Multiphase Flows with Digital and Traditional Microfluidics

Michael Andrew Nilsson

University of Massachusetts Amherst, mikeanilsson@gmail.com

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MULTIPHASE FLOWS WITH DIGITAL AND TRADITIONAL MICROFLUIDICS

A Dissertation Presented

by

MICHAEL A. NILSSON

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

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MULTIPHASE FLOWS WITH DIGITAL AND TRADITIONAL MICROFLUIDICS

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Approved as to style and content by:

_________________________________________________
Jonathan P. Rothstein, Chair

_________________________________________________
David P. Schmidt, Member

_________________________________________________
David A. Hoagland, Member

_________________________________________________
Donald L. Fisher, Department Head
Mechanical and Industrial Engineering
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ABSTRACT
MULTIPHASE FLOWS WITH DIGITAL AND TRADITIONAL MICROFLUIDICS
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MICHAEL NILSSON, B.S.M.E., UNIVERSITY OF MASSACHUSETTS AMHERST
M.S.M.E., UNIVERSITY OF MASSACHUSETTS AMHERST
PH.D., UNIVERSITY OF MASSACHUSETTS AMHERST
Directed by: Professor Jonathan P. Rothstein

Multi-phase fluid systems are an important concept in fluid mechanics, seen every day in how fluids interact with solids, gases, and other fluids in many industrial, medical, agricultural, and other regimes. In this thesis, the development of a two-dimensional digital microfluidic device is presented, followed by the development of a two-phase microfluidic diagnostic tool designed to simulate sandstone geometries in oil reservoirs. In both instances, it is possible to take advantage of the physics involved in multiphase flows to affect positive outcomes in both.

In order to make an effective droplet-based digital microfluidic device, one must be able to precisely control a number of key processes including droplet positioning, motion, coalescence, mixing, and sorting. For planar or open microfluidic devices, many of these processes have yet to be demonstrated. A suitable platform for an open system is a superhydrophobic surface, as surface characteristics are critical. Great efforts have been spent over the last decade...
developing hydrophobic surfaces exhibiting very large contact angles with water, and which allow for high droplet mobility. We demonstrate that sanding Teflon can produce superhydrophobic surfaces with advancing contact angles of up to 151° and contact angle hysteresis of less than 4°. We use these surfaces to characterize droplet coalescence, mixing, motion, deflection, positioning, and sorting. This research culminates with the presentation of two digital microfluidic devices: a droplet reactor/analyzer and a droplet sorter.

As global energy usage increases, maximizing oil recovery from known reserves becomes a crucial multiphase challenge in order to meet the rising demand. This thesis presents the development of a microfluidic sandstone platform capable of quickly and inexpensively testing the performance of fluids with different rheological properties on the recovery of oil. Specifically, these microfluidic devices are utilized to examine how shear-thinning, shear-thickening, and viscoelastic fluids affect oil recovery. This work begins by looking at oil displacement from a microfluidic sandstone device, then investigates small-scale oil recovery from a single pore, and finally investigates oil displacement from larger scale, more complex microfluidic sandstone devices of varying permeability. The results demonstrate that with careful fluid design, it is possible to outperform current commercial additives using the patent-pending fluid we developed. Furthermore, the resulting microfluidic sandstone devices can reduce the time and cost of developing and testing of current and new enhanced oil recovery fluids.
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Figure 56: A pictorial representation of the soft lithography technique for device fabrication using NOA-81.
1.1 Introduction

Fluids have long fascinated humankind, as our world is filled with instances of the beauty and complexity of fluid flow and its interaction with other objects. From the splashing of rain on leaves to the ebb and flow of the tides, humankind has sought to understand the physics and mechanics of fluid flows and interactions. While much work has been performed in the area of fluid research, there are many areas in which ongoing research is being performed to address many engineering challenges of today and tomorrow.

We have determined many properties of fluids, many of which were instinctively known to humankind long before they were characterized or studied. An important fluid property in this work is viscosity, a prominent variable when discussing moving fluids. Every person has a basic understanding of what viscosity is; a property that defines a fluid as “thick” or “thin”. Newton defined the viscosity as a constant coefficient of proportionality between the shear stress, $\tau$, and the shear rate, $\dot{\gamma}$, as

$$\tau = \mu \dot{\gamma}.$$ (1.1)

A non-Newtonian fluid is a fluid where flow properties differ from those of a Newtonian fluid. A common variety of non-Newtonian fluids possess viscosities that are some function of the shear rate of the flow. Depending on that relationship, many classifications of fluids exist such as: shear-thinning where the viscosity decreases with increasing shear rates, or a shear-thickening fluid where the viscosity increases over a
particular range of shear rates or in an extreme case at a critical shear rate. Another non-Newtonian effect is the concept of viscoelasticity, where a fluid has properties of both a liquid and also solid-like characteristics such as the material properties of elasticity.

At low Reynolds numbers, the viscosity plays an important role in determining the flow field. For incompressible flows of a Newtonian fluid, the Navier-Stokes equations reduce to

\[ \rho \frac{Du}{Dt} = \nabla p + \mu \nabla^2 u. \]  

(1.2)

Here the \( \rho g \) term is the gravity body force, and \( \nabla p \) is the pressure term, and \( u \) is the velocity. From Equation (1.2) it is clear that increasing viscosity requires a larger pressure drop to result in the same flowrate.

Of importance in fluid mechanics is the concept of multi-phase fluid systems, which is seen every day in how fluids interact with solids, gases, and other fluids. Multiphase systems require that the fluids involved be immiscible, meaning they do not completely mix but instead result in two distinct phases, with the profile of the interface between the two phases determined by the interfacial tension, an important parameter in multiphase flows. Interfacial tension can be measured by a tensiometer, which fits a curve using the Laplace-Young relationship that is based off of the principal radii of curvature in the drops.

This thesis will cover two multi-phase flow systems: droplet dynamics on a solid surface in a gaseous phase, and a two-phase liquid system within a solid microfluidic device. The microfluidic and digital, or one-drop-at-a-time microfluidic devices and phenomenon discussed in the proceeding sections allows for focus on the effects of
viscosity and surface tension. This thesis is broken up into multiple chapters, each highlighting a particular area of our research. Within each chapter is a section motivating the research, a section covering the experimental preparation and considerations, a section discussing and interpreting the results and a conclusion. The final chapter will briefly highlight the significant contributions of this research.

Chapter 1 continues with background information that is applicable to most, if not all, of the chapters in this thesis. It serves to both educate and reference other works for further study. It covers many of the physics, definitions, and history that is pertinent to the later chapters.

Chapter 2 covers our initial research into the development of a superhydrophobic surface as a platform for further experiments. This work, published as a full paper (Nilsson, Daniello et al. 2010) examines the results of mechanically sanding a Teflon surface with sandpaper of various grits. The resulting wettability modifications induced by various sandpaper grits serve as a platform for the work present in subsequent chapters. Chapter 3 presents our results of droplet coalescence and mixing on the superhydrophobic platform developed in the previous results. By colliding droplets on these surfaces, we demonstrated that surface permitting higher droplet mobility allow for more violent and interesting droplet coalescence, and also result in enhanced mixing over surfaces with reduced mobility. This work was also published as a full paper in 2011 (Nilsson and Rothstein 2011). Chapter 4 advances the understanding of droplet motion on superhydrophobic surfaces. After characterizing droplet motion on our superhydrophobic platform, we introduced discrete changes in wettability, and present the results of droplet motion over these changes for a range of approach angles. This
work was published as a full paper, and rounds out our research into the individual aspects of digital microfluidics (Nilsson and Rothstein 2012). Chapter 5 rounds out our research into digital microfluidics, presenting the development of two separate two-dimensional microfluidic devices that take advantage of the results of the previous chapters.

Chapter 6 begins our research using traditional enclosed microfluidics. Our work, motivated by enhanced oil recovery (EOR), examines the effectiveness of various fluids in extracting oil from a microfluidic device designed to mimic a small sandstone section. This work resulted in both patent pending devices, and also a patent pending fluid that outperformed a commercial additive in this small device. This work is submitted as a full paper (Nilsson, Kulkarni et al. 2013). A natural extension of this work is to test these fluids in a larger device, and also investigated if the differences in oil recovery and be observed in a single, representative pore. Chapter 7 presents the results of a single pore study, in which we examined the process of extracting oil from a representative pore. Chapter 8 presents the results of these fluids and their ability to recover oil from two devices of varying sandstone characteristics, but both significantly larger than the device in Chapter 6 such that over 26 of the smaller devices would not cover the same area as the larger devices in Chapter 8. The work is in preparation for submission.

Finally Chapter 9 is a brief conclusion of the significant contributions of this research, and highlights the current and future applications and directions of the results obtained in this work.
CHAPTER 2

A NOVEL AND INEXPENSIVE METHOD TO CREATE
SUPERHYDROPHOBIC SURFACES USING SANDPAPER AND TEFLON

2.1 Introduction

A great deal of effort has been spent over the last decade developing hydrophobic surfaces exhibiting very large contact angles with water (Girifalco and Good 1957; Saito, Takai et al. 1997; Chen, Fadeev et al. 1999; Nishino, Meguro et al. 1999; Miwa, Nakajima et al. 2000; Oner and McCarthy 2000; Tadanaga, Morinaga et al. 2000; Nakajima, Hashimoto et al. 2001; Kim and Kim 2002; Ou and Rothstein 2005; Gao and McCarthy 2006; Shastry, Case et al. 2006; Duez, Ybert et al. 2007; Gao and McCarthy 2007; Li, Huang et al. 2007; Li, Li et al. 2007; Daniello and Rothstein 2009). A number of strategies have been employed to increase the average contact angle between a substrate and water, including chemical modification of the substrate to lower the surface energy between the water and the surface (Chen, Fadeev et al. 1999). Reducing contact angle hysteresis is widely accomplished in practice by introducing either random or precisely patterned surface roughness to a hydrophobic substrate. For an excellent review of modern techniques please see Zhang et al. or Nakajima et al. (Nakajima, Hashimoto et al. 2001; Zhang, Shi et al. 2008).

There are many methods by which roughness may be introduced to a material, including chemical or mechanical processes, oftentimes in concert with each other (Quere, Azzopardi et al. 1998; Bico, Marzolin et al. 1999; Chen, Fadeev et al. 1999; Mahadevan and Pomeau 1999; Nishino, Meguro et al. 1999; Miwa, Nakajima et al. 2000; Oner and McCarthy 2000; Kim and Kim 2002; Lafuma and Quere 2003; Sakai, Song et
al. 2006; Shastry, Case et al. 2006). These methods generally necessitate extensive material or facility costs, however, there have been efforts made in minimizing these requirements (Gao and McCarthy 2006; Gao and McCarthy 2007). In an effort to further this work, we investigated a method that focuses on the simple mechanical surface alteration of polytetrafluoroethylene (PTFE), commercially known as Teflon, which is renowned for its water-repellent properties. Biological, commercial and industrial applications comprise a few of Teflon’s various uses. Teflon is naturally hydrophobic, featuring a smooth surface with contact angles, $\theta_d / \theta_r$, of 128°/78°, the average contact angle being 103°. The unaltered surface has large contact angle hysteresis, $\theta_d - \theta_r = 50^\circ$, restricting drop movement. Teflon’s low coefficient of friction with many materials and consequently its “non-stick” properties are its primary appeal for its wide use in cookware. Teflon is also applied to fabrics (Goretex) and structural components (dome roofs) which take advantage of its water repellency.

2.1.1 Three-Phase Contact Line and Contact Angles

In any multiphase system, a contact line develops between the three phases at the contact line. This contact line results from the differences in surface energy. In the case where one of the phases is a rigid solid, the contact line forms along the surface in its most favorable energetic shape. The behavior is analytically described by Young’s equation relating the contact angle with the interfacial free energies between the phases,

$$\cos(\theta) = \frac{\sigma_{12} - \sigma_{13}}{\sigma_{23}}.$$  \hspace{1cm} (1.6)
Here, $\sigma$ is the interfacial energy between the particular phases in the subscript. The result is an optimal contact angle that the two fluid phases have in relation to the solid phase. In the case that of a three-phase system of a solid, a gas, and a liquid, a small amount of liquid deposited onto the solid surface would develop a circular three-phase contact line, resulting a sessile drop. As more fluid is added, the drop would obviously grow to reach the required size. Upon stopping this addition of fluid, the droplet would then rest in a metastable state. This is referred to metastable because of the behavior of the contact line as the volume was increasing (Gao and McCarthy 2006).

### 2.1.2 Contact Angle Hysteresis

Contact angle hysteresis is defined as the difference between the advancing contact angle, $\theta_A$, and the receding contact angle, $\theta_R$, for a given surface and liquid, as shown in Figure 1. In this thesis, for the purpose of experiments with drops, we will focus on water as the liquid phase. Contact angle hysteresis inhibits the motion of the contact line, and as such also inhibits the motion of drops along a surface (Rothstein 2010), as it can be shown that the critical line force required to start a drop moving over a solid surface is directly proportional to the contact angle hysteresis

$$F_D \approx \sigma l (\cos(\theta_R) - \cos(\theta_A)).$$

Here $\sigma$ is the surface tension and $l = R \sin(\pi - \theta)$ is the radius of the contact area between the drop and the surface. Large contact angle hysteresis restricts the motion of droplets, and limits confined collisions to small Weber numbers (Wolfram and Faust 1978). With high hysteresis, before a drop can move it must deform and reach the receding contact
angle at the rear of the drop and the advancing contact angle at the leading edge of the drop. Therefore, varying the contact angle hysteresis should play a large role in droplet collisions, yet no study has yet been performed to understand how.

There has been some work investigating how contact angle hysteresis affects droplets impacting onto surfaces (Jayaratne and Mason 1964; Richard and Quere 2000; Reyssat, Pepin et al. 2006; Yarin 2006; Gatne, Jog et al. 2009; Vadillo, Soucemarianadin et al. 2009). Many of these studies looked at the dependence of various factors, such as spread diameter, crown height, jet height, and droplet rebound on important dimensionless parameters. They have shown that a droplet hitting a surface with minimal hysteresis can bounce, often producing satellite droplets dependant on the Weber number upon impact. If droplets collide with a surface with a large degree of hysteresis, they can be pinned and the dynamics significantly dampened. This observation highlights how the surface-droplet interaction and specifically the contact angle hysteresis during spreading is of importance to drop motion (Bartolo, Bouamrirene et al. 2006; Reyssat, Pepin et al. 2006).

2.1.3 Wettability

When a liquid phase interacts with a solid phase, the degree of wetting can be affected by surface roughness. There are two major models to describe water contact angles on rough surfaces: the Cassie, and the Wenzel model. In the Cassie state an air-water interface is supported between the surface roughness (Cassie and Baxter 1944). This phenomena modifies the contact angle, $\theta_c$, such that
\[
\cos(\theta_c) = \gamma(\cos(\theta)+1) - 1.
\] (1.8)

Here \( \theta \) is the equilibrium contact angle between a smooth surface sample and the liquid as defined by Young’s law, and \( \gamma \) is the area fraction of the solid-liquid interface. In order to maximize the equilibrium contact angle, the percent coverage of the air-water interface must similarly be maximized. It is also important to note that the shape and size of the surface protrusions affect the contact angle and resulting hysteresis (Oner and McCarthy 2000). There is, however, a lower limit on the solid fraction beyond which static pressure can deflect the interface such that it advances into the roughness, fully wetting the surface (Rothstein 2010). This fully wetted state is referred to as the Wenzel state (Wenzel 1936). The equilibrium contact angle for the Wenzel state, \( \theta_w \), is given by

\[
\cos(\theta_w) = r \cos(\theta).
\] (1.9)

Here \( r \) is the ratio of the wetted area to the projected surface area. For a smooth surface, \( r = 1 \), and increases with increasing roughness. For a hydrophobic surface, the equilibrium angle will increase in the Wenzel state, however the contact angle hysteresis is also typically very large. This is a consequence of the fluid resisting dewetting within the roughness, as reaching the receding contact angle required to move the three-phase contact line is challenging. It is important to note that in the case of both the Cassie and Wenzel state, it is only the wettability at the contact line that determines the advancing and receding contact angles and consequent hysteresis, and not wettability in the contact area, for a stationary drop (Gao and McCarthy 2007).
2.1.4 Superhydrophobic Surfaces

A surface with little to no contact angle hysteresis and an advancing contact angle greater than 150° is classified as a superhydrophobic surface (Tadanaga, Morinaga et al. 2000). There has been much effort in developing these surfaces (Chen, Fadeev et al. 1999; Nakajima, Hashimoto et al. 2001; Zhang, Shi et al. 2008; Nilsson, Daniello et al. 2010). Superhydrophobic surfaces were originally inspired by the unique water repellency of many plants, most notably the leaves of the lotus (Neinhuis and Barthlott 1997; Bush, Hu et al. 2007). When properly designed, these bio-mimetic surfaces can reduce the contact angle hysteresis of water by maintaining an air-water interface above the depressions between the peaks of the surface roughness, as seen in Figure 2a, with the resulting near-spherical drop shape shown in Figure 2b. Moreover, it has been shown that it is often advantageous to have multiple lengthscales of roughness in order to increase both advancing and receding contact angles while simultaneously minimizing hysteresis (Gao and McCarthy 2006). Superhydrophobic surfaces have demonstrated the ability to be self-cleaning. As water droplets move along these surfaces, they roll, collecting dust and particulates from the surface (Mahadevan and Pomeau 1999). Droplets move very easily along superhydrophobic surfaces because the drag force is proportional to the contact angle hysteresis. Minimizing the hysteresis allows drops to be easily dislodged by even the smallest perturbations (Bico, Marzolin et al. 1999; Kim and Kim 2002; Sakai, Song et al. 2006; Shastry, Case et al. 2006). The high level of water droplet mobility on superhydrophobic surfaces is desirable in many industrial applications. Some notable areas where the application of superhydrophobic surfaces is emerging include automotive, transportation, communication hardware, marine
technology, textiles, and biological applications. Specific examples of these applications being self-cleaning windows or antennas, stain-proof and water repellent clothing, and snow repellent satellite dishes (Kissa 1984; Schakenraad, Stokroos et al. 1992; Saito, Takai et al. 1997; Nakajima, Hashimoto et al. 2001; Ou and Rothstein 2005; Daniello and Rothstein 2009). These surfaces also facilitate the control and manipulation of individual drop-directed motion, allowing for the possible use of these surfaces in microfluidic applications. This is due to the contact line being pinned at each wetted feature as it recedes (Lafuma and Quere 2003).

In order to achieve superhydrophobicity with synthetic surfaces, two criteria must be met: chemical hydrophobicity and surface roughness. It has been shown both theoretically (Girifalco and Good 1957) and experimentally with water (Nishino, Meguro et al. 1999) that chemical alteration of a smooth surface can only achieve advancing contact angles, $\theta_a$, with water up to about $\theta \approx 130^\circ$ (Nakajima, Hashimoto et al. 2001). In order to achieve higher contact angles, the surface must have some degree of roughness to it, either precisely patterned or random. The combination of the chemical hydrophobicity with the surface roughness prevents the water from penetrating into the roughness and fully wetting the surface resulting in the superhydrophobic Cassie state. The Wenzel state can possess high advancing angles, but typically exhibits high contact angle hysteresis. Therefore, superhydrophobic surfaces are characteristically in the Cassie state of wetting.

With the increasing interest in superhydrophobic surfaces, and the ability to move and direct drops easily on low hysteresis surface, knowledge of drop motion, collisions, and coalescence is critical if these surfaces are to be utilized to their full extent as a
possible platform for digital (one drop at a time) microfluidics. These investigations and results are presented in Chapters 1-5. One of our primary motivations for sessile drop studies is coalescence of drops condensing onto a cold surface that would be advantageous in many commercial and research situations, such as radiators and space-based fluid recovery systems. In addition, very low contact angle hysteresis, droplet collisions will mimic those of unbounded droplets, allowing for greatly enhanced dynamics, deformations, and mixing.

2.2 Fabrication Method

Thin sheets of Teflon are very flexible, so we mounted each Teflon sample to pieces of aluminum using epoxy, in order to ensure a generally flat and secure Teflon surface. After letting the epoxy set, each sample was held stationary, and sanded by hand. Reasonable force was applied to impart a good representation of the grit size of the sand paper onto the Teflon. Sanding was performed in a random manner, as to show no preference in any particular direction. After approximately 20 seconds of sanding, the sanded surface was then cleaned with acetone briefly, then rinsed with reverse-osmosis deionized water, and dried with pressurized air. It is important to note that the final hydrophobic properties were not sensitive to additional sanding, excess pressure when sanding, or the use of a mechanical sander. The cost of a Teflon surface and sand paper is on the order of dollars, while more complicated methods can be on the order of hundreds to thousands of dollars for the materials and equipment required for production.

A range of commercial sand paper grit designations between 40-grit and 600-grit were used, with each sample being sanded by only one grit designation. Table 1 shows
the common grit designation for the sandpaper used, the average particle size on the paper, and the average RMS roughness of the Teflon surface following sanding. Surface roughness measurements were taken using a Zygo 7300 optical profilometer, with each surface measured three times in three different locations over an area of 0.045 mm². The resulting surface roughness imparted by the sanding exhibits a wide disparity between the various grit sizes. The smooth Teflon had the lowest average RMS roughness of 5.6 µm. As coarser sandpapers are used, the RMS roughness increased as expected. As seen in equations (1.8) and (1.9), this increase in surface roughness is a mechanism by which contact angle can be increased. This roughness, coupled with the innate hydrophobicity of Teflon, is enough to produce superhydrophobic surfaces with a variety of wettability states, as covered in the next section.

In order to explore the wettability states of these sanded Teflon surfaces, we examine the contact angles that are produced by this surface preparation. The contact angles were measured photographically using a goniometer constructed in-house and are listed in Table 1 and presented graphically in Figure 3. Each contact angle measurement was taken three times, each in a different location on the sanded Teflon surface. The volume of each drop was kept constant, and in each case the drop was well below a Bond number of one to ensure gravitational effects were negligible.

2.3 Results of Variation of Grit Designation

The Teflon prepared with the finest sandpaper, 600-grit, exhibited greater hysteresis than the smooth Teflon, as well as a larger advancing contact angle, suggesting that the added roughness exists primarily in the Wenzel state. As the grit size was
increased from 600-grit to 360-grit, the advancing contact angle continued to increase with little change in the contact angle hysteresis. At a grit size of 320-grit, corresponding to a RMS roughness of 10μm, the advancing contact angle reached a maximum value of $\theta_a = 151^\circ$ and the contact angle hysteresis showed a significant decrease. This data is suggestive of a transition from a mostly Wenzel to a mostly Cassie state of wetting. The contact angle hysteresis was further minimized as the grit size is increased from the 320-grit to the 180-grit. Of the surfaces with lower contact angle hysteresis, the 240-grit sanded Teflon had the least amount of hysteresis, 4°, which competes well with many of the published surface preparation techniques that posses similar hysteresis but are either much more expensive or require more complicated methods to produce (Nakajima, Hashimoto et al. 2001). As seen in Figure 3, two distinct regimes in the data become clearly apparent. The first at large sandpaper grits where the hysteresis remains fixed and advancing contact angle varies over a range of about 30°, and the second at lower sandpaper grits where the advancing contact angle is nearly constant at $\theta_a = 150^\circ$ and the contact angle hysteresis varies over more than 60°. It is important to note that contact angle hysteresis is a key component when determining whether a droplet will move freely on a surface, or adhere (Quere, Azzopardi et al. 1998; Chen, Fadeev et al. 1999; Lafuma and Quere 2003). The large variation of contact angle hysteresis in the second regime suggests that this surface preparation technique is well suited for systematically studying the effect of hysteresis on drop dynamics.

The advancing contact angle only marginally decreased as the grit size was increased from the 120-grit to the 40-grit, however, the contact angle hysteresis began to
increase for grit designations smaller than 120-grit. The largest grit designation tested, 40-grit, still possessed a highly hydrophobic advancing contact angle, though their contact angle hysteresis approached that of smooth Teflon. Scanning electron microscopy (SEM) in Figure 4 shows that this deterioration of superhydrophobic character is likely caused by the large spacing between the surface features resulting from the large grit size and a suspected transition back to the Wenzel state from the Cassie state achieved for grits between 240- and 120-grit.

SEM images were taken of a subset of the surfaces listed in Table 1 and are shown in Figure 4. The Teflon surfaces were sputter-coated with gold and measurements were taken at 20kV. While the untreated Teflon is relatively smooth, sanding with the 600 grit sandpaper introduces surface roughness by coarsening the Teflon surface. While this roughness serves to increase the advancing contact angles, the valleys are not deep enough to maintain an air-water interface, giving further support to the hypothesized Wenzel state of wetting. This results in lower receding contact angles because the water is pinned to the surface along the receding contact, increasing the hysteresis substantially, as shown in Figure 3. As the sandpaper increases in grain size (or decreases in grit designations), the amplitude of the surface peaks and valleys increases, while the second level of roughness becomes more obvious on the Teflon substrate. This is shown with the 320-grit sanded Teflon with noticeably deeper depressions in the surface, and furthermore with the 240-grit sanded Teflon. These deeper surface features and more pronounced secondary roughness likely allows for the formation of air-water interfaces typical of the Cassie state, resulting in even higher contact angles and reduced contact angle hysteresis. However, as the surface roughness increases even further, as seen with
the 80-grit in Figure 4 some of the valleys and depressions become large, making the support of an air-water interface less likely, resulting in the gradual transition back into the Wenzel state.

In summary, sanding Teflon results a method of surface fabrication that allows for the creation of superhydrophobic surfaces which depending on the grit-designation used, can result in surfaces with similar advancing contact angles, but with varying degrees of contact angle hysteresis (Nilsson, Daniello et al. 2010). This platform is ideal for isolating effects from the advancing contact angle and varying the contact angle hysteresis.
Figure 1: Schematic of a drop moving from left to right, with the measurements of the advancing and receding contact angles, $\theta_A$ and $\theta_R$ respectively, shown.
Figure 2: Superhydrophobic surfaces. a.) Water (blue) being partially supported by the microstructure of a superhydrophobic surface (green) with air within pores. b.) A droplet on the superhydrophobic gingko leaf as can be acquired on campus.
Table 1: Characterization of both the sandpaper used and the resulting surface roughness and wetting properties of water and the sanded Teflon surfaces.

<table>
<thead>
<tr>
<th>Grit designation</th>
<th>Mean Particle Diameter (μm)</th>
<th>RMS Roughness Teflon (μm)</th>
<th>Contact Angle (θ_s / θ_w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smooth</td>
<td>---</td>
<td>5.6</td>
<td>128°/78°</td>
</tr>
<tr>
<td>600</td>
<td>25.8</td>
<td>7.6</td>
<td>132°/71°</td>
</tr>
<tr>
<td>400</td>
<td>35.0</td>
<td>4.6</td>
<td>140°/80°</td>
</tr>
<tr>
<td>360</td>
<td>40.5</td>
<td>5.5</td>
<td>136°/99°</td>
</tr>
<tr>
<td>320</td>
<td>46.2</td>
<td>10.9</td>
<td>150°/119°</td>
</tr>
<tr>
<td>240</td>
<td>58.5</td>
<td>13.7</td>
<td>150°/146°</td>
</tr>
<tr>
<td>180</td>
<td>82</td>
<td>15.4</td>
<td>148°/141°</td>
</tr>
<tr>
<td>120</td>
<td>125</td>
<td>16.3</td>
<td>151°/134°</td>
</tr>
<tr>
<td>80</td>
<td>201</td>
<td>14.5</td>
<td>146°/129°</td>
</tr>
<tr>
<td>60</td>
<td>269</td>
<td>18.2</td>
<td>146°/125°</td>
</tr>
<tr>
<td>40</td>
<td>425</td>
<td>17.5</td>
<td>143°/108°</td>
</tr>
</tbody>
</table>
Figure 3: Hysteresis as a function of advancing contact angle for smooth ▼ Teflon, as well as a series of Teflon surfaces, sanded with sandpaper of grit designation ● 600, ▲ 400, ▼ 360, ◇ 320, ▼ 240, ◇ 180, ▼ 120, △ 80, ○ 60, and □ 40.
**Figure 4:** SEM images of a series of Teflon surfaces sanded with sandpaper of various grit designations, (a) smooth at 100x, (b) smooth at 200x, (c) smooth at 1000x, (d) 600-grit at 100x, (e) 600-grit at 200x, (f) 600-grit at 1000x, (g) 320-grit at 100x, (h) 320-grit at 200x, (i) 320-grit at 1000x, (j) 240-grit at 100x, (k) 240-grit at 200x, (l) 240-grit at 1000x, (m) 80-grit at 100x, (n) 80-grit at 200x, and (o) 80-grit at 1000x.
CHAPTER 3

INVESTIGATING THE EFFECT OF CONTACT ANGLE HYSTERESIS ON
DROplet COALESCENCE AND MIXING

3.1 Background and Motivation

The study of droplet collisions and subsequent coalescence has generated significant interest and a wealth of research in the past few decades because of its importance in a number of commercial fields including combustion, spray coatings, and more recently microfluidics. The majority of the research has been performed on unconfined droplets collisions in air or other fluids (Adam, Lindblad et al. 1968; Ashgriz and Poo 1990; Orme 1997; Qian and Law 1997; Eggers, Lister et al. 1999; Willis and Orme 2000; Mashayek, Ashgriz et al. 2003; Quan, Lou et al. 2009). In these experiments and simulations, the droplets are not in contact with a solid substrate and the complexity introduced by the three-phase contact line does not need to be considered. A number of these studies were concerned with the classification and study of the different types of droplet interactions.

Four distinct classifications of droplet interactions are typically identified when droplets collide in air: coalescence, bouncing, disruption, and fragmentation (Orme 1997). The coalescence regime is defined by full combination of two droplets into one, and typically occurs at lower Weber numbers, $We < 20$ for unconfined droplets (Ashgriz and Poo 1990). Within the bouncing regime, droplets collide, but coalescence is prohibited by a thin gas lubrication layer. This is primarily seen in hydrocarbon droplet collisions at Weber numbers between $0.5 < We < 8.6$ (Qian and Law 1997). Bouncing of
water droplets was only observed for glancing collisions at high impact numbers \( (I \geq 0.8) \) and Weber numbers larger than \( We > 5 \). Disruption and fragmentation are two regimes where the droplets separate after initially coalescing. In disruption, the coalesced droplet separates back into two droplets, typically of similar size. In fragmentation, the coalesced droplet separates more violently, resulting in two or more main drops and many satellite droplets. Both disruption and fragmentation generally occur at Weber numbers greater than \( We > 20 \) (Qian and Law 1997).

Unlike unconfined droplet collisions, there has only been a limited amount of work done on the coalescence of sessile drops where the presence of the contact line plays an important role in the dynamics of droplet coalescence (Meakin 1992; Andrieu, Beysens et al. 2002; Narhe, Beysens et al. 2004; Narhe, Beysens et al. 2005; Kapur and Gaskell 2007; Boreyko and Chen 2009; Boreyko and Chen 2009; Boreyko and Chen 2010; Karpitschka and Riegler 2010). The main fields examined are the coalescence of sessile drops deposited on a substrate either by condensation or by the addition of volume to one drop, and the dynamics of the meniscus bridge in the early timescales of coalescence.

To begin, it is necessary to use high-speed cameras or imaging in order to observe the dynamics of coalescence because of the small timescales involved (Thoroddsen, Etoh et al. 2008). For sessile drops, droplet impacts are typically limited to the coalescence regime due to the relatively low Weber numbers that can be achieved. In these low Weber number collisions, surface tension dominates the flow and drop deformations are limited. The surfaces studied in the literature did not examine surfaces with a high level of hydrophobicity (Andrieu, Beysens et al. 2002; Narhe, Beysens et al. 2004; Narhe,
Beysens et al. 2005; Kapur and Gaskell 2007; Karpitschka and Riegler 2010). The contact angles present on the surfaces studied were indicative of hydrophilic surfaces. These drops were driven to coalesce by either placing them placed directly next to each other and deforming the drop very slowly through the addition of water from a syringe (Narhe, Beysens et al. 2004; Narhe, Beysens et al. 2005) or through a hole in the test surface (Kapur and Gaskell 2007; Karpitschka and Riegler 2010) or through continuous condensation and growth of droplets on a surface in a saturated environment (Andrieu, Beysens et al. 2002; Narhe, Beysens et al. 2004; Narhe, Beysens et al. 2005; Boreyko and Chen 2009; Boreyko and Chen 2009; Boreyko and Chen 2010). The resulting Weber numbers were vanishingly small. These studies investigated the role of initial conditions prior to coalescence (Narhe, Beysens et al. 2004; Narhe, Beysens et al. 2005), the effect of dissipation at the contact line and how that affected contact line movement and the relative position of the coalesced drop (Andrieu, Beysens et al. 2002). They showed that by increasing volume through deposition from a syringe, capillary oscillations are introduced that can greatly increase the relaxation rate of the resulting drop by orders of magnitude over a drop coalesced as a result of condensation-driven volume increase (Narhe, Beysens et al. 2004; Narhe, Beysens et al. 2005). They also argued the importance of dissipation along the contact line, and how evaporation has little influence on the motion of the three-phase contact line (Andrieu, Beysens et al. 2002). For partially wetting drops, it was shown that coalescence dynamics are affected by the interaction of the contact line motion with the rise in bridge height caused by negative pressure in the meniscus bridge (Kapur and Gaskell 2007). The wetting characteristics can be affected by vibration, and even in low Weber number, condensation-driven droplet
coalescence it is possible for large-scale dynamics to occur, including ejection from the surface (Boreyko and Chen 2009; Boreyko and Chen 2009; Boreyko and Chen 2010). It has been shown that the coalescence characteristics between two different but miscible fluids depends largely on the surface tension difference between the two fluids (Karpitschka and Riegler 2010). In the study of the meniscus bridge there has been much theoretical and experimental work (Eggers, Lister et al. 1999; Wu, Cubaud et al. 2004; Thoroddsen, Takehara et al. 2005; Ristenpart, McCalla et al. 2006; Sellier and Trelluyer 2009; Wang, Zhu et al. 2010). Much of this is concerned with the rate of the spreading of the meniscus bridge. It has been shown that for spherical drops, there is a weak logarithmic relationship with the drop diameter (Eggers, Lister et al. 1999), while in thin films the relationship more closely resembles a power-law dependence (Ristenpart, McCalla et al. 2006). The exact dependence of this relationship is very difficult to ascertain, and in experiments, there is much difficulty in exactly replicating the conditions of the initial coalescence (Thoroddsen, Etoh et al. 2008). However, there has been success with aligning experimental results to theoretical results (Wu, Cubaud et al. 2004; Thoroddsen, Takehara et al. 2005). Also, it has been shown that in experiments, meniscus spreading is volume-dominated, while more recent models have simulated the coalescence as being capillary induced (Sellier and Trelluyer 2009) which was then confirmed (Wang, Zhu et al. 2010). None of these experiments were concerned with contact angle hysteresis and its effects on the dynamics of droplet coalescence at higher Weber numbers.

There has been some work investigating how contact angle hysteresis affects droplets impacting onto surfaces (Jayaratne and Mason 1964; Richard and Quere 2000;
Reyssat, Pepin et al. 2006; Yarin 2006; Gatne, Jog et al. 2009; Vadillo, Soucemarianadin et al. 2009). Many of these studies looked at the dependence of various factors, such as spread diameter, crown height, jet height, and droplet rebound on important dimensionless parameters. They have shown that a droplet hitting a surface with minimal hysteresis can bounce, often producing satellite droplets dependent on the Weber number upon impact. If droplets collide with a surface with a large degree of hysteresis, they can be pinned and the dynamics significantly dampened. This observation highlights how the surface-droplet interaction and specifically the contact angle hysteresis during spreading is of importance to drop motion (Bartolo, Bouamrirene et al. 2006; Reyssat, Pepin et al. 2006).

The mixing of fluids at a micro-scale has been studied extensively as performed in a micro-fluidic device. These devices are enclosed, and make use of many low Reynolds number effects, as well as many different driving mechanisms in order to effect mixing at micro-scales. Microfluidic devices will be covered later in this manuscript.

The most recent work on droplet mixing focuses on the mixing of two droplets of water on a surface with varying contact angles and minimal contact angle hysteresis (Lai, Hsu et al. 2010). Because of the lensing effect of the drop, quantifying mixing in a drop is daunting, as you need at least two views (top, side) to make a quantitative assessment of the mixing, and even then it can’t resolve internal mixing (Paik, Pamula et al. 2003). Methods such as micro-PIV, using fluorescent dyes and particles have been used to study mixing in drops (Wang, Nguyen et al. 2007; Lai, Hsu et al. 2010). These experiments avoided some of the lensing issue by interrogating droplets with low contact angles on transparent cover slips from below using an optical microscope (Kinoshita, Kaneda et al. 2006).
It was shown that based off of the rate of the mean velocity decay, diffusion effects became dominant at long times when the Peclet number became less than $Pe = \frac{LV}{D_{12}} \leq 1$. Here, $L$ is a characteristic lengthscale and $D_{12}$ is the diffusion coefficient. Therefore, important convection-based mixing, as would result from coalescence on low hysteresis surfaces, occurs at smaller timescales. They also are able to visualize internal flow fields, and show that the fluid in contact with the surface experiences a drag force, enhancing mixing of droplets in a microfluidic channel. Unlike the previous work in this area, our experiments will focus on the short-time dynamics of mixing on surfaces with varying hysteresis where the Peclet number is large and the flow is dominated by convection.

On an open device in which droplets are driven to coalesce, the surface will affect the coalescence dynamics. The following subsections will cover our efforts in this area. Specifically, we address the need to move the droplets into one another to allow for coalescence, the effect of contact angle hysteresis on the observed dynamics of the drop coalescence, the effect of the contact angle hysteresis on internal mixing of two drops following coalescence, and how discrete changes in contact angle hysteresis affect droplet path deflection, if at all.

### 3.1.1 Droplet Creation

The first challenge when performing single droplet digital microfluidics is the production and the placement of the drop itself. Droplets can be produced manually from either a syringe or dropper. Using either a syringe pump or a micropipetter allows for accurate volume control. Another option would use a similar drop production method;
however the input tube would pass through the substrate. Finally, condensation can produce drops on a surface. However, when condensing onto a superhydrophobic surface, any roughness on the surface is completely wet by the drops as it forms, resulting in drops forming in the Wenzel state. Mobilization of the drop then requires sufficient mechanical perturbations to create the transition back to the high mobility Cassie state (Boreyko and Chen 2009).

3.1.2 Droplet Motion

Droplet motion across superhydrophobic surfaces has also generated much interest. By tracking a single particle near the surface of a drop, Richard et al have shown that viscous droplets with high contact angles on a surface tend to roll across the surface (Richard and Quere 1999). The solid-body motion of the rolling drop greatly reduces the resistance to motion and has been shown to reduce the drag on the drops by as much as 99% (Kim and Kim 2002). Gogte et al. (Gogte, Vorobieff et al. 2005) later showed that for water on superhydrophobic textured surface, droplets initially slide at times near the onset of motion. They found that as the droplet accelerates it transitions to rolling motion. During the early stages of drop motion, the droplets trajectory approaches the free fall limit and interestingly it accelerates faster than a solid sphere rolling down the same inclined surface (Reyssat, Richard et al. 2010).

Droplets can be moved based on wettability gradients in patterned superhydrophobic surfaces (Chaudhury and Whitesides 1992; Ito, Heydari et al. 2007; Sun, Zhao et al. 2008). For example, Wier et al. (Wier, Gao et al. 2006) has showed that they can produce spontaneous droplet motion by spatially varying the surface chemistry
and the advancing contact angles across a surface with minimal contact angle hysteresis. A number of active methods exist for manipulating drops. These including mechanical actuation of the surface, aerodynamically driving drop motion through a puff of air or building electrodes into the surface to induce motion of the droplets through electrowetting (Pollack, Fair et al. 2000). Krupenkin et al. (Krupenkin, Taylor et al. 2004) demonstrated the ability to change wettability characteristics by using an electrode inserted in a droplet and a DC electrical field to drive a droplet from a superhydrophobic state to completely wetting. Optical-electric devices can be used to direct a motion of a drop as it falls by optically sensing the position of drops and then activating a charging device to alter drop trajectory (Link, Grasland-Mongrain et al. 2006). Electro-wetting devices can also be used to perform coalescence, mixing, and sorting of droplets (Li, Fu et al. 2010).

3.2 Experimental Design

Sanded Teflon surfaces were prepared as described in Chapter 2. Teflon surfaces with a backing treated to accept adhesive and epoxy were used. The Teflon was affixed to the aluminum slats as seen in Figure 5. Teflon was sanded with various grits of sandpaper, resulting in superhydrophobic surfaces (SHS) with high advancing contact angles and variable hysteresis which depends only on the grit size of the sandpaper chosen. The SHS were then placed on a precisely leveled surface attached to a vibration-reducing optical table. This was critical because droplets on low hysteresis surfaces can move with even the smallest perturbations. All of the surfaces had an advancing contact
angle of 150°, but a variable hysteresis making it possible to explicitly investigate the effect of hysteresis on droplet coalescence. The surfaces used in this study had a hysteresis of 3° which corresponds to Teflon sanded with 240 grit-designation sandpaper; a hysteresis of 15° which corresponds to Teflon sanded with 120 grit-designation sandpaper, and a hysteresis of 30° which corresponds to Teflon sanded with 320 grit-designation sandpaper.

In order to facilitate drop movement, pressurized air was used to impart momentum onto a single moving drop while keeping the second drop stationary. The drops were initially separated by 18 mm allowing for the moving drop to develop a steady velocity and minimizing the impact of the pressurized air on the stationary drop. The pressure of the air used to propel the drop varied, but was varied between 13 to 34 kPa. A cowl with inner diameter of about 3 mm was attached to the end of the tube which aided in dissipating the direct jet of air formed in the tube and reduced the likelihood of atomization of the drops and minimized the amplitude of capillary waves the surface of the moving drop. A sketch of the set up is shown in Figure 5.

In order to view the collision from multiple angles simultaneously, a pentaprism was mounted just above the drops to make both the side and top view visible. The collision and subsequent coalescence were captured using a Phantom v4.2 high-speed camera with a resolution of 384x512 at a frame rate of 2900 frames per second, outfitted with a Mitutoyo compact lens. Two Northstar 250W lamps were employed to provide adequate illumination for these high speed experiments. These lights provided enough illumination for a relatively large f-stop on the lens to be used. This was crucial because
it resulted in a depth of field large enough to keep both the side and top view of the drop in focus simultaneously.

The high-speed video was broken out into a series of individual images so that important measurements could be made. ImageJ™ was used to measure pre-collision quantities such as the initial droplet diameters, droplet velocities, and the impact factor from the offset in the droplet centers just before impact. A number of additional measurements were made after the collision. These include the deformation of the coalesced drop in both the collision direction the in-plane direction normal to the collision as well as the rotation rate of the coalesced drop for indirect impacts. As seen in Figure 5, the direction of droplet motion is taken to be the x-direction, the direction normal to droplet motion and in the plane of the SHS is the y-direction, and the direction normal to the surface is the z-direction.

In order to quantify mixing, we investigated two methods: dyes, and particle seeding. The fluorescent dye (Flourescein) used was not bright enough when illuminated to achieve the frame rates necessary to observe the mixing dynamics desired, and it was also found to change the contact angle properties of the drop which was undesirable for this study. Particles (11μm diameter Sphericel) were used to seed the moving drop and illuminated by a Northstar 250W lamp. The diffusion time of the particles to travel through the drops is many orders of magnitude larger than our window of observation, so any particle motion observed (order μs) is dominated by convection as the resulting Peclet number is very large. This is similar to prior work (Lai, Hsu et al. 2010) with the exception that in this study the droplet collisions occur at much higher Weber numbers on opaque surface with much larger advancing and receding contact angles. As such, the
camera cannot observe the internal flow from below, and the surface tension-driven
dynamics resulting from coalescence cause a very uneven and quick-changing drop
surface. Coupled with the lensing effect of the droplet surface, this leads to a difficulty in
precisely knowing the location of the observed particles within the drops. As a result,
although the results we will present in the following section show that mixing is
enhanced on low-hysteresis surfaces, the results are strictly qualitative.

3.3 Droplet Coalescence Results and Discussion

One measurement of great interest is the maximum deformation of the drop
following coalescence. It is our hypothesis that lower contact angle hysteresis will result
in considerable enhancement of drop deformation because it mobilizes the three-phase
contact line. In order to determine the maximum deformation, it is important to first
characterize when full coalescence has been achieved. In this work, we report a
maximum deformation only after the two drops become indistinguishable in the final
coalesced drop. Figure 6 - Figure 10 present image sequences of droplets coalescing at
various Weber numbers and impact numbers on substrates of various contact angle
hysteresis. An example of a collision reaching the criteria can be seen in the fourth
images of both Figure 6 and Figure 7. The maximum deformation is typically observed
just after this point.

To begin, it is prudent to comment on the overall observations of the collisions
themselves. The range of Weber numbers observed in this study were generally limited
to between $0 \leq We \leq 6$. There were some higher Weber number collisions observed over
the course of this study, however, in the case with surfaces of higher contact angles, these
usually were characterized by the impacting drop being airborne before impact as a consequence of the large lift forces exerted by our air propulsion system. The other reason for the low Weber number range is that higher Weber numbers usually led to the coalesced droplets quickly leaving the field of view of the high speed camera which prevented the complete measurement of the impact dynamics. Both of these factors lead to an upper limit in Weber number. Furthermore, it is important to note the maximum achievable Weber number decreased strongly as hysteresis increases. This is primarily due to the fact that with higher contact angle hysteresis, a larger driving force is required to induce droplet motion, as seen in equation (1.7). Although these Weber numbers are rather small compared to unconfined collisions, it should be noted that the Weber number limit we observed is much higher than Weber numbers in other sessile drop studies previously discussed, which were typically much less than $We < 1$ (Andrieu, Beysens et al. 2002; Narhe, Beysens et al. 2004; Narhe, Beysens et al. 2005; Thoroddsen, Takehara et al. 2005; Kapur and Gaskell 2007; Boreyko and Chen 2009; Boreyko and Chen 2010; Karpitschka and Riegler 2010).

Three general regimes of droplet coalescence were observed in droplet coalescence. A phase diagram is presented in Figure 11 and in Figure 12 which presents the general delineation of each regime as a function of Weber number and impact number for a surface with a contact angle hysteresis of $3^\circ$ and $30^\circ$ respectively. The first regime is characterized by an oscillation-dominant drop motion following droplet coalescence. This typically occurs at low impact numbers, head-on collisions, and is characterized by the droplet oscillation alternating between elongations in the x- and y-directions. An example of an oscillation droplet collision is shown in Figure 6. Each image sequence in
Figure 6 - Figure 10 represents a droplet coalescence progression with similar Weber numbers and impact numbers, but with varying hysteresis. The time in milliseconds is also displayed, with 0.0s occurred just prior to the coalescence, and shown as the top image in each sequence. The images were chosen to reflect similar instances of each part of the oscillation process. In each image, the side view is on the bottom half of each image, and the top view is the upper half of each image. The top view is where the oscillation in the surface plane is most visible. Analysis of the frequency of oscillation as a function of contact angle hysteresis will be presented later.

The second main mode of collisions is characterized not by oscillations, but by rotation of the droplets after coalescence. This regime occurs at high impact numbers following an indirect or glancing collision of the drops. The rotation is a result of the large amount of angular momentum transferred from the impacting drop to the stationary drop. This mode has been seen for unconstrained droplet collisions in air (Qian and Law 1997). Rotation is not observed for more direct collisions dominated by droplet oscillations. An example of rotation dominated dynamics is represented in Figure 8. The images show the progression of the drop coalescence dominated by rotation. As in parts of Figure 6 - Figure 10 the images were chosen to highlight similar stages of the three instances of droplet coalescence. From the images, it is apparent that droplets on the 15° hysteresis surface takes longer to achieve the same state of deformation than on the lowest 3° hysteresis surface. Interestingly, droplets on the highest 30° hysteresis surface proceed through their coalescence more quickly. As seen in Figure 11, this mode is typically present only for impact numbers greater than \( I > 0.5 \) and Weber numbers greater than \( We > 1 \). This lower Weber number and lower impact number limit, which
has been observed in freely coalescing drops, remains present as hysteresis increases, but shifts to lower Weber numbers and impact numbers. This demonstrates that the rotation of these droplets is strongly retarded as the hysteresis is increased. Another interesting observation is that even at high Weber numbers $We > 7$, our droplets were found to fully coalesce. This contrasts with the observations of droplet coalescence in air in the same Weber number range where droplets do not coalesce, but instead bounce off of each other (Qian and Law 1997).

The third type of collisions is a combination of both the rotation and oscillation regimes. As such, it possesses characteristics from both the oscillation dominant and rotation dominant regimes. In this regime the oscillations are observed to rotate about the new center of mass of the coalesced drop rather than maintaining oscillations in the x-y plane. This regime is encountered predominantly in the middle range of impact numbers, anywhere from $0.2 \leq I \leq 0.6$. This range, however, has a strong Weber number dependence. At low Weber numbers ($We < 1$), this regime stretches from about 0.5 to 1.0. There is a transition regime for Weber numbers between $1 \leq We \leq 3$, and at the largest Weber numbers tested, this regime settles into the impact number range of $0.2 \leq I \leq 0.6$. Figure 7, Figure 9, and Figure 10 show a progression of collisions occurring at middle impact numbers highlighting the effect of the Weber number. In Figure 10, the collisions possess more oscillation than rotation, while as you increase Weber numbers in Figure 9, and further in Figure 7, more rotation is witnessed. In the case of the higher Weber number, middle impact number cases in Figure 7, the droplet collisions on the 3° hysteresis surface tends to be dominated by more droplet rotation than by droplet oscillation. On the higher 30° hysteresis surface, the opposite trend occurs with
the droplet dynamics dominated by oscillation rather than rotation. As hysteresis increases, the oscillation effect for mid-impact coalescences appears to be emphasized. As we decrease the Weber number in Figure 9 and Figure 10, a similar effect is observed. Finally, we observe that as the contact angle hysteresis increases, the width of the mixed-dynamic coalescence narrows, and the rotation regime at higher Weber numbers extends to a range between $0.35 < I < 1.0$ as seen in Figure 12.

In Figure 13, the maximum deformation of the drops after coalescence is plotted in the form of three-dimensional plots with Weber number on the x-axis, impact number on the y-axis, and the maximum deformation on the z-axis. In Figure 13, the maximum deformation in the x-y plane is normalized by dividing it by the diameter of the impacting drop. In addition to the individual data points, a splined surface is superimposed over the data to help guide the eye and illustrate trends.

Upon inspection of the data in Figure 13, a number of qualitative observations about the role hysteresis on drop deformation following coalescence can be made. An increase is observed in the maximum deformation with increasing Weber number. This is expected, as there is an increase in kinetic energy in the colliding drops. Additionally, this is a trend that has been observed many times in the past for airborne collisions (Qian and Law 1997). Higher levels of deformation are observed at both low and high impact numbers than at middle impact numbers. At high and low impact numbers, there is kinetic energy is transferred into a single mode of motion, either rotation or oscillation. In the middle regime of impact numbers, energy is transferred into both rotation and oscillation and the resulting deformation in each mode is not always additive resulting in reduced deformation induced by this more complex drop motion.
One general observation that can be made from the images in Figure 6 - Figure 10 and the data in Figure 13 is that as the hysteresis increases, the overall magnitude of the droplet deformation decreases. In the case of the lowest hysteresis in Figure 13a, a maximum deformation nearing three times the original drop diameter is achieved at large Weber and impact numbers. As the hysteresis increases, the droplet deformation following collisions consistently decreases. In the case of the highest hysteresis tested, the maximum deformations are slightly over two times the original droplet diameter. Note that for two drops of equal volume coalescing on a surface with a contact angle of $\theta_a = 150^\circ$, the final steady-state diameter of the coalesced drop should be approximately 1.4 times larger than the original diameter. Thus for high hysteresis, little real deformation is observed during the droplet coalescence. Additionally, these higher hysteresis cases have less overall variation in the deformation with varying Weber and impact numbers than in the lower hysteresis cases. The deformation surface shown in Figure 13c for the 30° hysteresis case is essentially flat with only variation in the data provided by fluctuations in the data. When compared to the 3° hysteresis surface, the effect of increasing hysteresis is most obvious at high impact numbers where hysteresis is found to limit drop rotation and the resulting deformation.

For a more quantitative analysis, a statistical analysis was performed on the data by averaging the data over narrow windows in both impact numbers and Weber numbers. The results of this analysis are presented in Figure 14 and Figure 15. This averaging serves to more clearly illustrate the effect that contact angle hysteresis has on the droplet dynamics following coalescence. Each point in Figure 14 and Figure 15 represent at a minimum two data points, and at a maximum four data points, sorted by either impact
number or Weber number as is appropriate. Figure 14 is the collected data sorted into three impact number regimes to illustrate the effect of changing Weber number.

It is at the higher Weber numbers that the effects of hysteresis become most noticeable. For the lower \((0.0 < I < 0.3)\) and middle \((0.3 < I < 0.6)\) range of impact numbers shown in Figures Figure 14a and Figure 14b respectively, there is less variation in deformation and similar trends across all Weber numbers and contact angle hysteresis. At the high impact numbers \((0.6 < I < 1.0)\), the deformation of the lower hysteresis surfaces continues to increase with increasing Weber number; however, the deformation of the highest hysteresis studied remains unchanged and perhaps even decrease slightly at the highest Weber numbers investigated. These observations further illustrate that the contact angle hysteresis has the largest impact on the dynamics of the rotation dominated coalescence.

In Figure 15, the data is sorted into three Weber number regimes. For Weber numbers less than \(We < 2\), shown in Figure 15a, there is similar, minimal deformation across all impact numbers and hysteresis studied. Figure 15b shows Weber numbers from \(2 < We < 4\). Unlike the data in Figure 15a, the deformation in Figure 15b increases significantly as the impact number is increased, especially for the low hysteresis case. Figure 15c includes collisions at Weber numbers greater than \(We > 4\). As seen in the 3D plots at both low and high impact numbers, there is significantly higher deformation than at the middle impact numbers. Furthermore, as the hysteresis is increased at the higher and lower impact numbers, the impact of hysteresis on drop deformation becomes clear. Unlike the low hysteresis cases, the 30° hysteresis case results in lower deformation at all impact numbers and a qualitatively different response to changes in impact number. For
the two low-hysteresis cases a minimum is observed around an impact number of \( I \approx 0.5 \) and a large increase is observed as the impact number approaches \( I \approx 1.0 \). For the high hysteresis surface, the rotational motion is greatly suppressed and the maximum deformation is found to decrease monotonically with increasing impact number.

Hysteresis can have an effect on both droplet deformation and the dynamics of coalescence. One area in which the effects of hysteresis are prominent is on the oscillation frequency of coalesced drops following low impact number collisions, and the angular velocity of the coalesced drops following high impact number collisions. We chose to examine collisions from higher Weber numbers because the greatest affect of the hysteresis can be seen in this range. In Figure 16a, the frequency of oscillation of the low impact number collisions \( I = 0.06 \pm 0.02 \) is plotted as a function of contact angle hysteresis. As hysteresis increases, the frequency of the drop oscillations decreases for head-on collisions. It is possible to compare the rates of oscillation to work of Rayleigh (Rayleigh 1879), who showed that the natural frequency of a free droplet is

\[
f_R = \frac{1}{2\pi} \sqrt{\frac{8\sigma}{\rho R}} = 94\text{Hz}
\]

where \( R \) is the droplet radius, \( \gamma \) is the surface tension, and \( \rho \) is the density of the liquid. This natural frequency neglects the effect of the surrounding gases, droplet viscosity, and any second-order effects, all of which are known to reduce the natural frequency. Smithwick and Boulet (Smithwick and Boulet 1989) showed that the natural frequency for a drop on a surface with a pinned contact line goes as

\[
f_N = \frac{1}{2\pi} \sqrt{\frac{\sigma}{\rho R \lambda_n}}
\]

where \( \lambda_n \) are the eigenvalues of each mode and are dependent on the contact angle (Smithwick and Boulet 1989). For a contact angle of \( \theta = 150^\circ \), the natural frequency of the second mode of vibration is \( f_2 = 44\text{Hz} \) (McHale, Elliott et al. 2009).
This value is significantly smaller (40\%) than the predictions for a free drop. As seen in figure 7a, the effect of the surface for the 30° contact angle hysteresis case results in an oscillation frequency that compares well with the predictions of theory (Smithwick and Boulet 1989; McHale, Elliott et al. 2009). As hysteresis decreases, the natural frequency is found to increase, moving away from the result for a pinned contact line and towards the predictions of McHale et al. (McHale, Elliott et al. 2009) for a sessile drop with a fully mobile contact line \( f_{MCL} = 138 \text{Hz} \) (McHale, Elliott et al. 2009).

In Figure 16b, the rotation rate of a series of coalesced drops at varying impact number and a Weber number of \( We \approx 4 \) are presented. The rate of rotation is found to decrease from 3° to 15°, but then increase at 30° to a rate higher than the lowest hysteresis case. This observation can be explained if one considers not the angular velocity, but the angular momentum of the rotating drops. Assuming the final shape of the coalesced drops is ellipsoidal; the angular momentum of the rotating ellipsoidal drop can be calculated from its major and minor axis. The data in Figure 16b is recast as angular momentum as well. For the case of the highest hysteresis, although the angular velocity is large the droplets deformation is significantly smaller than the drops on lower hysteresis surfaces. This limits the moment of inertia of the drop, and as a result the drop rotates faster while maintaining approximately the same angular momentum in all three cases.

### 3.4 Droplet Mixing Results and Discussion

Naturally, the effect of contact angle hysteresis on droplet mixing is important, as many processes require mixing in many microfluidic devices. In order to adequately mix
on a two-dimensional surface, we need to gain insight onto how it occurs and is affect by the wettability properties. We hypothesized that lower hysteresis would lead to enhanced mixing. A preliminary investigation into the mixing occurring within the drop was performed. Shown in Figure 17 is a comparison of two droplet coalescence video sequences, with the top sequence representing a surface with contact angle hysteresis of $3^\circ$, and the bottom sequence of a surface with $50^\circ$ contact angle hysteresis. Both collisions were of low Weber number, $We \leq 0.15$, and low impact numbers $I \leq 0.04$. As one can see, the particles move about the low hysteresis coalesced drop more violently following paths that efficiently stretch and fold fluid elements from the two droplets together, reducing the distance fluid needs to diffuse and fully mix. With the higher hysteresis, the footprint of the drop changes only slightly on coalescence and as a result the mixing is confined to the area where the meniscus bridge is formed, reducing the overall magnitude of the internal flow of the drop. With lower hysteresis, there is larger undulations of the drop, as it behaves more akin to a freely suspended droplet collision, instead of one bounded by a surface. Additionally, the surface serves to reflect much of the capillary waves that occur, adding to the greater amount of mixing. It is clear from the images in Figure 17 that after mixing for only $t = 50\text{ms}$ the drop on the low contact angle hysteresis surface is nearing complete mixing while the drop on the high hysteresis surface remains essentially unmixed. This acceleration in mixing far outpaces diffusive effects which for these drops results in a fully mixed droplet is many orders of magnitudes larger than the observation timescale. These observations were consistent for a number of other Weber numbers and impact number cases studied.
This qualitative result is further supported by Figure 18, which plots the degree of mixing as a function of time for the two drops shown in Figure 17. The degree of mixing is calculated as $\Phi = \frac{(\sigma_0 - \sigma)}{\sigma_0}$. Here, $\sigma_0$ is the initial standard deviation of the image at $t = 0$, and $\sigma$ is the standard deviation. For a perfectly unmixed sample of binary particles/fluorescent fluid, it would result that $\sigma_0 = 0.5$, and $\Phi = 0$, where a value of $\Phi = 1$ would represent fully mixed. In this case, the images contain both white particles and non-white regions, and regions of intensity anywhere between which result from uneven lighting, shadows, and lensing effects. The mixing is calculated by a Matlab code that first thresholds the image so that only the drops are considered, and the background surface as well as bright reflections from the uneven lighting are ignored. The standard deviation $\sigma = \sqrt{(D - \langle D \rangle)^2}$, measures the intensity of the image using the density of distribution, $D$, as calculated by the method of Stone (Stone and Stone 2005).

The results presented in Figure 18 show that on low hysteresis surfaces. The mixing rate following coalescence is significantly larger than that observed for surfaces with higher hysteresis. The degree of mixing for both high and low hysteresis cases increases very quickly after coalescence. However, the droplet dynamics and motion on the high hysteresis surface ceases very soon after coalescence with the majority of motion occurring in a small band located along the meniscus bridge, as has been observed in the prior works. As a result, the mixing in drops on the high hysteresis surface saturates very quickly and remains roughly constant at $\Phi = 0.35$ at the end of the experiment as convection decays away and the drop continues to mix, but by diffusion of the seed particles alone. For the case of the low hysteresis surface, the dynamics persist for much
longer and are of significantly larger amplitude (as seen in the previous section) resulting in faster and more significant mixing that continues to increase beyond $\Phi = 0.7$ as the experiment progresses past $t = 50\text{ms}$. The trends observed in the qualitative results are consistent for a broad range of Weber numbers and impact numbers studied.

### 3.5 Conclusions

In this paper, the effect of contact angle hysteresis on the dynamics of the coalescence of sessile drops was studied. Three superhydrophobic surfaces were examined having the same advancing contact angle of $\theta_a \approx 150^\circ$ and varied contact angle hysteresis values of 3°, 15°, 30°, and 50°. A range of Weber numbers from $0 \leq We \leq 12$ and impact numbers between $0.0 \leq I \leq 1.0$ were studied. Within the coalescence regime, we characterize three distinct modes: oscillation, rotation, and a blend between the two. The impact and eventual coalescence of each drop was observed to fall within one of these regimes based on the Weber number, the impact number, and the contact angle hysteresis of the superhydrophobic surface. At low contact angle hysteresis, the drop deformation and dynamics are especially violent with large oscillations observed in head-on collisions and large deformations and high rotation rates observed at large impact numbers. The low contact angle hysteresis surfaces result in droplet collisions similar to those observed in air and thus the influence of the surface is small. Its presence does, however, limit the Weber numbers that can be achieved for a sessile drop and regimes of bouncing, disruption, and fragmentation were not observed even on the low contact angle hysteresis surface because of this limitation. The frequency of oscillation for all surfaces tested were all found to be slightly above the predictions for a sessile drop with a fully-pinned
contact line, with the largest deviation from theory being observed for the low contact angle hysteresis surfaces. These drops approached the predictions for sessile drops with fully mobile contact line.

With increasing contact angle hysteresis, the droplet deformation following coalescence decreases, to the point that for the highest hysteresis studied, the maximum deformations are only marginally above the expected analytical radius of two drops coalesced. In these cases, the dynamics of impact observed to remain localized primarily to the meniscus bridge formed between the two drops upon contact. Interestingly, for glancing collision with very high impact numbers, the angular velocity increased with increasing contact angle hysteresis. This was found to result in the reduced deformation in the drop, as in all cases angular momentum was conserved. Each of these observations become more intensified with increasing Weber number. Finally, while numerical studies are likely needed to accurately quantify the mixing benefits of coalescence on low contact angle hysteresis surfaces, experimental collisions on a low contact angle hysteresis surface were found to significantly increase the rate and degree of mixing over collisions of similar Weber and impact number on surfaces with high contact angle hysteresis.
Figure 5: Sketch of experimental set up. The two water droplets (blue) rest on the sanded Teflon surface. The jet of air is provided through the gray tube to the right. The lights (not shown) would be located in front and behind the set up.
Figure 6: Comparison across hysteresis for collisions with high Weber numbers and low impact numbers. The top row is 3° (We = 4.21, I = 0.04), the middle row 15° (We = 4.45, I = 0.05), and the bottom row 30° (We = 4.34, I = 0.07). Time increases from left to right.
Figure 7: Comparison across hysteresis for collisions with high Weber numbers and moderate impact numbers. The top row is 3° (We = 4.84, I = 0.31), the middle row 15° (We = 4.81, I = 0.34), and the bottom row 30° (We = 5.38, I = 0.33). Time increases from left to right.
Figure 8: Comparison across hysteresis for collisions with high Weber numbers and high impact numbers. The top row is 3° (We = 5.08, I = 0.87), the middle row 15° (We = 5.12, I = 0.82), and the bottom row 30° (We = 4.24, I = 0.88). Time increases from left to right.
Figure 9: Comparison across hysteresis for collisions with moderate Weber numbers and moderate impact numbers. The top row is 3° (We = 2.54, I = 0.35), the middle row 15° (We = 2.30, I = 0.33), and the bottom row 30° (We = 2.63, I = 0.35). Time increases from left to right.
Figure 10: Comparison across hysteresis for collisions with low Weber numbers and moderate impact numbers. The top row is $3^\circ$ (We = 0.16, I = 0.42), the middle row $15^\circ$ (We = 0.18, I = 0.36), and the bottom row $30^\circ$ (We = 0.22, I = 0.36). Time increases from left to right.
Figure 11: Impact number vs. Weber number, highlighting the different regimes of sessile drop coalescence on a Teflon surface with $\theta$ contact angle hysteresis, with ■ representing oscillation dominant collisions, ▲ representing rotation dominant collisions, and ○ representing collisions exhibiting both oscillation and rotation. The dashed lines serve to illustrate the rotation dominant, rotating-oscillation, and oscillation dominant regimes, from top to bottom, respectively, and are intended only to guide the eye.
Figure 12: Impact number vs. Weber number, highlighting the different regimes of sessile drop coalescence on a Teflon surface with 30° contact angle hysteresis, with □ representing oscillation dominant collisions, ▲ representing rotation dominant collisions, and ● representing collisions exhibiting both oscillation and rotation. The dashed lines serve to illustrate the rotation dominant, rotating-oscillation, and oscillation dominant regimes, from top to bottom, respectively, and are intended only to guide the eye.
Figure 13: Three dimensional plots showing the maximum deformation as a function of both Weber number, and impact number. The amount of hysteresis in each case is a.) 3° top left, b.) 15° top right, and c.) 30° bottom.
Figure 14: Plots of Average maximum deformation versus Weber Number for each hysteresis case. In each graph, the 3° hysteresis results are designated by the solid line with the □ symbol. The 15° hysteresis case is designated by the dashed line and the ● symbol. The 30° hysteresis case is designated by the dotted line and the ▽ symbol. Each graph shows results from a range of impact numbers, from a.) $I = 0.0-0.3$, b.) $I = 0.3-0.6$, and c.) $I = 0.6-1.0$. The standard error is also shown for each point, which is averaged down from the previous charts.
Figure 15 a-c: Plots of Average maximum deformation versus impact number for each hysteresis case. In each graph, the 3° hysteresis results are designated by the solid line with the ■ symbol. The 15° hysteresis case is designated by the dashed line and the ● symbol. The 30° hysteresis case is designated by the dotted line and the ▼ symbol. Each graph shows results from a range of impact numbers, from a.) $We = 0.0 - 2.0$, b.) $We = 2.0 - 4.0$, and c.) $We \geq 4$. The standard error is also shown for each point, which is averaged down from the previous charts.
Figure 16: Oscillation frequency and angular velocity of coalescing drops as a function of contact angle hysteresis. All cases take place at Weber numbers of approximately $We = 4$. In (a) the oscillation frequency of low impact number, $We = 4.3 \pm 0.1$, $I = 0.06 \pm 0.02$, cases are represented by ■. In (b) the angular velocity and angular momentum of the middle impact number cases, $We = 5.1 \pm 0.3$, $I = 0.33 \pm 0.02$ are represented by ● and the high impact number, $We = 4.7 \pm 0.4$, $I = 0.82 \pm 0.03$, cases are represented by ▼. The open symbols represent the angular momentum corresponding to each case.
Figure 17: Particle-laden drops colliding with unseeded drops. The top surface possesses 3° contact angle hysteresis with water, and the bottom surface possesses 50° contact angle hysteresis with water.
Figure 18: Degree of mixing vs. Time as a function of hysteresis. The surface possessing 3° contact angle hysteresis is represented by the square symbols and solid line. The surface possessing 50° contact angle hysteresis is represented by the triangle symbols and the dashed line.
CHAPTER 4
CREATING SHARP TRANSITIONS IN CONTACT ANGLE HYSTERESIS ON A
SUPERHYDROPHOBIC SURFACE TO MOVE, DEFLECT AND SORT
DROPLETS

4.1 Introduction

Microfluidics has become an important and widely studied and implemented platform for diagnostics, material characterization, synthesis, and formulation over the past few decades (Manz, Harrison et al. 1992; Stone and Kim 2001; Reyes, Iossifidis et al. 2002; Stone, Stroock et al. 2004; Squires and Quake 2005; Whitesides 2006). The main advantage of microfluidics is that small volumes of fluid can be precisely controlled and manipulated. Microfluidic devices are typically enclosed devices, created in a polymer, such as polydimethylsiloxane (PDMS) or glass via photolithography. These are often single application or one-time-use devices due to the tendency for micro-scale channels to clog or degrade after sustained use. Additionally, in microfluidic devices, it is often advantageous to perform experiments using individual drops of fluid rather than streams. This is a field often referred to as digital microfluidics because the drop is manipulated one drop at a time rather than as a continuous flow. The major advantage of using droplets is that it allows one to manipulate individual plugs of fluid while avoiding dispersion effects.

In this field of digital microfluidics, there are a number of key challenges that must be addressed if the device is to be successful. These include droplet positioning, movement, coalescence and mixing, splitting, and finally droplet deflection. In this work
we will demonstrate a new method for addressing two of these challenges: droplet positioning and deflection. What makes our devices unique are that the droplets are manipulated and deflected on an open two-dimensional substrate without the use of an enclosed channel as is done in conventional microfluidic devices. Our microfluidic devices consist of planar superhydrophobic surfaces with discrete spatial variations in wetting properties, specifically contact angle hysteresis. Superhydrophobic surfaces can be fabricated in a number of ways (Zhang, Shi et al. 2008). Here the devices are fabricated by mechanically sanding Teflon with sandpaper of various grit-designations to produce a randomly rough surface (Nilsson, Daniello et al. 2010). The superhydrophobic surfaces are inexpensive and easy to fabricate. In addition, by varying the sandpaper roughness, surfaces with a wide range of both advancing contact angles and contact angle hysteresis can be fabricated, allowing for the systematic and independent variation of either property.

Contact angle hysteresis is defined as the difference in advancing and receding contact angles, \( \theta_H = \theta_A - \theta_R \). Contact angle hysteresis inhibits contact line motion through a sticking force that goes as (Rothstein 2010)

\[
F_D \approx \gamma l \left( \cos(\theta_A) - \cos(\theta_D) \right). \tag{4.1}
\]

Here \( \gamma \) is the surface tension and \( l = R \sin(\pi - \theta) \) is the radius of the contact area between the drop and the surface. In order for a droplet to move, the droplet must first deform such that the advancing contact angle is exceeded and the receding contact angle is surpassed. In this work, all of the Teflon surfaces have an advancing contact angle of \( \theta_A = 150^\circ \), but vary in receding contact angle resulting in contact angle hysteresis that
range from $3^\circ < \theta_H < 50^\circ$. In Chapter 2, these surfaces were utilized to investigate the effect of contact angle hysteresis on droplet coalescence and mixing (Nilsson and Rothstein 2011). They showed that reduction in contact angle hysteresis can dramatically improve droplet mobility, deformation, and mixing following droplet coalescence.

Over the last few years there has been quite a bit of work in the field of two-dimensional digital microfluidics with a focus primarily on droplet motion. Superhydrophobic surfaces are the primary platform for drop studies as they are inspired by the remarkable behavior of water droplets on the leaves of the lotus plant (Neinhuis and Barthlott 1997). Droplets on surfaces with little contact angle hysteresis have been found to be extremely mobile and as such are very sensitive to vibrations and small perturbations (Bico, Marzolin et al. 1999; Chen, Fadeev et al. 1999; Kim and Kim 2002; Sakai, Song et al. 2006; Shastry, Case et al. 2006). Droplet motion across superhydrophobic surfaces has also generated much interest. By tracking a single particle near the surface of a drop, Richard et al. (Richard and Quere 1999) have shown that viscous droplets with high contact angles on a surface tend to roll across the surface in agreement with theory (Mahadevan and Pomeau 1999). The solid-body motion of the rolling drop greatly reduces the resistance to motion and has been shown to reduce the drag on the drops by as much as 99% (Kim and Kim 2002). Gogte et al. (Gogte, Vorobieff et al. 2005) later showed that for water on superhydrophobic textured surface, droplets initially slide at times near the onset of motion. They found that as the droplet accelerates it transitions to rolling motion. During the early stages of drop motion, the droplets trajectory approaches the free fall limit and interestingly it accelerates faster than a solid sphere rolling down the same inclined surface (Reyssat, Richard et al. 2010).
each of the experiments described above, droplet motion was induced by placing the substrate on an incline. Droplet motion can be induced in a number of other ways as covered in earlier in Chapter 1.1.10.

A number of previous studies have investigated the motion of droplets traversing over discrete changes in surface wettability. Suzuki et al. have shown that a droplet’s trajectory can be passively altered by using different surface chemistries to create an array of wetting and non-wetting stripes aligned at an oblique angle to the primary direction of droplet motion (Suzuki, Nakajima et al. 2008). Both the wetting and non-wetting stripes had similarly degrees of contact angle hysteresis, \( \theta_H = 16^\circ \), but very different advancing and receding contact angles. In their work, a series of arrays of 500\( \mu \)m and 100\( \mu \)m stripes were placed on an incline at an angle of 35\(^\circ\) from horizontal and oriented at various in plane angles. The velocity of the droplets was found to oscillate as they progressed across the striped surface. For the smallest droplets tested, a maximum droplet deflection angle of 13\(^\circ\) was observed (Suzuki, Nakajima et al. 2008). The droplets were always found to deflect towards the directions of the stripes to minimize drag, in a manner similar to continuous flows past striped and grooved surfaces (Stroock, Dertinger et al. 2002; Stroock, Dertinger et al. 2002; Ou, Moss et al. 2007). A number of methods exist for sorting drops using either electrowetting or optical-electric methods. Krupenkin et al. (Krupenkin, Taylor et al. 2004) demonstrated the ability to change wettability characteristics by using an electrode inserted in a droplet and a DC electrical field to drive a droplet from a superhydrophobic state to completely wetting. Optical-electric devices can be used to direct a motion of a drop as it falls by optically sensing the drop width and then activating a charging device to alter drop trajectory (Link, Grasley-
Mongrain et al. 2006). Electro-wetting devices can also be used to perform coalescence, mixing, and sorting of droplets (Li, Fu et al. 2010). However, these devices tend to be expensive and complicated to fabricate. There have been no studies to date that examine the effective of a single, discrete wettability change.

A number of open questions still remain, the most interesting being what happens when a droplet flows past a singular wettability transition rather than an array of stripes because it addresses the underlying physics of droplet deflection. Weir et al. (Wier, Gao et al. 2006) hypothesized that a two-dimensional digital microfluidic device could be designed to utilize a drops reluctance to cross from a region of lower to higher advancing contact angle to affect droplet trajectory. They showed that the additional gravitational potential energy needed to advance from a region of low to high contact angle can often be enough to exclude a slowly moving droplet from advancing onto the high contact angle surface. In this way, they were able to demonstrate the ability to steer droplets along a surface by drawing boundaries of high contact angle on a low contact angle background. It could also be conceived that effects from the receding contact line could also be used to affect droplet motion.

4.2 Experimental Setup

When a superhydrophobic surface has a precisely patterned or randomly patterned surface roughness capable of supporting an air-water interface, it is said to be in a Cassie-Baxter state of wetting (Cassie and Baxter 1944). The Cassie-Baxter state typically has both high advancing contact angles ($\theta_a \geq 150^\circ$) and minimal hysteresis. As a result droplets tend to have high mobility. When the roughness is not ideal and is too wide,
shallow, or rounded to support an air-water interface the water permeates and fully wets roughened surface, resulting in a droplet in the Wenzel state (Wenzel 1936). The Wenzel state may have high advancing contact angles, but also characteristically has a high contact angle hysteresis. The work presented here will employ surfaces in both the Cassie and Wenzel states and utilize discrete transitions in droplet wetting from one state to the other to deflect droplets based on size, speed, and composition.

The basic surface preparation technique used in this experiment is Chapter 2 (Nilsson, Daniello et al. 2010). In their work, they showed that sanding Teflon with different grits of sandpaper can produce randomly patterned surfaces with different degrees of roughness. With this technique a wide range of advancing and receding contact angles could be achieved simply by choosing the appropriate sandpapers. In this study, we will focus on a series of sanded Teflon surfaces for which the advancing contact angle can be held fixed at $\theta_a = 150^\circ$, but which have a receding contact angle that varies from $120^\circ < \theta_r < 147^\circ$. To generate the superhydrophobic surfaces used in this study, small pieces of Teflon were initially mounted to an aluminum substrate with epoxy to ensure a flat level surface. To create the wetting transitions, the entire Teflon surface was initially sanded with a sandpaper of one grit designation. Non-marking model tape was placed over half of the surface and the exposed half was then re-sanded with a sandpaper of a different grit designation. Care was taken to not tear or rip the tape during the second sanding. The tape was removed, and the surface cleaned with acetone, deionized water, and blown dry with pressurized air. The resulting Teflon surface
contains two distinct regions of similar advancing contact angle \((\theta_a = 150^\circ)\) but varying receding contact angles, with a sharp transition between them as shown in Figure 19.

### 4.3 Results and Discussion

The patterned Teflon surfaces were then placed on a plane with an adjustable inclination angle, \(\alpha\), to induce droplet motion. The inclination angle required to initiate the motion of the water droplet is dependent on both the contact angle hysteresis and the droplet size. Only for droplets where the gravitation force exceeds the sticking force, \(mg \sin \alpha > F_D\), will the droplets move down the incline. Expanding both sides for near spherical droplets we find a critical inclination of \(\sin \alpha_{\text{crit}} = \frac{(\kappa^{-1})^2 \sin(\pi - \theta)(\cos \theta_k - \cos \theta_a)}{2/3 R^2} \). As a result, there are cases for very small droplets or large contact angle hysteresis surfaces where droplets will remain pinned even on vertically oriented surfaces. Here \(\kappa^{-1} = \sqrt{\gamma/\rho g}\) is the capillary length which for water is \(\kappa^{-1} = 2.7\) mm and \(\theta = (\theta_a - \theta_k)/2\) is the average contact angle used in the calculation of the length of the contact line. Once moving, Reyssat et al. (Reyssat, Richard et al. 2010) showed that on a superhydrophobic surface the total force acting on the droplet becomes the gravitational force minus the sticking force introduced by contact angle hysteresis, \(F_{\text{tot}} = mg \sin \alpha - F_D\). Substituting in for sticking force from equation (1.7) and expanding for nearly spherical drops, one finds

\[
\frac{F_{\text{tot}}}{mg \sin \alpha} = 1 - \frac{(\kappa^{-1})^2 \sin(\pi - \theta)(\cos \theta_k - \cos \theta_a)}{2/3 R^2 \sin \alpha} \tag{4.2}
\]
Reyssat et al (Reyssat, Richard et al. 2010) showed that for surfaces with very low contact angle hysteresis that the effect of the sticking force is minimal, accounting for only a few percent change in the total force acting on the droplet. In their study, droplets were observed to descend down the superhydrophobic surface following the law of free fall until a terminal velocity was reached as aerodynamic and viscous forces slowed and deformed the sliding droplet. Here we investigate the effect of hysteresis on the drag of a drop keeping the advancing contact angle fixed at $\theta_a = 150^\circ$. In Figure 20, the total force on the droplets is presented normalized by the force of gravity for droplets. Using a micropipette, droplets of deionized water were placed on a sanded Teflon surfaces inclined at $13^\circ$ above horizontal. All of the droplets were initially placed on and allowed to accelerate down a low hysteresis surface, $\theta_H = 3^\circ$, before transitioning to a surface with higher hysteresis. The droplets moved easily down the low hysteresis surface under gravity and accelerated towards the contact angle transition reaching it at a velocity of approximately $U \approx 0.12$ m/s. By bringing droplets onto the higher hysteresis surfaces with a non-zero velocity, it was possible to observe droplet motion and calculate drag forces on surfaces where the droplets were observed to decelerate at the inclination angle chosen.

A high-speed camera (Phantom v4.2) was used to capture the droplet motion at a frame rate of 2900 fps. The acceleration of the drops was measured from the high-speed video images at a position $x = 2$mm downstream of the contact angle transition and used to calculate the total force on the drop to compare with the theoretical predictions of equation (4.2). As expected, the total driving force is found to decrease with increasing
contact angle hysteresis as the sticking force increases. As seen in Figure 20, and predicted by equation (4.2), the sticking force on the droplets with $\theta_h \leq 30^\circ$ is less than the force of gravity and as a result the drops are observed to accelerate down the length of the inclined superhydrophobic surface. The hysteretic drag on droplets on the smooth Teflon (50° hysteresis), however, is much larger than gravity and the drops are quickly decelerated. Although the experiments and theory agree qualitatively, the experimentally observed drag on the droplets is underpredicted by equation (4.2). This is likely due to the fact that equation (4.2) ignores effects of viscous losses. In the Cassie-Baxter state, the presence of the air-water interface can induce slip and dramatically reduce drag (Reyssat, Richard et al. 2010; Rothstein 2010). In fact, for very low hysteresis surfaces the viscous drag can be completely ignored (Richard and Quere 1999; Kim and Kim 2002; Reyssat, Richard et al. 2010). Contrast this to the higher hysteresis surfaces in which the water is in contact with less trapped air and to some degree has reverted to the fully-wetted Wenzel state in which the droplet must flow over a rough no-slip surface. In both cases, increased hysteresis corresponds not only to an increased sticking force, but a small viscous drag component. Although the experiments and theory agree qualitatively, the experimentally observed drag on the droplets is underpredicted by equation (4.2) at low hysteresis and overpredicted at high values of hysteresis. This is likely due to the fact that equation (4.2) ignores effects viscous losses and assumes nearly spherical drop shape.

The difference in drag along a surface of different hysteresis suggests that if the transition were not perpendicular to the flow direction, but at some oblique angle, that the droplets could be deflected. Additionally, the large deceleration and drag measured on
the smooth Teflon suggests that it could be used to capture and collect a drop moving along a surface of lower hysteresis. To investigate these hypotheses, the sanded Teflon surfaces were mounted on a rotating stage to change the in plane angle of the transition, $\alpha_r$, while varying the incline between $10^\circ < \alpha < 13^\circ$ to achieve the desired variation in droplet velocity and Weber number. This experimental setup can be seen schematically in Figure 21. The deflection distance, $d$, is the distance a drop moves from the original trajectory after passing the sharp transition in receding contact angle. This deflection distance is measured at a location 15mm downstream of the transition because by the time the droplet passes this distance any lateral motion has ceased and the droplet motion again is straight downhill. The deflection distance is normalized by the droplet diameter in the figures that follow. The droplet diameters in this study were 3.6mm on average with a standard deviation of 0.1. Positive deflections indicate deflection to the left while negative deflections are to the right. The deflection is a function of Weber number, where on a given surface in this work the Weber number could be varied from $0 < We < 1.25$ and the angle of the transition line was varied incrementally from $0^\circ < \theta_r < 45^\circ$. A wide variety of hysteresis transitions were fabricated. The high speed camera was mounted atop a tripod with the camera tilted to allow for a view perpendicular to the surface. For consistency, the data presented here are for surfaces rotated clockwise. However, the behavior was symmetric and the resulting dynamics were found to be independent of rotation direction.

Regardless of the particular contact hysteresis involved, when a droplet moves from a surface of high contact angle hysteresis to one with low contact angle hysteresis,
the resulting deflection is always towards the left. This can be seen in the left hand figures in Figure 22 both as an overlay of several images of a drop as it progresses along the surface and as a schematic diagram that we will use to better explain the physics. Conversely, when a droplet moves from a surface with low contact angle hysteresis to one with high contact angle hysteresis the droplet is deflected is always towards the right. This is illustrated in the images and the schematic diagrams in the right hand side of Figure 22. The directionality of the deflections is caused by the dynamics of the receding contact line as it encounters the transition. Recall that in all cases the advancing contact angle is identical and only the receding contact angle is affected by the transition. In the case a transition from high to low contact angle hysteresis, upstream of the transition the droplet is initially moving with a lower receding contact angle. The droplet deformation required to move along the high hysteresis surface upstream of the transition results in significant interfacial energy being stored within the moving, deformed droplet. Upon reaching and passing the transition, the receding contact angle is reduced and the backside of the drop quickly retracts. The droplet becomes less deformed and approaches a spherical shape. The sudden release of stored potential energy provides a small force that acts to accelerate the droplet normal to the contact angle hysteresis transition. This is shown schematically in Figure 22. The small driving force is equivalent to the difference in the sticking force in equation (4.3) between the high and low hysteresis surfaces,

\[ F_{\text{Deflection}} \approx \gamma l \left( \cos(\theta_R)_1 - \cos(\theta_R)_2 \right) \]  

(4.3)

Here, \( (\theta_R)_1 \) corresponds to the receding contact angle of the upstream surface and \( (\theta_R)_2 \) to the downstream surface. This force is aligned perpendicular to the transition
angle. Conversely, for a transition from low to high contact angle hysteresis, the droplet is deformed from a nearly spherical shape to a more deformed shape. In this process some kinetic energy is removed from the drop and converted to an increase in interfacial energy. The result is a force that decelerates the drop in a direction normal to the transition line. As seen in Figure 22, the result is a deflection of the drop to the right. Note that this observation is different from that of Suzuki et al. (Suzuki, Nakajima et al. 2008) for flow of a droplet across a surface with stripes of variable wettability. In their experiments, droplet deflection was always found to occur towards the orientation of the stripes. In the context of our experiments, the droplet deflections observed by Suzuki et al. (Suzuki, Nakajima et al. 2008) would be to the right.

The magnitude of the resulting deflection for a given transition angle and transition in contact angle hysteresis is shown in Figure 23 for a wide range of Weber numbers between $0.05 < We < 1.25$. One clear observation is that the deflection of droplets is much larger when the droplet transitions from a surface with higher contact angle hysteresis to one with lower contact angle hysteresis. This is true even if the Weber number, transition angle, and the magnitude of the change in hysteresis is identical. The response of a droplet to a transition in receding contact angle is not reversible. This observation is not intuitive, as in this case the amount of energy added or removed by the receding contact line dynamics is the same. If you investigate the angle that the trajectory is altered when transitioning from both $30^\circ$ to $3^\circ$ and $3^\circ$ to $30^\circ$ contact angle hysteresis, the angle of identical magnitude for the same Weber number. At a Weber number of $We = 0.15$ and transition angle of $\alpha_r = 40^\circ$, both drop trajectories are altered by $14^\circ$, but to the left for the $30^\circ$ to $3^\circ$ transition, and to the right for the $3^\circ$ to $30^\circ$
hysteresis transition. Because the deflection angle is identical in both cases, the
difference in final deflection distance must therefore be a result of the droplet dynamics
that occur after the droplet passes the transition. Following the 30° to 3° transition, the
droplet passes onto a surface with much less drag than the following 3° to 30° transition.
As seen in Figure 20 the drag force on the 3° surface is roughly one third the drag on the
30° contact angle hysteresis surface. The force resulting from the receding contact line
motion is imposed only as the drop passes the transition while the gravitational driving
force is constant. As a result, the lateral motion induced by the transition dies away more
quickly on the surface with higher contact angle hysteresis resulting in a reduced overall
droplet deflection even though the initial deflection angles are identical in both cases.

The difference in deflection can be calculated from first principles. Assuming a
constant deceleration, $a_y$, on the sanded Teflon surfaces, the deflection, $d = 1/2 \ a_y \ t_f^2 + V_i \ t_f$, can be shown to be dependent on the initial lateral velocity imposed on the drop by the
transition, $V_i$, and the time for the drop to lose all its lateral velocity, $t_f = -V_i / a_y$. The
deceleration can be taken from the measurements in Figure 2, $a_y = g_s - a_{drop}$, or from the
predictions of theory in equation (4.2). The initial velocity can be calculated from a
simple energy argument assuming that the deflection force is exerted over a finite
distance which we estimate as the radius of the contact between the drop and the surface,
$R \sin(\pi - \theta)$. If we assume complete conversion of work performed at the transition into
kinetic energy of the drop, the initial lateral velocity becomes

$$V_i \approx \sqrt{\frac{3 \gamma \left( \cos(\theta_r) - \cos(\theta_l) \right) \sin^2(\pi - \theta) \sin(\alpha_f)}{2 \pi \rho R}}$$  (4.4)
Using equation (4.4) to calculate the deflection of a drop across a $\alpha_r = 40^\circ$ transition, one finds a maximum possible deflection of about $d / D \approx 1.8$ for a $30^\circ$ to $3^\circ$ hysteresis transition, $d / D \approx 0.7$ for a $15^\circ$ to $3^\circ$ hysteresis transition, and about $d / D \approx -0.20$ for a $3^\circ$ to $30^\circ$ hysteresis transition independent of Weber number. These calculations predict the extreme values of deflection in Figures 5 and 6 reasonably well, but do not represent all the data because this calculation ignores the dynamics and assumes that all of the energy is transferred between interfacial and kinetic energy of the drop.

A number of other observations can be made from the data in Figure 23. Increasing the difference in the contact angle hysteresis across the transition was found to increase the deflection. However, when a droplet transitions onto a surface with a contact angle hysteresis of $\theta_H = 50^\circ$, which is large enough to completely halt droplet motion, the droplet deflection is clearly minimized independent of transition angle. Often for these experiments this is because the droplet stops completely and is captured at the transition line. We can also observe that for these cases the deflection is maximized at transition angles of approximately $\alpha_r \approx 40^\circ$. The maximum deflections were observed for droplets starting on a surface with $30^\circ$ contact angle hysteresis and then transitioning to a surface of $3^\circ$ contact angle hysteresis. For these surfaces of a transition angle of $\alpha_r = 40^\circ$, a significant deflection was achieved over a wide range of Weber numbers, with a maximum observed deflection of $d / D = 1.4$. This deflection is sufficient to achieve efficient sorting, as it exceeds what we consider the minimum deflection of one diameter required to effectively sort drops. However, effective sorting also requires the
chosen device to be selective. For that reason, the Weber number dependence of the droplet deflection was also investigated.

In Figure 24, the normalized droplet deflection is shown as a function of Weber number for a transition angle of $\alpha_T = 40^\circ$ for transitions from $30^\circ$ to $3^\circ$ contact angle hysteresis, $3^\circ$ to $30^\circ$ contact angle hysteresis, and $15^\circ$ and $3^\circ$ contact angle hysteresis. For the $30^\circ$ to $3^\circ$ and the $15^\circ$ to $3^\circ$ contact angle hysteresis transitions, a clear maximum is observed in the deflection data with Weber number at $We = 0.15$. The droplets are found to reach a maximum deflection of $d/D = 1.4$ and $d/D = 1.1$ for $30^\circ$ to $3^\circ$ and $15^\circ$ to $3^\circ$ respectively. Additionally, only within a very narrow range of Weber numbers, $0.1 < We < 0.2$, are the deflections found to be large enough to deflect the droplet by more than a single diameter to either side. Outside of this range, the deflections are much less substantial, $d/D < 0.5$, and is essentially independent of the Weber number. Finally, note that no deflection data is presented for $We < 0.05$ because at these low velocities it was difficult to mobilize the droplets on the surface with $30^\circ$ contact angle hysteresis. At larger Weber numbers, the inertial forces are much larger than the deflection force imparted on the drop as it crosses the transition. This can be better seen if a new modified Weber number is formulated which directly compares the inertial force to the difference in sticking force experienced by the drop as it crosses the transition as defined in equation (4.3),

$$We_{\text{mod}} = \frac{\rho U^2 D}{\gamma \left[ \cos(\theta_R) - \cos(\theta_H) \right] \sin(\alpha_T)}.$$  

(4.5)

For the new modified Weber number the optimal range for large deflections occurs for $0.75 < We_{\text{mod}} < 1.0$ as seen in the inset of Figure 24.
The presence of this maximum deflection explains the spread in the data in Figure 24 which incorporated data over a wide range of Weber numbers including the optimal values. No maximum was observed for the transitions from low contact angle hysteresis to higher contact angle hysteresis over the range of Weber numbers accessible in these experiments. In fact, for transitions from 3° to 30° hysteresis the value of deflection is constant at roughly the value of \( d/D \approx -0.13 \) predicted by our theoretical analysis. This is likely because as the drop transitions from low to high hysteresis, the interfacial energy of the drop can only be increased by reducing the velocity of the drop and changing its kinetic energy. As a result, the assumption of perfect conversion of kinetic energy to interfacial energy is reasonable. However, when the droplet transitions from high hysteresis to low hysteresis, the assumption of perfect conversion of interfacial energy into kinetic energy of the drop clearly does not hold over all Weber numbers. This is because the interfacial energy can transfer not only to kinetic energy of the drop, but also to capillary waves on the surface of the drop or to the mixing and swirling of fluid within the drop. As a result, the efficiency of energy conversion is not perfect, but is extremely sensitive to the droplet dynamics as it crosses the transition. One might expect the efficiency of energy transfer would be maximized if dynamics of transition excited the droplet at its natural frequency. In other words, at \( We = 0.15 \), the non-dimensional natural frequency should be approximately one, \( f_n t_c = f_n R \sin(\pi - \theta) / U \approx 1 \) where \( t_c \) is the residence time for the drop crossing the transition in contact angle hysteresis. This is in fact the case. For the transitions from 30° to 3° hysteresis transition at the peak Weber number of \( We = 0.17 \) the drop takes approximately \( t_c = 0.023 s (1 / t_c = 44 \text{ Hz}) \) to cross the
transition. The resonance frequency of a water drop has been measured on the 3° hysteresis surfaces to be $f_n = 55\text{Hz}$ (Nilsson and Rothstein 2011). For the 15° to 3° transition, the results are even closer with $1/t_c = 50\text{Hz}$ at $We = 0.17$. Thus, it appears the maximum deflection is achieved when the transition excites the droplet at or near its resonance frequency.

A number of additional experiments were performed examining transitions at $We = 0.15$ for a range of transition angles with droplets transitioning from 30° to 3° contact angle hysteresis. The maximum droplet deflections were found to increase with increasing transition angle as predicted by our theoretical analysis in equation (4.4). However, for experiments for which the transition angles were much greater than $\alpha_r > 45°$, where experimentally challenging to perform consistently. The droplet deflections measured at these angles were not universally reproducible and the resulting data had large standard deviations.

A natural extension of this deflection phenomenon is to ask what occurs when a drop moves across a stripe or multiple stripes of different contact angle hysteresis, instead of a single transition. The addition of a stripe means that a droplet will undergo two transitions in the course of travel, one from low to high and another from high to low contact angle hysteresis. Of the surfaces tested, the maximum deflection of any water droplet was observed on surfaces of 3° and 30° contact angle hysteresis so only stripes varying between those surfaces were considered to maximize the observed deflection. The stripe widths were on the order of the droplet diameter, $w = 3.5\text{mm}$, allowing for full wetting on the stripe as the droplet passes over it. The maximum observed droplet
deflections were observed to occur at a transition angle of $\alpha_r \sim 40^\circ$. This is in agreement with the results for the single transition.

In Figure 25, the deflection of droplets moving past single stripes of $3^\circ$ contact angle hysteresis on a background of $30^\circ$ contact angle hysteresis and vice versa are presented for a transition angle of $\alpha_r = 40^\circ$ for a range of Weber numbers. Here the Weber number and transition angle are always evaluated using the velocity of the drop as it encounters the first transition. As described previously, a single transition from higher to lower contact angle hysteresis produces a deflection to the left and a single transition from lower to higher contact angle results in a deflection to the right. For the case of a stripe, the net droplet deflection is sum of the deflections produced by both transitions. As seen in Figure 25, the deflection is consistently to the left for the case of a stripe with $3^\circ$ contact angle hysteresis on a surface of $30^\circ$ hysteresis. The first transition the drop experiences from $30^\circ$ to $3^\circ$ hysteresis produces a deflection that is to the left, and as seen in Figure 5, always larger in magnitude than the right deflection of the $3^\circ$ to $30^\circ$ hysteresis transition at a given Weber number. Following the first transition, the droplet encounters the second transition with increased and at a smaller transition angle, $\alpha_r < 40^\circ$, resulting in a small secondary deflection back to the right. As was observed for a single transition, a maximum deflection is observed for $We = 0.15$, although due to the presence of the second transition, a maximum deflection of only $d/D \sim 0.8$ was observed.

The trends in the deflection data of droplets passing over a stripe of $30^\circ$ contact angle hysteresis on a surface of $3^\circ$ hysteresis are more complex. At smaller Weber numbers, $We < 0.2$, the net droplet deflection is to the right. The initial transition from $3^\circ$
to 30° hysteresis causes a deflection to the right. Due to the absorption of kinetic energy at the first transition, the droplet slows between the first and second transition. The droplet thus moves along the stripe and encounters the second transition at a lower angle and Weber number. At low Weber numbers, the deflection at the second hysteresis transition is minimal and a net deflection to the right is observed. However, for larger Weber numbers the first transition still creates a small deflection, but the deceleration of the drop is enough to reduce the Weber number to within the optimal range at the second transition. The result is a smooth variation from right or negative drop deflections at low Weber number to left or positive deflections as the Weber number increases beyond $We > 0.25$.

If a single stripe can produce measureable droplet deflections near the ideal Weber number and transition angle, then it follows that a series of stripes can be used in series to further amplify the response of the drop. In Figure 26, a device designed to maximize droplet deflection by incorporating multiple stripes on a surface is presented. This device achieves far more deflection than a single transition or a single stripe, by having parallel stripes of 30° hysteresis across a surface of 3° hysteresis. The result is a droplet deflection of $d/D = 3.5$ after 60mm of travel past 3 stripes. The droplet moves across the first transition at a Weber number of $We = 0.15$. This leads to the maximum possible initial deflection. However, as the drop continues to accelerate down the device, the Weber number at each subsequent stripe increases and the deflection from each of the subsequent stripes is smaller. Even so, as it is clearly shown in Figure 26, multiple stripes of different receding contact angles can be a very effective means of deflecting or even sorting drops on a two-dimensional digital microfluidics platform.
4.4 Conclusions

In this paper, the ability for sharp transitions in contact angle hysteresis to deflect droplets was investigated. It was shown that for a single transition, droplet deflection of more than one droplet diameter were possible. Superhydrophobic sanded Teflon was shown to be an excellent platform for these two-dimensional digital microfluidics experiments because of its high advancing contact angles and the ease in which variations in contact angle hysteresis could be achieved. By masking patterns onto the Teflon, sharp transitions in contact angle hysteresis were created using different grit-designation sand paper to create variations in surface roughness. We show that a drop moving over these sharp transitions in contact angle hysteresis experiences a small force from the contact line transition. This force results from the conversion of kinetic energy to interfacial energy and vice versa as the change in contact angle hysteresis transforms the shape of the drop. Orienting the transition at an angle to the principle direction of the drop results in a force normal to the transition line, deflecting the droplet from its original path. The sign of the force and thus the direction of this deflection are shown to depend on whether the drop transitions onto a surface of a higher or lower receding contact angle. The drop deflects towards the transition line when moving from a higher to lower receding contact angle surface, while when transitioning from a lower to a higher receding contact angle surface the drop deflects away from the transition line. The initial angle of deflection is identical in both cases. However, higher hysteresis on the downstream surface mutes the impact of the deflection force because it has higher surface drag, resulting in decreased overall deflection. It is shown that this deflection is a
function of the magnitude of contact angle hysteresis difference, the angle of the transition, and the Weber number of the drop. In this study, the optimal conditions for deflecting water droplets sliding on sanded Teflon were found using a transition from a surface region with 30° contact angle hysteresis to 3° at Weber number around $We \approx 0.15$. In our study, a transition angle of around $\alpha_r = 40^\circ$, but theory predicts that the deflection should increase with further increases in transition angle. Small changes in Weber number can have a significant effect on the deflection, with Weber numbers outside of $0.1 < We < 0.2$ experiencing minimal deflection when transitioning from 30° to 3° contact angle hysteresis. Within this range of Weber numbers the transition time was found to coincide with one over the resonance time of the drop. As a result, at these speeds the interfacial energy released by the receding contact line is most efficiently transferred into kinetic energy of the drop thereby maximizing its deflection.

It is possible to achieve measureable deflections with the addition of a stripe of different contact angle hysteresis alternating between 3° and 30°. The effect of encountering each transition is found to be additive. Finally, it is shown that a series of stripes can achieve even larger droplet deflections. This work has thus clearly shown that with both single contact angle hysteresis transitions and stripes of differing contact angle hysteresis, it is possible to target drops of particular size, velocity, and wettability and alter their path sufficiently to effectively sort droplets. In combination with our previous work in this area, we have now shown that superhydrophobic Teflon surfaces are an excellent platform for two-dimensional digital microfluidics, as it has now been shown to successfully perform many of the tasks needed for effective development of these
microfluidic devices. This includes droplet coalescence and mixing, (Nilsson and Rothstein 2011) and the motion, deflection, and sorting of droplets shown here.
Figure 19: Schematic diagram of the experimental set-up. The transition from one contact angle hysteresis to another is shown as a dashed line.
Figure 20: The normalized acceleration of a 2.5mm diameter droplet moving down an inclined plane of variable contact angle hysteresis and constant advancing contact angle of $\theta_a = 150^\circ$. 
**Figure 21:** Experimental set-up with important parameters overlaid. The dashed line represents the location of the transition in contact angle hysteresis transition.
Figure 22: Sample droplet trajectories for transitions (on the left) from higher to lower contact angle hysteresis and (on the right) from lower to higher contact angle hysteresis.
Figure 23: Deflection of Drops moving over a single transition in contact angle hysteresis presented as a function of the angle of transition, $\alpha_r$, for a range of Weber numbers from $0.05 < We < 1.25$. The data includes transitions from (■) 3° to 50°, (○) 3° to 15°, (●) 15° to 3°, (▲) 3° to 30°, and (▼) 30° to 3°.
Figure 24: Normalized droplet deflection as a function of Weber number for single contact angle hysteresis transitions from (▼) 30° to 3°, (●) 15° to 3°, and from (▽) 3° to 30° all at a transition angle of $\alpha_t = 40^\circ$. The inset contains the same data plotted against the modified Weber number proposed in equation (4.5).
Figure 25: Deflection of Drops moving over a stripe of varying contact angle hysteresis presented as a function of the Weber number at a transition angle of $\alpha_T = 40^\circ$. The data includes (▼) a 3.5mm stripe of 3° hysteresis among a surface with 30° hysteresis and (▽) a 3.5mm stripe of 30° hysteresis among a surface of 3° hysteresis.
Figure 26: A low contact angle hysteresis surface with high hysteresis stripes of 3.5mm in width. The resulting deflection is many times that of a single transition. The Weber number at the first stripe is $We = 0.15$, which is near the range of maximum deflection. Subsequent stripes result in further droplet deflection, however each contribution is diminished because the droplet encounters them at higher Weber numbers.
CHAPTER 5
DESIGN OF TWO-DIMENSIONAL MICROFLUIDICS DEVICES FOR
SORTING, MIXING, AND ANALYZING DROPLETS

5.1 Introduction

In microfluidics, small amounts of fluids (microliter and smaller) are manipulated using devices which are typically comprised of channels with dimensions on the order of micrometers or nanometers (Manz, Harrison et al. 1992; Stone and Kim 2001; Reyes, Iossifidis et al. 2002; Stone, Stroock et al. 2004; Squires and Quake 2005; Whitesides 2006). It is this small size scale that provides microfluidic devices with numerous advantages over macroscale devices in a number of important application areas including biochemical diagnostics and detection, chemical reactions and synthesis, and separation processes. Due to the small amounts of fluid samples and reagents that are required in microfluidic devices, experiments can be performed at a lower cost, in a shorter time, and on a smaller device footprint. In microfluidics, a number of design difficulties exist which are due primarily to the increased importance of interfacial phenomena. These include the fabrication cost associated with complex three-dimensional microfluidic devices and the frequent failure of these devices due to blocked or contaminated channels after a single use. A number of recent papers have introduced creative solutions that circumvented the problem of cost by developing paper-based microfluidic devices that rely on wicking of liquid through channels printed onto a porous substrate (Martinez, Phillips et al. 2007; Martinez, Phillips et al. 2008). In the work described here, we follow a different strategy but with the same end goal of developing a new class of inexpensive,
easily-fabricated and in our case reusable microfluidic devices.

Digital microfluidics is a microfluidics technique that manipulates fluid one drop at a time, rather than as a continuous stream. These droplets are easily generated within a immiscible continuous phase and can be readily manipulated within a three-dimensional microfluidic channel (Christopher and Anna 2007; Miller, Rotea et al. 2010). There are a number of inherent advantages to digital microfluidics. The use of droplets instead of continuous streams allows one to maintain spatially-resolved chemical or biological species in a number of droplets distributed across a single device. These drops can be convected and combine with a precisely-controlled sequence and timing. Additionally, droplets naturally confine material to a small, convecting volume with closed streamlines. This enhances mixing relative to pure diffusion while eliminating the axial dispersion that exists in continuous flows. Both of which can be a major challenge in microfluidics.

An open two-dimensional approach to the design of digital microfluidic devices was recently proposed by Wier et al. (Wier, Gao et al. 2006). Their concepts were based on the spatial manipulation of surface topology and wettability of a two dimensional substrate in order to manipulate and control the dynamics of individual liquid droplets. For a digital microfluidics device to be successful, it must be able perform a number of basic processes including droplet transport, sorting, coalescing, mixing, capture and analysis. There are a number of active methods which utilize electrowetting and/or optical-electric methods to move, sort and mix drops on a two dimensional substrate (Krupenkin, Taylor et al. 2004; Link, Grasland-Mongrain et al. 2006; Chiou, Chang et al. 2008; Li, Fu et al. 2010). In this work, we will present a series of devices built on top of superhydrophobic surfaces with spatially variable surface roughness that we will
demonstrate can passively accomplish all the above-mentioned tasks using gravity alone to initiate drop motion.

Superhydrophobic surfaces were originally inspired by the unique water repellent properties of the lotus leaf (Barthlott and Neinhuis 1997; Bhushan and Jung 2006). It is the combination of a very large contact angle and a low contact angle hysteresis that defines a surface as superhydrophobic. Due to the presence of surface roughness or chemical heterogeneity, a liquid droplet can actually exist over a range of contact angles between the receding contact angle, \( \theta_r \), and the advancing contact angle, \( \theta_a \) (de Gennes, Brochard-Wyart et al. 2004; Gao and McCarthy 2006). The lack of significant contact angle hysteresis, \( \theta_r - \theta_a \) makes a water drop on a superhydrophobic surface unstable to even the smallest perturbation and allows it to move very easily across these surfaces (Bico, Marzolin et al. 1999; Chen, Fadeev et al. 1999; Kim and Kim 2002; Sakai, Song et al. 2006; Shastry, Case et al. 2006). This can be seen explicitly if one calculates the critical line force per unit length of the perimeter required to start a drop moving over a solid surface (Wolfram and Faust 1978)

\[
F \propto \sigma R (\cos \theta_r - \cos \theta_a).
\]  

(5.1)

Here \( \sigma \) is the surface tension of the liquid and \( R \) is the radius of the drop. Any significant contact angle hysteresis can result in drop becoming pinned to a surface even as that surface is tilted often even through vertical. For superhydrophobic surfaces, drops tend to roll rather than slide because the large contact angle moves the center of mass well above the surface and viscous friction is reduced by the presence of air-water interface below the drop (Reyssat, Richard et al. 2010).
A simple technique for creating inexpensive superhydrophobic surface was presented in Chapter 2 (Mahadevan and Pomeau 1999; Nilsson, Daniello et al. 2010). The technique involved sanding a smooth hydrophobic Teflon surface with various grit sizes of sandpaper to impart different degrees of surface roughness (Nilsson, Daniello et al. 2010). Electron micrographs of the resulting superhydrophobic surfaces are shown in Figure 4. Depending on the coarseness of the sandpaper used, surfaces with advancing contact angles between $120^\circ < \theta_a < 165^\circ$ can be produced with a contact angle hysteresis that can be smoothly decreased from $60^\circ$ to $3^\circ$ as seen in Figure 3. Using these superhydrophobic surfaces, Chapter 3 presented the effect of contact angle hysteresis on the dynamics of droplets by choosing surfaces with a constant advancing contact angle of $150^\circ$, but with receding contact angles that varied from $120^\circ < \theta_r < 147^\circ$. Decreasing the contact angle hysteresis was shown to increase contact line mobility of the droplet and, as expected from equation (5.1) to significantly reduce the drag force on a moving droplet (Nilsson and Rothstein 2011). As we will show, this increased droplet mobility can have a large impact on a number of the basic processes required to produce a successful open digital microfluidic device.

The effect of contact angle hysteresis on mixing within a droplet was also investigated in Chapter 3 (Nilsson and Rothstein 2011). They found that, for a given impact velocity and angle, reducing contact angle hysteresis resulted in larger droplet deformations and a significant enhancement of the mixing rate following the droplet collision. For a head on collision of two droplets at a Weber number of $We = \rho U^2 D / \sigma = 0.15$ on a surface with $3^\circ$ of contact angle hysteresis, the resulting
coalesced droplet was found to be 70% mixed after just 50ms. Here $\rho$ is the fluid density and $U$ is the velocity of the droplet at impact, $\sigma$ is the surface tension and $D$ is the droplet diameter. For the same Weber number collision on a surface with 50° hysteresis, where the contact line was found to remains nearly fully pinned following coalescence, the droplets following coalescence were found to achieve only 20% mixing over the same time period (Nilsson and Rothstein 2011). This study demonstrated that low contact angle hysteresis is a prerequisite for enhancing mixing of two or more droplets following coalescence.

Weir et al. (Wier, Gao et al. 2006) showed that transitions from low to high advancing contact angles could be used to steer or direct droplet motion. They showed that the additional gravitational potential energy needed raise the center of gravity of a drop advancing from a region of low to high contact angle could be enough to exclude a slowly moving droplet from advancing onto the high contact angle surface. If, however, the droplet had sufficient kinetic energy they were found to easily move across such a transition in wettability. Our work in Chapter 4 (Nilsson and Rothstein 2012) studied the motion of droplets across wettability transitions on sanded Teflon surfaces where the advancing contact angle was held fixed at $\theta_A = 150^\circ$, but with receding contact angles was varied from $120^\circ < \theta_R < 147^\circ$. A schematic of surface with a transition in contact angle hysteresis aligned at an angle of $\theta_T$ from horizontal can be found in Figure 27b. Motion was produced by placing the surfaces on an incline and allowing the droplets to move down the surface under gravity. Chapter 4 showed that as a droplet transitions from a region of large contact angle hysteresis to a region low hysteresis, interfacial
energy is released and partially converted into kinetic energy of the droplet causing it to deflect to the left (Nilsson and Rothstein 2012). Conversely, when a droplet progresses from a surface with low contact angle hysteresis to one with high contact angle hysteresis, kinetic energy is absorbed by the droplet and converted to interfacial energy in order to deform the receding contact line. As a result, the droplet was found to deflect towards the right.

Chapter 4 found that the magnitude of droplet deflection increased with increasing transition angle, but was a non-monotonic function of Weber number (Nilsson and Rothstein 2012). For droplets moving across a transition in receding contact angle from a surface with $\theta_r = 120^\circ$ to $\theta_r = 147^\circ$, a sharp maximum in droplet deflection of about one and a half times the drop diameter to the left, $d/D = 1.5$, was observed for Weber numbers between $0.1 < We = \rho U^2 D/\sigma < 0.2$ and a transition angle of $\theta_t = 40^\circ$ from horizontal. Outside this range in Weber number, the droplet deflection was found to be relatively small, $d/D = 0.4$, and independent of Weber number. Similar observations were made for transitions from $\theta_r = 135^\circ$ to $\theta_r = 147^\circ$ and on surfaces with stripes of $\theta_r = 147^\circ$ on a background with $\theta_r = 120^\circ$. In Chapter 4 we hypothesized that this narrow range of Weber numbers for which large deflections could be achieved was likely the result of the transition exciting the droplet at or near its resonance frequency where the conversion of interfacial energy to kinetic energy should be maximized (Nilsson and Rothstein 2012). Interestingly, the deflections were always found to be significantly larger for droplet motion across transitions from high to low contact angle hysteresis. This was shown to be a direct result of the increase in drag on high contact angle
hysteresis surfaces as seen in equation (5.1). The high hysteresis, high drag surfaces dampen out any horizontal velocity imparted to the droplet by the transition over a very short distance reducing the droplet deflection. As a result, large deflections were not found to be possible on high hysteresis surfaces.

These measurements suggested that not only can transitions in receding contact angle or contact angle hysteresis be used to direct droplet across a two dimensional surface, but because of the high selectivity of droplet deflection based on Weber number, it should be possible to sort droplets based on their size, velocity or wetting properties. These observations, in combination with enhanced mixing observed for low contact angle hysteresis surfaces, motivated our design of a series of digital microfluidic devices on superhydrophobic Teflon surfaces which we present in the following section.

5.2 Experimental Design and Validation

Schematic diagrams of two different digital microfluidic devices are shown in Figure 27. In each case, the devices were designed to incorporate a number of wetting transitions to move, deflect or capture drops for analysis. In all cases, the angle of the transition was set at 40° from the horizontal as this was found to produce the maximum deflection (Nilsson and Rothstein 2012). In Figure 27a, a digital microfluidic device for reacting two drops is shown. In this design, the droplets initially start on a surface with an advancing contact angle of $\theta_a = 150^\circ$ and a receding angle of $\theta_r = 120^\circ$. The two drops are produced by depositing water from syringe tips mounted just above the surface. The drops of water are slowly fed by a syringe pump and simultaneously released with a quick pressure pulse. Once released, the droplets accelerate under gravity along the
device which is tilted up 13° from horizontal. The droplets then pass over a transition to a surface with an advancing contact angle of $\theta_a = 150^\circ$ and a receding angle of $\theta_r = 147^\circ$ causing the two droplets to be deflected towards the center of the device. The droplets collide, coalesce and mix very effectively on the low hysteresis surface (Nilsson and Rothstein 2011) before being captured on a patch of unsanded Teflon which has a contact angle hysteresis of 50°. Once captured, the droplets can be easily characterized or analyzed and the device rinsed off and reused.

An example of a functioning digital microfluidic reactor is shown in Figure 28. A series of images of drops moving across the device are superimposed to illustrate drop motion. To create the surface, different regions of a 5cm wide by 10 cm tall piece of Teflon was masked off using residueless tape. The surface was then sanded with different grit designation sandpapers in a random manner to create the desired variation in receding contact angle. Care was taken to insure as sharp a transition as possible. As has been observed in Chapter 4, the degree of droplet deflection was found to be a function of the Weber number of the drops upon crossing the contact angle transition (Nilsson and Rothstein 2012). At very low and high Weber numbers, the droplets were not deflected enough to coalesce and were not captured by the high hysteresis target at the bottom of the device. The maximum deflection was observed for drops having Weber numbers of approximately $We = 0.17$. At this Weber number, the droplets were observed to coalesce very near to the transition giving the drops more time to mix and facilitating the fabrication of smaller devices. As the Weber number was increased, the droplets were deflected at a smaller angle and coalescence was observed to occur further down the device.
In Figure 27b, a schematic diagram of a two dimensional microfluidics droplet sorter is shown. The principles at play in this device are similar to those seen in the microfluidic reactor/analyzer. A single droplet is deposited on a surface with an advancing contact angle of $\theta_a = 150^\circ$ and a receding angle of $\theta_r = 120^\circ$ and allowed to move down a $13^\circ$ incline. As the droplet passes over a transition to a surface with an advancing contact angle of $\theta_a = 150^\circ$ and a receding angle of $\theta_r = 147^\circ$ it is deflected to the left. A patch of $50^\circ$ hysteresis smooth Teflon is left downstream of the transition at a distance $d = 3.5\text{mm}$ to the left of the droplet’s initial path to capture the most highly deflected droplets. The ability of this device to sort drops was tested by releasing a series of droplets at different Weber numbers. The Weber number of the droplets was varied in this study by either changing droplet diameter or droplet velocity. To change the droplet velocity at the transition line, the droplets were released at different positions above the transition line thereby varying the distance they had to accelerate down the incline. Our studies found that the droplet were deflected a sufficient distance to the left to be captured by the high contact angle hysteresis patch at the bottom of the device only when Weber numbers were between approximately $0.1 < We < 0.2$. Outside this Weber number range, the droplets were not significantly deflected. This is demonstrated in Figure 29. Here the paths of two droplets with different Weber numbers are superimposed on a single image. Droplet 1 in Figure 29 had a Weber number of $We = 0.15$. It was deflected $d = 3.5\text{mm}$ to the left and was successfully captured by the high hysteresis patch. Droplet 2 had a Weber number of $We = 0.50$. Unlike the droplet 1, droplet 2 was deflected only $d = 1.1\text{mm}$ to the left. As a result, it was not captured by the high hysteresis patch and
flowed completely off of the device. Because the deflection was approximately $d \approx 1 \text{mm}$ for all droplets outside of the optimal Weber number range, Figure 29 is representation for all the droplet experiments that were performed with this sorting device. Additionally, because of the narrow range in Weber number over which large deflections are possible, this study conclusively demonstrates that two dimensional microfluidic devices can be designed to selectively capture and sort drops based on droplet size, density, surface tension and most easily droplet velocity. Finally, Chapter 4 showed that multiple stripes of a surface with low contact angle hysteresis on a high hysteresis background can linearly amplify the deflection from a single transition and therefore amplify the sensitivity of the sorting process described here (Nilsson and Rothstein 2012).
Figure 27: Schematic diagram of two digital microfluidic device designed to (a) impinge two drops together so they can be mixed, reacted and analyzed and (b) passively sort drops based on size, velocity or wetting properties. All transition lines are 40° from horizontal.
Figure 28: Demonstration of the digital microfluidic droplet reactor/ analyzer. Two drops are released at the top, deflected by a transition from 30° to 3° contact angle hysteresis, coalesce and mix near the middle of the device, and are finally captured on a high hysteresis patch at the bottom of the device where they can be analyzed. The dashed lines show the location of the transitions in wettability. At the point of the transition the Weber number of the droplets was $We = 0.15$. 
**Figure 29:** Demonstration of two designs for a two dimensional digital microfluidic droplet sorter. The path of two droplets with Weber numbers of $We = 0.15$ (droplet 1) and 0.50 (droplet 2) are superimposed to demonstrate ability of this device to sort drops based on Weber number. The dashed lines at the top show the location of the transitions in wettability $30^\circ$ to $3^\circ$ contact angle hysteresis and the dashed lines at the bottom show the $50^\circ$ hysteresis target designed for capturing droplets at the bottom of the device. Here the $We = 0.15$ drop hits the target and is captured while the $We = 0.50$ drop misses the target and is not captured.
CHAPTER 6
EXAMINING THE EFFECT OF FLUID RHEOLOGY ON ENHANCED OIL RECOVERY IN A SMALL MICROFLUIDIC SANDSTONE DEVICE

6.1 Introduction

As the global oil supply decreases, the ability to effectively recover all of the oil from a particular well becomes increasingly important. The recovery of oil generally takes place in 3 stages: the primary, secondary, and tertiary (Energy 2011). The primary stage occurs when the well is first accessed, and oil is produced thus relieve the internal pressure exiting in the well. This stage recovers approximately 10% of the total oil in the field. The secondary stage is characterized by pumping a fluid, generally water or a gas into the field, which results in an additional 20-40% of the original amount of oil being recovered (Energy 2011). With anywhere from 50-70% of the original oil remaining in the oil field, there is much interest in developing methods to access and recover that oil.

The tertiary stage of oil recovery has developed much interest in more recent decades (Needham and Doe 1987; Thomas 2008; Alvarado and Manrique 2010; Brandt and Unnasch 2010; Jamaloei, Kharrat et al. 2010; Energy 2011; Fathi, Austad et al. 2011). The goal of the tertiary stage is to be able to access and recover as much of the remaining oil in the fields as possible. The methods of tertiary oil recovery can be categorized into three main approaches: thermal, gas, and chemical. All three approaches aim to ease the recovery of the oil, either by changing the properties of the oil, the imbibing fluid, or the core material itself.
Thermal techniques involve injecting hot gasses or liquids, and were largely developed around the 1960’s (Alvarado and Manrique 2010; Brandt and Unnasch 2010). The increased temperatures lower the viscosities of the heavy crude oils, allowing for easier recovery of the oil for existing pressures and conditions. Thermal approaches account for a large portion of the enhanced oil recovery strategies currently implemented around the world (Alvarado and Manrique 2010; Energy 2011).

Gas injection methods are similar to thermal methods in that they seek to modify the viscosity. The gasses used include nitrogen and carbon dioxide. The former is no longer currently used. Carbon dioxide has seen much interest in US in the past few decades, and has shown promise as not only a viable method in enhanced oil recovery, but also offsetting carbon dioxide production by effectively storing it in the dead oil fields.

Chemical methods of enhanced oil recovery became widely popular during the 1980’s (Alvarado and Manrique 2010). Chemical methods aim to increase the amount of oil recovered by either increasing the effectiveness of water floods by modifying the water used to displace the oil, reducing the interfacial tension of the oil with the use of specific surfactants, or modifying the wettability of the oil fields substrate (Alvarado and Manrique 2010; Energy 2011; Fathi, Austad et al. 2011). Chemical methods use either alkali-polymers, surfactants, polymers, or more recently a combination alkali-surfactant polymer system (Alvarado and Manrique 2010). The larger challenge with chemical methods is that every possible variable with respect to fluid and substrate properties can drastically change from one oil reservoir to the next. There is a large body of work for conditions in and solutions to enhanced oil recovery in particular oil fields, summarized a
The main challenge with either the use of surfactants to lower the interfacial tension or polymers as a viscosifier is the very delicate relationships to the conditions of the oil field substrate, which is not always constant, and the oil properties, which can also vary. Oftentimes, the polymers or surfactants are applied too far into the initial water flood, or they can lose effectiveness midway through the field (Thomas 2008). Another challenge with chemical approaches to enhanced oil recovery is cost; depending on the fluctuating cost of oil and production, it can quickly become the prohibiting factor. While challenging, the vast amount of oil remaining within oil fields is only going to be a growing driving factor for EOR research as the easily-accessed oil is continually recovered. New fluid technologies will develop, and modifications of existing technologies will require testing, such as utilizing different rheological properties of the fluids.

With a wide range of oil fields, testing methods are varied. It is impossible to perform *in situ* measurements. Instead, experiments are generally performed with samples of the actual oil field drilled out from the field. These samples can be filled with oil directly from the field, or similar man made oils. This core can then be used to test the ability of penetrating fluids to either displace the oil from pressure flow or imbibitions, which is where the displacing fluid wets the substrate by either natural wettability or by some alteration process (Jamaloei, Kharrat et al. 2010).

Fluid testing is also performed on idealized representations of flows, often arrays of posts or cylinders. This allows for specific dimensions to be specified for precise control of particular fluid flow properties and examine dynamics at the micro- and nano-
scales (Jamaloei, Kharrat et al. 2010). This method does not account for the inhomogeneous nature of field conditions or the true geometric flow constraints that exist in the field.

In this chapter, a series of microfluidic devices were developed and used that were designed to precisely reproduce a two-dimensional slice from a sandstone core. Microfluidics is a relatively young and developing field that encompasses the development of devices that allow for observations of fluid phenomena at the microscale (Petersen 1982; Duffy, McDonald et al. 1998; Stone, Stroock et al. 2004; Atencia and Beebe 2005; Gao and McCarthy 2006; Whitesides 2006; Nie, Seo et al. 2008). A more in-depth microfluidics discussion is detailed in Chapter 1. In microfluidics, photolithography is used to transfer a pattern onto a silicon wafer using a photoresist such as SU-8 (Madou 2002). Once developed, the two-dimensional pattern in the photoresist is used as a master from which multiple daughters can be cast in (poly)dimethyl-siloxane (PDMS) or other cross-linking polymers, containing negatives of the pattern on the master (Duffy, McDonald et al. 1998; McDonald, Duffy et al. 2000; McDonald and Whitesides 2002). This soft lithography technique has been used for more than a decade to generate microfluidic devices containing features as small as 10μm (McDonald and Whitesides 2002; Makamba, Kim et al. 2003). Here we utilize this technology to probe the effect of fluid rheology on oil recovery from hydrophobic microfluidic sandstone devices.

The initial sections following the introduction will cover many of the constituent components to creating microfluidic devices for use in testing various rheological fluids. Following these sections, we will cover the device and fluid design and development.
Finally, the results will be presented with relevant discussions, and the last section will present conclusions and contributions of this chapter.

6.1.1 Microfluidics Overview

Three-phase flow is an important phenomenon in the field of microfluidics. Microfluidics is the study of fluids at a nanoliter scale or less, which is typically accomplished by completely bounding the fluid flow within a solid substrate where the limiting dimensions for fluid flow characteristics range from the 100’s of nanometers to 100’s of microns. At these scales, fluid flow is bounded by interfacial tension, viscosity and diffusion, and the effect of gravity and inertia become negligible. The theory of fluid flow at these scales have been developed since the mid-1800’s, however the practical study of microfluidics is relatively new, with the technology to create devices at this scale resulting from micro-electromechanical (MEMS) development in the 1980’s (Petersen 1982; Stone, Stroock et al. 2004). Its appeal was also a result from interest in using it as a platform for study in molecular analysis, defense concerns after the cold war, molecular biology, and electronics at the microscale (Atencia and Beebe 2005; Whitesides 2006). The benefits of microfluidic devices, such as using minimal amounts of fluid and high efficiency of heat and mass transfer, and decreased diffusion distances, have lead to microfluidics becoming commercially desirable as well (Atencia and Beebe 2005; Whitesides 2006; Nie, Seo et al. 2008).
6.1.2 Rheology

This section will provide an introduction to rheology, and rheological fluids. In Chapter 1, Equation (1.1) demonstrates the linear proportionality of the velocity gradient (or rate of shear strain) to the shear stress. Fluids that behave according to this relationship are classified as linear, or Newtonian fluids referring to Sir Isaac Newton who first proposed this relationship. Gases behave as Newtonian fluids. Most common liquids also behave this way. However, there are some fluids whose behavior lies somewhere between liquids and elastic solids, and these liquids are classified as viscoelastic fluids. Viscoelastic fluids are one example of non-Newtonian fluids which have viscosities that are not constant. The general study of non-Newtonian fluids falls under the study of rheology. Rheology is loosely defined as the study of deformation or flow of matter, under which all fluids fall. The more accepted convention for rheology has evolved into the study of non-Newtonian fluids and visco-plastic solids. The main tenets of rheology are kinematics which describes the deformation, conservation laws which relate forces and stresses with the deformation, and constitutive relations which relate the forces with the motion of a particular group of fluids (Tanner and Walters 1998).

Non-Newtonian flows, by definition, do not have a linear relationship between the shear stress and the rate of strain as given in equation (1.1). The shear stress in non-Newtonian fluids can be some function of any number of fluid parameters, such as the rate of strain, the amount of strain, time, temperature, etc. Because of the complex nature of these fluids, it is useful to develop simplified models by which to describe the behavior of these fluids.
The term viscoelasticity combines the concept of having a viscous component and an elastic component. Elasticity has been long understood, and was characterized by Hooke with his relationship that the stress, $\tau$, in a linearly-elastic solid is related to the strain, $\gamma$, experienced by a modulus, $E$,

$$\tau = E\gamma$$  \hfill (1.3)

In viscous flow of a non-Newtonian fluid, the shear stress is a complex function of the rate of strain. One of the more simple models is the generalized Newtonian model, in which the shear stress, $\tau$, is related to the rate of strain, $\dot{\gamma}$, by a ‘non-Newtonian viscosity’ that is a function involving the rate of strain,

$$\tau = \eta(\dot{\gamma})\dot{\gamma}$$  \hfill (1.4)

The source of the interesting behavior of viscoelastic fluids is a direct result of their composition at very small scales. The internal structure of viscoelastic fluids is often comprised of molecular units that frequently interact and even entangle in flow, allowing the storage or memory to be kept of the methods by which the fluid was deformed. This information can be stored for an amount of time, from which a timescale can be described by the non-Newtonian viscosity and what is the elastic modulus of the material, $G$, given by

$$\lambda = \frac{\eta}{G}.$$  \hfill (1.5)

There are many different approaches to developing analytical decryptions that describe the nature of the non-Newtonian viscosity. Some of the more common inelastic constitutive models like the Carreau-Yasuda model describe the viscosity as a power law fluid, where the viscosity is given as the shear rate raised by some power law index, and
multiplied by some viscosity index depending on the fluid. This helps develop generalized classes of fluids, where each class can be described by a particular model. Prominent viscoelastic models include the Maxwell model, the Oldroyd-B, and the Giesekus model.

There are a number of classes of non-Newtonian fluids including: polymeric, self-assembled systems, and suspensions. Polymeric solutions exhibit classical viscoelastic behavior by having well defined elastic and viscous components. Polymers are by definition many repeatable units of a basic small molecule covalently bonded along a long backbone. While existing in nature, they have also begun to be created synthetically, for many purposes, largely industrial. As such, the study of polymers has intensified as their wide array of uses and manufacturing processes widened (Treloar 1970).

Polymers, as the name hints, are comprised of many small repeating units. From the Greek ‘Polus’ and ‘meros’, it literally means ‘many parts’. The parts in polymers are either individual atoms or molecules (Treloar 1970). In a particular bulk polymer, individual chains may be identical in length, known as being monodisperse, or of different overall lengths, which results in polydispersity. Typically in polydisperse fluids, an average molecular weight is given which some indication as to the degree of polydispersity. Furthermore, polymers exist in single chains also as complex branched geometries, adding to the complexity of the bulk. As a result, polymers can have many varied arrangements when in fluids based off of the above properties as well as the concentration and molecular stiffness of each polymer, with bends and kinks creating a
sea of entangled polymer chains and large variations in rheological properties (Larson 1992).

A second class of non-Newtonian fluids is self assembled systems. An example of this type of system is a surfactant solution. A surfactant molecule classically consists of a two sections: a hydrophilic or water-favoring head group of atoms, and a hydrophobic or water fearing ‘tail’ groups of atoms (Larson 1992). In a solution, these individual particles can congregate to areas that lower the free energy of the particle such as an oil-water interface. The particle would orient such that the hydrophobic tail group penetrates the oil phase, and the hydrophilic head group would remain in the water phase, resulting in a decrease of the interfacial tension between such phases. Depending on the concentration, particle charges, and the solvent, these surfactants form micelles that have multiple shapes and arrangements and often strands of surfactants. These chains can have similar appearance to polymer based systems, but lack a chemical bond between individual units. This allows chains to reptate past one another like a polymer, or the surfactant chains can break, reform, or form completely new bonds, where the polymer chain cannot (Cates 1987). This can result in a much lower relaxation time and many complex behaviors in particular fluid flow situations not related to this thesis (Kadoma and van Egmond 1998; Rothstein 2003; Chen and Rothstein 2004).

A third type of non-Newtonian fluid is suspensions. Suspensions contain a solute that is large enough when mixed, it would settle out of the solvent. However, it can be made to uniformly distribute, usually by some mechanical means. Suspensions can consist of solids in liquids, liquids in liquids, liquids in solids, and solids and liquids in gases. Unlike polymer and surfactants described above, particles in a suspension can
generally flow past one another, and at low concentrations, the resulting fluid is generally
Newtonian in nature with simply a higher viscosity, which is dependent on particle size
and concentration (Barnes 1989). However, when the concentration of particles is
increased these fluids can display non-Newtonian behaviors including shear-thinning,
shear-thickening, and non-zero normal stress differences.

6.1.3 Shear Thickening

Shear thickening, and its counter behavior shear thinning, are non-Newtonian
behaviors. They are characterized by a non-linear relationship between the shear-rate and
the shear stress, so more technically for shear thickening, the increase of viscosity that
corresponds with increasing shear rate. This phenomenon is generally caused by the
interaction of components of the fluid with other components. An example of this is in a
particle laden fluid. At a low enough concentration, the fluid behavior is Newtonian. At
high concentrations, the viscosity is Newtonian until a particular shear rate range is
encountered. Within this range, the viscosity increases, and afterwards the behavior
returns to a Newtonian state. This effect is caused by the interaction of these particles.

While the flow is in shear, it can be thought of that the particles arrange into layers within
the flow, each traveling at different velocities (Barnes 1989). Another analogy would be
a group a race cars: It is more advantageous for one car to drive behind another car in
order to reduce aerodynamic drag on both cars. In the case of the particles, aligning
behind other particles occurs as shear develops for similar reasons, and in this range
shear-thinning would occur. As the shear rate increases, these bands narrow, until the
critical shear rate. This critical shear rate is dependent on the particle size (and
asymmetry), concentration, and the viscosity of the continuous phase. At this critical shear rate, the particles in adjacent begin to interact, and either form hydro-clusters induced by the hydrodynamic interactions between particles, or by polymer bridging across particles. The interaction of these particles results in further difficult of the flow past them, resulting in locally higher shear resistance, or viscosity. It is at this critical shear rate that this phenomenon occurs throughout the bulk. Shear thickening can also occur in polymer and self-assembling flows, so long as the individual chains or particle sizes are of a sufficient length to cause significant interaction in shear flow.

6.1.4 Shear Rheometry

Shear rheometers are used to measure a wide range of fluid properties associated with non-Newtonian fluids. A representative schematic of the test section of a rheometer is shown in Figure 30 using a cone for the top shearing plate and a flat plate for the bottom. The cone and plate geometries are most common because they allow for constant shear-rates and stresses across the sample regardless of radial distance. For shear thickening fluids, they can be used to determine the viscosity as a function of shear rate. They are capable of shearing fluids over a range of prescribed steady shear rates or shear stresses, with the difference being what variable is being controlled within the device. It is important to define what method is being used, as it may affect results at particular settings. As the top plate is applying the shear rate/stress to the top plate, the bottom plate is measuring the resistance to the flow. It is then possible to calculate the viscosity from equation (1.1).
A rheometer is also capable of measuring viscoelastic model properties such as the storage or loss modulus. The shear rheometer can rotate or oscillate the top plate and measure the resulting forces acting on the plate, and measure the torque produced on the bottom plate. From these values, the storage and loss moduli can be calculated, which are associated with the Maxwell model, as described in detail in Morrison (Morrison 2001).

A typical shear rheometer is versatile. It is capable of performing many more tests including creep capabilities, step-strain tests, and temperature sweeps when outfitted with plates capable of maintaining accurate temperatures. The cone and plate geometries can also be switched out for other geometries is they are more appropriate for the particular tests or fluids used.

6.2 Device Development and Experimental Setup

The device layout and properties are shown in Figure 31. The mask was created from an actual cross-sectional image of sandstone which was used as a template for a microfluidic device that approximates flow through sandstone. The microfluidic device was fabricated out of PDMS using standard photolithographic techniques. The microfluidic sandstone device is 200 microns thick, and has capillaries and pores with average sizes from 200 microns to 10’s of microns. The only modification to the sandstone that would affect the flow was that any “dead ends” were removed, and replaced with narrow passages. Even with these modest changes, we believe this design captures the essence of flow through sandstone using an easy-to-fabricate and extremely flexible experimental test bed.
The pressure ports allowed for the measurement of the pressure drop across the sandstone features. The ports were plumbed with blunt needle tips connected to polyethylene tubing. This tubing was connected through adapters to a differential pressure transducer (Honeywell TruStability™) with a range of ±1 psi. The pressure drop allows for the calculation of the permeability, \( \kappa = U \frac{\eta \Delta \Delta \kappa \kappa}{\Delta P} \), where \( U \) is the superficial velocity, \( \eta \) is the viscosity, \( \Delta \) is the thickness of the medium, and \( \Delta P \) is the pressure drop across the thickness. Common oilfields have permeability values of \( 0.1 \leq \kappa \leq 10.0 \). The pressure drop measured across the presented device resulted in a permeability value of \( \kappa = 60D \pm 2D \). The porosity of the device is \( \phi = 0.48 \). While these values are slightly above the range of most oilfields, (Han, Nur et al. 1986) it is realistic in its structure, and its complexities allow for valuable insights in testing rheologically complex fluids.

In order to determine the amount of oil recovered, images were taken when the device was fully flooded with oil. To increase contrast with the PDMS, the oil was dyed with Sudan Blue (Sigma Aldrich), which is an oil-soluble coloring. A representative image of the fully oil-filled device is shown in Figure 31. The original images were then compared against images of the flow cell at stages during and after the driving fluid had been pumped through the microfluidic device at a prescribed flowrate. In these experiments a syringe pump (kd Scientific, model 100) was used to impose a specific flow rate on the driving fluid. The experiment was terminated after it was determined that it had reached steady state. Steady state was defined as when no more oil was visibly being removed through the transparent exit tubing. The images were taken with a
Nikon D70 camera outfitted with a macro lens (micro-NIKKOR 105mm). Backlighting was provided by a uniform light sheet (Dolan Jenner model QVABL) which was supplied by a light source (StockerYale Imagelite Model 20). The images were then made grayscale and imported into a homegrown Matlab™ code. The code first applied a threshold to each image, causing any oil filled area to appear completely black and any non-oil area white. The images were inspected to insure that the threshold value accurately represented the oil filled condition. The program then counted black pixels and reported the percentage of the image that was oil. Comparing between the percent of oil from the before and after the fluid flood allowed us to determine the percentage of oil removed during the flooding process.

The baseline fluid used to displace oil from within the microfluidic sandstone device is deionized water. The microfluidic devices are initially filled with Miglyol oil 840, common oil used in cosmetics. The interfacial tension between water and Miglyol oil 840 is $\sigma = 20\text{mN/m}$ while the contact angle between water and Miglyol-wetted PDMS is $\theta_A/\theta_W = 160^\circ/144^\circ$. For all of the other driving fluids being used, we investigate variations in interfacial tension, contact angles, and fluid rheology. In order to modify the interfacial tension without modifying viscosity, CTAB (hexadecyltrimethylammonium bromide) was added to the water phase at a concentration of 5 mM. Creating a 5mM CTAB solution reduced the interfacial tension of water in oil by an order of magnitude, from $\sigma = 20\text{mN/m}$ of water in oil to $\sigma = 2.1\text{mN/m}$.

Modifying the viscosity of the driving fluid was achieved through the addition of nanoparticles and/or high molecular weight polymer additives to the water phase. Here
we are interested in investigating the impact of two different rheological characteristics on enhanced oil recovery: shear thinning and shear thickening. The shear thickening fluid was created by adding a small amount (0.4 wt %) of a moderately high molecular weight (poly)ethylene oxide (PEO) (Mw = 600,000 g/mol, Aldrich) to a nanoparticle solution of 4.0 wt% hydrophilic silica particles (12 nm size, Degussa AEROSIL® 200) (Kamibayashi, Ogura et al. 2008). The result is a fluid that shear-thickens by a factor of about five around a shear rate of 10 s$^{-1}$ (Kamibayashi, Ogura et al. 2008). As seen in Figure 32, the nanoparticle suspension initially shear thins. At a shear rate of $\dot{\gamma} = 10 s^{-1}$, the shear viscosity thickens by a factor of approximately five. The fluid maintains this high viscosity until a shear rate of $\dot{\gamma} = 30 s^{-1}$ beyond which it begins to shear thin again. This shear thickening is induced by the interaction of nanoparticles enhanced by the presence of the polymer which can absorb to and bridge between nanoparticles to produce long-range interactions and a perculated network structure (Kamibayashi, Ogura et al. 2008). In the absence of polymers, the nanoparticle suspensions at this concentration show no shear thickening and a significantly reduced viscosity. Small angle oscillatory shear measurements of this fluid do not reveal any elasticity over the range of shear rates that could be probed. The interfacial energy of the nanoparticle/polymer solution was found to be $\sigma = 20$ mN/m and the contact angles with PDMS in Miglyol oil was $\theta_A/\theta_R = 159^\circ/143^\circ$. Finally, a commercially available viscoelastic fluid ‘thickener’, Flopaam 3630 (SNF Floerger®) was mixed with deionized water at a concentration of 0.1 wt%. Flopaam 3630 is a proprietary mixture of high molecular weight co-polymers of polyacrylamide and polyacrylate. At a concentration of
0.1 wt% Flopaam 3630, the mixture shear thins over the range of shear rates probed, and had the same baseline viscosity of the shear-thickening nanoparticle suspension. As seen in Figure 32a, the viscosity of the 0.1 wt% Flopaam 3630 shear thins at roughly the same rate as the shear thickening nanoparticle suspension. There are two major differences between these fluids. First, the Flopaam does not shear thicken. Second, as seen in Figure 32b, the linear viscoelastic spectrum of Flopaam shows the fluid to be viscoelastic with a relaxation time of $\lambda = 22s$.

6.3 Results and Discussion

The most common driving fluid used for oil recovery is water. Thus, for this study water is used as the control for which other driving fluids are compared against. The flowrates of the driving fluid through the microfluidic sandstone device ranged between 1.5 ml/hr and 22 ml/hr. This corresponds to front speeds just before the sandstone features of 0.38mm/s to 5.5 mm/s and capillary numbers for water between $3.8 \times 10^{-5} < Ca = \frac{\eta U}{\sigma} < 5.6 \times 10^{-3}$. The results for water and the other driving fluids are presented in Figure 33. In Figure 33, the percentage of oil remaining in the microfluidic sandstone device after the flow has reached steady state is presented as a function of the flow rate of the driving fluid. At the lowest flowrates tested, approximately 65% of the oil remained after flooding with water at 1.5 ml/hr. As the flowrate was increased, more oil was recovered until the data approached an asymptotic value of roughly 40% residual oil at large flowrates. The general trend of increasing oil recovery with increasing flowrate or capillary number has been observed many times in the past (Taber 1980; Thomas 2008; Cottin, Bodiguel et al. 2010).
Rather than simply increasing the front velocity, an alternative approach to increasing the capillary number is to decrease the interfacial tension of the driving fluid. The 5 mM CTAB solution has a lower interfacial tension than water but has the same viscosity. As seen Figure 33a, the CTAB solution recovers approximately 10% more oil than water at every flowrate investigated. The lower interfacial tension reduces the Laplace pressure that must be overcome if the driving fluid is to displace the oil. This is especially true in regions of higher interfacial curvature like entrances to narrow capillaries from larger pores. Interestingly, when the data is recast as a function of capillary number, as seen in Figure 33b, the water and the surfactant data do not collapse onto a single master curve. The capillary number alone clearly does not capture all the physics in this complex flow.

The shear thickening nanoparticle/PEO fluid greatly outperforms both the water and the CTAB solution in oil recover at flowrates between 1.5 and 22 µL/min. At the lowest flowrates tested, the shear-thickening fluid roughly matches the oil recovery obtained using the surfactant solution. This is likely a result of the large viscosity of the nanoparticle solution even prior to shear thickening. The resulting capillary number is even larger than the surfactant solution at these flowrates. At a flowrate of approximately 1 ml/hr, a dramatic improvement in the oil recovery is observed, peaking at a flow rate of 1.5 ml/hr with just 14% of the oil remaining in the microfluidic sandstone device at steady state. As the flowrate was increased, the shear-thickening fluid continues to greatly outperform both the water and surfactant solution. At the highest flow rates, the performance benefits of the shear thickening fluid were found to decay somewhat. As seen in Figure 33b, the trends again do not collapse with capillary number. Here the
viscosity used to calculate the capillary number was taken at the representative shear rate within the device. However, it is of particular interest to replot the oil recovery not as a function of flow rate or capillary number, but as a function of shear rate. This is done in Figure 34, to obtain a better understanding of the underlying physics at work with a shear thickening fluid. The shear rate, $\dot{\gamma} \equiv \frac{U}{L}$, is approximated from the flow rate of the driving fluid. Here $U$ is the front speed and $L$ is the characteristic length. The device has a mean pore opening size of 200μm, and is $H=200μm$ in depth, thus the characteristic length was chosen to be $L = 200μm$. The average front speed is calculated as, $U = \frac{\phi Q}{HW}$, where $Q$ is the volume flow rate, $\phi$ is the porosity of the sandstone, $H$ is the depth of the microfluidic, and $W$ is the total width of the device. As seen in Figure 34, the onset of improved oil recovery coincides with the shear rates of approximately $\dot{\gamma} \sim 10s^{-1}$ at which the viscosity of the nanoparticle solution was found to increase. This observation suggests that the increased pressure drop resulting from the shear-thickening transition is sufficient to overcome the Laplace pressure supporting water-oil interfaces in small capillaries and side branches. Once the capillaries are opened, a larger fraction of the sandstone device is accessed by the driving fluid and as a result the local shear rate is reduced. In some cases, the reduced shear rate can drive the viscosity back below the shear thickening transition, reducing the pressure drop in the oil depleted portions of the sandstone device. While the oil recovery increases with the onset of the shear-thickening, the peak oil recovery was found to exist over a range of average shear rates larger than the shear thickening range of the fluid. This is likely the result of the complexity of the pores and capillaries within the device, as there are variations of shear
rates within the device for any given flowrate. At the very highest shear rate, the 
viscosity of the shear-thickening fluid begins to shear thin and the impact of the 
thickening is gradually lost. Thus it appears that for shear-thickening fluids, the impact 
on oil recovery is best observed at or around the shear rates corresponding to the shear 
thickening transition.

It is important to note that there exists uncertainty in these experiments that result 
from small variations in fluid preparations and the device fabrication. The shear-
thickening behavior is very sensitive in the small variations in fluid composition. The 
device fabrication can also result in small variations in the thickness of the capillaries and 
pores, which would affect the shear-thickening onset. In order to minimize the effect of 
these variations, the experiments were performed using multiple fluid preparations and 
device fabrications, and error bars are presented to demonstrate the confidence in these 
results.

As seen in Figure 33 and Figure 34, the viscoelastic Flopaam 3630 mixture was 
found to outperform the water and the CTAB solution, and followed the same general 
trend of increasing oil recovery with increasing flowrate even though the viscosity was 
found to thin over the entire range of shear rates tested. It also was found to outperform 
the shear thickening fluid in regions far outside of the shear rates where the thickening 
occurs. This is important, as it demonstrates that by designing a fluid that thickens at a 
target shear rate, oil recovery can exceed that of current enhanced oil recovery fluids in 
use today. To understand these results in detail, it is useful to interrogate the images 
taken before and after flooding with each of these driving fluids.
By examining the images used for determining the oil recovery, it is possible to
qualitatively assess regions where one particular fluid outperforms others in accessing
and mobilizing the trapped oil. Figure 35 compares three before and after images of oil
recovery experiments performed at a flowrate of 4.8 ml/hr. The initial oil-filled
sandstone is shown in Figure 35a. The steady state result for water is shown in Figure
35b. The water is observed to form canals that cuts through the most permeable areas of
the sandstone and allows additional water to flow through, with occasional drops of water
pinching off in smaller capillaries and pores alongside the main canals. With the shear
thickening fluid, there is substantially less oil remaining. As seen in Figure 35c, the
comparisons to the water case are quite striking. The sandstone features within which oil
is characteristically still trapped are small capillaries between larger pores, and ‘dead-
ends’, where there are no easily accessed exits. As seen in Figure 35d, the Flopaam 3630
recovers less overall oil than the shear thickening solution because it does not displace oil
from many of the small capillaries accessed by the shear-thickening fluid. It is, however,
more successful than the shear-thickening fluid at accessing oil from within these dead-
end pores. These effects likely result from the elasticity of the Flopaam 3630 solution,
which has a relaxation time of approximately $\lambda = 22s$. At the average shear rate at this
experiment $\dot{\gamma} \sim 170s^{-1}$ the Weissenberg number is much larger than $Wi = \dot{\gamma}\lambda >> 1$ and the
elastic effect will be important. As the fluid passes from a pore into a capillary, an
extensional flow is produced followed by a strong shear flow within the capillary. Flow
into and through the capillaries result in the deformation of the polymer chains in the
flow direction and the buildup of significant elastic normal stresses (Rothstein and
McKinley 2001). Upon exiting of the capillaries, some of the elastic stress is released as
the polymer partially recoils back towards its equilibrium configuration. Much like die swell during extrusion of polymeric fluids (Petrie and Denn 1976; Larson 1992), the elastic normal stresses within the Flopaam drive the fluid quickly outward to fill the pores it is entering. As a result, the Flopaam can access more oil from dead-end pores as seen in Figure 35.

Figure 36 shows a comparison between water, the shear-thickening fluid, and the Flopaam solution over flowrates of 1.5ml/hr, 4.8ml/hr, 8.4ml/hr, and 13.5 ml/hr. This range of flowrates encompasses the range in which the shear-thickening fluid recovers more oil than the Flopaam solution. The water displaces more oil as the flowrate is increased, and the Flopaam follows the similar trend with a higher baseline of oil recovered. It is also easy to notice that the shear-thickening fluid recovers more oil at the lower flowrates examined than it does at the highest flowrate.

In our proposed research, we also aimed to cover variations in wettability. Variations in contact angle have significant effects on two-phase flow, so its effect on both the sandstone devices is of great interest. Methods for altering the wettability are covered in Chapter 1. The method we chose was creating devices from NOA-81 molds cast in PDMS masters. Much time and effort was spent in attempting to create devices in this manner. Unfortunately, it was extremely difficult to create high-fidelity devices, and after successfully creating a limited number the seal would rarely hold, rending the device useless. However, there were important lessons learned, such as the need to use a fresh PDMS master for every device, and vacuuming the NOA onto the master reduces adhesion abnormalities. This experimentation resulted in one successful experiment, which did increase oil recovery when flooding with water. This work serves to suggest
that pursuing glass devices or a similar hydrophilic substrate would be the most efficient way to EOR results on a modified wettability surface.

Finally, an important consideration is the ability of an enhanced oil recovery driving fluid to recover additional oil out of a field previously flooded with water for second stage recovery. Our microfluidic sandstone devices were designed with multiple inlets to make sequential flooding experiments easy to perform. The results for sequential flooding with water followed by Flopaam and the shear thickening fluid are shown in Figure 37. At a flowrate of 4.8 ml/hr, water was initially used to flood the microfluidic sandstone device. The amount of oil recovered from initially flooding of the small sandstone device with water matches the average from multiple single flood measurements in Figure 3. This data is shown as an open square overlaid on the data in Figure 37a. Figure 37b shows the results of subsequently pumping the Flopaam mixture through at the same flowrate (4.8 ml/hr) until steady state was obtained. Interestingly, the secondary fluid managed to recover exactly the same amount of oil as was obtained by the single flood with the Flopaam. The net residual oil of the Flopaam 3630 two-stage flood is represented by the open star in Figure 37a. This indicates that an initial flood of water does not affect the overall recover in a two stage flooding. Another interesting point is that with the initial water flood, the water forms a path of lower viscosity the oil, but the subsequent Flopaam solution flood does not show preferential flow through that path. The resulting images shown in Figure 37b are largely similar, with a few noticeable differences. The device only flooded with Flopaam had many dead-end pores nearly empty of oil and the second stage Flopaam flood did not remove as much oil from those
pores. However, the second stage Flopaam flood did remove more oil from some of the smaller capillaries that the single stage Flopaam flood did not. Additionally, the Flopaam in the second stage flood was able to connect across some capillaries where water had been where the single stage Flopaam could not. This indicates that there are some preferential flow paths at smaller scales that a first stage water flood might enable the Flopaam to access. Figure 37c compares the result of the two-stage flooding process flooding with water first and following with the shear-thickening fluid to the result of a single stage flood using the shear-thickening fluid. The results of the two-stage flood agree extremely well with the result of a single stage flood using the shear-thickening fluid. The two-stage residual oil is represented by the open circle in Figure 37a. The only differences apparent between a single stage and two-stage flood with the shear-thickening fluid are some small areas where water helped mobilize oil in the two-stage flood that remain in the single stage flood. Even with these obvious differences, the overall oil recovery remains very similar between a single stage Flopaam or shear-thickening flood and their two-stage counterpart floods that flood with water before flooding with the Flopaam or shear thickening fluid.

6.4 Conclusions

Enhanced Oil Recovery is an increasingly important field, and this work presents the efforts of developing a microfluidic platform for quickly testing fluids of different rheological properties for the recovery of oil from hydrophobic sandstone. Water was tested in the microfluidic sandstone device as a baseline for oil recovery comparison. Systematic variations of fluid properties were examined for their ability to increase oil
recovery. A surfactant solution lowers the interfacial tension with the oil used by a factor of ten, and increased the recovered oil by 10% for the flowrates tested. Flopaam, a commercially available fluid thickener designed for enhanced oil recovery was tested. The Flopaam mixture is shear-thinning and viscoelastic, and outperforms the surfactant solution by 10% at all flowrates tested. A fluid that shear-thickens at shear rates present in the microfluidic sandstone device for the flow rates investigated was designed using a polymeric fluid with nanoparticles added. This shear thickening fluidic achieved oil recovery that outperformed the water, surfactant, and Flopaam solutions for flowrates that closely matches the shear thickening regime. It was demonstrated that a two-stage recovery process using water and a secondary fluid can recover as much oil as a single stage recovery with the secondary fluid. The microfluidic sandstone device was thus proven to be a relative quick diagnostic tool to investigate the ability of enhanced oil recovery fluids to be tested for effectiveness before more costly and time intensive methods are employed. For oil field applications, shear-thickening fluids show great promise for enhanced oil recovery in the future.
**Figure 30:** Schematic of a typical test section of a Rheometer outfitted with a cone and plate.
Figure 31: Schematic diagram of the small sandstone device used in these experiments. The inlet is any of the three ports on the left, and flow goes from left to right. The two ports aside the main chamber are available for pressure drop measurements, and the port to the right is the outlet port. The lower image is what the sandstone portion looks like when filled with the Miglyol oil dyed with sudan blue.
Figure 32: a.) Viscosity as a function of shear rate for ⭐0.1 wt% Flopaam 3630 and the shear-thickening ○ 4.0 wt% silica nanoparticles 0.4 wt% PEO Mw600,000. b.) The storage ($G'$, ⭐) and loss ($G''$, ⭐) modulus as a function of angular frequency for the 0.1 wt% Flopaam 3630. The cross-over point is at 0.045 rad/s, corresponding to a relaxation time of $\lambda = 22s$. 

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Figure 33: a.) The percent oil remaining in the sandstone microfluidic device after flooding with various fluids as a function of flowrate.  b.) The percent oil remaining in the sandstone microfluidic device after flooding with various fluids as a function of capillary number.  The driving fluids in both include: ■ water, △ 5 mM CTAB in water surfactant solution, ○ shear thickening fluid consisting of 4.0 wt% silica nanoparticle 0.4wt% PEO Mw600,000 in water, and ★ 0.1 wt% Flopaam 3630 in water.
Figure 34: The percent oil remaining in the sandstone microfluidic device after flooding with various fluids as a function of shear rate through the sandstone microfluidic device. The driving fluids include: ■ water, △ 5 mM CTAB in water surfactant solution, ○ shear thickening fluid consisting of 4.0 wt% silica nanoparticle 0.4wt% PEO Mw600,000 in water, and ★ 0.1 wt% Flopaam 3630 in water.
Figure 35: a.) The initial microfluidic sandstone geometry filled with Miglyol oil dyed with Sudan blue. The oil-filled microfluidic sandstone device is shown after reaching steady-state by single-stage flooding at 4.8 ml/hr with b.) water, c.) 5 mM CTAB in water surfactant solution, d.) 0.1 wt% Flopaam 3630 in water, and e.) shear thickening fluid consisting of 4.0 wt% silica nanoparticle 0.4 wt% PEO Mw600,000 in water.
Figure 36: The oil-filled microfluidic sandstone device is shown after reaching steady-state by single-stage flooding with a.) water at 1.5 ml/hr, b.) shear-thickening fluid at 1.5 ml/hr, c.) Flopaam solution at 1.5 ml/hr, d.) water at 4.8 ml/hr, e.) shear-thickening fluid at 4.8 ml/hr, f.) Flopaam solution at 4.8 ml/hr, g.) water at 8.4 ml/hr, h.) shear-thickening fluid at 8.4 ml/hr, i.) Flopaam solution at 8.4 ml/hr, j.) water at 13.5 ml/hr, k.) shear-thickening fluid at 13.5 ml/hr, and l.) Flopaam solution at 13.5 ml/hr.
**Figure 37:** a.) The percent oil remaining as a function of flowrate for ■ water, ○ shear-thickening solution, and ★ Flopaam 3630. The stars indicate two stage recovery residual oil, starting with a □ water flood, the secondary (larger ○) shear-thickening solution, and the secondary ★ Flopaam flood. b.) The initial oil filled microfluidic sandstone geometry and comparing the steady-state results after flooding with only the Flopaam 3630 solution against flooding first with water and a secondary flood with the Flopaam solution. c.) The initial oil filled microfluidic sandstone geometry and comparing the steady-state results after flooding with only the shear-thickening nanoparticle solution against flooding first with water and a secondary flood with the shear-thickening solution.
7.1 Introduction

The results in Chapter 6 demonstrate interesting multi-phase phenomena at the micro-scales and the resulting macro-variations in oil recovery that they produce. A natural extension of the work in Chapter 6 is to reduce the complexity of the device to the smallest unit of interest: a single narrow capillary that broadens into a pore, and then reduces back to narrow capillary. The physics involved in this process would yield more insight into methods by which to design fluids to remove more oil from pores within oil fields, as it is representative of conditions where oil can be trapped. Furthermore, these experiments would allow our BASF collaborators to compare and validated results generated from simulations of these geometries.

Citing an absence of previous research on this particular set-up, the processes involved in a single pore can be separated into some constituent processes that have generated interest: flow through the narrow capillary, and flow over a backwards facing step. Flow between parallel surfaces separated by a small distance have generated much research (Saffman and Taylor 1958; Homsy 1987), with an excellent review on the topic presented by Homsy in which they detail and discuss both miscible and immiscible fluids. These experiments were performed in Hele-Shaw flow cells which consist of closely spaced parallel plates, which allow for two-dimensional flow. One finding of interest was that above a critical flow velocity, the interface between two immiscible
fluids becomes unsteady, and results in viscous fingering. The other applicable area is flow over a backward facing step. There has been numerical work examining this phenomenon at a microscale (Xue, Xu et al. 2005; Hsieh, Hong et al. 2010; Kherbeet, Mohammed et al. 2012). Much of the focus of these works concern heat transfer at small scales either with gas as the working fluid or nano-fluids (fluids with suspended nanoparticles), and the effect of the step. In context to this work, they provide and understanding of the location and magnitude of the recirculation areas, which is instructive to hypothesizing where oil may remain in the single pore devices. The goal with these single pore devices is to allow for a more detailed understanding of how fluids with variations in interfacial tension, polymeric properties, viscosities, or viscosities that are shear-rate specific will react to the presence of a relatively large pore along a narrow capillary.

### 7.2 Single Pore Experimental Design

In order to simulate a single pore device, a SU-8 master slide was created. The dimensions and a representative diagram of the device are shown in Figure 38. After the inlet, the fluid will flow through a long, thin channel. The length of this channel is to remove any artifacts in the flow field resulting from the entrance into the thin channel. The pore measures 100μm tall, 250μm wide, and 500μm long. After the pore, there is a short thin section to the exit. The dimensions of the pore were determined in jointly with our BASF collaborators to mimic the actual size of a representative pore found in core samples recovered from oil fields.
In order to create both the channel and the pore, a two-stage photolithography process was used. First, a thin 25μm channel was created on a silicon wafer, and was completely exposed and developed. Then, a fresh layer of SU-8 was spun onto the existing developed channel and the pore was exposed and developed. This allows for the creation of the pore feature on top of the channel feature. The alignment was performed using the Suss MicroTec MA6 Mask Aligner. Once the SU-8 master is created, PDMS molds can be made from the master using the softlithography techniques described in Chapter 1.

The experiments consisted of initially flooding the device with light mineral oil and then examining how various fluids behave when being used to displace the oil out of the pore. The device is designed such that there is a completely flat surface through which to visualize the resulting dynamics. Light mineral oil was chosen as the oil phase because of its availability and its well defined properties and working knowledge within our lab. We chose water as our baseline fluid, because it is the most common fluid used to extract oil from oil fields. We then compared fluids exhibiting variations in interfacial tension, viscoelastic behavior, and shear-thickening behaviors. In order to modify the interfacial tension, CTAB (hexadecyltrimethylammonium bromide) was used. It reduces the interfacial tension of a 5mM Ctab solution in water with oil by an order of magnitude with oil, from 20mN/m of water and oil to 2mN/m. Inspired by the work of Kamibayashi et al, we added a small amount for mid-molecular weight PEO (0.7 wt.% mv. 200,000) to a nanoparticle solution of 5.5 wt% hydrophilic silica particles. (Kamibayashi, Ogura et al. 2008) This resulted in a fluid that shear-thickens by a factor of 10 around a shear rate of 10 s⁻¹ which was a target shear rate common to many oil field applications.
A commercially available viscoelastic fluid ‘thickener’ in use for current EOR application, Flopaam 3630 (SNF Floerger®), was used for comparison to the shear-thickening formula. Flopaam 3630 is a proprietary mixture of high molecular weight copolymers of polyacrylamide and polyacrylate which commonly mixed at various concentrations in water depending on the desired target viscosity. For this study, Flopaam 3630 was mixed with deionized water at a concentration of 0.1 wt%. At this concentration, the Flopaam solution shear thins over the range of shear rates probed, and had the same baseline viscosity of the shear-thickening nanoparticle suspension. Figure 39 shows the viscosity as a function of shear rate both the shear-thickening fluid, and the Flopaam solution. The shear-thickening fluid used in this work was created using a slightly altered protocol than the shear-thickening fluid in Chapter 6. The shear-thickening in this chapter was the original combination of nanoparticles and PEO. This mixture (5.5 wt% nanoparticle, 0.7 wt% PEO 200,000 mw) was very sensitive to small variations during manufacture of the fluid. It was also discovered that the fluid created a year after the original design possessed largely different rheological properties, which could have been caused by variations in the moisture content in the nanoparticles or the PEO, or from other potential known or unknown reasons. These experiments were preformed when the fluid was behaving as measured in Figure 39.

The fluid interactions were viewed with the inverted microscope (Nikon TE2000-U, Melville, NY) and video data recorded using a high-speed video camera (Vision Research, Phantom 4.6, Wayne, NJ). The flow rates of interest were chosen in order to capture physics, before, during, and after the shear thickening range. For the particular shear-thickening fluid we are using, this results in shear rates of 5s⁻¹, 15s⁻¹, and 90s⁻¹.
which correspond to volumetric flow rates between 1.2 to 21.1 µL/min. The flow was be
driven by two stepper-motor actuated micro-syringe pumps (New Era Pump System, NE-
500 OEM) using a 1 mL plastic syringes (BD, plastic Leur-Lok Tip) for fluids with
particles, 1 mL glass syringes (Perfektum, glass Leur-Lok Tip) for fluids without
particles 5 mL glass syringes (BD, glass Leur-Lok Tip) for the oil flooding. The goal of
this proposed research is to better understand the role of the interfacial tension, viscosity,
and non-Newtonian effects on the ability to displace oil out of a pore, and where
specifically oil remains in such geometries.

7.3 Results and Discussion

To begin, there are some general similarities between most of the driving fluids
use. These include droplet formation into the pore at low flow/shear rates, and small
pockets of oil remain just upstream of the pore after steady state has been achieved.
Figure 40 shows the results of water as a driving fluid pumped at the three shear rates
used. At the lowest shear rate shown in Figure 40a, the water pinches off to form
droplets in the pore. As a subsequent droplet is form, the new droplet quickly coalesces
with the existing droplet in the pore, forming a larger drop. Once this drop fills the pore,
additional water forces water out of the pore. At steady state, there is a noticeable
amount of oil remaining just upstream of the pore. At the intermediate shear rate of 15s⁻¹
shown in Figure 40b a similar process occurs, with the only difference being that less
residual oil remains upstream of the pore. Finally, at the highest shear rate of 90s⁻¹ in
Figure 40c two main changes are noticed: the water does not initially wet the wall and
resembles viscous fingering down the channel, and the droplets formed in the pore do not
coalesce before they exit the pore. In the steady state, there exists a more oil upstream of
the pore, and also a smaller amount downstream.

Figure 41 shows the time-sequence results of the shear-thickening solution in the
single pore. The results are largely similar to that of the water case, which is surprising
even in the shear-thickening regime. Figure 41a shows the time sequence of the shear
thickening at the lowest shear rate. As the droplets enter the pore, they pinch off as the
water did, but coalesce much more slowly. At steady state, the flow profile closely
resembles that of pure water, with small amounts of oil remaining upstream. Figure 41b
shows the time sequence of the shear-thickening flow in the pore in the shear rate where
the viscosity has increased to 0.9 Pa\cdot s, and near 5x increase from the lower shear rate. At
this shear rate, the droplets continue to pinch off and slowly coalesce. The main
difference is that the time to fill the pore increases substantially, however this remains the
main difference. Figure 41c shows the shear-thickening solution at the highest shear rate.
This largely mimics the behavior of the water at this flowrate, with drops forming in the
pore and being forced out before complete coalescence and a similar amount of oil
remaining upstream of the pore.

Figure 42 shows the time-sequences of the surfactant solution for the range of
shear rates investigated. In the lowest shear rate shown in Figure 42a, larger droplets
form and at a slower rate, but coalesce before leaving the pore. At the middle shear rate
shown in Figure 42b, the droplets do not coalesce before leaving the pore. This is a result
of the much lower interfacial tension. At lower interfacial tensions, the droplets are
larger, which results in a larger radius of curvature and a longer lasting oil film between
the drops delays the coalescence until after the initial droplets exit the pore. At the steady
state, there is more oil residing in the upstream channel, similar to the higher flowrates of the water flood. At the highest shear rates shown in Figure 42c, there is no initial droplet formation, only continuous filling. At steady state, the CTAB solution completely fills the channel and pore, recovering more oil than the water alone.

The final fluid investigated is the viscoelastic fluid thickener Flopaam 3630. This fluid exhibited the most interesting response to the presence of the pore over all the shear rates studied. As the Flopaam encounters the pore as seen in Figure 43a, two simultaneous phenomena occur. As a droplet begins to form, the Flopaam solution in the channel violently recedes. There is no droplet pinch-off. This phenomenon is likely the result from the elasticity of the Flopaam 3630 solution. This solution has a relaxation time of approximately $\lambda = 22s$. The shear rates in these experiments range from $5s^{-1} \leq \dot{\gamma} \leq 90s^{-1}$ resulting in Weissenberg numbers much larger than $Wi = \dot{\gamma} \lambda >> 1$. Consequently, the elastic effect will be important. As the fluid enters into the channel from the inlet, an extensional flow is produced followed by a strong shear flow within the $25\mu m$ channel. causing deformation of the polymer chains in the flow direction and storage of significant elastic normal stresses. (Rothstein and McKinley 2001) Upon entering the pore, some of the elastic stress is released as the polymer partially recoils back towards its equilibrium configuration. This effect is similar to die swell during extrusion of polymeric fluids, (Petrie and Denn 1976; Larson 1992) where the elastic normal stresses within the Flopaam drive the fluid quickly outward to fill the pores it is entering. This displaced oil mainly moves out of the downstream pore exit, but a noticeable portion exits into the upstream channel creating an elongated connection between the bulk and the droplet formation. At steady state for the low shear rate, there
is a similar amount of oil remaining upstream channel as the water flood, and slightly more downstream. Figure 43b shows the intermediate shear rate of 15s⁻¹. The initial drop filling process continues similar to the lower shear rates, with the release of elastic energy results in a dynamic dewetting of the upstream Flopaam solution. At steady state, there is no visible oil remaining in the channel of the pore. At the highest shear rate shown in Figure 43c, the elastic energy release is not as noticeable, but still present. The steady state recovers all observable oil from the pore.

The results seen in Figure 43 reinforce some of the small scale differences in oil recovery seen in Figure 35 and Figure 36 and discussed in Chapter 6. In those images, the Flopaam solution penetrated into pores and recovered more oil from those pores than the other fluids tested. The single-pore experiments presented in this chapter strengthen the argument in Chapter 6 that this is caused by the release of elastic normal stresses within the polymeric Flopaam solution. While on the small scale the Flopaam recovers more oil from a single pore, the results from the sandstone microfluidic device in Chapter 6 show that larger device-scale pressure and shear-rate effects result in the shear-thickening fluid outperforming the Flopaam solution over shear rates in the shear-thickening regime.

7.4 Conclusions

This chapter investigates the ability of fluids of various rheological properties to recover oil from a single pore. Water was used as a baseline fluid for this study, which occurs at three prescribed shear rates. At the lowest shear rate, water droplets were initially formed when entering the pore, quickly coalescing and filling the pore, with a
small amount of oil remaining in the upstream channel at steady state. This process was similar at the middle shear rate, however the highest shear rate prevented the droplets from initially coalescing before they exited the pore. A shear-thickening fluid exhibited largely similar characteristics to water, the only difference is that they occur at slightly longer timescales. The reduced interfacial tension fluid resulting in longer lasting pore droplets, with coalescence prevented at the middle shear rate. The polymeric viscoelastic thickener used produced the most dynamic results, with the upstream channel storing elastic energy in the high molecular polymer strands that released as a droplet formed in the pore. This release expelled pore oil downstream, and partially upstream, resulting in a sudden dewetting of the upstream solution. However, at steady state the Flopaam surpassed the other fluids in qualitative oil recovery.
Figure 38: A representative image of the single pore microfluidic device with dimensions. A representative image itself is not to scale.
Figure 39: a.) Viscosity as a function of shear rate for 0.1 wt% Flopaam 3630 and the shear-thickening 5.5 wt% silica nanoparticles 0.7 wt% PEO Mw200,000. b.) The storage (G’, *) and loss (G’’, *) modulus as a function of angular frequency for the 0.1 wt% Flopaam 3630. The cross-over point is at 0.045 rad/s, corresponding to a relaxation time of \( \lambda = 22 \tau \).
Figure 40: Water in the single pore device at shear rates of a.) 5s\(^{-1}\), b.) 15s\(^{-1}\), and c.) 90s\(^{-1}\) in the single pore device
Figure 41: The shear-thickening fluid in the single pore device at shear rates of a.) 5s\(^{-1}\), b.) 15s\(^{-1}\), and c.) 90\(^{-1}\) in the single pore device
Figure 42: The surfactant solution fluid in the single pore device at shear rates of a.) 5s$^{-1}$, b.) 15s$^{-1}$, and c.) 90$^{-1}$ in the single pore device.
Figure 43: The flopaam 3630 solution in the single pore device at shear rates of a.) 5s⁻¹, b.) 15s⁻¹, and c.) 90⁻¹ in the single pore device.
8.1 Introduction

As with the above investigation of the single pore dynamics that take place in the relatively small sandstone mimicking device in Chapter 6, the eventual goal is to investigate whether a small scale microfluidic device can successfully predict the flow behavior, characteristics, and ability for a particular fluid to drive fluid out of a large scale oil field. In the Chapter 6 experiments, a microfluidic sandstone device was developed using standard soft-lithography techniques to produce an idealized two-dimensional porous media. Images taken from sandstone were used to create a device with roughly 40 pores and 80 capillaries of sizes ranging from the 10’s to 100’s of microns. The experiments demonstrated that shear-thickening fluids can be utilized to recover nearly 90% of the oil from this idealized microfluidic sandstone device (Nilsson, Kulkarni et al. 2013). However, there are still some open questions from that work. Specifically, given a small scale and high permeability of their devices, one might ask about the applicability of the results to core floods or at the very least, more complex and less permeable microfluidic sandstone devices. In this chapter, we reexamine the same fluids used previously; however we examine their ability to recover oil from two significantly larger and more complex devices of with varying permeabilities. These
experiments are the logical next step to the work in Chapter 6 required for the eventual
development a quick and easy diagnostic tool set for EOR fluid testing. These large-area
devices were fabricated to closely mimic the cross-section of an actual sandstone core
sample from the field and provided by our collaborators at BASF, in order to capture the
complexity of the sandstone sample. Additionally, these experiments will facilitate
future comparisons to traditional core-flood measurements using the same EOR fluids.

8.2 Device Development

The mask was created from an actual cross-sectional image of sandstone which
was used as a template for a microfluidic device that approximates flow through a
sandstone core. We started this process with an actual image of a sandstone core sample
from an oil field (supplied by BASF). A representative image of this mask is shown in
Figure 44. The diameter of the sample is 6 inches, so we designed our device to be to
scale. The first step in creating a device based off this core sample was to convert the
image to grayscale. We applied a threshold to the image which resulted in the light areas
representing sandstone and the dark areas representing empty space. Because this is a
two-dimensional slice of a three-dimensional structure, the image was modified to allow
for continuous flow through the device, removing any “dead-ends”. Connections were
made between pores along boundaries between sandstone particles to accomplish this. A
schematic of this process with pictorial representations is shown in Figure 45.

The design was performed in Adobe Photoshop, which has the advantage of being
able to easily manipulate the permeability of the device. Two masks were created: an
original scale image of the sandstone (with no dead ends) with the smallest capillaries
being 40 microns wide and referred to as the ‘small permeability’ device. The second mask was modified such that every pore and capillary was enlarged, resulting in a device with “higher permeability” and smallest capillary widths so 200 microns. The device was also modified to align in any direction and able to be arranged in a tile fashion. In this spirit, minor modifications were made near the edge of each ‘tile’ such that all pores and sandstone structures would align to allow for seamless flow from one “tile” to another. Shown in Figure 46 is the final representation of the sandstone. This would be one unit, and is scalable vertically and horizontally, with no dead-ends resulting from this processes.

Figure 47 shows the resulting designs for the larger devices, with the larger permeability device shown in Figure 47a and the smaller permeability device shown in Figure 47b. The flow in this figure would be from top to bottom. In each device, there are 3 units arranged in a row, side by side, and it is clearly difficult to distinguish any repeatability in the sandstone pattern and equally as difficult to determine where one tile ends and another begins. The side walls of the device were also developed to mimic impermeable sandstone, instead of being simply a flat sidewall. This is done in order to reduce the effect of the wall on the overall fluid flow.

One consideration that will need experimentation is the inlet conditions. In order to perform these experiments properly, the initial front of the flooding fluid should encounter the sandstone uniformly. In order to accomplish this, many inlets will be needed to distribute the flow across the device. However, unlike macroscale flow where the flowrate is a function of the cross-sectional area, in microfluidics the flow is dominated by the shear length which in many cases is limited by the depth of the device.
Therefore, we’ve found that the most effective way to distribute flow is to have channels of identical dimensions split to distribute the flow across the inlet.

The microfluidic devices were fabricated using PDMS and standard soft-lithography techniques. (Petersen 1982; Duffy, McDonald et al. 1998; Stone, Stroock et al. 2004; Atencia and Beebe 2005; Gao and McCarthy 2006; Whitesides 2006; Nie, Seo et al. 2008) In microfluidics, photolithography is used to transfer a pattern onto a silicon wafer using a photoresist such as SU-8. (Madou 2002) Once developed, the two-dimensional pattern in the photoresist is used as a master from which multiple daughters can be cast in (poly)dimethyl-siloxane (PDMS) or other cross-linking polymers, containing negatives of the pattern on the master. (Duffy, McDonald et al. 1998; McDonald, Duffy et al. 2000; McDonald and Whitesides 2002) This soft lithography technique has been used for more than a decade to generate microfluidic devices containing features as small as 10μm. (McDonald and Whitesides 2002; Makamba, Kim et al. 2003) The resulting microfluidic sandstone devices were designed to be 100 microns deep for the higher permeability device, and 80 microns deep for the lower permeability device. The capillaries in the higher permeability device were 200 microns wide on average. The lower permeability device has capillary widths of 40 microns. The design process used to create both the higher and the lower permeability microfluidic sandstone device capture the essential physics of flow through porous media and results in an easy-to-fabricate, and extremely flexible two-dimensional, experimental test bed.

Pressure taps were installed upstream and downstream of the sandstone geometry in the microfluidic device to measure the pressure drop across the sandstone geometry. The pressure ports were plumbed with blunt needle tips connected to polyethylene
tubing. This tubing was connected though adapters to a differential pressure transducer (Honeywell TruStability™) with a range of ±1 psi. The pressure drop measurements were used to determine the permeability, \( \kappa = U \frac{\eta \Delta \xi}{\Delta P} \), of each device. Here \( U \) is the superficial velocity, \( \eta \) is the viscosity which can be a function of shear rate, \( \Delta \xi \) is the distance across the sandstone geometry, and \( \Delta P \) is the pressure drop across the sandstone geometry. Common oilfields have permeability values of \( 0.1 D < \kappa < 10.0 D \). (Nejad, Berg et al. 2011) The pressure drop measured across the higher permeability device using water as the driving fluid resulted in a permeability value of \( \kappa = 73D \pm 2.5D \), and the lower permeability device had a permeability of \( \kappa = 42D \pm 1.5D \). In the rest of this paper, these two devices will be designated SMD-73D and SMD-42D for the sandstone mimetic device (SMD) with permeability of \( \kappa = 73D \pm 2.5D \) and \( \kappa = 42D \pm 1.5D \) respectively. The device in Nilsson et al. (Nilsson, Kulkarni et al. 2013) had a permeability of \( 60D \), but had a much smaller area with a much less complex sandstone structure. The range in permeability of the devices presented in this work will compliment the results of Nilsson et al. (Nilsson, Kulkarni et al. 2013) and allow for examination of any complexity effects on oil recovery and permeability effect on oil recovery. The porosity of the higher permeability device is \( \phi = 0.47 \), which is similar to the porosity of the device of Nilsson et al. (Nilsson, Kulkarni et al. 2013) The lower permeability device had a porosity of \( \phi = 0.35 \). While these values are slightly above the range of most oilfields, (Han, Nur et al. 1986) it is realistic in its structure, and its complexities allow for valuable insights in testing the ability of rheologically complex fluids to displace oil from sandstone.
In order to determine the amount of oil recovered by a flood, images of the initial conditions were taken when the microfluidic device was fully filled with light mineral oil. After flooding the oil-filled device at a prescribed flowrate, the initial condition images were then compared to images after the flood once the flow had reached steady-state and no additional oil was displaced with continued flooding. Representative images of the oil-filled SMD-73D and SMD-42D devices prior to flooding are shown in Figure 47. In these experiments a syringe pump (kd Scientific, model 100) was used to impose a prescribed flow rate on the driving fluid. The experiment was terminated after it was determined that it had reached steady state. Steady state was defined as when no more oil was visibly being removed through the transparent exit tubing. The images were taken with a Nikon D70 camera outfitted with a macro lens (micro-NIKKOR 105mm). Backlighting was provided by a commercial flood light. The images were then made grayscale and imported into a homegrown Matlab™ code. The code first applied a threshold to each image, causing any oil filled area to appear completely black and any non-oil area white. The images were inspected to insure that the threshold value accurately represented the oil filled condition. The program then counted black pixels and reported the percentage of the image that was oil. Comparing between the percent of oil from the before and after the fluid flood allowed us to determine the percentage of oil removed during the flooding process.

The baseline fluid used to displace oil from both the large and small permeability microfluidic sandstone devices was deionized water. The oil used to initially fill the microfluidic devices was light mineral oil (Fisher Scientific). To increase contrast with the PDMS, the oil phase was dyed with Sudan Blue (Sigma Aldrich). The interfacial
tension between water and mineral oil light was measured to be $\sigma = 20 \text{mN/m}$ while the contact angle between water and mineral oil-wetted PDMS was found to be $\theta_A/\theta_R = 155^\circ/138^\circ$. Two rheologically complex fluids were also used: a shear-thickening nanoparticle solution and a viscoelastic shear-thinning fluid.

Modifying the rheology of the driving fluid was achieved through the addition of nanoparticles and/or high molecular weight polymer additives to the water phase. In this study, we were interested in investigating the impact of two different rheological characteristics on enhanced oil recovery: shear thinning and viscoelasticity. The shear thickening fluid was created by adding a small amount (0.4 wt %) of a moderately high molecular weight polyethylene oxide (PEO) (Mw = 600,000 g/mol, Aldrich) to a aqueous dispersion of 4.0 wt% hydrophilic silica nanoparticles (12 nm size, Degussa AEROSIL® 200). (Kamibayashi, Ogura et al. 2008) The resulting fluid was found to shear-thickens by a factor of about five. (Kamibayashi, Ogura et al. 2008) As seen in Figure 32, at low shear rates the nanoparticle dispersion initially shear thins. At a shear rate of $\dot{\gamma} \approx \gamma_{\text{L}} = 4 \text{s}^{-1}$, the shear viscosity thickens by a factor of approximately five from approximately 0.2 Pa·s to 1.0 Pa·s. Here $U$ is the front speed and $L$ is the characteristic length. The fluid maintains this high viscosity until a shear rate of about $\dot{\gamma} = 20 \text{s}^{-1}$ beyond which it begins to shear thin again. This shear thickening is induced by the interaction of nanoparticles enhanced by the presence of the polymer which can absorb to and bridge between nanoparticles to produce long-range interactions and a perculated network structure under flow. (Kamibayashi, Ogura et al. 2008) In the absence of polymers, the nanoparticle suspensions at this concentration show no shear thickening.
and a significantly reduced viscosity. (Khandavalli and Rothstein 2013) Linear viscoelasticity measurements of this nanoparticle dispersion do not reveal any elasticity over the range of shear rates that could be probed. The interfacial energy of the nanoparticle/polymer solution was found to be $\sigma = 20 \text{mN/m}$ and the contact angles with PDMS in light mineral oil were measured to be $\theta_d/\theta_r = 140^\circ/104^\circ$.

A commercially available viscoelastic fluid, Flopaam 3630 (SNF Floerger®) was mixed with deionized water at a concentration of 0.1 wt%. Flopaam 3630 is a proprietary EOR additive comprised of a very high molecular weight co-polymers of polyacrylamide and polyacrylate. As seen in Figure 32a, at a concentration of 0.1 wt% Flopaam 3630, the solution was found to shear thin over the entire range of shear rates probed. The concentration of Flopaam was chosen such that it had the same baseline viscosity at low shear rates as the shear-thickening nanoparticle suspension so that effects of shear-thickening and viscoelasticity could be separated more easily. As seen in Figure 32a, the viscosity of the 0.1 wt% Flopaam 3630 solution shear thins at roughly the same rate as the shear thickening nanoparticle suspension. There are two major differences between these fluids. First, the Flopaam does not shear thicken. Second, as seen in Figure 32b, the linear viscoelastic spectrum of Flopaam shows the fluid to be viscoelastic with a relaxation time of approximately $\lambda = 22s$. As a result, an elastic response can be expected from this solution for flows where the Weissenberg number, $\text{Wi} = \dot{\gamma}\lambda > 1$, or equivalently for flows where the shear rate is greater than $\dot{\gamma} > 0.05s^{-1}$.
8.3 Results and Discussion

The first fluid used in this device was water. This was to establish a baseline using the most common fluid used in oil recovery. The flowrates used for driving the fluids through both microfluidic sandstone devices ranged between 1.5 ml/hr to 175.5 ml/hr. This corresponds to front speeds between $0.0001 \text{m/s} < U < 0.014 \text{m/s}$ and shear rates in the sandstone features of $0.7 \text{s}^{-1} < \dot{\gamma} < 70 \text{s}^{-1}$ for SMD-73D, and front speeds of $0.0002 \text{m/s} < U < 0.021 \text{m/s}$ and shear rates of $4.8 \text{s}^{-1} < \dot{\gamma} < 600 \text{s}^{-1}$ for SMD-42D. For SMD-73D, these shear rates correspond to capillary numbers for water between $3.9 \times 10^{-6} < Ca = \frac{uU}{\sigma} < 3.5 \times 10^{-4}$. The shear rates in SMD-42D correspond to capillary numbers of $9.9 \times 10^{-6} < Ca < 1.2 \times 10^{-3}$.

The results for water and the other driving fluids in the high permeability microfluidic sandstone device are presented in Figure 48. The percentage of oil remaining after water flooding was calculated after the flow had reached steady state. This result is presented as a function of the shear rate of the driving fluid which will allow for a more direct discussion of the physics and benefits of the shear-thickening fluid. The shear rate, $\dot{\gamma} \approx \frac{i}{L}$, is approximated from the flow rate of the driving fluid. The characteristic length for this study was chosen to be the hydraulic diameter of the capillary width of the device. For SMD-73D, the mean opening size is 200$\mu$m and the channel height is 100$\mu$m, thus the characteristic length becomes $L = 4\phi L = 133 \mu m$. For SMD-42D, the mean opening size is 40$\mu$m and the channel height is 80 $\mu$m, thus the characteristic length becomes $L = 53 \mu m$. The average front speed is calculated as, $U = \frac{\phi Q}{\phi H}$, where $Q$ is the volume flow rate, $\phi$ is the porosity of the sandstone, $H$ is the
depth of the microfluidic device, and W is the total width of the sandstone geometry. At
the lowest flowrates tested, approximately 85% of the oil remained after flooding with
water at 1.5 ml/hr in the high permeability microfluidic device. With increasing flowrate,
additional oil was recovered approaching an asymptotic value of roughly 45% residual oil
at the largest flowrates tested. Similar trends were observed previously with increasing
flow in a variety of model porous medias (Taber 1980; Thomas 2008; Cottin, Bodiguel et
al. 2010; Nilsson, Kulkarni et al. 2013) In Chapter 6 with our work using a smaller, less
complex microfluidic device, the amount of residual oil was slightly lower than the
results in Figure 48 (Nilsson, Kulkarni et al. 2013) This is likely because of the larger
average size of the capillaries in the device in Chapter 6 (Nilsson, Kulkarni et al. 2013).

Next, the shear-thickening nanoparticle dispersion was tested in SMD-73D. The
shear-thickening nanoparticle/PEO fluid greatly outperformed the water in recovering oil
over all the flowrates tested. At the lowest flowrate tested, the shear-thickening fluid left
37% of the original oil behind in the sandstone device. As the flowrate increases, the oil
recovery was found to dramatically improve, reaching as little as 12% residual oil at a
shear rate of 8s⁻¹ and maintains this impressive oil recovery at the highest shear rates
examined. These trends are qualitatively similar to the improved oil recovery reported in
Chapter 6 for the smaller, less complex PDMS microfluidic sandstone devices (Nilsson,
Kulkarni et al. 2013). This suggests that the observations in Chapter 6 were qualitatively
independent of device complexity and capillary size. Figure 48 shows a sharp transition
in oil recovery beginning at or below shear rates of approximately \( \dot{\gamma} \sim 3s^{-1} \). This shear
rate is very closely tied to the shear rates at which shear-thickening of the viscosity of the
nanoparticle dispersion was found to occur. The direct correlation to the shear-
thickening transition suggests rise in pressure drop associated with shear-thickening is sufficient to allow the nanoparticle dispersion to access previously trapped oil by overcoming the Laplace pressure supporting water-oil interfaces in the small capillaries and side branches. Once the fluid permeates these capillaries, a larger fraction of the sandstone device is accessed and the resulting local shear rate is reduced. In some cases, the reduced shear rate can drive the viscosity back below the shear thickening transition. While the oil recovery increases with the onset of the shear-thickening, the peak oil recovery was found to exist over a range of average shear rates larger than the shear thickening range of the fluid. This likely arises from the complexity of the device and variations of the local shear rates across the device for any given flowrate.

It is important to note that there exists uncertainty in these experiments that result from small variations in fluid preparations and the device fabrication. The shear-thickening behavior is sensitive to small variations in fluid composition. The device fabrication can also result in small variations in the thickness of the capillaries and pores, which would affect the shear-thickening onset. In order to minimize the effect of these variations, the experiments were performed using multiple fluid preparations and device fabrications, and error bars are presented to demonstrate the confidence in these results.

As seen in Figure 48, the viscoelastic Flopaam 3630 mixture was found to outperform the water at all flow rates tested within SMD-73D and the shear-thickening nanoparticle dispersion at the lowest shear rates tested in the high permeability sandstone device. Unlike the shear-thickening fluid, the viscoelastic Flopaam solution was found to follow a more Newtonian-like recovery profile over the flowrates tested, with a gradual improvement in oil recovery as the flowrate was increased. This may in part be due to
the fact that the viscosity of the Flopaam solution was found to thin over the entire range of shear rates tested. At the lowest flowrate test, it slightly outperformed the shear thickening fluid. In this region, the shear rates are outside of where the shear-thickening was found to occur. This important result reinforced the results of Chapter 6. that a fluid designed to thicken at a specific shear rate can exceed the oil recovery of existing enhanced oil recovery fluids like Flopaam.(Nilsson, Kulkarni et al. 2013) To understand these results in detail, it is useful to interrogate the images taken before and after flooding with each of these driving fluids.

By examining the images used for determining the oil recovery, it is possible to qualitatively assess regions where one particular fluid outperforms others in accessing and mobilizing the trapped oil. Figure 49 compares before and after images of oil recovery experiments performed at a flowrate of 62.4 ml/hr and shear rate of 25s\(^{-1}\) in SMD-73D. The initial oil-filled device is shown in Figure 49a. The steady state result for water is shown in Figure 49b. The water tends to form preferential pathways through the sandstone structure. Once a pathway was formed through the entire sandstone structure, the water was not observed to permeate laterally through the device instead choosing to follow the path of least resistance. At the flowrate in Figure 49, multiple channels formed through the sandstone device by the water. Figure 49c shows the results after the Flopaam 3630 flood of SMD-73D. At this flowrate, the Flopaam recovers less overall oil than the shear-thickening solution. The Flopaam solution does not perform as well as the shear thickening at removing oil from behind large obstructions, although it exceeds at stripping oil away from ahead of and beside smaller obstructions as seen in Figure 49. These large remaining pockets of oil behind larger obstructions and in lateral
pores account for the increased remaining oil. These observations differ from those observed in a less complex microfluidic sandstone device in Chapter 6 (Nilsson, Kulkarni et al. 2013). In the device in Chapter 6, it was observed that an identical Flopaam solution would flood into small 'dead-end' pores or unswept volumes and recover a significant amount of oil. This effect was attributed to the observed viscoelastic nature of the Flopaam solution. As the Flopaam solution would pass through a narrow throat, an extensional flow would be produced followed by a strong shear flow in the narrow passage. In their sandstone device, this resulted in the deformation of the polymer chains in the flow direction and the buildup of elastic normal stresses (Rothstein and McKinley 2001). After exiting a narrow passage, this elastic stress would be partially released and polymer would partially recover back towards its equilibrium configuration and expand radially downstream of an expansion. This is similar to a die swell that occurs as a result of extrusion of polymeric fluids (Petrie and Denn 1976; Larson 1992). In SMD-73D, the extent of this effect is reduced, as the pores and capillaries are larger on average by design. The device used in Chapter 6 had much more variation in scale down to the 10's of microns, while in our high permeability sandstone device every open dimension is 200 microns wide by design. Therefore the extensional flows and subsequent shear flows in our device would be weaker through the most 'narrow' passages, with the result being less effective oil recovery in 'dead-end' pores and behind larger features. As seen in Figure 49d, the shear-thickening solution was much more effective at clearing oil from the whole SMD-73D. The remaining oil was found mainly within unswept volumes. There is an absence of preferential channels as observed in the case of water.
Figure 50 shows the remaining oil left in the SMD-42D after pumping the driving fluids through over a range of different flowrates. The trends in this device agree qualitatively to those of the SMD-73D. At the lowest flowrate, roughly 62% of the original oil remained after water pumped water had reached steady state. With increasing flowrate oil recovery improved to an asymptotic value of roughly 40% oil remaining. This is an increase in oil recovery when compared with the performance of the SMD-73D. The Flopaam solution outperforms the water at all flowrates, ranging from 49% oil remaining at the lowest flowrate tested, and improving to 27% oil remaining at the highest flowrate tested. Unlike water, this is a decrease in oil recovery when compared against the SMD-73D. As a result, the increase in performance relative to water is reduced as the permeability of the sandstone microfluidic device is reduced. The response of the shear-thickening solution in SMD-42D is comparable to the oil recovery of the Flopaam solution at low shear rates. As the shear rate increases into the range of the shear-thickening, the oil recovery sharply improves, with only 11% of oil remaining at the highest shear rates examined. The amount of oil recovered at high shear rates is slightly higher for the higher permeability sandstone devices. The presence of a critical shear rate for the onset of significant oil recovery for the shear-thickening fluids was observed for both the higher permeability devices, SMD-73D, as well as the smaller, less complicated devices developed and tested in Chapter 6. Figure 51 allows for more qualitative observations of the oil recovery. The initial oil-filled SMD-42D is shown in Figure 51a. The flow rate in these images was 62.4 ml/hr, corresponding to a shear rate of 206s⁻¹. Water appears to do a more thorough job in removing oil from SMD-42D compared to SMD-73D. This, however, is simply an optical illusion as the starting
volume of oil is these lower permeability and lower porosity devices is smaller. Roughly the same fraction of fluid is displaced by the water. One observes that there are still large ‘pockets’ of oil that remain in both larger pores and smaller capillaries. The Flopaam solution, shown in Figure 51c, recovered less oil in the SMD-42D than in the SMD-73D at the same flow rates. This is slightly because the shear rates present in this SMD-42D for a similar flowrate are about 10x higher. This increases the Weissenberg number by an order of magnitude and the elastic stresses, but also decreases the shear viscosity quite substantially. This results in a much stronger release of elastic stretches after passages through much narrower 40μm channels, resulting in greater displacement of oil on the downstream side of sandstone features. Finally, the shear thickening fluid in Figure 51d again clearly extracts the most oil of the three fluids tested. The oil remaining in these devices typically reside downstream of larger features, and at the end of some of the narrow capillaries. Despite the viscoelastic advantage of the Flopaam solution, the shear-thickening fluid outperforms the Flopaam solution in shear rates associated with its shear-thickening in all the permeabilities studied in both this Chapter and Chapter 6.(Nilsson, Kulkarni et al. 2013)

An important aspect of an enhanced oil recovery fluid is the ability to recover additional oil from a field that had been previously flooded with water. This analysis is easy to perform in our microfluidic sandstone devices. The results for sequential flooding with water followed by Flopaam and water followed by the shear thickening fluid in the SMD-73D are shown in Figure 52. At a flowrate of 62.4 ml/hr corresponding to a shear rate of 25s⁻¹, an initial water flood was perform, resulting in an identical amount of residual oil when compared against the results in Figure 48. This data is
represented by an open square overlayed on the data in Figure 52a. Figure 52b shows the results of the subsequent flooding with the Flopaam mixture through at the same flowrate (62.4 ml/hr) until steady state was obtained. Interestingly, the secondary fluid managed to recover exactly the same amount of oil (Figure 52a, open star) as was obtained by the single flood with the Flopaam. This reinforces the results from Chapter 6, that an initial flood of water does not affect the overall recovery in either the small or larger sandstone microfluidic devices in a two stage flood (Nilsson, Kulkarni et al. 2013). Similar to the results in Chapter 6, the Flopaam solution flood did not show a preferential flow through passages flooded during the first stage. Figure 52c compares the result of the two-stage water and shear-thickening flooding process to the result of a single stage shear-thickening flood at a flowrate of 62.4 ml/hr (25s⁻¹ shear rate). Similar to the two-stage Flopaam solution results, the results from two-stage shear-thickening flood (Figure 52a, open circle) agreed extremely well with the single stage shear-thickening flood. The agreement between a single stage Flopaam or shear-thickening flood and their two-stage counterpart in this more complex large device reinforces the usefulness of these carefully engineered EOR fluids in both native oil fields and those previously flooded with water.

Figure 53 directly compares the ability of each fluid to recover oil from devices of varying permeability and complexity. In Figure 53a, the oil recovery ability of water from the two devices covered in this chapter and the small scale device in Chapter 6 is presented as a function of Capillary number, which relates viscous forces to surface tension. While there are some small scale variations, the water largely collapses as a function of Capillary number. This is interesting because this agreement covers both variations in permeability and more importantly variations in device scale, serving to
suggest that the results of the smaller scale device in Chapter 6 can provide meaningful insight in recovery characteristics. Figure 53b shows the Flopaam oil recovery from the three devices studied in this thesis as a function of Capillary number. While the results do not collapse, the effect of permeability is still present. At higher permeability, oil recovery is increased as a consequence of the lower shear rates where the viscosity of the shear-thinning fluid is higher. In devices with lower permeability, the viscosity will decrease with higher shear rates. This observation suggests that the effect of improved recovery from small dead-end pores at higher shear rates is not as important as the overall viscosity in the device. Finally, Figure 53c compiles the oil recovery from the shear-thickening fluid across all of the EOR devices in this thesis. However, the average capillary width that is used as the characteristic length scale in the shear rate calculation in Chapter 6 is replaced by the hydraulic diameter. The hydraulic diameter is used in order to better approximate the representative length scale in rectangular capillaries present in our device, as the capillaries in each device varies in both scale and aspect ratio. As seen in Figure 53c, the increase in oil recovery corresponding to the shear rate the corresponds to the shear-thickening fluid behavior collapse to a shear rate of approximately $\dot{\gamma} = 5 \text{s}^{-1}$. This implies that the shear-thickening fluid can drastically improve oil recovery when compared to water regardless of device permeability, scale, or complexity. However, as seen on Figure 53c, at shear rates larger than $\dot{\gamma} = 5 \text{s}^{-1}$, the permeability has an effect on the amount of oil recovered. Oil recovery is increased in devices with higher permeability. As permeability decreases, the amount of oil recovered decreases. While this effect may seem small, it is critical when considering an actual oil
field. The results present in Figure 53 suggest that the microfluidic devices developed in Chapter 6 can provide meaningful insight in EOR fluid testing that compares closely to the results of a larger-scale, more complex device.

8.4 Conclusions

The field of Enhanced Oil Recovery is becoming a more important and necessary field, and this work presents the efforts furthering the development of a microfluidic platform for quickly testing fluids of different rheological properties for the recovery of oil from hydrophobic sandstone of various permeabilities. Water was tested in the microfluidic sandstone device as a baseline for oil recovery comparison in both devices. Additionally, a commercially available viscoelastic fluid thickener and a shear-thickening fluid were both examined for their ability to increase oil recovery. In both devices the Flopaam solution outperformed the water, reducing the residual oil by a slightly higher amount in the device with higher permeability compared to the lower permeability device. The shear-thickening device, designed to thicken at shear rates present in the microfluidic sandstone device achieved oil recovery that outperformed the water and Flopaam solution over flowrates that correspond to shear rates that match the shear thickening regime. It was demonstrated that a two-stage recovery process using water and a secondary fluid can recover as much oil as a single stage recovery with the secondary fluid in this larger, more complicated device. The results of the larger microfluidic sandstone devices are in close agreement with published results of a smaller scale microfluidic sandstone device, highlighting the versatility of these FOR fluids to improve oil recovery regardless of the permeability and porosity of the devices tested.
This agreement also reinforces the notion that these platforms can serve as a quick diagnostic tool to investigate the ability of enhanced oil recovery fluids to be tested for effectiveness before more costly and time intensive methods are employed. Further, shear-thickening fluids show great promise for enhanced oil recovery in fields of varying permeabilities and complexity.
Figure 44: Image of sandstone core sample courtesy of BASF. The overall core dimension is 6 inches in diameter.
Figure 45: Schematic detailing the process to allow for flow through the sandstone device. The image on the left is region of the sandstone image supplied from BASF after a threshold had been applied. Narrow channels were added along boundaries between individual sandstone particles that are more clearly visible in the center image. The result of this process is shown in the image on the right.
Figure 46: One unit, or tile, of sandstone device. All channels connect side-to-side and top-bottom allowing for seamless connection of multiple units.
**Figure 47:** Images of the section of the mask pattern containing the sandstone geometry for the a.) SMD-73D and b.) the SMD-42D used in these experiments. Flow in these images would flow from top to bottom. Each device comprises of 3 sandstone tile units arranged in a row. The left and right edges are modified to represent impermeable sandstone. The smallest capillary size for the a.) SMD-73D is 200µm and for the b.) SMD-42D is 40µm.
Figure 48: The percent oil remaining in the SMD-73D after flooding with various fluids as a function of shear rate. The driving fluids include: ■ water, ○ shear thickening fluid consisting of 4.0 wt% silica nanoparticle 0.4 wt% PEO in water, and ★ 0.1 wt% Flopaam 3630 in water.
Figure 49: a.) The initial SMD-73D geometry filled with Mineral oil dyed with Sudan blue. The oil-filled microfluidic sandstone device is shown after reaching steady-state by single-stage flooding at 62.4 ml/hr hr and shear rate of 25s$^{-1}$ with b.) water, c.) 0.1 wt% Flopaam 3630 in water, and d.) shear-thickening fluid consisting of 4.0 wt% silica nanoparticle 0.4wt% PEO in water.
Figure 50: The percent oil remaining in the SMD-42D after flooding with various fluids as a function of shear rate. The driving fluids include: ■ water, ○ shear thickening fluid consisting of 4.0 wt% silica nanoparticle 0.4wt% PEO in water, and ★ 0.1 wt% Flopaam 3630 in water.
Figure 51: a.) The initial SMD-42D geometry filled with Mineral oil dyed with Sudan blue. The oil-filled SMD-42D is shown after reaching steady-state by single-stage flooding at 62.4 ml/hr and a shear rate of 206s^{-1} with b.) water, c.) 0.1 wt% Flopaam 3630 in water, and d.) shear- thickening fluid consisting of 4.0 wt% silica nanoparticle 0.4wt% PEO in water.
**Figure 52:** a.) The percent oil remaining as a function of flowrate for ■ water, ○ shear-thickening solution, and ★ Flopaam 3630 for the SMD-73D. The triangle symbols △ indicate the two-stage recovery of residual oil, and are overlaid on the water flood, the shear-thickening solution, and the Flopaam flood. b.) The initial oil filled SMD-73D geometry and comparing the steady-state results after flooding with only the Flopaam 3630 solution against flooding first with water and a secondary flood with the Flopaam solution. c.) The initial oil filled SMD-73D geometry and comparing the steady-state results after flooding with only the shear-thickening nanoparticle solution against flooding first with water and a secondary flood with the shear-thickening solution.
Figure 53: a.) The residual oil cast as a function of Capillary number after flooding with water in the SMD-42D (hatched squares), the results from the device in Chapter 6 (solid squares), and the SMD-73D (open squares). b.) The residual oil cast as a function of Capillary number after flooding with Flopaam in the SMD-42D (hatched stars), the results from the device in Chapter 6 (solid stars), and the SMD-73D (open stars). c.) The residual oil cast as a function of a shear rate that uses the hydraulic diameter as the characteristic length scale after flooding with the shear-thickening fluid in the SMD-42D (hatched circles), the results from the device in Chapter 6 (solid circles), and the SMD-73D (open circles).
CHAPTER 9

CONCLUSIONS AND CONTRIBUTIONS

This chapter will highlight some of the contributions that this thesis presents. More detailed conclusions are at the end of each preceding chapter, this sections frames those results in the greater context, as well as suggest directions that would further contribute to the fields. To begin, we have characterized an easily fabricated superhydrophobic surface that can exhibit a range of wettability characteristics. Aside from the obvious benefits serving as a wettability experiment platform as done in this thesis, the simple fabrication method allows for these surfaces to be used as demonstration for college or high school students. This hands-on demonstration allows for direct observation of the importance of wettability in main important processes.

The results of the coalescence, mixing, deflection and sorting that culminate in the development of a prototype two-dimensional digital microfluidic device hold tremendous promise. The work presented here provides the foundation for assay development for use on this substrate. The two-dimensional platform holds many advantages over traditional microfluidic devices and current capillary paper-based systems. The main advantages are that it is capable of quickly analyzing droplet-based reactions repeatedly without channels being clogged, and that is can easily be cleaned and reused many times. These benefits are important in regions where access to expensive supporting devices that drive traditional microfluidic devices are not able to be procured or powered.
The later chapters detailing the development of microfluidic sandstone devices show great promise of becoming a desired tool for testing and development of new and customized EOR fluids for particular wells. The ability to easily mimic the scale, geometry and localized variations of oil field conditions can greatly reduce the time and cost over current testing methods. Further, we present a shear-thickening fluid capable of surpassing current commercial additives designed to thicken at representative shear rates present in these devices. This formulation is particularly suited for EOR: shear-thinning behavior is extremely important to make the initial well injection process require less effort, because of the extreme transition from small to large shear rates as the fluid enters the oil field. By creating a fluid that shear-thins, and only thickens at a targeted field-centric shear rate, this, and similar engineered fluids show great promise in recovering much more oil from both untapped and oil fields in use.

Further development of this platform would allow for simulation of water-wet rock. Our efforts in this work demonstrated the difficulty in making a water-wet device out of optical adhesive, which would have allowed for high output device fabrication. An alternative for this would be creating devices from glass. The material, facility, and financial costs of this method would be slightly higher, but it would result in access to wettability ranges in the hydrophilic and superhydrophilic ranges. For these devices, there are locally high aspect ratios that would need to be highly resolved. For this reason, plasma etching would be the likely fabrication method. This would allow for a wider range of oil field geometries and wettabilities to be replicated in the lab to quick testing to be performed on existing and new EOR fluids.
In summary, this work presents advanced in two different areas: development and characterization of a two-dimensional digital microfluidic device, and the development of both microfluidic sandstone platforms and shear-thickening fluids that outperform current commercial additives. Both of these advances manipulate multiphase flows to achieve new and improved functionality and can serve as a basis for further technological and biological development and improvements.
APPENDIX

PHOTOLITHOGRAPHY, SOFT LITHOGRAPHY, AND WETTABILITY MODIFICATION

Microfluidic Device Fabrication

The origins of microfluidic devices are closely tied with the development of MEMS in the 1980’s. As a result, the microchannels of the first generation of microfluidic device were created by etching glass or silicon. It became apparent that an alternative method would be required as the existing method had many drawbacks: the fabrication technique was costly and time-consuming; each new device would require the entire fabrication process be repeated which necessitated excessive clean room use, and the silicon wafers are not optically transparent which prohibits visual inspection of the process in question. As a result, the methods used currently involve the use of elastomers to achieve rapid prototyping. This is achieved by making a master negative of the desired pattern on a hard substrate, and then curing the elastomer on the pattern and peeling it off (Duffy, McDonald et al. 1998; McDonald, Duffy et al. 2000; McDonald and Whitesides 2002). Using this method, it is possible to create multiple devices from the same master, greatly increasing research productivity and minimizing the time spent in a clean room. The entire process consists of photolithography to create the negative master in a silicon wafer, using PDMS to make a mold off of the master, and then sealing the device. These steps will be explained in greater detail in the subsequent sections.
Photolithography

Photolithography is a process by which light is used to selectively remove regions of a layer of light-sensitive substrates. It is now the popular method by which to create patterns on silicon wafers for use as a master for microfluidic devices (Madou 2002). This process begins with the development of a mask of the pattern that is desired to be either transferred to the photo-resist layer. This mask is typically made from a thin chrome layer or from ink on a transparency. The advantage of a chrome mask is that it allows for resolution down to sub-micron length scales. However, chrome masks are expensive to make in both time and cost. Alternatively, ink on transparency masks only allow for resolution down to 10 microns, but are made much more quickly and the cost is significantly less. For most microfluidic applications, 10 microns is sufficient enough to resolve all aspects of the device. Additionally, the reduction in time for creating new masks allows for multiple iterations on a design pattern that is commonplace for research new ideas or concepts (McDonald, Duffy et al. 2000).

With a mask prepared, it is loaded into a device designed to expose a substrate to UV-light. The substrate in this case would be a silicon wafer with a thin layer of photosensitive material on it. The photolithography process is shown in Figure 54. When the UV light is on, only the transparent sections of the mask allow this light to pass through and onto the photo-resist layer. The rest of the photo-resist layer will remain unexposed. The photo-resist layer can be of two types: positive resist, or negative resist. In a positive resist material, exposed material would be removed in a later development process, and unexposed material would remain adhered to the surface. In the case of a negative resist layer, materials exposed to UV light remain after development, and unexposed material
would be removed during development. After the development process, the remaining adhered photo-resist pattern and silicon substrate are ready to use as a master for the soft-lithography process explained later.

**Photo-resist**

The photo resist that is used in our lab is SU-8 by the Microchem Corporation. It is a negative resist, such that any exposed section remains on the silicon wafer, and area prevented from receiving UV light by the mask will be removed during development. This yields a durable master negative from which many molds may be cast using a softer material such as polymers. The main methods of failure after creating a master with SU-8 are the SU-8 de-adhering from the silicon wafer, or damage caused by the user either to the wafer or the SU-8 (Anderson, Chiu et al. 2000).

SU-8 comes in a variety of formulations, each designed with a particular spin thickness to be targeted. The general technique for all the formulations is similar: spin coat the SU-8 onto the silicon wafer at a speed that will result in the desired layer thickness, soft bake the coated wafer to remove many of the solvents in the SU-8, exposed the wafer to ultraviolet light to cross-link the SU-8 where desired, post-bake the wafer for complete removal of the solvents, and finally develop the wafer with PGMEA which removes any unexposed SU-8. For a specific example, suppose a 200 µm layer of SU-8 is desired on a wafer. For this thickness, SU-2100 is the appropriate SU-8 composition. After applying a liberal amount to the silicon wafer, it is spun at 500 rpm for 10 seconds, then 1500 rpm for 30 seconds. Following the spinning, the wafer is soft baked at 65°C for 5 minutes, then at 95°C for 25 minutes. The reason for the two bake
temperatures is to allow the SU-8 to heat up gradually, without which small cracks would form in the SU-8. At the higher temperatures with SU-8 coatings thicker than 100 µm an oven is recommended for the 95°C bake because on a hot plate in a fume hood, convection would cause uneven heating throughout the SU-8 which can also result in cracking or other undesirable effects. After the soft bake, the wafer is cooled and then exposed with the UV light for an amount of time that yields 300 mJ/cm² of energy imparted, which is generally 35 seconds, however this time can vary based off of the age of the bulb and the thickness of the SU-8. The wafer is then post-baked at 65°C for 5 minutes and then 95°C for 20 minutes, removing any remaining solvents. The wafer is subsequently cooled and then submerged in the PGMEA developer. The developer is then manually agitated for 20 minutes or until all excess SU-8 is removed. The wafer is then cleaned with isopropyl alcohol and is ready for the soft-lithography process.

**Soft Lithography**

The SU-8 master allows for rapid prototyping, because many devices can be made after only one clean room session, which is the most time-consuming part of the process. The process by which devices are made from the silicon-SU-8 master is soft lithography, which is presented visually in Figure 55.

The polymer used for this process is poly(dimethyl)siloxane. There are two primary ways to use PDMS to create fully enclosed PDMS devices, both of which use the same primary process to create a mold from the SU-8 master. To begin, the wafer is first placed in a Petri dish. The PDMS base is mixed with the associated curing agent in a 10:1 ratio. For a fresh 3” silicon wafer, approximately 35-40 grams of the PDMS base is
required to allow for a device of sufficient thickness to reduce swell when flow is applied. After thoroughly mixing the base and curing agent mixture, it is poured onto the wafer, and then placed in the vacuum chamber to remove any bubble from the pouring and reaction process, about 20 minutes. The wafer is then placed in an oven at 60°C for 50-60 minutes. On days with less humidity, 50 minutes will suffice, whereas with higher humidity, 60 minutes may be required. After baking, the device can be carefully removed by using a sharp knife to cut around the desired device and carefully peeling the device off of the wafer and from the surrounding PDMS. Inlet/outlet holes are then punched through with a 20 gauge blunt tipped needle attached to a syringe filled with air. After punching through the device, the syringe is depressed, ejecting the PDMS plug from the syringe tip. The needle is then slowly retracted from the device, being careful to support the device during this retraction near the needle base, as the elasticity of the PDMS can be exceeded during this process with would cause tearing. After all ports have been created, tape is applied to the side that will be sealed in order to remove any dust or other particulates that may have accumulated on the surface. It is important to note that cleanliness is of utmost importance during the entire process, as even the smallest contamination can result in device or adhesion failure.

In order to seal the top half which is the negative of the SU-8/wafer master, two approaches have been taken: a PDMS mismatch method, or using a corona bonding method (McDonald and Whitesides 2002; Haubert, Drier et al. 2006). The PDMS mismatch method involves spin-coating cleaned glass slides with degassed PDMS that has been made using a 5:1 ration of base to curing agent. The coated slides are then placed in the 60º oven for 50-60 minutes, dependent on humidity. After the bake, the
slides are removed, and the mold created above is pressed onto the slide. The assembly is then returned to the 60°C oven for a minimum of 8 hours, more generally overnight. The bond is formed as a result of the abundance of the curing agent in the PDMS on the slide. It creates a bond that is as strong as the internal PDMS bonds in the bulk material (McDonald and Whitesides 2002). The main advantage of spin coating the glass slide is that it allows for the device channels to be completely encased by PDMS, so there is no wettability variation.

The corona bonding method more recently used in our lab also requires a glass slide with a thin layer deposited on it through spin coating. With this method, the PDMS for the glass slide is made using a 10:1 ratio of the base to the curing agent. The slide and the top mold should be fully cured overnight. The slide and the mold, bonding sides up, should be placed on a non-conducting surface in a fume hood. Using the hand-held corona treater (model BD-20AC with power-line filter, Electro-Technic, Products Inc), the corona is passed repeatedly over both the slide and the bonding side of the mold. The wire from the corona treater should be approximately ¼ inch above the surface being treated, and total treatment time is about 30 seconds per surface. After such time, the two parts are pressed together. After about 1 hour, they are solidly affixed, and even more so if left overnight. This process also increases wettability of the PDMS, temporarily causing it to become extremely hydrophilic. However, the wettability recovers to its original value after about 2 hours (Haubert, Drier et al. 2006).

Other methods have been performed in the literature (McDonald, Duffy et al. 2000), however they are more time consuming and have large facility and equipment requirements. Additionally, our lab has had limited success with them.
Poly(dimethyl)-Siloxane

Poly(dimethyl)-siloxane is a very popular choice for the polymer involved in the soft-lithography step of the rapid-prototyping process. PDMS has many characteristics that make it an ideal candidate for use in microfluidics. It is optically transparent allowing for either laser or traditional illumination often for high speed videography, it is air permeable allowing for degassing of experiments where the presence of air or air bubbles is detrimental, and it is also biologically inert (Makamba, Kim et al. 2003). Additionally, it polymerizes are relatively low temperatures, it molds easily to small features, and is elastic enough to be safely removed from the master without damaging the SU-8 on the master or the newly formed mold (McDonald and Whitesides 2002).

PDMS has a fixed wettability which is naturally hydrophobic. This leads to challenges of performing experiments in which varying wettability is desired. Also, performing oil-in-water experiments is extremely difficult, as the PDMS is naturally oil-wet and not water-wet. However, there are methods by which to modify the wettability of PDMS, covered in the subsequent section. Furthermore, the PDMS can swell if in contact with strong organic solvents.

Wetting Characteristics and Modification

PDMS has an average contact angle of 109° with water in air, making it hydrophobic (Hu, Ren et al. 2002). In microfluidic devices, it is generally desired to perform experiments with decreased wettability. The obvious solution would be to change the material that is being used for the substrate to one that is hydrophilic. This can challenge the rapid prototyping goal, as making devices out of a material such as
glass, which can be superhydrophilic requires the complete device making process to be performed each time. A more recent study has shown is it possible to combine the rapid prototyping concept with micro-pattern stickers in order to produce devices with identical size capabilities of the PDMS method in a device that is naturally hydrophilic (Bartolo, Degre et al. 2008; Wagli, Homsy et al. 2011). They used Norland Optical Adhesive (NOA-81) for a second lithography stage, a process detailed in Figure 56 in which the PDMS serves as the master from which multiple devices can be made. With the NOA in place in the PDMS mold, the UV-sensitive NOA is exposed to UV light and is cured; resulting is a solid negative of the PDMS master. The NOA is very similar to the PDMS in its optical transparency and it is biologically inert (Bartolo, Degre et al. 2008; Wagli, Homsy et al. 2011). Furthermore is has a higher elastic modulus (Bartolo, Degre et al. 2008) allowing for thinner devices which minimizing swell from pressure variations, and it also is more resistant to swelling to solvents than PDMS (Cygan, Cabral et al. 2005).

There are also ways of modifying the wettability of PDMS directly, such as exposure to oxygen plasma or UV radiation, plasma treatment, deposition of a surfactant layer, and radiation-induced graft polymerization. Exposure to oxygen plasma is a method to both alter the wettability of PDMS and also to bond the PDMS, however the bond strength is limited, and experience in our lab has shown little success with using this method to successfully withstand flows in microfluidic devices. However, the exposure does temporarily cause the PDMS to become hydrophilic (Makamba, Kim et al. 2003) which can then be reversed with exposure to air or heat, recovering its native wettability (Hu, Ren et al. 2002).
Both the methods of exposing PDMS to corona discharge or UV radiation alter the wettability of the PDMS by oxidizing the surface. This can be used to bond the PDMS together as described above (Haubert, Drier et al. 2006). Both methods result in the creation of silicon oxide, the depth of which is dependent on the exposure time and generally range from 7 – 160 nm. At the longer exposure times, the wettability can become superhydrophilic, with advancing and receding contact angles of \( \theta_a / \theta_r = 28^\circ / 21^\circ \) (Hillborg, Tomczak et al. 2004). This range is superhydrophilic with minimal contact angle hysteresis. However, with this method, the wettability is eventually recovered to its original state over time.

The approach of UV induced graft polymerization aims to create a permanent change of wettability of the PDMS. While similar to previous methods where the PDMS is exposed to UV light, this methods requires the PDMS submerged in a polymeric solution while being exposed to the UV radiation (Hu, Ren et al. 2004). The most stable and successful polymer additive was acrylic acid in a mixture of \( \text{NAIO}_4 \) and benzyl alcohol (0.5mM and 0.5wt% concentrations respectively). With the addition of acrylic acid, the PDMS possessed contact angles of 45° with water in air. This method can also be used in enclosed PDMS devices, even to selective patterning of areas of mixed wettability (Hu, Ren et al. 2004; Fidalgo, Abell et al. 2007; Wang, Nguyen et al. 2007).
Figure 54: A pictorial representation of the process of photolithography with potential outcomes dependent on the type of SU-8 photoresist used.
Figure 55: A pictorial representation of the soft lithography and device fabrication process.
Figure 56: A pictorial representation of the softlithography technique for device fabrication using NOA-81.
BIBLIOGRAPHY


