PRECISION ROTATIONAL RHEOMETRY

BY

MICHAEL T. JOHNSTON

THESIS

Submitted in partial fulfillment of the requirements
for the degree of Master of Science in Mechanical Engineering
in the Graduate College of the
University of Illinois at Urbana-Champaign, 2013

Urbana, Illinois

Adviser:

Professor Randy H. Ewoldt
Abstract

For rotational rheometers, alignment of rotating surfaces is of prime importance in conducting accurate, reproducible measurements. A custom glass bottom surface has been designed and fabricated that has $< 1 \, \mu m$ of planar misalignment with respect to the instrument axis of rotation. This also enables visualization of samples from below and precise alignment of custom top plates that are attached to a standard geometry by a temperature sensitive adhesive. The glass bottom plate has enabled research in two areas: (i) surface tension effects on torque measurement and (ii) effects of microtextured surfaces on shear stress under gap controlled conditions.

Surface tension results in a torque that should not occur in an ideal, rotationally-symmetric geometry. This work identifies and explains the effect, which is due to surface tension and contact line traction forces. The surface tension torque is reduced by maximizing rotational symmetry of the contact line, minimizing evaporation and the migration of the contact line, reducing the radial location of the contact line, and lowering the surface tension. Identifying and eliminating the surface tension torque is critical for low viscosities, intrinsic viscosities, soft materials, sub-dominant viscoelastic components, small gaps, and any circumstance where the low-torque limit is experimentally important.

1 Partially adapted from the authors' work; Johnston M.T. Ewoldt R.H, “Precision rheometry: Surface tension effects on low-torque measurements in rotational rheometers,” J. Rheology (2013)
Microtextured surfaces, or deterministic placement of μm scale surface asperities, have been shown to reduce shear stress in hydrodynamic systems by reducing surface shear forces and by producing lift to support a hydrodynamic film. We have developed a triborheometric setup that enables precise control of the gap in order to explore the effect of microtextures on shear stress. We have also correctly non-dimensionalized the system and validated it with numerical results. Results show that the reduction in shear stress is larger than numerical results predict.
# Table of Contents

1. Introduction ............................................................................................................. 1

2. Transparent Bottom-Plate ....................................................................................... 4
   2.1 Objective ............................................................................................................... 5
   2.2 Design .................................................................................................................. 6
   2.3 Validation of Alignment ....................................................................................... 9
   2.4 Example Images .................................................................................................. 11

3. Surface Tension ......................................................................................................... 14
   3.1 Introduction ......................................................................................................... 15
   3.2 Mathematical Model ............................................................................................ 16
   3.3 Experimental Setup and Methods ....................................................................... 23
   3.4 Experimental Results and Discussion ................................................................. 27
   3.5 Conclusions ......................................................................................................... 43

4. Microtextured Plates ................................................................................................. 46
   4.1 Introduction & Background .................................................................................. 46
   4.2 Dimensional Analysis ......................................................................................... 49
   4.3 Experimental Methods ....................................................................................... 58
   4.4 Results and Discussion ....................................................................................... 63
   4.5 Conclusions ......................................................................................................... 72

5. Conclusions ............................................................................................................... 73

References .................................................................................................................... 75
Chapter 1

1. Introduction

Rheology is the study of material flow and rheometry is the means by which materials are experimentally probed. This work presents various methodologies and measurements where precise control of a rheology experimental setup is used. The way we define a fluid's properties is by material functions and the way we mathematically model this behavior is through constitutive models. The simplest constitutive model is a Newtonian fluid,

\[ \sigma = \eta \dot{\gamma} \]  

(1.1)

where shear stress, \( \sigma \), is linearly proportional to shear rate, \( \dot{\gamma} \), by a constant. This constant is known as viscosity, \( \eta \). We can also define the material function steady-shear viscosity

\[ \eta(\dot{\gamma}) = \frac{\sigma}{\dot{\gamma}} \]  

(1.2)

If \( \eta \) is constant we recover the constitutive equation for a Newtonian fluid. There are a range of material functions that describe material responses including viscoelastic and normal force responses [1]. In this work only steady-shear viscosity is measured while various precise methods of rheological measurements are explored. The methods are aimed at addressing non-ideal experimental artifacts that are present in Figure 1.1, primarily those due to system misalignment in planar Couette flow. How the various non-ideal artifacts affect measurements will be explored in more detail in the following chapters.
Chapter 2 describes the design of a transparent bottom-plate for optical access of rheological measurements. A glass bottom-plate was developed that allows a full-field optical view of the sample. The system can be aligned to less than 1 μm of planar misalignment to the axis of rotation. This precision alignment is better than commercially available components and fundamentally enables the small-gap testing of microtextured surfaces in Chapter 4.

Chapter 3 shows experimentally and theoretically, for the first time, that surface tension can produce torque. A mathematical model and experimental measurements show that asymmetries in the contact line and contact angle produce what appears as a constant torque independent of rate. The value of the torque is non-deterministic and appears as apparent shear-thinning. Guidelines for avoiding artifacts are provided, in order to increase the experimental range of measurement for low-viscosity fluids, such as wafer-based systems.
Figure 1.1 Ideally, shear rheological properties are defined from stress $\sigma_{12}$ and strain rate $\dot{\gamma}(t)$ or strain $\gamma(t)$ in homogeneous simple shear. In reality, loads and displacements are measured at boundaries and non-ideal experimental artifacts must be considered.

Chapter 4 shows gap controlled normal force measurements of microtextured surfaces. Novel measurement techniques were developed, along with the precision aligned transparent bottom-plate described in Chapter 2, to eliminate experimental noise and explore how the design of microtextures effects hydrodynamic lubrication. We show that microtextures reduce torque and produce a normal force that would not be present with flat surfaces.
Chapter 2

2. Transparent Bottom-Plate

Visualization of samples during testing is generally not possible with off the shelf rheometers. Along with this, non-ideal experimental variations due to misalignments that are present in state-of-the-art systems make accurate experimental measures at small gaps not possible. A need to visualize and perform small gap rheological measurements is present for the current course of experimentation. Therefore, a transparent bottom-plate with sub-micron alignment was designed and fabricated to meet these needs Figure 2.1.

(a)  
(b)

Figure 2.1: (a) State-of-the-art setup with temperature controlled Peltier bottom-plate (b) Newly-designed and built transparent bottom-plate with room for optics
The design and fabrication of the transparent bottom-plate was completed in two steps. Initially the functional requirements did not include small gap measurement capabilities, e.g. $< 100 \ \mu m$. The experimental setup was later developed to be functionally accurate at small gaps. To be concise, the design process will be presented as though both steps were completed concurrently.

### 2.1 Objective

In general, state-of-the-art (SOA) experimental setups do not have the ability to visualize samples while loaded in the rheometer (Figure 2.1a). Visualization of samples is beneficial in several ways. For quality control, one can observe possible air bubbles or other non-desirable sample loading artifacts that would otherwise go undetected. Also, setups such as microscopes, high-speed and still-frame cameras, and gap measurement systems can be used to take images and perform analysis such as particle image velocimetry (PIV). The bottom-plate was chosen as the transparent surface, as opposed to the top plate, because it is the stationary plate.

Along with visualization of samples the transparent-bottom plate must be accurate for measurements at gaps $H < 100 \ \mu m$. This means that the plate must meet a flatness tolerance and be well aligned to the axis-of-rotation. Good alignment ensures that torque measurements are accurate due to the gap being constant radially and rotationally. Alignment also affects normal force measurements. If the gap is not constant, then normal forces due to hydrodynamic effects can develop [2]. By choosing the bottom-plate as the transparent surface, if designed appropriately, it can be manually aligned without need for high manufacturing precision of the entire assembly.
2.2 Design

From the objectives a list of functional requirements was developed:

2.2.1: visualization of the sample;
2.2.2: minimize compliance of bottom-plate under load;
2.2.3: minimize misalignment of bottom-plate to axis of rotation.

2.2.1 Visualization

A transparent bottom-plate is necessary for visualizing the sample. This limits the material to glass or plastic. Since microscopes and other optical setups will be used with the bottom plate, the superior optical qualities of glass make it a better choice than plastic. Glass has better light transmittance and is much harder, therefore it will wear better.

Considerations of the other functional requirements of alignment and compliance also make glass a superior choice. Glass has a much higher modulus than plastic, 50-400 GPa > 100-900 MPa, and can operate at varying temperatures with relatively little change in mechanical properties. Optical grade glass is also very flat and this ensures constant gap-height.

When taking into account the need for microscope access, which requires close proximity, the thickness of the plate should be as thin as possible. A well-established thickness of ~ 1 mm for microscope slides is a good design goal. However, when taking into account compliance due to load, the glass should be thick enough to meet maximum deflection requirements. This is considered in 2.2.2.
2.2.2 Compliance

Under testing the bottom plate could undergo up to 50 N of force (max force of normal force transducer) but typically this value will be less than 10 N. Maintaining a constant, known gap is important and therefore compliance will be important. This would dictate that the glass should be as thick as possible. A design criteria of < 1 μm of deflection under a 10 N load was used. This ensures that gap heights of down to 10 μm can be used with less than 10 % error.

To estimate the amount of deflection present in the system, Roark’s Formulas for Stress and Strain [3] was used. Our glass is circular with a clamped edge support. The max deflection, $y_{\text{max}}$, corresponds to Case 17 in Table 11.2

$$y_{\text{max}} = -\frac{Wa^2}{16\pi D} \quad (2.1)$$

where $W$ is load (dimensions of force), $a$ is effective radius, and $D$ is the plate constant defined as

$$D = \frac{Et^3}{12(1-\nu^2)} \quad (2.2)$$

where $E$ is Young’s modulus, $t$ is plate thickness, and $\nu$ is Poisson’s ratio.

Using the properties of quartz glass, $E = 72$ GPa, and our design goal of < 1 μm deflection under a 10 N normal load, the glass plate must be $t = 0.15$ in. thick. If sapphire glass is used, $E = 345$ GPa, the plate thickness only needs to be $t = 0.10$ in. thick. We choose glass $t = 0.1875$ in. for our design.
2.2.3 Alignment

Alignment of the bottom plate is a primary consideration. Figure 2.2 shows how rheological measurement systems will always have finite misalignments and offset error in knowing the gap. Typically the apparent gap height $H_a$ is much larger than gap-offset error $\varepsilon$ and planar misalignment $\alpha$, $H_a >> \varepsilon$ and $H_a >> \alpha$. In such a case misalignment and offset error can be neglected. In our system we desire to test at gaps that are as small as possible and these system misalignments must be taken into account.

Planar misalignment $\alpha$ can lead to torque and normal force measurement errors. Torque errors result from a non-constant gap, and an average gap that is larger than the apparent gap, $H_a$. Normal force errors come from hydrodynamic forces similar to thrust bearings, which would not occur with perfectly parallel plates aligned with the axis of rotation.

Gap-offset error $\varepsilon$ is always present in the system due to squeeze flow in the gap zeroing procedure. If $\alpha = 0$, then gap-offset error $\varepsilon$ more predictably lines up with squeeze flow theory [4].
A plane is defined by three points. With reducing planar misalignment a primary goal, the support structure was designed with three posts. The support assembly is made up of three main components: a bottom coupling to the rheometer, three riser posts and a top coupling to the glass plate. Riser posts can be removed easily and replaced with posts of different lengths, as necessary to provide optical access below or instrument range of motion above. The top coupling must be adjustable and high-thread count screws were used to attach it to the supporting post. Aluminum was chosen as the material for the supporting structure because of its machinability and lower weight than steel.

2.3 Validation of Alignment

Validation of the transparent bottom-plate is important to verify design and manufacturing quality. Figure 2.3 shows the technique used to align and measure the misalignment and non-uniformity of the glass to the axis of rotation. A jeweled dial indicator is attached to the axis of rotation using a custom fabricated coupling. The spindle is rotated and the deflection at each support structure is measured.
Adjustments are made until all three are equal. The dial indicator is jeweled at 1 μm increments with a needle width of approximately 200 nm. Thus, 200 nm is the effective resolution of the indicator.

Figure 2.3: Measurement technique using a dial indicator to align the transparent bottom-plate to the instrument axis of rotation. Screws are used to adjust height of the bottom-plate.

Table 1 shows the measured value of the manufacturer provided bottom-plate (Figure 2.1a) and the custom bottom-plate peak-to-peak misalignment. The peak-to-peak misalignment was measured over a full rotation of the dial indicator. These measurements were taken at \( R = 30 \) mm from the center of the plate. This is the radius of the largest geometry used. The misalignment measured for the manufacturer provided plate is ± 21.4 μm and for the custom transparent bottom-plate ± 0.10 μm. Measurement of the custom plate misalignment is limited by the dial indicator resolution. When aligning the glass to the axis-of-rotation, misalignment of the plate is minimized to the extent where the needle on the dial indicator does not move.
Table 1: Dial indicator alignment validation. Peak-to-peak misalignment at $R = 30\text{mm}$.

<table>
<thead>
<tr>
<th></th>
<th><strong>Vertical Deviation</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer provided bottom-plate (Peltier plate)</td>
<td>± 21.4 (\mu\text{m})</td>
</tr>
<tr>
<td>Custom transparent bottom-plate</td>
<td>± 0.10 (\mu\text{m})</td>
</tr>
</tbody>
</table>

### 2.4 Example Images

In this section, example images are shown for both local microscope imaging and full-field imaging of the full diameter of the measurement geometry. Figure 2.4 shows a full-field, bottom view of air bubbles in a loaded sample. The top plate geometry is black. The contact line is easily observed for the embedded air bubbles and the outer edge. Such visualization of the outer edge contact line will enable the surface tension research in Chapter 3. The capability of confirming sample integrity and proper fill of the geometry ensures accurate, precise experimental measurements.
Figure 2.4: (a) Bottom view of 40 mm plate with sample loaded. Air bubbles present from the loading procedure are present that would go undetected without a transparent bottom-plate. The sample contact line can also be seen. (b) Method for capturing bottom view still images of experimental test.

Figure 2.5 shows a digital microscope (Dino-Lite AD413ZTA Pro) image of a microtextured top-plate through the transparent bottom-plate. Microtextured surfaces have engineered asperities to induce hydrodynamic flow and are studied in Chapter 4. Microscopic imaging can be used for seeing boundary surfaces, as well as microstructure within fluid samples. At this length scale we are approaching the lower end of resolution of this particular digital microscope. Other optics could easily fit under the transparent plate which has a 4.5 in. clearance for situations needing higher resolution.
Figure 2.5: (a) Microtextured top-plate geometry viewed through transparent bottom-plate. Microtextures are approximately 200 μm wide and 50 μm deep. (b) There is room for a microscope underneath the glass surface. The microscope shown took the image at left.
Chapter 3

3. Surface Tension²

For rotational rheometers, surface tension results in a torque that should not occur in an ideal, rotationally-symmetric geometry. This work identifies and explains the effect, which is due to surface tension and contact line traction forces, and not surface rheology at the liquid-air interface. For water we show that this torque can be more than two orders of magnitude larger than the viscous torque. In steady shear flow, the effect appears as a constant torque independent of rate, which would appear inaccurately as apparent shear thinning of water. In oscillatory tests this may appear inaccurately as an elastic modulus. This surface tension torque is sensitive to wetting conditions and contact line asymmetries and cannot be deterministically corrected in experimental measurements. It therefore raises the lower bound of the instrument low-torque limit. The surface tension torque is reduced by maximizing rotational symmetry of the contact line, minimizing evaporation and the migration of the contact line, reducing the radial location of the contact line, and lowering the surface tension. Identifying and eliminating the surface tension torque is critical for low viscosities, intrinsic viscosities, soft materials, sub-dominant viscoelastic components, small gaps, and any circumstance where the low-torque limit is experimentally important.

² Adapted from the authors’ work; Johnston M.T, Ewoldt R.H, “Precision rheometry: Surface tension effects on low-torque measurements in rotational rheometers,” J. Rheology (2013)
3.1 Introduction

Surface tension should not produce a torque in rotational rheometers, based on the idealized assumption of rotational symmetry. Historically, rotational symmetry has been a primary assumption [1], [5], even when considering effects of surface tension [6], [7]. However, we will show that the rotational symmetry assumption can be violated easily. Finite deviations of contact line rotational symmetry allow surface tension to produce a torque which impacts measurements of shear rheological material functions. The effect causes Newtonian fluids, including water, to appear as shear-thinning with finite elastic modulus.

It is known that normal force is influenced by surface tension effects, by both traction line force and pressure changes across a curved free surface [8], [9]. Normal forces are dependent on the shape of the free surface [10] and corrections have been calculated for certain experimental conditions.

Torque in rotational rheometers is influenced by certain edge effects and non-ideal conditions, and some of these effects have been carefully documented. Interfacial rheology and resistance to shear at the free surface can contribute to torque and apparent shear thinning and elasticity [11], [12], although this requires surface active components at the liquid-air interface. This surface rheology phenomena is not present in our study. Excess sample can also contribute to torque measurements [7], [13]. In the study by Kalika et al., an excess torque offset of ~10% was observed after squeeze flow, and decreased to zero with time. This does not occur in our study here, and we therefore attribute the observed excess torque to a different phenomenon.
Here we demonstrate a new concept, that surface tension itself, via contact line traction forces, can produce torque in rotational rheometers. We observe surface tension torque up to \( \sim 1 \, \mu\text{N.m} \) for water in steady shear with various standard geometries. This is approximately two orders of magnitude larger than expected viscous torque at low shear rates. For oscillatory experiments at 100% shear strain, we observe elastic surface tension torque of \( \sim 1 \, \mu\text{N.m} \), corresponding to an apparent storage modulus \( G' \). These observed values are highly variable due to sample loading and contact line symmetry, but the origin of the surface tension torque can be explained with a mathematical model.

### 3.2 Mathematical Model

Figure 3.1 shows the geometries used here and how the orientation and location of the free surface varies. One can intuit how the loading method or small changes in sample volume, especially at small gaps with parallel plates, can further change the shape and location of the free surface.
Figure 3.1: Configuration of rotational flow geometries used in this study (cross-section views, not to scale). Torque is measured at the top cylindrical shaft in each case. The free surface contacts the measuring geometry at an angle \( \Psi(s) \) with respect to the horizontal, where contact line forces pull tangent to the interface.

Contact line forces pull tangent to the liquid-air interface. The free surface contacts the measuring geometry at an angle \( \Psi(s) \), defined here with respect to the horizontal inside the closed curve of the contact line. We define the interface angle \( \Psi(s) \) with respect to the horizontal, rather than using the contact angle with respect to the local solid surface, in order to derive a universal predictive equation for different geometries. For an underfilled parallel plate geometry, the interface angle \( \Psi \) is equivalent to the contact angle \( \theta \); for other geometries \( \Psi \) and \( \theta \) are related by the local orientation of the solid surface, and this will depend on the geometry and the possibility of overfilling, even for a parallel plate.

For any geometry in Figure 3.1, if a geometry and sample have perfect rotational symmetry about the axis, then the resulting surface tension torque is zero, since traction force vectors would pass through the axis of rotation. In our experiments, we do observe a torque and hypothesize that this is due to (i) contact line asymmetry and (ii) interface angle asymmetry. These non-ideal conditions are shown in Figure 3.2. Contact line asymmetry can arise from finite manufacturing tolerances, sample
overfill, sample underfill, or evaporation-induced contact line migration. Note that interface angle hysteresis occurs only during movement of the geometry. This is why no rotational drift occurs when the geometry is not manipulated by the rheometer.

Figure 3.2: Contact line and interface angle; ideal versus non-ideal. Non-ideal asymmetries are exaggerated compared to typical loading and can also occur as a result of over filling.

The torque due to broken symmetry of the contact line can be calculated by considering an arbitrary closed, parametric curve, \( \mathbf{r}(s) \), as shown in Figure 3.3. This closed curve represents the fluid-solid contact line, assumed to be in the plane \( z = 0 \). Any deviation in the vertical location \( z \neq 0 \) could be considered as an additional secondary aspect, as this is not necessarily required to generate the torque.

Contact line forces pull along the liquid-air interface defined by \( \Psi(s) \), and act perpendicular to the contact line. We consider the possibility of changes along the arclength, including variable radius \( \mathbf{r}(s) \), surface tension \( \Gamma(s) \), and interface angle represented by \( \Psi(s) \). While variable surface tension is unlikely, it is possible in the presence of thermal gradients or surfactant concentration gradients.
We define an orthogonal local coordinate system \( (\hat{l}_t, \hat{s}_t, \hat{n}) \) to analyze this scenario (Figure 3.3). The unit vector tangent to the contact line is denoted \( \hat{l}_t \). The unit tangent in the surface direction, the direction of contact line force, is \( \hat{s}_t \), defined as tangent to the liquid-air interface defined by \( \Psi(s) \) and normal to \( \hat{l}_t \). The vector \( \hat{n} \) completes the system, defined by \( \hat{n} \equiv \hat{l}_s \times \hat{l}_t \).

![Diagram of contact line in z=0 plane](image)

\( \Psi(s) \)

Figure 3.3: Contact line in \( z=0 \) plane represented by an arbitrary parametric curve, \( r(s) \)

The unit normal and two unit tangents form an orthogonal basis set that can be represented in Cartesian or polar coordinates, e.g. for \( \hat{n} \)

\[
\hat{n} = n_r \hat{e}_r + n_\theta \hat{e}_\theta + n_z \hat{e}_z \quad (3.1)
\]

\[
\hat{n} = n_x \hat{e}_x + n_y \hat{e}_y + n_z \hat{e}_z \quad . \quad (3.2)
\]
Torque about the origin, $\mathbf{T}$, due to surface tension line forces, $\mathbf{F}$, can be found by integrating along the closed parametric curve

$$
\mathbf{T} = \oint \mathbf{r}(s) \times d\mathbf{F}
$$

(3.3)

where $\mathbf{r}(s)$ locates the contact line with respect to the origin. We are only interested in the $z$-component of torque and Eq.(3.3) becomes

$$
T_z = \int \mathbf{r}(s) d\mathbf{F}_\theta.
$$

(3.4)

The contact line force acts in the direction of $\mathbf{\hat{l}}_s$, calculated by

$$
\mathbf{\hat{l}}_s = \mathbf{\hat{l}}_n \times \mathbf{\hat{n}}.
$$

(3.5)

Therefore the force vector acting on a line segment $ds$ is

$$
d\mathbf{F} = \Gamma(s) ds \mathbf{\hat{l}}_s.
$$

(3.6)

where $\Gamma(s)$ is the local surface tension, $\Gamma \equiv [\frac{\mathbf{F}}{\ell}]$, i.e. dimensions of force per unit length. From Eq.(3.4), only $F_\theta$ is relevant which is calculated as

$$
dF_\theta = \mathbf{\hat{e}}_\theta \cdot d\mathbf{F}.
$$

(3.7)

Combining Eq.(3.5) - (3.7),

$$
dF_\theta = \Gamma(s) \left[ \mathbf{\hat{n}}_z(s) \mathbf{\hat{l}}_{x,z}(s) - \mathbf{\hat{n}}_z(s) \mathbf{\hat{l}}_{x,z}(s) \right] ds
$$

$$
= -\Gamma(s) \mathbf{\hat{n}}_z(s) \mathbf{\hat{l}}_{x,z}(s) ds
$$

(3.8)

where $\mathbf{\hat{l}}_{x,z} = 0$ was used, from the assumption that the line is in the $z = 0$ plane.

From Figure 3.3 we can see that $\mathbf{\hat{n}}_z = -\cos(\psi(s))$ and Eq.(3.8) simplifies further to

$$
dF_\theta = \Gamma(s) \cos(\psi(s)) \mathbf{\hat{l}}_{x,z}(s) ds.
$$

(3.9)
Combining Eq.(3.9) and Eq.(3.4) gives the main analytical result for torque caused by surface tension,

\[ T_z = \oint \Gamma(s) r(s) \cos(\psi(s)) \hat{t}_{lr}(s) ds . \]  

(3.10)

Let us consider the implications of Eq.(3.10). For the commonly-assumed axisymmetric case that \( r(s) = \text{constant} \), we have a circle and the r-component of the line tangent is zero, \( \hat{t}_{lr}(s) = 0 \) always. Therefore the surface tension torque \( T_z = 0 \) for a concentric circle contact line, even for varying interface angle \( \psi(s) \) or surface tension \( \Gamma(s) \). This defines the ideal case for rotational rheometry, that the contact line is pinned on a perfect circle. In this case, all surface tension forces are directed through the center of rotation, and therefore surface tension torque \( T_z = 0 \). We note that if \( \Gamma(s) \) is non-constant, then finite Marangoni flows will occur that may produce a torque. In our experiments \( \Gamma(s) = \text{constant} \) and Marangoni torques are not a consideration.

From Eq.(3.10), torque is generated only when \( \hat{t}_{lr}(s) \neq 0 \) somewhere along the curve (radial deviations from a concentric circle). We will now show that this is a necessary but insufficient condition. The additional criteria is that either interface angle or surface tension must be non-constant to generate a torque. Consider the case with interface angle \( \Psi(s) = \text{constant} \) and surface tension \( \Gamma(s) = \text{constant} \). For this special case, Eq.(3.10) becomes

\[ T_z = \Gamma \cos \psi \oint r(s) \hat{t}_{lr}(s) ds . \]  

(3.11)

The term \( \hat{t}_{lr}(s) \) is related to deviations of the contact line in the r-direction. It is related to differential changes in the radial location as
dr = \mathbf{i}_{t,r}(s) ds \quad \text{(3.12)}

Substituting this into Eq.\,(3.11),

\[ T_z = \Gamma \cos \psi \oint C r(s) dr. \quad \text{(3.13)} \]

For a closed arbitrary curve, the integral will always be zero, since

\[ \int_{s=a}^{s=b} r(s) dr = \int_{s=a}^{s=b} r(s) \frac{dr}{ds} ds \]
\[ = \frac{1}{2} r(s)^2 \bigg|_{s=a}^{s=b} \]
\[ = 0 \quad \text{(3.14)} \]

for \( r(a) = r(b) \) to complete a closed curve. Thus, the torque from surface tension will be zero even for very complex contact line shapes \( r(s) \), if the surface tension and local interface angle are constant along the arclength. This proves that surface tension torque requires a non-constant surface tension, or non-constant interface angle, which is more likely. A varying interface angle may arise, for example, from advancing and receding contact angles at different portions of a contact line with deviations in the \( r \)-direction.

The precise shape of \( r(s) \) and values of \( \Psi(s) \) are not likely to be deterministic. Eq.(3.10) does predict that surface tension torque will increase with large contact line radius, large radial deviations, large surface tension, surface tangents oriented horizontally, and large deviations of the interface angle. We will show experimentally that the measured surface tension torque is highly sensitive to the volumetric filling and control of the contact line. This includes overfilling and underfilling (e.g. with either excess or insufficient fluid to fill the geometry gap). Evaporation is particularly
problematic when it causes a receding contact line. Decreasing surface tension helps reduce the effect, but only if evaporation is controlled. Even with best practices in place, the effects of surface tension torque can set the lower limit of the minimum torque accessible for rheological characterization.

3.3 Experimental Setup and Methods

Experiments are performed on a rotational rheometer with a single-head, combined motor-transducer (Discovery Series Hybrid Rheometer (DHR), model HR-3, TA Instruments). This instrument has a manufacturer-stated low-torque limit of 5nN.m in steady shear and 0.5 nN.m in oscillation. A variety of geometries were used, as shown in Figure 3.1 and defined in Table 2.

The system temperature was set to 25°C, unless otherwise noted, for all calibrations and tests using the Peltier control systems (bottom plate or outer cylindrical boundary, depending on the geometry used). Room temperature of approximately 23°C was used for tests using the glass bottom plate. A plastic shield was used during all calibrations and tests to block air drafts. To ensure negligible viscous heating, we calculate the Nahme-Griffith number at the highest velocities. The Nahme-Griffith number can be interpreted as relative change in viscosity due to temperature rise

\[ Na = \frac{\Delta \eta}{\eta} \sim \frac{\dot{\gamma} \Delta T}{\eta} \]  \hspace{1cm} (3.15)

where \( \eta \) is viscosity and \( T \) is temperature. The steady temperature rise \( \Delta T \) comes from a balance of viscous heating and conduction, \( \sigma \dot{\gamma} V \sim \kappa \frac{\partial T}{\partial x} A \), where \( \sigma \) is shear stress, \( \dot{\gamma} \) is shear rate, \( V \) is volume of fluid, \( \kappa \) is thermal conductivity, \( x \) is length
scale, and $A$ is area. The length scale of importance is the geometry gap, $h$, and if we assume a Newtonian fluid this becomes $\eta \dot{\gamma}^2 Ah \sim \kappa \frac{\Delta T}{h} A$. Solving for $\Delta T$ with top plate velocity $U = \dot{\gamma} h$, $\Delta T \approx \frac{\eta \dot{\gamma}^2}{\kappa}$. Combining this with Eq. (3.15) gives [1]

$$Na = \frac{\partial \eta}{\partial T} \frac{U^2}{\kappa}.$$  \ (3.16)

For both distilled water and n-Decane, $Na \sim 10^{-6}$ at the highest velocities tested and therefore viscosity changes due to shear heating are negligible.

Visualization of contact line profiles was achieved with a custom-fabricated glass bottom plate, shown schematically in Figure 3.4. The plate is used with experiments involving the cone or plate upper geometries. This setup has the advantage of allowing visualization of samples from below, even during the use of a solvent trap. The glass bottom plate is readily adjusted using high thread count screws and a 1µm increment dial indicator to ensure perpendicular alignment of the glass to the instrument axis of rotation. We have successfully adjusted the glass bottom plate to sub-micron alignment. That is, deviation from a perfectly perpendicular plane to the instrument axis of rotation to any point on the glass plate is less than ±0.5µm. Temperature is not controlled when using the glass bottom plate.
Figure 3.4: Custom glass bottom plate. Photos were taken using the mirror to visualize the sample and contact line from below.

Table 2: Measurement geometry details (cf. Figure 3.1)

<table>
<thead>
<tr>
<th>Geometry Name</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 mm steel (St) cone</td>
<td>Diameter, $D = 60$ mm, angle 0.49°</td>
</tr>
<tr>
<td></td>
<td>Truncation gap: 14.0 μm</td>
</tr>
<tr>
<td>40 mm aluminum (Al) plate</td>
<td>$D = 40$ mm; operating gap: 400 μm</td>
</tr>
<tr>
<td>20 mm Al plate</td>
<td>$D = 20$ mm; operating gap: 400 μm</td>
</tr>
<tr>
<td>Concentric Cylinders, Single Gap (DIN Standard)</td>
<td>Rotor diameter: 27.98mm; length: 42.2mm</td>
</tr>
<tr>
<td></td>
<td>Cup diameter: 30.35mm</td>
</tr>
<tr>
<td></td>
<td>Operating gap: 5912.87mm</td>
</tr>
<tr>
<td></td>
<td>$C_L = 1.10^*$</td>
</tr>
<tr>
<td>Concentric Cylinders, Double Gap</td>
<td>Inner cup: 30.19mm; rotor: 31.93mm</td>
</tr>
<tr>
<td></td>
<td>Outer rotor: 35.02mm; cup: 37.03mm</td>
</tr>
<tr>
<td></td>
<td>Immersed height: 53.01mm</td>
</tr>
<tr>
<td></td>
<td>$C_L = 1.027^*$</td>
</tr>
</tbody>
</table>

*The parameter $C_L$ is the end effect coefficient and is defined by $\eta_{\text{apparent}} = \eta_{\text{measured}} / C_L$ due to excess liquid beyond the shear region (Figure 3.1).

The fluids used are distilled water and n-Decane (Canon Instrument Company, N1.0 Viscosity Standard). These fluids have comparable viscosity, but n-Decane has a lower surface tension by a factor of about three. The viscosity of water at temperatures of 25°C, 23°C, and 5°C is 0.891, 0.933, and 1.52 mPa.s respectively and the viscosity of n-Decane at 5°C is 1.17 mPa.s. The surface tension of water and n-Decane at 5°C is 75.0 mN/m [14] and 25.3 [15] respectively.
Sample volumes were precisely controlled. For the cone-plate and plate-plate geometries the optimal sample volumes were determined by eye with the use of a micropipette. Once ideal fill volume was determined for a given geometry this value was used consistently throughout a set of data. The Single Gap (SG) sample volume was 22.371 mL and Double Gap (DG) was 11.252 mL. These volumes were calculated according to the geometry dimensions in Table 2. The solvent trap was used with all samples except when indicated in the discussion of results.

Calibrations included rotational mapping, which precisely measures the internal frictional torque in the system as a function of angular position (software option set to precision 2 or 3 iterations). Steady shear flow experiments were completed with controlled angular velocity from \( \Omega = 3.98 \cdot 10^{-3} \text{ rad/s} - 3.98 \text{ rad/s} \). Torque and velocity values were averaged over integer rotations of the geometry with a minimum of one rotation at each velocity. For the smallest velocity the total rotation period is \( t = 2\pi/\Omega = 1,579 \text{ seconds or approximately 26 minutes} \). Each sample was tested using a flow peak hold test with a three to thirty second pre-shear depending on the velocity. A five minute temperature soak was used for the single and double gap geometries prior to testing.

Residual torque tests, with no sample loaded, were also performed in order to measure residual internal friction and air friction contributions to the torque. These tests were completed with the geometries 45 mm above the peltier plate or 85 mm above the peltier cup zero position. The end-effect factor \( C_L \) (Table 2) was not used in residual torque results.
3.4 Experimental Results and Discussion

Figure 3.5 shows steady shear velocity sweeps down to or below the stated low-torque limit with various planar and cylindrical Couette flow devices. Shown are torque versus angular velocity curves compared with the instrument low-torque limit of 5 nN.m. Each data set has a minimum of six runs (new sample loading for each run) with three runs from high to low velocity (ramp down) and three from low to high (ramp up). These tests use current best practices, as described in the methods section. We observe a torque plateau for all geometries, except the Single Gap (SG). The torque plateaus are on the order of 10 to 100 nN.m, well above the instrument low torque limit.

For steady shear flow we can use a simple equation to show how the observed torque appears as a plateau superposed onto a Newtonian viscous response,

\[ T = A + B \cdot \Omega. \]  
(3.17)

We have fit Eq.(3.17) to several data sets in Figure 3.5. For the ramp down values for the 20mm plate, we see the torque plateau ranging from \( A = 3.49 - 11.1 \text{nN.m} \), demonstrating non-deterministic variability. The maximum plateau for the double gap (DG) geometry is \( A = 103 \text{nN.m} \), which is well above the low-torque limit of the instrument.

If we compare the torque plateaus of the three planar Couette geometries (the cone and the plates), we see a positive correlation between torque plateau and geometry radius. This is what we would expect if surface tension was acting as a traction force at a given radius. The average torque plateau for the 20mm plate, 40mm plate and 60mm cone are respectively 6.79 nN.m, 8.69 nN.m, and 42.1 nN.m. While the difference between the 20mm and 40mm plates is very small and within
experimental error, we believe that the torque plateau for the 20mm plate is higher than expected (and with high variance) as a result of evaporation and contact line migration. Notably, the solvent trap does not have a seal for this geometry, unlike the larger plates and cone geometries. We know from visual observations that evaporation was an issue for the 20mm plate. The effect of evaporation can also be observed if we look at the ramp down velocity sweeps versus the ramp up velocity sweeps. The ramp down values have an average plateau of 9.36 nN.m versus the ramp up average of 4.21 nN.m. When ramping velocity from high to low there is more time for evaporation to occur before reaching the low torque regime than when ramping from low to high where we begin in the low torque regime.
Figure 3.5: Steady shear flow of water with various geometries (described in Table 2). Torque plateaus appear at low velocities. This effect is due to surface tension, and could be mistaken as shear-thinning of viscosity. Torque plateau fit lines are Eq. (3.17); for lines (1)-(4) the fit parameters are $A = 11.1, 7.78, 3.49, 103$ and $B = 22.8, 22.6, 24.3, 3427$, respectively.

The average DG torque plateau is 52.2 nN.m where the SG is 6.23 nN.m. Some important distinctions between the DG and SG exist. First, the contact line of the SG is well above the shear region while the contact line for the DG is in the shear region. This affects interface angle hysteresis and asymmetry that may depend on velocity. Second, the free surface is at a larger radius for the DG, 16-18mm, than for the SG, approximately 4mm. We can see these differences clearly in Figure 3.1 and is consistent with the prediction that surface tension torque should increase with larger
radius and larger perimeter of the contact line (all other deviations being comparable), from Eq. (3.10).

Comparing the DG and 60mm cone torque plateaus we see they are of the same order, 52.2 nN.m and 42.1 nN.m respectively, with the DG being larger even though the free surface is at a smaller radius. This is because the DG geometry has two free surfaces, the inner and the outer, while the 60mm cone has one.

We now perform a multitude of experiments to test the hypothesis that surface tension forces produce the observed torque plateaus in Figure 3.5. We will measure residual internal friction of the instrument, reduce surface tension while holding other factors constant, and deliberately break the rotational symmetry of the contact line both by overfilling (with local out-wetting) and underfilling (with deliberate underfill and evaporation-induced underfill). All observations are consistent with the hypothesis of extra torque due to surface tension line forces. In steady shear, the effects appear incorrectly as viscous shear-thinning. We will then show that surface tension line forces can also generate an elastic torque signal in oscillatory tests, producing an apparent elastic modulus $G'$.

To ensure the torque plateaus in Figure 3.5 are not from internal friction or experimental noise, we performed measurements with no fluid, which we call residual torque tests. Shown in Figure 3.6 are residual torque tests with no sample, with and without a geometry attached to the rotating spindle. The data fits a linear viscous scaling very well which is the common method used by the instrument manufacturer to correct for velocity-dependent residual torque. To indicate precision of the measurement, dashed lines are shown in Figure 3.6 at two standard deviations from the linear fit, at ±1.4 nN.m and ±1.5 nN.m. These uncertainties are less than
the manufacturer specified low-torque limit of 5nN.m. In Figure 3.6a, because no geometry is loaded, the standard deviation of the linear fit can be viewed as the instrument experimental uncertainty. After the 40mm plate is loaded, Figure 3.6b, the residual torque increases but the deviation stays approximately the same. From this data we can see that torque plateaus on the order of 10 to 100 nN.m observed in Figure 3.5 cannot be explained by low-torque limits of the instrument.

![Figure 3.6](image)

Figure 3.6: Residual torque values with (a) no geometry and (b) D=40mm plate using integer rotations at each velocity. A separate rotational mapping of precise, three iterations was completed for each velocity sweep. Also shown are a linear fit with two standard deviation uncertainty. (values for lines in Table 3)

Manual residual torque tests were completed for various geometries loaded, but no fluid sample. Table 3 shows the linear fit and two standard deviation values for no geometry, planar Couette flow geometries ranging from 8 to 60mm diameters, and cylindrical Couette flow geometries. This linear fit we will call the friction factor, $F_f$, and is defined by

$$ T = T_{raw} - F_f \Omega $$

(3.18)
where $T_{raw}$ is uncorrected torque, $T$ is torque used to calculate material functions, and $\Omega$ is angular velocity. $T$ is the torque reported in our results, unless stated otherwise. The variation in the friction factor, $F_f$, can be explained by ambient air friction due to differences in surface area and radial extent of the geometries.

Table 3: Friction factor, $F_f$, of various geometries with the $2\sigma$ deviation

<table>
<thead>
<tr>
<th>Geometry</th>
<th>$F_f$ Linear</th>
<th>Two Standard Deviations ($2\sigma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[µN.m (rad/s)]</td>
<td>nN.m</td>
</tr>
<tr>
<td>No geometry</td>
<td>0.281</td>
<td>1.40</td>
</tr>
<tr>
<td>8mm Plate</td>
<td>0.284</td>
<td>0.702</td>
</tr>
<tr>
<td>20mm Cone</td>
<td>0.282</td>
<td>0.645</td>
</tr>
<tr>
<td>40mm Cone</td>
<td>0.284</td>
<td>1.49</td>
</tr>
<tr>
<td>60mm Cone</td>
<td>0.294</td>
<td>3.00</td>
</tr>
<tr>
<td>Single Gap Cylinder</td>
<td>0.287</td>
<td>2.75</td>
</tr>
<tr>
<td>Double Gap Cylinder</td>
<td>0.291</td>
<td>5.33</td>
</tr>
</tbody>
</table>

Reducing surface tension should reduce the torque plateaus in steady shear as predicted by Eq.(3.10). In Figure 3.7 we see two sets of velocity sweep data showing torque with distilled water (H$_2$O), and n-Decane (comparable viscosity, but with surface tension lower by a factor of three). We have performed these tests using the double gap (DG) geometry at a temperature of $5^\circ$C in order to reduce evaporation effects. Lowering surface tension should lower the observed torque plateau in two ways. First, it lowers any total effect because forces are directly proportional to surface tension. Secondly, low surface tension means the n-Decane is highly wetting, making the interface angle more vertical in this geometry (Figure 3.1) and also less variable. From Eq. (3.10), all of these aspects should reduce the torque due to surface tension.
In Figure 3.7 there are six data sets, with separate loading, for each fluid tested. For water we see high variability, presumably due to lack of determinism in the contact line. While some of the velocity sweeps for water do not display a torque plateau down to the terminal velocity, there are four sweeps that give torque plateaus of approximately 1 μN.m. Conversely, the n-Decane velocity sweeps show no torque plateau and are highly reproducible using the same sample loading techniques. The variation among sweeps is so small that the six data sets are almost coincident for n-Decane.

![Graph showing steady shear flow with different surface tension (water and n-Decane) using the Double Gap (DG) geometry. Six data sets are shown for each fluid, which appear coincident for the n-Decane. Temperature was set to 5°C to decrease saturated vapor pressure and evaporation effects. Viscosity as measured; surface tension from Claussen (1967) and Jasper et al. (1953).](image)

Rotational asymmetry of the contact line is required for surface tension torque, according to Eq.(3.10). For standard geometries, this may occur due to the finite
precision and roughness at the edge of the geometry, and/or lack of deterministic contact line pinning. Rotational asymmetries can be deliberately exaggerated, and if they are concomitant with variable interface angle, then low-velocity torque plateaus should increase. We test this prediction by breaking the rotational symmetry in multiple ways: overfill by discrete droplet inclusion at the edge, deliberate underfill, and evaporation-induced underfill.

Droplet inclusion increases the low-velocity torque plateau, as shown in Figure 3.8a, which appears as apparent shear-thinning in Figure 3.8b. As we increase the number of 10μL droplets from zero to one to three, we see the torque plateau increase from an average of 8.69 to 85.9 to 294 nN.m. If surface tension were not the source of these torque plateaus, we would simply observe a vertical shift in the constant viscosity line due to excess material at the edge.
Figure 3.8: Torque plateaus and apparent shear-thinning from droplet inclusions on the free surface of a $D=40$mm plate. Inset lines (view from below) indicate droplet contact lines with glass bottom plate. Room temperature $\approx 23^\circ$C.
Under-filling the fluid can also cause contact line asymmetry, and should therefore increase the surface tension torque effect. As seen in the inset image of Figure 3.9, by placing the initial sample volume off-centered a significant asymmetry can be achieved. Intuitively, underfill of a geometry should give a lower torque than normal, but this is not what we observe; the underfill gives a significant torque increase in the form of a superposed plateau torque.

In Figure 3.9, the three ramp up underfill tests at low velocity give torque and viscosity measurements more than two orders of magnitude larger than the expected viscous measurement. Yet, the underfill is visually quite small. For three separate loadings of underfill (ramp up) the initial low-velocity torque is similar, $T \approx 1 \mu N.m$. As velocity increases from $\Omega=10^{-2}$ to $\Omega=10^{-1}$ rad/s the torque values drop. This slight decrease is due to the self-centering of the sample as the geometry rotates, but the surface tension torque is still prominent. With each successive rotation the torque drops until $\Omega=0.04$ rad/s. At this point we see the typical torque plateau. Now if we focus on the three ramp down underfill tests, we see that the initial torque values at $\Omega=4$ rad/s are higher than for the ramp up tests. This is due to the sample being more asymmetric for the ramp down tests than for the ramp up, at this velocity. In other words, the ramp up tests have had time to self-center whereas the ramp down tests have not.
Figure 3.9: Torque plateau and apparent shear-thinning for $D=40\text{mm}$ plate with normal sample fill and sample underfill. Three data sets, with separate loading for each condition. Normal sample volume is $525\mu\text{L}$ and underfill sample volume is $475\mu\text{L}$. Tested at room temperature $\approx 23^\circ\text{C}$.
Evaporation induces underfill and lack of deterministic contact line pinning, and is therefore another mechanism where contact line asymmetries can occur. Time lapse images of evaporation-induced underfill are shown in Figure 3.10. Torque was measured over an extended period of 45 minutes. The photos in Figure 3.10 show the initial over-filled sample. As evaporation occurs, the torque decreases until it remains fairly constant (300-400 sec.) with the sample pinned on the edge of the geometry achieving maximum rotational symmetry and minimum surface tension torque. The sample volume then receded enough that the contact line de-pinned and a larger torque of \( \sim 25 \text{ nN.m} \) developed (600-800 sec). Torque then again remained fairly constant until another contact line de-pinning event (1600 sec) raised the torque to \( \sim 80 \text{ nN.m} \). These observations are consistent with the prediction of Eq.(3.10) that contact line asymmetries correlate with surface tension torque.
Figure 3.10: Evaporation-induced contact line migration causes surface tension torque. The geometry is a parallel plate (diameter 40mm) with constant velocity $\Omega = 0.01$ rad/s. Images show the evolution of the contact line. Expected viscous torque is 5.98 nN.m. Tested at room temperature $\approx 23^\circ$C. Sample volume initially 525 $\mu$L.

Oscillatory measurements of viscoelastic moduli can also be strongly influenced by surface tension torque. Frequency sweeps were performed with water using a 60mm diameter cone at 100% shear strain amplitude from a frequency of 0.1 to 10 rad/s. Three sweeps were performed, one with intentional underfill and two close to ideal fills using best practices. Figure 3.11a shows the results of these experiments along with bottom view images of the geometry after the sample has been loaded.

An apparent elastic modulus $G'$ can be observed for water, due to the surface tension torque. The values are highly variable, ranging from a plateau of $10^{-2}$ Pa for the underfill to a plateau of $10^{-3}$ for the 495$\mu$L sample. What is extraordinary about the results is that by reducing sample volume by only 5$\mu$L, from 495$\mu$L to
490µL, the elastic modulus $G'$ becomes sub-dominant as we would expect for water. Although this effect could be in part or whole a result of sample loading variability, this speaks to the high sensitivity to sample volume and loading. The pipette has a manufacturer stated precision of ±1µL.

Figure 3.11a also shows the low-torque limit in terms of $G'$ and $G^*$, identified as

$$G'_\text{min} = T_{\text{min}} F_\sigma / \gamma_0$$

$$G^*_\text{min} = T_{\text{min}} F_\sigma / \gamma_0$$

(3.19)

where $T_{\text{min}}$ is the low-torque limit in oscillation $T_{\text{min}} = 0.5$ nN.m, $\gamma_0$ is the strain amplitude, and $F_\sigma$ is the stress factor $F_\sigma = 17,680$ Pa/N.m for the 60mm cone. The stress factor relates stress to torque as $\sigma = F_\sigma T$. For a cone geometry the stress factor is

$$F_f = \frac{12}{\pi D^3}$$

(3.20)

where $D$ is the geometry diameter.

The surface tension effect, when present, produces apparent elastic modulus $G'$ values up to three orders of magnitude larger than the low torque limit. The dynamic viscous component, $G''(\omega)$ in Figure 3.11a, restated as $\eta'(\omega)$ in Figure 3.11b, is also influenced by the surface tension torque effect. This is most clear in Figure 3.11b. At the ideal fill of 490µL, $\eta'$ is constant, and consistent with the viscosity of water, $\eta' = 0.933$mPa.s. In contrast, the overfilled and underfilled tests show $\eta'(\omega)$ decreasing with frequency, a type of apparent viscous-thinning behavior, which we attribute to the surface tension artifact.
Notably, some recent studies have reported shear elasticity of water, glycerol, and other liquids at low frequency [16]–[18] using rotational rheometers. These studies make striking claims about solid-like elastic behavior of these simple liquids at low frequency. It is unclear at present if surface tension torque was properly managed in these studies.
Figure 3.11: Oscillatory shear test of $\text{H}_2\text{O}$ with a $D=60\text{mm}$ steel cone. Also shown is an image of the underfill sample load from below. White line indicates underfilled region. The 495$\mu\text{L}$ and 490$\mu\text{L}$ volume samples had no visual underfill or overfill. Strain $= 100\%$. 
Figure 3.12: Apparent shear viscosity of water for 40mm plate and SG geometries (data re-plotted from Figure 3.5 in terms of apparent shear viscosity). The observed data shows apparent shear thinning that results from surface tension torque plateaus seen in Figure 3.5 for the 40mm plate.

3.5 Conclusions

This work is the first to identify and explain an important surface tension phenomenon in rotational rheometers. Surface tension can produce a torque more than two orders of magnitude larger than the torque due to material deformation. We have shown that surface tension can apply a torque on rotational rheometers that in steady shear typically appears as a constant torque independent of rate. This signature appears inaccurately as shear thinning of viscosity, as shown in Figure 3.12 (data re-plotted from Figure 3.1). It also appears inaccurately as an apparent yield stress if the torque plateau is constant as a function of shear rate, e.g. with underfill of the $D=40$ mm parallel plate (Figure 3.9), the torque plateau of $1 \mu$N.m would
appear as an apparent yield stress of water $\sigma_y = 0.08$ mm. In oscillatory tests, the surface tension torque causes a signature of both shear-thinning of dynamic viscosity $\eta'(\omega)$ and the incorrect appearance of an elastic shear modulus $G'(\omega)$ plateau. Increasing the contact line asymmetry produces a larger torque plateau whether it is by contact line local outwetting or under filling.

A mathematical model is derived to explain the source of this surface tension torque: rotational asymmetry of the contact line with non-constant interface angle or non-constant surface tension around the contact line. Since the surface tension torque is sensitive to wetting conditions and contact line asymmetries, it cannot be deterministically corrected in typical experimental measurements. It therefore raises the lower bound of the instrument low-torque limit, and it may help explain studies showing a practical low-torque limit 20 times larger than that stated by the equipment manufacturer [19]–[21].

The results here raise an important question for any low-velocity or low-torque measurement of rheological properties. Striking observations have been reported for elastic shear modulus of water, glycerol, and other simple liquids at low frequency using rotational rheometers at small gaps [16]–[18]. The surface tension torque phenomenon described here serves as a competing hypothesis to explain such observations.

The surface tension torque is reduced by maximizing rotational symmetry of the contact line, minimizing evaporation and the migration of the contact line, reducing the radial location of the contact line, and lowering the surface tension. Control of the contact line depends on proper sample volume, which is especially important at small gaps as changes in sample volume can easily influence underfill or overfill. This
breaking of the contact line symmetry causes surface tension torque that is more important than variation in viscous torque due to sample volume changes. With these guiding principles for reducing the surface tension torque, the geometry in our study that best meets these requirements is the cylindrical single gap. When planar Couette geometries such as the parallel-plate and cone-plate geometries are necessary, we recommend precise control of the contact line, e.g. by matched diameter plates or surface treatment. For example, it has been shown that a 200\(\mu\)m wide hydrophobic strip applied with a graphite tip can pin the contact line at a given radius [22], and this may also be beneficial for minimizing surface tension torque.

Identifying and reducing the surface tension torque phenomenon is critical for rheological measurement for low viscosities, intrinsic viscosities, soft materials, sub-dominant viscoelastic components, small gaps, and any circumstance where the low-torque limit is experimentally relevant. These results also apply to interfacial rheometry including the double wall-ring geometry [23], even in the absence of surface active components, if the precise rotational symmetry is broken in the contact line location and surface orientation angle. Low-torque limits are especially important with low-frequency or terminal regime oscillatory tests, asymptotic nonlinearities [24]–[26], and low apparent yield stress fluids [27], [28]. We expect this phenomenon to be especially important in aqueous systems, including biological materials, due to the high surface tension of water.
Chapter 4

4. Microtextured Plates

Microtexturing of surfaces, or deterministic placement of \( \mu m \) scale surface asperities, has been shown to reduce friction and increase the film thickness of surfaces in lubricated dynamic contact. Numerical investigations have shown evidence of both inertial and viscous mechanisms for the hydrodynamic pressure. In this work we perform gap controlled measurements of a microtextured plate in shear. We use a rotational rheometer with system misalignments eliminated such that we can carefully control the gap. In part one we lay out the objectives of this work and review relevant research in the literature. Part two explains our non-dimensionalization of the problem, provides evidence of its accuracy and provides design reasoning for the microtextures. In part three we explain our experimental methods and the development of a triborheometer that is used to perform gap-controlled tribological experiments. Part four discusses the results of our work and finally, in part five, we provide conclusions.

4.1 Introduction & Background

Microtextured surfaces have been shown to reduce friction compared to flat plates both numerically [29]–[31] and experimentally [32], [33]. Multiple mechanisms have been suggested for this. First, in boundary or mixed lubrication, the contact area of the two surfaces is reduced, thus reducing friction and providing a source for lubricating fluids. In hydrodynamic lubrication, the larger gap at the location of the microtextures reduces the local shear rate. A second mechanism for friction
reduction is that microtextured surfaces produce a hydrodynamic pressure that can support a load and move the system from a mixed or boundary regime into a hydrodynamic regime.

Another mechanism by which microtextured surfaces reduce friction is super hydrophobic slip when the fluid is in a Cassie-Baxter wetting state [22], [34]–[36]. Microtextures trap air bubbles. This produces a slip boundary condition over the microtextured region and in turn reduces friction. Reduction of friction due to super hydrophobic slip is not our interest here. The present study is concerned with durable materials and applications where trapped air pockets are not likely to be maintained within the microtexture.

Experimentally, friction reduction has been observed by using a tribometer with constant normal force applied to samples. In a pin-on-disk configuration Ramesh et al. found that optimized microtextures can support a film with normal pressures of 4.0–8.1 MPa [33]. Qiu & Khonsari used a disk-on-disk configuration and found a reduction in friction compared to flat plates [32]. However, due to increased wear it appears a hydrodynamic film was not supported. The limit of the tribometer method is that the gap between the surfaces or film thickness, $H$, is not controlled or known. Therefore, there has been no systematic study of gap-dependent or Reynolds number dependent friction reduction with hydrodynamic lubrication and microtextured surfaces.

We have developed a custom glass bottom plate that has enabled the development of a gap-controlled triborheometer (Figure 4.1). A triborheometer is a rheometer developed to take tribological data by carefully eliminating small misalignments in the system that result in experimental errors. Normal force
controlled triborheometric measurements have been made and shown to provide accurate data [37]–[40]. To achieve gap control, we have eliminated planar misalignments, $\alpha$, and carefully controlled the gap or film thickness, $H$, in order to make constant gap measurements. Flatness of the plates is also considered and controlled.

This work aims to identify the correct dimensionless parameters, develop experimental capability of a triborheometer, and compare computational results with constant gap experiments for friction reduction due to microtextured surfaces.
Figure 4.1: (a) Our experimental setup uses a rotational rheometer where hydrodynamic pressure is produced from the microtextured plate as it rotates with angular velocity $\Omega$ and torque $T$. The resulting normal force $N$ is measured with a force rebalancing transducer. Cylindrical dimple microtextures of varying width and depth were designed using numerical analysis and fabricated onto flat plates. The gap or film thickness $H$ can be controlled with a resolution of 0.1 $\mu$m with parallelism $\leq 25$ nrad. For all microtextured geometries $R_i = 14$ mm and $R_o = 19.5$ mm. Microtextures are located in a radial band around the outside with microtexture width $W$ and periodic length $L$. The radial distance between each microtexture band is 500 $\mu$m. (b) Custom designed and fabricated glass bottom plate with custom plate attached to top plate. Angular misalignment $\alpha$ is controlled by the precisely aligned glass bottom plate. Radial alignment is controlled by manual application of force with radial alignment tools.

4.2 Dimensional Analysis

We have selected the microtexture dimensions for our experiments by a combination of numerical results and evidence from the literature. Two sources in the literature have experimental setups similar to ours but were completed using constant normal force tribometers in a pin-on-disk configuration [32] and a disk-on-
disk configuration [33]. We only consider cylindrical microtextures in a deterministic layout.

For our numerical setup we assume steady-state conditions and solve the 2D Navier-Stokes equations,

\[ \nabla \cdot \mathbf{u} = 0 \]  
\[ \rho (\mathbf{u} \cdot \nabla) \mathbf{u} = -\nabla p + \eta \nabla^2 \mathbf{u} \]

where \( \mathbf{u} \) is the velocity, \( \rho \) is the fluid density, \( \eta \) is the fluid viscosity and \( p \) is the pressure. We use the second-order upwind scheme for momentum discretization and the coupled scheme for the pressure discretization with a convergence criteria for all residuals of \( 10^{-7} \). The fluid is assumed to be isoviscous and constant density. The energy equation is not considered.

4.2.1 Dimensionless Parameters

Our model system is a 2D representation as shown in Figure 4.2. We assume no slip boundary conditions on the walls with periodic boundary conditions on the inlet and outlet. Cavitation is not considered. The two quantities we are interested in measuring are normal pressure on the top plate, \( P \), and shear stress on the top plate, \( T \). For a simple 2D case these measures are dependent upon the seven dimensional variables shown in Figure 4.2. This general relation is,

\[ \text{Measured Quantities} = (P, T) = f(H, L, D, W, \rho, \eta, U) \]

where \( H \) is the hydrodynamic film thickness, \( L \) is the periodic length of the cell, \( W \) is the width of the microtexture, \( D \) is the depth of the microtexture, \( U \) is the top plate velocity, \( \rho \) is the fluid density and \( \eta \) is the fluid dynamic viscosity.
Figure 4.2: There are seven dimensional variables used to define our model 2D microtexture with a Newtonian fluid. \( H \) is the hydrodynamic film thickness, \( L \) is the periodic length of the cell, \( W \) is the width of the microtexture (diameter of cylindrical microtextures), \( D \) is the depth of the microtexture, \( U \) is the top plate velocity, \( \rho \) is the fluid density and \( \eta \) is the fluid dynamic viscosity.

Using the Buckingham Pi Theorem results in four dimensionless variables which are shown in Table 4. \( D^* \equiv D/W \) and \( W^* \equiv W/L \) are defined by the microtexture while \( H^* \equiv D/H \) and \( \text{Re}_H \equiv \rho U D H / \eta \) are defined by the film thickness and fluid. Naturally the Reynolds number results defined in terms of \( H \), since this is well-defined in the limit of a flat plate. We did not choose \( H \) to normalize all length scales. Instead we chose a microtexture aspect ratio \( D^* \) and microtexture density \( W^* \) that follows previous work [30], [33], [41]. The third dimensionless length scale of importance is the microtexture gap ratio \( H^* \) defined as the ratio of the microtexture depth \( D \) to the film thickness \( H \). This results in four independent dimensionless variables that satisfy the Buckingham Pi Theorem.
Table 4: Four dimensionless variables that define the 2D numerical system. The aspect ratio $D^*$ and dimensionless density $W^*$ of each microtexture is independent of the gap thickness $H$. This leads to a framework of viewing $D^*$ and $W^*$ as part of the microtexture design while dimensionless gap $H^*$ and Reynolds number $Re_H$ are part of the operating conditions.

<table>
<thead>
<tr>
<th>Dimensionless Number</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D^* = \frac{D}{W}$</td>
<td>Microtexture Aspect Ratio</td>
</tr>
<tr>
<td>$W^* = \frac{W}{L}$</td>
<td>Microtexture Density</td>
</tr>
<tr>
<td>$H^* = \frac{D}{H}$</td>
<td>Microtexture Gap Ratio</td>
</tr>
<tr>
<td>$Re_H = \frac{\rho U H}{\eta}$</td>
<td>Reynolds Number $\sim$ inertial/viscous</td>
</tr>
</tbody>
</table>

The system degrees of freedom have now been reduced from seven to four. We also need to define the measured dimensionless pressure $P^*$ and shear stress $T^*$ which are dependent upon our four dimensionless variables,

$$(P^*, T^*) = \phi(Re_H, W^*, D^*, H^*).$$  \hspace{1cm} (4.4)

Shear stress is a viscously dominated quantity and we have chosen to non-dimensionalize by the expected Newtonian shear stress, $\tau_{21}$, with no microtexture present,

$$\tau_{21} = \eta \frac{du_i}{dx_2} = \eta \gamma = \eta \frac{U}{H}. \hspace{1cm} (4.5)$$

The resulting relation is,

$$T^* = \frac{T}{\eta U / H}. \hspace{1cm} (4.6)$$
\( T^* \cdot H/L \) has been previously used in literature and results from a linear combination of dimensionless variables \( D^*, W^* \) and \( H^* \) [29], [30].

It is not as clear how to appropriately non-dimensionalize normal pressure as the phenomena could be either viscously or inertially dominated [42]. Eq.(4.7) shows a viscous scaling with the chosen length scale as the periodic length \( L \).

\[
P_{v,L}^* = \frac{P}{\eta U / L}
\]

(4.7)

This length scale is not unique and any other in the system could be chosen. A viscous scaling with the chosen length scale as the film thickness \( H \) is,

\[
P_{v,H}^* = \frac{P}{\eta U / H}.
\]

(4.8)

However, because of the three independent dimensionless length groups we can relate the two dimensionless pressure scalings using a linear combination of the independent dimensionless variables,

\[
P_{v,H}^* = P_{v,L}^* \cdot \frac{H^*}{D^* W^*}.
\]

(4.9)

Dynamic pressure has been chosen as the inertial scaling for normal pressure,

\[
P_i^* = \frac{P}{\rho U^2}.
\]

(4.10)

Again, because of the use of the Buckingham Pi Theorem we can relate the inertial scaling to the viscous scalings through linear combinations of our independent dimensionless variables,
4.2.2 Validation of Dimensional Analysis

We have chosen to validate the non-dimensionalization of our system using FLUENT®, a well known CFD software, to solve the Navier-Stokes equations. If we have the correct dimensionless groups our system should only be sensitive to dimensionless variations. We have chosen arbitrary values for three microtextures (G1-G3) that have varying dimensional values but with geometric similarity. As can be seen in Table 5, the three dimensionless length groups are all equal.

Table 5: Designed microtexture geometry parameters for this work. G1-G3 are numerically tested to show the system has been non-dimensionalized correctly while G4-G7 are experimentally and numerically tested. The aspect ratio variation of the microtextures covers approximately two orders of magnitude. Variation in dimensionless texture density are much smaller.

<table>
<thead>
<tr>
<th></th>
<th>$D^*$</th>
<th>$W^*$</th>
<th>$D$ [μm]</th>
<th>$W$ [μm]</th>
<th>$L$ [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>0.1</td>
<td>0.5</td>
<td>10</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>G2</td>
<td>0.1</td>
<td>0.5</td>
<td>50</td>
<td>50</td>
<td>500</td>
</tr>
<tr>
<td>G3</td>
<td>0.1</td>
<td>0.5</td>
<td>100</td>
<td>100</td>
<td>1000</td>
</tr>
<tr>
<td>G4</td>
<td>0.25</td>
<td>0.5</td>
<td>50</td>
<td>200</td>
<td>400</td>
</tr>
<tr>
<td>G5</td>
<td>1</td>
<td>0.8</td>
<td>300</td>
<td>300</td>
<td>375</td>
</tr>
<tr>
<td>G6</td>
<td>0.23</td>
<td>0.8</td>
<td>70</td>
<td>300</td>
<td>375</td>
</tr>
<tr>
<td>G7</td>
<td>0.03</td>
<td>0.8</td>
<td>9</td>
<td>300</td>
<td>375</td>
</tr>
</tbody>
</table>

\[ P_i^* = \frac{P_{v,H}^*}{Re_H} = \frac{P_{v,L}^*}{Re_H} \frac{H^*}{D W^*}. \]
Figure 4.3 shows the numerical results of the three microtextures using FLUENT®. Normal pressure $P$ and shear stress $T$ vary over six orders of magnitude as velocity is increased from $10^{-2}$ to $10^2$ m/s. When the results are represented using the dimensionless measures $(T^*, P^*)$ they collapse onto one curve. Dimensionless shear stress $T^*$ shows almost no dependence on $Re_H$.

For the resulting non-zero average pressure on the top surface, $P$, it appears the inertial scaling is most appropriate for this particular design at $Re_H > 10^{-1}$. This is consistent with previous results [42] which show the importance of inertial effects and the need to use the full Navier-Stokes equations rather than the simplified Reynolds equation. There, inertial effects appear as a function of both $Re_H$ and $D^*$. 
Figure 4.3: Numerical verification of dimensional analysis using FLUENT®. (a) Dimensional plot showing average pressure and shear stress on moving flat boundary (Fig. 2) as a function of plate velocity $U$. Each microtexture geometry produces a different pressure and shear stress. Density $\rho = 1000$ kg/m$^3$ and viscosity $\eta = 1$ Pa.s was used. (b) The same results plotted as dimensionless groups showing shear stress and both forms of dimensionless pressure. The geometric dimensionless parameters ($H^*, D^*, W^*$) for all microtextures are equal and thus dimensionless pressure and torque at each $Re_H$ are equal.

4.2.3 Design of Experiment

Both published data and numerical models were used to design the microtextures tested. Figure 4.4 shows previous investigations in the literature with normal force controlled experiments (tribometer) [32], [33] compared with the current gap
controlled investigation (triborheometer). The \((D^*, W^*)\) plane represents both boundary, mixed and hydrodynamic lubrication where the film thickness \(H\) is unknown. This plane is independent of film thickness \(H\) and is only dependent on the microtexture geometry \((D, W, L)\). Our objective is to examine multiple \(D^*\) and \(W^*\) values to determine their dependence upon \(H^*\). Viewing the geometry design from this dimensionless perspective allows a simplified framework for future design of components.
Figure 4.4: The dimensionless domain experimentally explored by this work (red) compared to select previous experimental studies [32], [33]. Previous studies have not known or controlled the gap $H$. The $(D', W')$ plane defines where the gap is unknown and boundary, mixed or hydrodynamic lubrication is occurring. We are able to control the gap which enables a systematic exploration of the dimensionless gap $H^*$ and Reynolds number $Re_H$.

4.3 Experimental Methods

Experiments were performed on a single-head rotational rheometer [Discovery Series Hybrid Rheometer (DHR), model HR-3, TA Instruments]. The instrument has a manufacturer stated torque range of 5 nN.m to 200 mN.m, normal force range of 5 mN to 50 N and a maximum velocity of 300 rad/s. A custom bottom and 40 mm top plate were used for all tests unless otherwise indicated. The fluid used is a
highly refined mineral oil (Canon Instrument Company, S60 Viscosity Standard) with a viscosity $\eta = 123$ mPa.s at a temperature of 22°C. The thermal sensitivity at 22°C is $\frac{\partial \eta}{\partial \theta} = 6 \times 10^{-3}$ Pa.s/K.

4.3.1 Experimental Setup

Rotational rheometers have been used to perform constant normal force tribological measurements [37], [38]. We extend this method by performing gap controlled tribological measurements. The main challenge is to precisely control alignments and parallelism in the system. A custom transparent bottom plate has been fabricated to enable precision alignment of the rheometer plates (Figure 4.1). The tilt of the bottom plate is adjusted using high thread count screws at three support posts. A 1 μm increment dial indicator is used to verify alignment with respect to the axis of rotation as well as parallelism of the two plates.

For small gaps, the main error is caused by gap offset error $\varepsilon$, when the actual gap is larger than the calibrated value. The zero gap position is calibrated based on contact force at the first point of contact. Two issues arise. (i) A finite force is often observed before solid-solid contact due to viscous resistance of air flow in the squeezing gap [43], [44]. (ii) The parallelism is not perfect, and the average gap will often be larger than the “first point of contact” gap. Both of these effects contribute to gap offset error, so that the actual gap is larger than what the instrument thinks. The angular misalignment may also contribute to experimental measurements of normal forces, and this can be used to identify the relative importance of the two sources of gap offset error [45].
It is useful to define the various measures of gap we will refer to. In numerical results we have defined the gap $H$ previously (Figure 4.2). The apparent gap $H_a$ in experiments is that based on instrument zero-gap procedure. The corrected gap $H_c$ is the apparent gap plus gap errors resulting from the gap zeroing procedure $\varepsilon_{SF}$,

$$H_c = H_a + \varepsilon_{SF}.$$ (4.12)

### 4.3.2 Microtextured Plate

The microtextured plates are circular disks made of hardened stainless steel and were fabricated using electric discharge machining (EDM) with microtextures on one side. Due to being in a rotational frame the microtextures are in a radial band on a 40 mm diameter disk. This microtexture band extends from an inner radius $R_i = 14$ mm to an outer radius $R_o = 19.5$ mm (Figure 4.1). The radial spacing between each ring of microtextures is 500 $\mu$m.

Microtextured and flat plates are attached to the instrument by a thermally reversible adhesive compound (Crystalbond™). The parallelism alignment in the normal direction $\alpha$ (Figure 4.5) is controlled by self-alignment to the bottom plate while the alignment in the radial direction is controlled by hand tools. The standard 40 mm plate has a non-parallelism $\alpha \approx 2.5$ $\mu$m and radial misalignment $< 20$ $\mu$m. With our custom plate we are able to achieve parallelism $\alpha < 1$ $\mu$m and radial alignment $< 25$ $\mu$m.

To compare the 2D numerical result with our measurements we must carefully consider the method. We know that torque $M$ on a flat plate in a parallel rotating disk configuration, with constant viscosity $\eta$ is,
\[ M = \int_0^R 2\pi T(r)r^2 dr = \frac{\pi \eta \Omega}{2H} R^4 \]  

(4.13)

Where \( T(r) \) is the local shear stress and \( \Omega \) is rotational velocity. Our microtextured plates are patterned only in the region \( R_i < r < R_o \) and we must account for the modification of shear stress \( T(r) \) in the microtextured regions. This would result in the piecewise integral

\[ M = \int_0^R 2\pi T(r)r^2 dr + T^* \int_{R_i}^{R_o} 2\pi T(r)r^2 dr + \int_{R_o}^R 2\pi T(r)r^2 dr \]  

(4.14)

where \( R_i, R_o \) and \( R \) are defined in Figure 4.1 and \( T^* \) is our numerical result for dimensionless average shear stress, defined in Eq. (4.6), for a microtexture of a given \( D^*, W^* \) and \( H^* \). The velocity for each individual microtexture is not constant in our setup but numerical results show that \( T^* \) is nearly constant as a function of \( \text{Re}_H \) (Figure 4.3). We must make an assumption about \( T(r) \) for Newtonian fluids, \( T(r) = \eta \Omega r/H \) where \( r \) is the local radius.

Eq. (4.14) then simplifies to,

\[ M = \frac{\pi \eta \Omega R^4}{2H} \left[1 + (T^* - 1) \left(\frac{R_o^4 - R_i^4}{R_i^4}\right)\right]. \]  

(4.15)

The apparent viscosity for a parallel disk rheometry is defined as [46],

\[ \eta = \frac{M}{\pi \Omega R^4} = \eta_0 \left[1 + (T^* - 1) \left(\frac{R_o^4 - R_i^4}{R_i^4}\right)\right] \]  

(4.16)

where \( \eta_0 \) is for a known Newtonian viscosity.
4.3.3 Experimental Protocol

The glass bottom plate is aligned with high thread count screws. Each support post can be independently moved. Alignment is verified with a < 1 μm resolution dial indicator attached to the axis of rotation. The dial indicator can then be swept around the axis of rotation to measure a minimum and maximum deflection. This is what we report as the planar misalignment $\alpha$.

The custom top plate is attached to the standard top plate by heating the custom plate and applying a temperature sensitive adhesive on its top surface. The custom top plate is then placed onto the custom bottom plate and aligned beneath the standard top plate with hand alignment tools. These tools are two vertical line contacts that reduce the radial misalignment of the custom top plate. The standard top plate is then lowered into contact with the custom top plate until a normal force of 10 N is achieved. This is held until the adhesive has cooled.

Once cooled the alignment of the custom top plate is verified by the dial indicator. The displacement measurement tip of the dial indicator is placed beneath the edge of the custom top plate. The top plate is then lowered until it comes in contact with the dial indicator. The plate is then rotated with the rheometer controls and the resulting peak-to-peak deflection is the reported $\alpha$.

Microtextured surfaces have shown hydrophobic behavior known as the Cassie-Baxter wetting state. Prior to testing, the microtextured surfaces are pre-wetted by massaging the test fluid into the dimples to achieve the wetted Wenzel state [47].

With the custom bottom plate, temperature is not controlled. To ensure viscous heat does not build up, each data point is collected with only a two second pre-shear
to eliminate any start-up transient and a five second run time. Apparent viscosity $\eta_a$ is the average viscosity measurement over the test time.

### 4.4 Results and Discussion

We are concerned with accurately correcting for any gap errors in the system because this affects the shear stress measurements and Reynolds number calculation. We will first validate shear stress measurements in a flat plate system and then extend this methodology to microtextured plates. The viscosity of the sample fluid is known. We will present our results in terms of apparent viscosity $\eta_a$ and corrected apparent viscosity $\eta_c$ which is corrected for gap offset error due to squeeze flow $\varepsilon_{SF}$. This correction from $\eta_a$ to $\eta_c$ is performed by the following relation [43],

$$\eta_c = \eta_a \left(1 + \frac{\varepsilon_{SF}}{H_a}\right).$$

#### 4.4.1 Flat Plate Validation

The gap zero procedure entails lowering the top plate at a given velocity $\dot{H}$ until a predetermined normal force $N$ is achieved. This procedure is not ideal for small gap measurements as gap errors $\varepsilon \sim 10 \, \mu m$ can occur. Squeeze flow occurs and with perfectly aligned, parallel plates of finite radius $R$ where $R \gg H$ [48], the normal force is

$$N = \frac{3\eta_{air}\pi R^4 \dot{H}}{2H^3}$$

(4.18)
where $\eta_{\text{air}}$ is the viscosity of air. For our system $\dot{H} = 500$ $\mu$m.s$^{-1}$, $R = 20$ mm and the normal force criteria $N = 5$ N. Assuming $\eta_{\text{air}} = 1.4 \times 10^{-5}$ Pa.s then gap error due to squeeze flow $\varepsilon_{\text{SF}} = 9.1$ $\mu$m.

This squeeze flow gap error estimate is theoretical but in practice $\varepsilon$ has variations of approximately $3$ $\mu$m when $\alpha < 1$ $\mu$m. In Figure 4.5 the gap error for the standard plate $\varepsilon = 20.4$ $\mu$m is larger than the custom plate $\varepsilon = 12.6$ $\mu$m. This is due to elimination of misalignment $\alpha$ when the custom plate is attached. The custom plate data is also shown in its corrected form where it falls on the constant viscosity line. This validates the use of this correction method and enables us to confidently apply the technique to microtextured surfaces.
Figure 4.5: Gap offset error, \( \varepsilon \), causes gap-dependent apparent viscosity changes and is reduced when angular misalignent, \( \alpha \), is reduced. Correcting for \( \varepsilon \) shows no gap dependence with flat plates and Newtonian fluid. Fit line is Eq.(4.17) with \( \eta_c \) and \( \varepsilon \) as fitting parameters. Temperature = 25 C.

4.4.2 Microtextured Plate

Figure 4.6 shows the apparent viscosity data for all four geometries. Lines are also shown to connect points with either constant \( \Omega \) or constant \( \text{Re}_H \). The results show a significant decrease of raw apparent viscosity \( \eta_a \). This data is then corrected for gap error according to Eq.(4.17) using the squeeze flow value of \( \varepsilon_{SF} = 9.1 \, \mu m \) as shown in Figure 4.7. This not only increases the viscosity value (Eq.(4.16)) but also increases the gap (Eq.(4.12)), which shifts the data to the right. Cleary, gap offset error \( \varepsilon \) does not explain the decreased hydrodynamic friction seen with microtextures.
Figure 4.6: Uncorrected apparent viscosity, not corrected for gap offset error $\varepsilon$, of the four microtextured geometries (G4-G7). G4 is shown with constant viscosity lines while G5-G7 are shown with constant Reynolds number lines.

We want to compare our numerical and experimental results. Using our 2D numerical model, dimensionless shear stress $T^*$ was calculated, Eq.(4.6), for geometries G4-G7 at $H^* = 0.2, 0.5, 1, 2$ and 5 and $Re_H = 0.1, 0.215, 0.464, 1, 2.15, 4.64$ and 10 using the 2D model described in Section 4.2. As previously stated, $T^*$ showed almost no dependence upon $Re_H$. This gives shear stress predictions at five gaps for each geometry. The shear stress predictions $T^*$ are then used to calculate $\eta$ from numerical results using Eq.(4.16).
From Figure 4.7, comparing corrected apparent viscosity $\eta_c$ data with the numerical results shows that measured $\eta_c$ is lower than predicted for all geometries. G5 in particular shows a large reduction in shear stress over a wide range of gaps. At the smallest gap $H_c = 14.2 \, \mu m$ the corrected apparent viscosity $\eta_c = 30.4 \, mPa.s$ at $Re_{H} = 100$. This is approximately 75% lower than the sample fluid.

Geometries G4 and G6 have equal aspect ratios $D^* \approx 0.25$. However, G6 has a dimensionless density $W^* = 0.8$ greater than G4 of $W^* = 0.5$. Numerical results have shown decreasing shear stress with increasing texture density $W^*$ [30]. Our results are consistent with this trend as shown in Figure 4.7a and Figure 4.7c. As $H_c$ decreases, G6 decreases faster than G4. At $H_c = 20 \, \mu m$ $\eta_c \approx 85 \, mPa.s$ for G6 while $\eta_c \approx 95 \, mPa.s$ for G4.
Figure 4.7: Corrected apparent viscosity of the four microtextured geometries (G4-G7). G4 is shown with constant viscosity lines while G5-G7 are shown with constant Reynolds number lines. All geometries show a decrease in shear stress, or viscosity, as the gap decreases even when corrected for gap error $\varepsilon$. Sample fluid S60 has a viscosity $\eta_0 = 123$ mPa.s at a temperature $= 22^\circ$C.

Another pertinent comparison is among geometries G5, G6 and G7. All three geometries have $W^* = 0.8$ while $D^* = 1, 0.23$ and 0.03 respectively. From results in literature [33] we expect G5 to exhibit the lowest $\eta_c$ due to $D^* = 1$. Both experimentally (with a tribometer setup) and numerically it has been shown that $\eta_c$ decreases as $D^*$ increases [30], [33]. G5 does exhibit the lowest $\eta_c$ over the range of $H_c$ but G7 achieves almost the same $\eta_c$ lower gaps of $H_c \approx 10 \mu m$. This is lower than $\eta_c$ for G6 at approximately the same $H_c$. 
Our numerical results predict that $\eta_e$ is independent of $Re_H$. Our experimental results are consistent with that prediction except at $Re_H \geq 10$ at sufficiently small gaps. This indicates that the effect is actually dependent on $\Omega$. This is apparent in Figure 4.7a where $\Omega \geq 100$ rad/s exhibit lower $\eta_e$. Viscous heating could be occurring as $\Omega$ increases. The Nahme-Giffith number, $Na$, is the relative change in viscosity due to temperature rise [1],

$$Na = \frac{\partial \eta U^2}{\partial \theta \kappa}$$

(4.19)

where $\theta$ is temperature, $U$ is top plate velocity and $\kappa$ is thermal conductivity.

For S60 $\partial \eta / \partial \theta = 6 \times 10^{-3}$ Pa.s/K and $\kappa = 0.16$ W/(m.K). When $\Omega \geq 100$ rad/s the worst case at the edge of the plate gives $Na \geq 0.15$. This explains the $\Omega$-dependent decrease of $\eta_e$ in Figure 4.7a and can be interpreted as approximately a 15% decrease in $\eta_e$ from the low velocity limit due to viscous heating. This is consistent with our measurements. When $\Omega \leq 31.6$ rad/s, $Na \leq 0.015$ and no viscous heating effects contribute to decreasing $\eta_e$. The Nahme-Giffith number can also be interpreted as a function of $Re_H$.

$$Na = \left( \frac{\partial \eta \frac{1}{\kappa \rho^2}}{\partial \theta} \right) \frac{Re_H^2}{H^2}$$

(4.20)

This introduces a dependence on $H$ as well. Assuming a critical Nahme-Giffith number $Na_{crit} = 0.1$, at $Re_H = 1.68$ the gap where $Na = Na_{crit}$ is $H_{crit} = 123$ $\mu$m.

This is consistent with Figure 4.7a, Figure 4.7b, and Figure 4.7c.
For $\Omega \leq 10$ rad/s and $Re_\mu \leq 1.67 \times 10^{-2}$, viscous heating is negligible. There are other possible explanations for why the decrease in $\eta_c$ is greater than that predicted by numerical results. First, the gap offset error $\varepsilon$ used to calculate $\eta_c$ could be too small. An increase in $\varepsilon$ would shift the $\eta_c$ data up and to the right, closer to numerical predictions. Of the four geometries, only G7 could potentially be explained by this as it is the only geometry that fits the functional form. For the other geometries, when $\varepsilon$ is increased either the low gap viscosity measurements become larger than higher gap viscosity measurements (G4, G6) or $\varepsilon$ would have to approach 100 $\mu$m (G5), which is too large to be accurate.

Second, the assumptions in calculating $\eta_c$ from $T^*$ could be wrong. Presently, we take the 2D $T^*$ and assume it would be equivalent for a 3D geometry. In reality the microtextured surfaces have a texture density that is lower than the extrapolated 2D case. For example, G5 has a 2D texture density $W^* = 0.8$ or 80%. In the 3D case it would be lower by a factor of $\frac{4}{\pi} W^*$. Since 3D area coverage by circular textures is smaller than 2D line coverage. In terms of $\eta_c$ this would mean the numerical predictions would be higher so this cannot explain the lower values of measured $\eta_c$.

Third, air bubbles trapped in the microtextures could be forming an approximate shear-free boundary condition due to the viscosity of air being much lower than the viscosity of S60, $\eta_{air} \ll \eta_{S60}$. We addressed this issue in Section 4.3.3 where the microtextured surfaces were massaged to induce the Wenzel wetting state. No air bubbles should be in the microtextures during testing and this cannot explain lower measured $\eta_c$. 
Fourth, secondary flows can develop due to inertia and this affects the shear stress on the top plate. Reynolds number based on gap height squared is the critical parameter [46].

\[ \text{Re}_{H^2} = \frac{\rho \Omega H^2}{\eta} = \text{Re}_H \frac{H}{R} \]  

(4.21)

How the secondary flows affect measured torque \( M \) is found by [46],

\[ \frac{M}{M_0} = 1 + \frac{3}{4900} \text{Re}_{H^2} \]  

(4.22)

where \( M_0 \) is Eq.(4.13), torque due to simple shear flow. Figure 4.7c gives the maximum \( \text{Re}_H = 2.5 \), the maximum \( \text{Re}_{H^2} = 0.0125 \). In Figure 4.7a at the maximum velocity \( \Omega \) and gap \( H_c \), \( \text{Re}_{H^2} = 0.34 \). These show that secondary flow is not important. Moreover, even if it was present, Eq.(4.22) shows that secondary flows will always result in an increase in shear stress and cannot explain the decrease in measured \( \eta_c \).

Lastly, we know surface tension can produce a torque due to line traction forces (Chapter 3) [49]. This would increase torque by adding a constant torque independent of \( \Omega \). Torque due to surface tension \( T = \mathcal{O}(1) \, \mu\text{N.m} \) is much lower than torques measured in our system \( T = \mathcal{O}(10^5) \, \mu\text{N.m} \). This also cannot explain the decrease in measured \( \eta_c \).

Alternative explanations for the decrease in \( \eta_c \) do not hold up. Secondary flows and surface tension torques would increase \( \eta_c \). As would a more rigorous treatment of the \( \eta_c \) calculation from numerical results. The fluid is not in Cassie-Baxter wetting
condition due to pre-wetting the microtextures. We can firmly report a decrease in hydrodynamic friction that does not depend on $\Omega$ (or $Re_H$) up to $\Omega \leq 31.6$ rad/s.

4.5 Conclusions

We have defined the correct dimensionless parameter space by showing the collapse of numerical shear stress and normal force curves. This builds a simplifying framework for presenting and interpreting numerical results for microtextures. A tribohemeometric setup was developed and novel gap-controlled experiments were performed. Additionally a reduction in shear stress due to the presence of microtextures on the shearing surface was observed.

1. For a given microtexture geometry $(D^*, W^*)$ and gap $(H^*)$ dimensionless shear stress $T^* \neq \phi(Re_H)$; (Figure 4.3)

2. When planar misalignments $\alpha$ are controlled on both surfaces, the gap offset error $\varepsilon$ approaches the gap offset due to squeeze flow $\varepsilon_{SF}$, making corrections more precise;

3. Microtextured surfaces in gap controlled conditions exhibit shear stress reduction;

4. Shear stress reduction of microtextured surfaces is greater than predicted by 2D numerical models.

This work will enable the further study of microtextures and their potential to produce hydrodynamic normal pressure. With normal force measurements a primary concern for experimental error is normal force from planar misalignments similar to a slider bearing [2]. Our precise alignment of the top and bottom plates will mitigate those concerns. The precise alignment of the shearing surfaces also allows exploration of other studies such as small gap, gap dependent and high shear rate rheometry.
5. Conclusions

In this work, enhanced precision control alignment and parallelism of a rotational rheometer was achieved. A glass bottom plate that enables precise control of parallelism with respect to the axis of rotation was designed and fabricated (Chapter 2). This allowed control of the two shearing surfaces and non-parallelism was reduced to < 1 μm. Visualization of the sample during testing is also now achievable with room for optics such as microscope objectives.

Precise control of low torque measurements was also achieved (Chapter 3). We have shown that surface tension can apply a torque on rotational rheometers that in steady shear typically appears as a constant torque independent of rate. This signature appears inaccurately as shear thinning of viscosity. The surface tension torque is reduced by maximizing rotational symmetry of the contact line, minimizing evaporation and the migration of the contact line, reducing the radial location of the contact line, and lowering the surface tension. Control of the contact line depends on proper sample volume, which is especially important at small gaps as changes in sample volume can easily influence underfill or overfill.

Identifying and reducing the surface tension torque phenomenon is critical for rheological measurement for low viscosities, intrinsic viscosities, soft materials, sub-dominant viscoelastic components, small gaps, and any circumstance where the low-torque limit is experimentally relevant. We expect this phenomenon to be especially important in aqueous systems, including biological materials, due to the high surface tension of water.

The precise alignment of the rheometer was also used to study the behavior of microtextures in gap controlled hydrodynamic lubrication (Chapter 4). We defined
the correct dimensionless parameter space and verified it with numerical results. This builds a simplifying framework for presenting and interpreting numerical results for microtextures. A triborheometric setup was developed and novel gap-controlled experiments were performed. Additionally, a reduction in shear stress due to the presence of microtextures on the shearing surface was observed.

This work will enable the further study of microtextures and their potential to produce hydrodynamic normal pressure. A primary concern for experimental error is normal force from planar misalignments similar to a slider bearing. Our precise alignment of the top and bottom plates mitigates those concerns. The precise alignment of the shearing surfaces also allows other studies such as small gap, gap dependent and high shear rate rheometry to be explored.
References


