^2}{8\mu_f} \frac{2y/w_1}{1 + 4D_t N^{fa}} \left[ 2y/w_1 + 4D_t N^{fa} \text{Im} \left( \sqrt{(2x/w_1 + 2iy/w_1)^2 - 1} \right) \right]
\]

(6.12)

where \(\tau_\infty\) is the applied shear at \(y = H\), \(i = \sqrt{-1}\), \(D_t = d_{0,t} \text{erf} \left( \frac{\sqrt{\pi}}{8d_{0,t}} a_r \right)\) with \(d_{0,t} = 0.124\), and \(N^{fa} = \mu_f/\mu_a\) is the viscosity ratio between water and air. For this comparison, we considered a computational domain with \(H = 500\ \mu m\), \(L = 3000\ \mu m\), \(w_1 = 50\ \mu m\), and \(h_1 = 50\ \mu m\), and used a constant shear stress of 0.1 Pa for the moving wall at \(y = H\). Figure 6.2d shows excellent agreement between the streamlines obtained from our calculations (dotted lines) and those produced using the exact mathematical solution given in Eq. 6.12 (shown with solid lines). Note that the exact solution is only for the water flowing above the grooves. Therefore, these results are superimposed to our flow field calculation results which were for both the water and air (see Fig. 6.2d).

6.4 Slip Effect from Liquid–Infused Surfaces with Trapped Air

In this section, we compare the performance of a liquid-infused surface comprised of transverse grooves with its liquid-infused surface with trapped air counterpart. A Couette flow with arbitrary specifications, a height of \(H = 50\ \mu m\), a pitch of \(L = 100\ \mu m\), and an upper plate shear stress of \(\tau_\infty = 0.1\ \text{Pa}\), is considered for this study. We consider a solid area fraction of \(\varphi = 1 - \frac{w_1}{L}\) for
both liquid-infused surface and liquid-infused surface with trapped air designs. The rectangular groove encloses the lubricant film with a width of \( w_1 = 76 \, \mu m \) (leading to solid area fraction of \( \varphi = 0.24 \)) and height of \( h_1 = 10 \, \mu m \) and it is placed on the stationary bottom plate. For the double reentry design in this work, we assumed \( l_1 = l_2 = l_3 = 4 \, \mu m \) (note that \( w_2 = w_1 + 2l_1 + 2l_3 \)) and \( h_2 = 15 \, \mu m \). Dynamic viscosities of \( 10^{-3} \), \( 1.8 \times 10^{-5} \), and \( 3.2 \times 10^{-3} \) Pa·s are considered for water, air and lubricant (e.g., hexadecane C16H34), respectively. Unless otherwise stated, these parameters will be used in the remainder of this section.

To predict the slip effect generated by liquid-infused surface with trapped air, Eq. 6.4 is solved for water in the gap between the plates as well as for the lubricant and air in the grooves. Similar calculations are also conducted for the same Couette geometry but with the liquid-infused surface as the bottom surface. Figures 6.3a and 6.3b show the velocity field for a liquid-infused surface and its liquid-infused surface with trapped air counterpart using streamline contour plots and velocity vectors, respectively. Note the large dark blue region in the lubricant layer of the liquid-infused surface with trapped air in comparison to that in the liquid-infused surface in Fig. 6.3a, indicating a stronger lubricant circulation in liquid-infused surface with trapped air. Similarly, larger velocity-vectors can be seen in the lubricant layer in the liquid-infused surface with trapped air relative to those its liquid-infused surface counterpart. The resulting slip-velocity along the lubricant–water interface on the bottom plate is shown in Fig. 6.3c and is normalized with the maximum slip velocity \( (u_{max} = 78 \, \mu m/s) \) predicted for the liquid-infused surface at \( x = 0 \). It can be seen that the liquid-infused surface with trapped air design allows water to achieve a greater slip velocity near the bottom plate leading to a larger overall slip length. Figure 6.3d shows the velocity gradient \( \partial u / \partial y \) along \( y = 0 \) for liquid-infused surface and liquid-infused surface with
trapped air normalized with the maximum velocity gradient \((\partial u/\partial y)_{max} = 118.5 \text{ s}^{-1}\) obtained for the liquid-infused surface at \(x = -w/2\) and \(w/2\). It can be seen that overall velocity gradient (i.e., overall shear stress) across the lubricant–water interface is smaller in the case of liquid-infused surface with trapped air surface. This is thanks to the air layer underneath the infused lubricant allowing it to slip along the air–lubricant interface at \(y = -h_1\). Effective slip length values of \(\tilde{b} = 0.51\) and 0.66 µm are obtained for water over the liquid-infused surface and liquid-infused surface with trapped air designs shown in Fig. 6.3, respectively (29% increased slip length for liquid-infused surface with trapped air). The We and Ca numbers are calculated for this test case (for air–lubricant interface and lubricant–water interface as can be seen in Fig. 6.3) and these values are \(O(10^{-8})\) and \(O(10^{-4})\), respectively. This leads to indicating of no interface distortion or liquid penetration across the lubricant–water interface as well as air–lubricant interface.
Fig. 6.3: Stream function contour plots and velocity vector fields are shown in (a) and (b) for a liquid-infused surface and its liquid-infused surface with trapped air counterpart, respectively. Normalized slip velocity $\frac{u}{u_{\text{max}}}$ and velocity gradient $\frac{(\partial u/\partial y)_{\text{max}}}{(\partial u/\partial y)_{\text{max}}}$ along lubricant–water interface are shown in (c) and (d), respectively. Here $u_{\text{max}}$ and $(\partial u/\partial y)_{\text{max}}$ are the maximum slip velocity and the maximum velocity gradient obtained for liquid-infused surface at $x = 0$ and $w_1/2$, respectively. All dimensions are in micrometer.

Figure 6.4 presents a comparison between the slip length values obtained from the above-mentioned simulations in the form of slip length gain defined as,

$$E = \left( \frac{\bar{b}_{\text{LISTA}} - \bar{b}_{\text{LIS}}}{\bar{b}_{\text{LIS}}} \right) \times 100 \quad (6.13)$$

where the subscripts LIS and LISTA are for liquid-infused surface, and liquid-infused surface with trapped air, respectively. In this figure, slip length gain $E$ is predicted for different groove aspect ratios $a_r = h_1/L$ and solid area fractions $\varphi$. It can be seen that, $E$ decreases with increasing $a_r$. It
is interesting to note that, all parameters held constant, effective slip length increase with $h_1$ for a liquid-infused surface but decreases for a liquid-infused surface with trapped air. This is because increasing $h_1$ increases the area of the frictional (oleophilic) side walls of the groove relative to that of its shear-free bottom boundary. Therefore, increasing $h_1$ results in a decrease in the slip advantage of a liquid-infused surface with trapped air. Nevertheless, slip length obtained from a liquid-infused surface with trapped air design is always greater than that from its liquid-infused surface counterpart ($E$ is always positive). It can also be seen that $E$ decreases with increasing solid area fraction, when other parameters are held constant. This is because the shear-free surface along the air–lubricant interface decreases with increasing solid area fraction, while the surface area of the frictional side walls of the lubricant cavity remain the same.

Figure 6.4b shows slip length gain $E$ for lubricants with different viscosities (i.e., different $N^{la}$ where $\mu_a = 1.789 \times 10^{-5} \text{ kg/m/s}$) versus $N^{lf}$ which is the ratio of the lubricant viscosity to that of the working fluid (e.g., water). It can be seen that increasing $N^{lf}$ further improves the slip length of a liquid-infused surface with trapped air over its liquid-infused surface counterpart (note that the effective slip length of a liquid-infused surface decreases with $N^{lf}$). Similarly, $E$ increases with $N^{la}$. This is because friction in liquid-infused surface is higher for a more viscous lubricant in comparison to its liquid-infused surface with trapped air counterpart. As can be seen in Fig. 6.4b, $E$ varies more with $N^{lf}$ than it does with $N^{la}$ especially at low $N^{lf}$ values.
Fig. 6.4: Slip length gain for liquid-infused surface with trapped air over liquid-infused surface for transverse grooves with different aspect ratios and solid area fractions are shown in (a). Effects of the fluids viscosity ratios $N^{lf} = \frac{\mu_l}{\mu_f}$ and $N^{lg} = \frac{\mu_l}{\mu_g}$ on the slip length gain are shown in (b).

For completeness of the study, we also compare the performance of a liquid-infused surface with trapped air comprised of longitudinal grooves with its liquid-infused surface counterpart by solving a simplified form of Eq. 6.4 for both cases. Note that using 2-D formulations to describe longitudinal grooves can only be accurate when the grooves are infinitely long, or when the grooves have no ends (e.g., concentric circular grooves such as those used in the Refs. (32,33)).
The 2-D approach may also be relevant the lubricant is continuously pumped into the grooves in the same direction of as the working fluid flows (like the liquid-infused surface in Refs. (31,41,42)). Most recently, the drag reduction in turbulent flows in two concentric rotating cylinders was measured in Ref. (122). In the work of Ref. (122), there were comparisons between three different surfaces with different microstructure features (i) superhydrophobic (ii) liquid-infused surface and (iii) surface in Wenzel state and these surfaces are good example of longitudinal grooves.

For such special cases, the Navier–Stokes equations can be simplified to $\nabla^2 u = 0$ where $u$ is the velocity in the z-direction (flow direction) with $\frac{\partial u_f}{\partial x} = 0$ at $x = -L/2$ and $x = L/2$. The boundary conditions along the lubricant–water interface ($y = 0$) are $u_f = u_l$ and $\frac{\partial u_f}{\partial y} = N_{lf} \frac{\partial u_l}{\partial y}$. Similarly, the boundary conditions are $u_l = u_a$ and $\frac{\partial u_l}{\partial y} = \frac{1}{N_{la}} \frac{\partial u_a}{\partial y}$ along air–lubricant interface ($y = -h_1$). We solved this differential equation using a three-point finite different scheme and benchmarked our solution by comparing its results with the work in Refs. (4,14) (the comparison is not shown for the sake of brevity). Figure 6.5a shows the $u$-velocity near the bottom plate with longitudinal grooves in the aforementioned Couette geometry for both the liquid-infused surface and liquid-infused surface with trapped air designs. Similar to the case of transverse grooves, these velocities are normalized with the maximum slip velocity predicted for the liquid-infused surface at $x = y = 0$. It can be seen that liquid-infused surface with trapped air provides a greater slip velocity than its liquid-infused surface counterpart. Once again, note that these results are only relevant to surfaces comprised of grooves with no ends. For longitudinal grooves with finite length, we can only conjecture that the performance will be similar or perhaps somewhat better than that
of transverse grooves (more accurate assessment of this argument requires complicated 3-D calculations and will also depend on the dimensions of such longitudinal grooves). The inset in Fig. 6.5a shows the velocity profile across the gap between the upper and bottom plates at $x = 0$ for a bottom plates with liquid-infused surface and liquid-infused surface with trapped air grooves. This figure shows how the trapped air in liquid-infused surface with trapped air allows the lubricant layer to acquire a velocity comparable to that of water, in contrast to the case with liquid-infused surface.

**Fig. 6.5:** Slip velocity along lubricant–water interface is shown in (a) for liquid-infused surface and liquid-infused surface with trapped air having longitudinal grooves. The velocity values are normalized using the maximum slip.
velocity \( u_{\text{max}} \) obtained for liquid-infused surface at \( x = 0 \). Slip length gain for liquid-infused surface with trapped air over liquid-infused surface with longitudinal grooves having different aspect ratios and solid area fractions are shown in (b). Note that these results are only accurate for longitudinal grooves with no ends.

Figure 6.5b shows a parameter study on the effects of \( h_1 \) and \( \varphi \) on the relative slip length gain of liquid-infused surface with trapped air similar to the study presented in Fig. 6.4a. Similar to the case of transverse grooves, it can be seen that \( E \) decreases with \( h_1 \) and \( \varphi \).

### 6.5 Effect of Interfaces Curvatures

In this section, modeling the fluid–fluid interfaces is discussed for curved interfaces. The flow field is assumed to be laminar 2-D steady state. Therefore, the flow field is obtained by solving Navier–Stokes equations in each region with different fluid using Fluent Inc., New Hampshire. Figure 6.6 shows a sketch of a fluid–fluid interface and these fluids are numbered as (1) and (2). For example, in case of using superhydrophobic surfaces, the fluids (1) and (2) would be water and air, respectively. Along this interface, three basic boundary conditions need to be satisfied to obtain the correct matching between these fluids, i.e.,

\[
\begin{align*}
|v_1| &= |v_2| \\
\tau_1 &= \tau_2 \\
v_1 \cdot n &= v_2 \cdot n = 0
\end{align*}
\]

where \( v \) is the velocity vector, \( \tau \) is the tangential shear stress, \( n \) is the unit normal to the interface and the subscripts 1 and 2 are for fluids 1 and 2, respectively (119). Note that the first and second boundary conditions are for the continuity of the tangential velocity and shear along this interface while the third boundary condition is for no mass flow in (or out) across the fluid–fluid interface. Therefore, a user defined function (UDF) is written to satisfy the boundary conditions in Eqs.
6.14a-c for each of the following cases. In order to validate the present model, several benchmark cases are discussed in the following sections.

![Boundary condition of the fluid–fluid interface between two fluids 1 and 2.](image)

**Fig. 6.6**: The boundary condition of the fluid–fluid interface between two fluids 1 and 2.

Now, this model is used to determine the flow fields in liquid-infused surface. The computational domain is shown in Fig. 6.6a. The flow fields in liquid-infused surface are calculated for different geometries (i.e., different $\beta$) as shown in Fig. 6.6a. Again, the channel geometry and flow conditions will be held constant in these cases with $H = 100 \mu m$, $L = 100 \mu m$. The entrapped lubricant is assumed to be incompressible fluid for this reason. There was no curvature of the lubricant–water interface as can be seen in Fig. 6.6a. Also, a pressure drop of 40 kPa is used as a reference value. The reference groove’s width and height are $w = 60 \mu m$, $h = 10 \mu m$, respectively, with a wall angle of $\beta = 45^\circ$. Otherwise these values will be mentioned. For the analysis of the results, different operating pressures (i.e., $\Delta P = 40, 20, 0.4, -20, -40$ kPa) and different wall angle (i.e., $-45^\circ \leq \beta \leq 45^\circ$) will be used in this work.

Unlike prior sections, the effective slip length will be calculated for both shear base (i.e., $b_s$) and for mass flow rate base (i.e., $b_d$) as mentioned in Eqs. 6.15a and 6.15b:
\[ b_s = \frac{\langle v \rangle}{\langle n \cdot \nabla v \rangle} \]  
(6.15a)

\[ b_q = \frac{Q_{\text{LIS}} - Q_{\text{NS}}}{4Q_{\text{NS}} - Q_{\text{LIS}}} \]  
(6.15b)

where \( Q_{\text{SHP}} \) and \( Q_{\text{NS}} \) is the volume flow rate in a LIS channel and no-slip parallel plates, respectively. Now, the enhancement in Eq. 6.13 will be either \( E_q \) when the slip length is \( b_q \) or \( E_s \) when the slip length is \( b_s \) (Eqs. 6.13 and 6.15). This is because the pressure drop can be used to evaluate the performance of the liquid-infused surface with trapped air on its counterpart liquid-infused surface which rewritten to be in teerms of volume flow rate (see chapter 2).

The results of liquid-infused surface are shown in Fig. 6.7. The slip length(s) for different wall angles are shown in Fig. 6.7b. The results show that the slip length increases with increasing \( \beta \). Also, for demonstration purposes, the tangential velocity and shear stress are shown in Fig. 6.7c and 6.7d, respectively, above and below the lubricant–water interface.
**Fig. 6.7:** Sketch of computational domain liquid-infused surface in (a). The slip lengths based on shear and volume flow rates for different wall angle at pressure of 40 kPa in (b). Comparison between the tangential velocity and shear stress in (c), and (d), respectively, above and below the lubricant–water interface.

For liquid-infused surface, the interface is assumed to be flat and that is not the case for liquid-infused surface with trapped air. In the case of liquid-infused surface with trapped air, there are three phase flows (e.g., water, lubricant and air, see Ref. (123)) on liquid-infused surface with trapped air design. Therefore, the above mentioned boundary conditions will be applied at the two interfaces, i.e., lubricant–water interface and air–lubricant interface. Figure 6a shows an example of the flow fields in liquid-infused surface with trapped air. First of all in order to obtain the radii of curvatures $R_{wl}$ and $R_{la}$, the lubricant pressure (incompressible fluid) is calculated from both top and bottom sides of lubricant and they are
where the subscripts $w$, $l$ and $a$ are for water, lubricant, and air, respectively. Also, the two volumes resulted from the lubricant–water interface and air–water interface are the same, i.e.,

$$
\int_{-\frac{w}{2}}^{\frac{w}{2}} f_{wl} \, dx = \int_{-\frac{w}{2}}^{\frac{w}{2} + h \tan \beta} f_{la} \, dx
$$

(6.17)

These interfaces in two-dimensional calculations can be written as equations of arc of a circle (see for more details Ref. (97)), i.e.,

$$
 f_{wl} = \sqrt{R_{iw}^2 - w^2/4} - \sqrt{R_{iw}^2 - x^2}
$$

(6.18)

Now, Eqs. 6.17 and 6.18 can be solved simultaneously in order to calculate $R_{wl}$ and $R_{la}$ at different operating pressures. Note that the air–lubricant interface is assumed to be pinned to point B from both sides and double reentry structure can be used at this point (see Refs. (45,123)).

A test case is considered in this section with channel height and length of $H = 100 \, \mu m$, $L = 100 \, \mu m$, respectively. The groove’s width and height are $w = 60 \, \mu m$, $h = 10 \, \mu m$, respectively, and wall angle of $\beta = 45^\circ$. The operating pressure of $\Delta P = 40$ kPa is used. The curvature radii are $R_{wl} = 69.18 \, \mu m$ and $R_{la} = 178.03 \, \mu m$ by using Eqs. 6.17 and 6.18. The stream function and velocity vector are shown in Fig. 6.8b and 6.8c, respectively.
Fig. 6.8: Sketch of computational domain of liquid-infused surface with trapped air in (a) under different pressure. The velocity vector and stream function in the three-phase flow in (b).

Comparisons between the liquid-infused surface with trapped air and liquid-infused surfaces are discussed in this section (for instance Figure 6.7a shows an example of reference case of liquid-infused surface and its counterpart liquid-infused surface with trapped air in Fig. 6.8a). Also, the solid area fraction, groove aspect ratio, and channel height and length are held constant. The parametric study including the protrusion angle (as a result of different pressure drop across the channel) and wall angle ($\beta$) are taken into consideration. In addition, the fluid properties (viscosity of entrapped fluid) will be varied to see the best performance for liquid-infused surface with trapped air over its counterpart liquid-infused surface. From these results, there may be best design of liquid-infused surface with trapped air compared to its counterpart liquid-infused surface to obtain the maximum benefits.

Figures 6.9a and 6.9b show the enhancement $E$ between liquid-infused surface with trapped air and its counterpart liquid-infused surface for shear stress base and for volume flow rate,
respectively (see Eq. 6.15). As can be seen, at different pressures the results do not have the same trend. The preliminary results showed that liquid-infused surface is better than liquid-infused surface with trapped air in case of applying high pressure. However, the volume flow rate is always higher in liquid-infused surface with trapped air than in liquid-infused surface as can be seen in Fig. 6.9b. This work will be continue to be our next reasech project (see Ref.(124)).

![Graph](image)

**Fig. 6.9**: The enhancement $E$ of liquid-infused surface with trapped air over its counterpart liquid-infused surface based on shear and volume flow rate in (a) and (b), respectively.

### 6.6 Conclusions

A new design, in which a layer of air is entrapped underneath the lubricant layer in a Liquid-Infused Surface to enhance its drag reduction effect, is introduced in this chapter, and it is examined using in-house numerical simulations. To further enhance the stability of the lubricant in the liquid-infused surface with trapped air design, the groove’s inlet was enhanced with double-reentry geometry. The slip effect generated with our design, referred to here as liquid-infused surface with trapped air, is computed by solving the biharmonic equation for the water–lubricant–air three-phase system in transverse grooves placed in the Couette flow geometry, and is compared to that of its liquid-infused surface counterpart. This chapter is a proof-of-concept study to
introduce the liquid-infused surface with trapped air as a means of providing long-lasting measureable drag reduction effects for water (or other low-viscosity fluids) as the working fluid. For the arbitrary dimensions considered in our study, liquid-infused surface with trapped air designs showed 20–37% advantage over their liquid-infused surface counterparts. It was specifically found that the drag reduction benefits of a liquid-infused surface with trapped air over its liquid-infused surface counterpart increase when the lubricant viscosity is increased. Effects of lubricant layer thickness and solid area fraction of liquid-infused surface with trapped air are studied in relation to their liquid-infused surface counterpart and discussed in detail.
Chapter 7. Overall Conclusion

The main goal of this thesis is to evaluate the performance of SHP or slippery surfaces. For this reason, a mathematical framework to study the time-dependent drag-reduction effect achievable by using SHP grooves inside a microchannel is presented. Our formulations showed excellent agreement with prior numerical, analytical and investigations. It was found that for two- and three-dimensional textures, the surface was function dependent on the interplay between the apparent contact angle and the volume of the groove. More specifically, our results showed that both the critical pressure and longevity of the entrapped air increase with the apparent contact angle (e.g., for surfaces decorated with hierarchical structures). On the other hand, increasing the initial entrapped air volume decreases the critical pressure while the longevity increases with increasing the initial volume of trapped air. Also, the instantaneous effective slip length (or drag reduction) resulted from longitudinal SHP grooves are almost twice the effective slip length obtained from transverse SHP grooves. These findings can then be used to custom-design superhydrophobic surfaces for different applications.

The flow fields in liquid-infused surface—when the entrapped fluid is a lubricant fluid—are evaluated in the present work by solving Naiver–Stokes equations. Then, the slip length (or drag reduction) is calculated for this design. In this work, a new design is suggested by entrapping a layer of air underneath the lubricant fluid. This design is referred to liquid-infused surface with trapped air. By assuming flat fluid–fluid interfaces, a comparison between the effect benefits
resulted from liquid-infused surface and liquid-infused surface with trapped air are accomplished. A drag reduction of about 37% advantage of liquid-infused surface with trapped air over its counterpart liquid-infused surface was obtained for arbitrary geometries of transverse grooves. Moreover, liquid-infused surface with trapped air may also be used in other applications where this design may increase the slippery of the working fluid compare to its liquid-infused surface counterpart (e.g., anti-fouling, anti-couling and so many other applications).
Appendix A: Gemortic Terms used in Chapter 2

Several geometric terms are used in the numerical modeling of longevity in Chapter 2 and they are

\[
\varepsilon_0 = \left[ R_{cr}^{(2)} \right]^2 \left( \sin 2\theta_L^{app} + \sin 2\theta_R^{app} + 2\sin^{-1} \left| \cos \theta_R^{app} \right| + 2\sin^{-1} \left| \cos \theta_L^{app} \right| \right) / 4 \tag{A1}
\]

\[
\varepsilon_1 = \frac{1}{2} \left( y_R \frac{w_R}{R} - \left( w_R - w_i / 2 \right) \frac{\dot{y}_R}{R} \right) \tag{A2}
\]

\[
\varepsilon_2 = \left[ -\frac{\dot{w}_R}{R} + \cos \theta_R^{app} \right] \left[ \frac{-\delta \left( w_L + w_R \right) + \sqrt{R^2 - \delta^2} - R \left| \cos \theta_R^{app} \right|}{\sqrt{R^2 - \delta^2}} \right] \tag{A3}
\]

\[
\dot{w}_R / \dot{R} = \left[ \sqrt{R^2 - \delta^2} \right] \left[ \sin \theta_R^{app} + \delta \left| \cos \theta_R^{app} \right| - R \right] / \left[ \delta + \left( \sqrt{R^2 - \delta^2} \right) \tan \beta_R \right] \tag{A4}
\]

\[
\dot{y}_R / \dot{R} = -\tan \beta_R \left[ \frac{\dot{w}_R}{\dot{R}} \right] \tag{A5}
\]

\[
\varepsilon_3 = \frac{1}{2} \left\{ y_{R,ref} + \tau \right\} \frac{\dot{w}_R}{\dot{R}} + \frac{w_L - w_R - w_i}{\dot{R}} \tag{A6}
\]

\[
\varepsilon_4 = R \left[ -\frac{\dot{w}_R}{\dot{R}} + \frac{\dot{\dot{w}}_R}{\dot{R}^2} \cos \theta_R^{app} \right] \left( \sin \theta_L^{app} - \sin \theta_R^{app} \right) \tag{A7}
\]

\[
\varepsilon_5 = \left( w_L + w_{R0} + R_0 \left| \cos \theta_R^{app} \right| \right) \sqrt{R_0^2 - \left( -w_L - w_{R0} + R_0 \left| \cos \theta_R^{app} \right| \right)^2} / 2 \tag{A8}
\]

\[
\varepsilon_6 = -R_0^2 \left( \sin 2\theta_R^{app} + 2\sin^{-1} \left| \cos \theta_R^{app} \right| - 2\sin^{-1} \left( \left[ -w_L - w_{R0} + R_0 \cos \theta_R^{app} \right] / R_0 \right) \right) / 4 \tag{A9}
\]
Appendix B: Vita

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PEER-REVIEWED JOURNAL PUBLICATIONS


**CONFERENCES AND WORKSHOPS**


4. **A.A. Hemeda**, H.V. Tafreshi “Instantaneous Slip Length in Superhydrophobic Microchannels” 68th Annual Meeting of the APS Division of Fluid Dynamics, 60 (21), Nov. 2015, Boston, USA.

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**Aerospace and Math Departments, Cairo University, Egypt**

(2006–2013)

Algebra, Calculus, Linear algebra, Introduction to Aeronautics, Fluid mechanics, Compressible flow, Fundamental of Aerodynamics, Boundary layer, High speed Aerodynamics, Computational Fluid Mechanics, Turbo machinery, Introduction to combustions, Propulsion systems, Airplane Aerodynamics, Space propulsion, Orbital Mechanics, Aerodynamics Laboratory, and Computer Club CUF

**Virginia Commonwealth University**

(2014–2015)

**Mechanical and Nuclear Engineering Department**

Numerical Methods (ENGR 312), Simulation and Modeling (ENGR 591), Convective Heat Transfer (EGMN 602)

**GRADUATE COURSEWORK**

**Cairo University, Egypt**


**Virginia Commonwealth University, USA**

Mechanical and Nuclear Engineering Analysis (ENGR 591), Continuum Mechanics (EGMN 503), Advanced Fluid Mechanics (EGRM 561), Special Topic in Nuclear Engineering (EGRN 610), Convective Heat Transfer (EGRM 602), Ordinary Differential Equations I (MATH 532), Mechanical and Nuclear Engineering Materials (ENGM 603), Mechanical and Nuclear Engineering Dynamics Systems (ENGM 604), Intro. To Grant Writing (GRAD 614), Responsible Scientific research Conduct (OVPR 602).

**COMPUTATIONAL SKILLS**

**Engineering Packages**

- Fluent Inc., and CFX ANSYS, COMSOL.
- MSC NASTRAN and AutoCAD
Photoshop, Flash, and virtual reality (MATLAB toolbox)

**Mathematical Packages**
- MATLAB, MATLAB Simulink, FLEXPDE, MATHEMATICA, FREEFEM++ and MAPLE.

**Programming Languages**
- FORTRAN, Visual Basic, C++ and Oracle.
References


87. Reversible switching between superhydrophobic states on a hierarchically structured surface [Internet]. [cited 2016 Apr 26]. Available from: http://www.pnas.org/content/109/26/10210


