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UNIVERSITY OF CALIFORNIA,
IRVINE

Water Flow through Single Nanopipes and Spreading of Normal and Superfluid Helium
Drops

DISSERTATION

submitted in partial satisfaction of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in Physics

by

David Joseph Mallin

Dissertation Committee:
Peter Taborek, Chair
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2019

DEDICATION

To all my friends and family who have supported me in my endeavors, especially:

My parents, Michael and Susan, and brother, Sean, who have supported me since the beginning (literally)

My grandmother, Ann, who has been a persistent voice of gentle encouragement

Virginia Mac, who has been my refuge throughout the journey

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ABSTRACT OF THE DISSERTATION

Water Flow through Single Nanopipes and Spreading of Normal and Superfluid Helium Drops

By

David Joseph Mallin

Doctor of Philosophy in Physics

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Peter Taborek, Chair

The work presented in this thesis represents two research projects which, simply put, both explore the hydrodynamics of fluids flowing along a solid boundary. In practice, the two experiments take place under the extremes of their very different conditions: one taking place at room temperature, but on a nanoscopic scale at many times ambient pressure and the other visible to the naked eye, but over a range of low pressures and at temperatures colder than outer space. The first project probes the no-slip boundary condition with the direct measurements of the smallest pressure-driven water flow through single nanotubes. The no-slip boundary condition is tested by performing room-temperature water flow experiments in both bare silica hydrophilic nanotubes and polydimethylsiloxane (PDMS) coated hydrophobic nanotubes, in order to resolve conflict in current literature. Flow rates of water through hydrophilic and hydrophobic single pipes with diameters ranging from 10 μm to 200 nm have been measured. A method of coating the pipes with a hydrophobic polymer roughly 2 nm thick was developed and the hydrophobic nature of the pipes after treatment was verified. The exact diameters of the tubes were measured using a gaseous flow impedance test, imaged directly via scanning electron microscopy (SEM), or measured through atomic force microscopy (AFM). The flow rates through both the hydrophobic and hydrophilic pipes agree with theory for viscous Poiseuille flow and are effectively indistinguishable from each

other.

The second research project presents the first observation of the spreading of normal and superfluid helium drops from 1.0-5.2°K. Optical and interferometric measurements were taken from both side and below points of view within a custom designed and fabricated cryostat. Images were taken at both high-speed and low-speed to observe different spreading regimes for the drops. High speed measurements showed initial spreading speeds that follow the $r \propto t^{1/2}$ power law determined by inertia-capillary balance and show a weak viscosity dependence. The long-term measurements showed anomalously flat drop profiles and a defined contact line that persist for up to 15 minutes despite the completely wetting nature of liquid helium and the existence of a ≈ 40 nm standing film. The observed long-term spreading power law of $r \propto t^{1/7}$ was greater than those predicted by scaling solutions in lubrication theory for normal drops, and demonstrate the first experimental evidence of spreading controlled by contact line dissipation mechanisms. Superfluid drops had lifetimes too short to observe long-term spreading. The short superfluid drop lifetime is thought to be caused by superfluid outflow through the liquid film which covers the substrate. Several other phenomena were observed, but not rigorously studied, including apparent Leidenfrost at low ΔT and critical opalescence.

Chapter 1

Introduction

1.1 Slip and Nanoflows

The no slip boundary condition for viscous flow defines the velocity profile in a pipe by forcing the velocity to be zero at the walls. This boundary condition predicts macroscopic flow rates, but does not originate from any fundamental principle. If this assumption is untrue, the molecules at the wall have a nonzero velocity and “slip” along the boundary. As a result, the velocity profile (and net flow rate) changes. There are several factors that have been theorized to affect slip, including surface roughness, hydrophobicity, and trapped nanobubbles[14, 60, 48]. The effects of hydrophobicity in particular have been studied intermittently since the 1800’s[21]. The growth of microfluidics and nanofluidics devices in recent decades has produced an increased interest in slip, as the effects become more relevant at smaller length scales. Thus, determining the scale at which slip might occur could have implications for many fields, including biological systems, DNA sequencing, desalination, and refrigeration[36, 44, 45, 61, 69].

The current body of research concerning hydrophobic effects on slip includes many conflicting reports. Reports on slip length range from <10 nm[60] to tens of microns[48].

The studies finding the greatest slip lengths involved pressure-driven flows through porous carbon nanotube membranes, which may exhibit enhanced flows due to structural defects rather than actual slip. Flow rate enhancement in those experiments claim to be on the order of 10^4 , which would result in an effectively flat velocity profile within the pipe, akin to superfluid flow. Two other studies, by Byun[14] and Schaeffel[60], used the same hydrophobic material and found completely different results. Schaeffel et al. and Byun et al. both studied water flow in polydimethylsiloxane (PDMS) coated microchannels. Both groups also used photo image velocimetry (PIV) in order to determine the velocity field and subsequent flow rates. Schaeffel reported a slip length of less than 10 nm while Byun reported a slip length of 2 μm . This is a discrepancy of over three orders of magnitude, for which the cause is unclear. It is possible that the fabrication of the microchannel from multiple pieces or the tracer particles from the PIV affect the flow. In order to eliminate these possible sources of error, we developed a technique to directly measure the flow rate through a single nanoscale tube to achieve the highest precision measurement of slip length to date.

1.2 Helium and Drops

Helium

Helium-4 gas liquifies at a temperature of 4.2°K at a saturated vapor pressure of 1 atmosphere. At $T_\lambda = 2.17^\circ\text{K}$, the helium liquid undergoes another transition where the fluid enters a new state known as superfluid, a term coined by Kapitza after he performed early measurements on the fluid's properties[40]. The phase diagram for helium-4 shown in Figure 1.1 shows the border of the two phases, known as the λ -line. The transition temperature at saturation became known as the lambda point not due to the shape in the phase diagram, but that of the heat capacity at T_λ , shown in Figure 1.2. Kapitza observed that the liquid had incredibly low viscosity below T_λ . Daunt and Mendelssohn observed another peculiar effect, involving a suspended container filled with liquid helium[24]. When

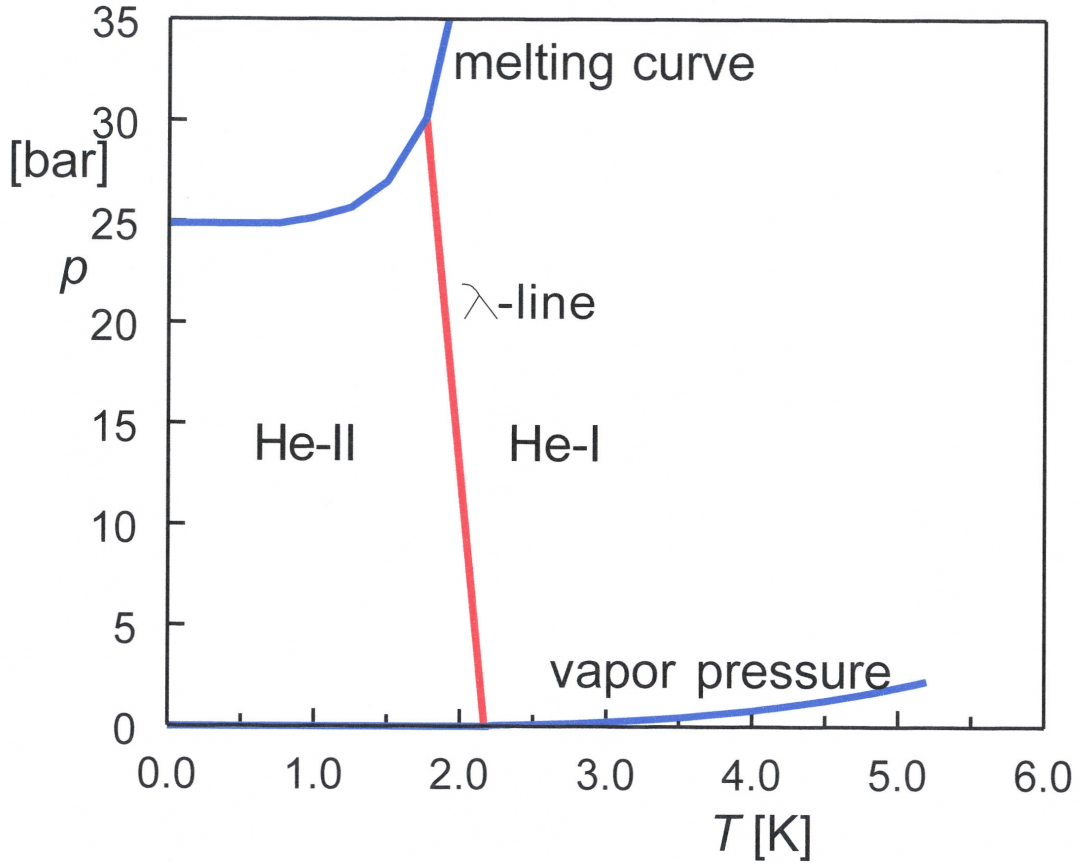


Figure 1.1: The phase diagram for helium-4. The λ -line (in red) is the border between normal and superfluid, also called Helium I and Helium II respectively.

brought below T_λ , the container empties itself via superfluid crawl through a microscopic film.

Landau developed a theoretical description for superfluid behavior, wherein the liquid is described then as a mixture of two interspersed components: normal and superfluid. This is known as the two-fluid model, and treats the measurable qualities of the fluid as a linear superposition of those of the classical normal fluid and quantum superfluid[41]. The total density of the fluid is the sum of the densities of the two parts, $\rho = \rho_s + \rho_n$. The normal and superfluid fraction is a function of temperature and is shown in Figure 1.3. The superfluid fraction begins at 0 at T_λ and increases with decreasing temperature, indicating a second order phase transition. Shortly after the observation and theory of Kapitza and Landau,

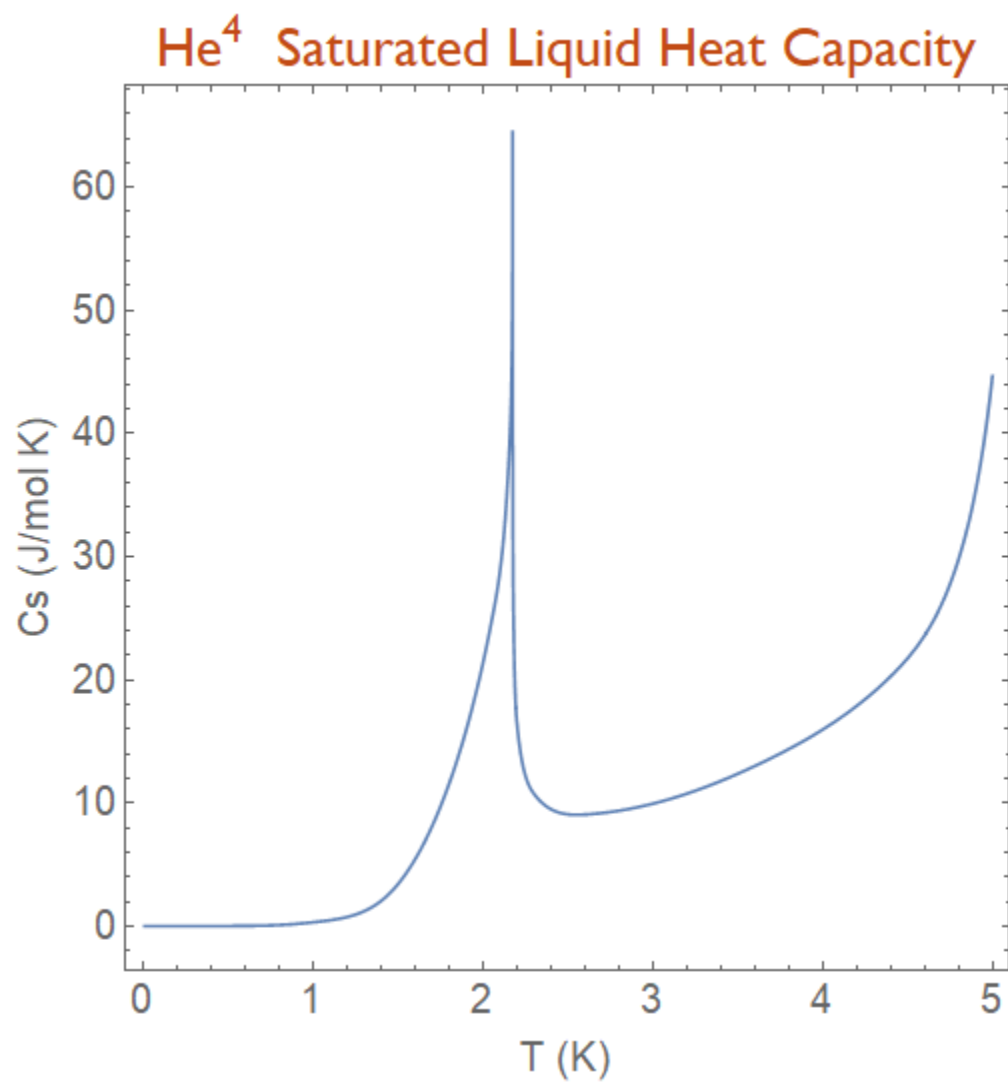


Figure 1.2: The namesake of the λ point. The heat capacity of liquid helium-4 at the superfluid transition at saturation looks like a λ .

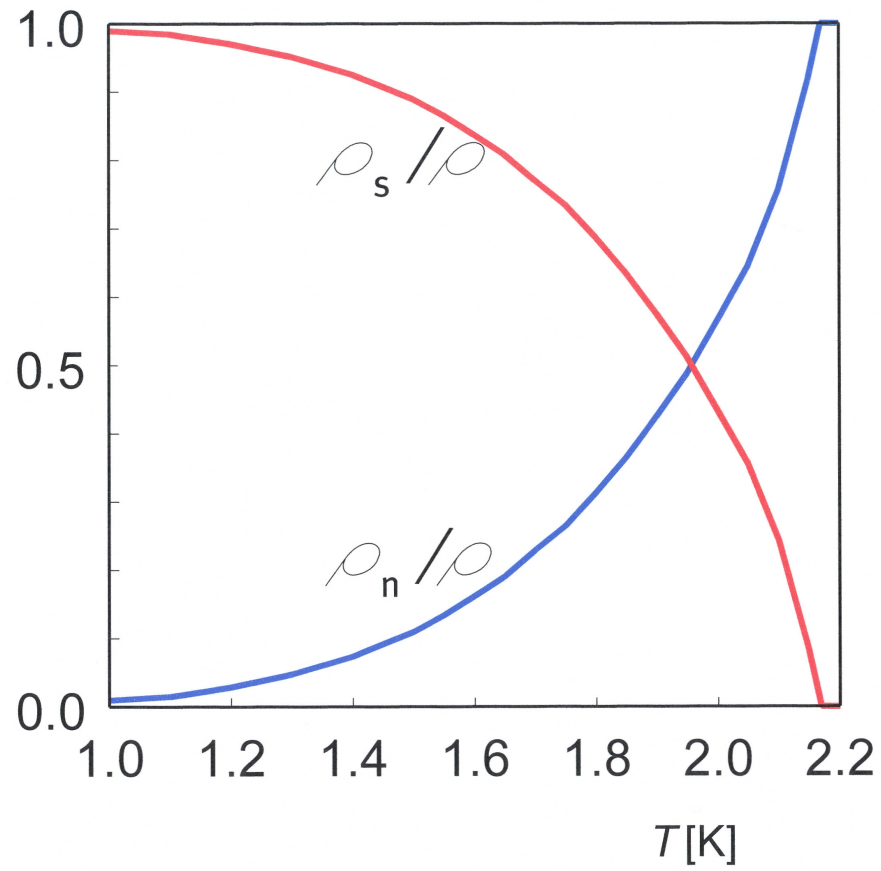


Figure 1.3: The normal and superfluid fraction as a function of temperature. The superfluid fraction begins at 0 at T_λ and increases with decreasing temperature.

London correctly suggested that the properties of superfluid helium originated from Bose-Einstein condensation[46]. Bose-Einstein condensation occurs when a collection of bosons all reach their lowest quantum energy state at very low temperatures and allows for previously microscopic quantum effects to become macroscopic and observable via bulk properties. As such, superfluid helium was the first observed Bose-Einstein condensate and remained the only one until Cornell and Wieman successfully observed the phenomena in a dilute rubidium gas over 50 years later[3].

Along with separate densities, the two fluids have independent velocity fields, v_s and v_n which obey different laws. The normal component follows the Navier-Stokes equation, while the superfluid follows a simplified version that assumes viscosity is negligible called the Euler equation for inviscid fluids. Another peculiar effect arises from the fact that the hydrodynamic equation for superfluid helium has a term that is the gradient of the chemical potential, $\nabla\mu$. Simply put, superfluid will flow towards regions where there is a smaller fraction superfluid. As stated earlier, the superfluid fraction is decided by temperature, meaning that superfluid will actively flow to eliminate any temperature gradient in the fluid. This makes helium ideal for cooling and maintaining low temperature applications, such as superconducting magnets for CERN’s Large Hadron Collider[42].

Drops

Drops are ubiquitous in everyday life, having little noticed but very important roles to play in many areas from clouds and precipitation[55] to emulsions in petroleum byproducts[1] to inkjet printing and other associated additive manufacturing techniques[49]. Despite the pervasiveness of drops in everyday life, an accurate description of a drop wetting a surface has been elusive. There are several motivations for studying spreading of liquid helium. Helium has a very low surface tension and wets all substrates except elemental cesium[59, 57, 54]. Even in the normal state, the viscosity is approximately a million times lower than silicone oils. Conventional room temperature spreading experiments take place in air, and the

spreading drop advances into a dry region with a possible precursor film[53] that advances ahead of the three phase contact line. The helium experiments are done in a saturated environment of its own vapor, so the drop advances into a "moist" region covered by a liquid film of typical thickness 40 nm which is stabilized by the van der Waals interaction with the solid substrate. The superfluid transition that occurs at $T_\lambda = 2.17^\circ\text{K}$ drastically changes the transport properties of the fluid. Because spreading in both the superfluid and normal state take place at near coexistence conditions, small changes in the chemical potential due to temperature gradients or even the droplet curvature can have surprisingly large effects.

Chapter 2

Water Flow Through Single Nanopipes

2.1 Theory: Poiseuille Flow and the No Slip Boundary Condition

2.1.1 Laminar Flow Through a Pipe

Laminar flow through a cylindrical pipe can be derived exactly from the Navier-Stokes equations in cylindrical coordinates. For laminar flow, the following assumptions are made:

1. The flow is in a steady state (all $\frac{\partial}{\partial t} = 0$)
2. The flow velocity is only in the z-direction ($u_r = u_\theta = 0$)
3. The flow is symmetric about the center (all $\frac{\partial}{\partial \theta} = 0$) and fully developed ($\frac{\partial u_z}{\partial z} = 0$)

Under these assumptions, the radial momentum equation yields $\frac{\partial p}{\partial r} = 0$, which means pressure will only vary in the z-direction (along the length of the pipe). The ϕ equation becomes

trivially satisfied. The z momentum equation reduces to:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial u_z}{\partial r} \right) = \frac{1}{\mu} \frac{\partial p}{\partial z}, \quad (2.1)$$

where μ is the dynamic viscosity and u_z is the velocity field in the z-direction. The solution to this differential equation is

$$u_z = \frac{r^2}{4\mu} \frac{\partial p}{\partial z} + c_1 \ln(r) + c_2. \quad (2.2)$$

The flow velocity cannot be infinite at $r = 0$, so $c_1 = 0$. Also, the pressure drop along the pipe is assumed to be linear, allowing $\frac{\partial p}{\partial z} = \frac{\Delta P}{L}$, where ΔP and L are the pressure drop across and length of the pipe.

The determination of c_2 is at the heart of this experiment. The value of c_2 determines the velocity of the fluid at the wall of the pipe. Traditionally, the no-slip boundary condition of $u_z = 0$ at $r = R$ (radius of the pipe) has been applied. However this is not the only theoretically acceptable boundary condition. It is also possible and completely acceptable to have a non-zero velocity at the walls of the pipe, as the no-slip boundary condition has no theoretical basis. It is a purely phenomenological boundary condition that yields correct flow rates for macroscopic flows. The velocity used for $u_z \neq 0$ at $r = R$ is

$$u_z(R) = b \frac{\partial u_z}{\partial r}, \quad (2.3)$$

where the velocity at the wall is proportional to the radial velocity gradient at the wall times a constant b , which is the slip length. The slip length has units of length as implied and represents the distance that the velocity profile extends past the physical wall of the

pipe. With the no-slip boundary condition, the parabolic velocity profile is

$$u_z = \frac{1}{4\mu} \frac{\Delta P}{L} (R^2 - r^2), \quad (2.4)$$

With slip allowed, the shifted parabolic velocity profile is

$$u_z = \frac{1}{4\mu} \frac{\Delta P}{L} (R^2 - r^2 + b \frac{\partial u_z}{\partial r}). \quad (2.5)$$

A representation of the difference in velocity profiles is provided in Figure 2.1. In order to extract a net flow rate, the velocity is integrated over the area of the pipe. In the no-slip case, this yields the equation for Hagen-Poiseuille flow,

$$Q = \frac{\pi R^4 \Delta P}{8\mu L}, \quad (2.6)$$

where Q is the volumetric flow rate. If slip is allowed, we see an additional flow term:

$$Q = \frac{\pi \Delta P}{8\mu L} (R^4 + 4bR^3). \quad (2.7)$$

For most macroscopic pipes, the normal contribution to the flow, proportional to r^4 , far outweighs the slip contribution unless the slip length is of the order of the pipe size. A given slip length becomes more relevant (and thus easier to detect experimentally) as pipe size decreases.

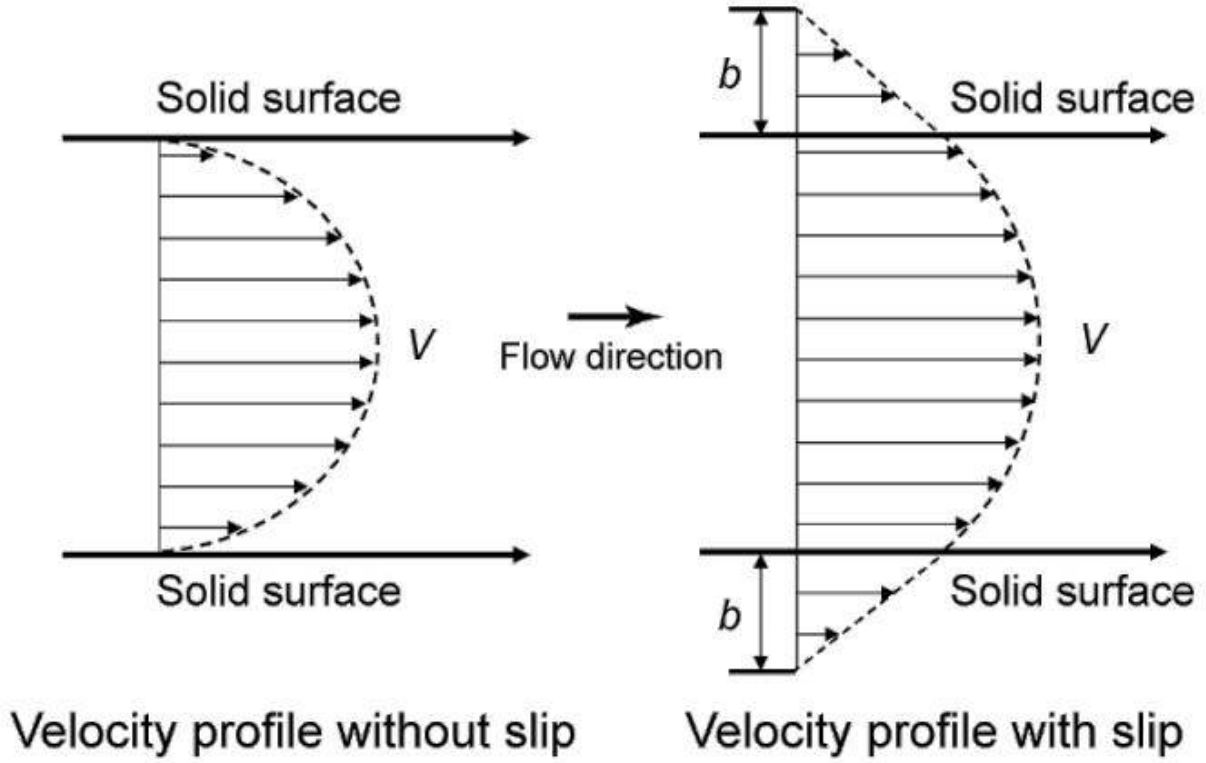


Figure 2.1: Cross sectional representations of no-slip and slip velocity profiles. The no-slip profile on the left shows a completely parabolic shape that reaches zero at the boundary. The slip profile on the right extends past the physical boundary by a slip length b . The velocity profile is linear after the boundary, taking on the slope of the tangential velocity at the boundary[6].

Contact Angle

While the consequences of slip flow (increased flow rate) are easy to understand, the origin of the slip itself is still poorly understood. Research on the subject has not reached a consensus on the cause, and often reaches conflicting conclusions. The common proposed causes of slip include surface roughness, hydrophobicity, and trapped nanobubbles[14, 48, 60]. In our experiments, we focus on testing the effect of hydrophobicity on slip length.

Contact angle is the common way to describe the degree of hydrophobicity. More generally, contact angle describes the wettability of a solid surface by a liquid. The relative interfacial energies of the gas, liquid, and solid dictate the shape of a drop of fluid on a solid surface. The relationship between these energies and the contact angle, shown in Figure

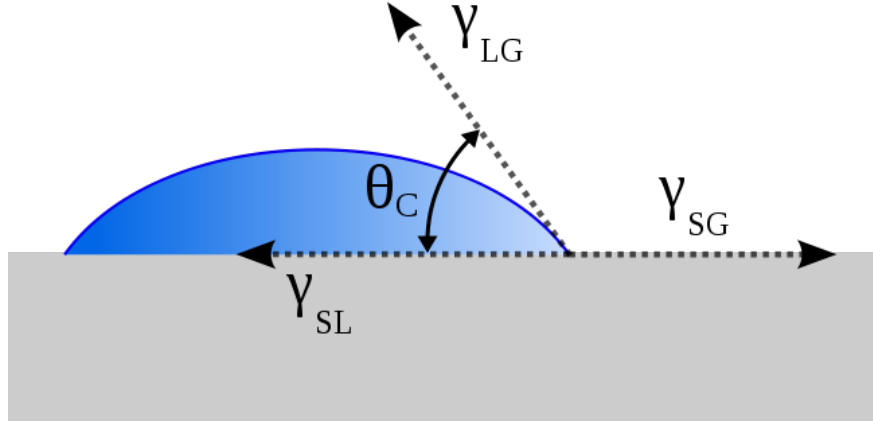


Figure 2.2: This contact angle diagram shows the relevant quantities in Young's equation, which controls the shape of the drop. The γ quantities refer to the interfacial energies between the different states and θ_c is the contact angle. If θ_c is greater than 90° , the surface is said to be hydrophobic, and if θ_c is less than 90° , the surface is said to be hydrophilic.

3.16, is given by Young's equation,

$$\gamma_{SG} - \gamma_{SL} - \gamma_{LG} \cos \theta_c = 0. \quad (2.8)$$

where θ_c is the contact angle and the γ terms represent the interfacial energies of the solid-gas, solid-liquid, and liquid-gas interfaces. If the contact angle is greater than 90° , the surface is said to be hydrophobic, and if the contact angle is less than 90° , the surface is said to be hydrophilic.

The fused silica used in our experiments is naturally hydrophilic, but can be made hydrophobic via coating with a hydrophobic material, such as the polymer polydimethylsiloxane (PDMS). In simple terms, water interacts more strongly with the fused silica surface than the PDMS surface. The decreased surface interaction between PDMS and water might allow water molecules to violate the no-slip boundary condition.

2.2 Direct Measurements of Water Flow through Single Nanopipes

The challenge of measuring fluid flow on the nanoscale is complex, and has been approached several different ways. Particle image velocimetry (PIV) is a common technique that involves seeding water with fluorescent tracer particles. The flow is then characterized by imaging the fluorescing particles[14, 60, 66]. By calculating the velocity of the particles in different sections of the flow, a velocity profile can be produced and from this a net flow rate. This technique has the advantage of measuring the velocity profile directly, but has a few disadvantages that led us to employ another method. First, it requires the construction a rectangular flow channel in order for the particles to be imaged. The construction of such a channel usually employs etching processes to create an open channel which is then closed by bonding a flat, transparent cover (often a simple microscope slide). The nature of the construction leads to questions of the uniformity of the channel and possible deformation under pressure (typical pressures for nanoflows can reach 50 atm). The other problem with PIV is the particle tracers that are employed. The particles themselves can be hundreds of nanometers or micron sized, giving them a non-negligible effect on the flow. There is essentially a lower limit on the channel size before the tracers become significant.

There are other methods as well, including using interferometry[20] or imaging[66] to measure the speed of a moving meniscus, using massive arrays of tubes and simply dividing a macroscopic flow by the number of tubes[48], or using a mass spectrometer[67]. Ideally, a direct measurement of the flow is made through a single tube. We perform such a measurement on successively smaller tubes from 10 μm to 200 nm. For previously stated reasons, the smallest tubes yield the most information on the no-slip boundary condition. Therefore, all the following procedural details are be told in the context of working with 200 nm tubes.

2.2.1 Measurement of Nanoscale Water Flow through Single Pipes

The basic concept of our experiment is to image a water droplet growing on the end of a nanotube over time. A pressurized water reservoir is attached to one end of the nanotube. The water was initially pressurized by helium gas tank. Helium was specifically chosen due to its low water solubility. As the experiments moved to smaller tubes, the pressures required for flow increased, and the formation of nanobubbles inside of the tube became a concern. The gas line was replaced with a high-pressure stainless steel syringe that is typically used for liquid chromatography measurement. In the syringe embodiment, there is no head space above the liquid reservoir, and all space is occupied by fluid. This made the pressure experiment very sensitive to temperature due to the different thermal expansion coefficients of the apparatus and the water inside. As a result, the entire experiment was placed in an insulated and temperature controlled box, where the experiments were performed at several degrees Kelvin above room temperature. Water flows out of the other side and into a reservoir of viscous oil, which contains the liquid bubble. The silicone oil prevents the water in an extremely small drop from evaporating immediately as it exits the tube. Diffusion is also severely limited by the silicone oil. The water creates a bubble on the end of the tube that grows over time. The bubble is periodically imaged and those images are processed to extract the volume. The volume as a function of time yields flow rate. A basic diagram is shown in Figure 2.3.

The Nanotubes

We acquired fused silica capillary tubing from Polymicro Technologies[®]. They produce high purity fused silica capillary tubing whose inner diameter can range from 2 mm down to 200 nm. The process of heating and pulling the capillary tubing leaves the inner surfaces clean, smooth, and chemically inert. This makes them ideal for flowing water through unaltered pipes, as well as for coating. The capillary tubing outer diameter is typically 125 μm or 350 μm , making them easy to handle. A yellowish brown polyimide coating supports

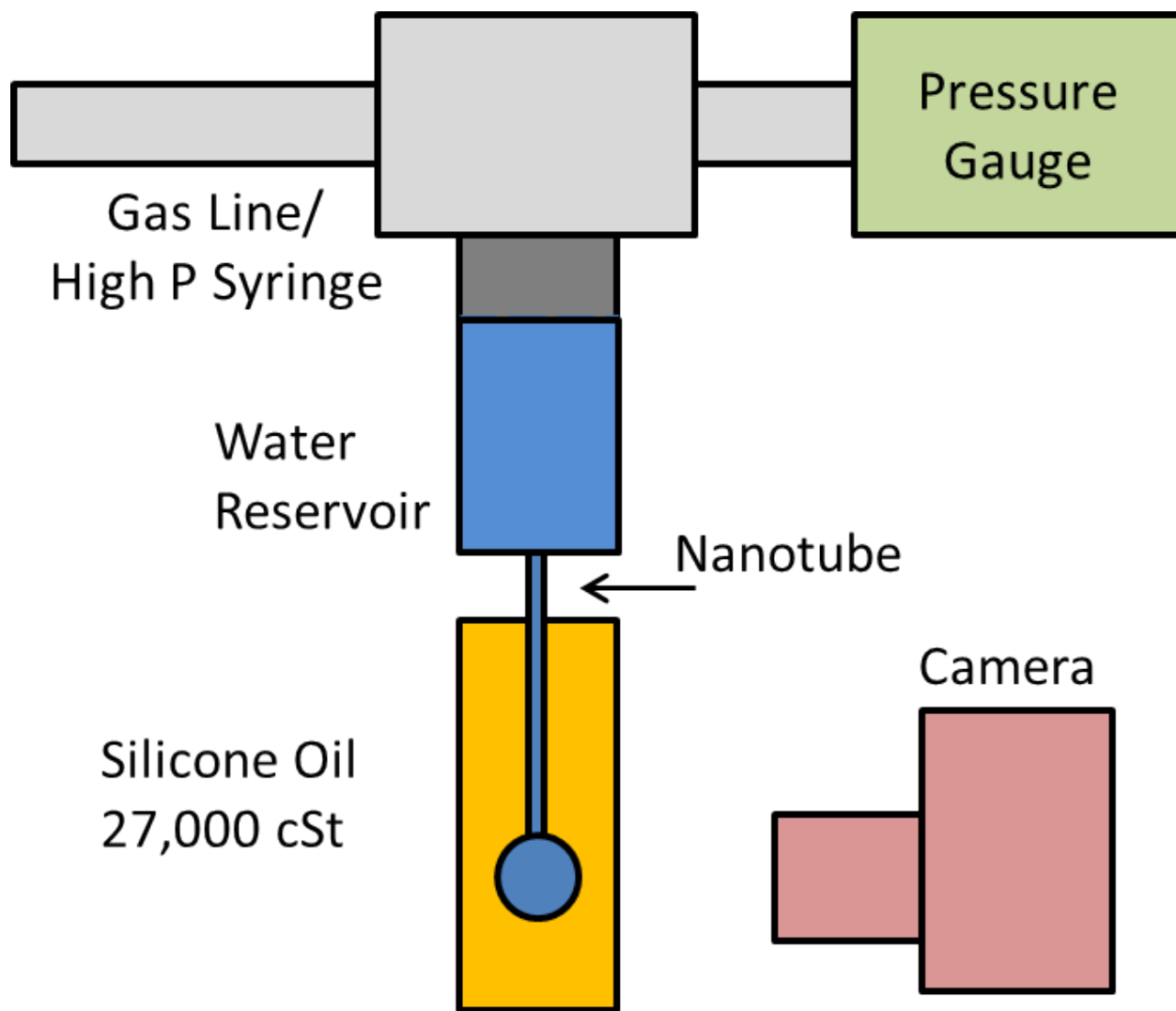


Figure 2.3: A diagram of the experimental setup.

and protects the fused silica.

When we acquire the tubing, which comes in a 10 m spool, we are given a diameter for the beginning and the end, which Polymicro Technologies[®] determined via scanning electron microscopy (SEM). The diameter of the tube is effectively constant over the length of a single tube for our experiment (roughly 25 mm), but can vary over longer lengths. This requires us to determine the tube diameter after each experimental run. Depending on the nominal tube size, this was accomplished in one of two ways. For larger tubes (greater than 2 μm), we use a mass spectrometer technique to measure gas flow of helium through the tube. The technique is one our lab commonly employs and is described by Velasco[67]. For small

tubes, we image the ends of the tubes via SEM. The fused silica nanotubes must be coated with metal before being imaged in an SEM. Both the metal coating and imaging are carried out at the Irvine Materials Research Institute (IMRI) user facility. A South Bay Technology Ion Beam Sputter Deposition and Etching System Model IBS/e is used to sputter roughly 2.5 nm of iridium onto the end of the tube. The angle and rotation of the coating process means that the diameter of the tube is effectively unchanged by this coating. The tube is then imaged in a FEI Magellan 400 XHR SEM. Figure 2.4 shows the entire end of the tube. Several images similar to Figure 2.5 of the inner diameter are taken. For each image, 20-30 points are taken around the circumference of the hole and fit to a circle profile in Mathematica. The resultant diameters from the fits are averaged for the final diameter used to compare to the water flow data. Typically, the diameters calculated from separate SEM pictures are within 2 nm of each other. Further efforts to reduce uncertainty in the inner diameter determination involve the use of atomic force microscopy (AFM). Preliminary work has shown that the nanotube can be mounted vertically in an Asylum Research AFM and that the hole can be imaged with a standard probe. In order to increase precision beyond that of the SEM, specialty tips have been provided by Nanotools USA for assessment. The tips, shown in Figure 2.6 have modified end to enable better measurement of the steep trenchlike wall of the nanotube inner diameter. The first (left), has a hammerhead shaped rectangular tip while the second (right) has a spherical tip. The evaluation of these tips will determine whether they can be used to reduce the calibration error.

There are several steps to preparing a nanotube for the experiment. The first is to separate a section of tubing from the spool. This is performed by scoring the tubing with a diamond scribe. It is important that the diamond scribe penetrates through the polyimide coating, but just barely scratches the fused silica. Once the silica is scored, pulling along the length of the tube causes it to break very cleanly. This is important since our experiment relies on the fact that the drop on the end of the tube is spherical (there is a correction that takes place in the image processing). If the tube face is not flat, the drop is misshapen and the

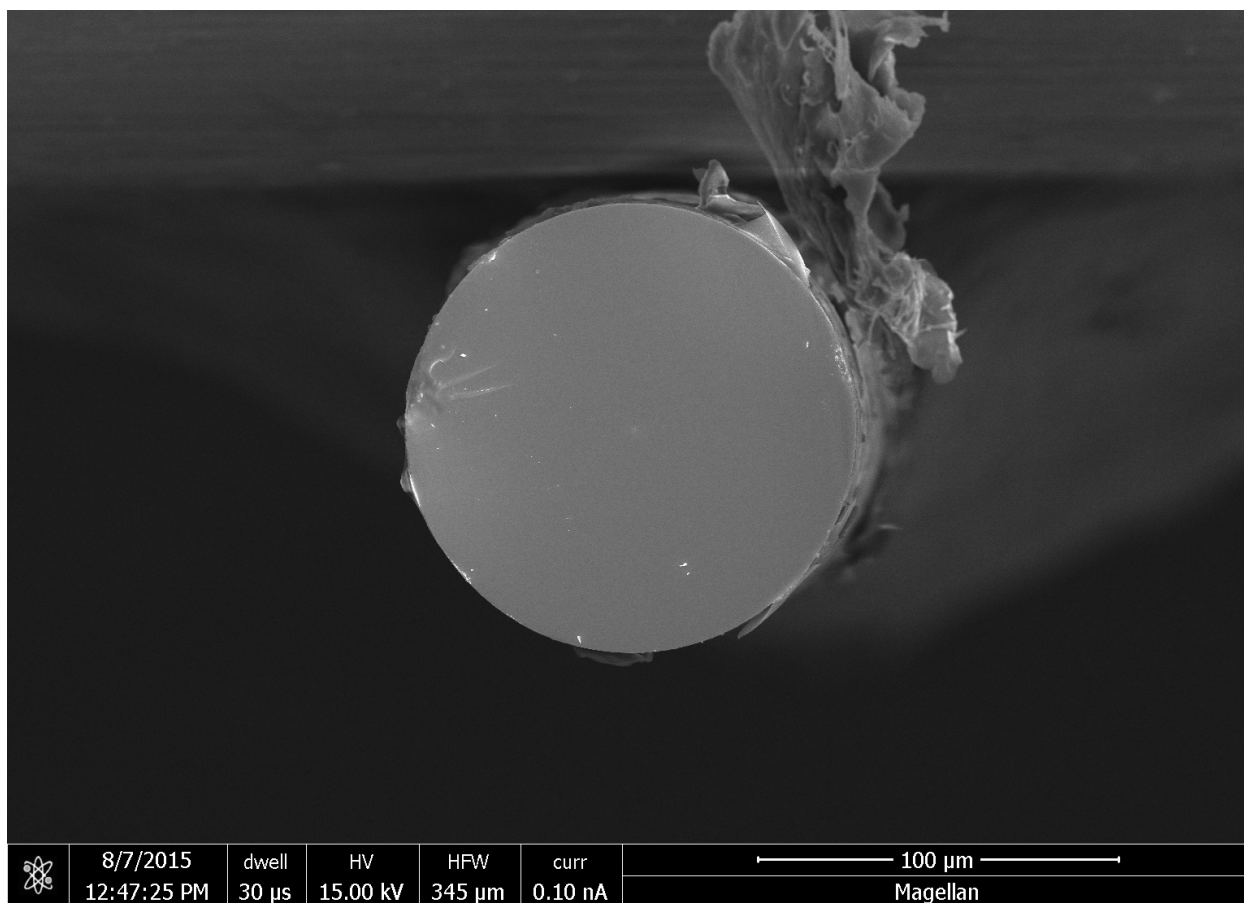


Figure 2.4: SEM image of the 200 nm inner diameter nanotube tip, coated in 2.5 nm of iridium. To give an idea of the scale, the 200 nm inner diameter can barely be seen in the center. The success of the cleave is shown by the smoothness of the face surface, showing only small imperfections where the diamond scribe nicked the edges.

volume cannot be calculated properly. This is an arduous process and one attempt in five is usually successful. The face is visually inspected under a microscope at 50x magnification to ensure the pipe was cleaved properly. In order to do this inspection, the polyimide coating near the tip must be removed, as is sometimes obscures or extends past the tip. This is accomplished by burning the coating off with a propane torch. Care is taken to burn the coating off without melting and deforming the fused silica.

After the tube is cleaved and inspected, is it epoxied into a 1/4" Swagelock VCR gland. The gland itself is a custom piece drilled out in two stages from a blank. A large bit around 3/8" is used to drill most of the way through, leaving roughly 1/4". This section forms

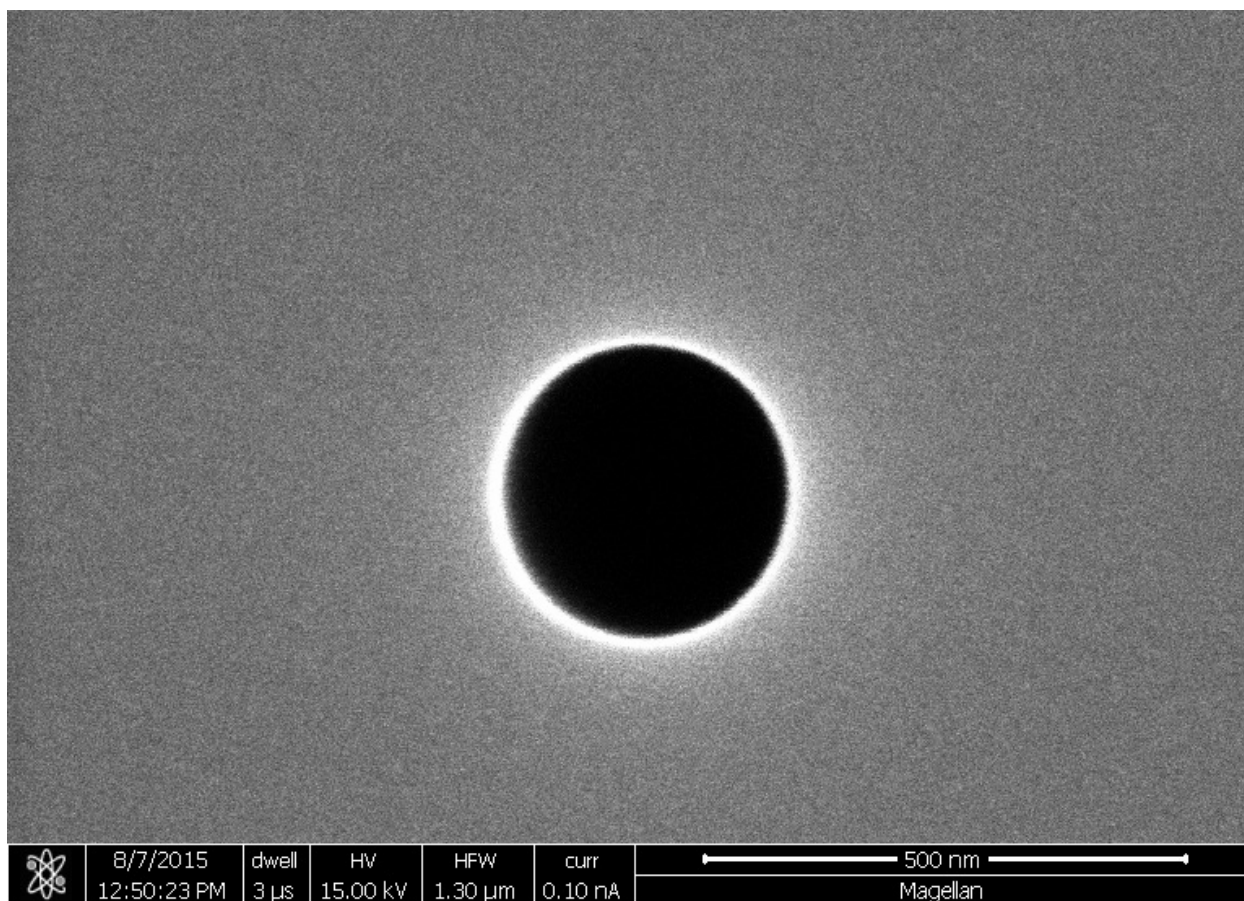


Figure 2.5: SEM image of the inner diameter of a 200 nm uncoated nanotube. The brightness in the center is a charging effect due to the iridium coating not penetrating down the tube. Several images such as this one are taken for single tube, and the average of the calculated diameter is used

the water reservoir for the flow. A smaller, 1/16" drill is used to break through. The tube is epoxied into this smaller hole. The two-stage shape helps the epoxy form a "plug" that prevents leaks. The smaller secondary hole also decreases the force on the epoxy, since pressures can reach up to 50 atm. We use Stycast 2850FT as an epoxy along with the 23LV catalyst. The epoxy is generally known for its uses at very low temperatures, but it works well here too. It is also very resistant to solvents, which means that the epoxy plug must be removed with a drill experimental between runs.

The VCR gland is pressurized by a high-pressure stainless steel syringe typically used for liquid chromatography. The syringe plunger is actuated by a high tension spring and a

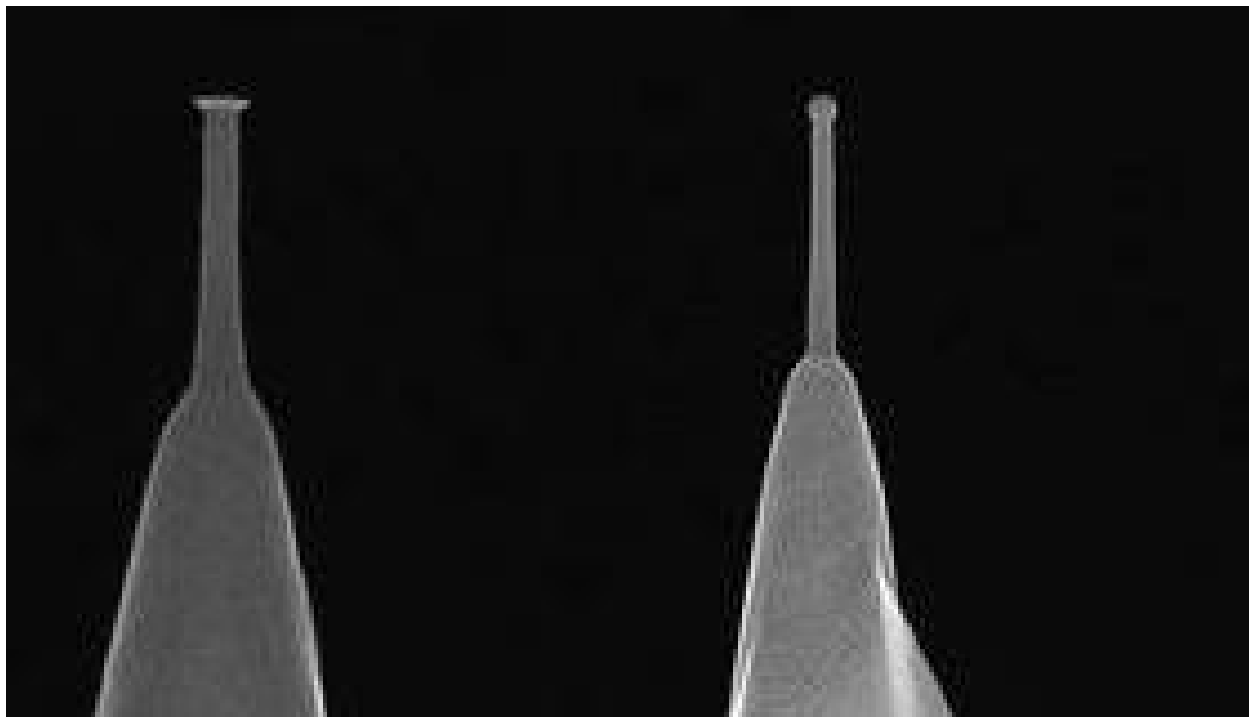


Figure 2.6: SEM image of specialty AFM tips provided by Nanotools USA. The first (left), has a hammerhead shaped rectangular tip while the second (right) has a spherical tip. The unique tip geometries are designed to image very steep features such as the inner walls of the nanotube.

set screw. The The pressure on this side is measured with an Omega Engineering®PX309-1KG5V pressure gauge with a 17V excitation. It is important that the tube is pressurized and has flowing water before the oil reservoir is raised to insert the tube. This prevents the oil from pushing into and clogging the tube.

The Hydrophobic Coating

In order to test the effects of contact angle on flow rate, both hydrophilic and hydrophobic nanotubes are required. Untreated tubes are naturally hydrophilic. They must be treated to be made hydrophobic. The first attempt to make the tubes hydrophobic used octadecyltrichlorosilane (OTS), an organometallic chemical that can produce a hydrophobic monolayer. The process involved cleaning the silica surfaces to be coated with acid in order to expose hydroxyl groups to which the OTS can bond. For the nanotubes, this means

flowing strong acid through the tubes at high pressure (in order to achieve acceptable flow rates). This coating process also requires a dry nitrogen environment, as OTS reacts with water. Several attempts yielded tubes through which there was no flow. We believe this to be due to water vapor contamination.

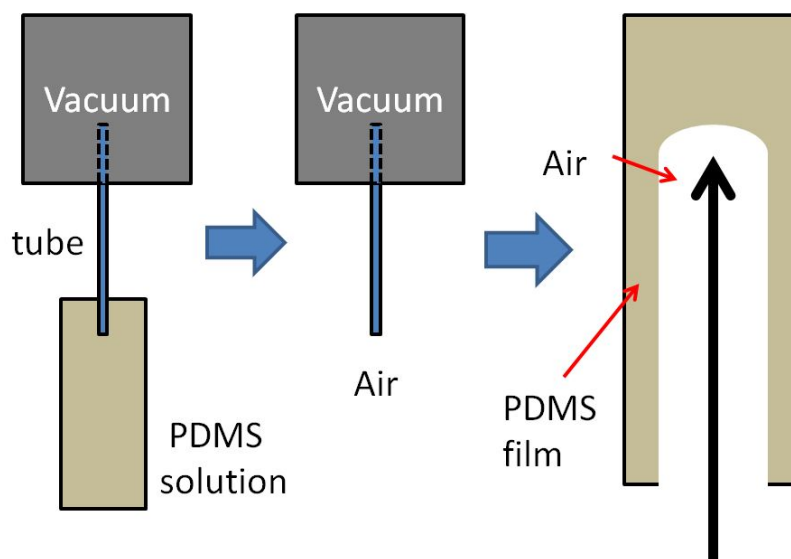


Figure 2.7: A diagram of the coating process. One end of a tube is dipped into a solution of PDMS and cyclohexane while the other end is exposed to vacuum. Then the tube is removed from the solution and exposed to air while the other remains under vacuum. An air bubble travels up the tube, leaving a thin PDMS film behind.

Coating the tubes with OTS was abandoned in favor of polydimethylsiloxane (PDMS), even though OTS has a greater contact angle (110°)[39] than that of PDMS (105°)[14, 60]. The coating method was inspired by Chen[19] and Bretherton[12] studying the film thickness around a bubble that travels through in a capillary. The idea is to fill the capillary with the desired liquid coating. Then, simply force an air bubble to travel the pipe, leaving a thin film. A diagram of the process is shown in Figure . The PDMS we use is Sylgard 186, which comes as two parts and has a high viscosity of 66.7 Pa·s. In order to achieve a thin coat of PDMS, the mixture is diluted 10:1 by mass with cyclohexane. Tubes roughly 10 cm long are fixed into a PDMS cap, with one side exposed to vacuum from a rotary vane pump and the other immersed in the PDMS-cyclohexane solution. The previously mentioned polyimide

coating is removed prior to coating. This ensures that the high temperatures involved in removing the polyimide does not affect the PDMS. The tubes stay immersed for roughly 20 minutes, which allows for the solution in the tube to be refreshed multiple times. The immersed end is then removed and exposed to air, allowing for a film to be created as the air passes through the tube. The tubes are then baked for one hour at 100°C. The thickness of the coating immediately after is estimated by[19]:

$$h = 1.337 r \left(\frac{\mu v}{\gamma} \right)^{\frac{2}{3}}, \quad (2.9)$$

where r is the radius of the pipe, μ is the dynamic viscosity of the fluid, v is the velocity of the bubble, and γ is the interfacial surface energy. For the diluted PDMS in a 200 nm fused silica pipe, we calculate the coating to be 20 nm thick before curing. The combination of the cyclohexane evaporation and curing reduces the thickness to under 2 nm.

On a flat surface, hydrophobicity is easily verified by measuring the contact angle. For PDMS, the contact angle with water has been well documented to be 105°[14, 60]. For a tube, especially a very small tube, it becomes a nontrivial matter. Several methods are used to verify the existence of the coating, depending on the tube size. All three methods rely on the concept of capillary action. If a tube is hydrophilic, it is energetically favorable for water to be in contact with the surface. If a tube diameter is small enough, this can manifest in water filling the tube upwards against gravity until it reaches a height in which the increase in gravitational energy equals the decrease in surface energy. The height at which this equilibrium occurs depends on the size of the tube, surface tension, and contact angle. For water and tubes 10 μm in diameter and smaller, this height is on the order of meters. If a tube is hydrophobic, it is energetically unfavorable for water to be in contact with the tube surface. Water resists filling a hydrophobic tube until it is forced by an external pressure.

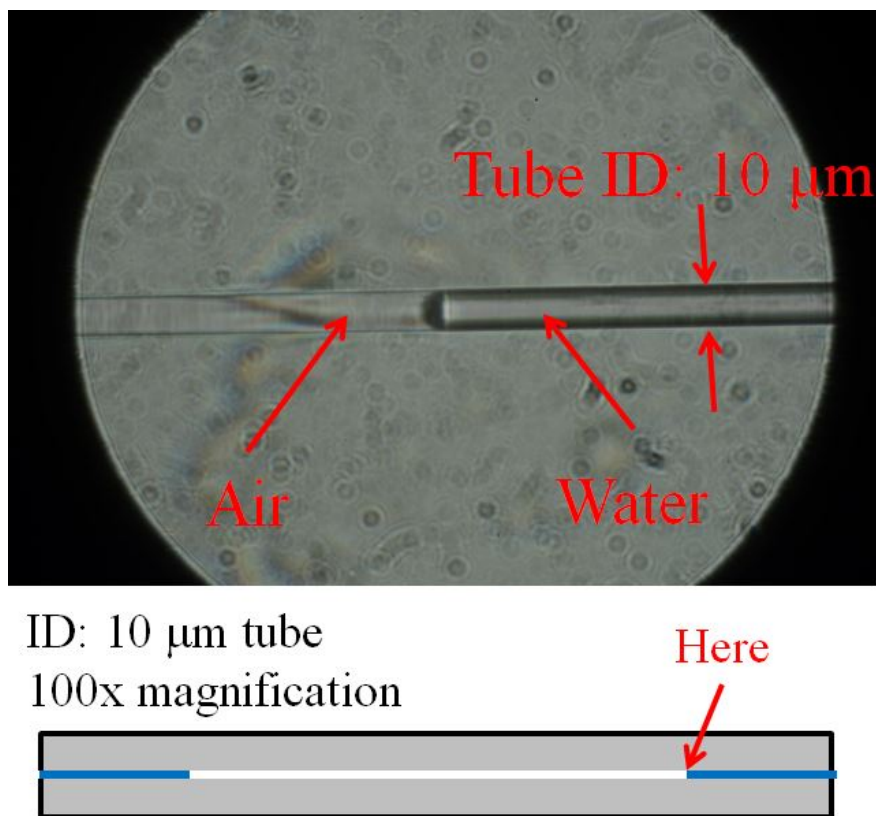


Figure 2.8: The observation of a meniscus inside a 10 μm tube confirms the hydrophobic condition of the tube and success of the coating process. The picture taken through a microscope objective shows the meniscus on the right side of the tube. To the right of the meniscus is water, while air is to the left. If the tube was hydrophilic, it would have completely filled with water.

The difference in behavior between hydrophilic and hydrophobic tubes makes it possible to verify the existence of the hydrophobic coating.

For large tubes (5 μm or larger), a meniscus can be viewed directly in a tube that is submersed in water. This is shown in Figure 2.8. A hydrophilic tube that is submersed in water will be filled. A hydrophobic tube resists filling up to a certain depth (and consequent pressure) , and then begins to fill from both ends. However, the filling compresses the gas remaining inside the tube and reduces the net pressure. This allows for a static meniscus to exist within the tube whose location will change based on the depth.

For medium tubes (1 μm or larger), fluorescence imaging is used. The tips of both coated and uncoated tubes are immersed in a saturated solution of Rhodamine 610 perchlorate in

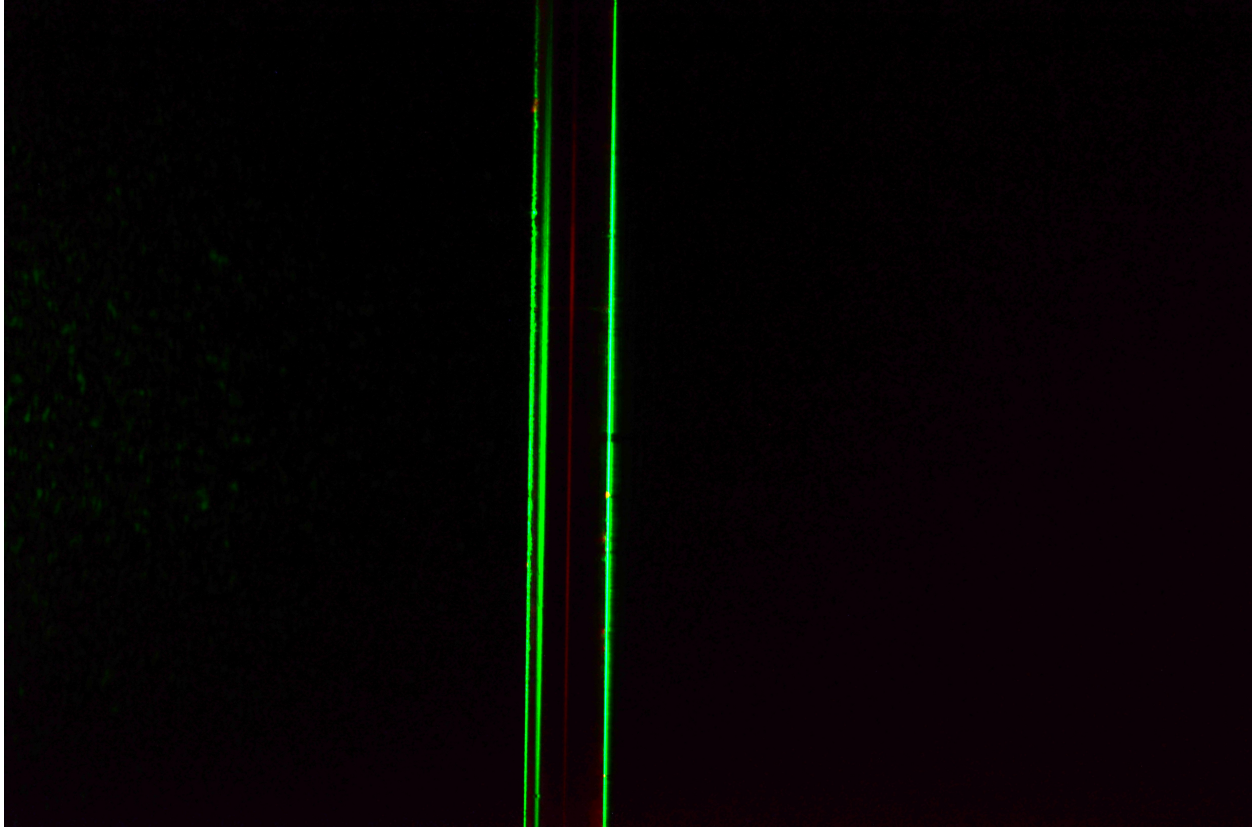


Figure 2.9: Example of fluorescence in a $2\ \mu\text{m}$ tube. The orange colored center stripe is the fluorescence from the saturated Rhodamine 610 solution. The green stripes are lensed laser light from the pump.

water. Rhodamine 610 absorbs light at a wavelength of $543.02\ \text{nm}$ and emits light at a wavelength of $610\ \text{nm}$. A diagram of the setup is shown in Figure .Both sets of tubes are dipped into the solution and imaged while being illuminated by a green laser at $532\ \text{nm}$. The uncoated tubes are hydrophilic, and should automatically fill with solution when they are dipped. The PDMS coated tubes should be hydrophobic and stay empty. The green laser light will pass through the coated tubes, while orange fluorescence is only seen in the uncoated tubes. The pictures are taken through two Thorlabs[®] FGL600 Longpass color filters which allows the orange fluorescence to be imaged while severely reducing the green laser light from the pump. An example of the tube fluorescence can be seen in Figure 2.9. The example shows that a substantial amount of laser light is bent towards the camera and penetrates the two filters. At $2\ \mu\text{m}$, it can be seen that the unwanted green light making it

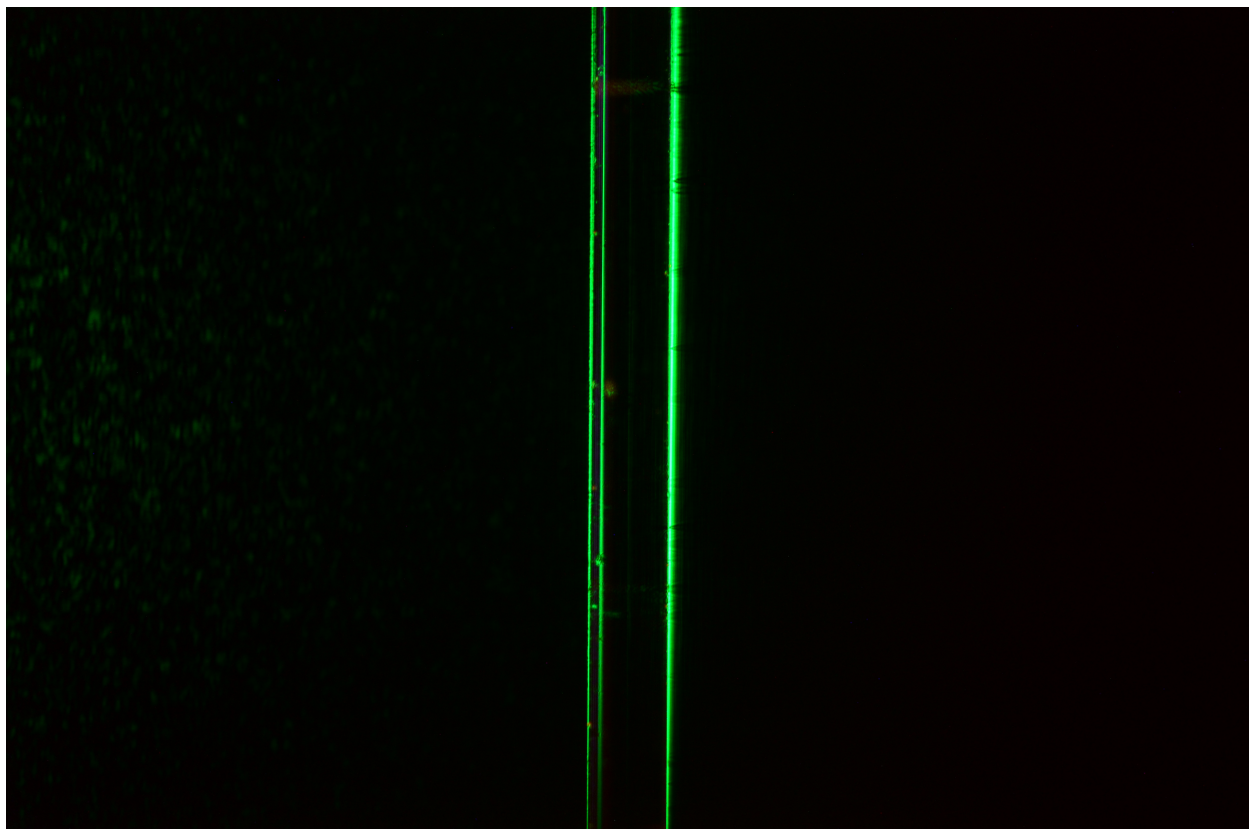


Figure 2.10: Any fluorescence signal is lost in the noise of the green pump laser, seen in the center of the tube.

through the filters is brighter than the fluorescence. The fluorescence signal is proportional to the volume, so it scales inversely with r^2 . For nanometer sized pipes, the green light that is bent by the inner diameter masks any fluorescence that may be taking place. This can be seen in Figure 2.10.

For tubes with diameters less than 500 nm, the coating is verified by observing the difference in pressure required to begin flow. Figure 2.11 shows the qualitative flow behavior for hydrophobic and hydrophilic tubes as a function of external pressure drop. The flow for uncoated tubes begins with any pressure drop and increases linearly with pressure. For hydrophobic tubes, the external pressure drop must first overcome the negative capillary pressure before flow will begin. Once the threshold is reached, the behavior will be the same as the hydrophilic tube (assuming no slip). A qualitative graph of this behavior is shown in Figure 2.11. This is due to the Young-Laplace pressure of the interface, given by

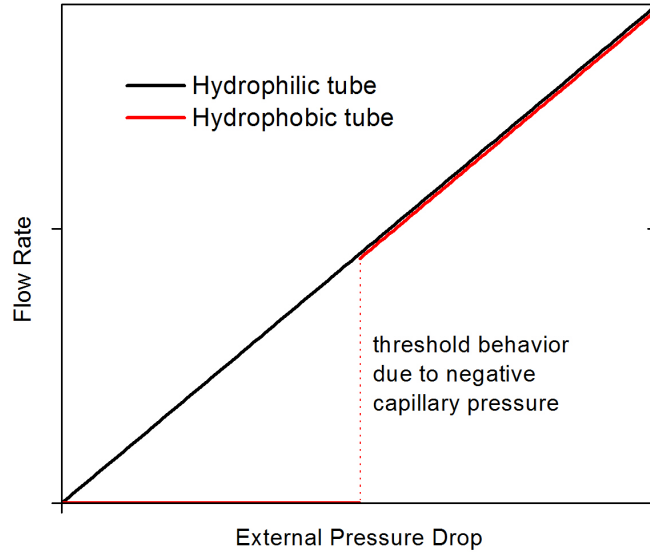


Figure 2.11: The theoretical flow behavior of a hydrophobic and hydrophilic tube as a function of external pressure drop differ due to capillary pressure. The hydrophobic tube negates any external pressure drop until a certain threshold, after which it adopts the same behavior as the hydrophilic tube (assuming no slip).

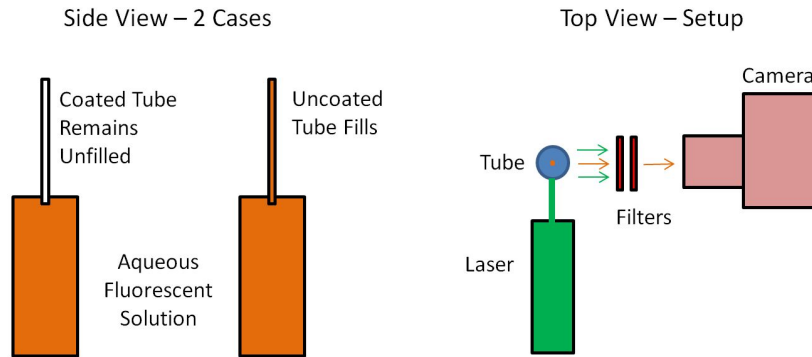


Figure 2.12: The setup used to verify the existence of the hydrophobic coating in $2\text{ }\mu\text{m}$ tubes relies on imaging of fluorescent dye in water. When the ends of the uncoated and PDMS coated tubes are dipped in fluorescent solution, only the uncoated tubes fill. Then, both tubes are illuminated with laser light, causing the solution in the uncoated tube to fluoresce. The light from the tube is filtered to remove the laser light before being captured by a camera oriented perpendicular to the laser.

$\Delta P = \frac{2\gamma \cos \theta}{a}$, where γ is the surface tension, θ is contact angle, and a is the radius of the pipe. For a 200 nm tube, it requires 3.72 atm to cause water to flow through the pipe. The

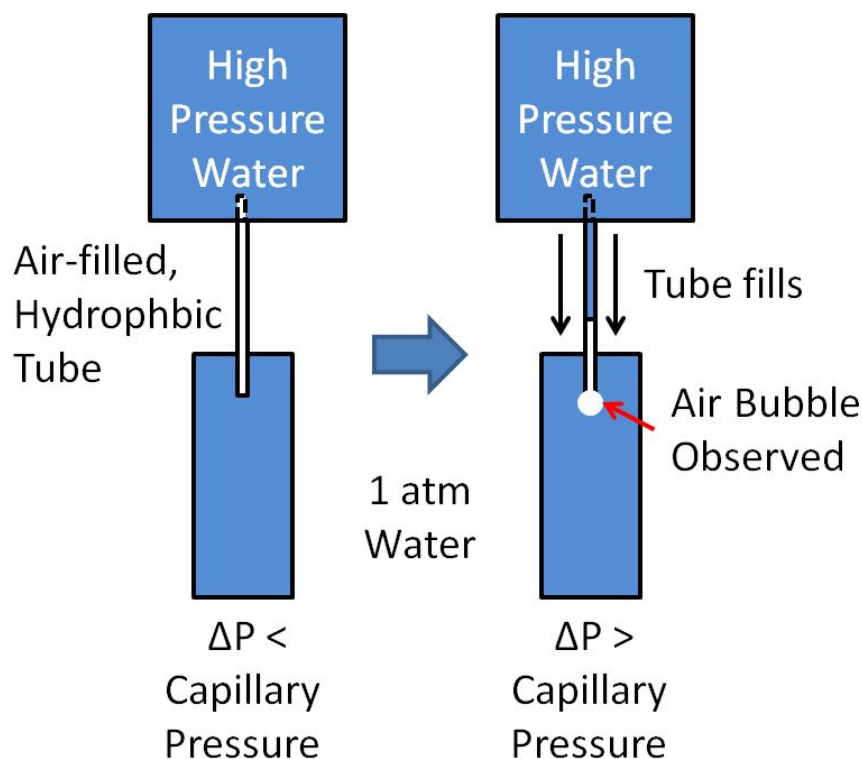


Figure 2.13: The coating in the 200 nm diameter tubes is verified by observing the threshold behavior of the flow with pressure. No flow is observed through an air-filled coated tube until the external pressure drop is enough to overcome the negative capillary pressure. Once this pressure is reached, the remaining air in the tube is pushed out and observed on the end of the tube.

coating is verified by observing the pressure-threshold behavior of the flow in the coated pipes. This is accomplished by raising the reservoir pressure of the tube while the other tip of the tube is placed in water instead of oil. When the Young-Laplace pressure is overcome, the water flow pushes the remaining air out of the tube, and the bubble is observed. A diagram of this is shown in Figure 2.13.

The Water and the Oil

There are two liquids of importance in this experiment. The first is the water flowing through the nanotube. We use water filtered by an EMD Milipore Synergy R[®]. A drop of bleach is added to 500 mL of the filtered water to prevent bacterial growth. This step was added after observing flow rates reduce and eventually stop at around 10 hours of flow.

Research into biofilms in microchannels[58] led us to believe bacterial growth was the cause. Adding this step allows for continuous flows greater than several weeks. This in turn allows us to use our smallest tubes. The mixture was tested to ensure the contact angle with PDMS remained unchanged.

The second liquid of importance in the experiment is the silicone oil in which the water forms a drop. The water cannot simply form on the end of the pipe and be exposed to air. At the operating flow rates of this experiment, the water would evaporate as it flows through, rather than forming a drop. A viscous oil with low water diffusivity is used to contain the droplet. We use Cannon[®] N5100 Viscosity Standard, which has a density 0.883g/mL. The lower density of the oil causes drops that are removed from the tube tip to sink out of the way. The density difference combined with gravity can cause deformation in larger drops from a spherical shape to a teardrop shape. To determine whether this effect is important, we look at the capillary length. If the largest dimension of the system (in this case the diameter of the drop) is smaller than the capillary length, the drop will remain spherical in shape. The capillary length is given by $\lambda_c = \sqrt{\frac{\gamma}{\rho g}}$, where γ is the surface tension between the two fluids, ρ is the density of the fluid in question, and g is gravitational acceleration. For this system, the capillary length is about 2.2 mm. The drops in the experiment have a maximum diameter of 1 mm, meaning the spherical approximation holds.

The Pictures

The pictures of the drops are taken with a Nikon[®] D7000 DSLR camera, in combination with an Olympus[®] LMPlanFL 10x microscope objective. A sample picture is shown in Figure 2.14. The camera is set to take a picture every two hours. The flow is on the order of picoliters per second and a single drop can take up to 120 hours to form. The image processing relies on us being able to discern a difference in the radius from one picture to the next. Depending on the flow rate, we may only process every other picture.

The outer diameter of the nanotube is used as a calibration for the pixel to distance

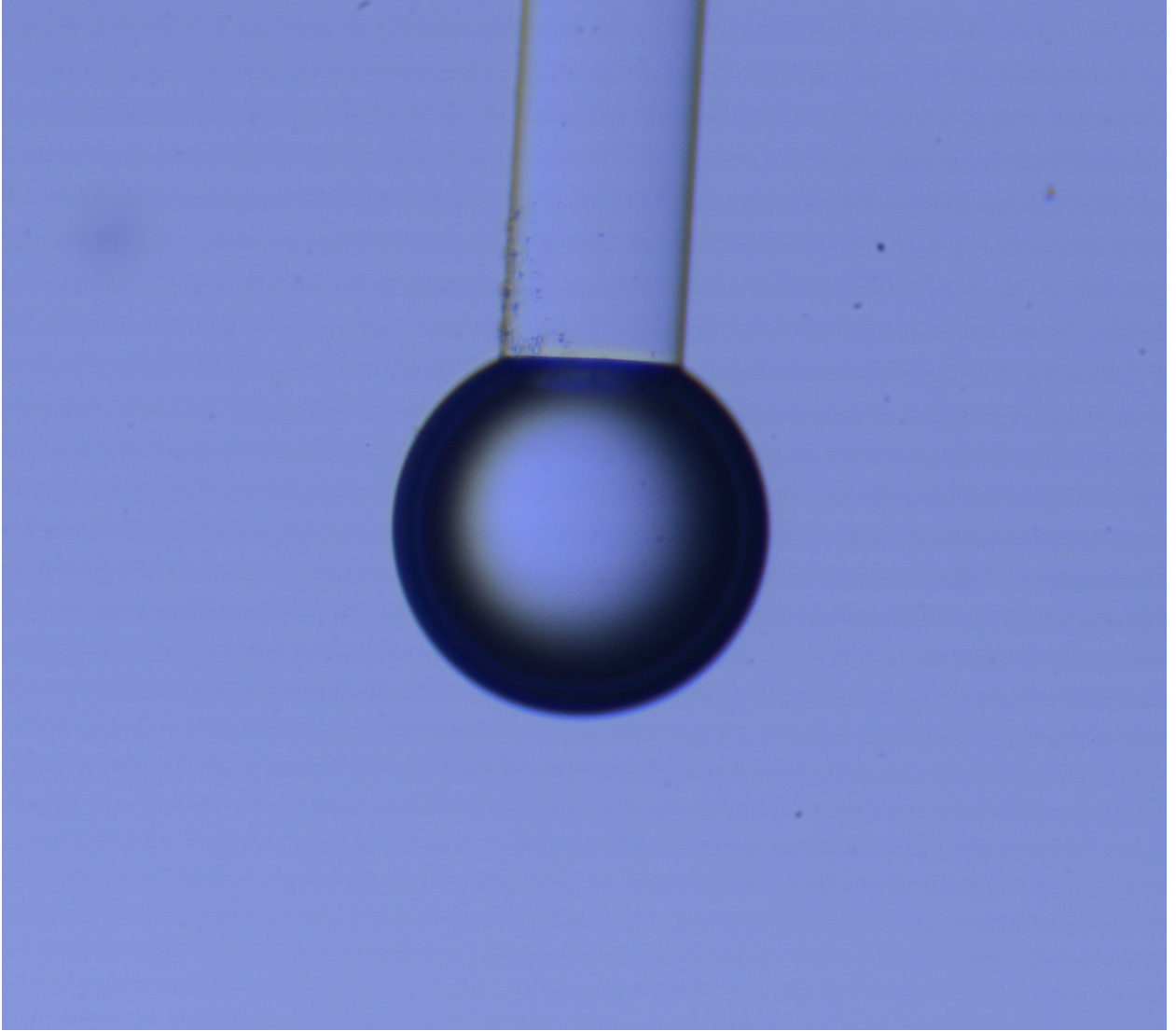


Figure 2.14: Sample of a drop picture. The picture was taken after 196 hours of flow through a 274 nm tube, with a pressure drop of 46.5 atm. The volume of this drop is 11.2 nanoliters.

conversion. The actual value is known from the same SEM imaging used to determine the inner diameter. The pixel diameter of the tube needs to be corrected for any tilt. Three points are taken from the picture, two on the left edge (A and B), and one on the right edge of the outer diameter (C). The perpendicular pixel distance is given by $|\frac{\vec{AB}}{|\vec{AB}|} \times \vec{AC}|$.

For each picture, roughly 20 pixel points are taken along the outer edge of the drop. These points are fit to a circular profile, and the radius and subsequent volume are calculated. This is not the final volume, as a correction must be made for the volume missing from the

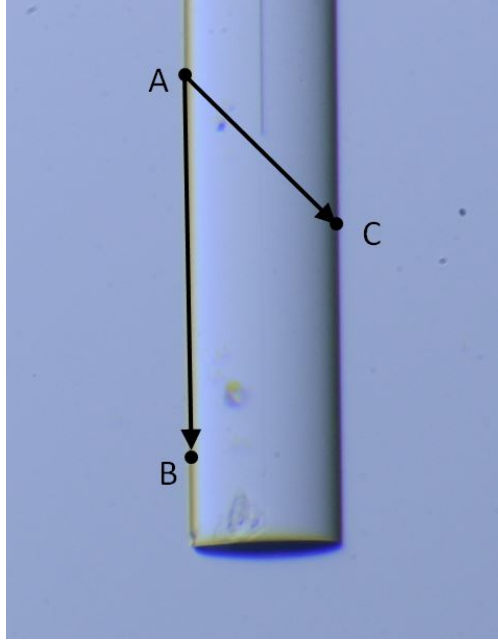


Figure 2.15: Diagram of the constructed vectors for the pixel to length calibration.

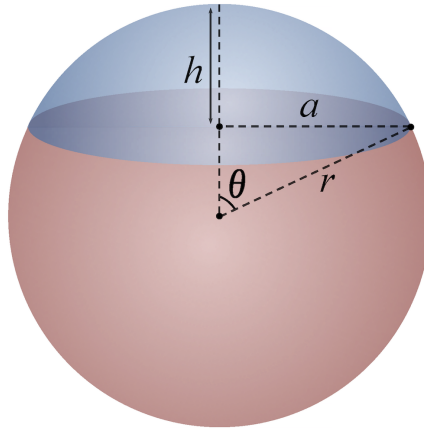


Figure 2.16: Diagram of the relevant parameters for the volume of a spherical cap.

“cap” of the drop where it comes into contact with the tube. The volume of a spherical cap is given by $V = \frac{\pi h}{6}(3a^2 + h^2)$, where a and h can be seen in Figure 2.16. The cap volume is subtracted from that of the sphere to give the total drop volume. The data of the drop volume over time is given a linear fit, where the slope of the fit is the flow rate.

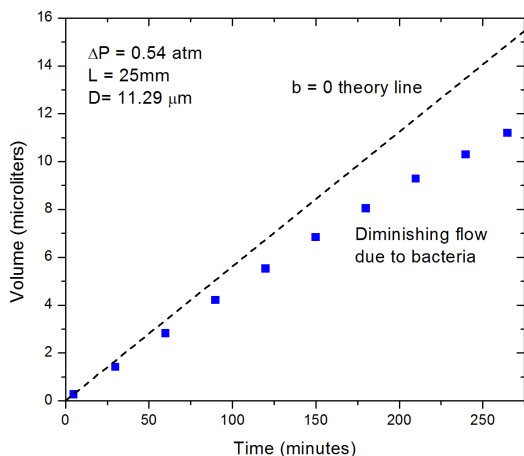
2.3 200 nm Indistinguishable Flows

Flow rates and slip lengths were measured through uncoated and PDMS coated tubes with diameters of 10 μm , 2 μm , and 200 nm for several pressures. The experiments are conducted in order of decreasing tube diameter. As diameter decreases, the experiment becomes increasingly sensitive to slip. The ratio of slip flow to no-slip flow is $\frac{4br^3}{r^4} = \frac{4b}{r}$, where b is the slip length. The capability to detect a 5% deviation in flow rate at each size would correspond to a specific slip length sensitivity. It is a slip length of 625 nm for 10 μm tubes, 12.5 nm for 2 μm tubes, and 1.25 nm for 200 nm tubes. The 200 nm tubes give the best sensitivity to slip, but the flow is much harder to measure experimentally. The larger tubes served to give an upper bound to the slip length value as well as provide experience and insight for the smaller tubes. They also hold the advantage of short trial runs (hours compared to days or weeks), which allowed for quick diagnosis and resolution of experimental challenges.

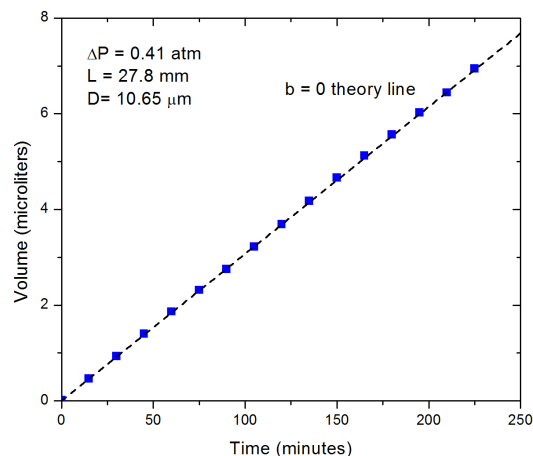
2.3.1 10 μm Data

Flows are measured through the tubes at room temperature with pressure drops ranging from 0.5 atm to 2 atm. Typical flow rates for 10 μm tubes are on the order of hundreds of nanoliters per minute. The first trials showed flow rates that follow theory at the beginning, but then reduced after 2-4 hours. This is unacceptable for trial runs in tubes smaller than 10 μm that require longer time (multiple days or weeks). The culprit for the reduced flow was found in bacterial growth, after reading about biofilm production in laminar flows in microchannels[58]. A simple solution to the problem was implemented in the form of adding a small amount of bleach (roughly 200 ppm) to the milipore water used for the experiment. The maximum time for flows is increased from a few hours to 2+ weeks. This allowed for longer experimental runs as well as multiple runs at different pressures on a single tube. Figure 2.17 shows the difference in a typical 10 μm flow run with and without bleach added

to the water.



(a) Flow run without bleach.



(b) Flow run with bleach.

Figure 2.17: Flow runs through 10 μm diameter tubes, one with pure milipore water and the other with bleach added to the milipore water to inhibit bacterial growth. This measure increased the maximum time for a flow run from a few hours to 2+ weeks.

Investigations into pressure drop dependence were performed at the 10 μm diameter level as well. Figure 2.18 shows multiple flow runs through a single coated tube at several pressures. The data follows the no-slip theory closely for all three pressures, with no trend in slip length with pressure. The diameter determined by the RGA and helium calibrated leak was 10.658 μm , while the diameters determined by the water flow were 10.682 μm , 10.675 μm , and 10.642 μm . If attributed to slip, the greatest difference in diameter between the calibration and flow measurement corresponds to a positive slip length of 93 nm.

The flow data between uncoated and PDMS coated 10 μm tubes was indistinguishable within a slip length of ≈ 100 nm. There is also no discernible dependence in the measured slip on pressure. In order to investigate slip lengths shorter than 100 nm, smaller tubes were used.

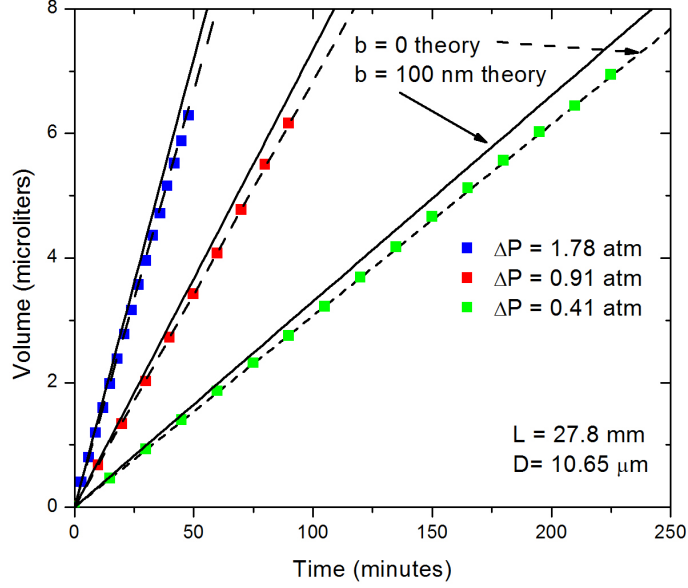
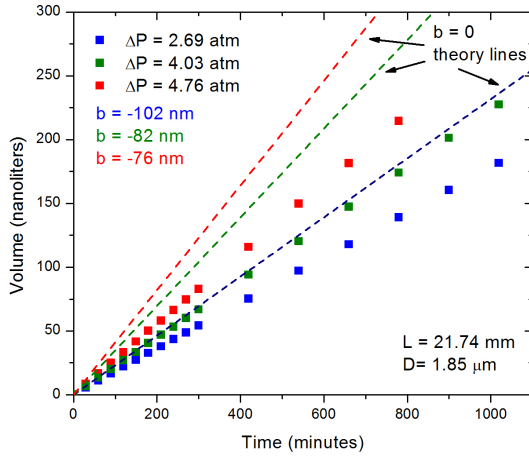


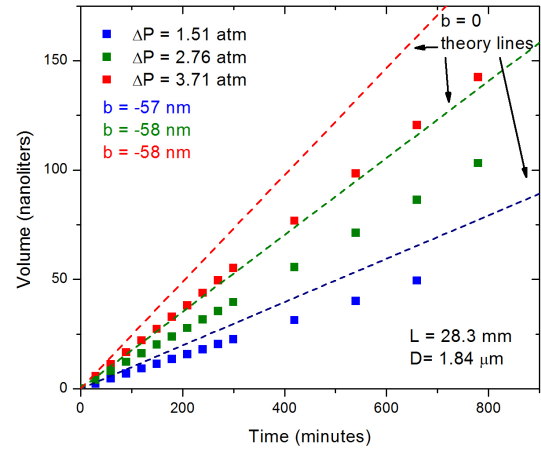
Figure 2.18: Flow data through a PDMS coated, 27.8 mm long, 10.65 μm diameter tube for pressure drops of 0.41 atm, 0.91 atm, and 1.78 atm. The measured flow rates for this tube yield slip length values of less than ± 10 nm.

2.3.2 2 μm Data

Flow data and slip measurement in 2 μm diameter tubes were performed with the methods and techniques learned from the 10 μm tubes. The pressure drops for the 2 μm flow data ranged from 1.5 to 5 atm, with typical flow rates on the order of nanoliters per minute. The 2 μm graph in Figure 2.19 visually shows higher deviation between the flow data and the theory than the 10 μm graph. This is because the 2 μm tubes are five times more sensitive than the 10 μm tubes. Small deviations from theory begin to appear much larger as tube diameter decreases. The average coated slip length (58 nm) and the average uncoated slip length (87 nm) differ by only 29 nm. This was roughly the same as the range of slip values that was commonly measured in a single tube (26 nm for the uncoated data shown). Therefore, it is not possible to tell if the difference is actually due to slip. It can be concluded from this data that the flow through the 2 μm coated and uncoated tubes is indistinguishable to within a slip length of 30 nm.



(a) Uncoated 2 μm flow data



(b) PDMS coated 2 μm flow data

Figure 2.19: Flow runs through 2 μm diameter, uncoated and PDMS coated tubes. The difference in measured slip length between uncoated and PDMS coated tubes was 29 nm, which was roughly the same as the range of slip lengths measured in a single tube. It can be concluded that the flows are indistinguishable within a slip length of 30 nm.

2.3.3 200 nm Data

Reducing the diameter by an order of magnitude from 2 μm to 200 nm decreases flow rates by a factor of 10,000. This is offset partially by increased driving pressure drops that range from 20 to 50 atm. The resultant flow rates are typically on the order of nanoliters per day. The main consequence is longer flow runs, taking usually 2 to 5 days. Considering a single tube may be used for 5 or 6 flow runs, several weeks can be spent on a single tube. Data from the longest flow run performed is shown in Figure 2.20. The data was taken over 5.5 days in an uncoated tube, and resulted in a calculated slip length of -1.2 nm. The inner diameter of the nanotube was measured via SEM.

The data shown in Figure 2.21 of uncoated and PDMS coated 200 nm diameter tubes exhibits the best slip length measurement sensitivity. The uncoated data follows no-slip theory exceptionally well, showing single nanometer slip lengths. The PDMS coated data also follows no-slip theory very well, while showing negative slip lengths between 4 and 5 nm. The difference between the coated and uncoated slip lengths can be attributed to the

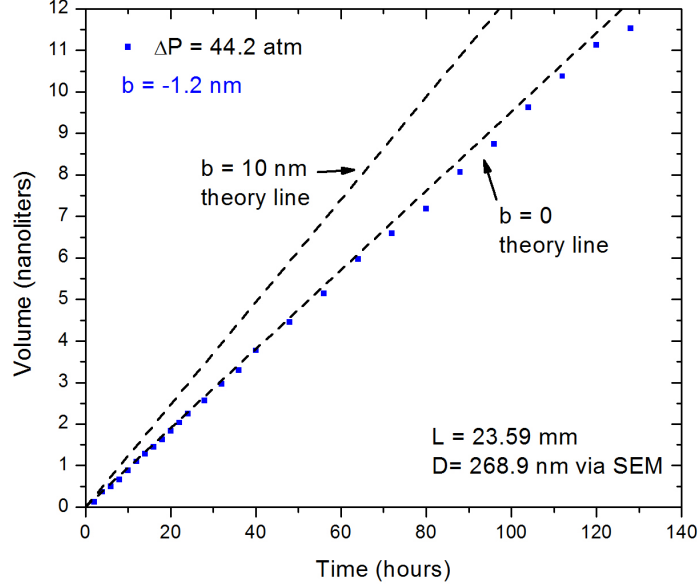
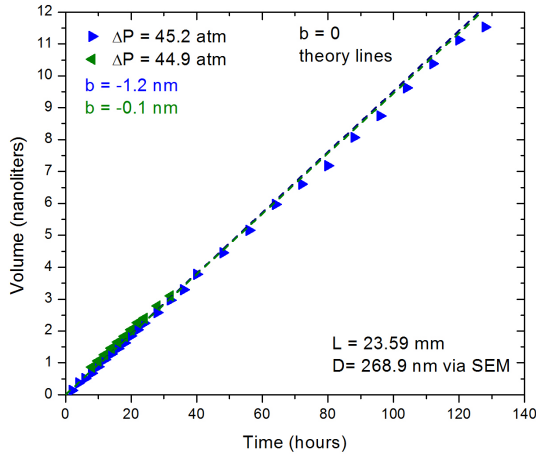


Figure 2.20: The longest single flow run performed in this experiment, lasting 5.5 days and reaching a final drop volume of 12.3 nanoliters. Data was taken for a 23.59 mm long, 268.9 nm diameter uncoated tube with a pressure drop of 44.2 atm. The calculated slip length was calculated to be -1.2 nm.

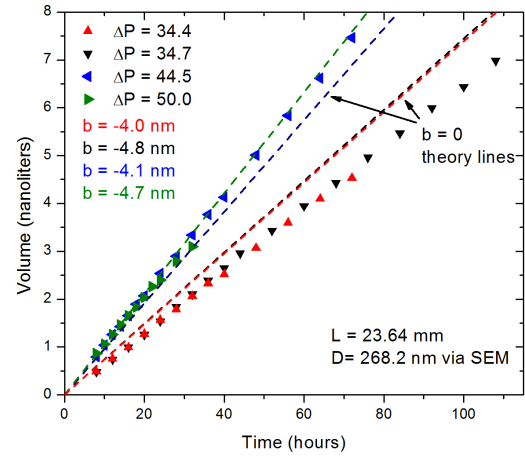
thickness of the PDMS coating, which was estimated to be less than 2 nm. The two flows are indistinguishable within a slip length of 3 nm.

2.4 Conclusion and Future Steps

Flow rate and slip length were measured in uncoated (hydrophilic) and PDMS coated (hydrophobic) single tubes of diameter 10 μm , 2 μm , and 200 nm. The flow experiments using the 10 μm diameter tubes showed that the flow through the hydrophilic and hydrophobic tubes followed the Hagen-Poiseuille equation and were indistinguishable within a slip length of 100 nm. They also showed no relation between the measured slip length and driving pressure. The 2 μm flow experiments showed negative slip values for both the uncoated and PDMS coated tubes that were indistinguishable within a slip length of 30 nm. The calibration method was changed for the 200 nm tubes, where the flow experiments showed



(a) Uncoated 200 nm flow data



(b) PDMS coated 200 nm flow data

Figure 2.21: Flow runs through 200 nm diameter, uncoated and PDMS coated tubes. The uncoated data agrees very well with no-slip theory, with small slip lengths on the order of 1 nm. The PDMS coated data also agrees well with no-slip theory with small, negative slip lengths between 4 and 5 nanometers. The difference between the coated and uncoated data can be explained by the thickness of the PDMS coating, which was estimated to be less than 2 nm. It can still be stated with certainty that the flows are indistinguishable within a slip length of 3 nm.

slip values less than 5 nm. The uncoated and coated flows were indistinguishable within a slip length of 3 nm, part of which maybe be due to the thickness of the hydrophobic coating itself. The results of the experiments support the no-slip boundary condition to the limits of the experimental sensitivity. It suggests that reports of greatly enhanced flows due to hydrophobicity may have been caused by experimental error. There are still other possible contributions for slip, such as nanobubbles, that need to be investigated to determine the correct boundary condition.

The method used to measure flows through single nanotubes can be further extended beyond 200 nm diameter tubes, but is only currently limited by finding a supplier or other way to fabricate said tubes. To address this, an atomic layer deposition (ALD) system has been fabricated and is being used to make smaller diameter tubes. ALD is a process in which a surface is exposed to diffuse amounts of alternating precursors which react with

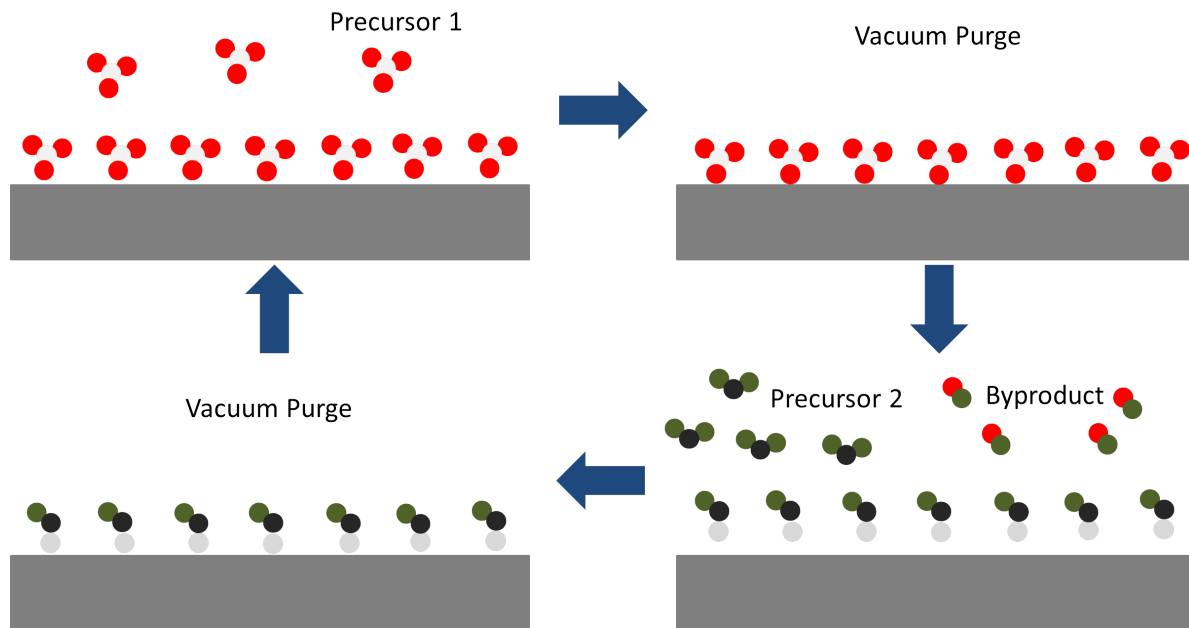


Figure 2.22: A basic diagram of the ALD process. A surface is covered by single layer a precursor when exposed to a rarefied gas of the same. Residual gas is evacuated, leaving only the molecules stuck to the surface by Van der Waals forces. The second precursor is introduced, reacting with the first precursor molecules on the surface and leaving behind a single atomic layer of (usually) metal oxide. The process is repeated as many times as necessary, and more complicated systems can many precursors to build novel multilayered materials.

reach other to form a self-assembled monolayer. A diagram of the process is shown in Figure 2.22. Most ALD systems cover the outsides of exposed objects that sit in a chamber. In our case, it is the inside of the tube we would like to coat in order to build arbitrarily small tubes. The 200 nm glass capillary tubes can be used as a base to make even smaller nanotubes. There are two potential difficulties that will arise in this process. First, we must ensure that enough of the dilute precursors is allowed to flow through the tube. As gas flows through the tube, the precursor is consumed as molecules stick to the walls. If material runs out, the cylindrical shape of the tube may be compromised. Second, as the atomic layers are built, the time it takes for the precursor laden gas through the tube will increase. This may cause a practical rather than theoretical limit on how small a tube can be made using this method. The ALD system has been designed and constructed using designs found in literature[34], and first attempts have been made at coating the insides of 200 tubes with aluminum oxide

using trimethylaluminum (TMA) and water as precursors. TMA was chosen because of the extensive literature regarding its use[56].

Chapter 3

Spreading of Superfluid and Normal Helium Drops

3.1 Drops and Spreading

When a drop of fluid impinges on a solid surface, surface tension and gravitational forces will cause it to spread. If the fluid partially wets the solid, the fluid drop will come to equilibrium with a contact angle θ_c given by the Young equation $\cos(\theta_c) = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv}$ where γ_{sv} , γ_{sl} , and γ_{lv} are the solid-vapor, solid-liquid and liquid-vapor interfacial energies, respectively. If the characteristic size of the drop is small compared to the capillary length $\kappa = \sqrt{2\gamma_{lv}/(g\rho)}$, the drop assumes a spherical cap shape which minimizes the surface energy, while if the characteristic size is greater than κ , the drop has a pancake shape which minimizes the gravitational potential energy[27].

In contrast, if the fluid completely wets the substrate (i.e. if $\gamma_{lv} < \gamma_{sv} - \gamma_{sl}$), the drop will eventually spread into a molecularly thin flat film. Because of its importance in coating technologies, the kinetics of the spreading process has been extensively studied both theoretically[47, 11] and experimentally[25, 71, 64]. Much of the experimental work has utilized silicone oil as the working fluid. The experiments show that drop radius R grows

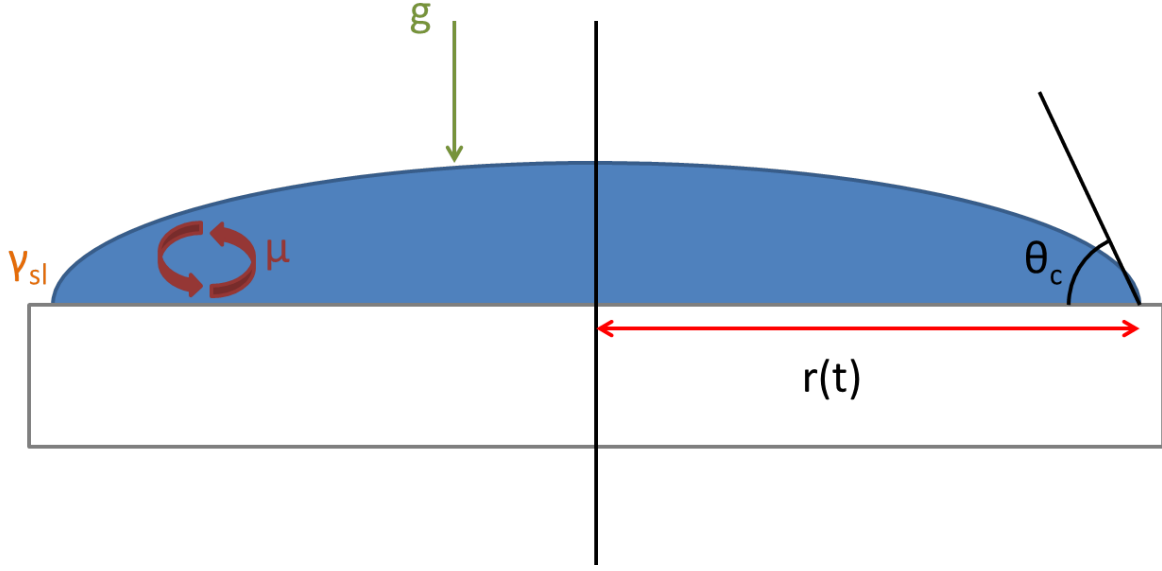


Figure 3.1: The forces that determine the spreading of a liquid drop on a solid surface, $r(t)$. Gravity (in green) always acts to flatten and spread the drop, and leads to $R \approx t^{1/8}$. Interfacial tension (in orange) leads to the familiar Tanner's Law, with $R \approx t^{1/10}$ and determines the equilibrium contact angle, θ_c . Viscous dissipation at the contact line (in red) as a controlling factor leads to $R \approx t^{1/7}$

as a power of t , t^α , with $0.1 < \alpha < .15$, and with a prefactor which depends on the fluid viscosity. One common theoretical approach is to model the fluid flow in the drop using the lubrication approximation. For axisymmetric drops driven by surface tension forces, a scaling solution can be found which yields $R \approx t^{1/10}$; this relation is often called Tanner's law[10]. For gravity driven spreading, the similarity solution yields $R \approx t^{1/8}$.

Another approach was adapted from molecular kinetic theory and applied to liquid wetting by Blake and Hayes[9]. Dodge further applied the theory specifically to the spreading of liquid droplets on solid surfaces[30]. He simplified the work of Blake and Hayes in the limit of the dynamic contact angle being very close to the equilibrium contact angle and incorporated surface physics to the static solution from hydrodynamics. His solution yields $R \approx t^{1/7}$, which he fit to his own experimental data. Further works in molecular dynamics simulations by deRuijter[26] predict that an intermediate spreading region where $R \approx t^{1/7}$ exists before the long time relaxation and an ultimate spreading law where $R \approx t^{1/10}$. It is

also predicted by deRuijter that there exists a characteristic crossover time between the two regimes which scales with viscosity as $t_2 \propto \eta^{-7/3}$. This means that the intermediate region with $R \approx t^{1/7}$ can last very long for low viscosity fluids. DeConinck theoretically attributed the behavior to dissipation due to molecular friction at the contact line[22].

3.2 Cryostat Design and Fabrication

In order to perform the helium drop experiments, a cryostat was designed and constructed. A cutaway of the cryostat model is shown in Figure 3.2 and an external picture of the actual cryostat is shown in Figure 3.3. The main design considerations, as well as a description of the key components will be described here. There were three main design constraints: multiple optical access ports, portability, and low base temperature. Optical access ports were required to take the measurements via high speed video. The funding grant dictated that the cryostat eventually be delivered to King Abdullah University of Science and Technology (KAUST) in Saudi Arabia, requiring a design that could be disassembled, shipped, and re-assembled with minimal downtime. This resulted in a smaller design than what would have been produced otherwise. The smaller footprint provided stricter tolerances in the design of the internal components. Finally, the experiments were to be performed with normal and superfluid, so the cryostat had to be able to maintain a temperature below 2°K while being illuminated for the high speed video. There are several subsystems within the cryostat that operate mostly independently from each other during normal operation. Keeping the cryostat at sub-liquid helium temperatures requires cooling power provided by a commercial pulse-tube cryocooler and a helium evaporative refrigerator and insulation provided by material choice, radiation filtering, and vacuum insulation. The bulk of the cooling power of the cryostat is provided by a commercial pulse tube cryocooler made by Cryomech. The package includes a compressor box and the cold head package. The compressor box is external to the cryostat and is connected to the cold head package which sits directly atop

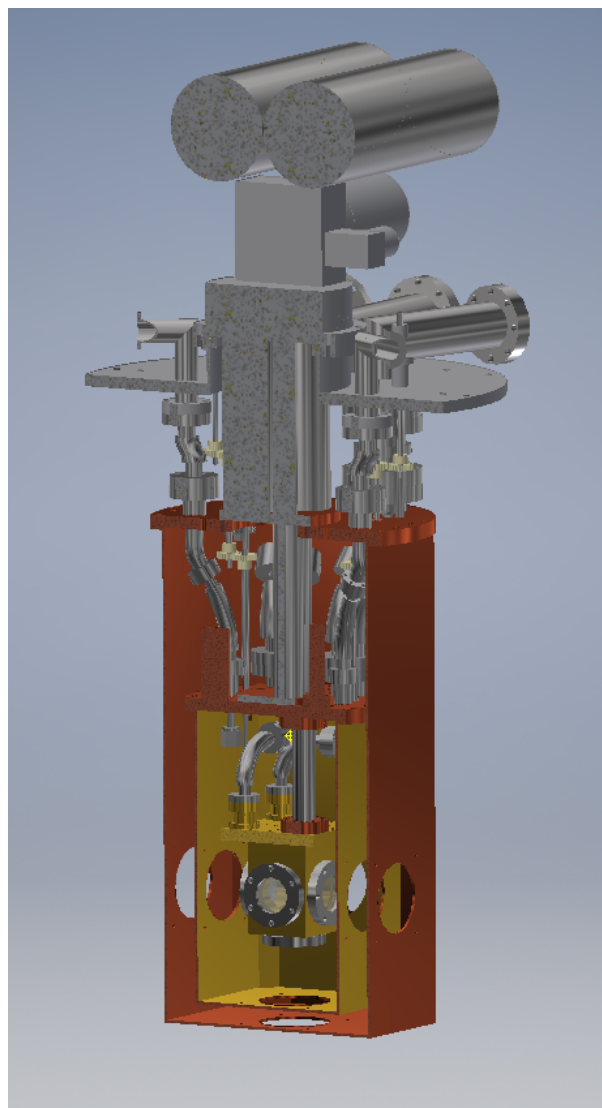


Figure 3.2: Cutaway of the cryostat design file showing the internal components.



Figure 3.3: Picture of the assembled cryostat from the outside, with the chamber closed.

the main chamber. They are connected via high and low pressure Aeroquip style gas lines to maintain the purity of the working fluid. The two offset, cylindrical cold heads protrude down from the top plate into the cryostat to provide the first two levels of cooling. The K and the second stage provides 1W of cooling power at a temperature of 4.2°K. As such, the two stages and their components are often referred to by their nominal temperatures, i.e. "40K plate," "4K thermometer," etc. The two cold heads are each attached to a larger copper plate to facilitate heat exchange between the cold heads and the many gas and electrical lines that need to be cooled. Figure 3.4 shows a picture of the installed 40K and 4K plates. Below the 4K cold head and plate is another plate, referred to as the 1K plate, which houses the last stage of cooling. Attached to the 1K plate is a helium evaporative refrigerator. The helium evaporative refrigerator consists of a high-pressure helium line that first passes through heat exchangers at the 40K and 4K plates. The gas liquefies while passing through the 4K heat exchanger before reaching an impedance. The impedance consists of one or more glass capillary tubes with inner diameter in the 50-100 μm range. The measure of impedance is defined by $Z = \frac{\Delta P}{Q\eta}$, where ΔP is the pressure drop, Q is the volumetric flow rate, and η is the dynamic viscosity. The amount of tubes, inner diameter, and length are tuned to give an impedance of roughly $5 \times 10^{18} \text{m}^{-3}$, a number experimentally determined and used in other evaporative refrigerators[13]. It was experimentally determined that the cooling power of the refrigerator is $\approx 30 \text{mW}$ at 1.5°K. The figure is approximate due to a complicated web of feedback that and temperature dependent properties. For example, the viscosity of the fluid drops dramatically when the helium reaches superfluid temperatures. One might naively assume that this would simply cause more helium flow and therefore more cooling power. However, with the increased flow, more heat load is put into the 4K plate which must cool down and liquefy the gas before it continues to the refrigerator. The temperature of the 4K rises and the helium delivered to the refrigerator is a high temperature. Due to the countless factors involved, the refrigerator is only manually tuned via the inlet pressure to optimize the cooling. As a rule of thumb, lower inlet pressure provides less cooling power but a lower

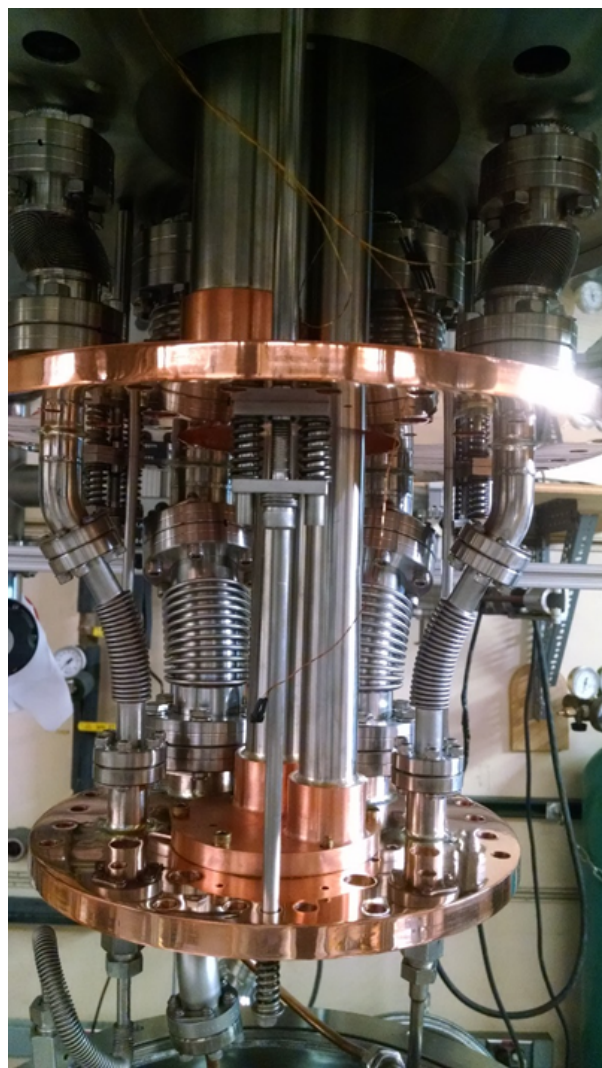


Figure 3.4: Picture of the 40K and 4K plate installed and connected to the cryocooler cold heads.

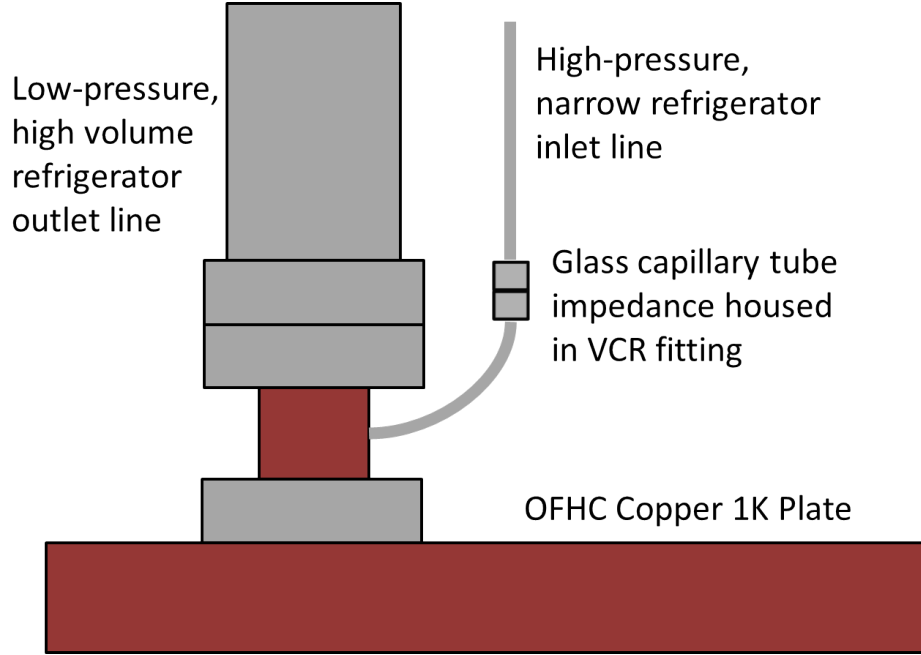


Figure 3.5: A diagram of the helium-4 evaporative refrigerator. Helium gas sourced from a tank outside the cryostat passes through heat exchangers on the 40K and 4K plates. The gas is liquefied while passing through the 4K heat exchanger and the liquid flows through a glass capillary impedance of $z \approx 10^{18} - 10^{19} m^{-3}$. The other side of the impedance is a low-pressure and low-impedance, causing the helium to evaporate and cool the refrigerator housing and the 1K plate to which it is attached.

final temperature and high inlet pressure provides more cooling power but a higher final temperature.

As the cryocooler and helium-4 refrigerator remove heat from the experimental cell, the rest of the cryostat is designed in such a way as to limit heat input from other sources into the cell. The potential sources of heat input into the cell are convection, conduction, and radiation. Convection is dealt with simply by evacuating the main chamber of ambient gas. The chamber is pumped on by a two-stage pump system consisting of a rotary vane mechanical roughing pump and a high-vacuum turbomolecular pump. The roughing pump is a Kurt J. Lesker RV 206 and the high-vacuum pump is a Varian V250. The chamber can reach pressures as low as 10^{-7} torr with this combination during cooldown. Once cold, the cold internal pieces of the cryostat will freeze gas molecules, causing further cryopumping that can lower the pressure even further.



Figure 3.6: A picture of the helium-4 evaporative refrigerator pot. The capillary tube impedance is housed in a VCR fitting that is attached to the small protruding pipe. The top of the pot connects directly to a larger diameter CF pipe to efficiently evacuate evaporated helium gas.

Conduction is limited into the cell from multiple sources. There are several gas lines that enter the cell as well as multiple electrical connections. To limit conduction through the gas lines, thin-walled stainless steel tubing of outer diameter 1/8" or 1/16" is used. Exact wall thickness was dependent on material availability and ductility needs based on the required pipe paths. Additionally, bending tubing into spiral shapes is a common practice employed to increase the tube length and decrease thermal conduction without drastically increasing the internal footprint of the tubing. Conduction from electrical wires is a balance between thermal and electrical conductivity and depends on the intended use. In the case of a low current thermometer, low thermal and electrical conductivity NiCo alloy wire is used. In the case of an ohmic heater used for temperature control, copper wire is used to ensure that the resistance, and therefore heat delivery, is concentrated at the desired locations. In both cases 30 AWG wire is used as a balance that reduces conduction vs thicker wire, but is still easy to handle without breaking.

Radiation into the cell can either come from the room via the optical view ports, or from internal parts of the cryostat that are still hotter than the cell. The cryostat contains two heat shields, one each anchored to the 40K and 4K plates. Each shield is nominally at the temperature of the plate to which it is attached. The shields are constructed from OFHC copper and are gold-plated, with polished external surfaces. The polished gold outside reflects more radiation than the bare copper, and provides much higher resistance to tarnishing. In order to facilitate the gold adhesion, a nickel layer of negligible thickness is deposited first. The shields have corresponding holes to maintain optical access. In order to limit the thermal radiation from the room, each viewport hole on the heat shields is covered by KG1 filter glass, which transmits optical light and blocks infrared as can be seen in 3.7. The downside to KG1 filter glass is its low thermal conductivity. This, coupled with its high infrared absorbance, can cause the glass itself to get relatively hot and radiate thermal radiation inwards toward the cell. To address this, the edges of the glass are lightly clamped to the heat shields with vacuum grease to facilitate heat transfer. Additionally, a sapphire

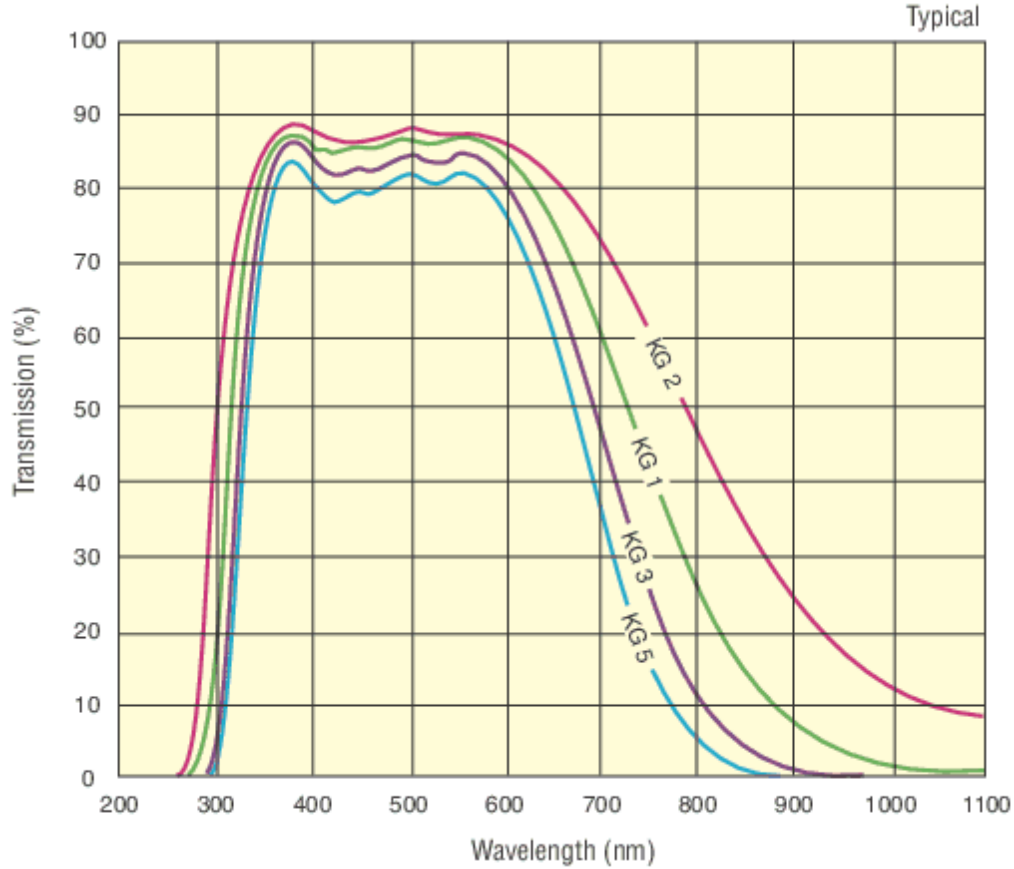


Figure 3.7: The typical transmission of radiation through various KG filter glasses as a function of wavelength[50].

window is placed in front of each KG1 window. The sapphire windows absorb some infrared radiation, and conduct the heat away much more quickly, reducing the heat load on the KG1 windows. There is an additional measure employed in the cryostat to obtain and maintain the very low temperature of the cell. The helium evaporative refrigerator only begins working once the heat exchanger on the 4K plate is cold enough to liquefy the helium. Before this point, the experimental cell and 1K plate is cooled by the 4K cold head. During this time, it is advantageous to facilitate heat transfer between the 1K and 4K plates to lessen cooldown time. Once liquid helium temperatures are reached, the evaporative refrigerator begins operating and the 1K plate and cell become much colder than the 4K plate. At this point, it is advantageous to reduce heat transfer between the 1K and 4K plates. This

is achieved with a gas controlled "heat switch," which connects the 1K plate to the 4K plate. The heat switch, shown in Figure 3.8 and 3.9, allows the operator to control the heat conduction between the two plates by either filling the switch with helium gas or pumping out the space and leaving vacuum conditions. Inside the switch, there is one OFHC copper pillar protruding downwards from the top and one protruding upwards from the bottom. They are not touching, so there is no conduction between them. The outside of the switch is thin-walled stainless steel that contributes little heat conduction. The gap between the copper pillars can be filled with helium gas, allowing convective heat transfer between the pillars via the gas. If the gas is pumped out of the switch, the convective heat transfer is "switched" off. The experimental cell reaches the lowest possible temperatures when the 1K plate and cell are isolated from the 4K plate in this fashion.

3.2.1 Cryostat Status Monitoring

The operation of the cryostat is monitored by multiple temperature and pressure sensors, as well as a mass spectrometry-based residual gas analyzer (RGA). Temperature measurement and control is based around a Lakeshore Cryotronics Model 336 Temperature Controller, for which a LabVIEW program was created to control the settings and log pressures and temperatures. The Model 336 contains 4 input channels and 2 output channels, capable of outputting up to 25W or 100W. All 4 input channels are typically utilized during normal operation. One thermometer is present on each cooling level, with the fourth thermometer reserved for the experimental cell. The thermometers on the 40K and 4K plate exist mostly for diagnostic purposes, to ensure the cryostat is operating normally. The thermometer on the 1K plate is used as feedback for the PID control loop built in to the temperature controller. Ohmic heaters are present on the 1K and 4K plates. The 1K heater is used for temperature control, while the 4K heater is typically used during warmup procedures to speed up the process. The thermometers are Cernox CX-1030-CU-HT thermometers, which operate between 0.3°K and 325°K. The thermometer sensitivity and accuracy is better at

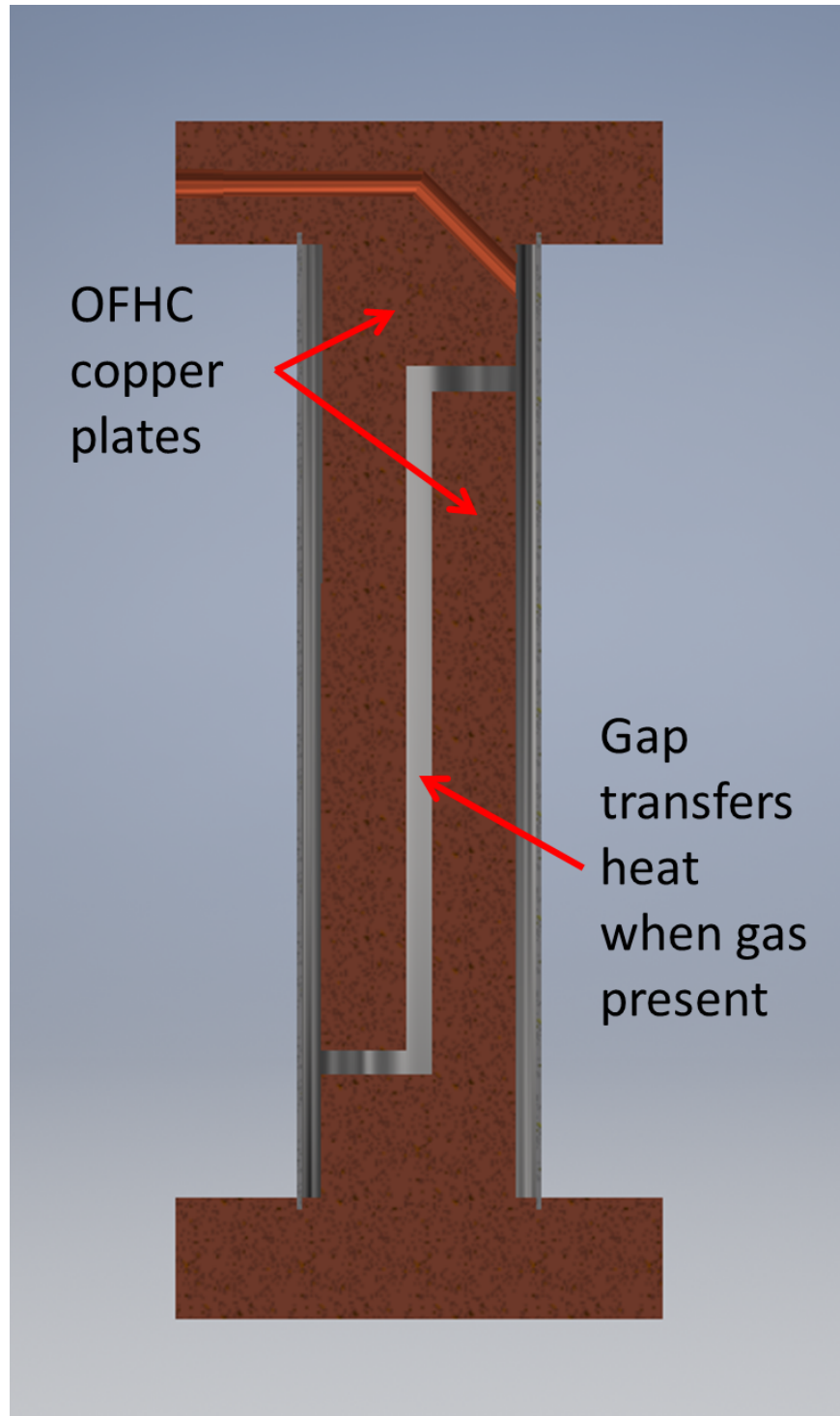


Figure 3.8: A cutaway model of the fabricated heat switch. Two OFHC copper pillars are offset and inserted into a sealed, thin-wall stainless steel cylinder, one from the top and the other from the bottom. When the gap space between the pillars is filled with gas, heat can be transferred between the top and bottom of the switch. If the gap space is vacuumed out, the convective heat transfer is stopped.



Figure 3.9: The heat switch before brazing assembly.

low temperatures, but the high-temperature data is only needed for diagnostic purposes for cooldown and warmup procedures.

Multiple pressure sensors are present in the cryostat to monitor the operation of certain subsystems. For the main chamber, two sensors are used. A KJLC 275 Series Convection Enhanced Pirani Gauge is used to monitor pressures from ambient down to 10^{-3} torr. These pressures typically only occur during the initial pumpdown, and are monitored for leak identification. For lower pressures, a KJLC 354 Series Ion Gauge is used. The ion gauge can measure pressures as low as 10^{-9} torr, though typical conditions in the cryostat only reach 10^{-7} torr. A high-pressure Omega PX-305 is used to monitor the refrigerator inlet pressure, which typically operates at pressures of 1-2 atm. The refrigerator outlet pressure is monitored with an additional KJLC 275, and serves as an indicator of healthy refrigerator operation.

Leaks in any cryogenic system are always a primary concern. A small leak of gas into the main chamber can destroy the effectiveness of the vacuum insulation. A leak in a liquid helium pipe is worse, as the liquid flowing out will expand by many times as it evaporates. Worst of all is a small leak in a section of pipe where superfluid is present. Due to the incredibly low viscosity of the superfluid helium, a leak that might be undetectable

if normal helium was present could be fatal to the experimental run. In the worst case, a leak occurs at superfluid temperatures, and disappears at room temperature so it cannot be found. The main tool used for leak checking various piping and chambers is a residual gas analyzer (RGA). We use a Stanford Research Systems RGA100 which was controlled by a freely provided software from Stanford Research Systems. The RGA is connected to the vacuum system, and consists of a hot filament that ionizes gas molecules, and collects the ions. The RGA is able to differentiate between different elements, and can be set to only scan for helium. Typically, the RGA operates in a pump mode, where the pump system is connected to the main chamber. The internal pipes and cell are pressurized with helium gas. If there is any leak outwards into the vacuum chamber, the RGA signal will indicate as such. Leak testing procedures of this type are typically performed before closing and cooldown. The RGA can also be used in a "sniffer" mode, in which a small $50\text{ }\mu\text{m}$ diameter, 10 cm long metal impedance is connected to the RGA-vacuum system. The impedance can "sniff" directly at possible leak sites, and is useful for identifying culprit leaking pieces.

3.3 Experimental Setup

The cryogenic and optical setup of our apparatus is shown in Fig. 3.10. Optical access was provided by sapphire windows on the front, back, and bottom of the cell with corresponding windows through the cryostat heat shielding and vacuum chamber. The imaging system consisted of an LED package, collimating lenses, high-speed camera, and a digital delay generator. The Phlatlight CBT 120 LED was used in pulsed mode in order to minimize heat input in the cell due to the light. A synchronization signal from the Phantom V2511 high-speed camera was used to trigger the Stanford Instruments DG535 digital delay generator, which in turn sent a pulse of controllable duration to activate the LED. The pulse duration was chosen to correspond with a given camera exposure time. The light from the LED travels through a series of collimating lenses limiting illumination to the area of interest.

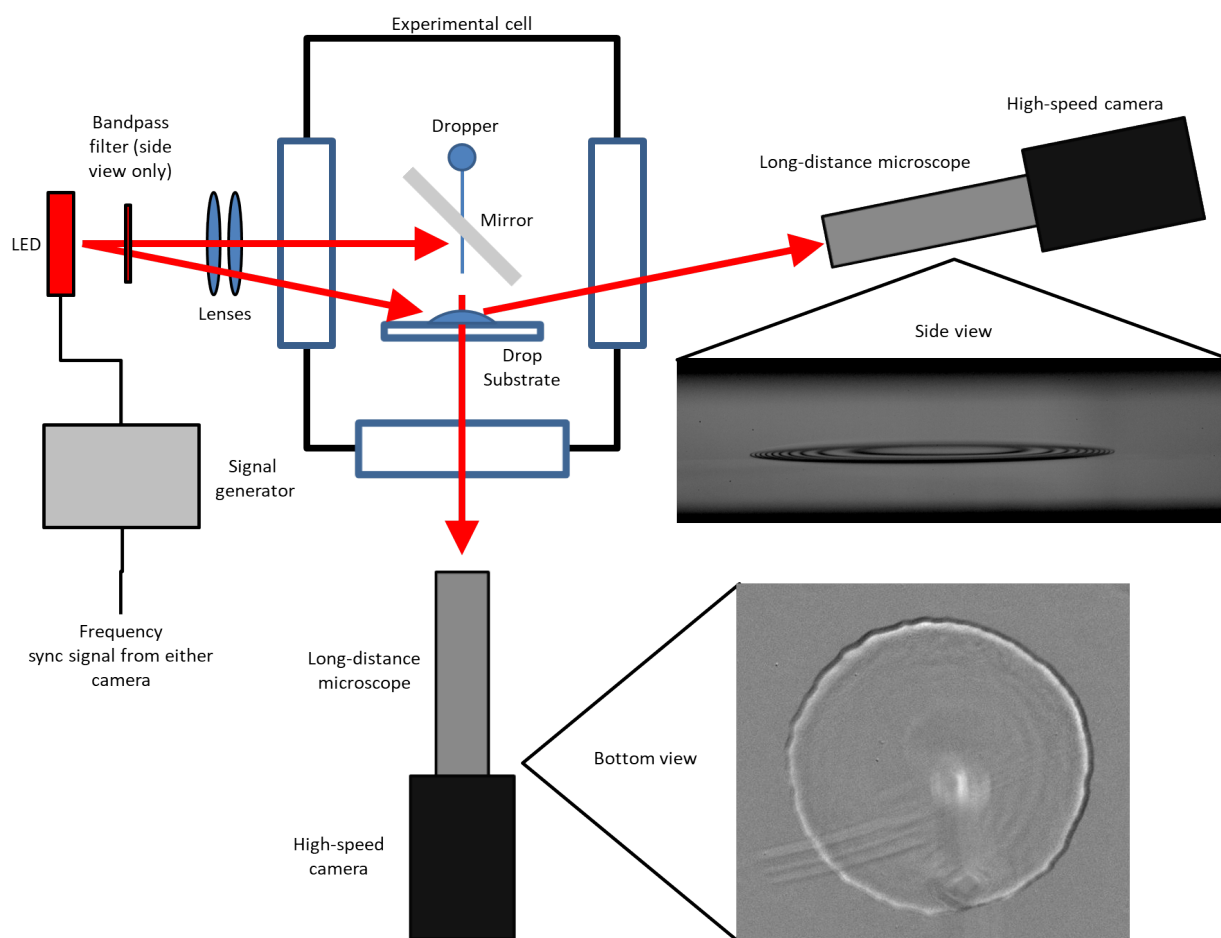


Figure 3.10: Schematic diagram of cryogenic and optical apparatus. Drops were delivered from a capillary tube approximately 1 cm above the substrate, which was usually a sapphire plate. The experimental cell had sapphire windows on the bottom and the sides. The spreading drop was illuminated with an LED, which was shone at a shallow angle for the edge-on view, or reflected from a 45 degree mirror to produce normal incident light for the bottom view.

In some configurations, an optical bandpass filter was placed in front of the LED in order to limit the wavelength in the interest of performing interferometry on the drops. The camera was mounted opposite and pointing toward the LED, or below and pointing upward towards the 45° mounted mirror. In the former configuration, the LED source and camera were be tilted downward at an angle of 6.4°. In the latter, the LED was horizontal and the camera was vertical. All experiments were performed with bulk liquid present, ensuring a saturated vapor environment. With bulk liquid present and liquid helium in the dropper line, the cell was able to sustain stable experimental conditions as low as 1.3◦K. This is higher than the minimum attainable temperature of the cryostat due to additional heat flux from the liquid helium in the dropper line. Helium drops were produced by increasing the pressure in the dropper line sufficiently above the cell vapor pressure for the given temperature. The microtube acts as a flow impedance to limit the drop rate. Typical ΔP values range from 10-100 torr, producing drops from once every 2 minutes to once every 20 minutes.

The drop impact and spreading substrate was covered in a film of liquid helium for all experiments. A quartz crystal microbalance (QCM) was used to measure the film thickness. The QCM, which has a thin, disk-like structure, replaced the sapphire as a substrate in some experiments, making the film thickness measurements very similar to conditions where the sapphire substrate was present. A QCM has incredible sensitivity to area mass density on its surface, with modern QCMs capable of measuring ng/cm²[52]. Electrodes deposited on the QCM surface are used to apply an AC voltage that, when on resonance with the QCM's natural frequency, increases in oscillation and drawn current. The natural frequency of the QCM will change when coupled to another mass, whether that be gas, liquid, or solid. The equation for the height, h , of a liquid film on the QCM, derived from the Sauerbrey equation, is

$$h = \frac{-\Delta f}{C_f \rho}, \quad (3.1)$$

where $-\Delta f$ is the change in resonant frequency, C_f is a constant unique to the exact model of QCM, and ρ is the density of the liquid which makes the film. The QCM used is a 5 MHz AT-cut quartz with a C_f of $56.6 \frac{\text{Hzcm}^2}{\mu\text{g}}$. Observed frequency shifts for normal helium varied from 30-40 Hz, resulting in film thicknesses of 36-49 nm. For superfluid, the frequency shift was measured to be 1.65-1.7 Hz at 1.6°K. This corresponds to a film thickness of 2.0 nm. However, this must be scaled by the normal helium fraction at that temperature, as the QCM only experiences viscous drag forces from the normal fraction. At 1.6°K, the superfluid fraction is 16.2%, and the corresponding corrected film thickness is 12.3 nm.

The existence of the helium film changes typical drop spreading conditions. In Figure 3.1, the forces which can cause drop spreading were described, with one being interfacial tension. More specifically, the interfacial tension determining dynamics is really difference between surface tensions of the three phases. There are a liquid-gas, liquid-solid, and gas-solid interfaces each with an associated surface energy. In the case of a completely wetting drop, it is energetically favorable for the drop to maximize the liquid-solid interface area, even at the cost of more liquid-gas interface area and less solid-gas interface area. In typical drop experiments where a drop impinges on a dry, this can be a dominating force. However, the drop in the experiments presented here impinge upon an already wet surface. While the liquid-gas and solid-gas contributions are still present, the larger liquid-solid contribution will be absent. This may result in the observation of behavior controlled by a different mechanism, such as viscous dissipation at the contact line.

3.4 Results and Discussion

3.4.1 Drop Shape

In impacts and spreading viewed from the side, the camera is tilted at a 6.4° angle, allowing interference fringes to be seen, as seen in Fig. 3.12 and 3.13. Fig. 3.15 shows a ray diagram of the interference occurring within the drop. The drop is flat enough for be

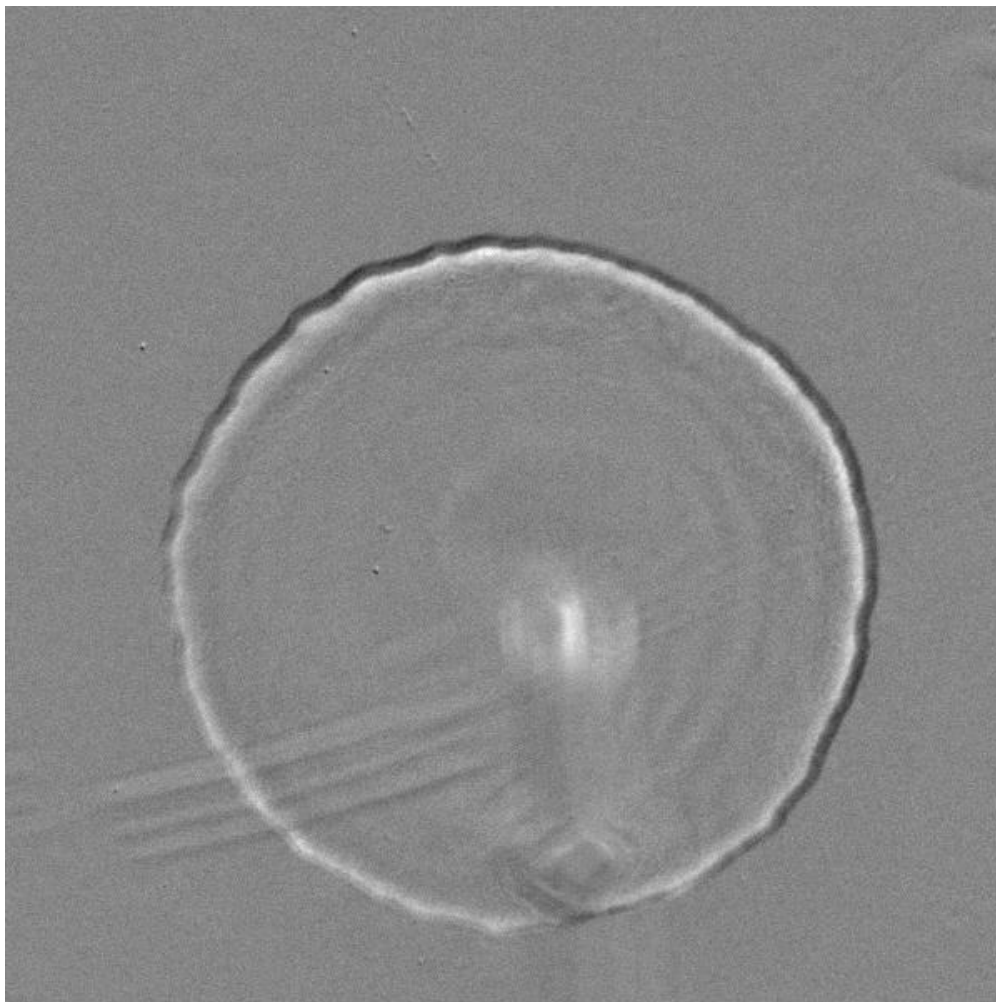


Figure 3.11: 1.6K Bottom view example

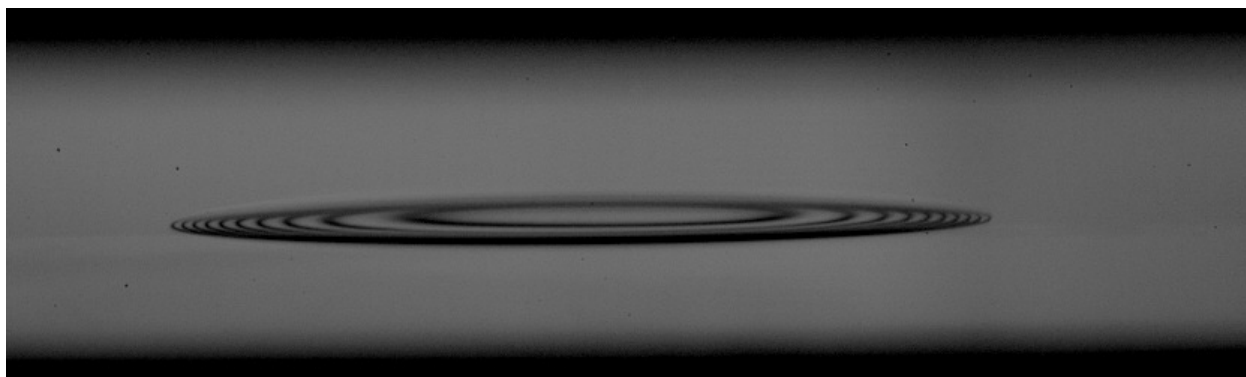


Figure 3.12: A 2.5°K drop seen from the side, approximately 2 seconds after impact. Interference lines show the changing thickness of the drop and are visible due to the slight angle of the imaging system.

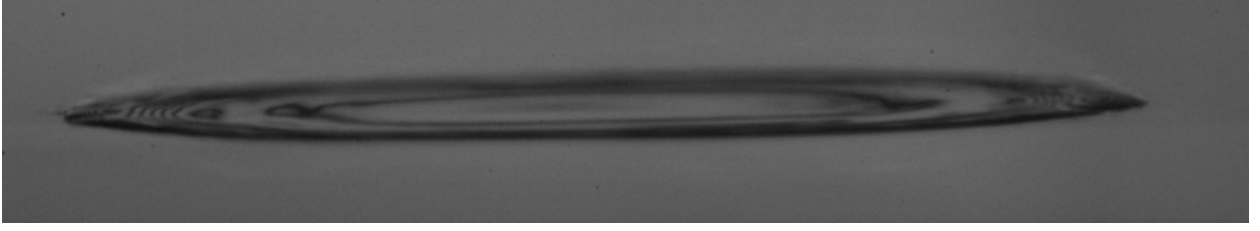


Figure 3.13: A 1.626°K superfluid drop seen from the side. The non-uniformity of the drop edges was typical for superfluid drops.

described as a thin film:

$$d = \frac{\lambda}{2n_{film} \cos \theta_t}, \quad (3.2)$$

where d is the change in film thickness per fringe, λ is the wavelength of light, n_{film} is the index of refraction of the liquid, and θ_t is the angle of the transmitted ray according to Snell's Law.

For a red LED with an optical bandpass filter centered at 632 nm, each fringe represents a 1174.5 nm change in drop height. Fig. 3.14 shows the drop profiles for several times, reconstructed from the interference fringes. The macroscopic contact angle calculated from the profile begins at 0.03° and approaches 0.018° over time, as shown in Fig. 3.16.

3.4.2 Drop Duration

Drop duration was measured from the time of impact to the total disappearance of the drop. Normal and superfluid drop duration exhibited clearly different behavior. Fig. 3.17 shows the maximum drop duration as a function of temperature. The duration of the superfluid drops is ≈ 1.5 s for most temperatures until close to the T_λ point, where it begins to sharply increase. Normal helium drop duration initially varied wildly, with a maximum duration of 15-16 min. It became apparent that the normal drop duration was highly sensitive to heat input, while the superfluid was not. Fig. 3.18 shows drop lifetimes

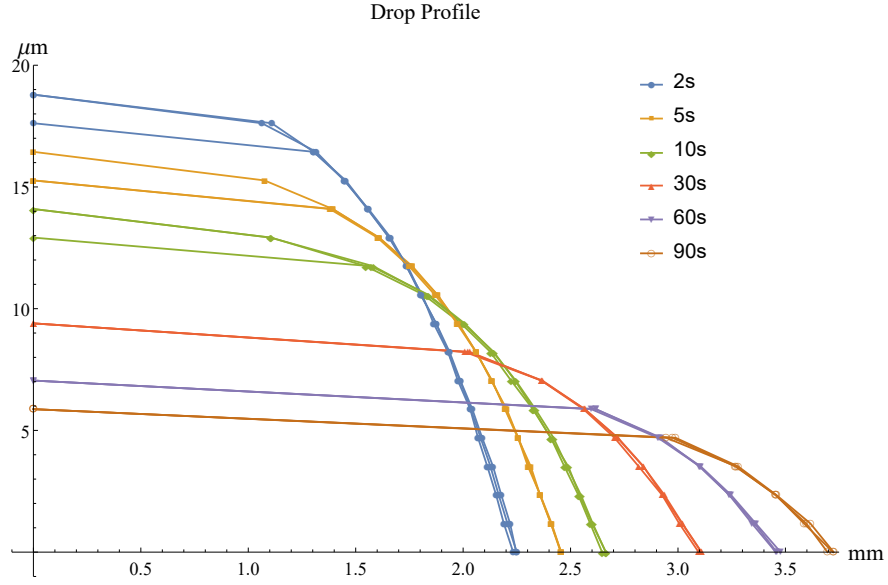


Figure 3.14: Profiles constructed from interference patterns. The data represents 3 individual drops, with profiles constructed for identical times. It is to be noted that the vertical axis is in units of μm while the horizontal axis is in units of mm. As a result, the reconstructed profile does not appear as flat as the actual drop.

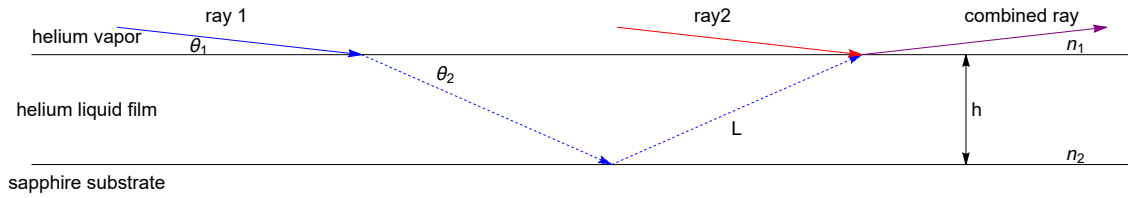


Figure 3.15: The basic interference model used to determine the height change between observed interference fringes on the surface of the helium drop. The difference in optical path length between the two rays leads to interference fringes. Each fringe represents a $\approx 1.2\mu\text{m}$ height change.

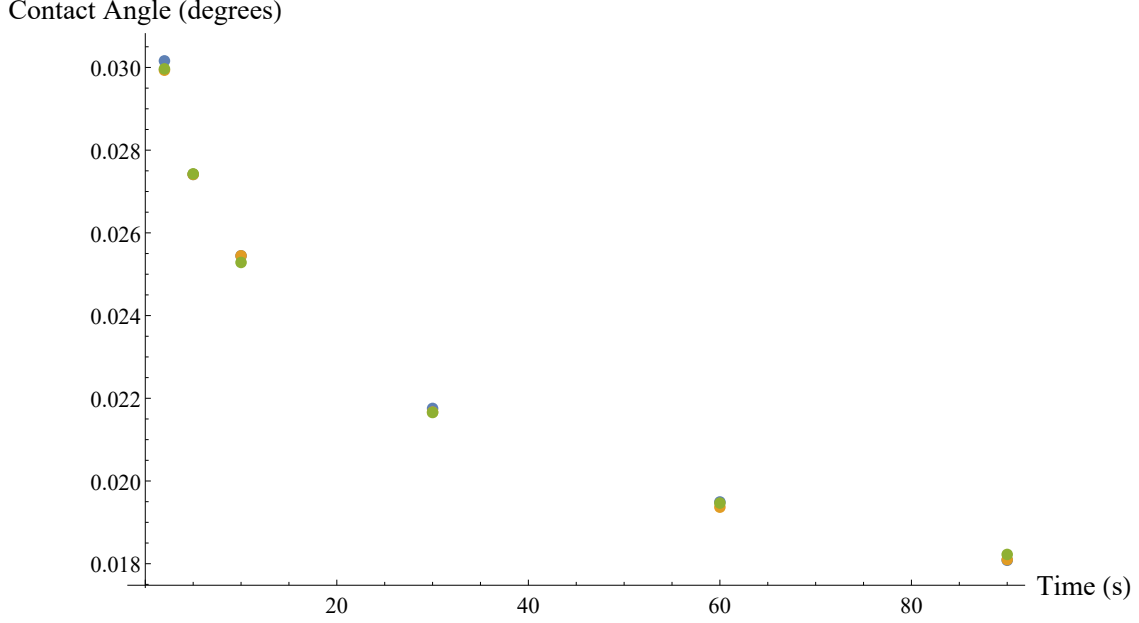


Figure 3.16: Macroscopic contact angle as a function of time. The small contact angle decreases further over time, consistent with a flattening drop profile.

as a function of power inserted into the substrate for various temperatures. The superfluid drop duration was unaffected by the power input, but varied with temperature. The normal helium drops were strongly affected by the heat input, with power inputs as low as $15 \mu\text{W}$ having an effect on the total drop duration.

Normal Duration

The sensitivity of the normal helium drop duration to heat input indicates evaporation as the controlling factor. The candidates for the driving force for evaporation are the Laplace pressure ($2\gamma h/R^2$), the liquid gravitational head inside the drop (ρgh), and the gravitational pressure difference in the vapor from the bottom of the cell ($mgHP/k_bT$). The pressure variations due to Laplace pressure and the liquid gravitational head are similar, and an order of magnitude less than the gravitational pressure difference to the bottom of the cell. The additional pressure from the height difference in the cell causes an outward flux of $\Delta P/\sqrt{2\pi mkT}$. For a typical drop at 2.5 K with a R_c of $300 \mu\text{m}$ (estimated from reconstructed drop profiles), this flux would evaporate the drop in seconds, much shorter than the observed

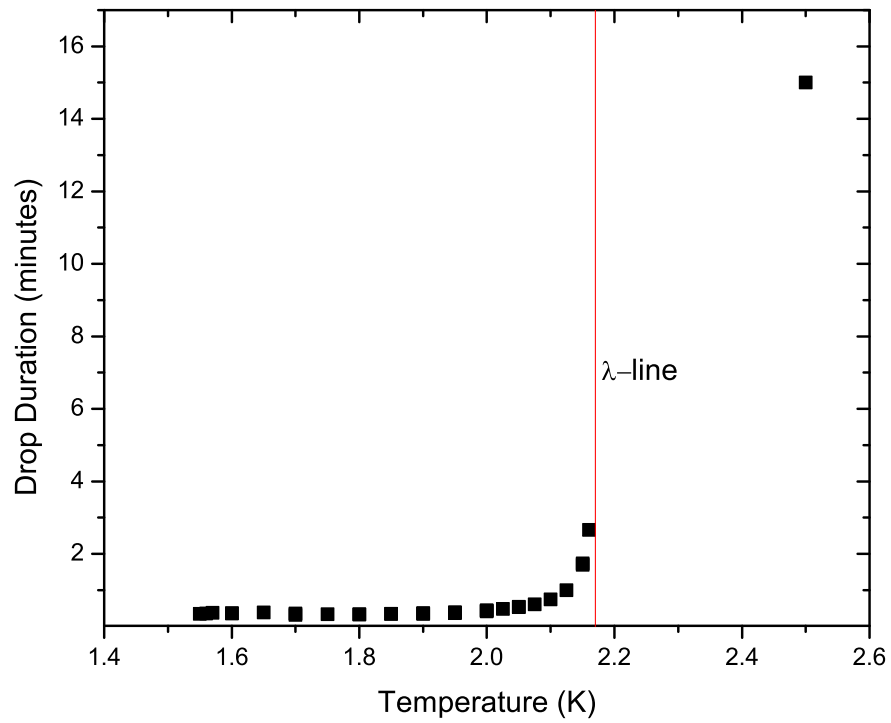


Figure 3.17: Maximum drop duration as a function of temperature. Superfluid drops had short lifetimes until temperatures close to T_λ . The maximum lifetime for normal drops was achieved at 2.5°K.

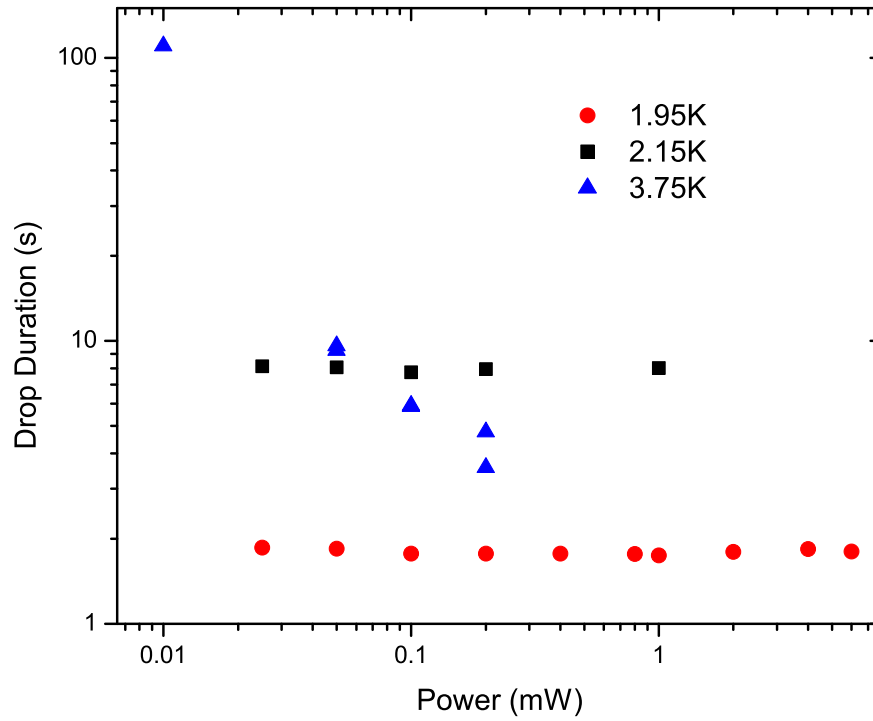


Figure 3.18: Drop duration as a function of heat input for various temperatures. Heat is applied to the sapphire drop substrate via an epoxied ohmic heater. Drop duration for superfluid drops was independent of heat input, while that for normal helium strongly dependent.

duration. However, the outward flux quickly cools the drop until the additional pressure due to curvature is offset by the reduced temperature of the drop. A drop in a 2.5 K environment only needs to be cooled by $\approx 30 \mu\text{K}$ to achieve this and reaches the reduced temperature in $\approx 70 \mu\text{s}$. The evaporation rate, then, is only dictated by the rate at which heat can be supplied into the drop.

Fig. 3.19 illustrates a simple model of heat transfer into the drop from the substrate. The sapphire substrate is assumed to have large thermal mass compared to the drop as well as a high thermal conductivity such that the surface in contact with the drop stays at a constant temperature, T_1 . The drop is modeled as mostly cylindrical with curved edges. The bottom surface of the drop is at T_2 , and the top surface of the drop is at T_3 . The pressure above the drop is the saturated vapor pressure at the same temperature as the substrate, T_1 . The pressure inside the drop is the saturated vapor pressure at $T_1 + T_2/2$ plus an additional due to the edge curvature, $2\gamma/R_c$. Two linear heat transfer equations used to determine the heat into the drop:

$$Q_{solid-liquid} = A \frac{T_1 - T_2}{R_k} \quad (3.3)$$

$$Q_{liquid-liquid} = \kappa A \frac{(T_2 - T_3)}{h} \quad (3.4)$$

Equation 3.3 describes the heat transfer between the sapphire substrate and the drop, where A is the contact area, T_1 and T_2 are the aforementioned surface temperatures, and R_k is the Kapitza resistance. The Kapitza resistance used is $R_k = 17.5T^{3.6} \text{ cm}^2\text{K/W}$ [2]. Equation 3.4 describes the heat transfer through the liquid cylinder without convection, where A is again the area, κ is the thermal conductivity of the helium drop, and h is the height of the drop. We then set the substrate (T_1) equal to 2.5 K and top drop surface



Figure 3.19: Simple heat transfer model for a drop on the sapphire substrate, not to scale.

(T_3) lower by $30 \mu\text{K}$ and solve for Q and T_2 . We find that $T_2 = T_3$, making the drop essentially isothermal. However, the calculated heat flux into the drop, $\approx 10 \text{ nW}$, would cause evaporation times on the order of days. We explore the predicted sensitivity of the experiment to heat and calculate what temperature difference between the substrate and drop would yield the observed evaporation times. We find that a 40 nK change in temperature difference can account for the missing heat flux. This sensitivity also implies that the cell is very isothermal. A substrate temperature difference of $1 \mu\text{K}$ would cause the drop to last only 11 seconds.

Superfluid Duration

Superfluid helium drops, with a typical duration of 1.5 s , would require a heat flux of 1.5 mW , roughly 600 times that calculated for the normal helium drops. The LED could not impart that much heat directly to the drop without changing the temperature of the entire experimental cell. Thus, another mechanism is needed to explain the anomalous drop duration. One possible solution that was explored was quantum evaporation of the superfluid. The phenomena was first reported by Johnston and King in 1966[38], when the velocity distribution of superfluid atoms evaporated from a 0.6°K bath was observed to be closer to that predicted for 1.5°K . Hyman, Scully, and Widom explained the process, later to be called quantum evaporation, where phonons and/or rotons traveling ballistically in the fluid impinge upon the fluid surface. The energy of the phonons or roton can be transferred to an atom on the surface, and if sufficient to overcome the latent heat of vaporization, send it into the vapor[37]. A source of phonon/roton production would be needed for quantum

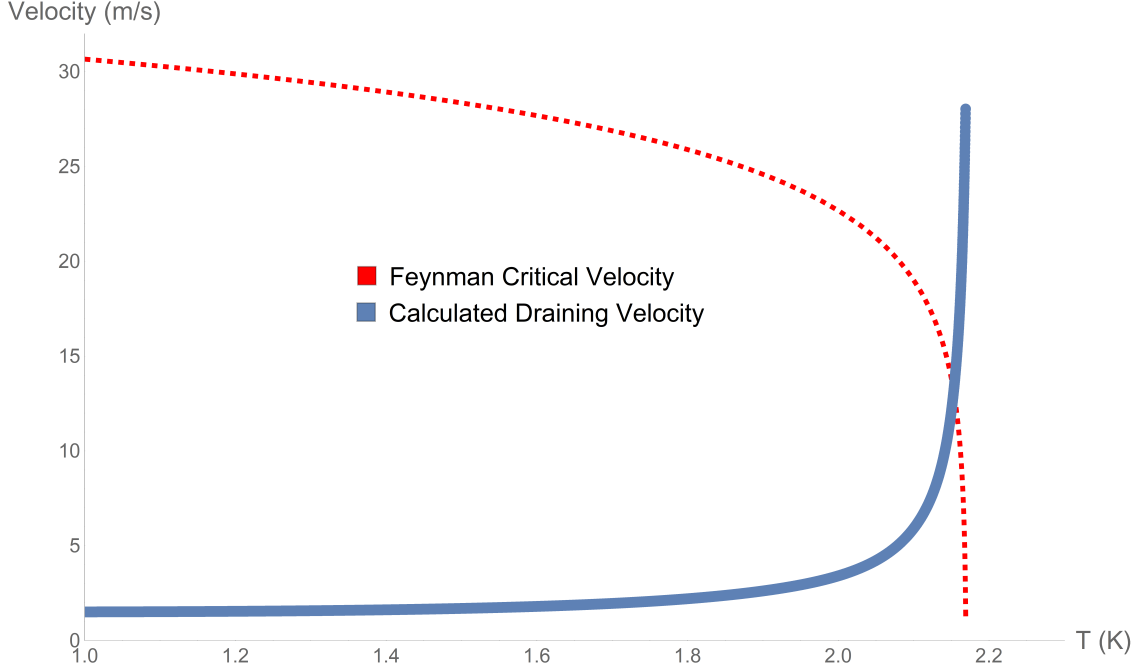


Figure 3.20: Feynman critical velocity (dashed, red) and required superflow velocity (solid, orange) as a function of temperature for a film thickness of 12 nm. Close to T_λ , superflow velocity may be limited, extending the duration of the drop.

evaporation to explain the short superfluid drop lifetime, and the rate of evaporation would be limited by the production. The data from Figure 3.18, showing the lifetime of drops as a function of heat input shows that the superfluid drop lifetime was mostly independent of heat input. Phonon production should be proportional to the heat input, implying that the drop lifetime should be strongly correlated with the heat input as well. As this is not the case, another explanation must be found.

Flow of the superfluid through the film on the substrate is a another possible explanation. To explore this, we compare the superfluid velocity required at the edge of the drop,

$$v_{req} = \frac{Volume}{2\pi r h t_{duration}(\rho_s/\rho)} \quad (3.5)$$

where r is the drop radius, h is the film thickness, and ρ_s/ρ is the superfluid fraction, to the Feynman critical velocity,

$$v_F = \frac{\hbar}{2mR} \ln\left(\frac{2R}{a_0}\right) \quad (3.6)$$

where m is the atomic mass of helium, R is a characteristic flow scale, and a_0 is the vortex core radius, in nm, that goes as

$$a_0 \approx \frac{0.32}{(T_\lambda - T)^{1/2}}. \quad (3.7)$$

In Equation 3.6, the characteristic flow scale would be determined by the height of the film, h and the current temperature. We can then plot both Equation 3.6 and Equation 3.5 as a function of temperature given the typical superfluid film thickness to see if superflow could be responsible for the reduced duration of the superfluid drops. Fig. 3.20 shows the required superfluid velocity and Feynman critical velocities as a function of temperature for a film thickness of 12 nm. For temperatures near T_λ , we can see that it is possible for the superflow to be limited by v_F , thus extending the duration of the drop. This is supported by the data in Fig. 3.17.

Further evidence for superfluid outflow is the oscillatory appearance of "exodrops" that appear outside of the main drop footprint and an associated suppression of drop recession during the exodrop appearances. Figure 3.21 shows several instances of exodrop appearance over the lifetime of a superfluid drop at 1.4°K. The exodrops manifest, and either disappear or are absorbed back into the main drop if they are close enough. The exodrops appear in all superfluid drops, and at anytime during the drop lifetime. A qualitatively similar effect is shown in 3.22 when heat was applied to the substrate that began in superfluid tempera-

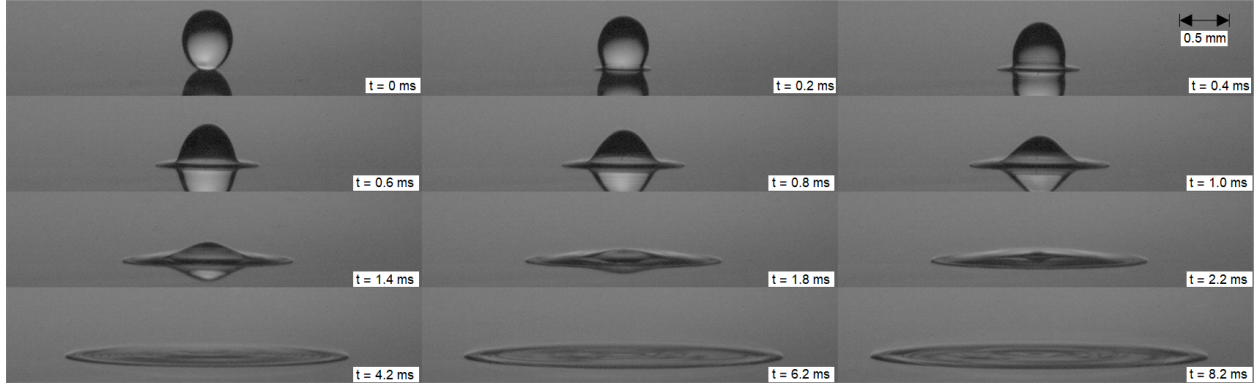


Figure 3.21: Instances of the appearance of exodrops over the lifetime of a superfluid drop at 1.4°K . The exodrops appear outside of the main drop, and either disappear or in some cases coalesce with the main drop. The exodrops appear throughout the entire lifetime of the drop. When exodrops manifest, the contact line seems to be pinned and recession halts until they have disappeared.

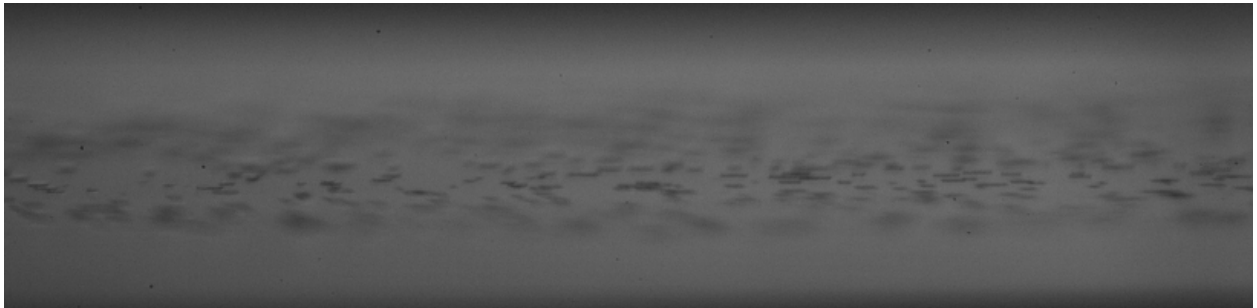


Figure 3.22: Similar in appearance to the exodrops, superfluid droplets spontaneously appear on the surface of the substrate when heat is applied. Approximately 1W of power was dissipated into an ohmic heater attached to the bottom of the sapphire substrate. The droplet duration is similar to that of the exodrops, being roughly 0.25 s .

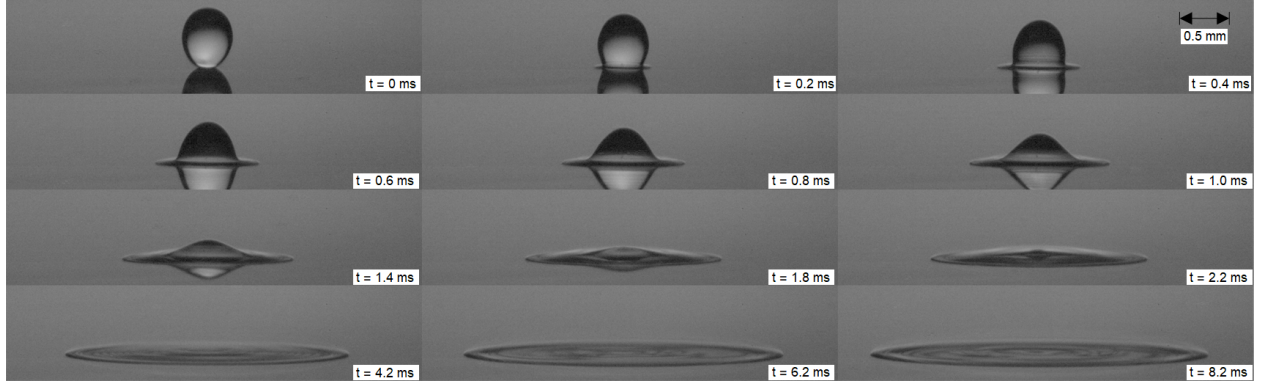


Figure 3.23: The short-term evolution of the drop impact for the first 10 ms. The inertia-capillary dominated regime is represented by the frames between 0.4 ms and 4.2 ms, where the "neck" has fully expanded but the inertia of the falling drop has not yet been dissipated.

tures, where small droplets spontaneously appeared all over the surface. We conjecture that the superflow through the film may become periodically unstable, allowing surface tension effects to form drops of the fluid that is no longer moving at high velocity and also temporarily stopping outflow.

3.4.3 Spreading

Short-term Spreading

In long term Tanner spreading, the behavior emerges from balancing surface tension and viscous dissipation at the contact line. The dynamics of the early stages of spreading, occur much faster[7, 8, 16, 23]. On contact, the drop immediately gains access to the liquid-surface interfacial energy. In both the completely wetting case[17, 31, 33, 70], and even partial wetting cases[68], it has been shown that there exists a regime in which the wet area grows as $r \propto t^{1/2}$. This occurs when there is a balance between the capillary pressure, $\propto \gamma R/r^2$, and the inertial pressure within the drop, $\propto \rho(dr/dt)^2$, where ρ is the density, γ is the surface tension, and R is the initial radius of the drop.

In Fig. 3.24, three regimes can be seen: the initial regime with no obvious power law, the inertia-capillary balance regime with $r \propto t^{1/2}$, and the beginnings of the crossover into

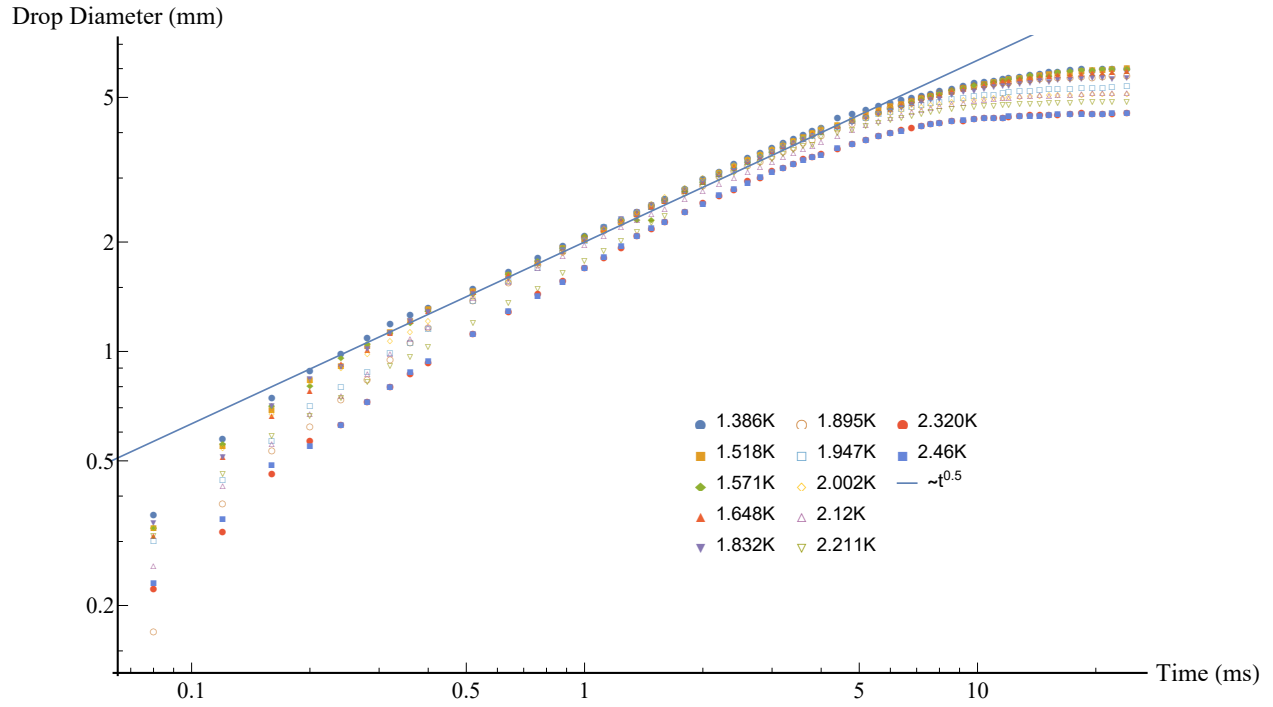


Figure 3.24: Diameter of wet surface of the drop impact for times between 10^{-4} s and 10^{-2} s. Also shown is a theoretical $D \propto t^{1/2}$ line to demonstrate the fit. The spreading exponent for the inertia-capillary balance dominated regime was found to be 0.52 ± 0.03 , in agreement with the law for intertially dominated coalescence.

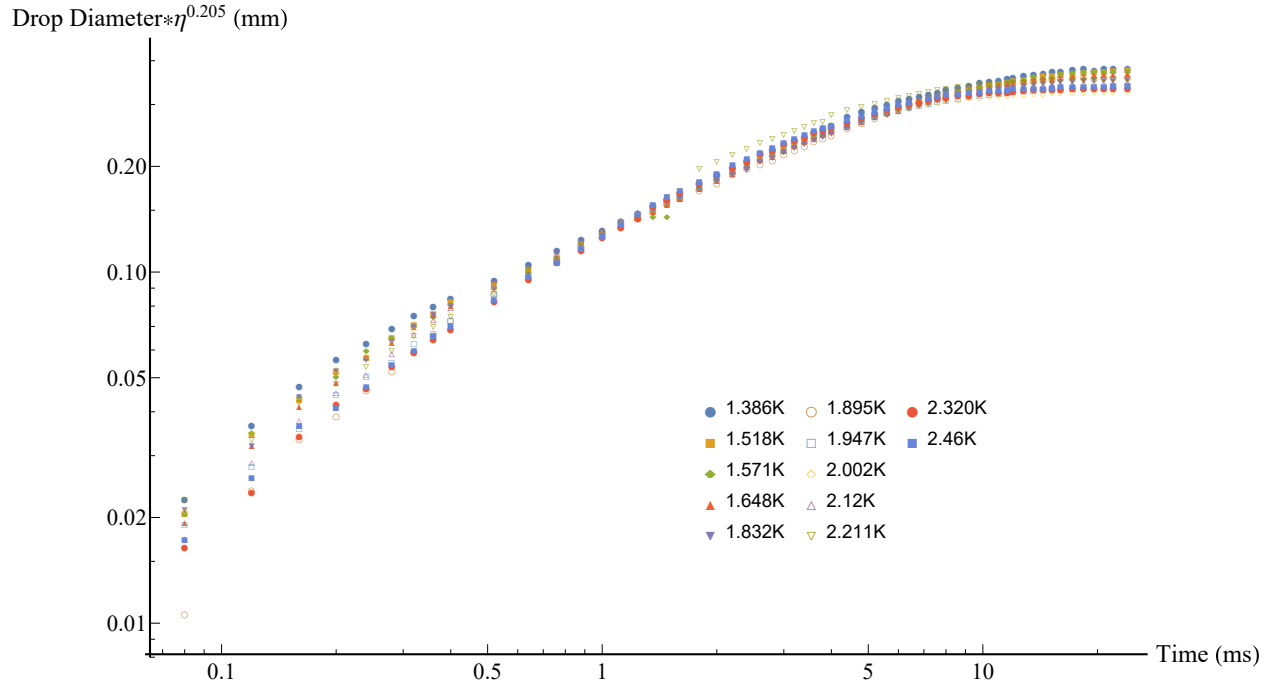


Figure 3.25: Diameter of wet surface normalized by a factor of the viscosity $\eta^{0.205}$ of the drop impact for times between 10^{-4} s and 10^{-2} s. The data, especially in the inertia-capillary balance dominated regime, collapses onto a single line. The $1/\eta^{0.205}$ dependence is much lower than $1/\eta$ as predicted by Carlson[15] and Eddi[32].

Tanner spreading. The inertia-capillary regime begins at $t \approx 0.5ms$ and continues until $t \approx 5ms$. It is of note that the spreading exponent is expected to be independent of the liquid viscosity. Eddi et al. have predicted that the speed of spreading have some viscosity dependence in some capacity weaker than $1/\eta$ [32]. As the data in Fig. 3.24 shows, the normal helium drops show slower spreading velocity than the superfluid drops, while maintaining similar power laws. The data was then scaled by an η^x factor, and the optimal value of the exponent was found to be 0.205. It can be seen in Fig 3.25 that the data, especially in the central inertia-capillary dominated regime, collapses onto a single line.

Long-term Spreading

In the normal state when the thickness of the spreading drop is small compared to its lateral extent, the spreading dynamics can be described by the lubrication approximation, which can be written in terms of the drop height $h(r, t)$ as a function of the radial coordinate and time:

$$\frac{\partial h}{\partial t} = \frac{1}{3\eta}(\nabla \cdot (h^3 \nabla (\rho g h - \gamma_{lv} \nabla^2 h))) \quad (3.8)$$

The first term in the inner parentheses describes the effects of gravity and the second term describes the effects of surface tension and curvature, both of which contribute to spreading. In an idealized case in which only one of these terms is important, self-similar solutions can be constructed which yield power law time dependence[18, 28] of both H and R_c , but for the general case of Equation 3.8, there are no self-similar solutions. If the typical height is H and the radial length scale is R_c , the gravitational term is of order $\rho g H$ while the surface tension term is of order $\gamma_{lv} H / R_c^2$. This leads to the somewhat counterintuitive conclusion that gravity becomes the dominant term when the drop footprint becomes large and the thickness is small. Pure gravitational spreading leads to disk shaped drops with sharp

corners, so it is important to retain both terms to get qualitatively correct drop shapes.

The long-term spreading results are shown in Figure 3.26. Three regions are shown: a transition region before Tanner spreading begins, the Tanner spreading region, and a region where spreading is suppressed by the evaporation of the drop. In the central region of concern, the best fit power law to the data was $r \propto t^{0.149} \pm 0.002$. While greater than any of the theoretical predictions, the observed value was closest to $1/7$, and represents the first experimental observation of its kind. Figure 3.27 shows the magnitude of the residuals for fits of experimental data to power laws from $r \propto t^{0.11-0.17}$. The minimum at 0.149 shows the best fit for the data as well as making clear the difference between the experimental data and the $1/8$ exponent. Figure 3.28 shows additional drop data that occurred when the drop substrate was heated. Heat inputs as low as $15 \mu\text{W}$ strongly affected spreading behavior and could easily lead to artificially low reported values of the spreading exponent. The sensitivity suggests the possibility that the true exponent could be even higher than the calculated 0.149 if the experiment could be performed in a completely isothermal environment.

The axially symmetric version of Equation 3.8 was put into non dimensional form using the capillary length κ as the length scale and $\eta/(g\rho\gamma_{lv})$ as the time scale. The non-dimensional equations were solved numerically with an initial condition of a gaussian or tanh shaped drop of width 1 and height 0.5 in reduced units. Using the lubrication approximation to propagate the contact line into a completely dry surface has well known numerical instabilities[29], so the initial condition included a thin film of liquid (of order 0.001 of the initial drop thickness) that covered the entire solid surface. Figure 3.8 shows the numerical solutions for the evolving drop profile. The calculated profiles are qualitatively similar to the experimental profiles, showing flat drops shapes with curvature close to the edges. However, the spreading power law was calculated to be $r \propto t^{0.121-0.123}$, in accordance with predictions for a gravity driven drop.

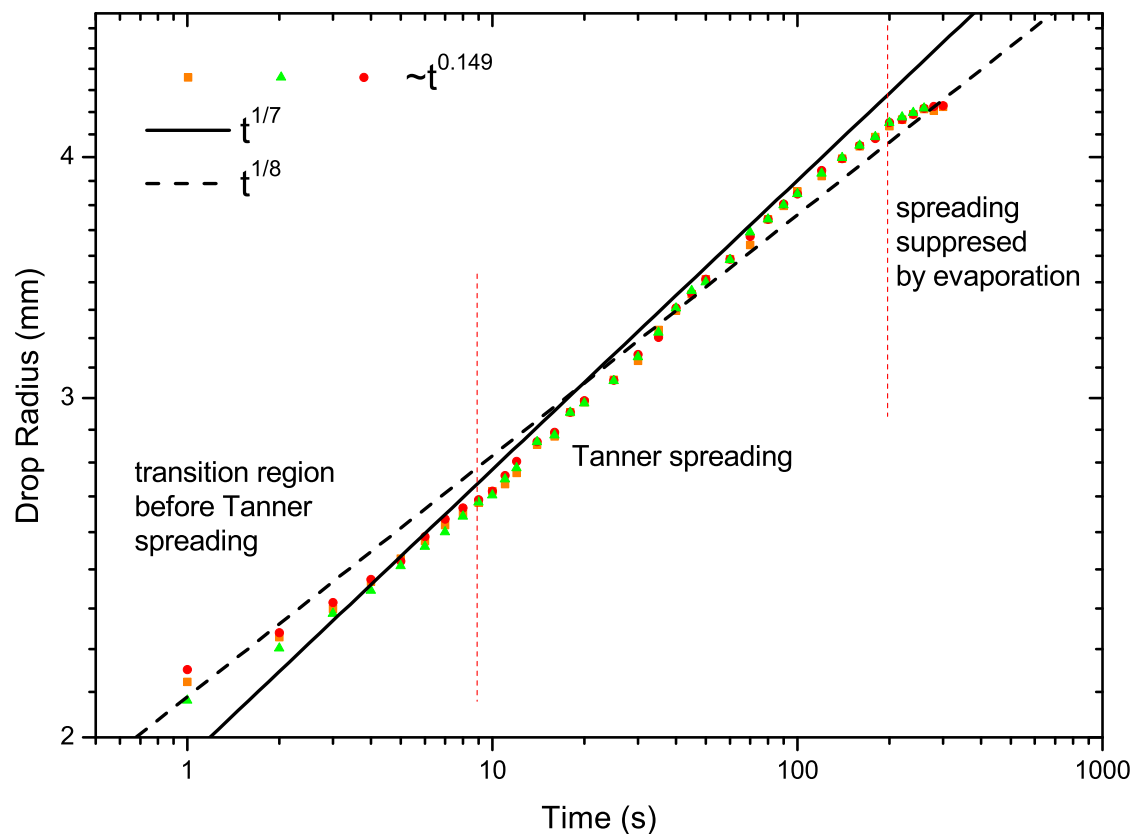


Figure 3.26: Drop radius as a function of time for three drops. The spreading is split temporally into three regions: a transition region before Tanner spreading begins, the Tanner spreading region, and a region where spreading is suppressed by the evaporation of the drop. The average spreading exponent of 0.149 ± 0.002 for the three drops in the Tanner spreading region is greater than $1/7 = 0.143$.

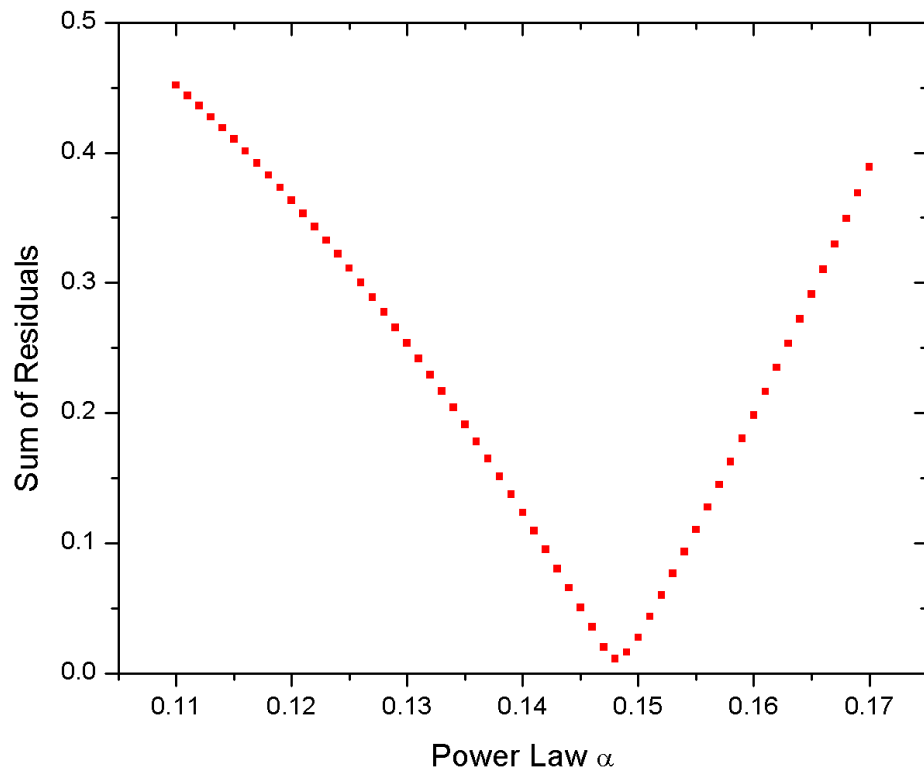


Figure 3.27: The magnitude of the sum of the residuals for fits of experimental data to power laws from $r \propto t^{0.11-0.17}$. The minimum of the residuals occurs at 0.149, and shows the clear deviation from the 1/8 power law.

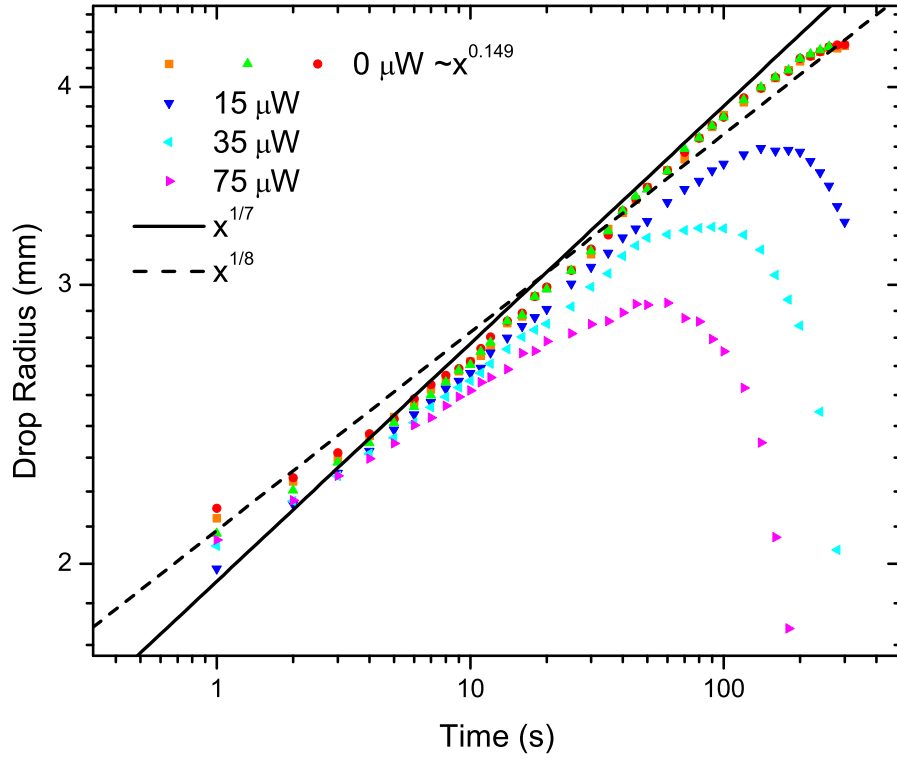


Figure 3.28: Drop radius as a function of time for long drops as well as the data for three other drops taken in similar conditions except that heat was added to the substrate. Power as low as $15 \mu\text{W}$ put into the bottom of the sapphire substrate strongly affects the spreading and could lead to artificially low values of the spreading exponent.

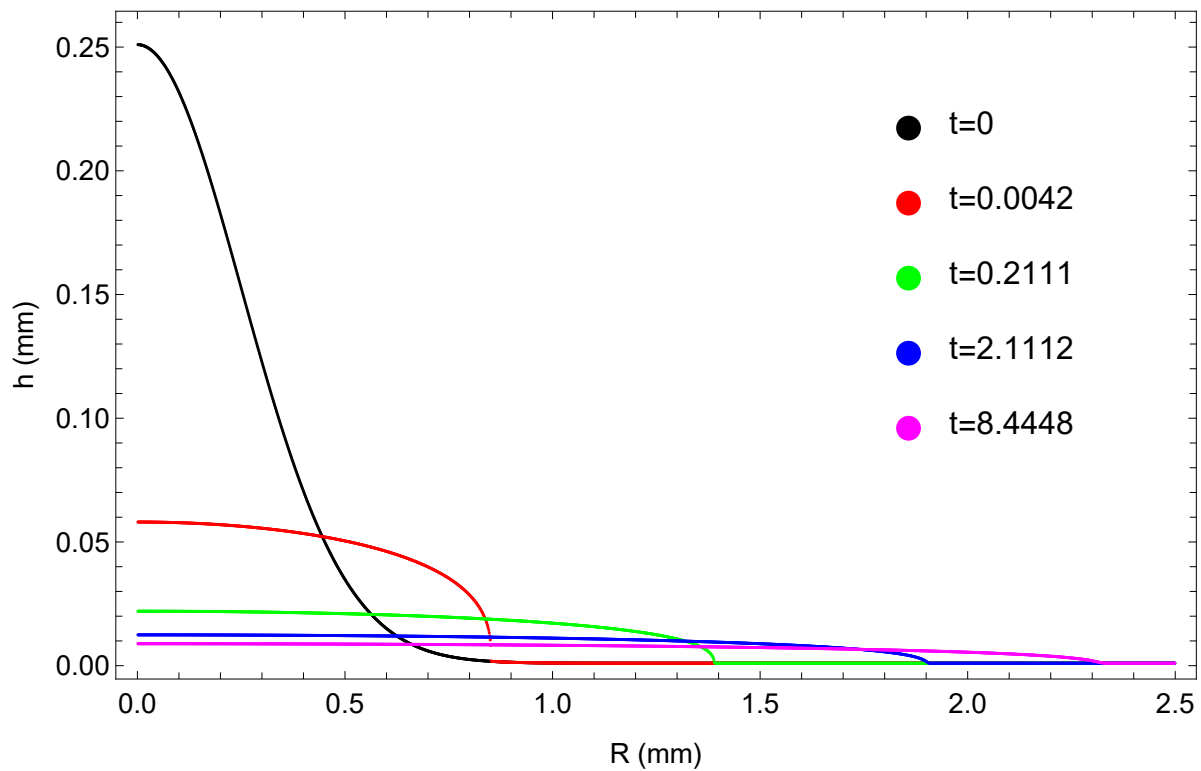


Figure 3.29: Numerical solutions for the evolution of the drop profile, showing drop profiles for various times. The solutions show qualitatively similar flat profiles with curvature concentrated near the edges.

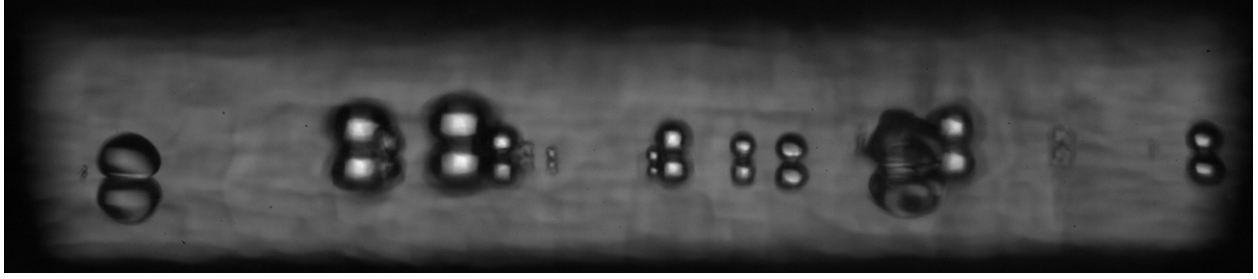


Figure 3.30: Many helium drops levitating on the sapphire substrate as 1 W is dissipated into an attached heater.

3.5 Other Observed Phenomena

Several other phenomena were observed over the course of the helium drop experiments, including apparent Leidenfrost effects at low ΔT and critical opalescence. While these were not extensively and systematically studied, they do provide possible future research projects. The results discussed will be mostly qualitative.

3.5.1 Leidenfrost

The Leidenfrost effect occurs when a liquid drop becomes levitated over a hotter surface by a cushion of its own vapor. Predictive formulas have been developed for the temperature difference, ΔT , between the surface and drop temperatures required for the onset of the effect. Several models have predicted a ΔT for helium of 1-2°K or even greater[62, 43, 5, 63, 35]. Shown in Figure 3.30, it was found that the Leidenfrost effect could be induced in the experimental cell by dissipating heat into the substrate. However, it was also found that even without the heater, some drops did not impact the surface as expected, instead bouncing before settling into a Leidenfrost state. Figure 3.31 shows a 5.1°K helium drop levitating over the sapphire substrate. The drop occurred under isothermal conditions, with temperature differences greater than 1 mK being very unlikely. Leidenfrost under these isothermal conditions was much more likely to occur at higher temperatures (3.5-5.2°K) and

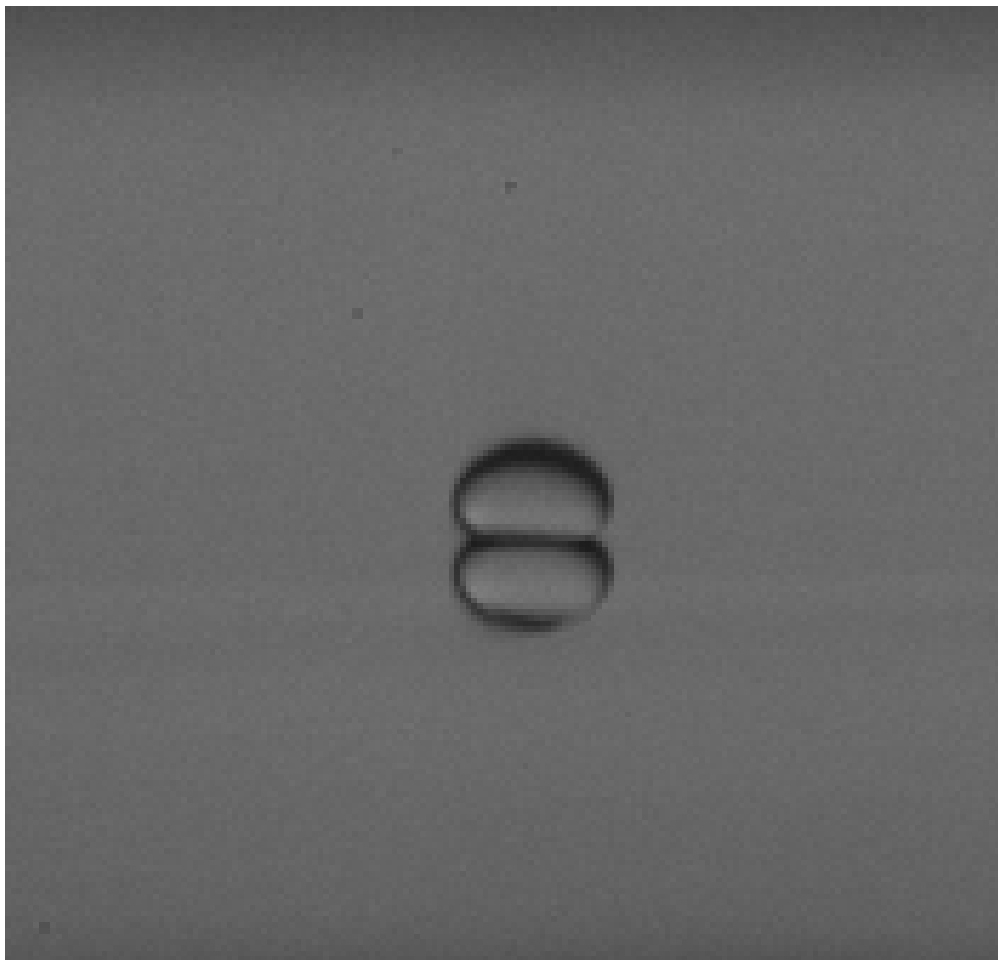


Figure 3.31: A 5.1°K helium drop levitating over the sapphire substrate. The experimental cell was under very isothermal conditions, with ΔT higher than 1 mK being very unlikely.

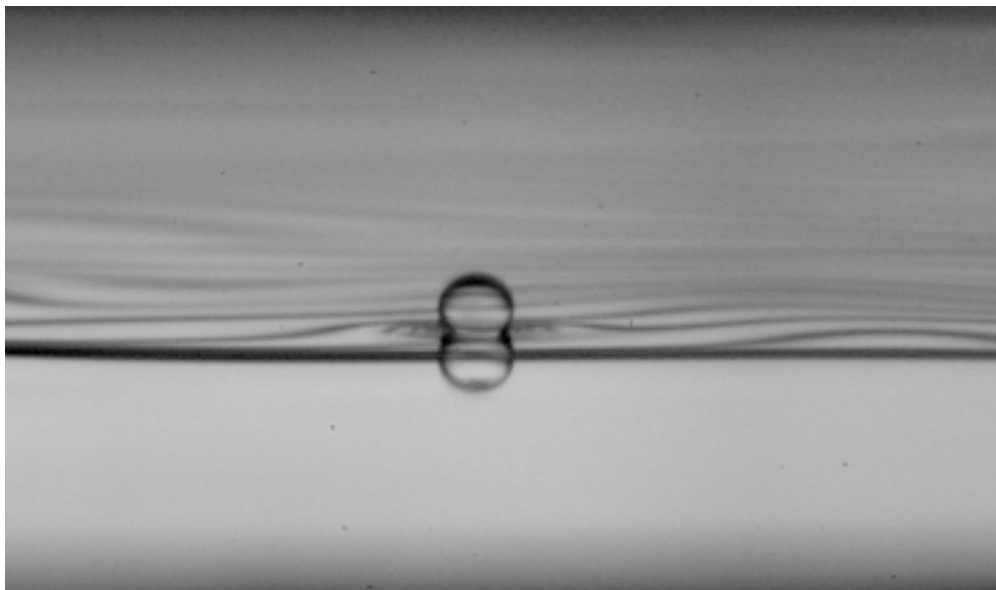


Figure 3.32: A 4.9°K helium drop levitating over a thin film of liquid helium.

even then was sporadic at times. Drops levitating on liquid surfaces was also observed, as can be seen in Figure 3.32. In initially evaluating the levitation over the liquid, the Marangoni effect was considered, where thermo-capillary driven convection currents within the drop or film could drag gas into the gap. However, Marangoni levitation was ruled out, as the spherical drop should be cooler than the surroundings due to its curvature and this would cause the convection currents to travel in the incorrect direction. Due to this, it is believed that the effect is indeed Leidenfrost, though it remains unknown why the effect is occurring under nearly isothermal conditions.

3.5.2 Critical Opalescence

The importance of critical opalescence was first recognized by Thomas Andrews while studying the liquid-gas phase transition of carbon dioxide[4]. It is striking example of peculiar behavior around the critical point. The critical point is the endpoint of a curve on a phase diagram, where the distinction between the two phases disappears. Most commonly, this

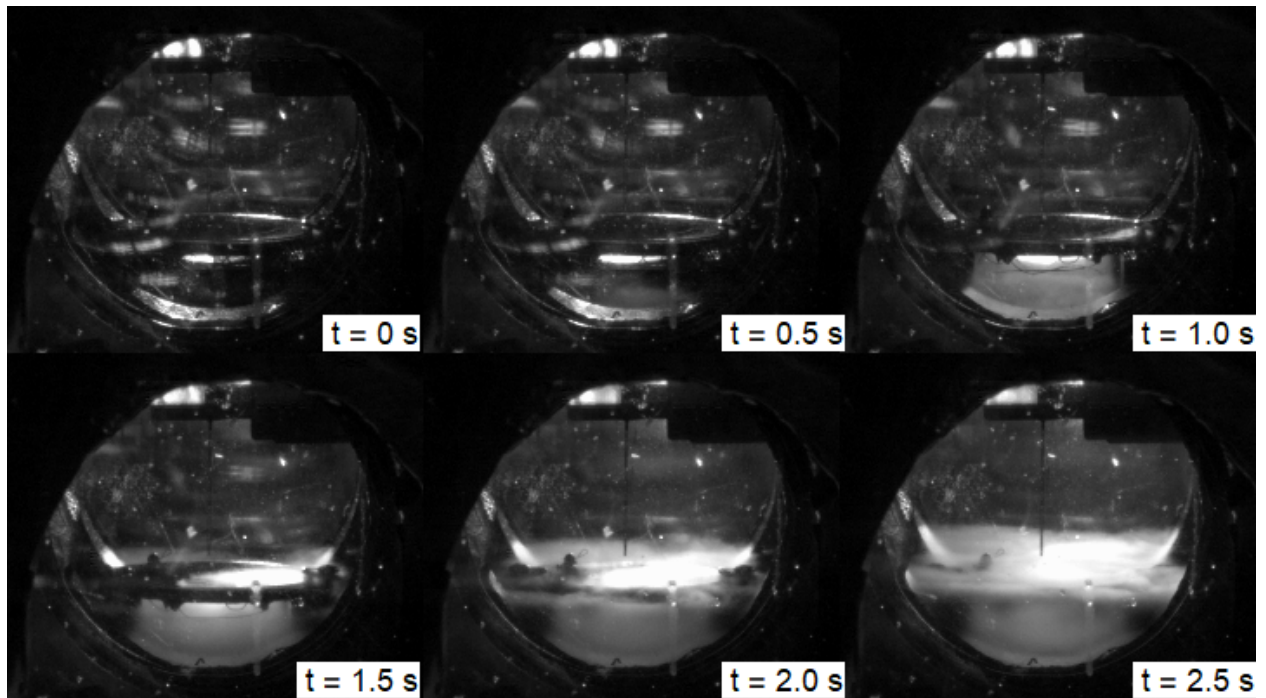


Figure 3.33: Critical opalescence induced by a temperature sweep from 5.25°K to 5.15°K . Opalescence originates at the bottom of the cell and rises to about mid-cell level.

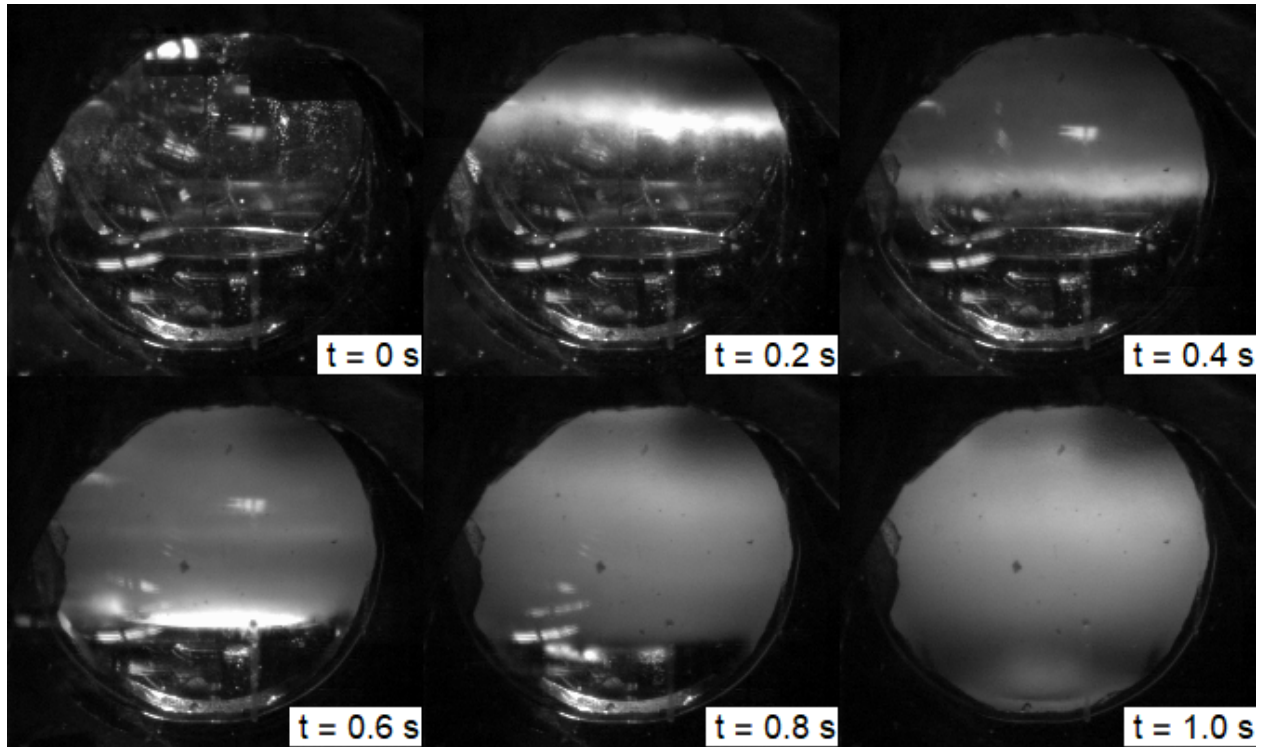


Figure 3.34: Critical opalescence induced by a pressure drop in the cell. Opalescence originates at the top of the cell and proceeds downwards until displayed by the entirety of the cell.

occurs along the gas-vapor curve, and beyond the critical point only "fluid" exists. Near the critical point, density fluctuations occur due to a divergence of the liquid correlation length, and as a result. When the density fluctuations become large enough, the regions begin to scatter light and a previously clear fluid becomes cloudy. This has been quantitatively studied in helium previously[65, 51] using scattered light intensity and pressure-volume correlation experiments.

To my knowledge, however, we have the first recorded video of the phenomenon in helium. Critical opalescence was induced in helium in two different ways. In both cases, the experimental cell was first fully filled at a constant temperature above the critical temperature of 5.25°K . Then, the cell was either cooled or exposed to a sudden drop in pressure via vacuum. In both cases the helium in the cell was brought across the critical point, and in the process displayed opalescence. In Figure 3.33, the evolution of critical opalescence due to a temperature sweep is shown. As the temperature was swept from 5.25°K to 5.15°K , the helium at the bottom of the cell began displaying opalescence, but the effect never proceeded further than mid-cell. The temperature sweep method was limited in speed, which when coupled with a small temperature gradient, may explain why only half the cell displayed the effect. Figure 3.34 shows the evolution of critical opalescence due to a pressure drop. In this case, the opalescence originates from the top of the cell and quickly moves downward to fill the entire cell. When using the pressure drop method, the onset of the full effect took only 1 second, much faster than the temperature sweep method which took 2.5 seconds and was incomplete.

3.6 Conclusion

A cryostat with optical access ports was designed and constructed in order to study the short- and long-term spreading of normal and superfluid helium drops. High-speed video was used to study the drop spreading under saturated vapor conditions. A QCM was used to

confirm the presence of a helium film that was ≈ 12 nm for superfluid and ≈ 40 nm for normal helium. Interference patterns produced from filtered LED light allowed the reconstruction of drop profiles, revealing remarkably flat, pancake-like profiles in both normal and superfluid drops. Normal helium drop lifetimes were long, but had large variations and were highly sensitive to small heat inputs. The driving force for evaporation has been attributed to the gravitational potential difference between the drop impact substrate and the bottom of the experimental cell, which was shown to have very high sensitivity to small inward heat flux. Superfluid drop lifetimes were much shorter, and were found to be insensitive to heat input. Quantum evaporation was not supported as a potential superfluid lifetime-controlling mechanism. Superflow through the substrate film that could drain the drop in the observed lifetimes was found to be a possible mechanism that is not forbidden by theoretical critical velocities. Short-term spreading of both normal and superfluid drops was found to follow the power law of $r \propto t^{1/2}$ suggested by inertia-capillary balance and the spreading coefficient had a weak viscosity dependence of $\eta^{-0.205}$. Long-term spreading of normal helium drops followed a power law of $r \propto t^{0.149}$, higher than those predicted by scaling solutions of lubrication theory that considered only surface tension or gravity. The first experimental measurement of a $r \propto t^{1/7}$ power law was made, in agreement with predictions from molecular theory that attributes spreading to dissipative mechanisms near the contact line. Several other phenomena, including Leidenfrost at anomalously low ΔT and critical opalescence were qualitatively observed but not rigorously studied. To our knowledge, however, the observations are the first of their kind and strong prospects for future study.

Chapter 4

Conclusion

The no-slip boundary condition has been experimentally investigated using water flows in nanopipes. The flow rate of water through 200 nm diameter single nanopipes was measured for both hydrophobic and hydrophilic surface conditions. A coating process was developed to coat the naturally hydrophilic glass capillary with PDMS to make them hydrophobic. Reference diameter data was obtained for the nanopipes through SEM imaging. Water flow in the hydrophilic tubes followed the predictions of the Hagen-Poiseuille equation with a no-slip boundary condition. Water flow in the hydrophobic tubes yielded similar results up to the limit of experimental error. The major source of uncertainty came from the SEM reference diameter data. Future steps involve fabricating smaller diameter nanopipes by using a novel flow-based atomic layer deposition system. Reduction in error from SEM reference diameter data may be achieved by switching to atomic force microscopy techniques. The work presented demonstrates the state of the art in measuring single nanoflows to identify potential slip conditions.

The short and long term spreading of normal and superfluid helium drops was experimentally studied. A cryostat with optical access ports was designed and constructed for the experiments. High-speed video was taken of drop impacts and spreading from the side and bottom. A QCM was used to confirm and quantify the presence of a nanoscale helium

film that was present on the drop substrate for all experiments. Notch-filtered LED light produced interference patterns in the side views that were used to reconstruct the drop profiles. Normal and superfluid drops showed remarkably flat, pancake-like profiles and distinct persisting contact lines. Normal helium drop lifetimes were long, but had large variations and were highly sensitive to small heat inputs. The driving force for evaporation has been attributed to the gravitational potential difference between the drop impact substrate and the bottom of the experimental cell. Superfluid drop lifetimes were much shorter, and were found to be insensitive to heat input. Quantum evaporation was not supported as a potential superfluid lifetime-controlling mechanism. Superflow through the substrate film that could drain the drop in the observed lifetimes was found to be possible except at temperatures very close to the lambda transition. Short-term spreading of both normal and superfluid drops was found to follow the power law suggested by inertia-capillary balance and the spreading coefficient had a weak viscosity dependence. Long-term spreading of normal helium drops followed a higher power law than those predicted by scaling solutions of lubrication theory that considered only surface tension or gravity. The experimental power law was consistent with predictions from molecular theory that attribute spreading to dissipative mechanisms near the contact line. This work represents the first experimental measurement of this power law. Several other phenomena, including Leidenfrost at anomalously low ΔT and critical opalescence were qualitatively observed but not rigorously studied. The work presented is the first to characterize the spreading dynamics of superfluid helium drops, and sets the stage for many future fluid studies of the same.

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