PHASE FIELD MODELING AND VERIFICATION
OF A WETTING MODEL FOR HYDROPHILIC AND
HYDROPHOBIC SURFACES

A Thesis in
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ABSTRACT

Wetting properties of surfaces are of interest due to their potential applications in many fields. Differences in surface tension between liquid and solid can allow hydrophilicity, attraction to liquid, or hydrophobicity, repelling liquid. In this study, a phase field model was implemented to study the effects of varied surface geometry on wetting properties.

Of particular interest are superhydrophobic surfaces, or surfaces with a contact angle exceeding 150°. This behavior is due to surface roughness. Such surfaces can be fabricated in a number of ways, including top-down and bottom-up approaches. Many surface geometries have been theorized, modeled, and tested for the purpose of creating a more effective superhydrophobic surface.

First, a 2-D phase field model was implemented in MOOSE (Multiscale Object-Oriented Simulation Environment) for a flat surface. Results were related to real materials for the Wenzel (fully wetted) and Cassie-Baxter (resting on a layer of air) states. The model’s accuracy was then verified for a pillared surface using the Cassie-Baxter and Wenzel formulas and experimental data.

After this verification, other patterned surfaces were created in MOOSE to relate microstructures’ shape, size, and wetting state to contact angle. Other patterns included raspberry-shaped particle-covered surfaces and a triangular saw tooth pattern.
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NOMENCLATURE

\( \alpha \) defines areas of liquid and gas (=1) or solid (= -1)

\( A \) functional term relating \( \phi \) in terms of location \( r \) (\( \phi = A(r) \))

\( \gamma \) interfacial surface tension

\( F \) free energy \( F(\phi) \)

\( \theta \) contact angle

\( j \) flux

\( \kappa \) liquid-gas interface width

\( L \) defect width of stripe defects resulting in a capillary effect

\( M \) mobility

\( \phi \) defines areas of liquid (=1) or gas (= -1)

\( r \) spatial term

\( V \) potential energy \( V(\alpha, \phi, A) \)
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Chapter 1

INTRODUCTION

Surface wetting behavior influences how liquids interact with solids. Some of these interactions can have a huge impact on certain properties relating to surface tension between the liquid and a solid surface. Potential applications include anti-stick or self-cleaning coatings, watercraft, metal refining, stain-resistant textiles [1], biomedical applications [2], and anti-fog coating [3]. Experimental and simulation work have been done to determine how to influence these behaviors. Creating surface topographies and using materials that either attract or repel liquids can obtain desired properties. This work focuses on modeling surface topography for the creation of superhydrophobic, or water-repelling, surfaces.

1.1 Wetting and Surface Roughness

Wettability of a flat surface is expressed in terms of the contact angle $\theta$ of a water droplet. Surfaces with contact angles less than 90° are classified as hydrophilic. Greater than 90° is considered hydrophobic, and greater than 150° superhydrophobic. The related prefix describing wetting by oil is oleo- (phobic and philic), while wetting by any liquid is described by hygro-, and any substance at all by omni-.

Figure 1.1: representation of water droplets on hydrophilic ($\theta < 90^\circ$), hydrophobic ($\theta > 90^\circ$), and superhydrophobic ($\theta > 150^\circ$) surfaces
A surface’s contact angle is determined by the interfacial tensions ($\gamma$) between solid (S), liquid (L), and gas (V), as shown by Young's equation:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$  \hspace{1cm} (1)

Differences in contact angle can be due to different materials. For example, flat, waxy surfaces with composition similar to the lotus leaf may have contact angles around 110° [4]. Superhydrophobic surfaces, however, are normally achieved through surface roughness. Micro- and nanoscale patterns or structures have the tendency to repel water, leading to higher contact angles [5]. Rough waxy surfaces can result in much higher contact angles, such as the lotus leaf, with a contact angle of 160° [4]. Surface roughness generally enhances existing properties, making hydrophilic surfaces’ contact angle lower and hydrophobic surfaces’ higher, as seen in Figure 1.2 [6].

![Figure 1.2: contact angle (\theta) as a function of roughness factor (Rf)](https://via.placeholder.com/150)

Two types of contact angles are used in the classification of surfaces: static, in which equilibrium is reached as the system’s total energy is minimized, and dynamic, as a drop is advancing or receding. The difference between advancing and receding angles is known as contact angle hysteresis. Flat surfaces have comparatively low hysteresis as compared to
some rough surfaces. Superhydrophobic surfaces have very little contact angle hysteresis [7].

Contact angle hysteresis can be measured by several different methods. Methods may employ vibrations, optical systems, tilted substrates, and more [8]. The overarching idea is to measure contact angle as a drop advances, such as when volume is being added, or recedes, as the drop’s volume is decreased. Hysteresis can also be measured as the maximum and minimum values reached by drops sliding along a tilted surface, as the contact angle is still a function of surface tension.

1.1.1 Cassie-Baxter and Wenzel States

Wetting on a rough surface can occur in two ways. The surface can be fully wetted, known as the Wenzel state. In this case, asperities are completely filled with liquid [9]. In the other case, the Cassie-Baxter state, liquid rests on a layer of air between surface asperities. This is also known as a composite state [10]. The two wetting states are shown in Figure 1.3.

![Figure 1.3: Wenzel (fully wetted) and Cassie-Baxter (composite) states](image)

Each wetting model can be described mathematically as functions of Young’s angle ($\theta$) and either surface roughness ($r$) for the Wenzel state, calculated in equation (2): 

$$\cos \theta_{\text{apparent}} = r \cos \theta$$

\[2\]
or fraction of the solid surface in direct contact with liquid ($f$) for the Cassie-Baxter state, as in equation (3):

$$\cos \theta_{\text{apparent}} = f (1 + \cos \theta) - 1$$  \hspace{1cm} (3)

Should a surface contain more than one type of asperity, phase, or material, the Cassie-Baxter state can be calculated based on the fraction of each surface ($f_1$ and $f_2$) covered by each and each solid’s contact angle ($\theta_1$ and $\theta_2$):

$$\cos \theta_{\text{apparent}} = f_1 \cos \theta_1 + f_2 \cos \theta_2$$  \hspace{1cm} (4)

It is assumed that the contact angle of liquid on air approaches 180° [6]. From these equations, it is evident that the highest contact angles will result from a large surface roughness value for the Wenzel state and as little surface contact as possible in the Cassie-Baxter state.

### 1.1.2 Surface Geometry

A number of types of roughness have been theorized and tested. Roughness can be single-scale, such as with pillars or other simple shapes, or multi-scale, like large pillars covered in smaller pillars, as in Figure 1.4.

![Figure 1.4: single-scale roughness (left) and two-scale roughness (right)](image)

Even a stripe defect across a surface can influence wetting behavior by causing a capillary effect between the two lines. The propagation of the meniscus over time is
influenced both by the shape and distance between stripe defects or width of microchannels, with smaller widths resulting in faster propagation [11].

The overall goal in designing surface geometry for Cassie-Baxter state wetting is to increase the ratio of air to solid in contact with a liquid. In the Wenzel state, more complex factors may be at play, but with surface roughness still having immense importance. Because there is no trapped air, roughness affects properties such as surface tension and flow behavior.

1.1.3 Bio-Inspired Surface Geometry

Many surfaces studied for their hydrophobic properties were originally found in nature. One of the most famous examples is the lotus leaf. Its waxy coating’s water repellency is enhanced by its multi-scale roughness, achieving a contact angle of 160° [12]. This causes water droplets to slide very easily off the leaf. The leaf and its microstructure are shown in Figure 1.5.

![Figure 1.5: (a) lotus leaf, (b) SEM image of lotus leaf prepared by glycerol substitution showing multi-scale roughness of papillae, wax clusters, and wax tubules, (c) wax tubules [12]](image)
The high contact angle actually causes a water droplet to roll as it slides off. This results in a self-cleaning property as the drop picks up anything lying on the leaf’s surface [13] (Figure 1.6).

![Figure 1.6: sliding (a) and rolling (b) droplet [13]](image)

Water striders’ legs also utilize a texture to repel water. They are covered in tiny hairs, or setae (Figure 1.7). The large length to width ratio of the setae results in Cassie-Baxter surface wetting with an extraordinarily low solid to air contact ratio. This allows a very high surface tension, thus allowing the bugs to move along the water’s surface. The resulting contact angle is $167.6 \pm 4.4^\circ$ [14].

![Figure 1.7: (a) water strider leg with many microsetae, (b) nanoscale grooved seta [14]](image)

Many other surfaces in nature have interesting wetting behavior both in the Cassie-Baxter state, such as many types of feathers and fur, and in the Wenzel state, such as aquatic
life. One surface that has been investigated for practical use is shark skin, to be discussed later in section 2.1.

1.2 Surface Fabrication

Since creating a rough surface is essential to enhance hydrophobic and hydrophilic behavior, surface preparation must consider the material to be used, but also how to treat or alter it to create texture. Surface fabrication falls into two basic categories: top-down and bottom-up. These terms were first used by the Foresight Institute in 1989 to categorize nano-scale fabrication methods [15]. Top-down, or subtractive, approaches such as lithography or etching take away from the original material. Bottom-up, or additive, approaches build on an existing surface via some type of deposition or bonding. Multiple steps can also be used and can combine top-down and bottom-up methods. This could be a particularly useful way of creating multi-scale roughness.

1.2.1 Top-Down Fabrication

Top-down methods can encompass anything related to machining, molding, carving, or otherwise removing an existing part of a surface. Specific methods used to create superhydrophobic surfaces include, as listed by Li et al., lithography, templation, micromachining, and plasma treatments. Lithography uses chemical processes to engrave or etch. Templation molds a surface by placing a template on top. Templates can include surfaces prepared by lithography or even natural surfaces such as leaves. Negative molds taken from a template can even be used to re-create the positive structure by repeating the templation process. Micromachining involves cutting away from a surface. Plasma treatments anisotropically etch a surface [1].
1.2.2 Bottom-Up Fabrication

With bottom-up methods, it is possible to create more complex geometries at the molecular level. These often involve self-assembly and self-organization. More than one material can be included in the surface’s structure by combining methods. Various methods as listed by Li et al. include chemical bath deposition, chemical vapor deposition, colloidal assembly, electrochemical deposition, layer-by-layer deposition by electrostatic assembly, sol-gel methods, hydrogen bonding, and chemical synthesis. Chemical depositions can result in nanotube, nanopin, or nanorod structures. Colloidal assemblies form tightly packed assemblies due to van der Waals forces, and multiple materials can be used together to form hierarchical roughness. Layer-by-layer deposition uses electrostatic charge interactions and requires hydrophobization due to polyelectrolytes’ hydrophilicity. Sol-gel methods use a gel-like liquid-solid solution, which is either applied directly or combined with fillers. Hydrogen bonding and chemical synthesis also bond molecules to a surface [1].

1.3 Experimental Methods

Surfaces are prepared in numerous ways and tested for contact angle. As discussed in section 1.1, advancing and receding angles, also known as contact angle hysteresis, can be measured either as drops slide across a tilted surface or as volume is added or subtracted. Contact angle is measured from images taken of a droplet.

1.4 Modeling Methods

Modeling can be classified either as mathematical or molecular in nature. Mathematical models follow known behavior by using formulas that have proven to be true. Molecular models follow the behavior of each molecule as it reacts with every surrounding molecule.
1.4.1 Phase Field

Phase field modeling mathematically solves interfacial problems. The microstructure of a material is described by continuous variables, where each phase is given a specific numerical value and the variables smoothly transitioning between values across the interface. Thus, interfaces have a finite width. The free energy of the system is represented with a free energy functional that is a function of the microstructure variables. The evolution of the microstructure variables is described by a set of partial differential equations that minimize the free energy functional. As the functional approaches its minimum, the system reaches its lowest-energy state.

As far as modeling wetting behavior, a number of different formulas have been used. The Ginzburg-Landau framework has been used to model a 2D view of a droplet from above [16, 17] and for 2D and 3D modeling of microfluidic junctions [18]. The Helmholtz free energy functional has been used for 2D wetting models viewed from the side [19, 20], as have parabolic PDEs resembling the Allen-Cahn equation [21]. Van der Waals free energy has been used to model flow over a surface [22].

MOOSE, used in this analysis, is one of a handful of simulation software packages and frameworks to utilize the phase-field method. It is a multiphysics finite element framework that uses C++ and was developed at Idaho National Lab.

1.4.2 Molecular Dynamics (MD)

Molecular dynamics modeling is a simulation method used to study the movement of atoms and molecules using numerical methods. Development of simulation methods began in the 1950s. Current capability allows accurate simulation of around $10^6$ simple molecules or single, very complex molecules. Newton’s equations of motion are normally used to determine particle interactions, but require an empirical potential describing the atomic
interaction. MD simulations accurately capture complicated material behavior by describing basic atom interactions rather than applying a single formula in which mechanisms must be specifically included such as with the phase field method. In MD, results vary every time since the model is stochastic. Main benefits include easily measuring all macroscopic parameters (surface tension, dynamic contact angle, etc.) and being able to run parametric studies, easily holding variables constant. This provides huge benefits over experimental methods. It should also be noted that contact angle must be determined using the circle extrapolated from the droplet's profile, not from the few molecules directly adjacent to the solid, and that this adjacent region's behavior is independent of droplet size [23].

1.5 Objectives

This work aims to create a phase field model in MOOSE that accurately represents wetting behavior. Surface geometry will then be varied in order to determine what types of surfaces should exhibit hydrophobic or hydrophilic properties. Previous models by experimentalists will be used in order to validate this model and expand upon their work.

1.6 Outline

Experimental and modeling results will be discussed and evaluated for their usefulness. Interesting results will be modeled and small parametric studies run to determine optimal sizes and shapes. Models will be compared to previous work.
Chapter 2

LITERATURE REVIEW

2.1 Experimental Results

Recent progress has been made in a number of microstructures and coatings that result in different wetting behaviors. The following will discuss several noteworthy experimental results of recent years.

2.1.1 Parametric Studies

In 2005, Suh and Jon created surfaces of rounded pillars of polyethylene glycol (PEG) using capillary lithography. Pillars were 150 nm in width with spacing of 500 nm, with varied heights. Images of the nanostructures and of water droplets on each surface are shown in Figure 2.1 [24].

![Figure 2.1: SEM images of molded PEG nanostructures and corresponding contact angles at 0 and 60 seconds; (a) flat surface, (b) 170 nm, (c) 310 nm, (d) 440 nm, (e) 500 nm [24]](image-url)
Ran et al., in 2008, varied hole diameter and depth in nanoporous alumina. Hole diameter, spacing, and depth were varied by using different anodization time, voltage, and pore opening time. Pore structures could be tuned to between 20 and 980 nm in diameter, and up to several hundred micrometers in depth. Several diameters and their corresponding contact angles are shown in Figure 2.2, and contact angles as a function of hole depth in Figure 2.3 [25]. Contact angle on flat, nonporous aluminum was measured as 85° [26].

Figure 2.2: porous alumina with fixed hole interval of 450 nm, diameters of (a) 85 nm, (b) 180 nm, (c) 290 nm, and (d) 420 nm (left); contact angle as a function of hole diameter with fixed hole depth 4.5 μm (right) [25]

Figure 2.3: contact angle as a function of hole depth in porous alumina [25]
In 2009, Park et al. compared theoretical Cassie-Baxter and Wenzel model predictions to actual wetting behavior for 5μm-thick pillars made of two different polymers. The pillars, of circular cross-section, were varied in height (5 different height/diameter ratios) and spacing (10 different spacing/diameter ratios). Fabrication methods are shown in Figure 2.4. Materials used were hydrophobic polydimethylsiloxane (PDMS), and hydrophilic Norland Optical Adhesive (NOA). Pillar width was held constant at 5 μm. The contact angle of a water droplet on flat PDMS is approximately 110°, and on NOA 70°. Contact angle was measured using a contact angle analyzer (Drop Shape Analysis System DSA100, Kruss, Germany) on drops of 6 μL over a time span of 1.5 minutes. Contact angle values, shown in Figure 2.5, were averaged over at least 6 locations on each sample [27].

Figure 2.4: fabrication procedure for PDMS and NOA pillared surfaces by using PUA [27]
2.1.2 Bio-Inspired Surfaces

Sun et al. used lotus leaves for templation using polydimethylsiloxane (PDMS) [28]. The process of replicating a lotus structure using templation directly from a leaf was continued later by others, including Dai et al. in 2013. A PDMS mold was taken of a lotus leaf to imprint the microscale pillar structures into a ZnO sol film. Hierarchical ZnO micro and nano structures were then fabricated using hydrothermal treatment, shown in Figure 2.6. Surfaces were modified using fluoroalkylsilane after hydrothermal growth. Flat surfaces of the same materials were found to have contact angles around 110°. Contact angles up to 158° were achieved on structures with 12 hours of hydrothermal growth [29].
In 2014, Zhao et al. published results on a hydrophobic shark-skin-inspired surface [30]. The diamond-shaped pattern of shark skin had previously been investigated and found to reduce drag [31]. The underlying principle was determined to be that grooved scales prevent the formation of vortices [32]. This work proposed and tested a new hydrophobic model to determine how size and arrangement of riblets affected wetting behavior. Micro-scale riblets were found to increase contact angles up to 103.9° from around 75° on a flat surface, and also trap air, creating a composite interface. An SEM image and a representation of the pattern used for biomimetic film are shown in Figure 2.7 [30].
In 2015, Watson et al. investigated water droplet behavior on actual gecko skin. The patterned surface resulted in impressive self-cleaning properties. Scales from the abdominal region, with diameter and spacing as large as 300 μm, were covered in silica particles. A 2 mm water droplet was introduced and the surface tilted to an angle of 2 degrees from horizontal. Progress of the droplet, as well as close-up images of the surface after its passing, can be seen in Figure 2.8. Contact angle was not reported, but self-cleaning properties were evident [33].

![Figure 2.8: (a) introduction and rolling of water droplet on silica particles, (b) droplet path after passing, (c) typical area under droplet after passing [33]](image)

2.1.3 Microfluidics

In the field of microfluidics, main concerns include controlling liquid flow and preventing biofouling. Controlling flow can be accomplished by microvalves, which serve to actuate, move, or seal off flow.

Yang et al., in 2011, related capillary width to wetting time, shown in Figure 2.9. The speed of the advancing meniscus agreed with the Washburn equation, which predicts that
the square of the advancing front’s position increases linearly with time. A modified equation was developed to account for different flow profiles [11].

![Graph](image)

**Figure 2.9: progress of liquid water meniscus x^2 over time t in open microchannels [11]**

In 2015, Wang et al. used chemically patterned striped surfaces to develop a microvalve for a microchannel. A micropatterned surface with alternating hydrophobic and hydrophilic stripes results in anisotropic wetting behavior due to the anisotropic wettability. Microscale features and dimensions influence flow, such as in a Y-shaped junction of certain dimensions, controlling the direction and speed of flow from inlet to outlet. Other factors influencing flow include applied pressure, period of the pattern, ratio of hydrophobic to hydrophilic area, and materials for each surface type. Microvalves perform best when the difference in surface free energies between the two materials is large. Smart valves may also be created by using thermo- or photoresponsive materials. SEM images and a schematic of the channel are shown in Figure 2.10 [34].
2.1.4 Other

In 2005, Hosono et al. used chemical bath deposition, which resulted in a nanorod structured surface as depicted in Figure 2.11. This surface was created using a solution of CoCl2 and NH2CO in water deposited on borosilicate glass. After deposition, surface was modified using lauric acid. The resulting nanorods had a tip diameter of 6.5 nm and the surface's contact angle was 178° [35].

In 2005, Ming et al. created a rough surface of raspberry-like silica particles, as shown in Figure 2.12. Epoxy-functionalized monodispersed silica particles of about 700 nm and aminofunctionalized silica particles of about 70 nm were prepared, with the smaller particles then covalently grafted onto the larger particles due to the reaction between epoxy and amine groups. Creating particles of varied sizes is simple, enabling manipulation of
The surface roughness. The surface is chemically modified with polydimethylsiloxane (PDMS) to enhance hydrophobicity. Resulting contact angles were as high as 165°. Contact angles on surfaces covered in small or large particles only were 148° and 151°, respectively [36].

![Figure 2.12: (a) TEM image, (b) AFM image of raspberry-like silica particles [36]](image)

A unique surface that is both non-wetting and non-sliding was presented by Zhao et al. in 2007. Constructed from polymethyl methacrylate (PMMA), which is hydrophobic, and amphibilic polyurethane, which is hydrophilic, the surface both attracts and repels water. The result is a surface with a high contact angle (160°) such that a static fluid is non-wetting, yet with a high surface tension that causes a droplet to adhere strongly to the surface without sliding. Its microstructure is shown in Figure 2.13 [37].

![Figure 2.13: SEM images of triple blend surface (PMMA, A-PU, F-PU) with A-PU/F-PU weight ratios a) 8/2, b) 6/4, c) 4/6, and d) 2/8; scale bar = 10 μm [37]](image)
In 2008, Xue et al. treated cotton fabrics with TiO2 sol, then coated with stearic acid and PFTDS either individually or together. Static contact angles as high as 163.5° were achieved. Past attempts at superhydrophobic textiles sometimes required extremely tight knits. All processes use some type of bonding or coating to achieve hydrophobicity [38].

T.S. Wong et al. have created an omniphobic surface that repels liquids by using a lubricating film, shown in Figure 2.14. Substrate materials are shown in Figure 2.15. Results were published in 2011. Porous solids (Teflon and epoxy-resin-based surfaces) were rendered more hydrophobic by sitting in a vacuum dessicator overnight with a vial of heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilan. Prefluorinated lubricating fluid (possibly 3 M Fluorinert FC-70, or DuPont Krytox 100 and 10) was added to form a coating layer. Due to compatible surface chemistry and roughness, the liquid spreads spontaneously due to capillary wicking. This spreading behavior results in the surface “repairing” itself when it loses some of the coating. Some coating is also trapped in the microstructure. When the surface is damaged, some combination of “chemical potential, concentration and pressure gradients” [39] aid in transporting more lubricant to the surface. Many potential applications exist, including in biomedical devices and anti-fouling or icing coatings.

Limitations include manufacturability and durability [40].

![Figure 2.14: comparison of stability and displacement of lubricating films on silanized and non-silanized surfaces [40]](image-url)
2.2 Modeling and Theoretical Results

2.2.1 Numerical

In 2004, Dupuis et al. applied a lattice Boltzmann solution of the equations of motion describing droplet spreading to model surfaces covered in microscale posts of square cross-section. Inputs include droplet size, surface tension, viscosity, and contact angle. Along with a free energy equation, these help to determine the evolution of a system over time. This analysis did take gravity into consideration [41].

In 2004, McHale et al. concluded that, for materials with a smooth surface contact angle of about 90°, the gain factor for amplification of contact angle is approximately equal to roughness factor for the Wenzel state. Young’s equation, along with the Cassie-Baxter and Wenzel equations, were used in this analysis. The relation is shown in Figure 2.16 [7].

Figure 2.15: SEM images of an epoxy-resin-based nanofabricated post array (left) and a Teflon-based porous nanofibre network (right) [40]

Figure 2.16: gain factors relating the response of Wenzel-state contact angle to surface roughness values of 1, 1.2, and 2 [7]
Ren, in 2014, used the string method to study the wetting transition on hydrophobic, microstructured surfaces for square pillared surfaces. The standard diffuse interface model was used. Transition states, energy barriers, and minimum energy paths were explored. Wetting was found to occur via the wetting of a single groove, followed by lateral propagation of wetting, as shown in Figures 2.17 (energy barriers between wetting states) and 2.18 (depiction of lateral propagation) [42].

Figure 2.17: overcoming energy barriers in Wenzel-state wetting from the innermost group of pillars (at wetting state W1) to outermost (W3) [42]

Figure 2.18: lateral propagation of droplet; W2 is a metastable state, S2 and S3 are transition states [42]
The model proposed by Nosonovsky and Bhushan in their 2005 paper combines “the effect of surface area, possibility of formation of composite interface and the effect of sharp edges” to predict contact angles as a function of surface characteristics, as plotted in Figure 2.20 [43].

![Figure 2.19: contact angle for surfaces with a sinusoidal profile, rectangular profile (dotted line), hemispherically-topped cylindrical profile solid line), and conical or pyramidal asperities [43]](image)

In 2006, Nosonovsky and Bhushan proposed a stochastic model for metastable wetting based on the Maxwell-Boltzmann distribution. Among other results, the relationship of the distance between asperities and contact angle was theorized, as plotted in Figure 2.19 [6].

![Figure 2.20: contact angle as a function of asperity spacing for (a) a stochastic model, (b) no air pockets, stochastic distribution of air pockets, and composite liquid-air interface (φ denotes roughness) [6]](image)
2.2.2 Molecular Dynamics

Koishi et al. modeled water droplets using Molecular Dynamics (MD) simulation in 2009. Droplets were introduced to the system from above at an impinging velocity, contacting surfaces of varied pillar heights to determine which regime (Cassie-Baxter or Wenzel) wetting will fall into under different conditions. It was found that there is generally a critical pillar height in which a bistable Cassie/Wenzel state occurs depending on the initial location of droplets. The free energy barrier between the wetting states, depicted in Figure 2.21, was found to be between a few tenths of $k_B T_0$ at critical pillar height and 8 $k_B T_0$ for pillar heights greater than the size of the water droplet, where $k_B$ is Boltzmann’s constant and $T_0$ is ambient temperature (298 K). Results also indicated that the free energy barrier is not particularly sensitive to the size of the water droplet. Results from two different initial conditions in MD simulations are shown in Figure 2.22, illustrating the ability of similar conditions to result in different wetting states [44].

![Figure 2.21: the free energy barrier ΔG separating the Cassie-Baxter and Wenzel states [44]](image-url)
Figure 2.22: MD model of water molecules over pillars with initial conditions (above) starting at (a) the top of the pillars and (b) between pillars, showing that different final wetting states (below) can occur given different initial conditions [44]

2.2.3 Phase Field

The Ginzburg-Landau framework, which expresses free energy in terms of a complex order parameter field, has been used to model droplets in 2D from above by Luo et al. in 2005 [17] and by Anantharaju et al. in 2009 [16], and for 2D and 3D modeling of microfluidic junctions by Liu and Zhang in 2009 [18]. Anantharaju et al. investigated wetting behavior on chemically heterogeneous surfaces, or surfaces of one material with squares of a second material embedded. Advancing and receding droplet behavior for such cases is shown in Figure 2.23.
In addition to the Ginzburg-Landau framework, Liu and Zhang also used a lattice Boltzmann model to simulate flow. Viscosity, contact angle, capillary number, and flow rate ratio were found to be important factors in droplet formation.

Luo et al. investigated contact line shape between stripe defects. Contact angle was not considered as simulations were viewed from above only.

The Helmholtz free energy functional has been used for 2D wetting models as viewed from the side by Borcia et al. in 2009 [19] and Wheeler et al. in 2013 [20]. Helmholtz free energy is a measure of thermodynamic potential, or useful work that can be obtained from a system. Wheeler et al. modeled molten metal droplets rather than water, using chemical potentials and a van der Waals diffuse interface approach. Borcia's model included gravity and measured stability of thin liquid films (as shown in Figure 2.24), static contact angles, and dynamic contact angles over sloped surfaces.
Parabolic PDEs resembling the Allen-Cahn equation have also been used in modeling 2D wetting from a side view, such as by Turco et al. in 2009. Both Dirichlet and Neumann boundary conditions were used to simulate advancing and receding drops both by changing drop volume and by tilting the solid surface. External force was also applied to drops in the Cassie-Baxter state to induce the Wenzel state, as in Figure 2.25 [21].

Van der Waals free energy has been used to model flow over a surface by Takada et al. in 2008. Navier-Stokes equations were used with the phase field model. Contact line
motions under gravity were accurately simulated (as in Figure 2.26), contact angle could be controlled by a wetting parameter, and capillary flow agreed with experimental data [22].

Figure 2.26: collapse of a 2-dimensional column of liquid under gravity [22]
Chapter 3

MODELING PROCEDURE

3.1 Formulation

A repeatable formula was chosen from Luo et al. [17] due to its simplicity and ease of implementation in the MOOSE framework and was modified to include several new features. The field’s equilibrium values are determined by the free-energy functional

\[ F(\phi) = \int d r \left[ \frac{V}{2} |\Delta \phi|^2 + V(\alpha, \phi, A) \right]. \]  \hspace{1cm} (5)

Potential energy \( V \), which describes different phases, is given by

\[ V = \frac{1}{2} (1 + \alpha) \frac{1}{4} (1 - \phi^2)^2 + \frac{1}{2} (1 - \alpha) \frac{\kappa}{2} [\phi - A(r)]^2, \] \hspace{1cm} (6)

where the liquid and gas phases are given by a double-well potential (\( \alpha=1 \)) and solid by a single well (\( \alpha=-1 \)). The liquid phase is given by (\( \phi=1 \)) and gas by (\( \phi=-1 \)). The solid phase has an energy minimum for \( \phi=A(r) \). The variables are evolved using a Cahn-Hilliard equation according to

\[ \frac{\partial \phi(r,t)}{\partial t} + \nabla \cdot M(\phi) j(r,t) = 0 \] \hspace{1cm} (7)

which allows local conservation of the field, and where \( j = \nabla \frac{dF}{d\phi} \). In this work we have modified the model to include a spatially varying mobility \( M \), where \( m \) is equal to zero within the vapor phase and 1 in the liquid phase, and is given by

\[ M = \frac{\phi+1}{2}. \] \hspace{1cm} (8)

Chemical potential can be obtained as \( \mu = \frac{\delta F}{\delta \phi} \). By inserting Equation (5) into Equation (7), we obtain the equation of motion,

\[ \frac{\partial \phi(r,t)}{\partial t} = \nabla \cdot M(\phi) \nabla \left( -\gamma \nabla^2 \phi + \frac{1+\kappa}{2} (\phi^3 - \phi) + \frac{1-\kappa}{2} \kappa (\phi - A(r)) \right). \] \hspace{1cm} (9)
As mentioned, this model is simple and allowed rapid implementation in the MOOSE framework. Due to its simplicity, two critical simplifying assumptions are made. First, we neglect gravity such that the only driving force for droplet evolution is the interaction with the surface. Second, we assume that the liquid moves according to diffusion rather than convection. Mass is conserved but gas concentration can diffuse through the liquid, which is not an accurate description of liquid behavior. More accurate models will be developed as future work.

### 3.2 Surface Texture Creation

Surfaces were designed graphically, mimicking prior (experimental and theoretical) results. Patterns were created in PowerPoint using built-in graphics features to exactly size and align shapes. These images are loaded into the image reader function in MOOSE, to be discussed further in section 3.3.

First, simple pillared surfaces were modeled in 2D. Goals for this preliminary modeling were to ensure that both Cassie-Baxter and Wenzel state wetting could be achieved.

Next, pillared surfaces with varied ratios of pillar height, width, and spacing were modeled after the experimental setup from Park et al. as shown in Figure 3.1. The surface was given a value of $A = -0.387$ or 0.2 which, on a flat surface, results in contact angles of 110° and 70°, the same as the contact angles of PDMS and NOA (polydimethylsiloxane and Norland Optical Adhesive).

![Figure 3.1: varied pillared surfaces](image)
After verifying how well the model fits with previous work in simple microstructures, more complex patterns can be explored. In 2D, this means moving from simple pillars to surfaces of multiscale roughness. Surfaces chosen included a triangular structure and raspberry-like silica particles, as in Figure 3.2 [35].

![Figure 3.2: multiscale rough surface of raspberry-shaped particles](image)

### 3.3 Initial Conditions

The surface roughness is included in the model by setting a spatially varying value of the α parameter, where we define α as -1 in the solid region and 1 within the region where fluid is free to move. For the flat surface, the values of α are set within a rectangular region using basic capabilities in MOOSE. The more complicated surfaces are created from images using image reading capabilities in MOOSE, which use RGB color values from an image file to determine which regions are defined by which variable value. For this case, black was defined as solid (α = -1) and white as fluid (α = 1). The initial state of the system is shown in Figure 3.3.

To differentiate between liquid and gas, φ was set to 1 inside the droplet and -1 outside. A finite interface width was defined between the two, forming a barrier of gradual decrease in φ from 1 to -1. As we solve the differential equations to predict the evolution of φ, the droplet is free to move about the system to reach its lowest energy state.
Finally, the parameter $A$, which defines the inherent contact angle of the surface, was defined with a single constant value, thus defining any solid surface in the model as having a specified value of hydrophobicity.

### 3.4 Solver

The PDE’s defining the evolution of $\phi$ are discretized using the finite element method in MOOSE. However, because the Cahn-Hilliard equation has fourth order spatial derivatives, it was divided into two second order equations and solved in the manner used by Zhang et al. [45]. The discretization with time is conducted using an implicit second order approach, where the nonlinear system of equations is solved using Newton’s method.
Chapter 4

RESULTS AND DISCUSSION

4.1 Droplet on a Flat Surface

Values of A, the wettability parameter, were varied between -1 and 1 at intervals of 0.1. Resulting contact angles were measured from the center of the liquid-gas interface, representing the meniscus, using gimp’s angle measuring tool. For this study, an interface width of around 1/6 of the droplet's radius will be used. Resulting contact angles were plotted as a function of A, as shown in Figure 4.1.

![Figure 4.1: lowest energy state of a droplet on surfaces of varied A values](image)

For this study, values of A from -1 to 0 are considered. These values were plotted against their resulting contact angle when run on a flat surface, as shown in Figures 4.2 and 4.3. The A values could then be related to the flat surface contact angles of a number of real materials by finding the value corresponding to that material's contact angle.
Figure 4.2: contact angle as a function of hydrophobicity parameter $A$ (negative values)

$$y = 55.828x^2 - 30.354x + 89.874$$

$R^2 = 0.99388$

Figure 4.3 contact angle as a function of hydrophobicity parameter $A$ (positive values)

$$y = -100.43x^3 + 143.41x^2 + 133.13x + 90.077$$

$R^2 = 0.99989$
4.2 Droplet on a Pillared Surface

Preliminary models on a simple pillared surface showed both Cassie-Baxter and Wenzel wetting states. A values were set to -0.387 and 0.2 to mimic PDMS and NOA, respectively, from the 2009 study by Park et al., in order to study behavior in each wetting regime as compared to theory and to experimental results. At a height to width to spacing ratio of 2:1:1, the PDMS surface was predicted theoretically and proved experimentally to be at a metastable state between Cassie-Baxter and Wenzel state wetting. Modeling results proved consistent with this behavior (Figure 4.4). Starting the droplet at varied initial y-values resulted in Wenzel, Cassie-Baxter, and partially wetted states.

![Figure 4.4: droplet on 2:1:1 spacing:height:width ratio, A = -0.387, with droplet started at varied initial heights](image)

A parametric study was then run for height and spacing ratios between 1 and 5 for a total of 25 simulations (Figure 4.5). Droplets were made bigger with respect to surface roughness size in order to obtain more accurate results.
Figure 4.5: pillars of varied height, width, and spacing ratios with contact angles given in black for Wenzel state wetting or white for Cassie-Baxter state (PDMS)

Resulting contact angles were plotted over lines representing theoretical predictions in both the Cassie-Baxter state (Figure 4.6). Color schemes were borrowed from the study by Park et al. for easy comparison to theoretical and experimental values.
Figure 4.6: contact angle as a function of pillar spacing ratio, plotted for varied height ratios (PDMS) (theoretical results from [26])

Modeled results for height ratios between 2 and 5 showed similar behavior to experimental results, though at contact angles about 15-25° lower. There was no discernible trend for pillars with a height ratio of 1, though some contact angles came extremely close to both experimental and theoretical values. This discrepancy could be due to the fact that in our simulations the droplet sizes are on the same order as the surface roughness. However, both the Cassie-Baxter and Wenzel models assume that the droplet is very large compared to roughness. Thus, it is not surprising that there are differences between the analytical models and the phase field solutions.

In an attempt to improve the ratio of pillar size to droplet size, a second round of simulations were run. Since trends for the larger pillar heights had previously proved to be similar, fewer height ratios were simulated. In order to determine if there was a contact angle drop-off at the transition from Cassie-Baxter to Wenzel state wetting at spacing ratios
between about 5 and 7 as found experimentally by Park et al, spacing ratios up to 7 were run (Figure 4.7).

A = -0.387 PDMS

Width : height

Contact angles were different for these simulations, but still on the same order of magnitude below experimental results. There was a small but promising dip in contact angles as expected between spacing ratios of 5 and 7 for h/d = 3. Results are plotted in Figure 4.8.
Next, simulations were run for Norland Optical Adhesive by using hydrophobicity parameter $A = 0.2$, a more hydrophilic value than used for PDMS (Figure 4.9).
Contact angles showed no resemblance to experimental or theoretical data (Figure 4.10).

![Figure 4.10: contact angle as a function of spacing (NOA) (theoretical results from [26])](image)

### 4.3 Droplet on a Triangular Surface

Effect of surface roughness size with respect to droplet size was briefly investigated on a saw blade-textured surface. An $A$ value of -0.387 was used to mimic PDMS. Droplet size remained constant as roughness height decreased. Contact angles on the largest- to smallest-textured surfaces were 70°, 115°, and 125° (Figure 4.11). Thus, a very large-textured surface could potentially render a hydrophobic material hydrophilic.

![Figure 4.11: varied droplet sizes on saw tooth textured surface](image)
4.4 Droplet on a Raspberry-Shaped Particle Surface

In order to compare to experimental results by Ming et al., raspberry-shaped particle shapes were created with a size ratio of 10:1. Images were also created for large particles only and small particles only with the same shape distribution for consistency. Experimentally determined values for the small, large, and raspberry-shaped particles were 148°, 151°, and 165°, respectively (Figure 4.12).

![Initial surfaces and modeling results](image)

Figure 4.12: initial surfaces (left) and modeling results (right) for PDMS-covered silica particles of (top) small size, (middle) large size, or 10 times small particles’ radius, and (bottom) raspberry-shaped particles comprised of both sizes

Although each simulation began with the same initial conditions, including droplet size and position, final droplet size varied. This, along with varied heights of the surface’s texture, certainly influenced measured contact angle. Resulting contact angle values were, similar to the pillars’, around 30° lower than predicted. Small particles resulted in a contact
angle of 123°, large at 122°, and raspberry-shaped at 129°. Note that the small-scale roughness is smaller than the interfacial width and therefore will not significantly impact the simulation results.

4.5 Analysis

When compared with results from Park et al., contact angles on PDMS surfaces were significantly lower but often followed similar trends.

NOA surfaces came close to theoretical values for lower spacing ratios, but when spaced further apart, were somewhat closer to experimental values. Lack of any definitive trend, however, makes the results inconclusive.

Raspberry-shaped particle results showed promising trends in increasing contact angle by adding multi-scale roughness, but factors such as the solid surface portion of the simulation “absorbing” too much of the droplet and too-tall surface roughness reaching too high on the droplet affected results.

Due to such a wide interface width with respect to surface features, contact between the surfaces and droplets were not as accurately represented as they could be. This affected all simulations.

4.5.1 Effectiveness of Surfaces

Pillared surfaces can be effective in many applications. Shorter, thicker pillars are more durable. Taller pillars have higher contact angles in the Cassie-Baxter state.

Large-scale saw tooth-shaped surfaces could potentially be useful in cases where hydrophobic materials cannot be coated but hydrophilic behavior is desired, such as in shape-changing surfaces designed to exhibit both hydrophilic and hydrophobic properties.
Smaller-scale patterned surfaces are unlikely to be as useful, as they either have low roughness or are tall enough to be very brittle at their triangular tips.

Raspberry-shaped particles and other surfaces with multi-scale roughness could be very effective in both Cassie-Baxter and Wenzel-state wetting due to their high contact angles.

4.5.2 Feasibility of Surface Manufacturing

Pillared surfaces and silica-particle-coated surfaces are easily manufactured on a small scale, but may become more difficult to fabricate for larger-scale applications. For preliminary work in determining easily created, durable surfaces, it should be considered that methods such as templation and deposition are fairly straightforward. It should also be noted that tall, thin structures are more likely to break or even to deflect under loads. This necessitates a trade-off between function and durability for a characteristic inherent in successful Cassie-Baxter state wetting.
Chapter 5

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

Although benchmarking values using pillared surfaces did not match up to experimentally determined values, the model shows promise in accurately depicting wetting behaviors. Goals include creating a more complex model with gravity so that the model represents more than just diffusion within a system. Also, a larger droplet with respect to surface size should be used, which will require a reduced interface width.

5.2 Recommendations for Experimental Work

Experimental work on surfaces that can be easily modeled in 2D would be particularly useful. This work was not extensive enough to determine useful surfaces to pursue, but easily modeled surfaces would include homogenous surfaces created by molding, surfaces with deposition of uniformly sized particles,

5.3 Future Work in Modeling and Optimization

Further work can be done in optimizing existing surface structures using parametric studies. These could include varied proportions of raspberry-shaped silica particles, shark skin pattern width, depth, and shape, and any other pattern that has not been adequately studied or is too costly to run parametric studies on.

Surfaces used for particular applications that involve flow or droplet rolling or sliding behavior could potentially be studied by adding gravity into the simulation. Advancing and receding contact angle of a droplet rolling on a tilted surface could give clues to such behavior within a droplet.
REFERENCES


