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Experimental Studies of the Growth Kinetics of Methane Clathrate Hydrates & Superfluid Hydrodynamics on the Nanoscale

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Experimental Studies of the Growth Kinetics of Methane Clathrate Hydrates & Superfluid Hydrodynamics on the Nanoscale

DISSERTATION

submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in Physics

by

Jeffrey David Botimer

Dissertation Committee:
Professor Peter Taborek, Chair
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2016
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J. Botimer, D. Dunn-Rankin, P. Taborek - Chemical Engineering Science, 142:89-96

Pressure Driven Flow of Superfluid through a Nanopipe

Quartz Tuning Fork Pressure Gauge for High Pressure Liquid Helium
J. Botimer, A. Velasco, P. Taborek - Under Review

Burning Ice - Direct Combustion of Methane Clathrates
M. Roshandell, J. Santacana-Vall, S. Karnani, J. Botimer, P. Taborek, D. Dunn-Rankin - Combustion Science and Technology (Accepted)

Surface Hall Effect and Nonlocal Transport in SmB$_6$:
Evidence for Surface Conduction
D. J. Kim, S. Thomas, T. Grant, J. Botimer, Z. Fisk, Jing Xia - Scientific Reports 3, 3150

Presentations

Pressure driven flow studies of superfluid helium-4 through single, high aspect ratio nanopipes
APS March Meeting - Baltimore, MD

Nanopipes, Hydrates, Physics, and Saving the World
Walla Walla University Physics Seminar

Experimental Evidence for Empty Cage Methane Clathrate Hydrates Grown Using Surfactants
APS March Meeting - San Antonio, TX

Surfactant Assisted Hydrate Growth
University of California, Irvine Engineering Seminar

The Effect of Surfactant on the Formation and Combustion of Methane Hydrates
APS March Meeting - Denver, CO

Imaging the Growth of Methane Hydrates on Various Substrates
Pacific Rim Workshop on Deep Ocean Power Science - Honolulu, HI
This thesis details the experimental findings of three distinct research projects. The first studies the growth kinetics of methane clathrate hydrates grown under the influence of multiple factors including surfactants, porous media, substrate wetting properties, and salt content. The second investigates the flow behaviors of superfluid helium through single, high aspect ratio nanopipes. The third models the frequency response of a quartz tuning fork in high pressure normal and superfluid helium and demonstrates how quartz tuning forks can be used as cheap, small, in situ, cryogenic pressure gauges.

The first project reports studies of the kinetics of growth of methane hydrates from liquid water containing small amounts of surfactant (<500 ppm of sodium dodecyl sulfate, SDS). The kinetics are monitored using simultaneous measurements of the uptake of methane detected by a pressure drop in the gas phase, and either visual observations of the amount of liquid water and solid phase in the reaction vessel, or in situ micro-Raman measurements or in situ NMR measurements. These diagnostics show that the uptake of methane and the conversion of liquid water to a solid phase do not occur simultaneously; the uptake of gas always lags the visual and spectroscopic signatures of the disappearance of liquid water and the formation of solid. The evidence suggests that the SDS causes water to form an
intermediate immobile solid-like state before combining with the methane to form hydrate. The growth mechanism is related to the surfactant and disappears for low SDS concentrations (< 25 ppm). Also reported are studies of the growth rates of methane hydrates as a function of substrate wetting properties, driving force, and growth media.

The second project studies pressure driven flow of superfluid helium through single high aspect ratio glass nanopipes into a vacuum has been studied for a wide range of pressure drop (0-30 atm), reservoir temperature (0.8-2.5K), pipe lengths (1-30mm), and pipe radii (130-230nm). As a function of pressure we observe two distinct flow regimes above and below a critical pressure $P_c$. For $P < P_c$, the critical velocity is approximately the Feynman critical velocity. As the pressure approaches $P_c$, there is a sudden transition to a new flow state with a critical velocity more than an order of magnitude higher. This effect is explained by a simple model which accounts for the fountain pressure generated by evaporative cooling at the outlet of the nanopipe.

The third and final project detailed here measured the quality factor $Q$ and the frequency $f$ of a 32 kHz quartz tuning fork immersed in liquid $^4\text{He}$ between 0.9 K and 3.0 K, over pressures ranging from the saturated vapor pressure to $\approx 25$ atm. At constant pressure, as a function of temperature, the quality factor and frequency have strong features related to the temperature dependence of the superfluid fraction. At constant temperature, $Q$ depends on the superfluid fraction while the frequency is a smooth function of pressure. The behavior is explained using a simple hydrodynamic model. The liquid helium viscosity is obtained from measured values of $Q$, and together with tabulated values of the helium density as a function of pressure and temperature, the frequency shift can be parametrized as a function of temperature and pressure. The observed sensitivity is $\approx 7.8$ Hz/atm. The quartz tuning fork provides a compact low power method of measuring the pressure in the bulk liquid.
Chapter 1

Introduction

This thesis is a collection of three distinct projects, the growth kinetics of methane clathrate hydrates, superfluid hydrodynamics on the nanoscale, and the behavior of quartz tuning forks in high pressure liquid helium. This chapter serves to briefly introduce these three research topics and provide some of the motivation for each. Each project will be motivated in more detail in their prospective chapters.

Chapters 2 and 3 focus on the growth kinetics of methane clathrate hydrates grown under the influence of multiple factors including surfactants, porous media, substrate wetting properties, and salt content. Clathrate hydrates, often referred to as simply hydrates, are ice-like crystalline compounds consisting of host water molecules forming a cage-like structure around guest molecules. Hydrates have many far reaching applications ranging from water desalination to alternative energy. In some cases researchers want to suppress hydrate growth, such as in natural gas pipelines where they often form and plug the flow of gas. In other cases, the desire is to enhance hydrate growth, such as when using hydrates as a means to turn salt water into fresh water. In all cases, a base understanding of the growth kinetics of hydrates is imperative before we can fully utilize or minimize them.
Chapter 4 introduces superfluid helium and some of the prominent theories that describe its behavior, while chapter 5 details an experimental study on the behavior of superfluid helium flowing through nanopipes. Superfluid helium has been the focus of extensive research for nearly a century[3, 37, 66, 121] and is still not fully understood. It is of great interest for both purely scientific reasons, as a quantum liquid, and for its practical application as both a cooling source[11, 1] and a sensor[94]. The study of superfluid helium flowing through nanopipes has direct application to evaporative helium cryostats[19, 62, 34, 23, 30, 105].

Chapter 6 studies the behavior of a quartz tuning fork oscillating in both normal and superfluid helium under pressures ranging from the saturated vapor pressure (SVP) to \( \approx 25 \) atm and looks at how these forks can be used as cheap, *in situ*, cryogenic pressure gauges. A simple hydrodynamic model is introduced which can be used to easily translate the measured frequency into a pressure. The tuning fork provides an extremely cheap and compact alternative to standard cryogenic capacitive pressure gauges.
Chapter 2

Clathrate Hydrates

This chapter deals primarily with the work published by the author in [13]. Additional details are given here and related studies performed are discussed in chapter 3. This chapter begins by giving a brief review of the clathrate hydrate research field and highlights the information that is most relevant to the work presented below. An excellent overview of the clathrate hydrate field can be found in Sloan[102].

2.1 Introduction to Clathrate Hydrates

Clathrate hydrates, often referred to as gas hydrates or simply hydrates, are non-stoichiometric ice-like crystalline compounds consisting of host water molecules forming a cage-like structure around guest molecules. Hydrates typically form in low temperature and high pressure environments. A large number of hydrate forming guest species exist and there is a wealth of literature devoted to the equilibrium phase diagrams of hydrates with various guest species [103, 102].

Hydrates were first discovered in 1810 by Humphry Davy [32] and were initially nothing
more than a scientific curiosity. In the early early 20th century, with the rise of the natural
gas industry, hydrates became much more than a mere curiosity when they were discovered
inside natural gas and oil pipelines hindering flow. Then, in the 1960’s, it was discovered
that hydrates, particularly methane hydrates, formed naturally and could be found in large
abundance if one knew where to look. These discoveries, hydrates forming in pipelines and
hydrates forming in nature, spawned an immense and diverse research field.

Hydrates of particular current interest include methane, carbon dioxide and hydrogen hy-
drates. Methane hydrates occur in large abundance in the ocean, typically between depths
of 800-1000 meters on the continental margins, and in permafrost, and may be exploitable
as an energy source [115, 111]. In petroleum exploration and transportation operations,
methane hydrates are a serious safety and economic concern. As mentioned previously, they
can form blockages in pipelines, not only restricting the flow of gas but also causing damage
if they become dislodged [24]. Methane hydrates are also being investigated as a means to
store and transport natural gas [103]. Carbon dioxide hydrates have been proposed as an
effective means of gas separation, and as a carbon capture mechanism [107, 27, 24, 98], and
hydrogen hydrates have been investigated as a means of hydrogen storage [54, 110].

For applications involving the storage and transport of gas, the efficiency and speed of
hydrate growth is a primary concern. Consequently, considerable attention has been devoted
to increasing the rate of hydrate formation, and it has been shown that surfactants greatly
increase the rate of formation for various hydrates [130, 127, 83, 68, 77]. In particular, sodium
dodecyl sulfate (SDS) at concentrations greater than 200ppm will increase the growth rate
of methane hydrate by one to two orders of magnitude compared to hydrate growth in pure
water. Although it is now clear that micelle formation is not required for fast growth[127],
there currently does not seem to be a consensus on how or why surfactants accelerate growth.
Other investigators have noted that the morphology of clathrate crystals are more porous
when grown from surfactant solutions[42, 83, 29], and that porous films coat the walls of the
reaction vessel. It is plausible that the porous clathrate adsorbs a film of water, and that the observed high growth rates are a consequence of the large interfacial area of contact between hydrate, water and gas. The project discussed in this chapter was focused on testing this hypothesis.

Our initial experiments utilized a reaction vessel with sapphire windows which allowed visual observation of the hydrate growth process. We corroborated previous reports of a porous fractal dendritic morphology, but a careful analysis of time lapse video together with gas uptake measurements showed that the apparent conversion of liquid to solid occurred distinctly before most of the methane was consumed. This transitional solid-like state presumably was not ice because the temperature \(3\degree C\) was too high, and was not conventional hydrate because the methane concentration was too low. The solid subsequently absorbed much more methane to reach a concentration consistent with a conventional hydrate without qualitative changes in its visual appearance. To explore the possible role of adsorbed or imbibed liquid water, we used two spectroscopic techniques, Raman and NMR, which can distinguish between liquid and solid phases at the microscopic level. The NMR signal of liquid water is quite strong, but it relies on motional narrowing, so immobile water in either an ice or hydrate phase is essentially invisible. The combination of the spectroscopic and visual evidence shows that the presence of SDS in water, under conditions that form methane hydrate, causes the water to form an immobile transitional state which only later combines with methane molecules to form hydrate. This state begins to disappear for low SDS concentration \(\leq 25\text{ppm}\).

### 2.2 Experimental Apparatus and Methods

We designed and built an optical cell capable of withstanding pressures up to 2500psi. The windows were 2 x 0.5 inch sapphire which could be switched out for stainless steel blanks if
desired. The cell was placed in a custom built cryostat with windows. The temperature inside the cell was monitored and controlled to within 0.06°C using a Stanford Research Systems CTC100. The pressure was monitored using an Omega-Dyne PX309 pressure transducer. The sodium dodecyl sulfate-DI water solution was made using SDS from Fischer Scientific with concentrations reported on a per unit mass basis. Methane gas was supplied by Airgas (99.5% pure). The volume of the cell was approximately 1.67 liters. Samples between 10 and 100 cm$^3$ of a solution of the desired concentration at room temperature were placed in a glass container and positioned near one of the windows of the pressure cell, which was also initially at room temperature. The cell was then mounted in the cryostat as shown in Figure 2.1 and the cell was pumped and flushed with methane three times and then pressurized to approximately 600-700psi. The valve to the methane supply was then shut and the cell temperature was reduced to approximately 275K over the course of 1-2 hours. These operating conditions were selected because the thermodynamic driving force was low enough that the cell could reach thermal equilibrium before clathration began, which ensured reproducible results.

As the clathrate hydrate forms, the pressure in the chamber drops by an easily measurable few percent ($\sim 10$ psi) because some of the methane gas is incorporated into the hydrate, which occupies less volume than the liquid water and methane gas separately. The number of moles in the gas phase is given by

$$n = \frac{PV}{zRT}$$

where $P$ is the pressure, $V$ the volume, $R$ the gas constant, $T$ the temperature and $z$ the compressibility factor determined from the Peng-Robinson equation of state. Although the maximum methane uptake in the clathrate at our formation conditions is less than the theoretical ideal stoichiometry of 5.75 water molecules per methane [71, 25], there is substantial variability in the literature regarding the appropriate value to expect [52] and so we use the
Figure 2.1: Schematic diagram of the apparatus, including the pressure cell, the cryostat and the micro-Raman setup. For visual observations, a computer controlled camera was positioned outside the cryostat.
ideal stoichiometry as our reference value, and report results on the degree of clathration relative this value. Because our clathrates were grown with a large excess of methane, all of the liquid water is eventually converted to clathrate. A Nikon D7000 with a Nikkor macro lens outside the cryostat at room temperature was used to take time lapse photographs of the SDS solution and the growth of solid clathrate.

The micro Raman spectrometer comprised a Princeton SpectraPro 2300i spectrometer, 532nm CW laser, and an Olympus long working distance 50x microscope objective lens, which was mounted inside the cryostat. In addition, a dichroic beamsplitter from Thorlabs, pin hole aperture, Semrock 532nm long-pass edge filter, and a Thorlabs 700nm shortpass filter were used as shown in Figure 2.1.

For the Raman measurements a solution of SDS in DI water was placed in a glass cuvette which in turn was placed in the optical pressure cell. The cell was evacuated and flushed three times and then pressurized while still at room temperature. The micro Raman spectrometer was then focused a few mm below the water line and data was continuously taken throughout the remainder of the experiment. The cell was then allowed to cool to 275K.

Care was taken to minimize the Raman contribution from gaseous or dissolved methane. If the optical path through the high pressure methane gas in the cell was approximately 1 cm, a clear signal at peaked at 2917.3 cm\(^{-1}\) was observed. By placing the cuvette within 100 microns of the sapphire window of the pressure cell, the gas phase Raman signal was reduced to less than 1% of the hydrate signal. To assess the Raman contribution from dissolved methane gas, the Raman spectrum of our SDS-DI water solution in contact with high pressure methane was taken slightly above the clathration temperature; no signal attributable to any trace amounts of expected dissolved methane\[^{104}\] at 2911 cm\(^{-1}\) was observed, presumably because the cuvette was not stirred, so equilibrium was not reached within the few hours of our measurements.
NMR measurements were used to monitor the \textit{in situ} growth and dissociation of hydrate. The high pressure NMR was performed using a Bruker Avance 500MHz spectrometer and a Daedalus Innovations high pressure ceramic NMR tube (3.77mm ID, 4.6 mm OD, 92.2 mm long) rated to 5800psi. For the growth experiments, the high pressure NMR tube was charged with SDS-DI water solution at room temperature and placed in the Bruker Avance spectrometer. The tube was then pressurized with methane and allowed to cool to the desired temperature. The pressure, temperature, and NMR signal were simultaneously monitored as the hydrate formed. The temperature of the NMR tube was controlled and monitored using a stream of nitrogen gas that flowed through the magnet bore and around the tube and the pressure was monitored by an Omega-Dyne PX309 pressure transducer. The tube was initially charged with an amount of solution that was the result of a compromise between the desire to maximize the signal and the requirement that the hydrate solid that was formed remained within the 30 mm length of maximum sensitivity of the NMR pickup coil. We performed a series of tests using varying quantities of solution to establish the relation between the volume of solution and the length of the solid hydrate plug that was eventually formed. All of the reported measurements were made with an initial charge of 150 $\mu$L of solution, which filled the tube to a height of approximately 12 mm and resulted in a hydrate plug approximately 25 mm long. To monitor dissociation, the hydrate sample was formed in the NMR tube using an external cryostat and gas handling system for reasons described below. The tube was then cooled to dry ice temperature and transferred to the Bruker Avance 500 MHz spectrometer. The pre-formed hydrate sample was then heated to a desired temperature and allowed to dissociate inside the spectrometer. The pressure, temperature, and NMR signal were simultaneously monitored.
2.3 Results and discussion

2.3.1 Visual observation vs. gas absorption

![Start of Clathration](image1.png)

![1.1%](image2.png)

![3.6%](image3.png)

![6.9%](image4.png)

Figure 2.2: A sequence of images of a beaker of 500ppm SDS in water at a temperature of 275K and a methane pressure of 650psi. White translucent methane clathrate hydrate first forms at the liquid-vapor interface and then grows up the walls of the beaker while the liquid interface drops. The percentages under each image are the fraction of water converted to hydrate calculated from gas absorption assuming ideal stochiometry.

Figure 2.2 shows photographic images of a typical hydrate formation using high SDS concentration (500ppm). The pictures are of a glass beaker partially full of SDS-DI water solution inside the pressure cell. The liquid-gas interface can be seen in Figure 2.2a, just at the start of clathration. Subsequent pictures are taken at 6min (2.2b), 10min (2.2c), and 14min (2.2d) after clathration starts. It is apparent that the liquid-gas interface drops within a few minutes. In addition to pictures being taken from the side of the beaker as shown in Figure...
pictures were also taken looking down on the beaker from above, and they also confirm that the liquid water reservoir is rapidly depleted. It is interesting to note, however, that when the liquid-gas interface hits the base of the beaker and the water reservoir is exhausted, the pressure measurements show that only a small fraction of the water has combined with methane to form hydrate. The pressure data suggests that although the white mass growing up the walls of the beaker is nominally solid, it initially has less than 10% of the methane content of a conventional hydrate.

A careful quantitative analysis of a sequence of images like those shown in Figure 2.2 yields information on the amount of water consumed as a function of time measured by both visual observations of the meniscus position and from measurements of the gas uptake. For the data shown in Figure 2.3a, a 500ppm solution, the liquid level drops to zero in a few minutes, but the methane absorption requires several hours showing a clear disparity between the two measured growth rates. Figure 2.3b shows the same type of measurements but for a hydrate grown with a low SDS concentration (25ppm). Note the data shown in Figure 2.3 begins with the onset of clathrate formation as determined visually. Previous measurements[83] as well as our own have shown that the kinetics of growth change drastically for concentrations below ~200ppm. This change is evident in two distinct ways in Figure 2.3.

First, the disparity in growth rates is much less pronounced in the low concentration case. The growth observed visually appears to track more closely with the absorption of methane. These results were verified in repeated trials, each time with a fresh solution of SDS in DI water.

Second, in Figure 2.3a substantial growth can be seen almost immediately after the onset of clathration (corresponding to \( t = 0 \)). For the low surfactant case shown in Figure 2.3b, however, a hydrate film quickly forms across the liquid-gas interface, which is followed by a period of very slow growth. The growth rate speeds up dramatically near \( t = 3.5h \). The exact mechanism responsible for the dramatic increase in growth at 3.5 hours is unknown, although
a likely explanation is that as the hydrate grows the water level below the hydrate film drops causing the film to sag and crack under it’s own weight, thus opening up channels that fuel the faster growth. The formation of a thin hydrate film across the liquid-gas interface, preventing further growth is seen in pure water-hydrate systems. The role surfactants play in preventing this growth inhibiting film has been experimentally explored[42, 77] but is not well understood.

It is clear from observations such as those shown in Figure 2.2d that the bulk water reservoir disappears long before most of the water has been converted into a conventional clathrate. One possible explanation is that a diffuse low density solid clathrate framework initially forms which imbibes and supports the liquid water which gradually is converted into solid clathrate. If this hypothesis is valid, we would expect microscopic probes of the liquid water content to decrease at the same time and at the same rate as the methane is removed from the gas phase. In fact, the Raman and NMR spectroscopy described below does not support this hypothesis.

### 2.3.2 In Situ Micro-Raman

Raman spectroscopy provides a way to study some of the structural changes occurring during clathrate growth. The changes in the Raman signal from the O-H vibrational modes were used to monitor the conversion of water (Figure 2.4a) to hydrate (Figure 2.4b). The Raman signal from the C-H bonds provides an alternative way to measure the local methane concentration in the solid as the methane becomes encapsulated in hydrate cages. High resolution scans can distinguish between methane in structure I hydrate, in structure II hydrate, and in gaseous form [26]. The Raman signature from each sample we measured indicated a structure I hydrate, which has a prominent peak at $\sim 2905\, cm^{-1}$ and a smaller peak at $\sim 2915\, cm^{-1}$ [92, 93, 104], as shown in Figure 2.5. As discussed above, we took precautions
Figure 2.3: Amount of liquid water converted to hydrate as a function of time. Water consumption measured by direct visual observation of the meniscus position is shown in blue open symbols. Water consumption deduced from the methane uptake pressure measurements are shown in solid black symbols. (a) shows the results for 500 ppm SDS, for which the liquid water appears to be consumed within a few minutes, but the absorption of methane requires about 2 hours. (b) shows the results for 25 ppm SDS where the water consumption measured by the two methods happens at approximately the same rate. In both cases, the initial pressure was 650psi and the temperature was 275K.
to minimize the contributions of gaseous methane to the signal and we verified that in our experimental setup, very little methane gas dissolved in the water during the course of our experiments. Thus Figure 2.5 only has the characteristic sI methane hydrate peaks.

Figure 2.6 shows the evolution of the Raman signal in time during the growth of a 500ppm SDS concentration sample. Spectra corresponding to the start of clathrate formation, 20%, 50%, and 75% formation, as measured by methane absorption, are shown. At the start of clathration, as determined visually when clathrate first appears, the Raman microscope sees only liquid water because it is focused below the surface of the water. As the hydrate grows, the O-H signal morphs from a characteristic water shape to one consistent with a distinctly structure I hydrate \[92, 104\], and the C-H peak grows. Note the small bump \(\sim 2917\text{cm}^{-1}\) at the start of clathration. This is the Raman contribution from the gaseous methane. It is quickly dwarfed by the Raman contribution of the methane in hydrate form. Using a finer spectroscopic grating to better resolve the methane peak yields Figure 2.5. As with the pictures shown in Figure 2.2, the liquid water reservoir is depleted by the time \(\sim 10\%\) of the gas has been absorbed, but the Raman spectra shows that the white solid structure seen in the pictures (Fig 2.2d) is clearly not purely structure I hydrate.

Since the methane peak in Figure 2.6 is due almost entirely to the methane in hydrate cages, the intensity of the methane peak is proportional to the number of methane molecules in the local part of the hydrate measured by the Raman spectrometer. Because of the turbidity of the hydrate, the volume of the sample contributing to the Raman signal is difficult to determine quantitatively, but we estimate that it is a few cubic microns. Despite the relatively small sample volume, the local methane concentration measured by the methane peak Raman intensity and the overall methane concentration, as measured by the pressure drop, were very similar, as shown in Figure 2.7. The data has been scaled by a single constant in order to normalize the two curves to fractional outcomes. The agreement between these two
Figure 2.4: Raman intensity as a function of wavenumber. a) Raman signal for pure water (black) and a typical Gaussian basis set used to represent it (dashed red). b) Raman signal for a fully formed methane hydrate and a typical Gaussian basis set used to represent it (red). The difference between the raw data and the fit using a weighted sum of Gaussians is indistinguishable on this plot.
Figure 2.5: High resolution Raman spectrum of fully grown clathrate hydrate, showing features characteristic of a structure I hydrate.

Figure 2.6: *in situ* micro-Raman spectra of 500ppm surfactant solution transforming to hydrate. The colors of the spectra listed in the legend correspond to the fraction of gas absorbed as measured by the pressure drop in the cell. The peak near 2900 cm\(^{-1}\) is due to methane in clathrate cages, while the broad structure between 3000 and 3700 cm\(^{-1}\) is due to O-H vibrations of water in either liquid or hydrate form.
Figure 2.7: Fraction of methane absorbed in a 500ppm SDS sample as a function of time deduced from the area under the methane peak in the Raman spectra (blue) and from the gas pressure (red).

measures of methane concentration was insensitive to the precise position of the focus of the beam, indicating that the sample was reasonably homogeneous on the scale of the Raman sampling volume.

Just as the methane peak gradually increases as the clathration proceeds, the liquid water phase is transformed into solid clathrate, and this process should be discernable in the Raman signal. A simple method for quantifying the concentrations of mixed phases from Raman spectra is to represent the mixed phase spectra as a linear combination of the spectra corresponding to the constituent pure phases. Decomposition of spectra using a Gaussian basis set, as shown in Figure 2.4, is a well established procedure for both water [40, 70, 112] and methane hydrates [101, 110]. To test whether liquid water was converted to hydrate at the same rate at which methane was incorporated, we attempted to represent our observed Raman signals in terms of a signal from liquid water molecules, hydrate $H_2O$ molecules, and $CH_4$ molecules alone:
\[ \Psi_{\text{sample}} = \alpha \psi_w + \beta \psi_h + \gamma \psi_m \]

where \( \Psi_{\text{sample}} \), \( \psi_w \), and \( \psi_h \), and \( \psi_m \), are the spectral signatures of the growing sample, pure water(2.4a), hydrate(2.4b), and methane, respectively, and \( \alpha \), \( \beta \), and \( \gamma \) are weighting coefficients proportional to the concentrations of the phases in the mixture. If we subtract off the contribution from the methane and include the constraint that water molecules can only be in the liquid or hydrate phase, we obtain an expression for the signal due to the O-H bonds.

\[ \Psi_{O-H} = (1 - \beta) \psi_w + \beta \psi_h \quad (2.1) \]

where \( \beta \) is the fraction of the water molecules in the hydrate phase. The data in Figure 2.7 shows that \( \beta \) can be determined from either the methane peak in the Raman signal or from pressure measurements; in the subsequent analysis, we have used values derived from pressure measurements.

If \( \beta \) accurately measures both the methane absorption and the conversion of water from a liquid phase to a solid hydrate phase, then subtracting \( \Psi_{O-H} \) in Eq. 2.1 from our sample signal \( \Psi_{\text{sample}} \)

\[ \Delta \Psi = \Psi_{\text{sample}} - \Psi_{O-H} \quad (2.2) \]

should be identically zero for all wavenumbers, and also should be independent of \( \beta \). Figure 2.8 shows that this is not the case. The resulting spectrum is flat from the start of clathration
Figure 2.8: Residual O-H Raman signal after subtraction of water and hydrate fit using Gaussian deconvolution fits for a 500ppm sample.

until about 5% clathration (the peak at $\sim 2910\text{cm}^{-1}$ is the methane peak, excluded from the Gaussian fit). For clathration fractions greater than 5% the spectrum begins to deviate significantly from 0. This deviation grows until it reaches a maximum around 40% clathration before decreasing back to 0 by 60% clathration, where it stays through the remainder of the growth process. We verified that this result was independent of the details of the basis set used to parameterize the pure component spectra $\psi_w$ and $\psi_h$ by performing the analysis with varying numbers of Gaussians and using splines to fit for each signal; in each case the deviation remained unchanged.

To further demonstrate that this deviation is associated with the influence of SDS on clathrate formation, we followed the same procedure for a low surfactant sample, such as the one shown in Figure 2.3b. As before, when we saw that the difference between the visual and gas pressure drop was less pronounced at low surfactant concentration, we again see a decreased but still present effect on the fitting residual in Figure 2.9. The Raman analysis
suggests that when SDS is present during the formation of methane hydrates, an intermediate state appears that cannot be classified as either liquid water or hydrate. To further explore the possibility of some kind of intermediate state of water in the hydrate growth process, in-situ NMR tests were carried out, as discussed in the following section.

![Residual O-H Raman signal after subtraction of water and hydrate fit using spline fits at low SDS concentration (25ppm).](image)

Figure 2.9: Residual O-H Raman signal after subtraction of water and hydrate fit using spline fits at low SDS concentration (25ppm).

### 2.3.3 In Situ NMR

We next turned to NMR to investigate the intermediate state of water that is indicated by the above-described discrepancies between gas uptake rates, caged methane Raman signal level, and visual disappearance of liquid water when SDS is present at levels high enough to accelerate clathrate formation. The NMR signal intensity is proportional to the number of hydrogen atoms in a magnetic environment that is typically specified by the relative resonant frequency shift, or chemical shift, with respect to a standard. For liquid water, the NMR signal is very narrow and well defined, while the signal for hydrate, though not as broad as
ice [41], is nearly zero in comparison to liquid water within the narrow bandwidth of a liquid state NMR detector. The integral of the NMR spectrum with respect to chemical shift is therefore proportional to the total amount of liquid water in the sample. In contrast to the micro-Raman probe which is sensitive to only a few cubic microns of the sample, the NMR spectrometer is sensitive to the sample in the entire NMR tube. By integrating the NMR signal we were able to monitor the quantity of liquid in the entire sample as the hydrate either formed or dissociated. As discussed in the “Experimental Apparatus and Methods” section great care was taken to insure that no water or hydrate left the volume seen by the NMR spectrometer.

The growth environment in the high pressure NMR tubes is quite different from that in the large glass beakers or cuvettes discussed previously. The tubes are necessarily small, so only a few drops of surfactant solution could be used. The tubes are opaque, so the only other measurable signature of hydrate growth is the pressure drop due to absorbed gas, which is also small. We therefore ensured that the volume of the gas handling system attached to the tube was also very small. An interesting experimental challenge was that while we could easily grow hydrates in the NMR tube when the tube was mounted in our custom cryostat, when the NMR tube was placed inside the Bruker NMR spectrometer, the hydrate would not grow, even under identical pressure and temperature conditions (650psi and 275K). We tested growth at a variety of pressures (from 600psi to 2000psi) and temperatures (from 265K to 275K) and found that reliable growth inside the Bruker NMR spectrometer was only achieved for temperatures below 267K and pressures in excess of 1000psi. We did not identify a reasonable explanation of this issue. Forming the hydrate below the freezing point of water raises questions about the formation of ice, but this seems unlikely for reasons that will be discussed shortly. Because of the small sample size and the larger thermodynamic driving forces used to initiate growth, the sample was converted to hydrate within a few minutes, instead of the hours required for the Raman and visual observation measurements.
Figure 2.10: NMR spectra of water turning to methane hydrate using a 1000ppm SDS solution at a temperature of 266K and a pressure of 1550psi. Blue is the initial water signal just before start of hydrate formation. (a) shows the full intensity range and a small chemical shift range. (b) shows the same data over a wide range of chemical shift.

(a) NMR spectra over narrow range of chemical shift.

(b) NMR spectra over wide range of chemical shift.
Figure 2.10 shows a sequence of NMR spectra obtained as water turns to hydrate inside the NMR spectrometer. The signal becomes less smooth as the hydrate grows due to spacial inhomogeniety across the NMR sample space during formation. Integration of these spectra, which give the liquid water content as a function of time, is shown in Figure 2.11 together with the fraction of remaining water computed from the pressure measurements. The data show, consistent with all of the other measurements, that there is a distinct lag between the disappearance of liquid water as measured by the NMR and the corresponding uptake of methane. This supports the hypothesis that the intermediate state discussed earlier is an immobile, solid-like state of water. The bump around 350s in Figure 2.11 is likely a result of sample heating due to latent heat evolution during hydrate formation. The heating temporarily slows the formation until the sample starts cooling down again. Given the temperature at which the hydrate formed (T= 266K) we recognize that some of the NMR signal loss may be due to water turning to ice at the same time. However, this seems unlikely to be a significant contribution for a number of reasons. First, the pressure (~1550psi) makes formation of hydrate highly favorable to that of ice at 266K. In addition, the magnitude of the pressure drop was consistent with all of the companion experiments done outside the NMR spectrometer at higher temperatures, indicating that all the water was converted into hydrate. Finally, when the sample was removed no traces of ice were observed.

Because the NMR signal measures the total liquid water content of the entire tube, it was feasible to make measurements during hydrate dissociation. To have samples consistent with our previous Raman and visual results, hydrate samples were grown in the NMR tube in our cryostat at T=275K and then chilled in dry ice, and transferred in the sealed NMR tube to the pre-cooled Bruker spectrometer. The hydrate was then allowed to come to equilibrium at a temperature just below the hydrate stability temperature. Once the temperature was stable, the temperature was raised to slightly above the stability temperature and the hydrate was allowed to dissociate.
Figure 2.11: Measurement of the fraction of water remaining in a sample grown *in situ* in the NMR spectrometer as a function of time. Red points are computed from measurements of the pressure drop. Blue points are obtained from the NMR spectra. Temperature is 266K, pressure is 1550 psi.

Figure 2.12: Quantity of liquid water as a function of time as measured by the change in pressure (red points) and NMR signal (blue points) as the methane hydrate dissociates at a temperature of 282K.
Figure 2.12 shows the result of a typical dissociation NMR measurement. During dissociation, the pressure increase leads the NMR signal corresponding to liquid water. This implies that as methane gas desorbs from the hydrate structure it leaves behind a solid structure that converts into liquid water at a later time. The time scale in Figure 2.12 indicates that this intermediate solid structure persists for several minutes after the methane gas has been released. These results were repeated over multiple trials with different methane hydrate samples.

2.4 Conclusion

Direct measurement of methane uptake together with visual observations, in situ Raman, and in situ NMR techniques during the formation of methane hydrates seem to be inconsistent with a simple growth model in which liquid water is imbibed in a porous structure and is slowly converted directly into a hydrate. The visual observations show that a solid-like structure which can support gravitational shear stresses is formed with remarkably low concentrations of methane. The Raman spectra show that the methane uptake and the conversion of water to clathrate occur at different rates. The NMR measurements show that during hydrate formation, the signal from mobile liquid water decreases before methane is consumed. This experimental evidence suggests the existence of an intermediate, immobile state of water that is stabilized by the presence of surfactant. This intermediate state disappears as the surfactant concentration approaches zero. We hypothesize that stabilization of this immobile intermediate state may be a key property of the surfactant that allows it to enhance hydrate growth.

Our experiments do not provide direct information about the structure of the intermediate state, but one intriguing speculation is that the surfactant allows the water to form empty clathrate cages that are later filled with methane. The possibility that SDS causes empty
clathrate like cages in an SDS-cyclopentane system is suggested in the work done by Lo et al[72]. However, if empty cages are possible the question of how they are later filled remains. Alternatively, the surfactant might be causing the water to form highly ordered, immobile layers that snap into the cage structure when approached by a methane molecule. Hints of this type of structure are visible in experimental observations[73] and in computer simulations of hydrate water interfaces which do not include surfactants [58, 99, 80, 126]. Although empty cage structures are known to be slightly energetically unfavorable at the temperatures of our measurements [58], it would be interesting to extend these simulations to incorporate the effects of surfactants to see if they stabilize cage precursor structures.

In addition, another interesting future research possibility is that of in situ neutron scattering during hydrate formation in the presence of SDS. Similar experiments have been performed by Thompson et al[116] on pure water-methane hydrates. Extending this work to surfactant laden samples could shine light on the structure of this transitional state.
Chapter 3

Tailoring Hydrate Growth

This chapter summarizes a few of the more promising hydrate projects that were never formulated into official publications due to time constraints. They were presented on at various conferences but were ultimately put on hold indefinitely so that time and resources could be focused on other projects. The projects are detailed here for any who may wish to continue this work in the future. Each project includes a brief description of the project, the preliminary findings, and suggested future work.

3.1 Experimental Setup

Each project described in this chapter utilized the same experimental setup described in Chapter 2 with only slight variations. Most notably, none of the following projects utilized a Raman spectrometer. The basic experimental setup can be seen in Figure 3.1. Additional experimental details about each project can be found in their respective sections.
Figure 3.1: Schematic diagram of the apparatus, including the pressure cell, cryostat, and DSLR camera.
3.2  Wetting Effects on Hydrate Growth Kinetics

3.2.1  Introduction

As discussed in Chapter 2, it has been well established that certain surfactants, such as sodium dodecyl sulfate (SDS), greatly enhance hydrate growth\[130, 127, 83, 68, 77\]. Furthermore, it has been observed that hydrates grown using surfactants tend to start at the liquid-gas interface and grow up out of the water, crawling up container walls as seen in Figure 3.2a\[13, 42, 83\]. While hydrates grown from pure water tend to start at the liquid-gas interface and grow down into the water as seen in Figure 3.2b\[82\].

(a) Hydrate growth behavior in the presence of surfactants such as SDS.
(b) Hydrate growth behavior using pure water.

Figure 3.2: Comparison of general hydrate growth behavior in the presence of surfactants vs in pure water.
Furthermore, it is known that when a fluid comes in contact with a solid substrate, such as a water droplet on a metal surface as seen in Figure 3.3, the fluid will spread until it minimizes it’s energy. The minimum energy configuration is determined by the ratio of the potential energy of the interaction between two fluid molecules and a fluid molecule and the substrate [39]. If the fluid molecules interact more strongly with each other than they do with the substrate then the fluid will tend to bead up, forming a large contact angle with the substrate, while if the opposite is true the fluid will spread out forming a low contact angle.

![Figure 3.3: Water droplet on copper substrate forming a wetting angle $\theta$ with the substrate.](image)

A key property of surfactants is they lower the surface tension between two liquids or between a liquid and a solid. When added to water, surfactants can lower the wetting contact angle between the water and a given substrate causing the water to spread out and cover a larger surface area than it normally would have.

It has been theorized that the enhanced hydrate growth rates in the presence of surfactants is due, at least in part, to the surfactants ability to enhance the liquid-gas interface surface area [13]. The project described in this section was designed to test this idea. The project studies the effect the wetting contact angle of a substrate or container has on the growth rates of hydrates.
3.2.2 Experimental Details

This project utilized the experimental setup shown in Figure 3.1, wherein a container of either water or a water-surfactant mixture was placed inside a custom optical pressure cell. The optical cell was pressurized and cooled to the desired experimental conditions. The growth was observed both visually, with a Nikon D70 DSLR camera, and experimentally by monitoring the pressure and temperature during growth. Pressure and temperature readings were used to monitor the water’s conversion to hydrate as described in Chapter 2.

For this project, three substrates were compared simultaneously for each experiment. Figure 3.4 illustrates the substrate arrangement inside the optical pressure cell. The three substrates stood vertically and were partially submerged in the same water or water-surfactant bath. The experiments were done in a Teflon container, to minimize growth up the walls of the container. The Nikon camera, taking images from the side, could visually monitor hydrate growth up each substrate.

All hydrates measured in this project were grown using methane gas.

3.2.3 Results and Discussion

Figure 3.5 illustrates a common growth sequence for three substrates with significantly different wetting angles grown from deionized (DI) water. The substrates, from left to right, are Teflon \((\theta \approx 95^\circ)\), copper \((\theta \approx 60^\circ)\), and glass \((\theta \approx 5^\circ)\). These substrates were chosen because they span a wide range of contact angles.

It can be seen in Figure 3.5 that the glass substrate is covered with hydrate in less than a minute, while the copper is covered much slower and no hydrate grows on either the Teflon substrate or the Teflon container walls.
Figure 3.4: Experimental setup to compare growth on multiple substrates simultaneously. $S_1$, $S_2$, and $S_3$ represent three different substrates. The experiment was done in a Teflon container, to minimize growth up the walls of the container.

From the images taken of hydrate growth, a surface growth rate can be extracted which characterizes how quickly the hydrate grows on, and covers, a given substrate. By comparing this surface growth rate on substrates with varying contact angles we can characterize a relation between the hydrate growth rate and the substrate’s contact angle.

Figure 3.6 shows the rate at which a growing methane hydrate spreads across a substrate surface for various contact angles. It can be seen that the hydrate growth rate on a substrate drops off dramatically as the contact angle increases. No growth was observed for substrates with contact angles higher than $\theta = 90^\circ$ up to $t = 12$ hours when the experiment was ended.

The same behavior can be seen for methane hydrates grown using 500ppm SDS in Figure 3.7, although the growth rates are roughly an order of magnitude higher. The inclusion of SDS lowers the contact angle on each of the substrates. While it appears as though the contact angle of the substrate has a significant effect on the growth rate of the hydrate, it
Figure 3.5: A sequence of images showing hydrate growth on three different substrates. The hydrate was growth from DI water at a temperature of 275K and a methane pressure of 650psi. From left to right the substrates are, Teflon, copper, and glass. It can be seen that hydrate grows very quickly on glass, very slowly on copper, and not at all on Teflon. Time = 0 is taken at the first visual evidence of hydrate growth.
does not appear to be the main reason that surfactants enhance hydrate growth. It can be seen by comparison of Figures 3.6 and 3.7 that even at high contact angles of \( \theta \approx 60^\circ \), the hydrates grown using SDS have growth rates higher than any seen using DI water.

Figure 3.6: The rate that methane hydrates, grown using DI water at 275K and 650psi, spread across a substrate during growth measured for substrates of varying contact angles.

Glass, which has a very low contact angle (\( \theta \approx 5^\circ \)), can be treated with Octadecyltrichlorosilane (OTS) to increase its contact angle between the glass and pure water to more than 90\(^\circ\). The glass substrate used in Figure 3.5 was treated with OTS using the method described by Yang et al.[129] and the experiment was repeated. The effect was dramatic and can be seen in Figure 3.8. Some water condensation can be seen on the OTS treated glass, but hydrate still does not form. The resulting surface growth rate for OTS glass is included in Figures
Figure 3.7: The rate that methane hydrates, grown using 500ppm SDS surfactant at 275K and 650psi, spread across a substrate during growth measured for substrates of varying contact angles.
3.6 and 3.7.

Figure 3.8: A sequence of images showing hydrate growth on three different substrates. The hydrate was growth from DI water at a temperature of 275K and a methane pressure of 650psi. From left to right the substrates are, Teflon, copper, and glass treated with OTS. It can be seen that, unlike with regular glass, hydrate does not appear to grow on glass treated with OTS. Hydrate once again grows very slowly on copper, and not at all on Teflon. Time = 0 is taken at the first visual evidence of hydrate growth. Some water condensation can be seen on the OTS treated glass, but hydrate still does not form.

3.2.4 Conclusion and Suggested Future Work

This project illustrates a clear link between hydrate growth rate on a substrate and the substrate’s wetting contact angle. As the wetting contact angle increases from zero, the growth rate of the hydrate on the substrate decreases dramatically. This behavior appears for methane hydrates grown using both DI water and a 500ppm SDS - water solution.

While it appears as though the contact angle of the substrate has a significant effect on the growth rate of the hydrate, it does not appear to be the main reason that surfactants enhance hydrate growth. It can be seen by comparison of Figures 3.6 and 3.7 that even at high contact angles of $\theta \approx 60^\circ$, the hydrates grown using SDS have growth rates higher than any seen using DI water.
In the future this work could be repeated for other hydrates, such as \( CO_2 \), to see if the same behavior is exhibited in all hydrates. This contact angle - growth rate relation could also be explored for various temperatures and pressures.

An interesting application for this work pertains to the issue of hydrates growing in natural gas and oil pipelines as described in Chapter 2. Hydrates form in the pipelines causing blockages, and they can cause damage if/when they become dislodged. It may be feasible to coat the pipelines with a hydrophobic material to discourage hydrate growth. Taking it a step further, it may be possible to control where the hydrates grow by building in easily accessible, and exchangeable, portions of the pipeline that have cartridges made from a hydrophilic material that would encourage any hydrates that may grow to grow on the cartridges.

Alternatively, in applications that require high hydrate growth rates, such as in carbon capture plants or with gas storage, selecting hydrophilic substrates can greatly enhance hydrate growth rates.

### 3.3 Stable Growth, the Driving Force, and Various Growth Media

The following projects are less developed, but nevertheless, the results are enlightening and the projects hold promise for future work and possible publications.

#### 3.3.1 Stable Growth

One seemingly simple, yet exceedingly important, realization that paved the way for all the hydrate projects described in this document involved the experimental conditions used to
grow hydrates. The results discussed in this section were all grown using SDS.

The phase diagram of methane hydrates is well established\[\text{102}\] and can be seen in Figure 3.9. In all experiments performed, we held the temperature above 273.15K, the freezing point of water, to ensure that no ice formed in our system. However, early on we would set the pressure to $\sim 1000\text{ psi}$, well above the required pressure for hydrate formation, in order to ensure that we saw hydrate growth. We soon discovered that operating so far above the equilibrium line produced chaotic, and unrepeatable growth rates.

Figure 3.9: Phase diagram for methane hydrates, constructed from data given in Sloan[\text{102}]. The red 'x' indicates the old experimental conditions, the blue 'x' indicates experimental conditions that yielded more consistent results.

Figure 3.10 shows the growth of three consecutive hydrate samples grown under identical conditions, 275K and 1000psi with 500ppm SDS. The hydrate growth is characterized as a percent of the total about of clathrate hydrate that could be obtained from the amount of
water used. This number was calculated using the pressure, temperature, and volume of the cell as described in Chapter 2. In addition to monitoring the pressure and temperature, each run was visually observed using a Nikon camera and the experiment was allowed to continue until no additional growth was observed.

Figure 3.11 again shows the growth of three consecutive hydrate samples grown under identical conditions, but this time at 275K and 650psi with 500ppm SDS. In comparing Figures 3.10 and 3.11 two things become apparent. First, the shapes of each clathration curve when grown at 650psi are smoother and there is more consistency between each run. Secondly, when the hydrate is grown at 650psi the growth takes significantly longer.

3.3.2 Driving Force

The second point noted above, that the hydrate growth rate appears tied to the pressure at which the hydrate is grown spurred a study of what is termed ”the driving force” during hydrate growth. A number of papers detail the theory behind the driving force[60, 6], which, put simply, states that the further above the equilibrium line you are, the faster the hydrate will grow. The distance from equilibrium can either be characterized in terms of a $\Delta T = T_{eq} - T_o$, where $T_{eq}$ is the temperature corresponding to the measured experimental pressure and $T_o$ is the experimental temperature, or in terms of a $\Delta P = P_o - P_{eq}$. There has been a some experimental work looking at growth rate as a function of $\Delta T$[6, 61]. We briefly looked at the relation between growth rate and $\Delta P$, and found it to resemble that found in studies of $\Delta T$, which is to be expected.

The equilibrium pressure for methane hydrates at 275K is measured to be $\sim 515$psi[102], but the value of the equilibrium line is often determined by melting the hydrate. It is difficult to solidify a liquid, whether it be water to ice or water to hydrate, when very close to the equilibrium conditions because one must overcome the energy required for nucleation. For
Figure 3.10: Methane hydrate growth, given as the percent of total, ideal growth as a function of time. Red, blue, and green represent three consecutive hydrate samples grown under identical conditions, 275K and 1000psi with 500ppm SDS.
Figure 3.11: Methane hydrate growth, given as the percent of total, ideal growth as a function of time. Red, blue, and green represent three consecutive hydrate samples grown under identical conditions, 275K and 650psi with 500ppm SDS.
this reasons the lowest pressure methane hydrates were grown at, while at 275 K, was 580psi.

Figure 3.12 shows the growth rate of methane hydrate at 275K for pressures ranging from 580psi-760psi. Over this pressure range the growth rate appears to depend linearly with P, although presumably the growth rate approaches 0 as the pressure approaches the equilibrium pressure. Tests were done for various SDS concentrations, ranging from 10ppm to 2000ppm. It was found that above 100ppm SDS, all data fell on the same curve and therefore everything above 100ppm has been lumped together. Below 100ppm growth rates began dropping off very quickly, in agreement with what has been measured before[83, 13].

What is very interesting, is the amount of hydrate that forms at different growth rates. The final clathration percentage, or the final amount of hydrate formed with respect to the ideal amount that could be formed, is often used as a way of quantifying a hydrate growth method’s quality. Achieving final clathration percentages in the 80 – 90% range is often considered very good. Figure 3.13 shows that the final clathration percentage is independent of the growth rate for pressures between 580-760psi.

Finding ways to enhance hydrate growth is valuable for multiple applications, as has already been discussed. It is valuable to know that the growth rate can be increased by an order of magnitude without any loss in final clathration percentage. By and large, the topic of a driving force inhydrate formation has been fairly extensively studied, although most of the work that has been done did not include the use of surfactants. Any future work on this topic would first require a thorough review of the rather substantial literature on the subject. The possibility of future work on this project, given the amount of literature already existing, seems limited. This project is included here more to pass on the practical knowledge as it pertains to determining experimental parameters in other hydrate related studies.
Figure 3.12: Methane hydrate growth rate as a function of pressure at 275K. All data was taken with SDS enhanced growth. Black squares include data for SDS values of 100ppm, 250ppm, and 500ppm. Red triangles are 25ppm SDS, and blue diamonds are for 10ppm SDS.
Figure 3.13: Methane hydrate final clathration percentage as a function of pressure at 275K for the combined SDS values of 100ppm, 250ppm, and 500ppm.
3.3.3 Various Growth Media

We conclude the hydrate portion of this thesis by summarizing a few final observations that are simple but still of some interest, for if they are not recorded here they will likely be lost from memory.

Hydrate grown using surfactants is impressively robust, and when above the equilibrium line shown in Figure 3.9 hydrate growth is difficult to suppress. Using SDS, usually at 500ppm, hydrate growth has been observed in various media including glass beads of various diameters (100\(\mu\)m – 2mm), sand, and bentonite nanoclay. In addition, hydrate growth has also been studied as a function of salt concentration (details can be found in the master’s thesis of UCI graduate Mason Eastman), and observed in coffee.

In all the media tested with a water-SDS solution, growth was observed at roughly the same rate found in the case of no media (Figure 3.12). Although in finer media, such as micron sized beads or the bentonite, the hydrate grown was very cake like. While in the case of hydrate grown from a simple water-SDS pool, the resulting hydrate was very dendritic.

For SDS hydrate grown from sand, a very interesting observation was made. Starting with sand in a beaker, water-SDS solution was added until the sand was fully saturated with liquid and the water level was even with the sand level. As they hydrate formed, it crawled up the walls of the beaker much like what was observed for growth from a pool (Figure 2.2). Only this time the growth served as a way to separate the water from the sand. Figure 3.14 shows the resulting hydrate formed in sand using 500ppm SDS at 275K and 1000psi. The bulk of the hydrate could then easily be separated from the sand. The sand did contain some hydrate, enough to burn for a few seconds, but by far the majority of the hydrate formed separate from the sand.

Hydrate formed using SDS often has the appearance of snow, but occasionally when hydrates
Figure 3.14: Methane hydrate grown from sand with 500ppm SDS at 275K and 1000psi.
were inspected after formation it appeared as though two distinct structures had formed, with a clearly defined boundary between them. Figure 3.15 shows a hydrate grown from a pool with 500ppm SDS at 275K and 1000psi. Two distinct regions can be observed, region 1 which appears more dense, and region 2 which has the appearance of snow as is common. The regions are separated by a clear boundary.

Figure 3.15: Methane hydrate grown with 500ppm SDS at 275K and 1000psi. Two distinct structures appear, with a clear boundary between them.

The reason for these two regions is unclear, particularly the existence of region 1 which does not always appear. However, when region 1 did form it was always between region 2 and
the wall of whatever container was used. Furthermore, region 1 never appeared in hydrate samples which were prepared by loading large containers with a small amount of water, i.e. in situations where the hydrate had ample room to spread out as it grew. Therefore, it seems plausible that the region 1 is formed when hydrate that forms first is later crushed by pressure that is generated by the remaining water converting to hydrate inside a limited volume.

3.4 Conclusion

This chapter detailed a number of promising hydrate related projects that were never formulated into official publications but nonetheless produced interesting and useful results. The projects have been described here for any who may wish to continue them in the future.

The relationship between hydrate growth rate and substrate wetting contact angle has been studied. It has been shown the growth rate decreases dramatically with increasing contact angle for methane hydrates growth from both DI water and a water-SDS solution. In addition, it has been shown that for hydrates grown using SDS, the growth rate increases linearly with pressure for pressures up to \(\sim 250\) psi above the equilibrium pressure but the final clathration percentage remains independent of pressure over the same range.

Finally, it has been observed that methane hydrates grown in sand using SDS separate from sand and form, in large part, on top of the sand. In addition, two distinct regions appear in hydrates formed in containers that are charged with large amounts of water-SDS solution and it is plausible that these regions form due to the hydrate having limited space to grow.
Chapter 4

Superfluid Dynamics

This chapter shifts focus from the study of clathrate hydrates to low temperature physics. Here we introduce superfluidity and discuss a few of the landmark experiments and prominent theories of the field. This chapter serves to provide the background necessary to understand the Superfluid Nanoflow project described in Chapter 5.

4.1 Two-Fluid Model

Helium liquefies at 4.2K, and between 4.2K and 2.17K this liquid, often referred to as He I, behaves like a normal fluid. However, as the temperature drops below 2.17K, known as the lambda temperature ($T_\lambda$), the helium transitions into a unique fluid state (He II) known as a superfluid (Figure 4.1). This state earns its name from its ability to flow through small capillaries with no measurable resistance[59, 3]. It was initially presumed that superfluid helium could be described as a classical ideal fluid using the Euler equations of motion. However, it quickly became apparent that this was not the case, and a more complex theory was needed to explain the superfluid behavior[87].
Figure 4.1: Phase Diagram of $^4\text{He}$. 

---

**Figure 4.1: Phase Diagram of $^4\text{He}$**

- **Solid $^4\text{He}$**: This region represents the solid phase of helium-4.
- **Superfluid**: The superfluid phase is characterized by its unique properties, such as zero viscosity.
- **Normal Liquid $^4\text{He}$**: This is the liquid state of helium-4.
- **$\lambda$-line**: This line separates the superfluid and normal liquid phases.
- **Vapor Pressure**: The vapor pressure line indicates the boundary between the liquid and gaseous states.

The diagram shows the pressure ($P$) versus temperature ($T$) plot for $^4\text{He}$. The specific phase transitions and the behavior of $^4\text{He}$ under varying pressure and temperature conditions are illustrated through this graph.
In 1941, Lev Landau proposed using a two fluid model to explain He II. The model treated He II as a superposition of a viscous fluid, behaving as a normal fluid, and an inviscid fluid with quantum mechanical effects\cite{65, 64}. Landau’s two fluid description is a generalization of the Euler equations of motion, in which the total mass density (Eq. 4.1) and the mass flux (Eq. 4.2) are described, to first order, by a linear combination of the superfluid and normal fluid states.

\begin{equation}
\rho = \rho_n + \rho_s 
\end{equation}

\begin{equation}
J = \rho_n v_n + \rho_s v_s
\end{equation}

Below $T_\lambda$, the total density $\rho$ depends fairly weakly on temperature, staying near 145 kg/m$^3$, while the superfluid and normal fluid densities, $\rho_s$ and $\rho_n$ respectively, are highly temperature dependent as shown in Figure 4.2. It should be noted however, as it will become important in later sections, that the total density does depend upon the pressure (Figure 4.3). Furthermore, $T_\lambda$ shifts with pressure, decreasing with increasing pressure as can be seen in Figure 4.1.

For laminar flow, the normal velocity component, found in Eq. 4.2, is the solution to the Navier-Stokes equation for a laminar, viscous flow in a pipe (Eq. 4.3).

\begin{equation}
v_n = -\frac{\Delta P}{8\eta L}r^2
\end{equation}

Here $\Delta P$ is the pressure drop across the pipe, $L$ is the length of the pipe, $r$ is the pipe’s radius, and $\eta$ is the dynamic viscosity. For velocities below a critical velocity, the superfluid velocity is governed by Equation 4.4,
Figure 4.2: The superfluid ($\rho_s$) and normal fluid ($\rho_n$) densities, normalized to the total density ($\rho$), as a function of temperature along the saturated vapor pressure curve[35].
Figure 4.3: Total density $\rho$ of helium as a function of temperature at 0 atm (solid black), 10 atm (dashed red), and 20 atm (dotted blue). Graph reproduced from data given in ref [16].
\[
\frac{\partial \vec{v}_s}{\partial t} + (\vec{v}_s \cdot \nabla) \vec{v}_s = -\nabla \mu \tag{4.4}
\]

\[
d\mu = -sdT + \frac{1}{\rho} dP \tag{4.5}
\]

where \(\mu\) is the chemical potential in units of energy per mass. Unlike the normal velocity, which is driven by a pressure gradient, the superfluid velocity is driven by a chemical potential gradient \((\nabla \mu)\). This new velocity driving force is the source for many of the quantum mechanical effects displayed by He II, such as the fountain effect[2, 75].

Because He II is a quantum mechanical system, it can be described by a single, complex wavefunction \(\Psi\). The modulus squared, \(|\Psi|^2\), is the superfluid density \(\rho_s\) and the phase of the wavefunction, \(\phi\), is the order parameter. The superfluid velocity, \(v_s\) is related to \(\phi\) through Equation 4.6[5]. This requires that the superfluid be an irrotational fluid with quantized circulation around cores where the wavefunction is excluded. These quantized vortices are theorized to have a radial velocity that falls of inversely with radial distance, and cores with a radius \(a_0\) on the order of the coherence length \((\approx 0.3nm)\)[10]. The existence of these vortices leads to many interesting phenomena unique to He II including quantum turbulence, energy dissipation, and the quantization of the angular momentum in He II systems. Despite extensive research on each of these phenomena, their mechanisms are still not fully understood. The experimental research presented in Chapter 5 deals with, among other things, dissipation limited superfluid flow caused by energy dissipation due to vortices. Thus, the remainder of this chapter will focus on the phenomena of energy dissipation through quantum vortex dynamics. In Equation 4.6, \(m\) is the mass of a helium atom.
4.2 Dissipation Limited Superflow

The two fluid model predicted by Landau is valid up to a critical velocity $v_{sc}$, above which the flow is limited by various dissipation mechanisms. Landau predicted a critical velocity of $v_{sc} \approx 60 m/s$, above which he predicted the roton excitations generated in He II would be sufficient to destroy the superfluid state and restore the helium to its normal state. Experimentally, however, critical velocities are typically found to be much lower than Landau’s predicted $v_{sc}$.

Onsanger and Feynman introduced a new theory for dissipation in the form of quantized vortex lines and vortex rings within an irrotational superfluid. Feynman attempted to explain critical velocities in superfluid flows using the formation of these quantized vortices[38]. By equating the kinetic energy of the superfluid exiting a channel to the energy required to form vortices at a specific rate, Feynman was able to predict a steady state velocity.

Feynman also postulated that resistance to flow, and thus a critical velocity, developed due to vortex lines contacting the pipe walls. He envisioned a situation wherein a vortex line gets started somehow and is pinned to an abnormality along the pipe’s wall. The vortex line would then get dragged along by the fluid, stretching and producing a longer vortex line.

Feynman’s critical velocity is dependent upon the structure of the vortex, where the vortex could either be a ring or rectilinear. The Feynman critical velocity, $v_{sc}$, for ring and rectilinear vortices are shown in Equations 4.7 and 4.8 respectively. The velocity depends very weakly on temperature except very near $T_\lambda$ where $a_0$, the vortex core parameter, diverges[10].

\[
\frac{\hbar}{m} \nabla \phi = \vec{u}_s
\]
Feynman’s critical velocities do a much better job predicting experimental data than Landau’s critical velocity [53, 114, 56, 74], but the construction is still incomplete and cannot explain some results found in submicron channels [121]. Primarily two different critical velocity regimes are seen. A fast regime, usually in small diameter channels, which is temperature dependent, and a slow regime which is largely temperature independent. Complicating matters further, critical velocities measured can vary stochastically between research groups, and, in some cases, the critical velocity can stochastically switch between the two velocity regimes over the course of a single experiment [56, 132].

The two critical flow regimes are often attributed to two types of vortex generation, termed extrinsic and intrinsic nucleation. Feynman’s critical velocity is an example of extrinsic nucleation, where vortices are generated from a preexisting vortex or set of vortices. Glaberson and Donnelly proposed another form of extrinsic vortex generation, the quantized vortex mill model [43]. In the vortex mill model a vortex line is pinned at the wall of the pipe and is stretched by the superfluid flow, the stretching increases its curvature until at some critical velocity a recombination event pinches off a vortex ring, leaving behind the original vortex line to repeat the process (Figure 4.4). This vortex ring then expands, crossing all flow streamlines and reducing the overall phase difference by $2\pi$ until in annihilates at the pipe wall. A $2\pi$ reduction in the phase reduces the velocity by a step of $\kappa/L$, where $\kappa = h/m$ is the quantum of circulation. The frequency at which these vortex rings need to be created to maintain a steady state flow is the Josephson-Anderson frequency (Equation 4.9).

\[
\begin{align*}
\vec{v}_{sc,\text{ring}} &= \frac{h}{mr} \left( \ln \left( \frac{8r}{a_0} \right) - \frac{7}{4} \right) \quad (4.7) \\
\vec{v}_{sc,\text{line}} &= \frac{h}{2mr} \ln \left( \frac{2r}{a_0} \right) \quad (4.8)
\end{align*}
\]
Figure 4.4: An extrinsic nucleation process described by Hulin et al. in Figure 8 of reference [56]. A pinned vortex line in a superfluid flow grows (a-c) until at a critical flow velocity a vortex ring is emitted. A smaller vortex ring (d-f) can also be emitted.

Schwarz, through simulations, predicted a critical flow velocity in which the pinned vortex line responsible for the vortex mill would detach from the its pinning site and be swept out of the channel. Thus, at this critical depinning velocity $v_{s,\text{pin}}$ (Equation 4.10) the flow would transition from extrinsic to intrinsic[95].

$$v_{s,\text{pin}} = \frac{\kappa}{\pi r} \ln \left( \frac{b}{a_0} \right)$$

(4.10)

The fast flow regime discussed above is strongly temperature dependent, and often very stochastic. Properties that point toward a process of vortex nucleation by way of thermal...
activation above ~ 150 mK and by quantum tunneling below[121]. An intrinsic mechanism was first proposed by Langer and Fisher[66] in 1967. They postulated that vortices above an activation energy, \( \Delta E \), would be generated through thermal nucleation. Each vortex decreases the superfluid’s phase difference across the channel by \( 2\pi \), and through Equation 4.6, its velocity as well. The change in superfluid velocity was proportional to the thermal frequency \( f_T \) as shown in Equation 4.11, where \( f_0 \) is the fluctuation frequency[81]. The change in superfluid velocity can be related to the pressure drop across the pipe by equating the thermal frequency \( f_T \) to the Josephson frequency \( f_{J-A} \). The resulting relation is shown in Equation 4.12.

\[
\frac{dv_s}{dt} = \frac{\kappa}{L} f_T = \kappa \pi r^2 f_0 e^{\frac{\Delta E}{k_B T}} \tag{4.11}
\]

\[
\frac{dv_s}{dt} = \frac{\Delta P}{\rho L} \tag{4.12}
\]

\( \Delta E \), known as the free energy barrier, can be deduced from experimental data. From experimental evidence, two energy barriers have been shown to be consistent with observed superfluid flow behavior[81, 122, 4, 84, 108, 131].

For data that displays a \( v_s \propto \rho_s/T \), \( \Delta E \) is approximated by \( \beta \rho_s/\rho v_s \) where \( \beta \) is a weak function of \( v_s \) and temperature[81]. This approximation corresponds to the nucleation of a vortex ring with activation energy shown in Equation 4.13. The activation energy is minimized when the momentum, \( \vec{p}_r \), and superfluid velocity, \( v_s \), are perpendicular to each other. The energy and momentum of the ring are given in Equations 4.14 and 4.15 respectively. This model predicts an infinite velocity at \( T=0 \), which is of course impossible. At low temperatures the velocity must approach the Landau critical velocity where the superfluid fraction will transition into normal helium by the excitation of rotons.
\[ \Delta E = E_r + \vec{p}_r \cdot \vec{v}_s \]  
(4.13)

\[ E_r = \frac{1}{2} \rho_s \kappa^2 R (\ln(\frac{8r}{a_0}) - \frac{7}{4}) \]  
(4.14)

\[ p_r = \pi \rho_s \kappa r^2 \]  
(4.15)

In many experiments a linear dependence on temperature has been observed for the critical velocity\[122, 4, 84, 108, 131\]. A corresponding energy barrier, \( \Delta E_l \), with linear temperature dependence was necessary to reproduce the critical velocities seen. Currently no physical model has yet been found which accounts for this linear dependence, however, a phenomenological function (Equation 4.16) has been used. The corresponding free energy barrier is shown in Equation 4.17. The three phenomenological constants \( v_0, T_0, \) and \( E_0 \) can be acquired from a data fit. They are found to be on the order of 10 m/s, 1K, and 100K respectively. This linear treatment of the velocity is valid until quantum tunneling dominates over thermally activated vortices. The cross over from thermal vortices to quantum tunneling dominated flow has been shown to be between 150 mK and 400 mK\[31, 57, 121\].

\[ v_{sc} = v_0 (1 - \frac{T}{T_0}) \]  
(4.16)

\[ E_{sc} = E_0 (1 - \frac{T}{T_0}) \]  
(4.17)
Chapter 5

Pressure Driven Flow of Superfluid through a Nanopipe

This chapter deals primarily with the work found in ref [14] and explores pressure driven flow of superfluid helium through single high aspect ratio glass nanopipes into a vacuum has been studied for a wide range of pressure drop (0-30 atm), reservoir temperature (0.8-2.5K), pipe lengths (1-30mm), and pipe radii (130-230nm). As a function of pressure we observe two distinct flow regimes above and below a critical pressure $P_c$. For $P < P_c$, the critical velocity is approximately the Feynman critical velocity. As the pressure approaches $P_c$, there is a sudden transition to a new flow state with a critical velocity more than an order of magnitude higher. This effect is explained by a simple model which accounts for the fountain pressure generated by evaporative cooling at the outlet of the nanopipe.
5.1 Introduction

The flow of superfluid helium (He II) through channels has been a subject of great interest for decades [5, 66, 121]. At low flow velocities, superfluid will flow as an ideal dissipationless fluid, but as the flow velocity increases, quantized vorticity can be generated which leads to dissipation and pressure gradients. Vorticity can be generated from the irrotational background superflow via thermal [81] or quantum [57] (intrinsic) nucleation, or it can be generated from pre-existing (extrinsic) pinned vortex lines. For either mechanism, there is a critical velocity above which vorticity is generated very rapidly, so stable flow takes place at or near the critical velocity. Much of what is known about these critical velocities comes from two types of experiments. The first type measures the flow rate as a function of pressure through either a capillary [33, 74, 90] or a single hole [53, 56, 9] using a capacitive level sensor. These experiments had a complex phenomenology and were difficult to interpret and attention turned to experiments which utilized vibratory motion of a diaphragm with a hole; early experiments used micron sized holes [8, 89, 17], while more recent experiments use holes in the range of a hundred nanometers [108]. This type of measurement detects the onset of dissipation due to individual vortices, but does not directly monitor either flow rate or pressure drops. Theoretical models which describe the formation and motion of vorticity are based on nucleation theory [66, 63, 53], two fluid flow models [76, 78, 113], and Biot-Savart dynamics of vortex motion [95, 97, 119]. A recent review [121] summarizes over 50 years of superfluid flow data.

In most previous experiments on flow of superfluid, a capillary or orifice connects two reservoirs of bulk fluid with pressure differences of a few Torr or less. Recently, several experiments have explored a more complex flow regime in which superfluid flows from a bulk liquid reservoir into a vacuum through a nanoscale channel [91, 125, 36]. The high flow impedance of these channels enables the investigation of flows over a wide range of pressure drop. The reservoir pressure in the experiments reported here span the range from the saturated vapor
pressure to the solidification pressure. The evaporative cooling which takes place on the low pressure side of the channel produces temperature gradients which can directly drive superflows. The combination of large temperature and pressure gradients can generate unusual flows in which the superfluid-normal transition occurs inside the channel. These types of flows are interesting strongly driven nonequilibrium systems, and are also important in cryogenic engineering. Standard evaporative refrigerators utilize large pressure drops across micron and sub-micron capillaries in which liquid helium enters in the normal state and emerges in the superfluid state[20, 34]. Similar flows occur in porous plug pumps and phase separators which are used in zero gravity[62, 79].

In the work presented here we study the mass flow-pressure drop relation for superfluid helium flowing through single nanopipes with aspect ratios in the range of $10^4$ to $10^5$ for pressure drops ranging from 0-30atm. The data show a large flow transition at a critical pressure that depends on the reservoir temperature.

### 5.2 Experimental Apparatus and Methods

Figure 5.1 shows the experimental apparatus, which was composed of an input helium gas line, a copper pressure cell which served as a liquid reservoir, the glass nanopipe, and a vacuum pumping line. The flow apparatus was mounted in a continuous pulse tube - $^4$He evaporation cryostat. The flow rate of helium through the nanopipe was measured using a Stanford Research Systems Residual Gas Analyzer (RGA), a type of mass spectrometer. The RGA is a very sensitive detector of the partial pressure of helium in the pumping line. A calibrated helium leak was used at the start of each experimental run, before helium was inserted into the cell, to obtain a conversion between the partial pressure of helium and the helium mass flow. Details about the use of a mass spectrometer to measure helium flow rates have been documented previously [91, 124].

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Figure 5.1: Superfluid nanoflow experimental setup. The high pressure reservoir is at temperature $T_1$ and pressure $P_1$. 
The fused silica pipes acquired from Polymicro Technologies had a nominal ID of 0.2\( \mu m \) and an OD of 100\( \mu m \) and had a protective outer polymer coating. We independently measured the ID of our prepared pipes in situ using normal \(^4\)He flow measurements, and post measurement using scanning electron microscopy. Our measured diameters were slightly larger than the nominal values, but the flow and SEM measurements were consistent between each pipe.

The pipes were prepared by first breaking off a length of pipe longer than needed. The polymer coating was then slowly burned off, taking care to not melt or bend the silica pipe. The pipe was then either sealed in a 1/8\(^\circ\) Swagelok VCR male - male adapter in the case of the longer pipes (Figure 5.2), or sealed in a 1mm thick x 5mm copper disc with a small hole drilled in the center in the case of the short pipes (Figure 5.3), using Stycast 2850FT epoxy. The short pipes were then attached directly to a small copper pressure cell using the Swagelok VCR fitting, while the copper disc holding the short pipe replaced the traditional metal gasket used in the Swagelok VCR seals. Just before mounting the pipes to the copper pressure cell, the pipes were cleaved at the desired length. By saving this step until the last possible moment, the chance of contaminants entering the pipe was minimized.

A ruthenium oxide thermometer was mounted inside the copper cell and submerged in the liquid helium to measure the helium temperature, with care taken to insure the thermometer had minimal thermal contact to the cell walls. A thermometer was also mounted to the exterior of the copper cell for monitoring purposes. The volume of the cell was \( \sim 10^{-6} m^3 \).

A 1/16\(^\circ\) copper fill line connected the cell to a mechanically actuated, superfluid tight valve at the 0.8K plate. A 1/16\(^\circ\) stainless steel fill line ran from the valve to the 4K plate, where 1/4\(^\circ\) piping connected to an external helium pressure system. All measurements presented here were done with the valve open and the pressure measured by either an Omega PX309 pressure transducer (higher pressure) or a MKS Instruments Baratron (low pressure) at room temperature.
Figure 5.2: Long glass pipe sealed in a 1/8” Swagelok VCR male-male adapter. The pipe can be seen sealed in Stycast 2850FT epoxy. The pipe was cleaved to length just before it was mounted into the cryostat to minimize the chance of contaminants entering the pipe.
Figure 5.3: Short glass pipes sealed in custom made 5mm copper discs each with a small hole drilled in the center. The pipe can be seen sealed in Stycast 2850FT epoxy. The pipe was cleaved to length just before it was mounted into the cryostat to minimize the chance of contaminants entering the pipe.
The low pressure side of the pipe was connected to a turbo pump through a 1/4” stainless steel pipe. Maintaining a high vacuum is critical for the RGA to operate properly. In some experiments the mass flow became too large for the RGA to measure, so for higher mass flows a MKS Instruments Series 345 Pirani gauge was used. The RGA and Pirani gauge’s working ranges overlapped enough to allow for the Pirani gauge to be calibrated to the RGA each run. The RGA’s upper limit was $\sim 3.5 \text{ mTorr}$, and the highest flow rates produced a pressure of $\sim 4.5 \text{ mTorr}$, so the Pirani gauge was only used over a very short range.

The cell was thermally anchored to a copper plate with the base temperature of 0.8K. Ultra high purity $^4\text{He}$ gas from Airgas (99.999%) passes through sintered, stainless steel mesh filters with a 0.5 micron nominal pore size from Swagelok before entering and after exiting the cell. The filters were thermally anchored at 4K. The filters provided further purification of the ultra high purity $^4\text{He}$ from trace gases and prevented contaminants from entering the cell.

All experiments were performed with the cell full of liquid $^4\text{He}$. At pressures at or near the saturated vapor pressure (SVP), the cell was able to reach base temperature (0.8K). For higher pressures, the cell and part of the fill line were filled with liquid. In this configuration a heat load was carried by the liquid $^4\text{He}$ from the 4K plate to the base 0.8K plate and the lowest obtainable stable temperature was $\sim 1.1\text{K}$.

Experiments were done by either stepping the temperature and holding the pressure constant, or stepping the pressure and holding the temperature constant. In the case of the SVP temperature sweep, the pressure was allowed to move along the SVP curve. Before cooling down, the cell was flushed with helium gas at least three times. The cell was then pressurized to $\sim 0.6 \text{ atm}$ while the vacuum line was held at vacuum. Both the input line and vacuum line were then sealed with room temperature valves while the cryostat cooled down. Once cold, the cell and vacuum line were evacuated while held at 6K.
The density of liquid helium can be monitored in situ with the use of a quartz tuning fork[12, 28]. A fork similar to that described in ref [55] was used to verify the solidification of helium at high pressures.

5.3 Results and Discussion

5.3.1 Normal Flow Behavior

To insure that our system was working properly we first measured the flow of normal liquid $^4He$ at 2.3K. For laminar flow of a normal fluid through a pipe, the mass flow can be described by the Poiseuille mass flow equation,

$$Q_m = \frac{\pi \rho \Delta P}{8\eta L} r^4$$

(5.1)

where $\Delta P$ is the pressure drop across the pipe, L is the length of the pipe, r is the pipe radius and $\rho$ is the density, and $\eta$ is the dynamic viscosity evaluated at the temperature and pressure of the reservoir.

Figure 5.4 compares the mass flow through a 2mm glass pipe at various pressures with the prediction of equation 5.1. The fit gives a radius of 130nm ($\pm 3nm$). This radius was later checked using SEM measurements and found to be in good agreement. The deviation from linearity in Figure 5.4 is due to the pressure dependence of both $\rho$ and $\eta$. 

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Figure 5.4: Mass flow of normal $^4He$ through a 2mm glass pipe at 2.3K as a function of the pressure drop. The solid line is the prediction of Eq. 5.1 for a pipe of radius 130nm assuming that the liquid density and viscosity in the nanopipe have the same values as in the high pressure reservoir.
Figure 5.5: Mass Flow Isotherms for various temperatures as a function of pressure drop through a single $r=130\text{nm} \times 2\text{mm}$ long glass pipe. $1.2\text{K}$ (+), $1.4\text{K}$ ( ), $1.6\text{K}$ ( ), $1.8\text{K}$ ( ), $2.0\text{K}$ ( ), $2.3\text{K}$ ( ). There is an abrupt increase in the mass flow at a critical pressure $P_c$ that depends on temperature.

### 5.3.2 Flow Transition at Critical Pressure

Although the mass flow vs pressure of normal $^4\text{He}$ can be explained with an isothermal viscous flow model, the mass flow of He II proved to be considerably more complicated. Figure 5.5 shows a number of isotherms for flow through a $r = 130\text{nm} \times 2\text{mm}$ long single glass pipe. As the pressure is increased from SVP for each temperature, the mass flow suddenly goes through a substantial and sharp transition at a critical pressure $(P_c)$ to a much higher flow rate.
Figure 5.5 also shows that $P_c$ systematically increases with increasing temperature. In addition, $P_c$ did not exhibit any observable hysteresis when the pressure was swept up and back down through the transition. This flow transition was observed in multiple pipes of varying lengths and radii. The exact value of $P_c$, at a given temperature, varies only slightly for pipes with lengths that vary by more than an order of magnitude, as shown in Figure 5.6, but for each pipe the qualitative dependence on temperature is similar and lies in the 10-150 Torr range. For all pipes, the nature of the flow above and below $P_c$, particularly the temperature dependence of the superfluid velocity, is quite different as will be discussed in more detail below.

A quantitative model for the flow requires an assumption on the state of the fluid at the low pressure end of the pipe and in particular, the position of the liquid-vapor interface. For the mass flows measured in our experiments, the liquid-vapor interface cannot occur inside the pipe in steady state because the mass transport of the vapor in the pipe is far too small[125]. For some combinations of pipe diameter and driving pressure, superfluid helium can emerge from the end of a pipe in a continuous stream like water coming out of a garden hose [46], but that is not possible in our apparatus. Generating a continuous stream or a stream of droplets requires the formation of a large amount of liquid-vapor interface. The energy to do this must come from the kinetic energy of the flow out of the nozzle. For liquid flowing out of a hole or pipe, there is a critical velocity, $v_{jet}$ at which the kinetic energy of the fluid can supply the surface energy for a continuous liquid jet to be formed. Below this critical velocity no jet can be formed and the liquid drips out of the pipe[120]. This critical velocity is

$$v_{jet} = 2\sqrt{\frac{\gamma}{\rho r}}$$  \hspace{1cm} (5.2)

where $\gamma$ is the surface tension. Nanoscale pipes have a high surface to volume ratio, so the
Figure 5.6: Mass flow as a function of pressure drop through a 2mm (filled symbol) and 30mm (empty symbol) single r=130nm glass pipes at 1.6K (triangle) and 1.8K (square). There is an abrupt increase in flow at a critical pressure $P_c$ which depends on the temperature of the high pressure reservoir. $P_c$ is defined as the maximum curvature point at the foot of the rise, as shown for the 1.79K isotherm.
Figure 5.7: Schematic of a nanopipe connecting a high pressure reservoir at temperature $T_1$, pressure $P_1$ and chemical potential $\mu_1$ to pool of liquid that is held by surface tension to the glass surface at the low pressure exit. The pressure in the exit region is effectively zero, so the fluid pool evaporates and its temperature drops to a lower temperature $T_2$ at which the evaporative heat flux $Q_{\text{evap}}$ is balanced by thermal conduction from the glass. Fluid is blue and glass is gray.
critical velocity can be quite high. For a r=130nm pipe, \( v_{jet} \approx 8.4 m/s \), which is higher than any velocity we observe. Thus, as the helium flows out of the low pressure side of the pipe, the liquid will form a small pool around the low pressure region of the pipe as shown in Figure 5.7. The same type of analysis suggests that a pool of liquid will also form at the exit nozzle in several recent experiments involving flow into a vacuum [91, 36].

Because the low pressure side of the pipe is held at vacuum, the helium pool begins to evaporate with a mass flux density per unit time \( J_{evap} \) which is determined by the pool temperature \( T_2 \),

\[
J_{evap} = (P_{svp}(T_2) - P_{gas}) \sqrt{\frac{m}{2\pi k T_2}}
\]  

(5.3)

where \( P_{svp} \) is the saturated vapor pressure of the liquid, \( P_{gas} = 0 \) is the pressure of the surrounding gas, \( m \) is the mass of a helium atom, and \( k \) is Boltzmann’s constant. The RGA detector measures the total helium evaporating per unit time \( \dot{m}_{evap} \),

\[
\dot{m}_{evap} = A_p J_{evap}
\]  

(5.4)

where \( A_p \) is the surface area of the evaporating helium pool. In steady state, the temperature and size of the pool adjusts itself so that the mass flow out of the pipe is the same as the evaporated flux. Determining \( T_2 \) and \( A_p \) requires a careful consideration of the heat and mass flows in our system.

We begin with the simplifying assumption that the normal fluid flow in the nanopipe is negligible and that all of the flow in the pipe is due to superfluid; a comparison of Figures 5.4 and 5.5 shows that at the pressures corresponding to the flow discontinuity, the normal flow is never more than 5% of the total. The equation of motion for the superfluid velocity
$v_s$ is given by

$$\frac{\partial v_s}{\partial t} + \nabla ( \frac{1}{2} v_s^2 + \mu ) = 0$$  \hspace{1cm} (5.5)$$

where $\mu$ is the chemical potential. For steady state 1D flow in a pipe connecting fluid reservoirs at temperatures $T_1$ and $T_2$ and pressures $P_1$ and $P_2$, the velocity is

$$v_s = \sqrt{2(\mu_1(T_1, P_1) - \mu_2(T_2, P_2))}$$  \hspace{1cm} (5.6)$$

where we assume $\mu_1 > \mu_2$ and the $v_s$ is directed out of the reservoir and into the vacuum. When the inequality is reversed with $\mu_2 > \mu_1$, the superfluid will flow from the pool at the exit back into the reservoir. The chemical potential can be computed from available thermodynamic tables. Along the coexistence curve, the chemical potential is a monotonically decreasing function of temperature. For small deviations from coexistence, $\mu$ can be estimated using the thermodynamic formula $d\mu = -sdT + \frac{1}{\rho}dP$, where $s$ is the entropy per unit mass of the fluid. For temperatures above 1K, the entropic term dominates, so a finite pressure drop is required to force superfluid to flow from the warmer reservoir into the cooler exit pool. The critical pressure required to overcome the $\Delta \mu$ caused by evaporative cooling can be calculated if the pool temperature $T_2$ is known. The steady state heat balance of the pool is

$$L_v A_p (P_{svp}(T_2) - P_{gas}) \sqrt{\frac{m}{2\pi k T_2}} = \frac{\Delta T}{R_K} A_p$$  \hspace{1cm} (5.7)$$

where $L_v$ is the latent heat of evaporation, $\Delta T = (T_1 - T_2)$, and $R_K$ is the Kapitza resistance between glass and $^4$He, where we have used $R_K = 17.5T^{3.6}(cm^2K)/W$ as reported in Pollack[86]. The left hand side of Eq. 5.7 is the heat flow due to evaporation, and the right side is the heat conducted across the solid-liquid interface. Assuming that the solid substrate
is at temperature $T_1$, Eq. 5.7 can be solved for the pool temperature $T_2$. The values obtained for $T_2$ depend only weakly on $T_1$, and range from 0.7K to 0.8K in our system. Once $T_2$ is determined, the critical reservoir pressure $P_c$ required to drive superflow out of the reservoir is given by the solution to

$$\mu_1(T_1, P_c) = \mu_2(T_2, P_{svp}(T_2))$$  \hspace{1cm} (5.8)$$

The surface area of the pool, $A_p$, is determined by the balance between the mass flow rate through the pipe and the evaporation rate of the pool:

$$A_p J_{evap} = \rho \pi r^2 \sqrt{2(\mu(T_1, P_1) - \mu(T_2, P_{svp}(T_2))}$$  \hspace{1cm} (5.9)$$

For a given reservoir temperature $T_1$, pressure $P_1 > P_c$, and pool temperature $T_2$, equation 5.9 can be solved for the pool radius $r$ which rises from zero at $P = P_c$ to values in the range of 100 microns for reservoir pressures near 1 atmosphere. Above the threshold pressure $P_c$, this simplified model predicts a superfluid flow velocity that scales as $v_s \sim \sqrt{\frac{P_1}{P_c}}$ as shown in Figure 5.8. A comparison of experimental values of $P_c$ determined from the onset of the steep rise in flow as seen in Figure 5.6 and the predictions of the simplified model is shown in Figure 5.9.

Although the model predicts $P_c$ well, it does not explain the flow states above and below $P_c$. In particular, the simplified model predicts no flow for $P < P_c$, but a substantial flow much larger than the normal state flow is observed. For large pressure drops, the model predicts a mass flow that monotonically increases with pressure, but experiments show flow rates that are independent and even decrease with increasing pressure. These effects are discussed further below.
Figure 5.8: Calculated pressure dependence of mass flow using equations 5.6, 5.7, and 5.8 for a r=130nm x 30mm long glass pipe with $T_1 = 1.6K$. 
Figure 5.9: $P_c$ as a function of the reservoir temperature $T_1$. Solid curve is calculated from Eq. 5.8. Data points mark the beginning of the steep rise in flow rate from data such those in Figure 5.6.
5.3.3 Low Pressure Regime

An important feature of the simplified model described above is that the pool of liquid at the pipe exit reaches a low temperature that is independent of the area $A_p$ of the pool. If the pool is at a lower temperature than the reservoir, a finite pressure drop will be required to establish a chemical potential gradient in the direction which drives superflow from the reservoir to the exit pool. For pressures below $P_c$, superflow would tend to drain the superfluid in the pool back into the pipe and the reservoir. In contrast, experiment shows a temperature dependent flow from the reservoir into the vacuum that is over an order of magnitude higher than what can be accounted for by normal flow. Figure 5.10 shows the temperature dependence of the mass flow through two pipes, $r=130\text{nm}$ and $r=230\text{nm}$, where the driving pressure is the saturated vapor pressure, which is always below $P_c$.

Both the magnitude and the strong temperature dependence of the mass flow below $T_\lambda$ indicates that superfluidity is involved. One possible explanation for superflow into the vacuum even at small pressure drops is to invoke a more complex heat transfer model than described by Eq. 5.7. An implicit assumption in the simplified heat transfer model is that the temperature of the fluid in the pipe is the temperature of the reservoir $T_1$ throughout its length, and that the temperature drops abruptly at the exit. The actual situation is certainly more complicated but difficult to model exactly. When the pool area is small, it is plausible that even small residual heat flows from the pipe will raise the temperature of the pool so that smaller pressure drops are sufficient to drive superflow into the vacuum against the thermal gradient.

The mass flow data of Figure 5.10 can be converted into an average superfluid velocity $v_s$ in the pipe using

$$v_s = \frac{\dot{m} - \dot{m}_n}{\rho_s(T_1)\pi r^2} \quad (5.10)$$
Figure 5.10: Mass flow through single glass pipes with radii $r=130\text{nm}$ (filled squares) and $r=230\text{nm}$ (empty squares) as a function of the reservoir temperature $T_1$. The pressure in the reservoir is the saturated vapor pressure $P_{\text{sat}}(T_1)$, which is always below $P_c$. 
where $\dot{m}$ is the observed mass flow, $\dot{m}_n$ is the normal mass flow, taken to be the mass flow just above $T_\lambda$ multiplied by the normal fluid fraction, and $\rho_s(T_1)$ is the superfluid density at the saturated vapor pressure corresponding to the temperature of the reservoir $T_1$. It is interesting to note that, despite being below $P_c$, the superfluid velocity compares very closely to the Feynman critical velocity, given by

$$v_c = \frac{\hbar}{2mR} n\left(\frac{2R}{a_0}\right)$$

(5.11)

where $a_0$ is the vortex core radius which diverges as $T$ approaches $T_\lambda$[10].

$$a_0 \approx \frac{0.32}{(T_\lambda - T)^2}(nm)$$

Using equation 5.10 we can calculate the superfluid velocity and compare it to the Feynman critical velocity in Figure 5.11. It can be seen that $v_s$ at low temperatures is very similar to the $v_c$ predicted by equation 5.11 for both pipe diameters. The superfluid velocity is very temperature dependent, decreasing with increasing temperature. Similar temperature dependence has been seen before [36, 53, 131]. There is a pronounced dip in the data at temperatures near 1.5K which appeared in all the pipes we investigated.

### 5.3.4 High Pressure Regime

The mass flow rate data for pressures above $P_c$ are shown in Figure 5.12. The mass flow of normal helium (2.3K) which increases approximately linearly with pressure, is shown for a 2mm long pipe as a benchmark. For low temperatures (1.2K), the mass flow of superfluid is approximately independent of pressure up to pressures at which the bulk helium solidifies above 25 atm. The solidification of the bulk helium could be observed by a dramatic shift
Figure 5.11: Superfluid velocity through single r=130nm (filled) and r=230nm (empty) glass pipes with the reservoir at SVP which is less than $P_c$. The Feynman critical velocity from Eq. 5.11 for R=130nm (solid line) and R=230nm (dashed line).
in the frequency of a quartz tuning fork that was submerged in the bulk helium. For higher temperatures, the superfluid transition temperature depends on pressure. $T_\lambda$ decreases linearly with pressure, ranging from 2.172K at SVP to approximately 1.78K at 30 atm. Because there is a pressure gradient in the nanopipe, this implies that the high pressure end could be normal while the low pressure end could be superfluid, i.e. the superfluid transition could occur inside the pipe. At intermediate temperatures (1.8K) the flow rate actually decreases with pressure. Furthermore, although we have varied the nanopipe length by over an order of magnitude, the length appears to have little to no effect on the superfluid mass flow.

At pressures above $P_c$, the temperature dependence of $v_s$ is drastically different than at low pressure. Figure 5.11 shows the temperature dependence of $v_s$ at low pressures compared to the Feynman critical velocity (eq. 5.11) for pipes of $r=130\text{nm}$ and $230\text{nm}$. For $P < P_c$, the superfluid velocity decreased with increasing temperature. In Figure 5.13, we perform the same analysis for pressures above $P_c$, but for this case the velocity is largely temperature independent, even increasing slightly with increasing temperature before dropping sharply, very close to $T_\lambda$. This behavior is in sharp contrast to the power law behavior observed in ref [36]. Although $v_c$ is roughly proportional to $1/R$ as in the Feynman formula, the low temperature values of $v_c$ are much higher than the values observed for $P < P_c$, and to get even approximate agreement with the data, the predictions of Eq. 5.11 need to be multiplied by a factor of 11. A comparison of the flow rates through nanopipes of length 2mm and 30mm shows that for a given pressure drop, the flow is essentially independent of the nanopipe length. The flow transition at $P_c$ was observed in all of our pipes. It does not seem to occur in more conventional flow experiments [100, 123, 56, 114, 53] and was not observed in previous experiments on flow into a vacuum [91, 36].

The schematic diagram of Figure 5.7 implies that there are temperature and pressure gradients in the nanopipe. Although our data do not directly address the spatial dependence of the gradients, they do provide some qualitative insight. For relatively low pressure where the
Figure 5.12: Mass Flow as a function of pressure drop through short (2mm) and long (30mm) single \( r=130\text{nm} \) glass pipes for a range of temperatures of the high pressure reservoir \( T_1 \). 2mm-1.2K (■), 2mm-1.8K (▲), 2mm-2.0K (●), 30mm-1.6K (+), 30mm-2.0K (x). Normal state flow through a 2mm nanopipe at 2.3K (▼) is shown for comparison. \( P_c < 1\text{atm} \), so most of the data are in the high pressure regime. Note that the length of the nanopipe has very little effect on the mass flow.
Figure 5.13: Superfluid velocity through single \( r=130\text{nm} \) (filled squares) and \( r=230\text{nm} \) (open squares) glass pipes for a constant pressure above \( P_c \) as a function of temperature. The curves show the Feynman critical velocity for \( R=130\text{nm} \) (solid line) and \( R=230\text{nm} \) (dashed line) multiplied by a constant factor \( \alpha = 11 \).
pressure dependence of the superfluid transition temperature is negligible, our observations are consistent with the assumption that the temperature in the nanopipe is the same as in the high pressure reservoir, and the temperature gradients are confined to a short region near the exit. For example, the flow data shown in Figure 5.13 shows no sign of superflow for input reservoir temperatures above 2.17K, even though the temperature of the fluid pool on the low pressure end is certainly below $T_\lambda$. Similarly, for the normal state flow shown in Figure 5.4 there must be a superfluid-normal boundary somewhere in the nanopipe, but apparently it is near the end because the standard viscous flow equations using the nominal geometry explain the data. At high pressures, the superfluid transition temperature can be significantly depressed. Figure 5.14 compares temperature dependence of flow rates at high and low driving pressures. For $P = 23\text{atm}$, the superfluid transition is at $T = 1.82K$, so naively one would not expect superflow for reservoir temperatures above this value. The data nevertheless shows a small increase in flow rate at $T_\lambda$, but also a more significant but broader increase as the temperature drops below 1.82K. This behavior suggests that the combination of temperature and pressure gradients can affect the location of the super-normal boundary in the nanopipe.

An ideal dissipation-less superfluid cannot sustain steady state flow in a pipe subject to a chemical potential gradient; some form of dissipation is required to balance the pressure work done on the fluid. Dissipation in a superfluid is intimately related to the formation and motion of vortex lines. The Anderson-Josephson relation,

$$\Delta P = \frac{\rho\tilde{N}h}{m}$$

relates the pressure drop to the rate $\tilde{N}$ that vortices must be created and cross the flow lines to account for $\Delta P$. For a 20 atm pressure drop across a $r=130\text{nm} \times 2\text{mm}$ long pipe, such as that shown in Figure 5.13, the equation requires approximately $10^{11}$ vortices per second.
Figure 5.14: Mass flow through single $r=130$nm glass pipes 30 mm long as a function of the temperature $T_1$ of the high pressure reservoir for two values of the pressure in the high pressure reservoir. For $P_1 = 1.24$atm (filled circles), the superfluid transition temperature is 2.17K and the mass flow increases smoothly as the reservoir temperature is lowered below that value. For $P_1 = 23.0$atm, (filled squares) the superfluid transition temperature is 1.82K. As the temperature is lowered below 2.17K, the flow increases abruptly even though the fluid in the high pressure reservoir is normal (the fluid pool at the low pressure outlet is superfluid, however). As the reservoir is cooled further below its superfluid transition, there is another step-like feature in the flow rate which may be due to motion of the superfluid-normal boundary in the nanopipe.
to cross the flow path. If the pressure gradient is approximately constant and the vortex velocity transverse to the flow is approximately the same as the axial flow velocity in the pipe, the number density of vortices \( n \sim 10^{20}/m^3 \) and the mean spacing between vortices is \( \sim 220\text{nm} \).

The vortices can be produced either by thermal nucleation or by a "mill" process which amplifies pre-existing pinned vortices. The fact that the flow rate becomes essentially independent of temperature at low temperature rules out thermal nucleation. For a pinned vortex to bow out across the diameter of the pipe requires a time of order the pipe radius divided by the flow velocity, which for our pipes is approximately \( 10^{-7} \text{sec} \). This implies that for our pipes, at least \( 10^4 \) pinned vortices would be needed to generate the measured pressure drop. Schwarz has pointed out that pinned vortices in a finite pipe will be advected downstream and flushed out of the pipe, so they need to be continuously generated\[95, 96]. One proposal to accomplish this is to have several vortices with pinning sites outside the inlet. The other pinning sites can propagate down the tube in a helical wave which will interact and generate a vortex tangle if the velocity is above a critical velocity estimated to be \( 20\kappa/R \), where \( \kappa \) is the quantum of circulation. For our pipes, this critical velocity is approximately \( 30m/sec \), which is about an order of magnitude higher than the flow velocities we observe.

### 5.4 Conclusion

The behavior of superfluid helium flow through single nanopipes into a vacuum was studied for inlet pressures ranging from 0-30 atm. Surface tension effects require the superfluid exiting the nanopipe on the vacuum side to form a pool which subsequently evaporates at a rate determined by heat transfer from the substrate. The temperature of the pool typically reaches values near 0.7K and is only weakly dependent on the temperature of the high
pressure reservoir. The fact that flow through the nanopipe connects two liquid reservoirs at different temperatures has important implications for the analysis of this type of experiment. Superfluid flow is driven by changes in chemical potential which are generated by temperature and pressure gradients. Superfluid will flow towards regions of high temperature and low pressure, but these two gradients are opposed to each other for most operating parameters of our apparatus. We have observed a transition in flow regimes at a critical pressure which appears to be the pressure required to generate a net chemical potential gradient directed toward the low pressure end of the nanopipe. For pressures below the critical pressure $P_c$, our simplified model suggests that the flow would be directed toward the high pressure side of the nanopipe, which would drain the fluid pool at the exit and result in no net flow. In contrast, our measurements with $P < P_c$ show a strongly temperature dependent superfluid flow into the low pressure side of the apparatus. This discrepancy may be due to an oversimplification of the heat transfer model or to the onset of a more complex time varying or spatially inhomogeneous flow. Nevertheless, increasing the driving pressure beyond $P_c$ where the chemical potential gradient changes sign results in an abrupt increase in the mass flow rate by roughly an order of magnitude. Above $P_c$ the superfluid velocity is essentially independent of temperature and of the length of the nanopipe. For low temperatures and temperatures near $T_\lambda$, the mass flow is also independent of the pressure drop. At intermediate temperatures, the mass flow actually decreases with increasing pressure, which may be related to motion of the super/normal interface inside the nanopipe. Mass flow rates that are independent of pressure drop have been seen in previous experiments on superfluid flow connecting two nominally isothermal liquid reservoirs with pressure drops of only a few $Pa$ [100]; a remarkable feature of our data is that the pressure independence of the mass flow extends all the way to the solidification pressure. In a future study we hope to apply the Biot-Savart vortex tangle model [96, 118] and the detailed two fluid hydrodynamic models [106, 113] to produce a quantitative comparison with our experimental data.
Chapter 6

Quartz Tuning Fork Pressure Gauge for High Pressure Liquid Helium

This chapter shifts focus away from superfluid behavior in nanopipes, to the behavior of quartz oscillators in superfluids. For some projects it became desirable to have a cheap, compact, in situ, cryogenic pressure gauge. A gauge with the desired specifications was not available, so the following study was launched to explore the feasibility of using a micron sized quartz tuning fork as a high pressure detector in liquid helium. This chapter deals primarily with the work found in ref [15].

6.1 Introduction

Quartz tuning forks are small, cheap, high Q mechanical resonators which work well in cryogenic environments. Because of these valuable experimental attributes, they have been utilized to measure thermodynamic and transport properties of helium and helium mixtures[28, 12, 85, 55]. The primary measurable properties are the resonant frequency and quality factor
of the electromechanical oscillations of the tuning fork. Hydrodynamic interactions with the surrounding fluid can alter these values.

Using a hydrodynamic model, changes of the resonant frequency and quality factor can be related to variation of the total density, normal fraction density, and viscosity of the fluid. Below \( T_\lambda \) liquid helium can be regarded as a superposition of a normal fluid and an inviscid superfluid state, so both components must be incorporated in the model. Because the compressibility of liquid helium is rather high, relatively small changes in pressure result in easily measurable shifts of the resonant frequency.

We have exploited this effect to calibrate quartz tuning forks as in situ pressure gauges in bulk liquid helium. In contrast to most previous work[50, 51, 47, 49, 48], in addition to characterizing the frequency dependence on pressure and temperature, we measured the frequency response at constant density (\( \Delta \rho \approx 0.2\% \)). All data presented here, isothermal, isobaric, and isopycnic, can be modeled using a simple hydrodynamic model with a single set of parameters. The viscosity of He II has also been measured concurrently over the same range of temperatures (0.9 - 3.0 K) and pressures (SVP - 25 atm).

### 6.2 Experimental Procedure

An experimental cell with approximate volume \( \approx 1cm^3 \) was constructed from oxygen free high thermal conductivity (OFHC) copper. The cell was thermally anchored to a continuous pulse tube cryostat with an additional evaporative stage and a base temperature of \( \approx 0.83 \) K [19]. A vacuum sealed, quartz tuning fork from Citizen Fine Tech (CFS-206) with a resonant frequency of 32.764 kHz and a quality factor of \( Q \approx 8.5\times10^5 \) at room temperature was used. The corresponding values at 1 K were 32.710 kHz and \( Q \approx 8\times10^6 \). The tuning forks came sealed in metal cylinders. The cylinders were opened by carefully sanding off the top of
the cylinder. The tuning forks were then installed in the copper cell and remeasured under vacuum at room temperature to verify the quality of the resonance. A tuning fork similar to the one used in these experiments, with the metal can removed, can be seen in Figure 6.1.

An HP 8751A Network Analyzer was used to measure the frequency response of the tuning fork and the data was fit post-experiment using a LRC circuit model in Mathematica to be discussed shortly. A sweep time of 120 seconds, IFBW of 2, and a span of between 10 and 80 Hz were used for measurements, depending on the pressure. At 1K, when the forks quality factor was high, the error in frequency $\delta f \approx 0.015 Hz$ which corresponds to a $\delta P \approx 0.002 atm$. At 2.2K, when the quality factor is at its lowest, $\delta f \approx 0.15 Hz$ and $\delta P \approx 0.02 atm$. This sensitivity could be significantly enhanced with longer sweep times and averaging, as well as more careful wiring. The cell was equipped with a stainless steel fill line 150 microns in diameter.

Experiments were run in two experimental configurations, open cell and closed cell. When the cell was open, the pressure in the cell was monitored with a room temperature capacitance gauge, and with a custom built cryogenic capacitance gauge thermally anchored to the cell. The capacitance gauge was modeled after the gauge described in Figure 1 of ref [109] and had an electronic noise limited sensitivity of $\approx 8$ Torr at 30 atm and liquid $^4He$ temperatures. The capacitance gauge had a capacitance of $\approx 10pF$ and was measured using an Andeen-Hagerling 2500A 1kHz Ultra-Precision Capacitance Bridge, which had a sensitivity of 0.5 attofarads. When the valve was open a superfluid heat leak prevented the cell from reaching its base temperature. In this configuration, the lowest temperatures obtainable were 1.1K.

For the closed cell configuration a mechanically actuated, superfluid tight valve was installed in the fill line near the cell. The valve was a conventional Swagelok bellows valve with a stainless steel spherical stem tip. For the closed cell configuration the pressure in the cell was monitored using the custom built cryogenic capacitance gauge. In this configuration, the base temperature of 0.83K was obtainable.
Figure 6.1: Typical quartz tuning fork used in the measurements described here. The fork is 3.95mm long, 0.18mm thick, and each tine is 0.23mm wide.
The temperature of the He II was measured directly using a ruthenium oxide thermometer which was submerged in the helium a few mm away from the tuning fork.

The Network Analyzer measured the voltage $V_{\text{out}}$ across the tuning fork in response to a swept frequency input signal of amplitude $V_{\text{in}} = 5 \text{ mV}$ as described in ref [55]. The frequency response of the tuning fork was modeled as a Butterworth-Van Dyke circuit [117, 7] (Figure 6.2). The admittance of the circuit is given as $Y(\omega)$ in Eq. 6.1 and the quality factor $Q$ is defined in Eq. 6.2, where $\omega_0$ is the resonant frequency.

$$Y(\omega) = \frac{1}{R + \frac{1}{\omega C} + i\omega L} + i\omega C_0$$

(6.1)

$$Q = \frac{\omega_0 L}{R}$$

(6.2)

Figure 6.2: Butterworth-Van Dyke equivalent circuit for a quartz tuning fork resonator. Typical values used were $R = 298 \text{ k}\Omega$, $C = 3.173 \text{ fF}$, $C_0 = 13.31 \text{ pF}$, and $L = 7.88 \text{ kH}$.

6.3 Hydrodynamic Model of Frequency Shift and Quality Factor

The tines of a quartz tuning fork oscillate in an antisymmetric mode. A detailed analysis of the effect of the surrounding fluid on the vibrational modes of the tuning fork would be...
quite complicated, but useful qualitative insight can be obtained by considering the simpler
case of a single tine modeled as a cylinder oscillating perpendicular to its axis. General
considerations for small amplitude oscillations of any solid in a fluid show that the force due
to the fluid is the sum of two terms which are proportional to the velocity and the acceleration
of the solid, respectively[64]. The hydrodynamic force proportional to the acceleration is
present even in the limit of an ideal inviscid fluid and acts like an added mass term in the
equations of motion. The force proportional to the velocity is due to rotational flow in a thin
layer of thickness $\delta = \sqrt{\eta/\rho \pi f}$, where $\eta$ is the viscosity, $\rho$ is the density of the fluid, and
$f$ is the frequency of the oscillation. This force determines the dissipation and the quality
factor $Q$.

For a cylinder of radius $R$, exact formulas[22, 88] for the frequency ratio and $Q$ can be
expressed in terms of a complex dimensionless quantity $\Gamma(f)$

$$\Gamma(f) = 1 + \frac{4iK_1(-i\sqrt{i\text{Ren}})}{\sqrt{i\text{Ren}K_0(-i\sqrt{i\text{Ren}})}}$$

(6.3)

where $\text{Ren} = 2\pi \rho f R^2 / 2\eta$ is the Reynolds number and $K_0$ and $K_1$ are Bessel functions. The
ratio of the resonant frequency in vacuum $f_{\text{vac}}$ to the resonant frequency in the fluid $f$ is

$$\left(\frac{f_{\text{vac}}}{f}\right)^2 = 1 + \frac{\rho \text{Re}[\Gamma(f)]}{\rho_q}$$

(6.4)

where $\rho_q = 2659 \text{kg/m}^3$ is the density of quartz. The quality factor is given by

$$Q = \frac{\text{Re}[\Gamma(f)] + (\rho_q/\rho)}{\text{Im}[\Gamma(f)]}$$

(6.5)

where $\text{Re}$ and $\text{Im}$ denote the real and imaginary parts.
For our tuning fork, the effective radius $R$ of the tuning fork is $\approx 0.3 \text{ mm}$, so the Reynolds number is $\approx 4 \times 10^5$. This justifies the use of the asymptotic expressions for the Bessel functions, which leads to the simplified expressions for the Eqs. 6.4 and 6.5 which are valid for small values of $\delta/R$:

\[
\left( \frac{f_{\text{vac}}}{f} \right)^2 = 1 + \frac{\rho}{\rho_q} + \frac{2\delta \rho}{R\rho_q} \tag{6.6}
\]

\[
Q = \frac{R(\rho + \rho_q)}{2\delta \rho} \tag{6.7}
\]

The two fluid model of a superfluid assumes that superfluid $^4\text{He}$ consists of a superfluid fraction with density $\rho_s$, zero viscosity, and zero viscous penetration depth, and a normal component with density $\rho_n$ and a viscous penetration depth $\delta_n = \sqrt{\eta/\rho_n \pi f}$. Only the normal fluid contributes to $Q$, but both components affect the frequency. Summing the contributions from both components yields:

\[
\left( \frac{f_{\text{vac}}}{f} \right)^2 = 1 + \beta \frac{\rho}{\rho_q} + B \frac{2\delta_n \rho_n}{R\rho_q} \tag{6.8}
\]

\[
Q = \alpha \frac{R(\rho_n + \rho_q)}{2\delta_n \rho_n} \tag{6.9}
\]

We have introduced three dimensionless parameters, $\alpha$, $\beta$, and $B$ into Eqs. 6.8 and 6.9. For a cylinder, all three parameters are identically equal to 1, but for a realistic tuning fork, we expect these parameters to differ from 1, to account for the non-cylindrical tines and the presence of the second tine[50, 51, 47]. At low enough temperatures, $T < 0.5 \text{ K}$, the normal fraction approaches zero and the mean free path of the quasiparticles become larger than
the diameter of the tines and the hydrodynamic description breaks down. All of our results are for $T > 0.83$ K where the hydrodynamic regime is still valid. For numerical calculations, the temperature and pressure dependence of the total mass density $\rho[T, P]$ and the normal fluid density $\rho_n[T, P]$ were obtained from ref [16]. The viscosity was measured directly, as will be discussed shortly. Eq. 6.8 can be solved to give the frequency of the fork $f$:

$$f = \frac{f_{vac}}{\sqrt{1 + \beta \frac{\rho}{\rho_q} + B \frac{2\Delta \rho}{R \rho_q}}}$$

Lea et al.[67] showed that at He II temperatures the elasticity of quartz is dependent upon pressure $P$ and for high pressures an additional term, proportional to $P$, is needed to accurately predict the frequency response of a quartz oscillator. Therefore, Eq. 6.10 becomes:

$$f = \frac{f_{vac}}{\sqrt{1 + \beta \frac{\rho}{\rho_q} + B \frac{2\Delta \rho}{R \rho_q}}} + \gamma P$$

(6.11)

where $P$ is pressure and $\gamma$ is a constant with units Hz/atm. Lea, who used a shear mode quartz crystal resonator at $f = 20.5$ MHz, saw a $\gamma/f \approx 1.48 \times 10^{-6}$ atm$^{-1}$. As will be shown, our data yields a best fit of $\gamma/f \approx 11 \times 10^{-6}$ atm$^{-1}$. This difference could be due to geometric factors, as well as which elastic constant of quartz is most relevant for the oscillations of the fork. An oscillating beam, fixed on one end and free to move on the other, will have its first resonant frequency at

$$f = \frac{0.56 \sqrt{E_y I}}{L^2 \sqrt{\rho_q A}}$$

(6.12)

where $L$ is the length of the beam, $I$ is the moment of inertia, $A$ is the cross sectional area, and $E_y$ is the effective Young's modulus. For quartz, $E_y$ is pressure dependent. To first
order in pressure,

\[ f = f_0 + \frac{0.28 \sqrt{T \frac{dE_y}{dP}}}{L^2 \sqrt{\rho_y AE_y}} P \]  \hspace{1cm} (6.13)

where \( f_0 \) is the resonant frequency at \( P=0 \). The coefficient in front of \( P \) is equivalent to \( \gamma \). The elastic constants \( (c_{ij}) \) of quartz have dramatically varying pressure dependencies. Calderon[21] reports a typical pressure dependence of \( \frac{\partial c_{ij}}{\partial P} \approx 6 \). Some have reported \( \frac{\partial c_{ij}}{\partial P} \) values as high as 18 for \( \alpha \)-quartz[45]. For a beam similar to one of our tines \( (L=3\text{mm},\ r=0.3\text{mm}) \), \( \frac{dE_y}{dP} = 6 \) and \( E_y = 10 \text{ GPa} \), values similar to \( c_{12} \) in ref [21], we get \( \gamma \approx 0.28 \) and \( \gamma/f \approx 8.8 \times 10^{-6} \text{ atm}^{-1} \). The \( \gamma \) found in this work is still above this estimate, but given that \( \gamma \) is heavily dependent upon the geometry of the tine and the highly variable pressure dependence of the quartz elastic constant, the best fit for \( \gamma/f \) found in this work seems to be within reason.

While the total mass density \( \rho \) and the normal fluid density \( \rho_n \) were taken from tabulated thermodynamic data[16], we found that there was a fairly large spread in the reported values of helium viscosity below \( T_\lambda[128, 44, 18, 35, 69] \). Figure 6.3 shows reported values of heliums viscosity near \( T_\lambda \) along the saturated vapor pressure curve from a variety of sources. It can be seen that, while all the data follow the same qualitative behavior, the exact value of \( \eta \) between reported data sets differs by as much as 2x.

Given the variability in available data, we decided to calculate our viscosity through direct measurement of the quality factor \( Q \) in Eq. 6.9, where \( \delta_n = \sqrt{\eta/\rho_n \pi f} \). \( \alpha \) was determined experimentally to be \( \alpha \approx 0.36 \) by measuring \( Q \) along the saturated vapor pressure curve and matching the calculated \( \eta \) to the reported values in ref [128]. This \( \alpha \) was then used for all subsequent calculations of \( \eta \) at higher pressures. Some of the acquired values of \( \eta \) are shown in Figure 6.4. The measured quality factor \( Q \) can be seen in Figure 6.5 as a function of temperature at SVP, 8.5 atm, and 22 atm.
Figure 6.3: Reported helium viscosity $\eta$ values along the saturated vapor pressure curve as a function of temperature. Data is taken from NIST[69] (open circles), Bruschi[18] (filled diamonds), Woods[128] (empty triangles), Goodwin[44] (filled triangles), and Donnelly[35] (filled squares) compared to viscosity values calculated from $Q$ (*).
\[
\eta = \frac{f \pi R^2 \alpha^2 (\rho_n + \rho_k)^2}{4Q^2 \rho_n}
\]  
(6.14)

**Figure 6.4**: Viscosity \( \eta \) values calculated from \( Q \) at various pressures as a function of temperature.

### 6.4 Results and Analysis

Figure 6.6 shows a typical frequency response curve at 1.7K and 9.6 atm. Figure 6.7 shows how the frequency curve changes with temperature. At low temperatures, the normal fraction is low and the frequency response has a high \( Q \). As the temperature increases, and \( T \) approaches \( T_\lambda \), the resonant frequency decreases and \( Q \) drops. However, even at \( T > T_\lambda \),
Figure 6.5: The quality factor $Q$ at SVP, 8.5 atm, and 22 atm as a function of temperature.
when the helium is normal and $Q$ is at its lowest, we can still obtain a frequency curve with a defined peak (Figure 6.6 insert).

Figure 6.6: The frequency response of the tuning fork at 1.7K (open circles) and 9.6 atm, and the corresponding fit using Eq. 6.1. The parameters used were $R = 298$ k$\Omega$, $C = 3.173$ fF, $C_0 = 13.31$ pF, and $L = 7.88$ kH. The inset shows a similar scan at 2.3K and 8.4 atm.

The validity of Eq. 6.11 can be checked experimentally as both a function of pressure and a function of temperature. Figure 6.8 shows the pressure dependence of $f$ at 1.53K, 1.84K, and 2.0K for pressures ranging from 0 to 27 atm. The corresponding predicted $f$ using Eq. 6.11 is shown to be in good agreement with experiment. All fits are made using the same parameters, $\beta = 0.93395$, $B = 5.8342$, and $\gamma = 0.38$ Hz/atm. For the 1.84K and 2.00K isotherms, the curves change direction slightly when crossing $P_\lambda$, the $\lambda$-pressure corresponding to each temperature ($\approx 25$ atm at 1.84K and 13 atm at 2.0K). The solidification of helium can be
Figure 6.7: The evolution of the frequency response of the tuning fork for temperatures from 0.9K to 2.3K at \(\approx 9.6\) atm.
seen for pressures above the solidification pressure (≈ 25 atm at 1K). Above the solidification pressure the resonant frequency of the tuning fork shifts dramatically and is lost. Despite searching over a wide range of frequencies, we were unable to find the resonant peak of the tuning fork in solid helium.

Figure 6.9 shows the temperature dependence of $f$ at a variety of pressures ranging from 2.5 atm to 21.9 atm. The corresponding predicted $f$ using Eq. 6.11 is shown to be in good agreement for all pressures and temperatures measured. All fits were made using the same parameters used in Figure 6.8. The shift in $T_\lambda$ can be seen as the pressure is increased in each run.

Since the goal of this paper is to show the feasibility of a 32 kHz quartz tuning fork as a cheap, in situ, cryogenic pressure gauge we also measured the frequency response of the fork in a sealed, superfluid tight cell. The pressure was monitored in situ by the cryogenic capacitance gauge and the temperature was monitored with a ruthenium oxide thermometer. The cell was sealed with a mechanically actuated valve as described in the experimental section. In this closed cell configuration the density was nearly constant, changing only slightly as the volume changed due to the capacitance gauge. The density changed by $\approx 0.2\%$ from $T_\lambda$ to 1K.

In order to maintain a constant density as the temperature changes, the pressure must also change substantially. Thus, as the temperature of the cell was swept from 1K to 2.5K, the frequency $f$ reacted to both the changing temperature and the changing pressure. Figure 6.10 shows the change in frequency $\Delta f = f - f_{\text{min}}$ as a function of temperature when the valve is closed vs when the valve is open and $P$ is held constant. Here $f_{\text{min}}$ is the minimum frequency of the experimental run. The corresponding cell pressure during the closed valve run is shown in the Figure 6.10 inset. The $\Delta f$ of an open valve run at a similar pressure is also shown (7 atm run also shown in Figure 6.9). The predicted $\Delta f$ using Eq. 6.11 and the same parameters as before ($\beta = 0.93395$, $B = 5.8342$, and $\gamma = 0.38$ Hz/atm) is shown to be
Figure 6.8: The frequency $f$ dependence of the tuning fork on pressure at 1.53K, 1.84K, and 2.0K. The corresponding predicted $f$ using Eq. 6.11 is shown for parameters $\beta = 0.93395$, $B = 5.8342$, and $\gamma = 0.38$ Hz/atm.
Figure 6.9: The frequency $f$ dependence of the tuning fork on temperature at 2.5 atm, 7.0 atm, 10.0 atm, 13.7 atm, 17.3 atm, and 21.9 atm. The corresponding predicted $f$ using Eq. 6.11 is shown for parameters $\beta = 0.93395$, $B = 5.8342$, and $\gamma = 0.38$ Hz/atm.
in good agreement with experiment in the closed cell, constant density environment.

Figure 6.10: The change in frequency $\Delta f$ as a function of temperature for a closed cell (filled squares) configuration vs an open cell (empty triangles) configuration. The predicted $\Delta f$ for the closed cell run is also shown (solid line). The inset shows the corresponding cell pressure for the closed cell run.

6.5 Conclusion

In conclusion, we have shown that the frequency shift of a 32kHz quartz tuning fork can be calibrated to function as a cheap, in situ, cryogenic pressure gauge. In addition, the forks quality factor Q can be used to accurately measure the helium's viscosity up to $\approx 25$ atm. Our results show that for the range of temperatures (0.9 - 3.0K) and pressures (SVP
- 25 atm) presented here, the tuning fork frequency can be accurately predicted with a simple hydrodynamic model (Eq. 6.11) using a single set of parameters \( \beta = 0.93395, \quad B = 5.8342, \) and \( \gamma = 0.38 \) Hz/atm). The resonant frequency has a sharp feature as a function of temperature at \( T_\lambda \) while the frequency as a function of pressure is much smoother and the superfluid transition is much more difficult to discern as a function of pressure. Nevertheless, in both cases the simple hydrodynamic model presented here predicts the observed frequency behavior very well.
Chapter 7

Conclusion

This thesis details the results and implications of three distinct projects, the growth kinetics of methane clathrate hydrates, superfluid hydrodynamics on the nanoscale, and the behavior of quartz tuning forks in high pressure liquid helium. In chapter 2 it was shown that the growth kinetics of methane clathrate hydrates are fundamentally altered when grown under the influence of surfactants. By using simultaneous measurements of the uptake of methane detected by a pressure drop in the gas phase, visual observations of the amount of liquid water and solid phase in the reaction vessel, \textit{in situ} micro-Raman measurements, and \textit{in situ} NMR measurements it was shown that sufficient amounts of sodium dodecyl sulfate cause the water to form an intermediate immobile solid-like state before combining with the methane to form hydrate. Chapter 3 illustrated that hydrate growth rates can be further enhanced by increasing the hydrate driving force, or by growing the hydrates on a hydrophillic substrate. These results could have far reaching implications in hydrate based technologies that require high rates of hydrate formation, such as water desalination, gas storage, and carbon sequestration.

Chapter 5 reported on studies of pressure driven flow of superfluid helium through single
high aspect ratio glass nanopipes. It was shown that as a function of pressure, two distinct flow regimes above and below a critical pressure $P_c$ exist. For $P < P_c$, the critical velocity is approximately the Feynman critical velocity. As the pressure approaches $P_c$, there is a sudden transition to a new flow state with a critical velocity more than an order of magnitude higher. This effect was explained by a simple model which accounted for the fountain pressure generated by evaporative cooling at the outlet of the nanopipe. Above $P_c$ the superfluid velocity is essentially independent of pressure.

The discovery of a critical pressure $P_c$, as well as the pressure independence of the superfluid flow above $P_c$, has direct implications to the design of helium cooling systems, such as helium evaporative cryostats and porous plug pumps, which depend critically on the flow rates of superfluid through micron and sub-micron sized channels. In future studies it would be interesting to explicitly study the pressure and temperature profiles inside the nanopipes when the superfluid is subjected to high pressures, as the profiles are most certainly more complicated than what was modeled in chapter 5.

Finally, chapter 6 showed that a quartz tuning fork can be used as a low cost, compact, in situ cryogenic pressure gauge. The quality factor $Q$ and the frequency $f$ of a 32 kHz quartz tuning fork immersed in liquid $^4$He between 0.9 K and 3.0 K, over pressures ranging from the saturated vapor pressure to $\approx 25$ atm was reported. At constant pressure, as a function of temperature, the quality factor and $f$ have strong features related to the temperature dependence of the superfluid fraction. At constant temperature, $Q$ depends on the superfluid fraction while the frequency is a smooth function of pressure. All behavior was explained using a simple hydrodynamic model. The liquid helium viscosity can be acquired from $Q$, and together with tabulated values of the helium density as a function of pressure and temperature, the frequency shift was parametrized as a function of temperature and pressure. The observed sensitivity was $\approx 7.8$ Hz/atm.
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