Spectroscopic analysis of molecular fluids at the solid-liquid interface

Samantha Lynn Nania

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SPECTROSCOPIC ANALYSIS OF MOLECULAR FLUIDS AT THE SOLID-LIQUID INTERFACE

by

Samantha Lynn Nania

A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemistry in the Graduate College of The University of Iowa

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To those who have taught me about life, love, and supported me throughout,
Thank you.
Life is a journey to be experience, not a problem to be solved.
-A. A. Milne, Winnie the Pooh
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Abstract

Chemical and physical interactions play important roles in surface film formation and fluid slip at the fluid-solid interface. It has been shown that the fluid molecules at this solid interface behave differently than the molecules in the bulk. To investigate fluid film formation and the fluid’s transition between bulk and interfacial regions, a dynamic wetting technique is utilized. This technique allows the formation of variable thickness fluid films. When used in conjunction with vibrational spectroscopy and ellipsometry, direct analysis of variable thicknesses films, spanning the bulk to interfacial transition, can be obtained. Film thickness are predicted using the Landau-Levich model and the Lifshitz model, and comparisons generally agree with experimental results.

According to hydrodynamic no slip boundary condition, fluid molecules near a solid surface can have no velocity with respect to the solid substrate. Recent theories state more specifically that, if a fluid comes in contact with an ultra-smooth surface (< 5-7 nm RMS roughness), the no slip boundary condition might be violated. We confirmed violation of the no slip boundary condition in two specific cases for fluid layers on SAM-modified substrates. To understand how the fluid/solid properties affect this condition, an acetophenone and bare silver surface was studied. Our results show that the structure and ordering of fluid molecules within these films are highly dependent on the film’s thickness and confinement. Temperature control wetting studies also corroborate with these results showing that as a frozen film of large thickness approaches the melting point, a molecular reorganization occurs creating a crystalline structure before the film melts into an isotropic bulk structure. Structure dependence on alkyl-chain length was then investigated using a series of trialkylamine fluids. Results show significant changes in the vibrational profile as
a function of film thicknesses and rotational velocity as the alkyl-chains increase in length. These are ascribed to changes in primary carbon attached to the nitrogen as a function of shearing and the rigidity of the molecule.

These results reveal interactions taking place at the solid-liquid interface and have impacts on a broad spectrum of industrial, commercial, and research applications including lubrication and transportation vehicles.
Public Abstract

The layer of material present where a solid and a liquid meet is called an interface, and interfaces play an important role in many everyday applications like lubrication, transportation, and even bacterial infections. Understanding the chemical and physical properties of the microscopic interface will help scientists to make better materials more efficiently and improve the quality of life for everyone. Studying this chemical interface is very challenging because the dimension of these regions are very small, on the scale of 1/1000 of a human hair, so this work uses reflected light to study the formation of thin liquid films on a solid, mirror-like surface. This research aims to improve our understanding of how liquids slip, stick, or pack when it is very near the solid, within the interface.

Our results show that some fluids can slip completely from a surface, which changes the way scientists and engineers approach challenges in lubrication, transportation, and even bacterial infections. We also learned that other solid-liquid combinations create fluid films that have tunable behavior for varying size of the molecules or with varying film thicknesses. This gives future scientists and engineers new ways to control properties of the interface, and will allow improved performance for future devices like ships and medical implants.

Future studies in this area of chemistry will shed lights on the behavior of the molecules at this microscopic interface and continue to uncover chemical interactions that have impacts on industrial, commercial, and basic research applications.
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Chapter 1. Introduction

The chemical and physical interactions that occur at the solid-liquid interface play a crucial role in a wide range of chemical, biological, and mechanical applications.\(^1\) The interfacial region (determined by thicknesses from ca. 1 to 100s of nanometers from the surface) is the region in which molecules form layers planar to the solid surface. It is well known that molecules in this region experience forces which cause them to form anisotropic organization at the interface and therefore exhibit extremely different properties than the molecules in the isotropic bulk.\(^2^6\) Because of this, the fluid in this region is generally believed to behave very differently than the same material far from any surface, therefore being described as an entirely new phase of matter.\(^3^5\).

Interfaces are omnipresent making the region where a liquid comes in contact with a solid a very fruitful topic of investigation. Studying these interfaces will uncover a wide range of knowledge about the physicochemical properties and interactions that occur in this region. Our research aims to improve understanding of one such phenomenon with important ramifications in fluid flow: the motion and slip of fluid molecules at solid surfaces.

1.1 The No Slip Boundary Condition

For many years, chemistry, physics, and engineering have all attempted to spearhead the study of fluids at surfaces.\(^7^10\) As of late, it was widely accepted that the molecules in a fluid adjacent to a moving solid surface remains at rest at the solid interface, even under conditions of high shear stress such as rapid, pressure-driven fluid flow.\(^7^9^10\) This idea is known as the no slip boundary condition (Figure 1.1A), and is defined as the condition in
which a fluid in contact with a substrate has no velocity with respect to the substrate itself.\cite{7}

Between the 18\textsuperscript{th} and the 20\textsuperscript{th} century, hydrodynamic no slip boundary condition was extensively studied by distinguished scientist such as Bernoulli,\cite{12} Stokes,\cite{13} Coulomb,\cite{14} and Whetham.\cite{15} Ultimately, it was decided that there was no evidence of slip at the interface and that if slip did occur, it was too small to be measured or seen.\cite{7} Because of the low resolution of experimental techniques and instrumentation, the no slip boundary condition had been widely agreed upon and was used for all practical applications, until the end of the 20\textsuperscript{th} century when a rapid development in micro and nano-scale analysis and high sensitivity instrumentation occurred. This lead to increase in demand of a better understanding of the chemical and physical interactions taking place at the interface on such as small scale.

Recently, more research has been done to better understand the existence of a slip length which sheds light on the concept of molecular slip at the interface, uncovering a

\textbf{Figure 1.1} Schematic of (A) no slip, (B) partial slip, and (C) complete slip boundary conditions present at the solid-liquid interface. In the no slip boundary condition, the velocity of the fluid at the solid interface matches the velocity of the surface. In a partial or complete slip boundary condition, the fluid’s velocity at the solid interface can oppose the velocity of the surface. Adapted from Ref 7 and 10.
couple different scenarios that violate the no slip boundary condition, including the partial slip boundary condition (Figure 1.1B) and the complete slip boundary condition (Figure 1.1C). For a partial slip boundary condition, a finite slip length has been used to quantify any amount of slip actually present at the interface. This slip length is a theoretical length beyond the surface at which the velocity of the fluid is zero.\textsuperscript{7} This theoretical slip length can be related to the actual slip of a fluid molecule at a surface, which is the distance a fluid moves across the surface (parallel) in various experimental conditions per unit time. If this occurs, the no slip boundary condition is determined to be violated because the fluid adjacent to the surface has a velocity that is non zero with respect to the interface.\textsuperscript{7,9-11}

The idea that the no slip boundary condition could be violated was met with strong criticism, but that has not deterred research groups from investigating the violation and supporting it with a range of studies, including both partial and even complete slip in some cases.\textsuperscript{9, 11, 16-19}

Research efforts to define the limits of the no slip boundary condition have been productive, revealing unsuspected chemical and physical properties of fluids and solids near solid surfaces.\textsuperscript{2,3,4} Reviews have compiled a list of various experimental techniques used to study the phenomena of hydrodynamic slip.\textsuperscript{7, 10} Some techniques measure the slip indirectly by estimating the slip length based on the effect of slip on some macroscopic parameter; for example, slip length calculated from flow rate studies through a capillary by applying a pressure drop which yield slip lengths from tens of nanometers up to micrometers in length.\textsuperscript{10, 20-22} Other techniques such as particle image velocimetry use tracer molecules to investigate velocity profiles of fluids near surfaces.\textsuperscript{18, 23} With advancements in technology and instrumentation, a shift in views to much smaller domain
sizes has allowed for a molecular picture of the interfacial layers and has brought attention of the intermolecular chemical and physical forces.\textsuperscript{3, 24}

This breadth of research has shown that slip can be observed at the solid-liquid interface, and shed light on the various chemical and physical properties which may contribute to slip. It has been determined that properties such as surface wettability, viscosity, surface roughness, and shear rate among other properties can influence in slip at the interface.\textsuperscript{7, 10} For example, Granick et. al.\textsuperscript{11} studied the hydrodynamic slip boundary condition for surfaces containing various layers giving a range of RMS roughness values from 6 to 0.2 nm using a modified surface force apparatus (SFA), which vibrates once the surfaces approach one another, applying a oscillatory hydrodynamic force while squeezing the fluid. It was reported the hydrodynamic no slip boundary condition could be violated when the surface in question is an ultra-smooth surface(\textless{} 5 to 7 nm RMS roughness).\textsuperscript{11}

Thompson and Robbins used molecular-dynamic simulations of Lennard-Jones liquids to demonstrate that these model fluids have changes in the boundary condition as a function of the degree of order induced in the fluid at the interface. The simulations have also shown that crystallized layers at the interface correspond to a wetting phase and they only have two confined layers at most.\textsuperscript{25}

1.2 Nanoscale Confinement and Shear Flow

The idea of molecules behaving differently at the interface compared to the isotropic bulk\textsuperscript{2-6} has been extensively studied. Granick has reported that molecules confined to the interface, organize themselves into layers which run parallel to the solid boundary.\textsuperscript{26} This organization gives rise to an oscillating density profile seen in Error! Reference source
not found., which states that the density of the molecules packed at the interface is quite high, but decreases when the area between two packing layers is met until the next layer is reached in distance and the density profile increases again. As the distance from the solid surface increases, this oscillation decays until the bulk isotropic fluid is met and disorder is reached.\textsuperscript{6, 27} This rise in ordering at the interface is what gives rise to the vast change in properties at the interface.\textsuperscript{2}

Granick goes on to state that as the fluid layers become thinner at the solid interface, the resistance to flow (friction) causes the confined molecules to “solidify” in a sense that shear cannot be allowed.\textsuperscript{2} At these confined thicknesses, it is possible that the molecular arrangement of the fluid represents crystalline ordering. To understand this crystalline ordering, Israelachvili and co-workers used optical absorption spectroscopy in a SFA to analyze shear-induced ordering of an anisotropic cyanine dye molecule in aqueous solution. Their results show that crystallization of the molecules can be due to a combination of confinement, shear, and epitaxial interactions.\textsuperscript{28}

Dutta et al.\textsuperscript{29} reported molecular orientation and shear effects by confining a fluid between a silicon window and a magnetic seal rotating together in a custom sample

\textit{Figure 1.2} Schematic diagram of the density profile of molecules laying at solid interface vs the distance from the solid surface. Adapted from Ref 2.
chamber. The molecular ordering is then examined under the play of shear forces. It was determined that shear has an effect on molecular ordering, but that it varies depending on the molecule. Molecules with spherical shape order instantaneously at the interface without the effects of shear, however, when shear forces are applied, it was found that there is a decrease in ordered area but no change in the amount of ordered layers. For a molecule with a more polymeric structure which does not originally order at the interface, an increased ordered structure was found when a large amount of shear was applied. This was determined to be shear-driven disentanglement.\textsuperscript{29} Israelachvili and coworkers demonstrated ordering at an interface in contact with the shearing force for thick films (even up to ~800\textmu m in size) using a second-generation x-ray SFA to show. The results also exhibit a shear-induced boundary layer created by orientational “phase” separation behavior.\textsuperscript{30}

To investigate the interactions and ordering of molecules at the solid-liquid interface without the interference of the bulk molecules, a dynamic wetting technique is employed which allows for direct spectroscopic analysis using infrared and ellipsometry techniques.

1.3 Dynamic Wetting

Investigation of the interfacial region has been a difficult task due to the microscopic dimension of the region and its proximity to the bulk fluid, which can interfere with the interfacial region. In order to successfully analyze the interface, the bulk fluid must be minimized as much as possible.

To do this, we utilize a dynamic wetting technique. With this dynamic wetting technique, the fluid is introduced at the bottom of a vertically aligned, solid, disk-like silver
(Ag) substrate via glass capillary. The glass capillary is positioned ca. 2 mm from the surface allowing the bulk droplet to be held between the glass capillary and the surface, due to capillary forces, basically forming a bulk reservoir at the bottom of the surface. The surface, which is attached to a gearhead and motor, is allowed to rotate through the bulk droplet at a predetermined speed causing a thin film of controlled thickness to be extruded up and away from the bulk droplet onto the surface (Figure 1.3). Due to the nature of the technique, the residual film is constantly replenished forming a stable interfacial film. The film is then probed at the apex of the surface using spectroscopic methods in a reflection geometry, represented by the red beam in Figure 1.3. The infrared and ellipsometry beam can shed light on composition and orientation of the molecules in the interfacial region, along with the amount and thickness, respectively. The wetting technique is similar to emersion, in which a substrate is submerged into a bath of fluid and then slowly pulled out of the bath and probed using vibrational spectroscopy.31-33

![Figure 1.3 Cartoon schematics of dynamic wetting technique (left) and of film formation (right) as the surface is rotated through the bulk droplet. As the disk rotates through the droplet, an extruded thin film of the fluid may be formed which is probed at the apex of substrate rotation.](image-url)
The dynamic wetting technique provides direct analysis of molecules representing the interfacial matter that would naturally be present at a fully emersed solid-liquid interface without the effects of the bulk.\textsuperscript{34, 35}

The Pemberton group at the University of Arizona have undertaken multiple studies using this dynamic wetting technique in conjunction with infrared spectroscopy and ellipsometry.\textsuperscript{34-38} In one study, 11-mercapto-1-undecanol-modified silver surfaces were rotated through various aqueous and non-aqueous solvents and ellipsometry was used to determine the effect of emersion velocity and fluid viscosity on emersed film thickness. Based on the thickness vs velocity data, it was seen that at lower rotating velocities (0.005 cm s\textsuperscript{-1}) intermolecular forces can compete with hydrodynamic forces by showing a wide spread of thickness measurements throughout the various fluids; whereas, at faster velocities (0.037 cm s\textsuperscript{-1}) the thickness values are clustered suggesting hydrodynamic forces have a large effect on the thickness. It was also shown that some fluids (1-butanol and 1-pentanol) with large viscosities show no significant change in thickness over the range of velocities; however, others, such as water, acetonitrile, and methanol, show an increase in thickness with a decrease in velocity. The fact that some fluids show thickness changes over a range of velocities while others do not, can help our understanding of which interactions are at play at the solid-liquid interface. Pemberton et al. have also studied glycerol/D\textsubscript{2}O solutions on Ag substrates using infrared reflection spectroscopy to better understand the structural/adsorption contributions as a component of these forces.\textsuperscript{37}

This research utilizes the dynamic wetting technique in combination with a variety of spectroscopic techniques including polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS), IRRAS (which only contains p-polarized light),
and spectroscopic ellipsometry. The infrared techniques described throughout this dissertation are surface sensitive, therefore having enhanced signal at the solid-liquid interface and provide details on structure (at an angle perpendicular to the surface), chemical interactions, and thickness of the films present.\textsuperscript{1, 39-41} Ellipsometry is used to determine absolute thickness of the fluid films and may vary slightly from the thickness values determined using Beer’s law due to the selection rules of the infrared technique.

The results presented in this dissertation provide new chemical insight into various interfacial systems. This includes the construction of new ideas of the hydrodynamic no-slip boundary condition at the solid-liquid interface and a better understanding of the behavior of molecular fluids as a function of rotational velocity and thickness. With these findings, this research will be applicable to the development of innovative solutions to many longstanding challenges in industry and physical sciences, such as fouling on ships and bacteria anchoring to medical implants.

1.4 Scope of the Dissertation

The research in this dissertation aims to better understand the physical and chemical interactions that play a role at the solid-liquid interface. This is done with the spectroscopic techniques polarization modulation infrared reflectance absorption spectroscopy (PM-IRRAS), IRRAS, and spectroscopic ellipsometry using a dynamic wetting technique, which minimizes the influence of bulk fluid while forming a thin extruded film. These spectroscopic techniques probe molecules at the interface and their ordering nature, and provide a better understanding of how velocity affects film thickness.
Chapter 2 aims to analyze the no slip boundary condition and what role roughness plays in this boundary condition. For these experiments, chlorobenzene and dichlorobenzene were used as the fluids on a self-assembled monolayer (SAM) modified surface to be able to reach the velocity at which the transition between interfacial and bulk can be obtained. To investigate the surface roughness effects on the no slip boundary condition, both smooth, mechanically polished surfaces (2 nm roughness) and electrochemically roughened surfaces (7 nm roughness) were used. Based on this study, interesting results about the possible violation of the hydrodynamic no slip boundary condition were exposed.

Chapter 3 aims to further understand what effects play a role in the fluid slip at the solid interface by changing the system from chlorobenzenes to acetophenone, which has a very similar molecular structure but includes a larger side chain and changing the surface from a SAM modified Ag surface to a bare silver surface. This simplifies the system and allows for direct comparison of experimental film thickness to theoretically predicted film thickness, revealing that there is an agreement between the experimental and theoretical thickness which occur when molecules become confined to a surface.

Chapter 4 aims to analyze the effect of alkyl-chain length on the film formation at various velocities and the role in packing and ordering properties of the molecules at the interface. This is achieved by utilizing a series of trialkyamines with varying alkyl-chain lengths and systematically varying the velocity at which the surface is rotated through the film, revealing interesting details about the orientation of these molecules in thicker films.

Overall, the topics discussed in this dissertation focus on using a dynamic wetting technique to analyze the interfacial films of a wide range of solid-liquid systems, while
taking into account surface roughness, velocity, temperature, and orientation when a fluid comes in contact with a solid. A better understanding of the physical and chemical interactions taking place is achieved by use of spectroscopic techniques and theoretical comparisons uncovering a wealth of knowledge about the solid-liquid interface.
Chapter 2. Experimental Procedures and Methods

2.1 Materials

\( \text{H}_2\text{SO}_4 \) (ACS grade, BDH), \( \text{HClO}_4 \) (70\%, Sigma), and \( \text{NH}_4\text{OH} \) (28-30\%, BDH), were used as received. A 4.0 M solution of \( \text{CrO}_2 \) (99.9\%, Aldrich) and a 0.6 M solution of \( \text{HCl} \) (ACS grade, BDH) were prepared with Milli-Q water. Water was purified with a Milli-Q UV Plus System (Millipore Corp, 18.2 MΩ cm\(^{-1}\) resistivity, TOC \( \leq 4 \) ppb).

All glassware and Teflon materials used in these experiments were cleaned using two acid baths, first by submersion in NOCHROMIX acid for 6 hours to 1 day to get rid of organics, then rinsed with copious amounts of distilled water, and finally submersion in 50\% nitric acid for 6 hours to 1 day to get rid of inorganics. The glassware was then triply rinsed with distilled water followed by boiling Milli-Q water to dissolve and wash any remaining impurities. Sometimes glassware and Teflon materials were cleaned in a base bath for 6-12 hours followed by a distilled water rinse and a boiling Milli-Q rinse. The base bath consists of 250 g of KOH salt, 4 L of isopropanol, and 2 L of Milli-Q water.

2.2 Surface Preparation

Polycrystalline silver disks (14 mm diameter, 99.999\%, ESPI Metals) were mechanically and chemically polished. Each silver surface was mechanically polished using a large stainless steel dye and plunger in which the surface screws into. New surfaces were initially mechanically polished with 600 grit sand paper followed by 1000 grit sand paper for 25 minutes each. Then, the surface was polished successively using 9.5, 3.0, 1.0, and 0.3 \( \mu \)m aluminum oxide powders with water for 15, 10, 5, and 2 minutes, respectively. Specifically, for grit sizes \( > 1.0 \) \( \mu \)m, the surface was polished in a circle (Figure 2.1A).
until 5 minutes before the end time in which the dye was held in one position and pushed
in an up and down motion to ensure all the visible lines were going in one direction (Figure 2.1B); if this was true, the dye was rotated 90° and the process was repeated (Figure 2.1C). Once it was confirmed that the lines again were all going in one direction, the surface was polished in a figure eight motion until time finished (Figure 2.1D). Between each grit size, the surface was rinsed, sonicated in Milli-Q water for 5 minutes, and rinsed again with Milli-Q. For 1.0 and 0.3 µm grit sizes, the surfaces were only polished in a figure eight fashion since these two grit sizes yield mirror finish on the surface (Figure 2.1E). After the final sonication, the threads of the surface were covered in Teflon tape before chemical polishing.

Figure 2.1 Images of the surface throughout the polishing process. The surface is rotated in a circle for an allotted amount of time depending on the grit size (A). Then, the surface is moved in a forward and back motion to ensure the lines all go in one direction (B) before being rotated 90 degree and repeated (C). Finally before sonicating and moving on to a smaller grit size, the surface is move in a figure eight fashion on the pad (D). For grits above 1 µm, lines can be seen in the surface as shown in A-D; however, once the surface is polished at 1 and 0.3 µm grit powders, the surface holds a mirror finish (E).
Surfaces were then chemically polished using the chromate-etch process as shown in Table 2.1. Figure 2.2 shows the set up for the chemicals and beakers in the hood. To start the surface was submerged in H$_2$SO$_4$ for 5 minutes. This step removes any organics or dirt that was on the surface before the chromate-etch. The surface was then removed and rinsed using Milli-Q water, and the side of the surface was pressed against a KimWipe to remove excess water before submerging it in HClO$_4$ for 10-20 seconds. The surface was then removed from the HClO$_4$ and directly submerged in a 50:50 mixture of CrO$_3$:HCl and

Table 2.1 Steps needed to completely the chemical polishing procedure and the purpose of each step.

<table>
<thead>
<tr>
<th>Step</th>
<th>Time</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$_2$SO$_4$</td>
<td>5 minutes Removed organics and dirt on surface</td>
</tr>
<tr>
<td>2</td>
<td>HClO$_4$</td>
<td>10-20 seconds Puts an acidic environment on surface &amp; oxidizer</td>
</tr>
<tr>
<td>3</td>
<td>HCl:CrO$_3$</td>
<td>1 minute Oxidize and form AgCl to remove top layer</td>
</tr>
<tr>
<td>4</td>
<td>sonication</td>
<td>5 minutes Remove AgCl layer from surface</td>
</tr>
<tr>
<td>5</td>
<td>sonication</td>
<td>5 minutes</td>
</tr>
<tr>
<td>6</td>
<td>NH$_4$OH</td>
<td>5 minutes Reduced any left over CrO$_3$</td>
</tr>
<tr>
<td>7</td>
<td>H$_2$SO$_4$</td>
<td>5 minutes Last clean</td>
</tr>
</tbody>
</table>

Figure 2.2 Picture of the chemical polishing set up including order of which the chemicals should be set up.
jigged for a minute before being rinsed. This step caused a layer of AgCl to form on the surface which was then removed during two consecutive steps of 5 minute sonication in Milli-Q with a rinsing step in between and after. From this step, the Teflon tape was removed from the threads of the surface using tweezers and the surface was submerged in NH$_4$OH for 5 minutes to ensure that any leftover chromium was reduced from chromium VI to chromium III because chromium III is soluble in water. Lastly, the surface was rinsed with Milli-Q, submerged in H$_2$SO$_4$ for 5 minutes to remove any organics that may have been on the surface at the end, rinsed again, and finally, sonicated for 5 minutes in water. The surface was stored in water for no more than 1 hour before use. The final surfaces had RMS roughness of better than 5 nm verified via AFM.

2.3 Dynamic Wetting

The surface was attached to a shaft which was secured via a setscrew to a spur gearhead series 12/3 motor (Micromo). This motor was attached to a 12 V DC power supply to provide substrate rotational velocity control. The velocity range depends on the ratio of the gearhead used; the ratios used in these experiments include 30492:1, 13552:1, 529:1, and 104.4:1 which were calibrated by hand. Toward the end of the shaft was a ball bearing which allows this assembly to slide into a Teflon plunger and remain true while rotating; this was crucial to ensure a constant spot to probe during rotation. This Teflon plunger was then inserted into an in-house made Teflon cell which was airtight to allow environmental control for the duration of the measurement. The cell was held under an inert nitrogen gas atmosphere, which was either dry (pure N$_2$) or saturated with the vapor phase of the selected wetting fluid. Reference data were acquired for the system before introduction of the fluid or fluid vapor to verify purity and cleanliness of the substrate.
Once confirmed, the cell’s vapor phase was saturated with the wetting fluid by dispensing fluid into the bottom of the cell and waiting an allotted time for it to come into equilibrium. Complete saturation was vital to prevent evaporation of fluid from the substrate during analysis. Saturation was confirmed by infrared transmission-absorption measurements of the fluid’s gas phase vibrational spectra within the cell by continuing to collect spectra until they overlap, becoming a steady state. Finally, the tip of a glass capillary was brought near to the surface, and a droplet of fluid was dispensed from the capillary tip. The droplet (ca 0.2 mL) was held between the capillary and the bottom of the surface by capillary forces. **Figure 2.3** is a cartoon depiction of how the substrate was then made to slowly rotate through the droplet at a prescribed velocity, and a thin layer of fluid (held to the surface through intermolecular or physical forces against the downward force of gravity) was extruded as the surface rotates up and away from the droplet. Ultimately, fluid molecules in this film were spectroscopically probed at the apex of the substrate’s rotation.

**Figure 2.3 Left:** Cartoon schematics of dynamic wetting technique (left) and of film formation (right) as the surface is rotated through the bulk droplet. As the disk rotates through the droplet, an extruded thin film of the fluid may be formed which is probed at the apex of substrate rotation. **Right:** Actual experimental image of dynamic wetting.
2.4 Instrumentation

2.4.1 Atomic Force Microscopy (AFM):

Surface roughness was analyzed using an atomic force microscope (Asylum Research MFP-3D). Surfaces were screwed into a homemade aluminum block (ca. 1 cm thick, pictured in Figure 2.4) to minimize interference vibration. Because of the thickness of the surfaces and the aluminum block, the leg attachments were needed. Once the surface was placed, the tip was loaded. The tips used in this research were μMasch HQ.NSC 18/AIBS. The laser was then aligned where the sum falls between 7 and 10, and the deflection was zero or slightly negative. Depending on the resonant frequency, the autotuned range was set and the target percentage was set for -5%. The surface was approached using AC tapping mode. For this mode, the target set point was set between 1 -1.5 V and the set point was set to 80% of the target point or 800 mV.

Figure 2.4 Image of surface attached to aluminum block under the AFM head.
Once the tip was close enough to the surface, the mode was switched to Contact mode, and the set point was set to 0.1 V. At least 5 images were collected using contact mode and the RMS roughness was calculated by Asylum/IGOR software and averaged.

2.4.2 Contact Angle (C.A.)

A goniometer (Rame-Hart model 100) upgraded with a high-resolution CMOS camera (Figure 2.5) was used to characterize substrate contact angle and wettability. The camera was equipped with a 6x to 60x magnification lens (Thor Labs). The light was turned on to about 80% as to not over saturate the camera. Drops of the wetting fluid (~20 µL) were dispensed on to the surface using an EPPENDORF EDOS 5222 equipped with Eppendorf combitips plus 0.1 mL tips. Videos of the dispensing and retraction of the droplet were taken. From these videos, multiple still shot images of dispensing, resting, and retracting fluid droplets were captured (n ≥ 3) for statistical analysis of advancing, receding, and static contact angle. ImageJ software was used to quantify C.A.s on both edges of the droplet’s image for each surface/fluid combination.

![Figure 2.5 Side image of contact angle goniometer including high resolution camera, sample, pipette and lighting. Camera software is used to capture video and images of droplet on the surface.](image-url)
By using the angle tool in the software, the first line was placed along the bottom of the droplet, from one corner of the droplet to the other, and the second line was pulled up along the side of the droplet to be tangent to the triple point, which is the point where the liquid, solid, and air meet. This angle was determined at the contact angle and was averaged for multiple droplets for statistical analysis.

2.4.3 Fourier Transform Infrared (FTIR)

Measurements were acquired using a Thermo-Nicolet iS50 Fourier transform infrared spectrometer in the transmission orientation. The FTIR is equipped with both a DTGS/KBr and liquid nitrogen cooled MCT-A detector. For the experiments done here, the MCT-A detector was used for its increased sensitivity capabilities for lower signal input. A bare background was collected using cleaned KBr salt plates sandwiched either in a press-on demountable cell holder or a clamp sample holder. All KBr salt plates were cleaned before and after use with acetone and KimWipes. After the sample holder is placed in the FTIR compartment, the lid was closed and the compartment was purged from the instrument itself along with a beaker full of liquid nitrogen to speed up the process. The measurement was taken after 2 minutes of purging.

The ‘Transmission ESI’ experiment file was used. Each spectrum was collected at 4 cm\(^{-1}\) resolution for an average of 32 scans. This was the same for the FTIR of the samples. Sample spectra were collected by pipetting ~5-15 µL of sample, depending on fluid properties, between two clean KBr salt plates. Sometimes a Teflon spacer was used
between the two KBr plates to be able to determine molar absorptivity values for the sample. Spectra were baselined after collection if necessary.

2.4.4 Temperature Control FTIR (TC-FTIR)

The temperature control FTIR was completed using the same method as FTIR except that the compartment was equipped with a CryoTherm accessory (International Crystal Laboratories) shown in Figure 2.6. The CryoTherm accessory was comprised of a vacuum jacket and a cell holder/refrigerant chamber. The vacuum jacket was mounted to the accessory plate for the Thermo-Nicolet iS50 FTIR and sealed with KBr windows which allowed the source to enter and leave the jacket.

Figure 2.6 Left: Image of Cyrotherm accessory attached the FTIR compartment with temperature control chamber attached. Right: Top down view of the chamber with all the connections made including the thermocouple, the controller connection, the outgas hose for the liquid nitrogen chamber and the vacuum hose which evacuates any water present in the jacket.
The temperature control sample cell had seven parts including the top and bottom metal pieces which screwed together to hold all the pieces, the neoprene spacer, two Teflon spaces, CaF$_2$ windows (Figure 2.7). Bare backgrounds were taken with bare clean CaF$_2$ salt plates. The sample was then dispensed between the two salt plates and the cell was assembled. Once assembled, a light smear of silicone grease was place on the metal portions of the sample cell to ensure good thermal conductivity when clamped into the cell holder/refrigerant chamber. The refrigerant chamber was then dropped into the vacuum jacket and sealed. The vacuum line was attached to the refrigerant chamber along with the service connections to the CryoTherm box.

Once all the attachments were made, the stainless-steel disc is dropped into the bottom of the refrigerant chamber, followed by the mushroom. The mushroom used depended on the temperature range for the experiment; the larger diameter mushroom was used for temperature between -100 °C and ambient, whereas the smaller diameter mushroom was used for temperatures between -190 and -80 °C. If going above -100 °C, the mushroom was changed between liquid nitrogen refills when the temperatures fell between -80 and -100 °C. The refrigerant chamber was then filled with liquid nitrogen and
plugged with the bung which has an attached hose, seen in Figure 2.6, that allows any refrigerant to boil off away from the top plate of the chamber. Depending on the duration of the experiment and reachable temperatures, sometimes it was required for numerous refills of the refrigerant chamber.

The ‘Transmission ESI’ experiment file was used. For these experiments, background spectra were collected every 10 °C in the range of interest. Spectra were then collected referencing the background of the closest temperature background spectra. Spectra were collected on a wide range of temperatures until the temperatures of interest were discovered in which spectra were collected in a narrower scope. Spectra were baselined after collection if necessary.

2.4.5 Infrared Reflection Absorption Spectroscopy (IRRAS)

Measurements were acquired using a Thermo-Nicolet iS50 Fourier transform infrared spectrometer in combination with an external optical bench. This external bench was necessary in order to accommodate the wetting cell used in this research shown in Figure 2.8. The IR source can be followed in this figure. The IR beam leaves out the side of the FTIR where it was reflected off a focusing mirror and through a polarizer. The polarizer only allowed p-polarized light to pass through which was then focused onto the surface at 78° ± 3° with respect to surface normal. This angle was of high importance because it is said that this is where max mean squared electric field strength (MSEFS) is acquired which is proportional to absorbance.
Figure 2.8 Image of external optical bench which includes multiple focusing mirrors, the polarizer, photoelastic modulator (which is turned on for PM-IRRAS experiments only), the sample wetting cell, and the MCT-A detector. A red line has been added to represent the path of the source from the FTIR to the MCT-A detector.
With this angle and the p-polarized light, along with the geometrically thin fluid films created by dynamic wetting, the IRRAS selection rules\textsuperscript{39, 43} seen in Figure 2.9 allow for the exclusive examination of interfacial molecules of the extruded film.

Importantly, only molecular vibrations with a dipole component oriented at some angle perpendicular to the metallic substrate will be observed in this geometry while molecular vibrations with dipoles parallel to the interface will not be probed due to these specific selection rules. Analysis of the resulting vibrational energies and line-shapes were used to provide chemical information on the structure, orientation, and local chemical environment of the fluid molecules contained within the wetting film.

The ‘SKS IRRAS’ experiment file was used which sets the gain=1, the optical velocity=1.8988 cm/s and the aperture=100 with no attenuation; the output file for this experiment file was absorbance. The surface is aligned to yield max peak to peak signal in the bench tab of the experimental set up. Before any measurement was taken, the signal change was checked while the surface rotates to ensure that it does not vary more than 10% of the total signal. All spectra in these experiments were averaged over either 2500 or 1000 scans with a 4 cm\textsuperscript{-1} or 2 cm\textsuperscript{-1} resolution depending on the experiment. A background

\textbf{Figure 2.9} Schematic of the selection rules for IRRAS showing enhancement of the p-polarized light at the interface.
spectrum was initially acquired of a bare silver rotating surface. Once a saturation environment was reached and the surface was being wetted with the fluid, sample spectra were taken with reference to the original bare silver surface background spectrum. Spectra were baselined after collection if necessary.

2.4.6 Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS)

PM-IRRAS measurements were acquired using the same set-up as IRRAS only with the addition of a photoelastic modulator (HINDS Instruments) and a synchronous sampling demodulator (SSD, GWC Instruments). The selection rules. 39, 43 remain the same for this technique but because of the additional two components, there is the s-polarized light which gets canceled at the interface (Figure 2.10) and the signal is enhanced enabling the analysis of sub-monolayer species on the metal surface.

![Figure 2.10 Schematic of the selection rules for PM-IRRAS which modulated between s- and p-polarized light. The s-polarized light gets cancelled at the interface whereas the p-polarized light gets enhanced at the interface.](image)
Although the set-up was mostly the same between IRRAS and PM-IRRAS, the collection process was much more complex for PM-IRRAS. The ‘SKS PMIRRAS’ experiment file was used for PM-IRRAS experiments which sets the gain=1, the optical velocity=1.8988 cm/s and the aperture=100 with no attenuation; the output for this experimental file was single beam/arbitrary units because the spectrum is a ratio of channels in this case and not absorbance. The alignment of the surface in these experiments affected the signal, the phase and the Bessel function making it a very difficult technique to align. Before any measurement was taken, the surface was aligned to obtain max peak to peak signal, and the signal change was checked while the surface rotates to ensure that it does not vary more than 10% of the total signal. Then, the phase was checked by connecting the two phase cords to the oscilloscope; a good phase consists of the bottom of the sin-wave matching the right most line of box signal seen in Figure 2.11A. This was adjusted using the phase adjustment dial but was found to get the best phase when the dial was turned to 5-50. It was important to ensure that the phase does not change while the surface was rotating. Once the signal and phase were correct, the Bessel function was adjusted. This was done by setting the PEM controller box to the wavenumber of choice. This wavenumber essentially determined where the top of the Bessel function fell on the wavenumber axis and was set to enable the peaks of interest to fall on a high intensity linear portion of the Bessel function seen in Figure 2.11B. This allowed for easier baselining once the spectra were analyzed. The Bessel function could be visualized when the switches on the SSD box were moved from local and sum to Ext and Diff, the external A feature was checked in the SST menu and the bench in the experimental setup was set to single beam.
Figure 2.11 A. Picture of the display from the oscilloscope showing the phase. Note that the right line of the box feature falls on the minimum of the sin wave. B. Image of the Bessel function centered around 2500 cm\(^{-1}\). C. Image of the dual-channel box showing the A and B channel readings where A should always be larger than B.
The PM-IRRAS experiments in this thesis were collected with the “WAV” set to 2500 cm\(^{-1}\) and 1300 cm\(^{-1}\) on the PEM controller. This “WAV” values is the wavenumber where the Bessel function will have a maximum feature. Once the Bessel function was optimized, a spectrum was collected; if the Bessel function did not look good, the surface and detector were realigned and the process was started over.

All spectra in these experiments were averaged over 2500 scans with a 4 cm\(^{-1}\) resolution. To collect a spectrum, the dual-channel was checked which allowed a popup box to show the A and B channels seen in Figure 2.11C. The gains on the SSD box were adjusted to ensure that the A channel read out was larger than the B channel. The ‘ok’ button was then clicked to complete the dual channel check which was the last step before collecting. To start the measurement, collect sample from the SST menu was clicked; it was important not to use the collect sample on the toolbar. Measurements of the bare silver rotating surface were collected before any fluid was introduced to ensure the surface was clean. Once this was confirmed, a saturation environment was reached, and then the surface was wetted with the fluid; measurements were taking for both saturation and wetting. After the spectra was collected, it was added to the window where both the A and the B channel spectrum show up. To obtain the spectrum of interest, the ratio of the B channel over the A channel spectrum was taken. Spectra were baselined after collection due to Bessel function shape.

2.4.7 Ellipsometry

Spectroscopic ellipsometry was performed using an M-2000 spectroscopic ellipsometer (J.A. Woollam Co., Inc.). Most ellipsometry was collected using focusing probes which decreased the spot size from ca. 1 mm to 250 µm in diameter. Data was
acquired at an incidence angle of 75° in the dynamic wetting cell. The ellipsometry set up is pictured in Figure 2.12.

All measurements were taken for 5 seconds with a minimum of 3 measurements per velocity. Depending on the experiment, the measurement was either taken while the sample was stopped at the same location on the surface or taken while the surface was rotating but starting the measurement at the same location on the surface. The ellipsometer reports Ψ and Δ values which were sensitive to changes in refractive index and extinction coefficients from 370 nm to 1000 nm for films ranging in thickness from several hundred nanometers to less than 1 nm.

Figure 2.12 Left: Front view of the ellipsometer with wetting cell and focusing probes attached. Right: Top down view of the set-up with a view into the cell to see the surface position.
The $\Psi$ and $\Delta$ parameters were used to analyze changes directly in film thickness at the solid-fluid interface. The data was also analyzed using models in the Complete Ease software. Models used are shown in the appendices.

### 2.4.8 Differential Scanning Calorimetry (DSC)

Thermal analysis was done using a Q100 differential scanning calorimeter (TA Instruments) with liquid nitrogen cooling accessory. Samples were prepared by pipetting ca. 4 mg of sample into an aluminum pan. No lid was used to prevent leakage of sample out of the pan during clamping process. An empty pan with no lid was used as a blank. The blank heat flow data is subtracted from the sample data later using Excel. The sample chamber is purged at 20 ml min$^{-1}$ with equal part ultra-pure helium (Praxair 99.998 %) and ultra-pure nitrogen (Praxair 99.998 %). An initial temperature of 25℃ is set before the sample is cooled to -140 ℃ at a rate of 10 ℃ min$^{-1}$. The heat flow is then left to equilibrate at -140 ℃. Once equilibrium is reached, the sample is heated to 25 ℃ at a rate of 5 ℃ min$^{-1}$ and set to equilibrate at the final temperature of 25 ℃. Measurements are replicated three times, with a new sample each time. The peak temperature is determined using TA Instrument TRIOS software.
Chapter 3. Analysis of Fluid Film Behavior using Dynamic Wetting at a Smooth and Roughened Surface

Note: This chapter was published in Analytical Methods (Anal Methods) titled “Analysis of Fluid Film Behaviour using Dynamic Wetting at a Smooth and Roughened Surface,” in 2015 by Samantha L. Nania and Scott K. Shaw. The TOC figure shown above represents the slip profiles predicted as a function of surface roughness using the dynamic wetting technique.

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3.1 Abstract

A dynamic wetting technique is described and used to create and aid analysis of ultrathin (1-5 nm) fluid films on vertically aligned silver substrates of varying roughness (RMS roughness between 1 and 7 nm) prepared by chemical and mechanical polishing and electrochemical roughening. Chlorobenzene and 1,2-dichlorobenzene fluids are applied to hexanethiol monolayer modified Ag substrates. The dynamic wetting approach allows direct investigation of the solid-liquid interface and provides a platform for investigating possible deviations from the hydrodynamic no slip boundary condition. Surface analysis is carried out by contact angle measurements, vibrational spectroscopy, and ellipsometry. Data describe effects of the surface roughness, surface chemistry, fluid viscosity, and dynamic wetting velocity on the properties of the wetting film. Results indicate that fluid films are not present on very smooth (better than 5 nm RMS) or intermediate roughened substrates (RMS roughness around 7 nm), despite varying surface chemistry and varying wetting velocities. These results provide evidence to support the possibility of molecular slip at solid surfaces.

3.2 Introduction

The solid-liquid interface plays many roles in applications from fuel cells to biomedical implants. This is due to drastic changes in the properties of matter within the interfacial region, specifically defined as a planar layer parallel to the solid surface with a thickness of ca. 1 to 100s of nanometers. Matter within this region is generally believed to behave very differently than the same material far from any surface (i.e. in the bulk phase). In fact, in this thin interfacial layer, materials have been described to behave as entirely new phases of matter. Our research aims to improve understanding of one such molecular
interaction with important ramifications in fluid flow: the motion and slip fluid molecules at solid surfaces.

3.2.1 The No Slip Boundary Condition

Chemistry, Engineering, and Physics, have intersected in the study of fluids at surfaces for many years.\textsuperscript{7-10} Until recently, the idea that fluid molecules adjacent or near to a solid surface remained in static contact with that surface, even under conditions of high shear stress (i.e. rapid, pressure-driven fluid flow), was widely accepted.\textsuperscript{7, 9, 10} This observation was formalized by the no slip boundary condition, which posits that a fluid layer adjacent to a solid surface moves at the same velocity as the substrate itself.\textsuperscript{7, 9-11} This no slip boundary condition precludes the possibility of fluid slip and was widely agreed upon through much of the 20\textsuperscript{th} century. More recently, the existence of a finite slip length ($b$), measured beyond the interface and at which the velocity of the fluid approaches zero (Figure 3.1),

\textit{Figure 3.1} Schematic of (a) no slip, (b) partial slip, and (c) complete slip boundary conditions present at the solid-liquid interface. In the no slip boundary condition, the velocity of the fluid at the solid interface matches the velocity of the surface. In a partial or complete slip boundary condition, the fluid’s velocity at the solid interface can oppose the velocity of the surface. Adapted from Refs 7 and 10.
has been used to quantify the boundary condition and any possible fluid slip.\textsuperscript{7} This is directly related to the actual slip of a fluid molecule at a surface, which is simply the linear distance, parallel to the surface, over which a fluid molecule will move under varying experimental conditions. When a fluid and an adjacent solid surface move at different velocities, the no slip boundary condition is violated.\textsuperscript{7,9-11} The suggestion that this behavior was physically possible was once met with severe criticism. However, a growing body of literature now exists that supports the idea that, in certain circumstances, partial or complete slip may in fact be observed.\textsuperscript{9,11,16-19}

Research efforts to define the limits of the no slip boundary condition have been productive, revealing unsuspected chemical and physical properties of fluids and solids near solid surfaces.\textsuperscript{2,3,4} Some of the most recent studies have examined slip boundaries by tracing velocity profiles of fluids near surfaces using fluorescent tracer particles,\textsuperscript{18,23} whereas other studies have relied on applying shear forces and monitoring friction or fluid displacement via controlled motions of multiple plates or capillaries.\textsuperscript{7,11} Technological advancements have facilitated analysis of continually smaller sized domains, allowing for increasingly detailed characterization of the fluid molecules that participate in creation of the boundary condition. This shift in vantage point has provided a molecular view of the interfacial system, and has led to the consideration of intermolecular chemical forces along with physical forces.\textsuperscript{3,24} For a chemically generic system, it has been reported that when an ultra-smooth surface (< 5-7 nm RMS roughness) comes in contact with a fluid, the hydrodynamic no slip boundary condition can be violated and a slip boundary can be achieved Figure 3.1).\textsuperscript{11} Lauga et. al. describe multiple circumstances in which the no slip boundary condition has been apparently violated, providing multiple examples of studies
showing slip lengths that range from nanometers to microns, all determined via different experimental methods. They are quick to point out multiple physical processes that may lead to results which could be construed as slip; the takeaway message being that an overall disagreement exists on if slip is actually observed, and to what extent surface and fluid properties might contribute to slip at the fluid-solid interface. Since the effects of surface roughness on the slip boundary condition have yet to be agreed upon, our measurements aim to examine the surface roughness at the nanometer scale using a dynamic wetting technique in combination with spectroscopic methods.

3.2.2 Dynamic Wetting

Because of the microscopic dimensions of the interface and the proximity of the bulk solution, it is very difficult to exclusively analyze material contained within the solid-liquid interface. To provide an advantage in our measurements, we employ dynamic wetting. Dynamic wetting is a technique in which a droplet of a liquid is held near the bottom of a solid, disk-shaped substrate. The plane of the substrate is vertical, and the substrate is slowly rotated through the droplet. This creates an extruded film, or residual film, as the substrate rotates up and away from the fluid droplet. The fluid film is ultimately probed via spectroscopy in a reflection geometry at the apex of rotation as shown in Figure 3.2. The reflected light yields information pertaining to the interfacial region’s architecture, including amount, composition, and orientation of fluid molecules within the probe area. The wetting technique is similar to emersion, and provides direct analysis of molecules that represent interfacial matter that would naturally be present at a fully emersed solid-liquid interface.
The film interface is analyzed using a combination of polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) and spectroscopic ellipsometry, which provide details on chemical interactions, structure and film thickness. Results from these data allow the construction of new chemical insight into the systems in which the solid-liquid interface plays an important role. If the slip boundary condition is dependent on surface roughness, this research will be applicable to the development of innovative solutions to many longstanding challenges in industry and physical sciences.

3.3 Experimental Section

3.3.1 Materials

H₂SO₄ (ACS grade, BDH), HClO₄ (70%, Sigma), NH₄OH (28-30%, BDH), Chlorobenzene (99.9%, Alfa Aesar), and 1,2-dichlorobenzene (99%, Alfa Aesar) were used as received. 4.0M solution of CrO₃ (99.9%, Aldrich), 0.6 M solutions of HCl (ACS grade, BDH), and 0.1 M solution of KCl (99.995%, Alfa Aesar) were prepared with Milli-
Q water. Water was purified with Milli-Q UV Plus System (Millipore Corp, 18.2 MΩ cm⁻¹ resistivity, TOC ≤ 4 ppb). 5 mM hexanethiol (96%, Acros Organics) solutions were prepared in ethanol (200 Proof, Pharmco-Aaper).

3.3.2 Surface Preparation

Polycrystalline silver disks (14 mm diameter, 99.999%, ESPI Metals) were mechanically and chemically polished. Each silver surface was mechanically polished using 600 and 1000 grit sand paper followed by successive 9.5, 3.0, 1.0, and 0.3 µm aluminum oxide powders. Surfaces were then chemically polished using a chromate-etch. The final surfaces had RMS roughness of better than 5 nm verified by multiple contact mode images from an atomic force microscope (Asylum Research MFP-3D). These polished surfaces were examined directly or roughened electrochemically in aqueous 0.1 M KCl solution by passing 5 mC cm⁻² of oxidative current. Surfaces to be modified with hexanethiol self-assembled monolayer (SAM) layers were placed in a 5 mM hexanethiol in ethanol solution for at least 24 hours. Each surface was doubly rinsed with ethanol and water and sonicated in water to rid the surface of any excess physisorbed hexanethiol. The surfaces were stored in water for at least 12 hours before use.

3.3.3 Dynamic Wetting

The surface is attached to a shaft housing a 12-volt DC motor and gearhead (Micromo) to provide substrate rotational velocity control. This assembly is inserted into a Teflon cell which is made airtight to allow environmental control for the duration of the measurement. The cell is held under an inert nitrogen gas atmosphere, which is either dry (pure N₂) or saturated with the vapor phase of the selected wetting fluid (i.e.
chlorobenzene). Reference data are acquired for the system before introduction of the fluid or fluid vapor to verify purity and cleanliness of the substrate. Once confirmed, the cell’s vapor phase is saturated with the wetting fluid. Saturation is confirmed by infrared transmission-absorption measurements of the fluid’s gas phase vibrational spectra within the cell. For chlorobenzene fluids used here, complete saturation requires ca. 2 hours. Complete saturation is vital to prevent evaporation of fluid from the substrate during analysis. Previous studies, on Ag-SAM-Water systems, have shown the formation of condensation films in a complete saturation environment.\textsuperscript{45} Finally, the tip of a glass capillary is brought near to the surface and a droplet of fluid is dispensed from the capillary tip. The droplet (ca 0.2 mL) is held between the capillary and the bottom of the surface by capillary forces. The substrate is then made to slowly rotate through the droplet at a prescribed velocity, and a thin layer of fluid (held to the surface through intermolecular or physical forces against the downward force of gravity) is extruded as the surface rotates up and away from the droplet. Ultimately, fluid molecules in this film are spectroscopically probed at the apex of the substrate’s rotation.

3.3.4 Instrumentation

3.3.4.1 Contact Angle (C.A.)

A goniometer (Rame-Hart model 100) upgraded with a high resolution CMOS camera is used to characterize substrate contact angle and wettability. The camera is equipped with a 6x to 60x magnification lens (Thor Labs). Drops of the wetting fluid (~20 µL) are dispensed on to the surface using an EPPENDORF EDOS 5222 equipped with Eppendorf combitips plus 0.1 mL tips. Multiple images of dispensing, resting, and retracting fluid droplets are captured (n ≥ 3) for statistical analysis of advancing, receding,
and static contact angle. ImageJ software is used to quantify C.A.s on both edges of the droplet’s image for each surface/fluid combination.

3.3.4.2 PM-IRRAS

Measurements are acquired using a Thermo-Nicolet iS50 Fourier Transform spectrometer in combination with a photoelastic modulator (HINDS Instruments), a liquid nitrogen cooled MCT-A detector, and a synchronous demodulator (GWC Instruments). These components are assembled on an external optical bench to create an infrared beam incidence angle of 78° ± 3° with respect to surface normal. Each spectrum shown here is averaged over 2500 scans and acquired at 4 cm⁻¹ resolution. Spectra are acquired at selected substrate rotation velocities over the range of 0.009 and 2.00 cm s⁻¹. The combination of PM-IRRAS selection rules²⁰,²² and the geometrically thin fluid films created by dynamic wetting, allow for the exclusive examination of interfacial molecules of the extruded film. Importantly, only molecular vibrations with a dipole component oriented perpendicular to the metallic substrate will be observed in this geometry due to these specific selection rules.³⁹,⁴³ Analysis of the resulting vibrational energies and line-shapes are used to provide chemical information on the structure, orientation, and local chemical environment of the fluid molecules contained within the wetting film.

3.3.4.3 Ellipsometry

Spectroscopic ellipsometry is performed using an M-2000 spectroscopic ellipsometer (J.A. Woollam Co., Inc.). Data is acquired at an incidence angle of 75° in a cell identical to that described above for infrared experiments. Data are analyzed using Complete Ease software and film thickness results are used to corroborate the PM-IRRAS data.
The ellipsometer reports \( \Psi \) and \( \Delta \) values which are sensitive to changes in refractive index and extinction coefficients for films ranging in thickness from several hundred nanometers to less than 1 nm. The \( \Psi \) and \( \Delta \) parameters are used to analyze changes directly in film thickness at the solid-fluid interface.\(^{44}\)

### 3.4 Results and Discussion

Care is required in selection of an appropriate fluid/substrate pairing for these studies. The ideal fluid would have: 1) a low vapor pressure, 2) a low viscosity, and 3) a unique and strong infrared absorption profile. Using Newtonian fluids is important because it ensures that the velocity of the surface, and any resulting shear induced in the fluid, will not affect fluid’s viscosity. A Newtonian fluid is one whose behavior is purely viscous, meaning the viscosity does not depend on the shear rate.\(^7\) Chlorobenzene and 1,2-dichlorobenzene are liquids at room temperature and they both have surface tensions and vapor pressures that are lower than that of water (Table 3.1),\(^{46-48}\) which is desirable because these properties would allow for uniform thin film formation without evaporation. Hence, chlorobenzene and 1,2-dichlorobenzene are chosen for this work. The chlorobenzenes also have fairly strong and unique vibrational spectra (Figure 3.3) which permits direct analysis of wetting films with PM-IRRAS.

---

**Table 3.1** Properties of different solvents being used in wetting experiments. Values taken from: references 46(a), 47(a), and 48(all others).\(^3\)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>mp (^\circ)C</th>
<th>Vapor Pressure (kPa)</th>
<th>Viscosity, ( \eta ) (mPa s)</th>
<th>Surface Tension, ( \gamma ) (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0</td>
<td>3.17</td>
<td>0.890</td>
<td>71.99</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>-45.3</td>
<td>1.6</td>
<td>0.753</td>
<td>32.99</td>
</tr>
<tr>
<td>1,2-Dichlorobenzene</td>
<td>-17.0</td>
<td>0.18</td>
<td>1.324</td>
<td>37.00(^a)</td>
</tr>
<tr>
<td>1,3-Dichlorobenzene</td>
<td>-24.8</td>
<td>0.252</td>
<td>1.044</td>
<td>35.42</td>
</tr>
<tr>
<td>1,4-Dichlorobenzene</td>
<td>53.1</td>
<td>0.231(^b) (solid)</td>
<td>(solid)</td>
<td>(solid)</td>
</tr>
</tbody>
</table>

---
We expect surface roughness to show an effect on the interfacial structure of the alkanethiol used here to modify the hydrophobicity of the solid surface. This roughness could have an effect on the residual film’s behavior and properties, which can also play a role in slip / no slip boundary condition. We begin by reporting RMS roughness of each surface obtained from AFM images (Figure 3.4). These confirm that mechanically/chemically polished bare silver substrates and electrochemically roughened (5 mC cm$^{-2}$) silver substrates have an average RMS roughness of 2.3 ± 0.3 nm and 7.1 ± 2.7 nm, respectively. We note that the value for the smoothest of our substrates is significantly below the theoretically proposed 5-7 nm range for attaining a complete slip boundary condition.$^{11}$

![FTIR transmission spectra of chlorobenzene (top blue) and 1,2-dichlorobenzene (lower red) acquired using KBr salt plates. Spectra are offset vertically.](image)

$^{11}$ Figure 3.3 FTIR transmission spectra of chlorobenzene (top blue) and 1,2-dichlorobenzene (lower red) acquired using KBr salt plates. Spectra are offset vertically.
Figure 3.4 AFM images of 1 x 1 μm sections of both (A) smooth and (B) roughened silver substrate with 2.3 ± 0.3 nm and 7.1 ± 2.7 nm average RMS roughness, respectively.
Control of the substrate’s rotational velocity is crucial in a dynamic wetting measurement. At low velocities of rotation, the fluid film is comprised exclusively of molecules that interact with the substrate; we deem these as ‘interfacial’. When the velocity of rotation increases beyond a system dependent, critical value, the film thickens and includes bulk fluid that is dragged from the fluid bath on account of viscous interaction between the fluid molecules. These extra fluid molecules create a thicker film and can reach the apex of rotation where the spectroscopic beam is probing. These molecules are not specifically interacting with the solid surface and therefore, are deemed ‘bulk’ phase material. The critical velocity at which this transition takes place depends on the interaction potentials (Hamaker constants) between the fluid and surface species. These are adequately summarized by the critical capillary number ($C_a$), which is calculated using the receding contact angle of our chlorobenzene fluids via Egger’s equation\textsuperscript{49}

$$V_{crit} = \frac{C_a \gamma}{\eta}$$ \hspace{1cm} \textit{Equation 3.1}

where $V_{crit}$ is the critical dewetting velocity, $C_a$ is the critical capillary number, $\gamma$ is the surface tension (N m$^{-1}$), and $\eta$ is the viscosity (N s m$^{-2}$). These parameters for the chlorobenzene fluids are shown in Table 3.2. For the hexanethiol modified, smooth, silver surfaces used here, $V_{crit}$ is calculated to be 0.20 cm s$^{-1}$ and 0.20 cm s$^{-1}$ for chlorobenzene and 1,2-dichlorobenzene, respectively.

C.A. measurements shown in Table 3.3 were acquired for both fluids on silver surfaces modified with hexanethiol SAM. The receding C.A. was used to calculate the critical dewetting velocity due to the similar geometry of the extruded film formation.
Table 3.2 Parameters used for calculating the critical dewetting velocities ($V_{crit}$) for smooth and roughened surfaces with both chlorobenzene (blue/top) and 1,2-dichlorobenzene (orange/bottom). Surface tension ($\gamma$) and viscosity ($\eta$) from reference 48. Critical capillary number ($C_a$) is calculated from J. Eggers equations.\textsuperscript{49}

<table>
<thead>
<tr>
<th></th>
<th>Chlorobenzene</th>
<th>1,2-Dichlorobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Smooth (2 nm)</td>
<td>Roughened (7 nm)</td>
</tr>
<tr>
<td>$C_a$</td>
<td>4.61E-05</td>
<td>6.33E-05</td>
</tr>
<tr>
<td>$\gamma$ (N m$^{-1}$)</td>
<td>3.30E-02</td>
<td>3.30E-02</td>
</tr>
<tr>
<td>$\eta$ (N s m$^{-2}$)</td>
<td>7.53E-04</td>
<td>7.53E-04</td>
</tr>
<tr>
<td>$V_{crit}$ (cm s$^{-1}$)</td>
<td>0.20</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table 3.3 Contact angle (C.A) for smooth and roughened hexanethiol-modified Ag surfaces with both chlorobenzene and 1,2-dichlorobenzene. Receding C.A. values are used for calculating $V_{crit}$.

<table>
<thead>
<tr>
<th>Ag-Hexanethiol</th>
<th>Chlorobenzene</th>
<th>1,2-Dichlorobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smooth (2 nm)</td>
<td>37.5±2.4°</td>
<td>9.1±1.7°</td>
</tr>
<tr>
<td>Roughened (7 nm)</td>
<td>28.7±3.1°</td>
<td>10.2±1.2°</td>
</tr>
</tbody>
</table>
during the wetting process. The receding C.A.s for a smooth (ca. 2 nm) SAM-surface with chlorobenzene and 1,2-dichlorobenzene are 9.1±1.7° and 10.7±2.3°, respectively. These C.A.s are similar to what is found for a rough surface (ca. 7 nm), with chlorobenzene and 1,2-dichlorobenzene receding C.A. was 10.2±1.2° and 13.4±1.9°, respectively. Receding contact angles, which are used for calculation of the critical dewetting velocity and best mimic the dynamic wetting process, are statistically identical for smooth and rough surfaces.

**Figure 3.5A** shows PM-IRRAS spectra acquired from the SAM modified surface in the absence of the chlorobenzene fluid (in a dry N₂ environment). The SAM’s CH-stretching vibrations are clearly seen between 2800 cm⁻¹ and 3000 cm⁻¹. By using the Beer-Lambert law and the ideal gas law,⁵⁰ we compare our experimentally observed saturation condition to the reported vapor pressure of the fluid. For all of our measurements, our observed vapor pressures match or slightly exceed the reported values of vapor saturation.⁴⁸ With the saturated environment achieved, but before introducing the bulk fluid, PM-IRRAS data are acquired to assess if a condensation layer is present on the surface. The surface film would be clearly indicated by infrared absorption features of the condensate. Our spectra acquired under these conditions are displayed in **Figure 3.5B** and **Figure 3.6**, and show only infrared absorption due to the hexanethiol SAM layer, which is a clear indication that no condensed fluid layer is present.
Figure 3.5 (A) PM-IRRAS spectra of SAM-modified Ag surface in the wetting cell during N₂ purge, before fluid introduction. (B) IRRAS spectra of SAM-modified Ag surface during in the cell during saturation of the vapor phase with chlorobenzene. Spectra acquired at 1.0 and 1.5 hours are completely superimposed, showing the vapors have reached saturation in the cell.
Figure 3.6 (A) IRRAS Spectra show saturated vapor levels of chlorobenzene fluids over 22 hours. (B) PM-IRRAS spectra over time after a saturated vapor environment was reached in the cell. No surface-fluid chlorobenzene peaks are present even after 22 hours of exposure to the saturated gas phase indicate that no condensation layer is formed.
Finally, Figure 3.7 shows PM-IRRAS spectra of the surface during dynamic wetting both mono- and di-chlorobenzene fluids at various velocities. In these spectra, the SAM’s alkane C-H stretching vibrations between 2800 cm\(^{-1}\) and 3000 cm\(^{-1}\) are present, but there are no absorption features present between 3000 cm\(^{-1}\) and 3200 cm\(^{-1}\) (aromatic C-H stretches), which would indicate the presence of a chlorobenzene film. In fact, no film is observed despite increasing the substrate’s rotation velocities well above (and below) the critical dewetting velocity.\(^{49}\)

![Figure 3.7 PMIRRAS spectra acquired from hexanethiol modified Ag during wetting with chlorobenzene fluids. (A) and (B) show results for smooth (2 nm RMS) surfaces. (C) and (D) show data for surfaces roughened to 7 nm RMS.](image-url)
We have previously shown PM-IRRAS to be sensitive to single monolayers of fluids.\textsuperscript{51} However, spectroscopic selection rules dictate that PM-IRRAS is only sensitive to molecular vibrations with a component of the changing dipole that is perpendicular to the interface. Hence, these results could illustrate one of two scenarios: 1) a fluid film is not being formed, or 2) the fluid molecules’ molecular vibrations are oscillating in a plane that is perfectly parallel to the Ag substrate’s interface.\textsuperscript{43} This type of orientation might be plausible for chlorobenzene due to π–π stacking found between aromatic rings.\textsuperscript{52} To aid in determining which case best describes our chemical system, spectroscopic ellipsometry data were also collected.

Ellipsometry is a powerful technique used to quantify film thickness with single nanometer resolution. Since it is sensitive changes in refractive indices, even if π–π stacking is occurring, any chlorobenzene film should be detected. The ellipsometric measurement generates Ψ and Δ values from the differing absorption of UV-Vis light under varying polarization conditions. The Ψ and Δ values change as a function of thickness of layers on the surface. Figure 3.8 and Figure 3.9 show the Ψ and Δ data acquired from the bare silver (Bare Ag dry) surfaces, the hexanethiol modified silver surfaces (SAM Ag dry), and the SAM-modified Ag surface while wetting with chlorobenzene fluids at various substrate velocities. A significant shift in the Ψ and Δ values is observed between the bare Ag data and the SAM-modified Ag data. This is due to the addition of the hexanethiol monolayer with a thickness of 1.4±0.3 nm. However, when the surfaces are wetted with the chlorobenzene fluids, no additional change in the Ψ and Δ values is observed regardless of substrate velocity, substrate roughness, or mono- or di-chlorinated fluid.
Figure 3.8 Ellipsometric data obtained before and during the wetting process with fluids and velocities as listed on 2 nm RMS surfaces. Ellipsometric parameters from the dry, bare Ag surface is highlighted with arrow to distinguish the shift observed after modifying with hexanethiol. (A) and (B) show the $\Psi$ and $\Delta$ values when wetting the surface with chlorobenzene. (C) and (D) show $\Psi$ and $\Delta$ values when wetting the surface with 1,2-dichlorobenzene. We note that the critical dewetting velocities for chlorobenzene and 1,2-dichlorobenzene are both 0.20 cm s$^{-1}$ on smooth SAM-Ag.
Figure 3.9 Ellipsometric data obtained before and during the wetting process with fluids and velocities as listed on 7 nm RMS surfaces. Ellipsometric parameters from the dry, bare Ag surface is highlighted with arrow to distinguish the shift observed after modifying with hexanethiol. (A) and (B) show the $\Psi$ and $\Delta$ values when wetting the surface with chlorobenzene. (C) and (D) show $\Psi$ and $\Delta$ values when wetting the surface with 1,2-dichlorobenzene. We note that the critical dewetting velocities for chlorobenzene and 1,2-dichlorobenzene are both 0.28 and 0.37 cm s$^{-1}$, respectively on roughened SAM-Ag.
Although there are slight variations in the wetted in some of the wetting measurements (Figure 3.10), there is no clear trend and is most-likely due to human measurement errors during alignment. These results support the assertion that no fluid is present at the solid-liquid interface. Ultimately, these results support a slip boundary condition on surfaces as rough as 7 nm RMS, which is at the upper limit of what has been predicted.\textsuperscript{11}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image}
\caption{Zoom in of the several representative, independent $\Psi$ (A) and $\Delta$ (B) ellipsometry measurements collected with roughened (7 nm) Ag-SAM surface during wetting process. The variance in the data does not follow any clear trend and is due to small changes in alignment as the substrate rotates.}
\end{figure}
3.5 Conclusions and Future Work

The slip boundary condition is investigated using a model system of hexanethiol-modified silver substrates of controlled roughness (2 and 7 nm RMS) and varying velocity of wetting with respect to system dependent $V_{crit}$ values. Data from two sensitive techniques, PM-IRRAS and spectroscopic ellipsometry, are shown and both indicate that no fluid remains on the substrate regardless of roughness or wetting velocity. PM-IRRAS and ellipsometric results show only features associated with the hexanethiol monolayer. The clear observation of these SAM-related features demonstrates that our measurements are probing the interfacial region and are sufficiently sensitive to detect the presence of fluids at the interface. Ellipsometric measurements also clearly confirm the presence of the SAM layer and also would be adequately sensitive to detect a film of chlorobenzene if it were present. We suggest that this set of experiments, carried out by the dynamic wetting technique, supports the presence of a slip boundary condition.

It is important to investigate additional combinations of fluids, substrates, and roughness values. These will allow examination of a wider range of chemical and physical interactions between fluid and substrate to further develop our understanding of which intermolecular forces are indeed in control of the fluid slip phenomena. The dynamic wetting method, combined with spectroscopic techniques, is a powerful method for this analysis.
Chapter 4. Structural Changes in Acetophenone Fluid Films as a Function of Nano-Scale Thickness

Note: This chapter was published in Langmuir titled “Structural Changes in Acetophenone Fluid Films as a Function of Nanoscale Thickness,” in 2017 by Samantha L. Nania and Scott K. Shaw. The TOC figure shown above represents the ordering that takes place as a film thins from a thick film to a confined film at the interface.


DOI: 10.1021/acs.langmuir.6b04206

URL: http://pubs.acs.org/doi/pdf/10.1021/acs.langmuir.6b04206
4.1 Abstract

We report experimental observations of a developing solid-liquid interface by examining acetophenone films of varying thicknesses, supported on solid silver substrates. A dynamic wetting technique provides experimental control of fluid film thickness as a function of rotational velocity. Ellipsometry and infrared reflection absorption spectroscopy data are analyzed to provide absolute film thickness and details of the changing chemical environment for varying film thickness. This data is compared to theoretical models that predict fluid film thicknesses based on physical-chemical properties of the acetophenone/silver pair. As the velocity of the substrate is varied from 0.003 cm s\(^{-1}\) to 1.872 cm s\(^{-1}\), the fluid film’s thickness changes from a ca. two hundred nanometers to two microns. This increase in film thickness with increasing velocity follows a Landau trend, which is linear with respect to velocity\(^{2/3}\). Our data also show clear evidence of molecular orientation changes as a function of film thickness, which take place as the thinner films are increasingly comprised of acetophenone molecules within a confined, interfacial environment. The spectral changes for the thinnest fluid films (< 100 nm) are shown to exhibit features similar to transmission FTIR data of frozen acetophenone, suggesting that these films are highly ordered as a result of their nanometer scale confinement.

4.2 Introduction

Molecules adjacent to a surface experience forces that lead them to form anisotropic organizations significantly different from those found in the bulk. It has been determined that these interfacial molecules may behave differently than the bulk fluid making this a fascinating topic to explore.\(^4, 5, 53\) Interfaces are ubiquitous; therefore, it is important to
understand the unique physicochemical properties and interactions that ensue in these interfacial regions and how they differ from the bulk regions. The interfacial region is challenging to study because it is often difficult to distinguish between molecules in the interfacial region compared to the bulk fluid at the surface. While probing, the interfacial region presents distinct analytical challenges, the last few decades have seen development of advanced sampling and analysis techniques for this task which include probe microscopies, X-ray photoelectron spectroscopy, surface enhanced Raman and infrared spectroscopy, non-linear techniques, spectroscopic ellipsometry, and secondary ion mass spectrometry. These and many other techniques provide data that allow advanced understanding of molecules’ behavior in the interfacial region, and how the surface at that interface plays a role

Uncovering details about the interface becomes increasingly important for better understanding boundaries between the bulk and interfacial material behaviors. Recent work that is relevant to our own includes that by Nathanson and coworkers, in which thin liquid films are formed via rapid emersion, and the retained fluid film is thinned to a uniform thickness on the order of hundreds of microns via a scraper.54 Using a molecular beam, it has been shown that the scattering and trapping of these gas phase molecules at the liquid interface can aid in distinguishing which molecules and functional groups are present.54 Hemminger and coworkers also examine molecules at the liquid-vapor interface using ambient pressure X-ray photoelectron spectroscopy. This study reveals that the concentration of ions at an interface is dependent on the properties of the liquid and is supported by MD simulations.55 To analyze orientation of molecules in interfacial thin films, Pemberton et. al. use infrared spectroscopy to study water/D₂O films. The diagnostic
stretching vibrations of the D$_2$O were fit to model line shapes to determine distinct environments of water at the interface.$^{38, 56}$ Dutta and coworkers report at molecular orientation and shear effects by confining a fluid between a silicon window and a magnetic seal rotating together in a custom sample chamber. The molecular ordering is then examined under the play of shear forces. It was determined that shear has an effect on molecular ordering, but that it varies depending on the molecule.$^{29}$

The molecular composition at the interface and the specific orientation of molecules in the interface remain fruitful topics of investigation. A major objective of our work is to report the properties and molecular orientation of a fluid film as a function of its thickness. In doing so, we are able to understand how the molecules behavior within fluid films is affected as a function of their confinement within an interfacial region. Spectroscopic studies of the interfacial region are convenient because they are non-invasive and very descriptive of chemical environment and orientation. However, standard spectroscopic probes of the microscopic interfacial regions are challenged by large interference from relatively thick, bulk layers.

In these studies, we mitigate the bulk contribution to the signal by using dynamic wetting to provide systematic variations of a fluid film’s thickness. The dynamic wetting technique affords the experimentalist continuous and systematic control of a fluid layer thickness as it is supported on a solid substrate. Often this thickness can be varied across the interfacial and bulk phase regimes. A relationship between the substrate’s velocity and the fluid film thickness can be developed and classified into two regimes as is shown in Figure 4.1.
At velocities below a system dependent critical value \( v_{\text{crit}} \), intermolecular forces in the substrate-fluid system combine to create fluid films of a characteristic thickness as described by the Lifshitz equation\(^{57} \) seen in \textbf{Equation 4.1},

\[
  h = \sqrt[3]{\frac{A_{123}}{6\pi \left( \frac{RT}{V_m} \right) \ln \left( \frac{P}{P_0} \right)}}
\]

\textbf{Equation 4.1}

where \( h \) is thickness (m), \( A_{123} \) is the Hamaker Constant (J), \( R \) is the gas constant (J (K mol\(^{-1}\)), \( T \) is the temperature (K), \( V_m \) is the molar volume (m\(^3\) mol\(^{-1}\)), \( P \) is the pressure of vapor, and \( P_0 \) is the saturated vapor pressure. This film thickness does not vary with substrate velocity, and (for molecular fluids) is generally on the order of single nanometers. Above \( v_{\text{crit}} \), the film’s thickness begins to show velocity dependence. \( v_{\text{crit}} \) can be identified as the intersection point between the Lifshitz and Landau models\(^{49} \) and verified experimentally.

\textbf{Figure 4.1} Theoretical film thickness vs. substrate velocity\(^{(2/3)} \) for the Landau and Lifshitz models. The solid black line traces predicted thickness of the Landau model, and the dashed red line traces predicted thickness of the Lifshitz model. The intersection of these two predictions defines the critical dewetting velocity.
by monitoring film thickness as the substrate velocity is varied. Film thicknesses above the \( v_{\text{crit}} \) are predicted to follow a velocity\(^{(2/3)}\) dependence, as described in the Landau equation\(^{58}\) seen in Equation 4.2.

\[
h = 0.299 \frac{\left( \frac{V \eta}{\gamma} \right)^{2/3}}{\sqrt[3]{\rho g}} \quad \text{Equation 4.2}
\]

where \( h \) is thickness (m), \( V \) is velocity of withdrawal (m/s), \( \eta \) is the viscosity (Pa s), \( \rho \) is the density (kg m\(^{-3}\)), \( g \) is the acceleration of gravity (m s\(^{-2}\)), and \( \gamma \) is the surface tension (N m\(^{-1}\)). This dependence allows direct control of the experimental system. This velocity\(^{(2/3)}\) dependence persists until, at very fast substrate rotations, centripetal forces overcome chemical interactions and the system enters a new regime analogous to spin casting. Our work focuses on the substrate velocities that provide film experimental thicknesses of ca. 100 nm to 1000 nm. This provides a tunable level of fluid confinement and allows observation of the transition from a film that contains both interfacial and bulk components to a system comprised almost entirely of interfacial species.

This study further analyzes interfacial films of acetophenone; Acetophenone is a an organic, molecular fluid with a low vapor pressure (0.049 kPa), and low viscosity (1.681 mPa s).\(^{59}\) The C=O overtone and the C-H stretching modes at 3351 cm\(^{-1}\) and 3062 cm\(^{-1}\), respectively, provide good spectroscopic handles for vibrational analysis of the fluid.\(^{60}\) Table 4.1 shows the relevant properties for acetophenone, chlorobenzene, and water direct comparison.\(^{59}\) This study continues a series of molecular fluid films examined by our group.
We previously reported data for chlorobenzene and 1,2-dichlorobenzene fluid films at alkane-thiol SAM-modified silver surfaces. Both chlorobenzene and 1,2-dichlorobenzene did not form films on surfaces with RMS roughness of ≤ 7 nm, regardless of a wide range of substrate velocities. Acetophenone contains a benzene ring, similar to chlorobenzene, but has a side chain which includes a ketone. The π-π interactions present in chlorobenzene liquids should be at least partially disrupted by the ketone group, and it provides a useful spectroscopic handle for data analysis. Based on the physical properties of acetophenone, we predict that acetophenone fluid films will be stable and that the thickness of these films will follow the existing models, increasing thickness with velocity. Confirming this prediction will advance the chemical model of the interfacial region, revealing fundamental knowledge of interface formation behavior and advancing applications such as lubrication, microfluidics, and biofouling.

4.3 Experimental Section

4.3.1 Materials

\[ \text{H}_2\text{SO}_4 \text{ (ACS grade, BDH), HClO}_4 \text{ (70\%, Sigma), NH}_4\text{OH (28-30\%, BDH), and Acetophenone (98\%, Acros Organics) are used as received. 4.0M solution of CrO}_3 \text{ (99.9\%, Aldrich) and 0.6 M solutions of HCl (ACS grade, BDH) are prepared with Milli-Q water.} \]
Water is purified with Milli-Q UV Plus System (Millipore Corp, 18.2 MΩ cm$^{-1}$ resistivity, TOC ≤ 4 ppb).

4.3.2 Surface Preparation

Polycrystalline silver disks (14 mm diameter, 99.999%, ESPI Metals) are mechanically and chemically polished via established methods$^{42, 62}$ to create smooth surfaces with RMS roughness ≤ 5 nm as verified with atomic force microscopy. Optical constants of the surfaces are routinely checked with ellipsometry and compared to literature values$^{59}$ to verify they are flat and clean. Cleaned surfaces are immersed in ultrapure water for < 60 minutes to protect the surface before use. Surfaces are taken out of the water and blown off with nitrogen before it is put in the nitrogen purged cell.

4.3.3 Dynamic Wetting Apparatus

The clean Ag surface is mounted to a gear box and variable voltage (0-12 volt) DC motor. This assembly is mounted to a PTFE plunger and inserted into a gas tight PTFE cell to allow control of environmental conditions. The motor/gearbox assemblies allow for substrate rotation velocities between 0.003 and 1.913 cm s$^{-1}$ (0.04 to 26.08 R.P.M.) The PTFE cell is fitted with CaF$_2$ windows which provide spectroscopic access for infrared and ellipsometry studies. A small volume (ca. 200 μl) of the fluid of interest is dispensed into the bottom of the cell. A portion of this droplet evaporates to form a saturated fluid-vapor environment in the cell volume. This vapor mitigates evaporation of fluid films from the substrate during dynamic wetting measurements.
Infrared reflection absorption spectroscopy (IRRAS) data of the gas phase is used to confirm saturation vapor pressure is met. Previously studied systems have shown solvent layers that condense from the vapor phase. To monitor for this behavior we acquire PM-IRRAS spectra during the time required to create the saturated vapor phase. Ultimately, a droplet of the wetting fluid (ca. 200 μl) is dispensed from a 1 mm I.D. glass capillary and held in hanging meniscus contact with the bottom of the Ag disk (Figure 4.2). The substrate’s rotation through the bulk droplet extrudes a fluid film on the surface. The film is spectroscopically probed at the apex of the surface’s rotation. Lab temperatures are monitored and range between 20 – 21°C.

4.3.4 Instrumentation

4.3.4.1 Transmission FTIR

A Thermo-Nicolet iS50 Fourier Transform spectrometer with liquid nitrogen cooled MCT-A detector is used for bulk fluid analysis. ~15 uL of fluid is dispensed and sandwiched between two KBr salt plates with a 0.25 um Teflon spacer to control path length. Each spectrum is an average of 128 scans acquired at ≤ 4 cm⁻¹ resolution at an
optical velocity of 1.8988. The transmission data at fixed path length is used to quantify molar absorptivity values via Beer-Lambert Law analysis. These values are used to corroborate ellipsometry data of the wetting films’ thicknesses.

4.3.4.2 TC-FTIR

Temperature controlled FTIR measurements are obtained using the same FTIR spectrometer and detector. A variable temperature cell and a high stability temperature controller (International Crystal Laboratories) are fitted into the FTIR’s main transmission compartment. The transmission windows are 4 mm thick, CaF₂. This apparatus provides temperature control from -180 °C to 250 °C. Each temperature controlled spectrum shown here is acquired at 4 cm⁻¹ resolution and averaged over 32 acquisitions.

4.3.4.3 IRRAS

The output of the FTIR described above is directed to an external optical bench and associated optics contained inside a custom enclosure which is purged with dry, CO₂ omitted air (Purimetrics, Model KADW-13AS). The wetting cell is placed in the beam path and the substrate is aligned for an IR beam incidence angle of 78° ± 3° with respect to the surface normal. IRRAS measurements are acquired under static p-polarization, selected by a standard wire-grid polarizer. IRRAS spectra here are averaged over 2500 or 1000 scans (as noted) with a resolution of ≤ 4 cm⁻¹. Polarization modulated (PM)-IRRAS is used to test for presence of condensation layers due to increase in sensitivity. IRRAS is used to analyze the wetting films due to relatively large thicknesses which provide adequate signal to noise ratios. For this reason, a background scan is collected after vapor phase saturation has been reached within the dewetting cell, and applied to all IRRAS spectra to remove any interference of gas phase acetophenone in the fluid film spectra.
4.3.4.4 Ellipsometry

Spectroscopic ellipsometry is performed using an M-2000 spectroscopic ellipsometer (J.A. Woollam Co., Inc.) equipped with focusing probes to create ca. 250 μm diameter spot size. The incidence angle is fixed at 75.0° from normal. The cell used for ellipsometry is identical to that used for infrared reflection measurements. The ellipsometer acquires refractive index and extinction of the sample from 370 nm to 1000 nm. These data are fitted using Complete Ease software to quantify film thicknesses.\(^{44}\)

4.4 Results and Discussion

Figure 4.1 shows theoretical curves for Lifshitz (dashed line) and modified Landau (solid line) model predicted film thicknesses for a generic fluid substrate pair, plotted with respect to substrate withdraw velocity. The two models intersect at the critical wetting velocity, \(v_{\text{crit}}\), in the lower left of the plot. Below this velocity, the predicted fluid film thickness remains constant due to the solid-liquid intermolecular interactions. Above \(v_{\text{crit}}\), the predicted thickness varies with a \(v^{2/3}\) dependence, as originally observed by Landau-Levich.\(^{58}\) For the specific set of conditions presented for acetophenone, Ag metal substrates, and nitrogen gas environments, the critical dewetting velocity is calculated to be 0.00010 cm s\(^{-1}\).

Figure 4.3 plots experimental data for film thicknesses with the model-predicted thicknesses from Landau (solid black line) and Lifshitz (dashed red line) models. We note that the x-axis is plotted on a non-linear scale, to show the predicted relationship between film thickness and substrate velocity\(^{(2/3)}\).
Figure 4.3 (A) Theoretical and experimental film thickness with respect to velocity. The x-axis has been scaled to velocity$^{2/3}$ to highlight linear response. Data points represent film thicknesses determined by ellipsometry (red triangles), the absorbance of C=O overtone peak at 3062 cm$^{-1}$ (blue circles), and absorbance of C-H stretching peak at 3351 cm$^{-1}$ (green squares), calculated using Beer-Lambert Law. Error bars of one standard deviation are included for all experimental measurements but are smaller than the data point in some cases. Data in (B) expands the view of low velocity data in A, for substrate velocities < 0.073 cm s$^{-1}$ which show the linear dependence with velocity$^{2/3}$. 
Comparison between the experimental and model data show that films created at substrate velocities between 0.003 cm s\(^{-1}\) and 0.073 cm s\(^{-1}\) have thickness values that correlate to the Landau model as shown in Figure 4.3B. Films created at substrate velocities faster than 0.073 cm s\(^{-1}\) and up to our maximum examined velocity of 1.872 cm s\(^{-1}\) deviate significantly from the trend predicted by Landau as shown in Figure 4.3A. The experimental film thicknesses are calculated via two methods: 1) Beer-Lambert Law analyses solve for films’ path length using molar absorptivity values acquired from transmission IR measurements, and 2) film thicknesses are directly measured via spectroscopic ellipsometry. Figure 4.4 shows the two characteristic IR transitions of acetophenone that are used for the Beer-Lambert Law analysis; the C=O overtone mode at ~3350 cm\(^{-1}\) and the C-H stretching mode from the aromatic ring at ~3060 cm\(^{-1}\).

**Figure 4.4** IRRAS spectra of acetophenone films on Ag substrates acquire at various substrate velocities. Data show showing intensity changes in C-H stretching peak (3062 cm\(^{-1}\)) and C=O overtone peak (3351 cm\(^{-1}\)) corresponding to thickness changes.
These modes are chosen because they are strong IR absorbers and do not significantly change their center frequency or FWHM as a function of the film thickness. The data in Figure 4.3B shows nearly quantitative agreement between the Landau model and our Beer’s Law analysis of film thickness for C=O overtone (green squares) and C-H stretching (blue circles). We expect variations in these two IR data sets are due to changes in orientation of the fluid molecules near the solid surface which affects the molar extinction coefficient of the respective vibrational modes. Ellipsometry data for velocities between 0.003 cm s$^{-1}$ and 0.073 cm s$^{-1}$ are shown by red triangles in Figure 4.3. Ellipsometry thicknesses for substrate velocities above 0.073 cm s$^{-1}$ could not be obtained because of sharp increases in optical depolarization which reduces the quality of the ellipsometry data. Ellipsometry thickness values display a positive slope that is linear with velocity$^{(2/3)}$. This data is similar to the thickness data from IR and matches the Landau model. The ellipsometry data suggests consistently thicker films than those calculated by Beer’s Law. This systematic positive deviation from the theoretical model may be due to a non-uniform film thickness across the probe beam’s area on the substrate which complicates the required models to calculate film thickness. At very slow substrate velocities, the experimental film thicknesses approach the Lifshitz model limit of velocity independence ($v_{crit}$) thickness. For this system, the Lifshitz model predicted minimum thickness is 0.00723 um, achieved at velocities $v_{crit} < 0.0001$ cm s$^{-1}$. A table providing numerical comparison of the thicknesses from the IRRAS data, ellipsometry data, and the model predictions is available in Table 4.2.

The Lifshitz model is not velocity dependent and represents the lower bound of our predicted thickness values.
Table 4.2 Experimental and theoretical film thickness values with respect to velocity IR measurements of the C-H stretching peak (3351 cm\(^{-1}\)), C=O overtone peak (3062 cm\(^{-1}\)), Landau model, and Lifshitz model. Values for vibrational modes are calculated using Beer’s law from absorbance intensity.
Uncertainty values are pooled standard deviations from \( n \geq 3 \) independent samples (acquired on different days), and \( \geq 3 \) unique measurements per sample.

<table>
<thead>
<tr>
<th>Velocity (cm s(^{-1}))</th>
<th>IR Thickness (nm)</th>
<th>Ellipsometry Thickness (nm)</th>
<th>Landau Model (nm)</th>
<th>Lifshitz Model (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003</td>
<td>80 ± 4</td>
<td>80 ± 5</td>
<td>240 ± 1</td>
<td>70</td>
</tr>
<tr>
<td>0.004</td>
<td>91 ± 21</td>
<td>88 ± 12</td>
<td>261 ± 1</td>
<td>84</td>
</tr>
<tr>
<td>0.006</td>
<td>148 ± 38</td>
<td>119 ± 41</td>
<td>319 ± 5</td>
<td>111</td>
</tr>
<tr>
<td>0.014</td>
<td>280 ± 30</td>
<td>270 ± 20</td>
<td>329 ± 4</td>
<td>195</td>
</tr>
<tr>
<td>0.016</td>
<td>233 ± 45</td>
<td>198 ± 35</td>
<td>566 ± 7</td>
<td>213</td>
</tr>
<tr>
<td>0.035</td>
<td>450 ± 40</td>
<td>390 ± 10</td>
<td>589 ± 2</td>
<td>359</td>
</tr>
<tr>
<td>0.056</td>
<td>580 ± 20</td>
<td>450 ± 30</td>
<td>734 ± 9</td>
<td>491</td>
</tr>
<tr>
<td>0.073</td>
<td>660 ± 10</td>
<td>510 ± 20</td>
<td>860 ± 6</td>
<td>585</td>
</tr>
<tr>
<td>0.356</td>
<td>1160 ± 30</td>
<td>750 ± 10</td>
<td>-</td>
<td>1684</td>
</tr>
<tr>
<td>0.892</td>
<td>1650 ± 40</td>
<td>910 ± 40</td>
<td>-</td>
<td>3107</td>
</tr>
<tr>
<td>1.415</td>
<td>1960 ± 140</td>
<td>960 ± 70</td>
<td>-</td>
<td>4226</td>
</tr>
<tr>
<td>1.872</td>
<td>2060 ± 130</td>
<td>960 ± 90</td>
<td>-</td>
<td>5093</td>
</tr>
</tbody>
</table>
As mentioned above, experimental thickness approach the Lifshitz predicted thickness for our lowest obtainable substrate velocities (ca. 0.003 cm/s). As the substrate velocity is increased, experimental thickness data falls along the predicted trend of the Landau equation as defined in Equation 4.2. We note that the prefactor in this equation (currently 0.299) has been adjusted by a factor of $10^{0.5}$ from an earlier publication\textsuperscript{64} to accommodate dimensional analysis.

**Figure 4.5** shows IR data between ca. 1000 cm\(^{-1}\) and 2000 cm\(^{-1}\) for the distinctly different vibrational profiles of acetophenone films of varying thickness which depict the evolution of the interface, along with one transmission IR spectrum of frozen acetophenone. We highlight two absorption peaks of interest in the lower frequency region of the transmission IR data. These peaks, at 1679 cm\(^{-1}\) and 1262 cm\(^{-1}\), are attributed to C=O stretching and C-CO-C bending respectively\textsuperscript{60} from the ketone functional group. As the film thickness decreases (indicated by direction of the dashed arrows in **Figure 4.5**), the absorption features at 1666 cm\(^{-1}\) and 1247 cm\(^{-1}\) representing interfacial acetophenone shift by ca. 10 cm\(^{-1}\) to higher frequency and decrease in FWHM. Two other features at 1695 cm\(^{-1}\) and 1274 cm\(^{-1}\) representing bulk acetophenone do not shift their center frequency as thickness decreases but do show a drop in intensity until they vanish entirely in the thinnest films. Careful analysis of these spectral details reveals two simultaneous processes: an exclusion of the bulk material as the film thins, and simultaneous enhancement in the ordering of remaining ‘interfacial’ fluid. To understand these processes, we make comparison to the transmission IR data of a frozen acetophenone sample, shown at the top (black trace) of **Figure 4.5**.
Figure 4.5 Infrared spectra of acetophenone. A transmission spectra of frozen acetophenone (at top) is compared to a series of IRRAS spectra acquired at various substrate velocities (film thicknesses). Two absorption features at ca. 1265 cm\(^{-1}\) and 1680 cm\(^{-1}\) are highlighted with arrows to show the significant wavenumber shift towards the profile of the frozen spectra as the film thins.
The absorption features at 1679 cm\(^{-1}\) and 1268 cm\(^{-1}\) in the frozen spectrum coincide with the acetophenone peaks at 1679 cm\(^{-1}\) and 1262 cm\(^{-1}\) in the thinnest fluid film (red trace) in Figure 4.5. The shift to higher energy and narrowing of these two features supports an increasingly ordered arrangement of interfacial acetophenone molecules in response to the increasingly confined environment presented by the thinning fluid film. Because the absorption features in the thinnest films are very similar to those in the frozen acetophenone spectra, we suspect a similar molecular arrangement. This is despite the temperature of the thin films (21° to 22° C) being several degrees above the freezing point of acetophenone, which may provide useful insights into surface freezing and surface melting phenomena reported previously,\(^{65, 66}\) as well as confinement or shear-induced molecular ordering transitions in other systems.\(^{2, 5}\)

### 4.5 Conclusion

Acetophenone fluid films of variable thickness are investigated with IRRAS and spectroscopic ellipsometry. Theoretical thicknesses for the films are calculated using both Landau and Lifshitz equations, and a direct correlation to the experimental data is observed for substrate velocities of between 0.003 cm s\(^{-1}\) to 0.073 cm s\(^{-1}\). Film thicknesses from ellipsometry measurements show a constant positive deviation from the theoretical predicted thicknesses and the experimentally measured Beer-Lambert Law thicknesses. At substrate velocities faster than 0.073 cm s\(^{-1}\), experimental thickness values diverge significantly from the theoretical prediction, indicating additional forces, such as centripetal forces, acting to thin the film.

The acetophenone fluid films also show significant changes in vibrational profile as a function of their thickness. Analysis of the vibrational line shapes and comparison to
a spectrum of frozen acetophenone indicates that thinner films create an increasingly ordered, or crystalline-like structures that we ascribe to the increase in confinement experienced by the fluid in the thinnest films. Vibrational modes in the lower frequency region are used to characterize this evolution of the interface, and indicate that the acetophenone in films < 250 nm thick adopts an ordered structure, although distinct structural changes are seen in films as thick as 1000 nm. Additional studies of these and similar interfacial systems will be necessary to improve understanding of the intermolecular interactions affecting the solid-liquid interface, and the distance over which a solid surface can affect a fluid’s structure when creating an interface.

4.6 Acknowledgements

The authors are grateful for several helpful discussions and assistance from thank Dr. James Hilfiker and Dr. Nina Hong at J.A. Woollam company along with Taylor Fetrow for her help with CrystalMaker and creating the TOC. Research funding support for this work was provided via a Cottrell Scholar award to SKS from the Research Corporation for Science Advancement. SLN gratefully acknowledges financial support from the University of Iowa’s Graduate College Research Fellowship.
Chapter 5. Structural Changes in Acetophenone Fluid Films as a Function of Temperature

Note: This chapter is being prepared for publication in by Samantha L. Nania, Jaclyn Wrona and Scott K. Shaw. The TOC figure shown above represents the ordering that takes place in a room temperature thin, confined film (80 nm) compared to that of a 500 nm film. Also shown is the 500 nm film at 17 °C, after freezing exhibiting the same crystalline ordering seen in the thin, confined film.
5.1 Abstract

We find evidence of an ordering process in 500 nm films through repeated cooling-heating cycles, consistently generating a crystalline-like long-range ordering as frozen films approach the melting point. We characterize the solid-liquid phase transition of thin (ca. 500 nm) films of a simple molecular liquid, acetophenone, via vibrational spectroscopy. Results of multiple temperature cycles show a possible need for conditioning upon the first temperature cycle before any significant vibrational changes can be observed in the following cycles. For subsequent cycles, there is evidence of frozen films showing crystalline ordering when heated until the film eventually melts. Melting spectrum and initial rotating spectrum are nearly identical proving the fact that the films do not change thickness throughout the process. Trends in the absorption spectra recorded as a function of film temperature (heating) also bear a resemblance to spectral trends toward crystallinity as a function of increases thickness in room-temperature interfacial films. We suggest that these vibrational changes as a function of temperature confirm crystalline ordering in thin (80 nm), confined films previously studied, providing evidence that these confinement effects can extend to significant distances (100 nm) from a wall or other surface. This crystalline ordering at the interface in liquid films could play a role in the alterng of properties that appears in the molecules are the solid-liquid interface.

5.2 Introduction

Solid-liquid interfaces play a role in a wide range of everyday applications. Since interfaces are ubiquitous, knowledge of the interactions which take place in these regions is essential to recognizing their role in these applications. Though this region is difficult to study because of its small dimensions and interaction with bulk fluid, advances in
analytical methodology have revealed that molecules at this interface order, and behave differently than those in the bulk.$^{4, 5, 53}$

The ordering of molecules at the interface can be described using a density profile, as seen in Figure 5.1. The oscillation seen in the density profile results from the fact that interfacial molecules often order in parallel layers, breaking the symmetry of the bulk liquid and creating anisotropy. The density increases at each layer of molecular packing, then decreases between the layers, reflecting the absence of molecules. As the distance from the surface increases, the density profile decays and the fluids eventually becomes isotropic bulk.$^{2}$ This packing at the interface could alter the properties of the films to behave more solid-like.

Solid-like properties are exhibited by thinned films confined to the interface, resisting all shear until a critical point is reached. This behavior has been observed in a variety of fluids.$^5, 26, 27, 67-71$ Solid-like behavior at the interface has been shown, for
instance, by Israelachvili et. al.\textsuperscript{5} who used a surface force apparatus (SFA) equipped with a lateral sliding mechanism to probe shear-induced ordering across a variety of systems (spherical, chain-like, and branching molecules) to better understand the effects of molecular geometry on the interfacial ordering phenomenon. All liquids showed liquid-like behavior when unconfined by the SFA plates (gap size > 5 layers) but solid-like behavior when confined by SFA plates (gap size < 5 layers). These results indicate that confining a liquid between two surfaces may be a route to creating order and solid-like properties.\textsuperscript{5} And, in multiple studies,\textsuperscript{4, 29, 72} Dutta et al. have reduced the number of necessary surfaces to one, showing that layering occurs even at a single solid surface for tetrakis(2-ethylhexoxy)silane (TEHOS), where the liquid films diverge from the ideal, isotropic structure. Since the ordering of these molecules at the interface can change the properties in the region and therefore play a role in many applications, this concept is a fruitful topic to study.

Previously, our group studied this ordering phenomenon at a single surface using a dynamic wetting technique (\textbf{Figure 5.2}).\textsuperscript{73} With this technique, the film on a vertically-
held disc is constantly replenished by its rotation through the bulk droplet, creating a stable film of controlled, constant thickness.

By varying the velocity of the substrate at which it rotates through the bulk droplet, ordering of the molecules can analyzed as a function of film thickness at room temperature. The data from this study showed that as the film thins, changes are seen in the vibrational profile, which represents ordering of the molecules as a function of film confinement. We found that the thin film spectrum of acetophenone was comparable to that of a bulk frozen transmission, and proposed that as the film thins and the molecules become confined to the interface, a crystallization occurs where ordering of confined molecules resemble that of the molecules in a frozen, or solid, crystalline film.\(^\text{73}\)

Studying acetophenone films under the influence of temperature changes can aid in understanding the crystalline like ordering which occurs in thin, confined films. Hence, we focus on using thermal analysis to qualitatively identify phase transitions, such as: crystallization; glass-transitions\(^\text{74}\); cold crystallizations, in which a sample’s crystallization feature is observed upon heating\(^\text{75}\); and melting. Recognizing these phase changes is critical when analyzing this crystalline ordering seen in liquid films using spectroscopy, and can help when manipulating these liquid films under the influence of temperature changes.

Herein, we report the molecular behavior and ordering of acetophenone at the solid-liquid interface as a function of film thickness and temperature. Using the dynamic wetting technique described above, we perform temperature-controlled studies of thin (500 nm) films, varying the temperature of the surface through consecutive freeze-and-melt cycles. Infrared reflectance absorption spectroscopy (IRRAS) is used to probe the films and reveal information about the fluid’s ordering as a function of temperature and location in a freeze-
melt cycle. We seek to understand the ordering seen in thin confined films by studying temperature change effects on the organization or crystallization of the molecules at the interface, and whether such ordering can be induced at longer range, perhaps extending into the bulk.

5.3 Experimental Section

5.3.1 Materials

H_{2}SO_{4} (ACS grade, BDH), HClO_{4} (70%, Sigma), NH_{4}OH (28-30%, BDH), Acetophenone (98%, Acros Organics) are used as received. 4 M solution of CrO_{3} (99.9%, Aldrich) and 0.6 M solutions of HCl (ACS grade, BDH) are prepared with Milli-Q water. Water is purified with Milli-Q UV Plus System (Millipore Corp) to reach 18.2 MΩ cm resistivity, TOC ≤ 4 ppb.

5.3.2 Surface Preparation

14 mm diameter Ag disks (Polycrystalline, 99.999%, ESPI Metals) are mechanically polishing using aluminum oxide abrasive powder and chemically polished using a chromate etch procedure described in previous publications.\textsuperscript{42,62} Surface roughness is confirmed to be < 4 nm RMS roughness using contact mode atomic force microscopy while cleanliness is confirmed using a polarization modulation-IRRAS.

5.3.3 Instrumental Methods:

5.3.3.1 Temperature Controlled Dynamic Wetting

A brass shaft is attached to a gear head-variable voltage (0-12 Volts) DC motor combo (MicroMo) and enclosed in a hollowed out Teflon plunger. The brass shaft contains two ceramic, non-lubricated ball bearings with a separation distance of 41 mm. These ball
bearings allow the brass shaft to be pressed into the hollow Teflon plunger forming a sealed chamber around the brass shaft. A polished silver substrate is mounted on the end of the brass shaft and the plunger is inserted into the nitrogen purges Teflon cell body. The cell is made to be air-tight with a controlled environment. The cell is fitted with two CaF$_2$ windows for spectroscopic access using IRRAS. Before wetting, a droplet of fluid is dispensed into the bottom of the cell using a glass capillary inserted through the front of the cell and the nitrogen purge is stopped. This allows the fluid at the bottom of the cell to evaporate into the gas phase of the cell forming a saturated vapor environment. Once a saturated vapor environment is reached (monitored by IR absorbance), the same glass capillary is re-positioned ca. 1 mm from the Ag surface and a droplet of fluid is deposited at the bottom of the substrate. The droplet is held between the silver substrate and the tip of the glass capillary. The droplet volume is ca. 250 μL. The silver substrate is then rotated through the bulk droplet at a desired velocity, forming a thin film on the surface.

Once the film is formed, the capillary is pulled away from the substrate prior to cooling. The temperature of the substrate is regulated by controlling the temperature of the brass shaft from which it is mounted. Good thermal conductivity of the brass shaft conducts heat to and from the substrate. The brass shaft temperature is controlled by passing heated or cooled fluid around the section of the shaft enclosed within the hollowed Teflon plunger. This section is separated from the sample chamber by sealed ball bearings. To regulate the temperate, the fluid passes through a series of cooling or heating elements. The heated or cooled nitrogen gas exits the Teflon chamber through the opposite side of the cell. The fluid temperature and flow rate allow control of the rate of cooling or heating of the silver
substrate to its final temperature. The temperature of the sample surface and the cell are measured continuously using calibrated thermocouples.

The substrate continuously rotates through the bulk droplet as the temperature is varied from room temperature to the point at which the film freezes. Once the film freezes, the rotation of the substrate is stopped so that the bulk droplet is positioned below the IR spot, to reduce the interferences from frozen bulk droplet. The surface is then warmed until the film melts, at which point the surface is rotated again to ensure the film thickness remains stable. This temperature cycle is run anywhere from 2-4 times before it is started again with a new clean surface. Spectra are collected continuously throughout the entire temperature cycle.

5.3.3.2 IRRAS

The infrared beam from a Thermo-Nicolet iS50 Fourier Transform spectrometer is directed to an external optical table, which is enclosed and purged with dry and CO2 free air. The IR beam is reflected from a collimating mirror and passed through a wire grid polarizer, which transmits p-polarized light. The polarized IR beam enters the dynamic wetting cell through a disk-shaped CaF2 window. The cell is positioned so the beam reflects off the surface at an incident angle of 78 ± 3° with respect to surface normal, and exits the cell through a second CaF2 window. The beam is then focused by an additional collimating mirror onto a liquid nitrogen cooled MCT-A detector element. Both a background IRRAS spectrum of bare silver in a nitrogen gas environment and bare silver surface in an acetophenone saturated vapor environment are taken for reference. The background spectra contain 1000 scans, which are signal-averaged with a resolution of 4 cm⁻¹. All IRRAS spectra of extruded films are collected automatically by acquiring consecutive spectra.
During the freezing cycle, spectra are averaged over 100 scans with a resolution of 4 cm\(^{-1}\) until the film is frozen and a change is seen in the spectrum. For the heating cycle, spectra are averaged over 10 scans with a resolution of 4 cm\(^{-1}\) to decrease the time needed to acquire each spectrum, thus enabling the observation of small changes in spectra as a function of temperature.

### 5.4 Results and Discussion

In room temperature studies, as a film thins to 80 ± 6 nm, the molecules at the interface exhibit solid-like crystalline ordering.\(^73\) **Figure 5.3** shows a series of

![Image of infrared spectra](image)

**Figure 5.3** Various infrared spectra of acetophenone. A transmission spectrum of frozen acetophenone (at top) is compared to a series of IRRAS wetting spectra acquired at room temperature for various film thicknesses. The absorption feature at ca. 1265 cm\(^{-1}\) is highlighted with an arrow to show the significant wavenumber shift towards the profile of the frozen spectrum as the film thins. Spectra are offset vertically for clarity.
acetophenone wetting spectra highlighting this change in the absorption features in the 1100 cm\(^{-1}\) to 1500 cm\(^{-1}\) region.

These peaks are attributed to bulk and interfacial modes of the C-CO-C bending from the ketone functional group on the molecule.

As the film thickness decreases from 1280 ± 40 nm to 80 ± 6 nm (Seen in Table 5.1), the molecules in the film become confined to the interface, and the absorption feature at 1250 cm\(^{-1}\) shifts by ca. 12 cm\(^{-1}\) to 1262 cm\(^{-1}\). This shift is tracked using the dotted arrow, and the absorption feature now at 1262 cm\(^{-1}\) matches the peak at 1268 cm\(^{-1}\) in the frozen (17 °C) transmission infrared spectrum of acetophenone (top). On the other hand, the feature seen at 1274 cm\(^{-1}\), which is attributed to bulk acetophenone, does not shift the center of frequency, but as the liquid film thins, the feature does decrease in intensity until, in the thinnest film (80 nm), it disappears. These results indicate two simultaneous processes: 1)

<table>
<thead>
<tr>
<th>Velocity (cm s(^{-1}))</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003</td>
<td>80 ± 6</td>
</tr>
<tr>
<td>0.004</td>
<td>90 ± 20</td>
</tr>
<tr>
<td>0.006</td>
<td>130 ± 40</td>
</tr>
<tr>
<td>0.014</td>
<td>270 ± 30</td>
</tr>
<tr>
<td>0.016</td>
<td>220 ± 40</td>
</tr>
<tr>
<td>0.035</td>
<td>420 ± 30</td>
</tr>
<tr>
<td>0.056</td>
<td>520 ± 20</td>
</tr>
<tr>
<td>0.073</td>
<td>580 ± 20</td>
</tr>
<tr>
<td>0.356</td>
<td>960 ± 20</td>
</tr>
<tr>
<td>0.892</td>
<td>1280 ± 40</td>
</tr>
<tr>
<td>1.415</td>
<td>1440 ± 110</td>
</tr>
<tr>
<td>1.872</td>
<td>1510 ± 110</td>
</tr>
</tbody>
</table>
the loss of the bulk material and its disorder as the film thins and, 2) the ordering of molecules to resemble that of a frozen or crystalline acetophenone.
To investigate the ordering behavior seen in previously in these confine films and confirm crystalline ordering, a film of stable, constant thickness is studied using temperature control wetting. For these experiments, a silver substrate was rotated at a constant velocity of 0.076 cm s$^{-1}$, creating a constant film thickness of 500 ± 70 nm. When the film is at room temperature, this thickness allows us to see isotropic bulk-liquid-like behavior. The 500 nm film was taken through a series of cooling and heating cycles until the film froze and melted, repeating the cycle multiple times. During the first cooling cycle, the surface was taken well below the freezing point before the film froze. It is possible that at this point, the film was supercooled and a small defect was needed in order for freezing to be initiated. The resulting first frozen cycle spectra of the 500 nm film are shown in Figure 5.4. The wavenumber region 1230 to 1300 cm$^{-1}$ analyzed in Figure 5.3 is highlighted with a box in Figure 5.4. A sharp feature at 1272 cm$^{-1}$ is seen and remains throughout the temperature range until the film melts and becomes liquid again, at which point the spectrum again resembles that of a liquid-like fluid thick film being rotated at 0.076 cm$^{-1}$.

After the system has passed through the liquid-to-solid phase transition once (cycle 1), subsequent temperature cycles (cycles 2-4) show a vastly different set of features. Figure 5.5 shows multiple trials for each cycle. The sharp feature at 1272 cm$^{-1}$ seen in the first temperature cycle disappears in subsequent cycles (cycles 2-4). It could be that the first cycle generates a conditioning process needed before more characteristic spectral changes can be seen. In cycles 2-4, the spectra observed immediately after the fluid freezes, at 11.2 ± 2.6, is seen in Figure 5.5A, °C. These vary slightly over multiple trials. For
instance, the population of the peaks varies throughout the trials. This could be due to various domains of ordering occurring immediate freezing.

Figure 5.4 A series of IRRAS spectra acquired after the first cooling cycling and during the first warmed cycle until the films melt (bottom to top). The absorption feature at ca. 1265 cm$^{-1}$ is highlighted to show the feature of interest.
Figure 5.5 Series of IRRAS spectra collected after the second cooling cycle for (A) Domain like frozen and (B) Crystalline Frozen. The absorption features at ca. 1265 cm$^{-1}$ is highlighted with a box.
However, as the frozen/refrozen film warms and approaches the melting point of 19 °C in each cycle, the spectra shift, and exhibit much more similar features across cycles 2-4. Spectra in Figure 5.5B, acquired at 17.3 ± 0.4 °C, show this change. These data show the emerging of a single peak around 1268 cm⁻¹ which we propose is the interfacial, crystalline peak for C-CO-C bending.

Figure 5.6 may give insight into this feature by comparing spectra of frozen acetophenone (17 °C, FTIR), liquid room-temperature 80 nm film, and 500 nm film after it has been frozen and then warmed to 17.3 ± 0.4 °C (both IRRAS). The profile of the feature at 1268 cm⁻¹ of the frozen 500 nm film at 17.3 ± 0.4 °C, matches both the thin 80 nm film and the frozen transmission infrared spectra of acetophenone, suggesting that warming the frozen film causes the molecules to release energy and rearrange in crystalline fashion, as in a cold-crystallization phase transition.  

Figure 5.6 Comparison of the temperature controlled frozen transmission infrared spectrum at 17 °C (black), the IRRAS wetting spectrum of the thinnest film (80 nm @ rotational velocity of 0.003 cm s⁻¹) (purple), temperature controlled crystalline frozen spectrum of 500 nm film (green), and the IRRAS wetting spectra of the same 500 nm film at room temperature (decreased by a factor of 1/3 for scaling) (red). A dotted line has been place to show resemblance between frozen FTIR, wetting 80 nm film, and crystalline 500 nm film.
The reordering noticeably resembles what was observed in our earlier study, as the liquid film thinned and became confined to the interface (purple).\(^7\) Finally, the bottom two spectra, show the 500 nm film below melting and above melting. The growth of the peak at 1274 cm\(^{-1}\), and the shifting of the peak from 1268 to 1247 cm\(^{-1}\) as the thick film warms, shed light on the vastly different features present between crystalline ordering and liquid-like isotropic bulk.

A series of spectra outlining the vibrational changes which take place during a post-conditioning temperature cycle is outlined in **Figure 5.7**. Starting at the top of the figure, the film is rotated at 0.076 cm s\(^{-1}\) resulting in a stable film thickness of 500 nm at room temperature (red dashed).

![Figure 5.7](image-url) **Figure 5.7** From top to bottom: IRRAS spectra collected at temperature points of the 500 ± 70 nm thick acetophenone film post conditioning through the cooling and heating cycle. The top and bottom spectra have been decreased by a factor of 1/3 for scaling. The absorption feature at ca. 1265 cm\(^{-1}\) is highlighted with an arrow to demonstrate that the same features are seen in the warming film as in the thinning films.
The second spectrum is the spectrum immediately after freezing at 11.2 (cyan), followed by the sequential spectra collected during the heating cycle until the film melts at 18.5 ± 0.2 °C (solid red). Given the spectral similarities between the initial rotating spectrum and the final melted spectrum, it can be concluded that the film thickness does not change from start to finish of the temperature cycle. An arrow has also been added to the figure to highlight the same peaks of interest highlighted in thickness study at room temperature in Figure 5.3, as well as to better track the shifting of the peaks as the film melts. A side-by-side of the two series of spectra can be seen in Figure 8 for comparison. The features seen between 1230 and 1300 cm⁻¹ for both sets of spectra in Figure 5.8 are strikingly similar, but are performed under very different conditions: varying temperature and varying thinning and confinement, respectively. This study sheds light on crystalline ordering of the molecule in both thicker films when crystallized and thin films as a function of surface confinement.
5.5 Conclusions

To understand the crystalline-like behavior of molecules as they become confined to an interface, temperature-controlled studies of molecular fluid films were performed in a series of freeze-melt cycles. During the first temperature cycle, the temperature was taken well below the freezing point, by 20-30 °C to see freezing in a thick 500 nm rotating film. This first temperature cycle resulted in a sharp feature at 1272 cm$^{-1}$. This sharp feature persists over the range of temperatures until the film melts again and is not present in subsequent cooling and heating cycles. It is hypothesized that a conditioning process is necessary before more characteristic changes in molecular ordering can be observed throughout freezing and melting.

In the subsequent temperature cycles (cycles 2-4), immediate freezing resulted in spectra with varying peak populations, which may resemble frozen domains, and therefore we surmise that it indicates isotropic freezing. This variance disappears as the film warms and approaches the melting point (19 °C). At 17.3 ± 0.4 °C, the feature at 1268 cm$^{-1}$ emerges which represents the interfacial, crystalline peak for C-CO-C bending. This closely resembles what is seen in the thin film IRRAS film and the frozen transmission FTIR of acetophenone. Comparing the series of spectra seen in the heating cycle of a thick 500 nm film, as it progresses from solid to liquid, and the series of spectra seen as a film thickens from 80 nm to 580 nm, we see the sequential changes in the two series are strikingly similar. We suggest that these similarities in the vibrational changes as a function of temperature and thickness confirm crystalline ordering in thin films providing evidence that these confinement effects can extend to significant distances (100 nm) from a wall or
other surface. This ordering can play a major role in the properties of fluids at the solid-liquid interface.

5.6 Acknowledgements

The authors are grateful for the assistance from Taylor Fetrow for her help using CrystalMaker and creating the TOC graphic. Research funding support for this work was provided via the NSF Career Award (NSF-CHE #1651381) to SKS from the National Science Foundation. SLN gratefully acknowledges financial support from the University of Iowa’s Chemistry Department and the University of Iowa’s Graduate College Ballard Seashore fellowship.
Chapter 6. Velocity Dependent Orientation Changes of Trialkyamines at a Solid Silver Interface

Note: This chapter is being prepared for publication by Samantha L. Nania and Scott K. Shaw. The TOC figure shown above represents the spectra changes seen as a function of velocity for a single trialkylamine. The peaks at 2800 cm\(^{-1}\) and 2900 cm\(^{-1}\) are assigned to the “primary” CH\(_2\) next to the center nitrogen. Analysis of these peaks give rise to the idea that faster velocities are needed to see changes in short-chained trialkylamines compared to longer chained trialkylamines.
6.1 Abstract

This research utilizes a dynamic wetting technique in conjunction with spectroscopy and spectroscopic ellipsometry to analyze combined effects of substrate rotational velocity and film thickness on ordering across a series of trialkylamine liquids. Our data shows effects of substrate velocity on film thickness and effects of shear and confinement on the conformation of the fluid molecules as they are confined between the solid substrate and overlying vapor phase. Our results show that film thicknesses follow theoretical Landau-Levich model predictions over three orders of magnitude in substrate velocity (0.10 to 10 cm s\(^{-1}\)). The film thicknesses over this range span from ca. 1 µm to over 10 µm, with the longer alkyl chains creating the thickest films. Vibrational data show significant changes in absorbance profiles of the trialkylamines through the mid-IR range, which trend with substrate velocity and alkyl-chain length. Specifically, we analyze vibrational modes at 1438 cm\(^{-1}\), 2800 cm\(^{-1}\) and 2900 cm\(^{-1}\) which are affected by changes in the ‘primary’ CH\(_2\) groups, attached to the center nitrogen atom. It was shown that shorter alkyl-chains require higher substrate velocities for these modes to be affected, and we assign the changes to shearing induced by the rotating substrate. This causes the fluid molecules to rearrange, adopting molecular orientations that differ from those in the isotropic bulk. Temperature controlled transmission FTIR data for the trialkylamines are used to clarify these effects, and to correlate trends as function of alkyl-chain length.

6.2 Introduction

Any liquid in contact with a solid surface forms an interface, and interfaces play key roles in a wide range of biological, chemical and mechanical applications. At the solid-liquid interface, which often spans a few to several tens of nanometers, molecules breaks
their centrosymmetric symmetry and order in a wide range of patterns which are characteristic of the intermolecular interactions present.\textsuperscript{2, 4} Such ordering behavior significantly impacts the properties of the fluid at the interface, affecting material and device performance in lubrication, fluid transport, and numerous other technologies.

The interfacial region is very difficult to study because the dimensions are small, and the entire interface is often confined between a solid surface and a bulk fluid. Although advances in micro- and nano-technology and instrumentation allowed increasing levels of detail on these microscopic systems, studying the chemical interface continues to be a challenge. Dynamic wetting is employed here to allow direct access to the interfacial region (i.e. mitigating interference of the bulk fluid). In dynamic wetting, a glass capillary is positioned ca. 2 mm from the bottom of a vertically aligned solid disk, which is in turn mounted at the end of a DC electric motor. The capillary is used to dispense a droplet of fluid that, when held between the surface and the capillary, creates a thin, extruded interfacial film across the substrate as it passes through the droplet. The motor includes a gearbox and variable DC voltage to allow control of the substrate’s rotational velocity, and therefore control of fluid films’ thickness. The residual film is ultimately probed at the apex of the substrate’s rotation surface using spectroscopic techniques. Combining dynamic wetting with infrared reflectance absorption spectroscopy (IRRAS), a surface and orientation sensitive technique, and spectroscopic ellipsometry, chemical and physical information about fluid layers at the interface are directly probed.

Dutta et al. reported results of shear effects on both spherical molecules and linear polymeric molecules.\textsuperscript{29} The results show that shear flow affects interfacial structure of both liquids, however the extent of the effect was dependent on the molecular shape. For
spherical molecules, ordering at the interface occurs simultaneously, without shear flow. When shear is applied, it limits the area in which ordering occurs, but does not affect the number of ordered layers present; whereas, for long polymeric liquids, large increases in shear play a role in inducing layering and ordering; this is known as shear-driven disentanglement.\textsuperscript{29} Israelachvili et al. have reported that within relatively thick films (ca. 800 \( \mu \text{m} \)), a small amount of applied shear (amplitude ca. 20 \( \mu \text{m} \)) induces an orientation transition and molecular ordering in the layers in contact with the shearing surface.\textsuperscript{30} Our own group previously reported measurements of thin (ca 100 nm) acetophenone films on a bare silver surface.\textsuperscript{73} The films’ thicknesses vary systematically with rotational velocity as predicted using the Landau-Levich behavior. Interestingly, molecular ordering behavior at the interface is also observed as a function of the film’s confinement between the solid substrate and overlying vapor phase.\textsuperscript{73} These results indicate liquid like to solid like behavior of molecules under confinement.\textsuperscript{2, 5} In addition to confinement, shear or centrifugal forces from the rotation of the surface and gravity have also been known to induce ordering of the molecules at the interface. This is in addition to earlier work that shows special cases for violating the hydrodynamic no slip boundary condition, where fluid layers are not observed regardless of the rotational velocity or shear rate applied. Here, thin films of chlorobenzene and 1,2-dichlorobenzene were studied on self-assembled monolayer modified silver surfaces with varying roughness between ca. 2 and 7 nm RMS roughness. Results from this study using both reflectance vibrational spectroscopy and spectroscopic ellipsometry show no fluid present at the interface at rotational velocities ranging from 0.01 to 1.90 cm s\(^{-1}\), supporting the presence of a slip-boundary condition.\textsuperscript{61}
Our research objective in the present work is to understand the complex relationship between fluid film thicknesses, rotational velocity of the substrate and shear forces, and the theoretical models for film thicknesses (i.e. Landau-Levich), and their roles on the fluid’s ordering and therefore, properties at the interface. We predicted that studying a series of trialkylamines with varying alkyl-chain lengths would allow elucidation of effects of alkyl-chain length due to the variable rigidity of the alkyl arms and overall molecular size on the ordering occurring at near the surface. Ultimately, our experiments identify multiple factors which influence the behavior of the molecules at the solid-liquid interface.

6.3 Experimental Section

6.3.1 Materials

H$_2$SO$_4$ (ACS grade, BDH), HClO$_4$ (70%, Sigma), NH$_4$OH (28-30%, BDH), tripropylamine ($\geq$ 98%, Sigma), tributylamine ($\geq$ 99.5%, Sigma), tripentyamine (> 98.0%, TCI), and trihexylamine (96%, Sigma) are used as received. 4.0 M solution of CrO$_2$ (99.9%, Aldrich) and 0.6 M solutions of HCl (ACS grade, BDH) are prepared with Milli-Q water. Water is purified with Milli-Q UV Plus System (Millipore Corp, 18.2 M$\Omega$ cm$^{-1}$ resistivity, TOC $\leq$ 4 ppb).

6.3.2 Surface Preparation

Polycrystalline silver disks (14 mm diameter, 99.999%, ESPI Metals) are polished and smoothened using mechanical and chemical methods previously established. Optical constants and smoothness are routinely measured using ellipsometry and atomic force microscopy, respectively. Cleaned surfaces are stored in ultrapure water for no more than 60 minutes before being blown off with nitrogen and inserted into a nitrogen purged cell.
6.3.3 Instrumental Methods

6.3.3.1 Dynamic Wetting Apparatus

A custom cell (PTFE) houses a silver surface mounted on a PTFE plunger which contains a variable voltage (0-12 V) motor and gearhead (MicroMo). The cell has two UV grade CaF$_2$ windows to allow access to the substrate by various light sources employed here. An adjustable but air-tight front plate allows positioning of a glass capillary into the cell to deliver the fluid of interest to the substrate. The entire cell geometry holds the surface in the vertical plane for rotation and measurement. The cell is made air tight to allow control of the local environment, which is typically maintained under a blanket of UHP nitrogen gas at room temperature and a slight (1-2 psi) positive pressure. For wetting experiments, fluid is dispensed into the bottom of the cell to establish a saturated vapor environment before wetting. Once a droplet of fluid is suspended between the capillary and the substrate, the substrate is rotated at various velocities between (0.117 – 9.602 cm s$^{-1}$) to create films of various thicknesses. The films are probed at the apex of the surface rotation to avoid any interaction of the probe beam with the bulk droplet near the capillary.

6.3.3.2 IRRAS

A Thermo-Nicolet iS50 Fourier Transform spectrometer produces an IR beam which is directed into an external-optical bench. The bench is a custom enclosure purged with dry, CO$_2$ scrubbed air and contains focusing mirrors, a polarizer, a custom sample enclosure (the cell), and a liquid nitrogen cooled MCT-A detector. The cell is situated in the beam path such that the IR beam traverses its center and reflects from the substrate at 78° from normal. All IR spectra are recorded at ≥ 4 cm$^{-1}$ resolution and averaged over 1000 scans. For these experiments, background spectra are collected using the dry, clean Ag
surface and again after a saturated vapor phase of the desired fluid is achieved within the cell volume. All spectra are corrected against the saturated vapor phase background to eliminate contributions from the vapor phase in the final data sets. Variations in gas phase absorption data are typically < 0.05 abs units over the course of an experiment (10-24 hours). Two spectra are acquired at each rotational velocity to ensure that the film has reached a stable thickness.

6.3.3.3 TC-FTIR

Temperature control transmission FTIR was done with the use of the same Thermo-Nicolet iS50 Fourier Transform spectrometer as stated above except the internal FTIR transmission compartment was equipped with a Cryotherm accessory (International Crystal Laboratories). The accessory is fit with KBr windows (external) and CaF_2 windows (internal). The external windows allow the cooled sample to be maintained under vacuum, eliminating condensation of water vapor. Background spectra are collected at all temperature of interest to reference when taking sample spectra. Once background spectra are collected, 15 µL of the sample fluid is dispensed between the two salt plates and spectra are collected every 10 ºC.

6.3.3.4 Spectroscopic Ellipsometry

Ellipsometry measurements are collected using a M-2000 Spectroscopic ellipsometer (J.A. Woollam Co., Inc.) with focusing probes which reduce the spot size to ca. 250 µm in diameter. Ellipsometry measurements for dynamic wetting utilize the same cell as the IRRAS set up, but the incidence angle is made to be 75º from normal. All measurements are five seconds long and are taking while the substrate is rotating. At least three data points are collected at each velocity, and variation in the thicknesses are reported
as pooled standard deviations in our results. Our instrument collects psi and delta values from 370 nm to 1000 nm, and film thickness is calculated by fitting this data using the CompleteEASE software. The model employed here consists of three layers: 1) the bare silver substrate, 2) an intermix layer, and 3) a general oscillator layer.

6.3.3.5 DSC

Thermal analysis was done using a Q100 differential scanning calorimeter (TA Instruments) with liquid nitrogen cooling accessory. Samples were prepared by pipetting ca. 4 mg of sample into an aluminum pan. No lid was used to prevent leakage of sample out of the pan during clamping process. An empty pan with no lid was used as a blank. The blank heat flow data is subtracted from the sample data later using Excel. The sample chamber is purged at 20 ml min\(^{-1}\) with equal part ultra-pure helium (Praxair 99.998 %) and ultra-pure nitrogen (Praxair 99.998 %). An initial temperature of 25°C is set before the sample is cooled to -140 °C at a rate of 10 °C min\(^{-1}\). The heat flow is then left to equilibrate at -140 °C. Once equilibrium is reached, the sample is heated to 25 °C at a rate of 5 °C min\(^{-1}\) and set to equilibrate at the final temperature of 25 °C. Measurements are replicated three times, with a new sample each time. The peak temperature is determined using TA Instrument TRIOS software.

6.4 Results and Discussion

Error! Reference source not found. is a compilation of the properties of the various trialkyamine fluids that are explored in this chapter. Superscript numbers 59, 76, 77 These fluids are transparent, slightly viscous, and make good fluids for dynamic wetting due to their low vapor pressures and moderate surface tensions. These factors are important to ensure that the fluids do not evaporate when in the thin wetting film, and that the thin films are stable (to not rupture)
Table 6.1 Properties and the generic chemical structure of trialkylamines used in wetting experiments. Values taken from references 59(a), 76(b), and 77(c).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>mp (°C)</th>
<th>Vapor Pressure (Torr)</th>
<th>Viscosity η (mPa s)</th>
<th>Surface Tension γ (mN m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tripropylamine</td>
<td>-93.5⁰a</td>
<td>2.9⁰b</td>
<td>0.598⁰c</td>
<td>23.2 ± 0.1</td>
</tr>
<tr>
<td>Tributylamine</td>
<td>-70⁰a</td>
<td>0.3⁰b</td>
<td>1.258⁰e</td>
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<tr>
<td>Tripentylamine</td>
<td>N.O</td>
<td>1⁰b</td>
<td>2.416⁰e</td>
<td>26.3 ± 0.1</td>
</tr>
<tr>
<td>Trihexylamine</td>
<td>N.O</td>
<td>&lt; 1⁰b</td>
<td>3.911⁰e</td>
<td>27.2 ± 0.1</td>
</tr>
</tbody>
</table>

over reasonable time periods for measurements. Melting points are important to understanding trends in spectral changes that might correlate with solid-liquid phase transitions. We note in the table that the values for the melting point for the long-chain trialkylamines are not reported in literature. DSC measurements on these fluids shows a crystallization peak for tripropyl- and tributylamine, but no features are seen for the other fluids. A visual melting point test was done for the tripentyl- and trihexylamines, and the fluids became gels before turning to liquid which may explain why a clear melting point was not observed in DSC. Figure 6.1 shows FTIR spectra of tripropylamine, tributylamine, tripentylamine, and trihexylamine.

Figure 6.1 Transmission FTIR spectra of each trialkylamine used in these studies. The absorption feature around 2900 cm⁻¹ (vertical dashed line) appears at short chain lengths but is obscured at longer chain lengths. The shaded boxes represent additional regions of interest for this work. Spectra are offset vertically for clarity.
The expected ratio of methyl to methylene stretches is apparent in the C-H stretching region (2850 cm\(^{-1}\) to 2980 cm\(^{-1}\)). A particular region of interest in this region is highlighted with a vertical dashed line at 2905 cm\(^{-1}\). An absorption peak is observed here in tripropylamine, the shortest chain length molecules, but slowly becomes less apparent as the alkyl-chain length increases. This peak is assigned to an overtone vibration of the -CH\(_2\) group directly adjacent to the central nitrogen atom of the trialkylamine, and is denoted as CH\(_2\)(1) or the “primary CH\(_2\)” in the figures and text of this manuscript. The changing shape of this absorbance feature will be further analyzed in the thickness dependent IRRAS spectra discussed below (Figure 3). Additional interesting changes in the spectral profiles are observed at 1150-1200 cm\(^{-1}\), 1440 cm\(^{-1}\), and 2800 cm\(^{-1}\) which are associated with the C-N stretching mode for a tertiary aliphatic amine, the C-H deformation for CH\(_2\)(1), and symmetric stretching of the CH\(_2\)(1), respectively.\(^{60}\)

Dynamic wetting approach was used to create fluid films of the trialkylamine fluids on Ag substrates. The film thickness is controlled by varying the rotational velocity of the substrate. Predicted thicknesses are generated using the Landau-Levich model from Equation 6.1,

\[
h = 0.299 \frac{(V \eta)^{2/3}}{\sqrt{\rho g \gamma}}
\]

*Equation 6.1*

where \(h\) = thickness (m), \(V\) = velocity of withdrawal (m/s), \(\eta\) = viscosity (Pa\(^s\)), \(\rho\) = density (kg/m\(^3\)), \(g\) = acceleration of gravity (m/s\(^2\)), and \(\gamma\) = surface tension (N/m).
These predicted thicknesses vs. substrate velocity are shown in Figure 6.2 as solid lines. Experimental data points, shown by solid data points, agree well with the predictions. The thickness data are present as linear trends vs velocity\(^{2/3}\). It is clear that the fluids with longer alkyl substituents become thicker at much lower velocities than the short alkyl-chains. The slopes for the different fluids vary as predicted by the Landau-Levich model due primarily to increasing viscosity of the fluids with increasing length of the three alkyl-substituents. Values in Error! Reference source not found. for viscosity and surface tension increase with increasing length of the alkyl substituents. Specifically, as the viscosity changes from 0.598 mPa s to 3.911 mPa s for tripropylamine to trihexylamine,
respectively, the film becomes thicker by a factor of ca. 3.5 whereas the changes in surface tension, from 23.2 to 27.2 mN m\(^{-1}\), doesn’t show any significant change in thickness. Based on these data and Equation 1, viscosity of the fluid plays the major role in thickness of these films.

**Figure 6.3** show series IRRAS spectra for films of tripropyl-, tributyl-, tripentyl-, and trihexylamine as the velocity of the substrate is varied. Changes in the spectra are highlighted with dashed vertical lines and labeled **I**, **II**, and **III**, which represent **I** the C-H bending vibration attached to the nitrogen, **II** the shifting of the sym CH\(_2\)(1) stretch, and **III** the overtone of the stretch seen in (I). The spectral features broaden with increased velocity. Because IRRAS is sensitive to the orientation and chemical environment of molecular dipoles, this broadening could be due to overlap of multiple absorption peaks arising from the same molecular dipole as it exists in different environments in the thicker films.

The shoulder at 1438 cm\(^{-1}\) in **Figure 6.3**, **I**, has been assigned to the C-H bending vibration for the primary CH\(_2\). This peak increases in intensity as the substrate rotation is increased, which creates thicker films and increases shear forces within the film. Based on the selection rules for IRRAS, this feature’s behavior could be due to rearrangement and ordering the alkyl-chains on the molecule. This change also may also be supported by growing intensity of the peak centered around ca. 2900 cm\(^{-1}\) (dashed line **III**) which is assigned as overtone peak of the vibration previously discussed and found at 1438 cm\(^{-1}\).
Figure 6.3 Infrared spectra of tripropylamine, tributylamine, tripentylamine, and trihexylamine at various rotational velocities. Significant changes in the spectra as the velocity are marked by dashed black lines I, II, and III. I (1438 cm\(^{-1}\)) represents the C-H bending vibration attached to the nitrogen, II (2800 cm\(^{-1}\)) represents the shifting of the sym CH\(_2\)(1) stretch, and III (2900 cm\(^{-1}\)) can correlate to the overtone of the stretch seen in I.
The feature at ca. 2800 cm\(^{-1}\) (II) is associated with the symmetric C-H stretch of the primary CH\(_2\), and clearly shifts from 2797 cm\(^{-1}\) to 2812 cm\(^{-1}\) as the substrate velocity is increased. This shift in energy is plotted vs. substrate velocity in Figure 6.4. The trend seen in this plot is very similar to the trend seen in the shift of the peak around ca. 2900 cm\(^{-1}\), discussed fully in Figure 6.5, indicating that the two modes both experience changes in chemical environment, and supporting their assignment the primary CH\(_2\) unit.

Figure 6.4 (A) Spectra of trihexylamine demonstrating how the peak at ca. 2800 cm\(^{-1}\) was analyzed by shift in center of frequency. (B) Plot of wavenumber vs velocity for tripropylamine (black box), tributylamine (red circle), tripentylamine (green triangle), trihexylamine (blue triangle) in order to understand the shift in the peak as a function of chain length.
Figure 6.5 A) Spectra of trihexylamine demonstrating how the slope of the peak at 2900 cm$^{-1}$ was analyzed. (B) Plot of the slopes as a function of velocity for tripropyl- (black box), tributyl- (red circle), tripentyl- (green triangle), and trihexylamine (blue triangle). Each line is fit with an trendline, and the equation is used to calculate the velocity as which the slope equals zero. (C) Plot of velocity vs the number of carbons (defined for B) for the chain with cartoons to represent the freedom of rotation in longer alkyl-chained molecules.
Further analysis of the peak centered around ca. 2900 cm\(^{-1}\) was done to understand the trend with alkyl-chain length shown in Figure 6.5. At lower velocities, the peak appears as a shoulder of the peak at 2940 cm\(^{-1}\); this peak grows in and shifts with increase velocity until it appears to be a peak of its own and then ultimately, becomes a shoulder of the peak at 2875 cm\(^{-1}\). This shift can be represented by the slope of the line around 2900 cm\(^{-1}\) as shown in Figure 6.5A and is plotted vs velocity (Figure 6.5B). By fitting this slope data with a trendline, the velocity at which the slope is zero can be identified for each of the four liquids examined here. The result is shown in Figure 6.5C, and based on this plot it is clear that higher velocities are required to produce a similar changes in the primary CH\(_2\) for the shorter alkyl-chains as opposed for longer alkyl-chains. We generally interpret this as a measure of alkyl-substituents’ flexibility. We reason that the longer alkyl chains should be more easily deformed (at lower velocities) due to their increased interactions, and resulting molecular entanglements, with the neighboring alkyl chains. This is represented by the cartoon of the molecule shown in Figure 6.5C.

To test if these spectroscopic features might be due to ordering/crystallization of the fluid as it is confined within the thin film environment, temperature controlled FTIR (TCFTIR) measurements are provided in Figure 6.6. Figure 6.6 shows the TCFTIR spectra for tripropyl-, tributyl-, tripentyl- and trihexylamine for comparison. The areas in which significant changes are observed for the dynamic wetting spectra discussed above are marked on these spectra with gray dashed lines. As the fluid freezes, there is a slight increase in absorption features at ca. 1440 cm\(^{-1}\) and 2900 cm\(^{-1}\), corresponding to the similar growth seen in the wetting spectra as the fluid film becomes thicker, but there is no change in the peak at 2800 cm\(^{-1}\) which contrasts the wetting data.
In addition to comparisons with wetting films, interesting changes in the TCFTIR spectra appear during the cooling sweep. For example, the blue box in Figure 6A at ca 1200 cm\(^{-1}\) clearly shows only one peak (at 1192 cm\(^{-1}\)) for tripropylamine, but a broad combination of peaks for the trihexylamine spectra. The single peak in tripropylamine is the only peak that appears throughout the range of temperature, from 0 to -120 °C. The fluids with longer alkyl substituents (tributylamine, tripentylamine, and trihexylamine) exhibit multiple peaks that change intensity as the fluid decreases in temperature, and eventually freezes (or forms a glass). Specifically, trihexylamine (Figure 6.B) displays a broad absorbance peak at ca. 1165 cm\(^{-1}\). As the temperature decreases, the peak at 1165 cm\(^{-1}\) decreases in intensity while a relatively sharp peak at 1180 cm\(^{-1}\) grows in. This new peak at higher frequency is observed in all the longer chained trialkylamines (tripentyl- and trihexylamine), as the temperature decreases, but the frequency of this peak differs depending on the fluid. For tributylamine, the peak is already present but increases in intensity. As the films decrease in temperature, the freedom of the atoms to move decreases, therefore longer alkyl-chained molecules, such as trihexylamine, more closely resembling a rigid, short alkyl-chain, molecule such as tripropylamine. Based on this data and the energy of the vibration, we assign both of these features to the C-N stretching mode of the aliphatic amine.\(^{60}\) This could indicate a change in the local environment of some fraction of the molecules which form crystalline domains within the cooled, likely glassy phase balance of the material.
Figure 6.6 Temperature control transmission infrared spectra of each trialkylamine (tripropylamine, tributylamine, tripentylamine, and trihexylamine) at various temperatures while cooling. Significant changes seen in the IRRAS spectra are marked by dashed black lines I, II, and III on this spectra. Another significant change can be seen in the 1150-1200 cm\(^{-1}\) region and is marked with a blue box. Spectra is scaled by 3 on the left of the break for clarity.
The heating sweep for tripropylamine from -140 °C to 0 °C after freezing is also noteworthy. A series of spectra in Figure 6.7 show the heating process, and clear changes as the phase transition temperature is reached and surpassed. In this figure, as the fluid approaches the melting point (-93 °C), the spectra changes and the peaks look much more resolved, sharp, and narrow as seen in the -80 °C spectra. Once the temperature goes beyond -80 °C, the spectra changes again and the minor changes seen in the cooling process repeat in the heating process. We believe that as the fluid approaches the melting point, there is a cold crystallization takes place before the fluid melts. Clear evidence of this transition is observed in the DSC heating scan seen in Figure 6.8, seen at a peak temperature of -121 °C before the melting peak at a peak temperature of -102 °C. We note that this is only seen for tripropylamine in vibrational spectroscopy.
6.5 Conclusion

A series of trialkylamines are examined as they exist as thin films on bare silver surface as functions of film thickness and substrate velocity. Thickness data collected from ellipsometry indicate that the fluid films follow the Landau-Levich model for thickness vs. velocity for our system. Data trends clearly show that longer alkyl-chained molecules became thicker at much lower velocities than shorter alkyl-chained molecules as driven by viscosity.

To better understand how these fluids interact at the interface, infrared reflectance absorption spectroscopy is used because of its sensitivity to molecular orientation at the interface. As the films change thickness, changes are seen in characteristic peaks at 1438 cm\(^{-1}\), 2800 cm\(^{-1}\), and 2900 cm\(^{-1}\) which are due to the CH\(_2\) attached to the center nitrogen atom. By analyzing the shift in the peak at 2800 cm\(^{-1}\) and at 2900 cm\(^{-1}\), we conclude that higher velocities are needed for short alkyl-chained molecules than larger alkyl-chained

![Figure 6.8 DSC heating trace from -140 to 25°C from tripropylamine. This trace includes the cold crystallization peak (peak temperature of -121 °C) and the melting peak (peak temperature of -102).](image)
molecules to see changes in these peaks. This velocity dependence on peak shifts could be caused of the need for increase shear forces on rigid, shorter alkyl-chained molecule compare to the longer alkyl-chains molecules which have increase in freedom of rotation of the atoms. This same trend is seen in the peak at 2800 cm\(^{-1}\).

Temperature controlled transmission infrared spectroscopy was done to better understand the changes seen in the wetting spectra of all the fluids. Although, there is slight increase in intensity of the peaks at 1438 cm\(^{-1}\) and 2900 cm\(^{-1}\), it doesn’t appear that there are significant changes in these infrared spectra in comparison to the wetting IRRAS spectra. Despite this, there is significant changes in C-N stretching mode of longer alkyl-chain molecules to more closely resemble shorter-chained molecules at lower temperatures and therefore lack of movement regimes. It is worth noting that interesting changes were seen once the fluid was frozen and then warmed. As the fluid approaches the melting point, the peaks become much more well resolved around -95 °C and stay that way until -80 °C where it then returns to the spectra seen at that temperature on the cooling sweep.

These studies allow us to better understand the changes that take place when a fluid comes in contact with a solid interface. Further studies of these fluids and other fluids at this solid interface will help to continue to shine light on the role the solid-liquid interface play in various applications.

6.6 Acknowledgements

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Chapter 7. Conclusions and Future work

The main focus of the research discussed in this dissertation was to better understand the physical and chemical interactions occurring at the solid-liquid interface. Due to bulk interference, the interfacial region at a solid substrate is difficult to probe. Here, we show the advantage of using dynamic wetting technique to interrogate the interface. This technique allows for a substrate to rotate through a bulk droplet causing an extruded film of varied thickness depending on controlled rotational velocity to be formed on the surface as it pulls up and away from the bulk. This extruded film can then be probed with spectroscopic techniques. By combining dynamic wetting with various spectroscopic techniques, such as polarization modulation infrared reflectance absorption spectroscopy (PMIRRAS), IRRAS, and spectroscopic ellipsometry, information about the molecules at the interface including information about the composition, amount or thickness, and ordering of the molecules at the interfacial region can be uncovered.

Using these techniques, we have studied a variety of systems and concepts. In Chapter 3, a chlorobenzene/1,2-dichlorobenzene fluid on a SAM-modified Ag surface was used to understand the slip boundary conditions and a possible violation was discovered. To further understand this, in Chapter 4, an acetophenone fluid on a Ag surface was used to simplify the system by eliminating the SAM-modification but also keeping molecules with similar properties and structure to chlorobenzene but with a larger side chain. By varying the velocity and temperature, changes in the vibrational profile was seen suggesting a change in ordering of the molecules in the film. Finally, in Chapter 5, a series of trialkylamines were used to better understand how the length in the side chains and changes in velocity can affect packing and ordering at the interface.
7.1 Chlorobenzenes and the Study of the Hydrodynamic Slip Boundary Condition

Granick et al. reported that when a surface is smooth to < 5-7 nm RMS roughness, the hydrodynamic no slip boundary condition can be violated. To experimentally study this, a chlorobenzene and 1,2-dichlorobenzene fluids were studied on smooth (2 nm RMS roughness) and roughened Ag surfaces (7 nm RMS roughness). Because violation of the no slip boundary condition could mean no fluid is present at the surface, a hexanethiol (SAM) layer was added to the surface as a sort of “standard” to ensure the surface was being probed. It was shown with PMIRRAS that hexanethiol layer was present at the interface, but no evidence of fluid was there for either the smooth or roughened surface. The rotational velocity was varied both above and below the $V_{\text{crit}}$ for the system but still no fluid was seen. Because PM-IRRAS is only sensitive to dipoles perpendicular the interface, it was possible that the molecules were lying flat on the surface which could be confirmed using ellipsometry due to changes added chlorobenzenes causing a change in layer thickness. Using ellipsometry, a change in film thickness from a bare silver surface to a SAM-modified surface was shown but again, there was no evidence of a fluid film at the interface for either smooth or rough surface, confirming these results. Because no fluid was present, it is possible that with this system, the hydrodynamic no slip boundary condition was violated but the change in RMS roughness of the surface from 2 nm to 7 nm was not a factor. Future work could aim to study surfaces with an RMS roughness much greater than 7 nm, but to better understand what properties contribute to the violation of the hydrodynamic no slip boundary condition, different liquid-solid systems can be studied, such as acetophenone on a bare silver surface.
7.2 Acetophenone and the Study of Confinement and Crystallinity

To better understand what properties effect the violation of the hydrodynamic boundary condition, another system was studied which included a bare silver surface and acetophenone which is a fluid that has very similar properties and a similar ring structure as chlorobenzenes but this molecule has a large side chain. This simplified the system and allowed the formation of films. The thickness of these films was controlled by systemically varying the rotational velocity of the surface and measured using both IRRAS and spectroscopic ellipsometry. This allowed for direct comparison of experimental film thickness to theoretically predicted film thickness determined by the Landau-Levich model, revealing that there is great agreement between the experimental and theoretical thickness when the rotation velocity < 0.073 cm s$^{-1}$.

As the rotation velocity decreases and the films begin to thin, interesting changes in lower frequency region of the vibration profile were observed. The spectrum of the thinnest film was compared to an FTIR spectrum of acetophenone below the freezing point (19 °C), and it was seen that the molecules are confined to the interface (<250 nm thickness), the film creates an increasingly ordered structure resembling the frozen acetophenone spectrum. Although the convergence to the frozen acetophenone spectrum is seen at very thin films (80 nm) shifts in the series of spectra are seen in films as thick as 1000 nm. Because of this, temperature controlled wetting was done to see if these changes occur in thicker films when the temperature is varied.

For temperature controlled wetting studies, the surface was rotated at 0.076 cm s$^{-1}$ and then the temperature was cooled until the film frozen and then warmed until the film melted again. Consecutive spectra were collecting during the process. It was seen that in
order to freeze the film the first time, the films must be taken well below the freezing point and the temperature at which this first freezing occurs varies greatly. It could be that the surface has to be super cooled before a defect causes the initiation of freezing and these spectra all had a derivative feature is believed to be an annealing process needed before any real spectra changes can be seen. Upon freezing and melting again, it was seen that as the film approaches the melting point, it takes on the same vibration profile of a thin (80 nm) film even at such large thicknesses (503 nm). The series of spectra taken as the film continues to warm but thickness remains the same, show a similar vibrational profile changes seen previously when film thickness was varied at room temperature.

7.3 Trialkylamines and the Study of Shear Effects on Ordering in Films

To analyze the role of size of the molecules on film thickness, packing, and ordering, a series of trialkylamines (tripropyl-, tributyl-, tripentyl-, and trihexylamine) with increasing alkyl-chain length from 3 up to 6 carbons in chain length was studied as a function of velocities. The thickness of these films was studied using ellipsometry. It was found that the experimental thickness agreed with the theoretical thickness, and the longer chained molecules became increasingly thicker at lower velocities than the shorter chained molecules.

These experiments also revealed interesting details about the orientation of these molecules as a function of chain length and rotational velocity. For all the molecules, spectra became much broader as the films became thicker due to the overlap of multiple absorption peaks for a single vibrational mode in different environments. Beyond the broadening, changes were seen in the peaks that are associated with the “primary” CH₂
attached to the center nitrogen atom. By analyzing these peaks, it can be concluded that it requires higher velocities, and therefore shearing forces, to see changes in shorter alkyl-chained molecules that longer chained molecules. We ascribe this to the rotational freedom of longer chained molecules and their increased interactions with neighboring alkyl chains compared to shorter chained molecules.

Overall, the topics discussed in this dissertation focused on using a novel dynamic wetting technique in combination with a variety of spectroscopic techniques to investigate a range of solid-liquid systems including chlorobenzenes, acetophenone, and trialkylamines. These experiments studied the effects of surface roughness, velocity and temperature dependence, and chain length-size on film formation, thickness, and ordering. The results shed light on the physical and chemical interactions which take place at the solid-liquid interface and therefore uncover a wealth of information of how these interfaces can be modified and adjusted to better suit a range of industrial and research applications.

Future work could aim to investigate a variety of other solid-liquid systems including looking at fluids with different functional groups to better understanding the chemical interactions within the films and how those change or play a role in the ordering of the film as a function of confinement and temperature. Another system could include biological systems for better understanding how surfaces play a role in biological applications such as biomedical implants.
Appendix A  In House Made Wetting Cells

Preface: This appendix contains pictures of the in-house made cells designed to enable wetting experiments while probing with spectroscopic techniques including, polarization modulation infrared reflection-absorption (PM-IRRAS), infrared reflection-absorption (IRRAS) and ellipsometry. Cells have gone through multiple versions throughout my tenure at the University of Iowa but have ultimately been designed to function in the same manner. The most up-to-date version of the cell is pictured below with descriptions of each important cell aspect. All cells pictured here are composed completely of Teflon.

A.1 IRRAS/Ellipsometry

Figure A.1 In house made Teflon IRRAS and ellipsometry dynamic wetting cell containing 1. Teflon window holders, 2. Teflon front plate, and 3. In-cell in and out ports for N₂ gas purge.

Figure A.2 shows the cell being used for IRRAS. The cell is equipped with 25 x 1 mm UV-Vis grade CaF₂ windows, which allow the probing beam (IR and Ellipsometry) to enter and exit the cell, Teflon front plate, gas in/outlets, and a plunger. The front of the cell contains an elongated slot that has the width of the capillary, but enough height to allow the capillary to move from the center of the surface to the bottom of the surface. This slot
is encompassed by a depressed ring, which allows for the placement of an o-ring, enabling the front plate, which has just a big enough hole to fit the capillary tightly through it, to form an air tight seal when attached to the cell. The gas inlets allow for control of the environment inside the cell by providing a place for nitrogen gas in and out. For the experiments in this dissertation, the outlet port is plugged and the capillary is used as the outlet until the purge is turned off and the fluid is introduced. The plunger for this cell houses the gearhead, motor, brass shaft, and ball bearings, allowing the brass shaft free rotation while still holding a seal to the inside environment. Finally, the plunger tightly fits into the cell to ensure that the cell truly is as air tight as possible.

A.2 TC-IRRAS

Figure A.1 shows the cell used for temperature controlled IRRAS (TC-IRRAS). Much like the cell used for IRRAS and ellipsometry, this cell is equipped with 25 x 1 mm UV-Vis grade CaF\textsubscript{2}, windows which allow the probing beam (IR and ellipsometry) to enter and exit the cell, Teflon front plate, gas in/outlets, and a plunger. The plunger differs from the previously described plunger to enable temperature control. The plunger is hollowed out, resulting in a chamber within the plunger that is sealed on either side by ball bearings. The ball bearings have a dual purpose of ensuring that the shaft remains true while rotating and sealing the air chamber inside of the plunger, keeping it isolated from the wetting environment. When the plunger is pushed into the back of the cell, slits on the side of the plunger line up with the in and out ports on the back of the cell enabling the flow of temperature controlled nitrogen gas to the chamber. This flow of gas is what is used to regulate the temperature of the surface in the cell due to thermal conductivity between the brass shaft and the metal surface. In this set-up is it extremely important that the plunger is
extremely tight when being pushed into the cell in order to maintain sealed, separate environments between cell and plunger.

Figure A.2 In house made Teflon TC-IRRAS dynamic wetting cell containing 1. Teflon window holders, 2. Teflon front plate, 3. cell in- and out ports for N₂ gas purge, 4. plunger chamber in and out ports for temperature controlled N₂ gas, 5. thermocouples, and 6. plunger with gas chamber.
Appendix B  Calculations

Preface: This appendix contains screen shots of Excel files used for calculations along with brief descriptions for use. These files are functional, but there is room for improvement. The user must add literature and experimental values to cells in order for the calculation to adjust for fluids of interest. These files might be found digitally by searching the author's backup data files for the file name stated under the sub chapter.

B.1 Landau-Levich and Lifshitz Models

*File name: Landau Levich and Lifshitz Model Calculations.xlsx*

The Landau-Levich model and the Lifshitz Models are theoretical models used to determine thickness, \( h \), of bulk and interfacial films, respectively. The equation for the Landau Levich model (Equation B.1) is as follows:

\[
h = 0.299 \frac{\left( \frac{V \eta}{\gamma} \right)^{\frac{2}{3}}}{\sqrt[3]{\frac{\rho g}{\gamma}}} \quad \text{Equation B.1}
\]

where \( h \)=thickness (m), \( V \)=velocity of withdrawal (m/s), \( \eta \)=viscosity (Pa*s), \( \rho \)=density (kg/m\(^3\)), \( g \)=acceleration of gravity (m/s\(^2\)) and \( \gamma \)=surface tension (N/m).

The equation for the Lifshitz model (Equation B.2) is as follows:

\[
h = \sqrt[3]{\frac{A_{123}}{6\pi R T V_m \ln \left( \frac{P}{P_0} \right)}} \quad \text{Equation B.2}
\]

where \( h \)=film thickness (m), \( A \)=Hamaker constant (J), \( R \)=gas constant (J/(K*mol)), \( T \)=Temp (K), \( V_m \)=molar volume (m\(^3\)/mol), \( P \)=pressure of vapor, and \( P_0 \)=saturated vapor
pressure. The Excel spreadsheet (Figure B.1 and Figure B.2) is set up for the Landau-Levich equation, columns B3, C3, and D3 need to be filled in with constants for the system, and for the Lifshitz equation, columns Q3, R3, S3 and T3 need to be filled in with constants for the system, along with the velocity (cm/s) columns for both set ups (A6+ for Landau-Levich and R6+ for Lifshitz) with the velocities of interest. The rest of the cells have equations which Excel will do the calculations for you.

For example, to calculate the thickness from the Landau-Levich model for acetophenone liquid at the solid silver interface, the viscosity (Pa s) [cell B3], the density (kg/m³) [cell C3], and the surface tension (N/m) [cell D3] along with the range of velocities (cm/s) [cell A6+] need to be put in (Seen in Figure 2.1). It is worth noting that Excel will do calculations for thousands of cells, so start the velocity at zero and increasing by a small amount. This can be done by clicking in the cell below the first velocity cell and typing “=A6+’value to increase by” and then double clicking the small box in the bottom right corn. Once those values are put in, the velocity will be converted to (m/s) and then the thickness (m) will be calculated using the Landau-Levich equation above. This value will then be converted to nm for later reference.

![Figure B.1 Screen shot of Excel spreadsheet used to calculate thickness from the Landau-Levich Model.](image-url)
To calculate the thickness from the Lifshitz model for acetophenone liquid at the solid silver interface, the temperature (K) \([\text{cell Q3}]\), molar volume \((\text{m}^3/\text{mol})\) \([\text{cell R3}]\), pressure ratio \([\text{cell S3}]\) and Hamaker constant \([\text{cell T3}]\) along with the range of velocities \((\text{cm/s})\) \([\text{cell R6+}]\) need to be put in (Seen in Figure 2.1). It is worth noting that the molar volume \([\text{cell R3}]\) can be calculated in the cell by using the mw and the density \([\text{cell C3}]\) and a conversion factor. To do this type “\(=\text{mw}/(1000*\text{C3})\)” into the box. Once those values are put in, the thickness \((\text{m})\) will be calculated using the Lifshitz equation about in \text{cell P5} and converted to nm in \text{cell P6} in which the cells in column \text{S6+} will reference from.

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<th>Q</th>
<th>R</th>
<th>S</th>
<th>T</th>
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<td>(\text{Mol Vol (m}^3/\text{mol)})</td>
<td>(\text{Pressure})</td>
<td>(\text{Hamaker (J)})</td>
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</table>

*Figure B.2 Screen shot of Excel spreadsheet used to calculate thickness from Lifshitz Model.*

**B.2 Critical Dewetting Velocity**

The critical dewetting velocity \((V_{\text{crit}})\) is the rotational velocity at which a film transitions from the interfacial region into the bulk. At \(V < V_{\text{crit}}\), the thickness of the film remains constant over a range of velocity and is known as the interfacial film. At \(V > V_{\text{crit}}\) the thickness of the film increases as the velocity increases and added bulk layers get added to the interfacial layer. There are two ways to calculate the critical dewetting velocity. In Chapter 3, Egger’s equation was used, whereas in Chapters 4 & 5, the intersection point
between the Lifshitz model and the Landau-Levich model was used because of the simplicity of the system. Both procedures are described below.

**B.2.1 Eggers Equation and Excel Spread Sheet**

*File name: Eggers VCrit Calc Ag System Fluids.xlsx*

The Excel spreadsheet (Figure B.5) is set up so columns A, B, C, E, G, and H need to be filled in with constants for the system; the rest of the cells have equations, which will allow Excel to do the calculations. Hamaker constants $A_1, A_2, A_3$ represent different layers of your system. The two tabs of the .xls sheet allow for calculation of the two phase or three phase system. For example, to input data for a system of chlorobenzene liquid at the solid silver interface, $A_1$ will be chlorobenzene and $A_2$ will be silver. These values will be used to calculate $A_{12}$ (or $A_{123}$) in column D using **Equation B.3**:

$$A_{12} = ((A_1)(A_2))^{1/2}$$

Or

$$A_{123} = (\sqrt{A_1} - \sqrt{A_3}) \times (\sqrt{A_2} - \sqrt{A_3})$$

**Equation B.3**

Later, this combined Hamaker constant is used to calculate the slip length, $\lambda$.

In Column E enter the contact angle of fluid at the interface in degrees. Pick the row that best represents your contact angle. For instance, for a contact angle of 22, replace 20 in column E row 7 with 22. Column F converts this to radians via **Equation B.4**:

$$\theta(rad) = \frac{\theta(^\circ)}{360} 2\pi$$

**Equation B.4**

125
Finally, $\gamma$ (surface tension in N/m), $\eta$ (viscosity in N s/m$^2$), and $\rho$ (density in kg/m$^3$), constants for the fluid, are entered into columns G, H, and I respectively. To calculate the unitless value for $\lambda$ the slip length ($\lambda_m$) and the capillary length ($l_c$) must be calculated using the equations from **Equation B.5** and **Equation B.6**:\(^{49}\)

\[
\lambda_m = \sqrt{\frac{A_{12}}{6\pi\gamma}} \quad \text{Equation B.5}
\]

\[
l_c = \sqrt{\frac{\gamma}{\rho g}} \quad \text{Equation B.6}
\]

Once these values are known, the unitless value $\lambda$ (Column L) is calculated by dividing $\lambda_m$ (Column K) by $l_c$ (Column J) Once columns A-L are complete, the values necessary to calculate $Ca_{crit}$ are present. This will be done by solving **Equation B.7** below:\(^{49}\)

\[
Ca_{crit} = \frac{\theta_{rad}^3}{9} \left[ \ln \left( \frac{Ca_{crit}^{1/3} \theta_{rad}}{18^{1/3} \pi [A_i(s_{max})]^2 \lambda \theta_{surface}} \right) \right]^{-1} \quad \text{Equation B.7}
\]

where the constants $a$ and $b$ can be solved for and represented by the following **Equation B.8**:\(^{49}\)

\[
a = \frac{\theta_{rad}^2}{9} \quad \text{and} \quad b = \frac{\theta_{rad}}{18^{1/3} \pi [A_i(s_{max})]^2 \lambda \theta_{surface}} \quad \text{Equation B.8}
\]
These values (Columns M and N) will then be used to identify $C_{a_{\text{crit}}}$. This is achieved by plotting $e^{a/x}$ vs. $bx^{1/3}$ on opposing y-axes with $C_{a_{\text{crit}}} = x$ on the x-axis shown in Figure B.3:

![Figure B.3 Double y plot of $e^{a/x}$ and $bx^{1/3}$ vs $C_{a_{\text{crit}}}$](image)

Smaller intervals of $x$ allows for more significant figures in $C_{a_{\text{crit}}}$. This $x$ interval can be adjusted by clicking in the second cell for $x$ (D20) and adjusting the equation. This equation adds some factor of 10 to the original cell. Once the equation is edited, you need to double click the small box in the bottom right hand corner of that cell (Figure B.4), so the equation is applied to the rest of the (10,000) cells in that column. This will also adjust the lines on the graph. The intersection point of these lines on the graph will be used to determine $C_{a_{\text{crit}}}$. Find the graph and data that corresponds to your contact angle. The scaling of this graph should be set so the intersection point can be seen; if the intersection is not seen, adjust the x and y-axis scale on the graph. For systems examined so far, $C_{a_{\text{crit}}}$

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seems to range between $10^7$ and $10^3$. To identify the intersection, the $y$-values of the two lines corresponding to the $x$-values will be subtracted. The point at which this becomes 0 is the intersection. The corresponding $x$-value is $C_{\text{crit}}$. It is important that when the values of the difference between the two $y$-values change from negative to positive values (around 0), the variance of $C_{\text{crit}}$ ($x$-values) should be less than 1% around this area. By using a lookup function, Excel will find the value closest to 0 and select the $x$-value at that point. This will be the value put in for $C_{\text{crit}}$ (Column O). This is then used in the final calculation of $V_{\text{crit}}$ via Equation B.9:

$$V_{\text{crit}} = \frac{C_{\text{crit}} Y}{\eta}$$  \hspace{1cm} \text{Equation B.9}$$

where $V_{\text{crit}}$ (column P) is in $\left( \frac{cm}{s} \right)$ and can be converted to $\left( \frac{\mu m}{s} \right)$ (column Q).

**Figure B.5** Screen shots of the Excel sheet used to calculate $V_{\text{crit}}$ from Egger’s.
B.2.2 Intersection of Landau-Levich and Lifshitz Models

Since the Lifshitz model represents the interfacial layer thickness and the Landau Levich model represents the added layers as the film becomes bulk, by setting these two equations equal to each other and solving for velocity (V) as seen below in Equation B.10, the \( V_{\text{crit}} \) can be calculated.

\[
\frac{\left( \frac{A_{123}}{6\pi \left( \frac{RT}{V_m} \ln \left( \frac{P}{P_0} \right) \right)} \right)^{1/2} (\rho^2 \gamma^3)^{1/4}}{0.163 \eta} = V_{\text{crit}}
\]

Equation B.10
B.3 IRRAS Beer-Lambert Law

File Name: IR Beer's Law.xlsx

For IRRAS, Beer-Lambert Law (Equation B.11) is used to calculate film thickness from the absorbance feature in the spectrum

\[ A = \varepsilon b c \]

where \( A \) is the absorbance, \( \varepsilon \) is the molar absorptivity of the peak of interest, \( b \) is the path length, and \( c \) is the concentration. In the case of IRRAS, the equation will be solved for the path length. This value will give you the distance that the beam travels which is through the film at an incident angle of 78° and back out the film after it reflects off the surface.

Referring to the blue triangle Figure B.6 Screen shots of the Excel sheet used to Thickness using Beer-Lambert Law below, this distance pertains to the hypotenuse of the right triangles. To calculate the thickness of the film (labeled \( x \) in the diagram), the total path length (\( b \)) is divided by 2, and then multiplied by the cos (78°). An Excel file has been set up to do the calculation where the user needs to insert concentration (cell C1), the molar absorptivity. (cell C2), and the absorbance from the peak (column A).

![Figure B.6](image-url)

**Figure B.6** Screen shots of the Excel sheet used to Thickness using Beer-Lambert Law.
Appendix C  Data Collection and Work Up

Preface: This appendix contains various techniques used for data collection and data work up and have been separated by instrumental technique.

C.1 IRRAS

C.1.1 Macros

Screen shots of Macros files used to collect continuous spectra and determine peak heights are seen below. These Macros Basic files might be found digitally by searching the author's backup data files for file names stated below. Each macro will require the user to open OMNIC Macros Basic software before opening the file and saving it with user’s parameters set. To set parameters, double click on the layer that needs to be edited. To run the macro in OMNIC, the user will have to create a button in the OMNIC toolbar to activate the macro by going to the edit tab > edit toolbar > add item > Run Basic Macros > Browse > Select Macros file > open > Ok > drag to current item. These buttons can be save to the toolbar for later use by saving the configuration with them in place as the default configuration.
C.1.1.1 IRRAS Data Collection

File Name: IRRAS.mac

Figure C.1 Macros box for setting up continuous handoff collection of IRRAS spectra including the number of spectra, the experimental setup and file save.

With the Macros IRRAS (Figure C.1), OMNIC will collect spectra automatically for the number of spectra set into the loop amount. The user should configure the experimental setup exactly like would be done if collecting the spectrum manually, ensuring that the background file is accurately selected, along with the number of scans, resolution, gain, optical velocity, and attenuation. In order to get the program to save each spectrum separately and not overwrite each one, the file name should be selected and then #index# can be added anywhere in the file name which will make the software assign a consecutive number to each spectrum. This feature ensures that if something happens to the program in the middle of the running Macros, no data is lost.
C.1.1.2 Peak Height

File Name: Peak Height.mac

With the peak height Macros (Figure C.2), OMNIC will determine the height of
the peak location indicated within the in Peak Height box. If the center of frequency for
the peak shifts, it is best to check the box that says, “seek closest peak”. The ‘corrected’
peak height will be determined according to the baseline given by the start and end points
identified in the baseline section. To run through an entire set of spectra, open all spectra
in OMNIC and set the loop amount to all which will allow to the program to run through
every spectrum in the open window. Data which props up in the peak height box will need
to be recorded in the notebook; some experimenting with the log file in OMNIC has been
done but not to satisfactory standards.
C.1.1.3 Find Peak

*File Name: Find Peak.mac*

![Image of Macros box for finding a peak in an IRRAS spectrum by the sensitivity and threshold for search and by setting the region to search.]

*Figure C.3* Macros box for finding a peak in an IRRAS spectrum by the sensitivity and threshold for search and by setting the region to search.

With the find peak Macros (Figure C.3), OMNIC will determine the peaks present in a spectrum based on the sensitivity set, the threshold, and the region. Some experimenting with this Macros has been done, but it is not satisfactory when it comes to shoulders and other very small peaks. This Macros takes some work understanding sensitivity and threshold adjustments.

C.1.2 Baselining

Baselining is a data work-up technique used to give IR spectra clean and straight baselines for publication. For FTIR and IRRAS, the baseline should be mostly corrected by referencing a background file. It has been determined that the baseline in the lower frequency region is very environmentally and experimentally sensitive, making slight baselining necessary for most spectra. To baseline an FTIR or IRRAS spectrum, follow the steps below:

1. Select spectrum which needs baseline
2. Go to process tab and click baseline correct

3. Add a few points along the axis (for consistency purposes, wavenumber of baseline points is recorded). Points should never get to close to actual peaks and should be placed on the outskirts of the peaks

4. Auto Y points so they attach to the spectra at those point

5. Go through and zoom in on sections using the white bar at the bottom to adjust the points to the curve of the baseline and pulling points away from peak locations.

6. Once the point are in position, replace original spectrum with baselined spectrum

7. Save file with the same name to a “Flattened” folder within that day’s experiment file. MAKE SURE YOU DO NOT SAVE OVER ORIGINAL RAW DATA.

Baselining for PM-IRRAS is quite different since the final spectrum has the Bessel function feature (Seen in Figure C.4) which will need to be baselined out. To baseline PM-IRRAS data, the above steps should be followed up to step 3 where baseline points are added on the outskirts of peaks of interest. For PM-IRRAS, in areas where there are no peaks present, enough baseline points needed to be added to ensure the curvature of the Bessel function is covered without creating peaks that are not real (this may require A LOT of baseline points). Once this is done, the steps above can be completed so the spectrum comes out with a straight baseline (Figure C.5)
Figure C.5 Example spectrum of a PM-IRRAS measurement of self-assembled monolayer on a silver surface. The Bessel function shape can be seen along with the baselining line (black dotted line).

Figure C.4 Resulting baselined spectrum of self-assembled monolayer on a silver surface see in figure 3.4. The Bessel function shape is no longer present and there is a clean, straight baseline throughout the entire spectrum.
C.2 Ellipsometry

Ellipsometry measures the change in polarization of the light as it reflects or transmits from a material. This change is polarization is represented by the change in amplitude (\(\tan \Psi\)) and phase change (\(\Delta\)) and can be seen in the equation below

\[
\tan \Psi \cdot e^{i\Delta} = \rho
\]

*Equation C.12*

where \(\rho\) is the combination of the change in amplitude and the phase. These \(\Psi\) and \(\Delta\) is what the raw data consists of. In order to make sense of the data and be able to determine thickness, these two parameters need to be fit to models. Snapshots of these models and data might be found digitally by searching the author's backup data files.
C.2.1 Model Fitting

C.2.1.1 Bare Silver

A bare silver surface is fit to a B-spline model (seen in Figure C.6) with the starting material being Ag and the fit turned on for the E Inf and the IR Amp. Once the model is pulled up and the measurement file is opened, the model is generated as a layer on the file and fitted. This fit will allow the program to come up with optical constants for the Ag surface. These optical constants can be obtained by right clicking on B-Spline and saving layer optical constant as tabular. These optical constants will be used as the bottom layer when other layers are added.

Figure C.6 Bare silver model fit to the $\psi$ and $\Delta$ data collected from a bar silver surface.
C.2.1.2 Acetophenone

Acetophenone films on a bare silver surface is fit using a multi-layer model (seen in Figure C.7) which includes both the substrate layer, which will be set as the optical constants saved from the bare silver surface, and the Gen-Osc layer. A Gen-Osc layer is used for an organic film layer. For this model, the thickness is fit along with the UV Pole Amp, UV Pole En, and the Amp1 from the fit type. Once the fit is generated, each parameter must be adjusted until the fit looks relatively good. It can then be fit and the thickness can be recorded.

C.2.1.3 Trialkylamines

Trialkylamine films on a bare silver surface is fit using a multi-layer model (seen in Figure C.8) which includes the substrate layer, which will be set as the optical constants saved from the bare silver surface, and intermix thickness layer, which represents a layer where the solid and liquid intermix, and the Gen-Osc layer. Again, the Gen-Osc layer is
used for an organic film layer. For this model, the multiple sample analysis mode is used to allow elements to be fit along a range of that multiple measurements while other parameters get fit individually for that specific sample. This enables the fitting of the intermix layer to be the same across all the measurements. The parameters that were left to fit individually for each measure was the thickness from the Gen-Osc layer, which will be the overall thickness of the film, the % thickness non-uniformity, and the UV Pole Amp. The UV Pole En was set to 11 to help fit the models without allowing so much variation. Again, once the fit is generated, each parameter must be adjusted until the fit looks relatively good across all measurements in this case. It can then be fit and the thickness can be recorded.

Figure C.8 Model used to fit acetophenone thin films on a bare silver surface.
References


76. Sigma-Aldrich: Analytical, Biology, Chemistry & Materials Science products and services. https://www.sigmaaldrich.com/catalog/ (June 07),