Integration of van der Waals superconductors into 2D-3D Hybrid Superconducting Circuits

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Abstract

van der Waals materials as a field have boomed in the last decade for multiple reasons. Not only are air stable vdW materials comparatively inexpensive and easy to work with, but they can be used to create structures that would have previously been impossible or extremely expensive to fabricate. The vdW superconductors are just as fascinating for their own properties, such as Ising superconductivity and 2D superconductivity, as they are fascinating for their ability to interface seamlessly with other van der Waals materials. Atomically-thin two-dimensional (2D) transition-metal dichalcogenide superconductors enable uniform, flat and clean van der Waals tunneling interfaces, motivating their integration into conventional superconducting circuits. We cover the properties and characteristics of the TMD superconductors before turning to focus more on how their properties and characteristics can best be used to build new things. The largest part of this body of work is integrating 2D and 3D superconductors. However, fully superconducting contact must be made between the 2D material and three-dimensional (3D) superconductors to employ standard microwave drive and readout of qubits in such circuits. We present a method for creating zero-resistance contacts between 2D NbSe$_2$ and 3D aluminum that behave as Josephson junctions (JJJs) with large effective areas compared to 3D-3D JJs. The devices formed from 2D TMD superconductors are strongly influenced by the geometry of the flakes themselves as well as the placement of the contacts to bulk 3D superconducting leads. We present a model for the supercurrent flow in a 2D-3D superconducting structure by numerical solution of the Ginzburg-Landau equations and find good agreement with experiment. These results demonstrate a crucial step towards a new generation of hybrid superconducting quantum circuits. Lastly, we take a step into that new generation of hybrid superconducting circuits by integrating 2D superconductors into RF resonant circuits in addition the the prior DC circuits.
Preface

My journey through more than twenty four years of school has been supported every step of the way by my parents, brother, and grandparents. My parents always enthusiastically supported my boundless curiosity and they instilled me with a love for learning from a young age. Every night my dad’s last words to me before turning off my bedroom lights were "always keep learning," and then I proceeded to stay awake reading a book with a flashlight. My mom was always one of the most involved parents in the entire school district, and it wasn’t until I was much older that I realized she had stepped away from her law career to provide my brother and I with unwavering parental support, care, and encouragement as we grew up. My teachers and principles were often on a first name basis with my mom because she spent so much time organizing school events, chaperoning field trips, and ensuring I had the opportunity to participate in any extracurricular learning experience I was interested in, but also partly because she got the phone calls when my teachers caught me reading in class. My brother played an early role in my education, staying up late at night when we shared a bunk bed to teach me some of the math he was learning three grades ahead of me in elementary school. I eventually followed him to undergrad at Miami University where we diverged slightly in our studies. He focused on mathematics while I fell deeper in love with physics and first discovered the joys (and sorrows) of working in experimental research.

I had taken AP calculus and AP statistics in my junior year of high school, and after loving those classes taught by Sharon Volpe and Luke Lester I had thought at the time that I would study math & stats in college. However, my love of physics was fostered in my last year of high school when I was encouraged by Jack Kernion to take his AP Physics course. His contagious excitement for the subject pushed me through when I was struggling with difficult concepts and his class was my first inspiration to pursue physics in college and I will forever be grateful to him for this. When I first visited Miami University I was given a wonderful tour of the physics department by the Department Chair, Mick Pechan, not knowing that a year and a half later he would be my research advisor. He showed me around the entire department, poking his head into the various offices and research labs where he greeted every student by name. I am grateful to Jeff Clayhold for welcoming me into his research lab my freshman year when I had little physics knowledge or skills to bring with me. I learned a lot of problem solving skills that year, and I still work with PCBs more
than I would have thought. After joining Dr. Pechan’s lab the next year I learned a great deal about working in an experimental research lab from Brian Kaster, the senior graduate student. Although I’ve since moved from magnetic materials to 2D superconductors, my time in Dr. Pechan’s lab was very formative for me and I would not be the physicist I am today without those four years of working with and learning from him. I would also like to thank Perry Rice and Samir Bali who taught amazing lessons both inside and outside the classroom. My time at Miami University was not spent entirely inside a physics lab, though at times it may have seemed that way to my friends. I am so very fortunate to have found myself surrounded by wonderful and caring friends and formed friendships that continue strong over a decade later. Andy & Jaimee, Carson, Micah, Joanna, Blonde Charlie, Prashant: always remember after you beat me in Fantasy Football that I have another chance next season!

After moving back to Pittsburgh and starting grad school at CMU I quickly bonded with several other physics first-years. I spent innumerable hours in our sub-basement closet sized office working on QM and E&M homework problems with Dacen Waters, Aklant Bohmick, and Nicholas Jin. Without their help and assistance in our qualifying exam study group I would certainly not have passed. My first year at CMU I was fortunate to be able to work with Sara Majetich, from whom I learned the necessity of persisting past adversity. I greatly appreciate the generosity of Michael McQuade for the fellowship that let me do research while taking classes this first year. I switched labs and became Ben Hunt’s second graduate student. A fact which his first graduate student, Deva Gopalan, is always happy to remind me. Working with Ben, Deva and our first postdoc, Sergio de la Barrera, to build our lab from the near empty room that I first walked into has been a great experience and I have learned so much from all of them along the way. Deva and I bonded like brothers over the years, and I hope we can do another roadtrip sometime. Sergio taught me a great deal in the years we worked together, the lab would not function half as smoothly as it does today without his early work and influence. After stacking and fabricating well over a hundred van der Waals heterostructure devices to test and measure, my favorite Device Under Test remains the lab that I helped assemble with some truly amazing people. Ben has been a wonderful mentor over the last 5+ years. He is a constant voice of encouragement to try new experimental techniques and play around with new ideas for projects, but his voice of care and planning for success when approaching a new project has been so very valuable to temper my own optimistic brashness. I would be well served in the future to imagine his voice over my shoulder at such times rather than blindly and excitedly jumping into some new project headfirst. It has been a great experience to work with and teach the younger students. The undergrads’ time with us seems so ephemeral before they move on, but I’m glad to have worked with Jingyi Wu, Nathan Drucker, and Jiwoo Seo. Working with the younger graduate students who spend years learning from and with you is very different than working with undergrads, in part because you know that they will be taking over your work and equipment after you graduate. I’m happy to be leaving the care of the
lab in the steady hands of Joe Seifert (or at least until he soon graduates), Qingrui Cao, Erin Grimes, and John Lyons. May your cooling water be cold (and remain in the pipes rather than on the floor), your dil fridge rarely be warm, your cryogen dewars full, and your glovebox always over-pressured. I’d like to thank the members of HatLab both past and present who have contributed so much to our collaboration. Michael Hatridge is unwavering in his efforts to inoculate students with knowledge, even when we at first seem resistant to his treatment. I first met Olivia Lanes in the Quantum Computing class taught by Dr. Hatridge before we had any idea that our labs would collaborating on a project. We then spent 4+ years working together on that project and the work that spun out of it. We’ve commiserated after devices died, celebrated the working ones, and I’ve grown to value her friendship. Additionally, Olivia was the first person to buy my homemade candles, encouraging me as my hobby turned into a side gig. It feels good to finally have our names together at the top of our published paper. HatLab is such a tight family, I have often felt like I’m a distant cousin who visits intermittently, but when I do visit the whole family is extremely kind and helpful. Tzu-Chiao and Xi Cao have always been helpful with nanofab and fridge issues and HatLab’s first postdoc Gangqiang Liu was very helpful in getting Olivia and I started with our project. The younger members of HatLab are meeting and exceeding the gold standard set by the original crew, and I look forward to working with them more closely this coming semester as a postdoc.

In my personal life, Bianca Palmisano has been a constant presence for so many years. Though we are often separated by long distances, your friendship is an unwavering companion in times of difficulty. My lifelong friend Andrew Kuremsky left us a lifetime too soon, but I always remember him and the times we spent growing up together every time I pick up a hammer, wrench or power tool. Especially if I’m about to invent a new way of misusing or breaking said tool.

Like so many other people, I never imagined that I would be finishing grad school in the midst of a global pandemic. 2020 was a tumultuous year in many respects, but one of the most positive aspects in my life this past year has been the deepening relationship that Kristy Xu and I have built while living alone in an apartment with two cats. Our outdoor hiking, kayaking and camping adventures have been curtailed by the changing of seasons, but I am looking forward to having more outdoor adventures with you in the spring. For now, we will have to find that same pleasure with our culinary adventures. Nobody knows what the future will hold, but I look forward to facing that future with you side by side as we build our lives together.

I was going to thank my cats, Pico and Nano, for surviving grad school with me, but I just had to clean up another one of Pico’s hairballs earlier...so I’d like to thank Nano for surviving all of these years of grad school with me.

I’d like to end where I began, by thanking my parents. There is no doubt in my mind that none of this would have been possible without them and their support. The past 6+ years of school and life would have been unimaginably more difficult if I had not had my family nearby. This work is dedicated to both of you.
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Chapter 1

Introduction to Superconductivity and 2D vdW Materials

I will begin this chapter by introducing some key concepts in superconductivity before jumping back more than a century to walk along the historical path of superconductor research and theoretical models. After discussing their bulk properties and behavior in the presence of magnetic fields I will explore some of the changes that occur in superconductors as they approach and cross over the two-dimensional limit(s). This introduction to superconductivity will then finish the with an overview of Josephson junctions and their parallel combination to form superconducting quantum interference devices (SQUIDs). In the last portion of the chapter I will provide an overview of common van der Waals (vdW) materials with an emphasis on vdW superconductors and their properties. These 2D materials have attracted large amounts of research attention and funding over the last decade and a half largely because of the new parameter spaces of experimental exploration that they have opened.

1.1 Introduction to Superconductivity

Superconductivity as a phenomenon is characterized by two properties (and several associated limits): superconductors appear to exhibit both perfect conductivity and perfect diamagnetism [1]. These two properties, shared by no other phase of matter, have been the prime force pushing superconductivity research forward for over a century. While it took more than four decades after the discovery of superconductivity for the first high-field superconducting electromagnet to be built, the next seven decades of superconductor research steadily produced new superconducting materials that repeatedly established new upper bounds on the limits of critical temperature, magnetic field, and current density [2].

Perfect conductivity in superconductors exists as a state where there is zero drag on the movement of electrons, allowing the flow of an electrical current around a superconducting loop to persist nigh indefinitely in the absence of external forces. Unlike
all other diamagnetic materials, which have a much weaker volumetrically distributed response that only slightly reduces their internal magnetic field, perfect diamagnetism in superconductors is observed as an applied magnetic field being excluded from entering a superconductor. This is explained by induced surface currents forming on the perfect conductor to cancel the magnetic field at the surface. As shown in the top row of Figure 1.1 where solid cylinders are cooled below a transition temperature after which an external magnetic field is applied and both materials expel the field via induced surface currents. When the magnetic field is removed, both materials return to a static state. However, superconductors diverge from theoretically perfect conductors when they are cooled in the presence of an applied magnetic field, where they will expel all magnetic flux from their interior during the superconducting transition such that their internal magnetic field is always zero. In contrast, the onset of perfect conductivity in a material would result in the freezing of the internal magnetic flux to a constant value, such that a change in the applied field would not change the internal magnetic flux, as shown in the second row of Figure 1.1. The expulsion of magnetic fields from the interior of superconductors was discovered by Meissner in 1933 by measuring an increase in the magnetic field between two parallel superconducting rods as the magnetic flux was expelled from the rods during the superconducting transition, this effect was subsequently named after him [3]. The Meissner effect also points to some of the limits of superconductivity, demonstrating that the superconducting state is a thermodynamically stable state, and that the critical magnetic field, \( H_c \) (critical flux density, \( B_c \)), which destroys the superconducting state occurs when the magnetic field energy per unit volume is equal to the difference in the Helmholtz free energies per unit volume between the superconducting and normal states, Equation 1.1 using SI units[1].

\[
F = (f_N - f_S) = \frac{\mu_0 H_c^2}{2} = \frac{B_c^2}{2\mu_0} \tag{1.1}
\]

In the example of a hollow superconducting cylinder, applying a magnetic field will induce circulating surface currents on the cylinder walls such that the magnetic flux through the body and hole of the hollow cylinder is canceled, with the direction of the currents switching if the direction of the field is switched. The same behavior will also occur in a perfectly conducting hollow cylinder. However, these cases diverge when a magnetic field is already passing through the hollow cylinder before the onset of a perfectly conducting state or a superconducting transition. In the case of a perfect conducting hollow cylinder, the magnetic flux through the hole and body of the cylinder will be locked in place at the originally applied value, with no variation due to changes in the applied field. The final row on the right side of Figure 1.1, looking much like the prior row, shows that a multiply connected perfect conductor behaves akin to the simpler geometry. Quite unexpectedly, as a superconducting hollow cylinder transitions into the superconducting state with non-zero applied magnetic flux, an induced current will spontaneously appear in the superconducting cylinder’s inner
Figure 1.1: Superconductors vs. perfect conductors
Superconductors (Left: red/hot & blue/cold) are contrasted with perfect conductors (Right: pink/hot & green/cold) in three different scenarios. Cylinders cooled in the absence and presence of a field, as well as field cooled hollow cylinders. Axial sheet current directions are denoted by arrows and color.

and outer surfaces, expelling magnetic flux from the body of the cylinder. However, rather than fully cancelling the magnetic flux through the hole in the cylinder, the
circulating current produces a magnetic field which quantizes the total magnetic flux in multiples of $h/2e = \Phi_0$, the magnetic flux quantum (in SI units). If the applied magnetic flux is between two adjacent multiples of $\Phi_0$, the current will circulate in the direction that results in an integer total magnetic flux through the hollow cylinder which is closest to the applied magnetic flux, essentially rounding the magnitude of the magnetic flux to the nearest integer multiple of $\Phi_0$. This is shown in the bottom left of Figure 1.1, where the greater and lesser integer multiples of the magnetic flux quantum are shown explicitly. If the applied field is then changed or removed, the induced current will respond in kind to maintain the constant integer flux $n\Phi_0$ through the hollow cylinder, including changing sign if the applied magnetic flux passes through the integer value. This quantization was one of the first pieces of evidence that superconductivity is a quantum phenomenon and is further discussed in Section 1.1.6.

1.1.1 History of Superconductivity

Superconductivity was discovered in elemental mercury in 1911 by Kamerlingh Onnes soon after he first liquefied helium [4]. Onnes demonstrated that mercury submersed in liquid helium had an electrical resistance indistinguishable from zero, while also proving that liquid helium is an insulator, as he was using non-insulated bare-metal measurement lines [4]. Initial experimental work continued to focus on elemental superconductors such as lead, tin, indium and thallium, probing their response to currents, temperatures and magnetic fields, experimentally determining the dependence of the critical field on temperature (Equation 1.2)[1].

$$H_c(T) = H_c(T = 0) \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right]$$

(1.2)

After the Meissner effect was discovered, phenomenological theories developed by Gorter and Casimir (two fluid model) and the London brothers (London equations) accurately modeled the influence of temperature on critical fields and how the exponential decay in magnetic fields at the surface of a superconductor relates the current distributions and critical fields [5]. The exploration of superconducting alloys lead to the discovery of type-II superconductors, which remain in a superconducting state while penetrated by a limited amount of flux. Two decades later, Russian physicists Ginsburg and Landau (GL) published a macroscopic theory using a superconducting wave function that agreed with the London equations at surfaces, incorporated the recent idea of a superconducting coherence length alongside magnetic penetration depths as its characteristic length scales and explained type-II superconductors [5]. Later that decade Bardeen, Cooper and Schrieffer (BCS) proposed what became known as BCS theory, which fully explained all currently known superconductors by describing them as a condensate of electron pairs functioning as bosons in a superfluid state.
After another two decades of research, the experimental discovery of high temperature superconductors, unexplained by BCS theory, has led to ongoing and extensive basic research into the mechanisms behind unconventional superconductivity, as well as a flurry of applications that can more easily integrate superconductors operating a liquid nitrogen temperatures. The steady stream of new superconducting materials has driven the integration of superconductors into ever more applications, including high-field electromagnets (used in MRI scanners, nuclear fusion confinement systems, NMR systems, scientific research labs and particle accelerators), DC power supply cables, magnetometers, maglev trains, conventional and quantum computing circuits, particle detectors, telescope sensors and single-photon detectors. As the number and scale of applications for superconductors grow, the call for newer and more capable superconducting materials grows ever louder.

1.1.2 London Equations & Penetration Depth

In 1935 the London brothers, Fritz the theorist and Heinz the experimentalist, together proposed two equations (1.4) that included a phenomenological parameter (1.3) to govern the local average electric and magnetic fields in "superconductors", as they were often called in that era (Heinz would later propose the concept of dilution refrigerators, so I’m doubly grateful to him) [1, 6, 7]. Experiments on superconductors prior to 1935 had shown stark disagreement with Ohm’s law, which states that an applied electric field in a conductor produces a constant current \( J = \sigma E \), or \( V = IR \). So the London brothers started with the commonly discussed substitute for Ohm’s law in superconductors, the so called "acceleration equation" \( E = \frac{\partial}{\partial t} \lambda J \) [6]. Using SI units in the proceeding derivations, the phenomenological constant \( \lambda \) is dependent upon the material specific London penetration depth \( \lambda_L \), which is related to the superconducting charge carrier density \( 2n^*_s = n_s \), charge carrier mass \( m^* = 2m_e \), charge \( e^* = 2e \) and vacuum permeability \( \mu_0 \) [1, 6, 8]. The acceleration equation agreed with experiments that observed persistent currents in the absence of an electric field, but the London brothers believed it to be overly general and proposed Equations 1.4. The first equation limited the generality of the acceleration equation by including the gradient of the charge density, they then took the curl of that combination and applied Faraday’s law to obtain the second London equation [6]. Subsequent experiments by Heinz London in 1937 showed that \( \nabla \rho = 0 \) in superconductors, reducing the first equation to the acceleration equation and resulting in the London equations we are familiar with today (Equations 1.5) [8].
\[ \lambda = \mu_0 \chi_L^2 = \frac{m^*}{n_e^* e^2} \]  

(1.3)

1935: \[ \vec{E} = \frac{\partial}{\partial t} A \vec{J}_s + \nabla \rho \]  
\[ \vec{H} = -\nabla \times (A \vec{J}_s) \]  

(1.4)

1937: \[ \vec{E} = \frac{\partial}{\partial t} A \vec{J}_s \]  
\[ \vec{H} = -\nabla \times (A \vec{J}_s) \]  

(1.5)

\[ \nabla^2 \vec{H} = \frac{\vec{H}}{\chi_L^2} \]  

(1.6)

\[ H(r) = H(0)e^{-r/\lambda_L} \]  

(1.7)

\[ H(r) = H(0)e^{-r/\lambda_L} \]  

(1.8)

Combining the second London equation with Maxwell’s formulation of Ampere’s law yields Equations 1.6, 1.7 which show an exponential decay of magnetic field from the maximum at a superconductor’s surface [1]. This was the first theory that showed the perfect diamagnetism of superconductors only holds true in the bulk, and that magnetic fields can penetrate short distances in from the surface of superconductors. Accounting for magnetic field penetration at the surface of a superconductor reduces the total energy cost on the superconducting state of excluding the magnetic field. From the volume averaged perspective used in Equation 1.1, magnetic field penetration reduces the volume from which the magnetic field is excluded and therefore, when averaged over the total volume of the material, reduces the average magnetic energy per unit volume associated with excluding the field from the whole superconductor. This could be calculated by integrating \( \mu_0/2 \) times the square of Equation 1.7 over the superconductor’s volume and then normalizing by that volume to find the decrease in the average magnetic energy per unit volume, \( u_{\text{pen}} \). Comparing the reduced magnetic energy per unit volume \( \mu_0 H^2/2 - u_{\text{pen}} \) with the difference between the Helmholtz free energies per unit volume in the normal and superconducting state \( F = (f_N - f_S) = \mu_0 H_c^2/2 - u_{\text{pen}} \) we can see that the critical field is increased slightly above initial calculations in which magnetic fields were excluded from the entire volume of the superconductor (Equation 1.1)[1, 5].

From Ampere’s law, we know that so long as the current density has radial symmetry, current can be anywhere between the center and the surface of a cylinder to produce the same constant magnetic field at the surface of the cylinder and beyond. In concert with previous experiments that showed that the critical current of a superconducting cylinder produces the critical field at the superconductors surface, the London equations show that the current density in a superconductor is greatest at the surface and decreases exponentially over the penetration depth (Equation 1.9).

\[ \vec{J}_s(r) = \frac{\partial H(r)}{\partial r} = -\frac{H(0)}{\lambda_L} e^{-r/\lambda_L} \]  

(1.9)
Next, with the condition that net charge carrier momentum in the superconductor must be zero in the ground state with no electric or magnetic fields, London set the canonical momentum equal to zero \((\vec{p} = m\vec{v} - e\vec{A} = 0)\), to show that the average local charge carrier velocity is proportional to \(\vec{A}\). Multiplying that average local charge carrier velocity by the total local charge \(n_se\) allows the supercurrent density to be written as shown in Equation 1.10. However, this supercurrent equation is only physical for a particular choice of gauge. Pulling from his work on superfluids, Fritz London introduced the London gauge (Equation 1.11) [1]. The London gauge requires Equation 1.10 to describe the current through a surface as proportional to the component of \(\vec{A}\) normal to the surface [1]. Therefore, under this gauge, the vector potential is zero in the bulk since the supercurrent density must be zero far from any surface.

\[
\vec{J}_s = -\frac{\vec{A}}{\Lambda\mu_0} = -\frac{n_se^2\vec{A}}{m}
\]

\[
\nabla \cdot \vec{J}_s = \nabla \cdot \vec{A} = 0
\] (1.11)

London theory is a phenomenological masterpiece that tremendously advanced the understanding of superconductivity prior to the second world war [5]. The London equations provided the first mathematical explanation of the Meissner effect while also explaining persistent supercurrents in a ring, but key questions in search of a theoretical explanation for critical current densities and the larger critical fields in alloy superconductors remained open [5, 6]. A disadvantage of London theory is part of the reason it was so successful in the first place; it is a phenomenological theory that wasn’t rigorously derived from first principles. [6]. Answers to these problems would require more than two decades of further research before they were provided by the macroscopic Ginzburg-Landau theory, with the microscopic picture of superconductivity subsequently explained by BCS theory.

1.1.3 Band structures & quasi-particles

To enable a conceptual discussion of the microscopic BCS theory we need to start out with some background on band structures and quasi-particles. In any microscopic picture of a system we must start with the idea that in any physical system there are a finite number of discrete states that the system’s electrons can exist in, and at \(T=0\) electrons will occupy states with the lowest energy [9, 10]. The Pauli exclusion principle forbids electrons from occupying the same quantum state, as they are indistinguishable fermions (spin 1/2) they are antisymmetric under exchange [10, 11]. This means that if two electrons swap quantum states the sign of the wave function will flip. So if two electrons occupying the same state were exchanged the wave function would...
have its sign flipped, but the system would remain exactly the same, a contradiction for non-zero wave functions. In the case of a single atom’s orbitals this prohibits two electrons from having the same spin and angular momentum [11]. For a system of many atoms close together, such that electrons can move between the orbitals of multiple atoms, rather than speaking of the orbitals associated with individual atoms we consider combinations of the many individual atomic orbitals. These combinations of atomic orbitals form molecular orbitals that are delocalized across the extent of the system and conserve the system’s total number of orbital states [9, 11]. As the Pauli exclusion forbids electrons from occupying the same quantum state, identical atomic orbitals are combined to form symmetric/antisymmetric molecular orbitals with split energy levels. Electrons in the outermost occupied atomic orbitals that are highly overlapping and interacting are affected much more than electrons in orbitals closer to the atomic nucleus. The splitting of atomic orbitals into an equal number of molecular orbitals with different energies results in the average energy difference between states being inversely proportional to the size of the system [9, 11]. On the monumentally larger scale of macroscopic systems with $10^{23}$ or more atoms, the combination of atomic orbitals and splitting of their energy levels creates an effectively continuous distribution of quantum states with minute $(10^{-22} \text{ eV})$ energy differences between adjacent momentum states $\vec{k}_n$ and $\vec{k}_{n+1} = \vec{k}_n + d\vec{k}$ [9]. This nearly continuous distribution of quantum states is called an electronic band. The band exists in a system’s momentum space, and the agglomeration of all such bands is a band structure which can have energy gaps between bands with energies not associated with any momentum state [9]. In the momentum space (reciprocal space or k-space) of a crystal the momentum of an electron wave function is periodic with the reciprocal lattice vectors, so a larger momentum vector can be reduced to some remainder after subtracting an integer number of reciprocal lattice vectors [9]. This remainder will then fall inside the Brillouin zone, which is composed of the irreducible momentum states $\vec{k}$ in a crystal [9]. Because a band structure fills momentum space we can reduce it to the Brillouin zone using the same process applied to the periodic momentum vectors, seemingly as if it were folded back over itself at a higher energy level. Band structures are sensitively shaped by a material’s composition, structure, and environment and altered by changes in those factors [9]. So the shape of a band structure can provide immense amounts of information about a material’s properties such as electrical conductivity and optical absorption [9]. Despite their utility, they are only an approximation of a system’s quantum state and as such they can fail to accurately describe the system near surfaces, inhomogeneities, and strongly correlated electron systems [9]. At this point, it’s important to note that we are now inherently discussing quasiparticle electrons rather than a conceptualization akin to a single electron bound to a single proton in the hydrogen atom. The motion and scattering of a single electron through macroscopic systems involves immensely complex many-particle interactions [9]. Fortunately, the shape of the band structure is influenced by and includes contributions from such interactions in the uniform bulk of system [9]. This allows us to let many
complexities lay in the background while we study the behavior of electron quasiparticles in the fore [9]. Electron quasiparticles have the same charge and spin as a single electron, but they emerge from the collective motion of individual electrons in the system. This enables us to treat the quasiparticles as free electrons moving through a vacuum and scattering only due to interactions with other quasiparticles (including, but not limited to, other electron quasiparticles) or local impurities in the system [9]. The band structure is their dispersion relation \( E(\vec{k}) \), lumping many complex interactions into a momentum dependent effective mass for the free quasiparticle [9].

With a few notable exceptions, bands are parabolic with \( E \propto k^2/m_{\text{eff}} \) in the regions of \( \vec{k} \)-space surrounding their local maxima and minima, with the effective mass in those regions proportional to the degree of curvature. So the effective mass can vary by several orders of magnitude above or below \( m_e \), or even be negative in regions near a band maximum where the quasiparticles will move in the opposite direction due to an applied force [9]. If we imagine a system’s electron configuration in its ground state (\( T=0 \)) we would assign electrons to occupy momenta states of progressively increasing energy along the bands. We could continue this process until all of the electrons in the system are assigned to some state, and no electron is occupying a state with a higher energy than an empty state. We can then pinpoint the energy below which all states on the bands are filled and above which all are empty. We then subtract the energy of the lowest occupied state to obtain the Fermi energy, \( E_F \), which is used to calculate a number of related quantities for a given system [9].

At any temperature, the highest energy filled state defines an energy level called the Fermi level, with this energy creating the Fermi surface in momentum space below which the filled energy levels are termed the Fermi sea [9]. An electron quasiparticle in the Fermi sea requires an energy input sufficient to be excited into an empty state on a band above the Fermi level. We can now treat the excited quasiparticle as a free electron since it requires very little change in energy to move into adjacent empty states [9]. Simultaneously, this excitation leaves an empty state in the Fermi Sea that can freely move around as adjacent electrons fill the empty state and leave an empty state in their prior location. This allows us to treat this empty state as a quasiparticle hole that has opposite mass, charge and spin to a quasiparticle electron that would fill that state; allowing the recombination/annihilation of the electron and hole to conserve mass, charge and angular momentum [9]. This leads to the common renormalized ideation of the Fermi Sea ground state as a vacuum where the excitations of electron/hole pairs are a free exciton quasiparticle moving through space, known as second quantization [9]. The same picture is used for any other variety of quasiparticle in the lattice including phonons (quantized sound waves) and magnons (quantized spin waves) [9].
1.1.4 Microscopic BCS theory

The idea of an energy gap in superconductors had been postulated previously, but it wasn’t until the mid 1950’s that experimental evidence supported the concept. Experiments on the specific heat of superconductors below $T_c$ measured exponential behavior in $C \propto e^{\Delta/T}$ where the constant $\Delta$ is material dependent and proportional to the critical temperature of each superconductor [1]. Further evidence came from electromagnetic absorption measurements in the microwave and far-infrared spectrum which showed a minimum excitation energy of $\sim 2\Delta$. This minimum excitation energy is consistent with the specific heat measurements if the excitations always occur in pairs [1]. Around this time Bardeen, Cooper and Schrieffer (BCS) proposed a microscopic theory in which superconducting charge carriers are bound pairs of electrons in a degenerate ground state [1].

The gap energy in BCS theory is temperature dependent, increasing from zero at $T_c$ to its maximum $\Delta_0$ at $T=0$ [1]. Moreover, experimental data agrees with the BCS calculation that $\Delta_0 = 1.764k_BT_c$ [1]. At zero temperature the superconducting ground state is maximally occupied, and as observed in the microwave absorption experiments an energy $2\Delta_0$ is required to create an exciton quasiparticle [1].

A key insight by Cooper just prior to the development of BCS theory was that electrons on the surface of the Fermi sea can form a bound state with energy less than the Fermi energy in the presence of even a very weak attractive force [1]. More precisely, in the presence of any such attractive force the surface of the Fermi sea is unstable against the formation of a single bound pair of electrons with opposite momenta, this instability continues to increase the occupation of the superconducting state until the energy required to bind another pair of electrons is greater than $2\Delta_0$ [1]. This explains the superconducting charge carrier having mass $2m_e$ and charge $2e$, with the Cooper pair density $n_s^*$ being $1/2$ of the superconducting number density $n_s$. BCS theory is typically discussed in terms of electrons, but it equivalently describes superconductors in which the charge carriers are electrons or holes. While charge carriers will repel each other in free space, inside the superconductor this repulsion is screened out by the positive nuclei over distances larger than the interatomic spacing which is accounted for by the band structure and second quantization [1].

BCS theory shows that electron-phonon coupling is the source of the attractive force between electrons that causes Cooper pairing. Cooper pairs in a superconductor are composite bosons that occupy a degenerate ground state described by a coherent wave function, similar in concept to a Bose-Einstein condensate (BEC). In the proceeding discussion we will consider the simplest case of the S-wave superconductors. In an S-wave superconductor Cooper pairs form between electrons with opposite spin (total spin $S=0$), opposite momenta ($k,-k$), and zero net angular momentum ($L=0$), and their wave functions are written in the form of a plane wave. From the momentum space viewpoint, and with allusion to second quantization (but without any formality) electrons that form a Cooper pair initially start with equal and opposite
momenta (k & -k). An electron with momentum k (-k) scatters to a slightly different momentum k’ (-k’) via the exchange of a created (destroyed) phonon with momentum 
\[ p = k - k' = (-k) - (-k'). \]
So long as the change in electron energy \( E_{k-k'} \) is less than the energy of the phonon, \( \hbar \omega_p \), this results in an attractive force between the electrons\[1, 9\]. Because this interaction occurs through the exchange of a phonon it occurs over distances much greater than the interatomic spacing.

From a real space viewpoint the two S-orbital electrons with equal and opposite momenta have spherically symmetric probability distributions, and their superposition produces a spherical standing wave \[12\]. This standing wave results in an onion-like concentrically layered probability distribution, and thus a similar charge distribution \[12\]. This layered charge distribution distorts the lattice to create a virtual phonon with energy \( \hbar \omega_p < 2\Delta_0 \). The spherical standing wave and lattice distortion extend over a radius \( \sim \xi_{BCS} = \hbar v_F/\pi \Delta_0 \) (more than a micron in some materials) which lowers the Coulomb energy and thus the free energy of the superconducting state by \( 2\Delta_0 \). The net reduction in free energy from all of the Cooper pairs present in a superconductor makes the superconducting state more favorable than the normal state below the critical temperature. The lattice distortion would then move like a phonon as the Cooper pair moves through the superconductor \[12\]. This extended radius means that many Cooper pairs are overlapping at all times \[1\].

A key distinction between the BCS state and a BEC is the overlap of Cooper pairs. Which is in direct contrast with the non-overlapping bosons in a BEC. The coherence of Cooper pairs acts to minimize the exchange energy, keeping phonon exchange interactions small and in the attractive regime by restricting electrons in the condensate from scattering with large energy exchanges\[9\].

Although BCS theory is an accurate microscopic quantum model of conventional superconductors (by definition of conventional), and it provides corrections to the values of quantities like \( \lambda \) and \( \xi \) in various geometries, the macroscopic phenomena I will discuss in later chapters can be modeled using Ginzburg-Landau theory instead. Although Ginzburg-Landau theory was developed prior to BCS theory it can be derived as a special case of BCS \[5\]. The above treatment of BCS theory should be sufficient for a conceptual understanding of any references in later sections and chapters; as no quantitative exploration of BCS is undertaken herein. For instance, Chapter 3 covers our work with Ising superconductivity, a phenomenon that results from Cooper pairs forming in specific regions of the Brillouin zone from electrons with spins pinned out of the plane of a 2D superconductor due to spin-orbit coupling. Chapter 4 then focuses on macroscopic phenomena at interfaces between two and three dimensional superconductors, which we modeled using Ginzburg-Landau theory.

### 1.1.5 Ginzburg Landau Theory

Jumping back several years from BCS theory historically, the concept of a characteristic coherence length, \( \xi \), was developed by Pippard to explain how superconducting
charge carriers are influenced by the average of any applied fields over a volume of radius \( \xi \) \cite{1}. He successfully fit the current experimental data on lead and tin using a non-local generalization of Equation 1.10. Ginzburg-Landau theory is a macroscopic theory that describes the quantum mechanical behavior of superconductors close to the critical temperature. Realizing that superconductivity is a second order phase transition (the second derivative of the free energy has a discontinuity at the transition); they introduced a complex order parameter, akin to a quantum wave function, which describes the local carrier density \( |\psi|^2 = n^*_s \) \cite{1}. The order parameter \( \psi(\mathbf{r}) = \sqrt{n^*_s} e^{i\theta(\mathbf{r})} \) has an associated phase \( \theta \) that can vary smoothly and continuously in space over a characteristic coherence length \( \xi(T) \) \cite{1, 9}. This Ginzburg-Landau coherence length is approximately equal to Pippard’s coherence length well below \( T_c \) in pure superconductors. The magnitude of their complex order parameter can also vary over this coherence length, accurately describing the interface between a superconductor and a normal metal, where the superconducting order parameter grows from zero to its bulk value over a length \( \xi(T) \) from the interface, while a magnetic field in the normal metal will penetrate into the superconductor a distance limited by the penetration depth \cite{1}. Incorporating both a coherence length and a penetration depth they combine the two characteristic lengths into the dimensionless Ginzburg-Landau parameter, \( \kappa = \lambda/\xi \). Near \( T_c \) the Ginzburg-Landau coherence length diverges like \( \xi(T) \propto (1 - T/T_c)^{-1/2} \), and the London penetration depth behaves similarly since \( n^*_s \to 0 \) as \( T \to T_c \). Therefore, the Ginzburg-Landau parameter \( \kappa \) is both dimensionless and approximately temperature independent near \( T_c \), leading to its widespread use in characterizing superconductors. The most studied superconductors in these early decades were mostly pure elemental superconductors, with \( \lambda \ll \xi \) so that \( \kappa \ll 1 \) \cite{1}. Although several alloy superconductors had been studied that did not follow this pattern, Ginzburg and Landau did not consider them in their initial work \cite{5}. With the constraint that \( \psi \) varies smoothly in the superconductor (i.e. not using the London gauge), they expand an expression for the superconductor’s Helmholtz free energy (Equation 1.12) about the critical temperature (hence the theory’s validity near \( T_c \)), using Landau’s prior work on second order phase transitions \cite{5}. Their result is the Ginzburg-Landau equation (Equation 1.13); a differential equation in terms of the spatially varying \( \psi \), the vector potential \( \mathbf{A} \), and the two temperature dependent Ginzburg-Landau parameters \( \alpha \& \beta \) which are functions of the critical field and penetration depth \cite{1}.

\[
 f_S = f_N + \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{2m^*} \left( \frac{\hbar^2}{i} \nabla - e^* \mathbf{A} \right) \left( \frac{\hbar^2}{i} \nabla - e^* \mathbf{A} \right) |\psi|^2 + \frac{\mu_0 H^2}{2} \quad (1.12)
\]

\[
 \alpha \psi + \beta |\psi|^2 \psi + \frac{1}{2m^*} \left( \frac{\hbar^2}{i} \nabla - e^* \mathbf{A} \right) \left( \frac{\hbar^2}{i} \nabla - e^* \mathbf{A} \right) \psi = 0 \quad (1.13)
\]

The temperature dependence of the Ginzburg-Landau parameters produces two distinct regimes of solutions of the free energy near \( T_c \). In the absence of EM fields
and phase gradients we can simplify Equation 1.12 down to $f_s = f_n + \alpha |\psi|^2 + \frac{1}{2} \beta |\psi|^4$ [1]. When minimizing this free energy we find the trivial solution of $|\psi|^2 = 0$, based on the definition of $|\psi|^2$ this is equivalent to saying the superconducting carrier density is zero and the free energy is equivalent to that of the normal state. To avoid infinite carrier densities, $\beta$ must be positive, leaving the only nontrivial solution of $|\psi|^2 = \frac{-\alpha}{\beta}$, plotted in Figure 1.13 alongside a three dimensional view of the wave function with $\alpha < 0$ in complex space, [1, 13]. We can see that when $\alpha$ changes sign from negative to positive we are left with only the trivial normal state solution. This implies that there is a phase transition at $\alpha = 0$, so according to how we define $T_c$, $\alpha \propto (1 - T/T_c)$ which circles back around to our earlier contention that $|\psi|^2 = n_s^\star \rightarrow 0$ as $T \rightarrow T_c$ [1]. This shows that the superconducting state is a favorable energy state for the system below the critical temperature, which is when the superconducting carrier density becomes finite. Moreover, Figure 1.2b shows the revolution of 1.2a in complex space, showing that the two minima in 1.2a form a ring of minima in 1.2b. This proves that the wave function’s phase can hold any value in the superconducting ground state without changing the energy of the superconducting state, and that it can change throughout the extent of a superconductor so long as it is continuous everywhere.

$$\mathcal{F}(\mathbf{r}) = \frac{e^* h}{m^*} |\psi|^2 \left( \hat{\nabla} \phi(\mathbf{r}) - \frac{e^*}{\hbar c} \hat{A}(\mathbf{r}) \right)$$

(1.14)

The Ginzburg-Landau equation can also be used to rewrite Equation 1.10, which was written using the London gauge where net charge carrier momentum must be zero in the absence of electric or magnetic fields. The third term in the Ginzburg-Landau equation (Equation 1.13) is equal to the kinetic energy. A factor of $1/2m^*$ makes it clear that the squared parenthetical is the momentum per charge carrier. So we can
then write an updated equation for the supercurrent density as Equation 1.14 [1].

By taking the curl of this supercurrent equation we can again return to the second London equation, as the curl of the scalar phase is zero.

### 1.1.6 Flux vs Fluxoid quantization

Returning to the flux quantization thought experiment discussed in the introduction, which compared a hollow superconducting cylinder with a hollow cylinder of perfect conductor, we can apply the supercurrent equation from Ginzburg-Landau theory to understand how accounting for penetration depth in the interior wall of the cylinder alters our calculations. Let us consider the case of a superconducting cylinder cooled below \( T_c \) in the presence of a magnetic field. If we examine a cross section of a hollow cylinder far from the ends the London equations derivation of magnetic field strength inside the superconductor (Equation 1.7) tells us that the magnetic field will actually penetrate slightly into the interior wall of the cylinder, with the magnitude of the field inside the superconductor falling off exponentially over several penetration depths, \( \lambda_L \), such that for a distance \( r=3\lambda_L \) from the surface, \( H(r)=0.05H(0) \). Fluxoid quantization follows from integrating Equation 1.14 around a contour \( C \) inside a superconductor, but first we can clean up some constants by converting to \( \mathcal{E} \) in Equation 1.15.

Next, recognizing that the phase \( \phi(\vec{r}) \) must be continuous and the contour integral is a closed loop, so the integral over the gradient of \( \phi \) must be an integer multiple of \( 2\pi \). We can also apply Stokes’ theorem using the identity \( \overrightarrow{B} = \nabla \times \overrightarrow{A} \) to swap the third term to a surface integral.

\[
\Lambda \oint_C (\vec{J}(\vec{r})) \cdot d\ell = \frac{\hbar}{e^*} \oint_C (\nabla \phi(\vec{r})) \cdot d\ell - \oint_C (\overrightarrow{A}(\vec{r})) \cdot d\ell \tag{1.15}
\]

\[
\Lambda \oint_C (\vec{J}(\vec{r})) \cdot d\ell = 2\pi n \frac{\hbar}{e^*} - \oint_S (\overrightarrow{B}(\vec{r}) \cdot \vec{n}) \cdot dS \tag{1.16}
\]

\[
\oint_S \overrightarrow{B}(\vec{r}) \cdot \vec{n} dS + \Lambda c \oint_C (\vec{J}(\vec{r})) \cdot d\ell = 2\pi n \frac{\hbar}{e^*} = 2\pi n \Phi_0 \tag{1.17}
\]

Equation 1.17 is the fluxoid quantization condition, a generalization of flux quantization, for which the first term is zero. Applying this to the case depicted in Figure 1.3, if we select the contour \( C_1 \), the first term of Equation 1.17 is equal to the magnetic flux through the surface \( S_1 \) which covers the hollow region of the cylinder, but because the cylinder walls are penetrated by the magnetic field, this term is a non-integer multiple of \( \Phi_0 \). The second term integrates the supercurrent around the inner wall of the cylinder, and because the magnitude of this supercurrent is dependent on the strength of the magnetic field penetrating further into the cylinder, the
Figure 1.3: Flux vs fluxoid quantization in a superconducting cylinder

A cross-sectional view of a long hollow superconducting cylinder (considering only the interior magnetic field). A magnetic field $\vec{B}$ was applied before the cylinder was cooled below $T_c$, producing a supercurrent density $\vec{J}_s$ which quantizes the flux. Three contours ($C_1 : r = \xi$, $C_2 : r = \xi + 2\lambda$, $C_3 : r \gg 5\lambda$) and their associated enclosed surfaces are drawn for reference.

A combination of the second term and the first will be an integer multiple of $\Phi_0$. Contour $C_2$ behaves similarly, except now surface $S_2$ covers $\sim 2\lambda_L$ into the cylinder walls, and the magnetic flux through $S_2$ is increased by $\sim 90\%$ of the total flux penetrating the superconductor, while the integral of the supercurrent around $C_2$ has fallen to $\sim 10\%$ of the value around $C_1$ because the supercurrent density is lower further from the surface of the superconductor. Lastly, if we select contour $C_3$, which is deep in the bulk of the cylinder body, the entire magnetic flux is measured and the first term of Equation 1.17 produces an integer multiple of $\Phi_0$, while the second term must be zero because the supercurrent density in the bulk of a superconductor is zero. While the generalized fluxoid quantization is produced here starting from the Ginzburg-Landau equation, Fritz London had earlier worked out a more limited flux quantization condition from a quantum mechanical interpretation of the London equations, only off
by a factor of 2 due to the then unknown superconducting charge carrier $e^* = 2e$ [14].

1.1.7 Type-II Superconductors & Abrikosov Vortices

Abrikosov considered the case of superconductors with $\xi < \lambda$ such that $\kappa > 1$ and calculated the surface energy following in the footsteps of Ginzburg and Landau. They had found a positive surface energy at superconductor/normal metal interfaces for values of $\kappa \ll 1$, and declined to significantly explore the other scenario for lack of experimental relevance [5]. Abrikosov conducted similar calculations and found that superconductors with $\kappa > \frac{1}{\sqrt{2}}$ have a negative surface energy at such interfaces, making them energetically favorable [1]. Starting from the original Meissner era relation, Equation 1.1, we can see that any region within a coherence length of the
surface effectively lowers the volume averaged free energy of the superconducting state $f_S$ as the superconducting state dies off exponentially towards the surface in that subvolume. Symmetrically, and proceeding from the London era correction to the critical field calculation, any region within a penetration depth of a surface lowers the volume averaged free energy because the superconducting state isn’t excluding the magnetic field in that region [1]. This means that for $\xi/\sqrt{2} > \lambda$ (type-I), the energy per unit volume in regions $\xi/\sqrt{2} > r > \lambda$ is positive, but for $\xi/\sqrt{2} < \lambda$ (type-II), the energy per unit volume for the region $\xi/\sqrt{2} < r < \lambda$ contributes to a negative surface energy per unit area. Ginzburg and Landau concluded that a positive surface energy contribution limits the formation of domains in the superconductor to a scale much larger than $\xi$ up to the macroscopic sample size [1]. In contrast, Abrikosov found that type-II superconductors, as he named them, in the presence of an increasing magnetic field greater than some minimum magnitude will subdivide into smaller and smaller domains until the domain size is limited by $\xi$ [1]. These domains consist of normal metal regions surrounded by a multiply connected superconducting domain through which supercurrents continue to flow. Each normal metal domain is confined to a region with radius $\xi$ passing through the superconductor and channeling the magnetic field lines, as schematized in Figure 1.4a. This explained the alloy superconductor experiments from earlier decades that found critical fields significantly larger than predicted by Equation 1.1.

This allows a zero resistance superconducting state to persist in higher applied magnetic fields limited by the upper critical field $H_{c2}$. Although magnetic flux begins penetrating through the type-II superconductor at the lower field $H_{c1}$ than the critical field of type-I superconductors $H_c$ ($H_{c2} > H_c > H_{c1}$). Once the $H_{c1}$ minimum magnetic field level is reached, vortices don’t need to force their way into the superconductor, they can pop in (and out if they have an anti-vortex pair). Unlike the previously discussed case of a field applied to a superconducting hollow cylinder cooled in zero field, where an induced supercurrent forms to cancel the magnetic field inside the cylinder, in type-II superconductors the formation of this normal region by the penetration of magnetic flux is energetically favorable [1]. A supercurrent circulates around the normal core forming a vortex, concentrating most of the magnetic field inside the normal core (Figure 1.4). Similar to the case of a field cooled hollow superconducting cylinder, the flux inside is quantized, but each Abrikosov vortex only carries one flux quantum, since it is energetically more favorable for multiple vortices to form than for one vortex with a larger core to contain multiple flux quanta (this maximizes the domain wall surface area, which due to the negative surface energy of domain walls when $\kappa \geq 1/\sqrt{2}$, minimizes the energy of the superconducting state).

Revisiting Ginzburg and Landau’s treatment of a superconductor/normal metal interface where they showed the magnitude of the order parameter as increasing from zero in the metal to its bulk value over approximately a coherence length, we apply the same thinking to the vortex core. If we look at the cross sectional schematic of the vortex in Figure 1.4a, the red line plots the superfluid density as it drops
from its bulk value on either side to \(|\psi|^2 = n_s = 0\) at the center of the vortex. This change can occur on no shorter a length scale than that set by the coherence length, so the radius of the normal vortex core is a coherence length \([1]\). This leads to Equation \(1.18\), which calculates the upper critical field, \(H_{c2}\) by dividing the flux quantum by the cross-sectional normal area within the superconductor through which flux penetrates \([1]\).

\[
H_{c2} = \frac{\phi_0}{2\pi \xi^2(T)} = \sqrt{2}\kappa H_c
\] (1.18)

Equation \(1.18\) shows that the upper critical field in type-II superconductors is limited only by how tightly these flux carrying vortices can pack together before they overlap and destroy the superconducting state. Equation \(1.18\) also shows how this upper critical field can be rewritten in terms of the Ginzburg-Landau parameter \(\kappa\), using the GL definitions of penetration depth and coherence length, clearly showing the importance of \(\kappa = 1/\sqrt{2}\) as a crossover point between type-I and type-II superconductors.

Figure \(1.4a\) depicts the magnetic field strength across the vortex using a blue line and arrows, with an obvious maximum in the center of the normal core. For the case of a single vortex in a type-II superconductor with \(\kappa \gg 1\), Ginzburg-Landau theory approximates the magnetic field in each of the three domains as broken down in Equation \(1.19\) \([1]\). The magnetic field is approximately constant inside the normal vortex core, just outside of which it decays like \(\ln(\lambda/r)\), and then decays exponentially out to infinity. The vortex supercurrent according to the London equation is, of course, the derivative of these values, so it is zero inside the vortex, drops as \(1/r\) up to a penetration depth away, and falls exponentially from there.

\[
h(r) \approx \frac{\phi_0}{2\pi \lambda^2} \left[ \ln \frac{\lambda}{\xi} \right] \quad r \leq \xi
\]

\[
h(r) \approx \frac{\phi_0}{2\pi \lambda^2} \left[ \ln \frac{\lambda}{r} + 0.12 \right] \quad \xi \ll r \ll \lambda
\] (1.19)

\[
h(r) \rightarrow \frac{\phi_0}{2\pi \lambda^2} \left( \frac{\pi \lambda}{2r} \right)^{1/2} e^{-r/\lambda} \quad r \rightarrow \infty
\]

When multiple Abrikosov vortices form in a type-II superconductor, within several penetration depths of each other they will have a slightly repulsive force between them, this results from the interaction of the supercurrents (moving charges) with the fixed magnetic flux passing through the vortex, a form of the Lorentz force. Then the force on each vortex is \(\overrightarrow{F} = \overrightarrow{J}_s \times \overrightarrow{\Phi}_0\), where \(\overrightarrow{J}_s\) is the absolute supercurrent at the vortex’s position, and \(\overrightarrow{\Phi}_0\) is used as a vector pointing in the direction of the magnetic flux through the superconductor \([1]\).

The lattice constant for a square lattice is precisely \(a = (\phi_0/B)^{1/2}\), but since the interaction between vortices is repulsive, and the lattice constant for a triangular
lattice in an equal field is 7.5% larger, the triangular lattice is energetically more favorable \[1\]. In Figure 1.4b, we can see that supercurrents surround each normal vortex core, and by symmetry \( \mathbf{J} = 0 \) along the hexagonal boundaries in the triangular lattice. Using flux quantization on the contour \( \mathbf{C} \), we can see that a single flux quanta is fully contained within the bounds of this hexagon. For a triangular vortex lattice in a 1T magnetic field, the lattice constant \( a \approx 50 \text{nm} \). Depending on the penetration depth \( \lambda \), which is large compared to \( \xi \) for these calculations, the magnetic field at radius \( r \) according to Equation 1.19 could be decaying slowly compared to the vortex lattice parameter \( a \). For the triangular vortex lattice shown in Figure 1.4b we would expect the magnetic field to be at a non-zero minimum along the bounds of the hexagon, but the magnetic field at every point in the superconductor will be a summation of the decaying fields from every vortex. Using an argument from symmetry again, the total magnetic flux from a vortex outside of its hexagonal unit cell, will be equal to the total flux inside its hexagonal unit cell from every other vortex, tallying up to a single flux quanta in each hexagon. The same symmetry argument shows that in a uniform stable vortex lattice, a vortex will feel no net force from other vortices because their supercurrents will all cancel out. However, the Lorentz equation includes not just supercurrents from other vortices, but any and all supercurrents at the location of the vortex. So if an experimental physicist is sourcing a current through their superconducting sample in an applied magnetic field greater than \( H_{c1} \), they should expect vortices in their sample to experience a force due to that current. The cross product in the Lorentz force causes a vortex to move transverse to the direction of current flow. However, a moving vortex directly causes a change in magnetic flux and from Faraday’s law this results in an electric field anti-parallel to the supercurrent, decelerating the Cooper pairs, and dissipating energy i.e. creating resistance \[1\]. This would seem to imply that type-II superconductors cannot be used to create electromagnets. However, defects and grain boundaries in type-II superconductors can pin vortices in place, requiring some energy barrier be overcome for the vortex to be freed, as can external artificial defects such as magnetic nanoparticles \[1, 16\]. The statics and dynamics of vortices create several interesting states in type-II superconductors beyond the triangular vortex lattice such as melting into vortex liquids and vortex glasses, all dependent on how vortices move collectively \[17–21\].

Direct observation of vortices was originally accomplished via the process of Bitter decoration, in which small magnetic particles are deposited on a material to visualize magnetic field lines, but now scanning tunneling microscopy/spectroscopy (STM/STS) can image vortices by probing the density of states in a superconductor \[15, 20, 22, 23\]. STM uses an atomically sharp metal tip that is scanned over the surface of a sample while a bias voltage is applied between the tip and the sample. The measured tunneling current through the vacuum between tip and sample depends on the sample’s local density of states, the bias voltage, and the tip position \[15, 20\]. An STM can be operated with a constant current feedback loop connected to the
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Figure 1.5: Vortex lattice graph obtained via STS mapping

Graphs of the vortex lattice in NbSe$_2$ at 4.2K are plotted with a node representing each vortex and edges connecting nearest neighbors. Six such graphs are extracted from STM scans as the applied magnetic field is increased incrementally. The colored dots represent lattice defects. The standard triangular lattice gives each vortex 6 nearest neighbors, colors represent vortices with 4, 5, 7 or 8 nearest neighbors (pink, red, blue and green respectively). Black bars are 1 µm. Figure from [20]

z-axis piezo of the STM tip, such that the height of the tip as it scans across the sample changes rapidly to maintain a constant tunneling current. Here, the z-axis piezo voltage contains information about the sample height and the electron density at the energy of the bias voltage, without a clear method of deconvolution [15, 20]. STS is performed by varying the bias voltage while the scanning tunneling microscope tip is held at a fixed location and height [20, 23, 24]. The measured tunneling current can then be used to plot an I-V curve, or the dI/dV derivative of the I-V curve, which will be proportional to the local density of states over the range of bias voltages [15, 20, 23, 24]. A superconducting gap is visible in an STS spectrum as a dip in the dI/dV curve centered at the Fermi energy, therefore the core of a vortex
in a superconductor is seen as a location without the superconducting gap \([15, 20]\). 
\(dI/dV\) can be obtained directly during an STS measurement by using a lock-in amplifier to apply a small high-frequency AC voltage on top of the slowly varying DC bias voltage, resulting in the same measurement circuit described in Section 2.3.3 \([15, 20, 23, 24]\). STM and STS can be combined to directly produce a map of the differential conductance across the sample at a set bias voltage during an STM scan by using the same lock-in amplifier circuit. When the bias voltage is set to slightly less than the superconducting gap energy, the \(dI/dV\) map at will reveal the normal cores of vortices, where there is no superconducting gap with sub-nanometer resolution \([15, 20]\). While the resolution of Bitter decoration is limited by magnetic particle size and the large penetration depth in type-II superconductors, STM/STS images the normal core of a vortex directly with the full resolution of the instrument. This not only images the location of vortices in the superconductor, but also the shape of the vortex core which can be distorted in anisotropic superconductors with tilted fields \([15, 20, 25]\). Figure 1.5 shows graphs of a vortex lattice in bulk NbSe\(_2\) at six increasing perpendicular magnetic field setpoints. Extracting the vortex positions from STM/STS scans, each node (also known as a vertex, but that might get confusing in this discussion) on the graphs represents a vortex core, with edges connecting it to its nearest neighbors \([20]\). Nodes representing vortices pinned at or near lattice defects where the number of nearest neighbor vortices is fewer or greater than the 6 nearest neighbors expected in an ideal triangular vortex lattice are marked by colored dots \([20]\). As the field is increased the density of the vortex lattice increases, as does the number of defects. After each jump in field, the defects mostly remain in place, and the regions around pre-existing defects are more likely to gather new defects than regions with no defects \([20]\). This type of flux pinning is how type-II superconductors function in electromagnets where they carry large supercurrents. They must have enough sufficient defect density to pin their vortices in place, inhibiting flux flow and the associated dissipation.

### 1.1.8 2D superconductivity

Physicists often study condensed matter systems with reduced dimensionality in search of behavior in sharp contrast to three-dimensional behavior. One reason for this is that thermal fluctuations are enhanced in one & two dimensional systems as compared with 3 dimensional condensed matter systems \([27, 28]\). These enhanced thermal fluctuations disrupt the typical ordering seen in three dimensional systems as temperature is reduced. The Mermin-Wagner theorem proved that in one & two dimensions no spontaneous symmetry breaking of long range orderings can occur at finite temperatures in systems with only short range interactions \([29]\). This was first presented as a prohibition on ferromagnetism and antiferromagnetism in reduced dimension systems, but was shown to be generalizable to other types of ordering as well \([29]\). However, many 2D phenomena that seem to have long range order have been
Figure 1.6: Superconductor-Insulator quantum phase transition in WS$_2$

The quantum phase transition between superconducting and insulating states is shown in R(T) curves of ionic liquid gated WS$_2$, where the resistance is varied above and below the resistance quantum by tuning the carrier density. States above or below the resistance quantum go insulating or superconducting respectively at low temperature. Figure from [26]

identified as doing exactly this and are well studied. Monolayer graphene crystals have extremely small out of plane fluctuations [30]. Magnets lack long range order due to spin orbit coupling anisotropy. 2D superconductors have a continuous transition into the superconducting state, which was shown by Kosterlitz, Thouless, and Berezinski to be a topological transition involving quasi-long range order, now known by their initials as the BKT transition [27, 28]. BKT transitions at finite temperatures in superconductors involve spontaneous vortex-antivortex unbinding and motion, which
are easier to observe in clean limit systems than in dirty/disordered systems \[28\]. Figure 1.10 provides a timeline on the study of very thin superconductors in the clean and dirty limits.

Figure 1.10: Timeline on the study of very thin superconductors

A key signal of the crossover from 3D to 2D superconductivity is the angular dependence of the upper critical field near the in-plane orientation. The 3D anisotropic Ginzburg-Landau model predicts a smooth and rounded peak, while the 2D Tinkham model predicts a sharp cusp with local linear behavior on either side. Figure from \[31\]

We have observed signs of the BKT transition as a broadening of the bottom of the superconducting transition in many of our samples. However because \(T_{BKT}\) is so close to \(T_c\), it is difficult to study it further in these samples. 2D superconductors exhibit a quantum phase transition between superconducting and insulating states as disorder is added via any of several means such that the normal state resistance crosses \(R = \frac{\hbar^2}{4e^2} = 6.450 \Omega\), above which the would-be 2D superconductors transition to an insulating state \[32, 33\]. Experimental observations of this SI transition have been performed using magnetic fields, electrostatic gating (shown in Figure 1.6), and varying elemental dopant densities in a series of samples \[26, 34\]. In thin films of superconductors, many of the assumptions, limits and rules that apply in the bulk limit fall away. For instance, in applications of GL theory, if the film thickness \(d\) is less than the coherence length, you can make the assumption that neither the magnitude nor the phase of the order parameter can change along this axis of the superconductor, out-of-plane applied magnetic fields can be handled as constant throughout the
superconductor, and the superconductor can be treated in general as uniform sheet currents. Additionally, for in-plane applied magnetic fields, orbital pair breaking effects are completely suppressed when electrons cannot have out-of-plane momentum components and vortices cannot form.

Figure 1.8: In-plane and out-of-plane vortices in anisotropic SC
Radii of vortex core (dark blue) and flux penetration ring (grey) for in-plane and out-of-plane vortices in an anisotropic superconductor. To convert between conventions, in this schematic \( \lambda_{ab} = \lambda_{||} \) & \( \lambda_c = \lambda_{\perp} \). Adapted from [1]

Anisotropic layered superconductors offer an interesting example of 2D superconductivity. Depending on the coupling between layers, they can behave more like independent free-space 2D superconductors, or fully 3D superconductors, but are often somewhere in between. These anisotropic layered systems are common in the high-\( T_c \) variety of superconductors which are based on copper oxide layers with many and various additional elemental components (YBCO, BSCCO, TBCCO, etc.) [1]. However, for several decades these were all studied in their bulk forms (an exception is YBCO, see Figure 1.10), it wasn’t until the advent of van der Waals superconductors that anisotropic layered superconductors were studied in the few layer and monolayer limit. However, recently research has come full circle and some high-Tc superconductor monolayers have been isolated and measured, finding the \( T_c \) to be identical with optimally doped bulk samples in one instance [35]. In these layered superconductors with weak coupling between layers, in-plane vortices that form between layers are termed Josephson vortices (see Figure 1.9). As the layers are weakly coupled to each other, these vortices are analogous to the vortices that form across flux biased Josephson junctions.

\[
\left( \frac{H_c(\theta) \sin(\theta)}{H_{c\perp}} \right)^2 + \left( \frac{H_c(\theta) \cos(\theta)}{H_{c\parallel}} \right)^2 = 1
\]

\[
\left| \frac{H_c(\theta) \sin(\theta)}{H_{c\perp}} \right| + \left( \frac{H_c(\theta) \cos(\theta)}{H_{c\parallel}} \right)^2 = 1
\]
Figure 1.9: Diffuse Josephson vortex lattice in a layered superconductor. Josephson vortices can exist in between the layers of a layered superconductor, as the weak links between layers act like the weak link in an extended Josephson Junction. Figure from [36].

The difference in the behavior of a 3D anisotropic superconductor and a superconductor in the 2D limit is clearest in the angular dependence of their critical field near the in-plane orientation. As shown in Figure 1.7, the 3D Ginzburg-Landau equation gives the formula in Equation 1.20 that produces a rounded peak as the magnetic field direction crosses through the planar axis of an anisotropic 3D superconductor. By comparison, a superconductor in the 2D limit also has anisotropic critical fields, but the 2D Tinkham model in Equation 1.21 produces the sharp cusp in the critical field shown in Figure 1.21 when the magnetic field is applied precisely in-plane with near linear behavior at small angles in either direction [1, 31].

It is important to note that in the literature, when working with anisotropic superconductors, \( \lambda_\perp = \lambda_c \) (typically larger) and \( \lambda_\parallel = \lambda_{ab} \) (typically smaller) refer to the direction of the screening currents, not the direction of a magnetic field being screened, while \( \xi_\perp = \xi_c \) and \( \xi_\parallel = \xi_{ab} \) refer to the actual direction of coherence [1]. So a vortex through the plane has core radius \( \xi_{ab} \) and flux penetration radius \( \lambda_{ab} \), but an in-plane vortex will have anisotropic geometry with core height \( \xi_c \) and width \( \xi_{ab} \), but magnetic flux height \( \lambda_{ab} \) and width \( \lambda_c \).

**Pearl Regime**

\[
\lambda_{Pearl} = \frac{2\lambda^2}{d} \tag{1.22}
\]

In his thesis work, Dr. Judea Pearl was the first to explore vortices in the regime for which a thin film type-II superconductor is significantly thinner than its penetration depth, \( d \ll \lambda \). Using fluxoid quantization, Pearl found that the effective penetration depth for these films (Equation 1.22) is significantly greater than in thicker films [1, 38]. In some cases with \( d \ll \lambda \), the penetration depth \( \lambda_{Pearl} \) can be many microns or even millimeters long. The import of this is that vortices in these films will
The history of 2D superconductor fabrication has generally moved from thicker to thinner, and from higher disorder to the clean limit. New data points for TaS$_2$ and magic angle twisted bilayer graphene could extend the plot in the bottom right corner. Figure from [37].

behave fundamentally differently than Abrikosov vortices. Pearl vortices will have supercurrents surrounding them that follow the behavior of Equations 1.23 instead of Equations 1.19.

$$\vec{J}_s(r) = \frac{\Phi_0}{\pi} \frac{d}{2\lambda^2 R} \hat{r} r \ll \frac{2\lambda^2}{d}$$

$$\vec{J}_s(r) = \frac{\Phi_0}{\pi} \frac{1}{r^2} \hat{r} r \gg \frac{2\lambda^2}{d}$$

Comparing a Pearl vortex to an Abrikosov vortex, the $1/r$ current behavior (and $\ln(1/r)$ field behavior) is the same within a radius of a penetration depth. The penetration depth for a Pearl vortex is the Pearl length, so its magnetic flux is spread out over a significantly larger region than Abrikosov vortices despite having identical normal core radii [38]. This results in films with dimensions on the order of the Pearl length, $\lambda_{Pearl}$, being effectively uniformly penetrated by the magnetic field while remaining in a zero resistance state. Secondly, beyond a Pearl length from the vortex, the associated supercurrents transition to falling off with a $1/r^2$ behavior, rather than the exponential die off seen in Abrikosov vortices. This results in long range forces proportional to $1/r^2$ causing interactions between Pearl vortices that don’t occur in thicker superconducting films. These long range interactions would cause any vortex-antivortex pair to be attracted towards mutual annihilation no matter what their initial separation in the film. On the same note, it also prohibits clustering of Pearl
vortices without strong pinning forces holding them in place. They will repel each other even with significant separations, maintaining a strict lattice ordering. This long range force also disallows the spontaneous formation of vortices at equilibrium when any vortices already exist in the film. New Pearl vortices can only form when the film is out of equilibrium with the applied field. Pearl stated this in terms of a magnetic pressure that is required for vortex formation. His last observation is that in films on roughly the scale of the Pearl length, because of how broadly the supercurrents of a vortex are spread, the magnetic moment of a Pearl vortex is large because it is related to the diameter of the entire film, and independent of film thickness [38]. In anisotropic superconductors, where penetration depths for fields applied in-plane and out-of-plane differ ($\lambda_\perp \neq \lambda_\parallel$), the appropriate penetration depth for a calculation based on the plane the screening currents are moving in rather than the magnetic field vector. So in the case of a magnetic field being applied to an anisotropic superconductor in the out-of-plane direction, the superconductor is in the Pearl regime if $d \ll \lambda_\parallel$, since the screening currents are parallel to the superconductor’s plane. Following this, the Pearl length is then: $\lambda_{Pearl} = 2\lambda_\parallel^2/d$.

Clearly the strongest condition on the 2D nature of a superconductor is the material being a single atomic layer thick. However, a second atomic layer doesn’t necessarily change the superconductor’s properties (although in some cases it does, as shown in Chapter 3). A strong condition for classifying a superconductor as 2D is for it to be thinner than it’s out-of-plane coherence length, completely suppressing orbital pair breaking effects and all vortex formation due to in-plane fields. Clearly the superconductor’s behavior above and below this thickness will be distinct. However, I believe that is worthwhile to consider another, somewhat weaker, condition for what can also classify as a 2D superconductor. The Pearl regime provides a looser 2D limit for a sample’s thickness $d \ll \lambda$, but as discussed above the behavior of thin superconductors in this regime is radically different from that of thicker superconductors.

1.1.9 Josephson Junctions

Brian Josephson, in his thesis research, first identified the nature of a current tunneling through an insulating barrier between two superconductors in the absence of an applied voltage. This current results from weak interactions between the out-of-phase wave functions in the superconducting electrodes (see schematic Figure 1.11) [1, 39]. Later theoretical and experimental investigations showed that the tunnel barrier was not a fundamental part of this result, and that any form of weak link (insulating barrier, normal barrier, superconducting constriction, dissimilar superconductors, etc...) between superconducting reservoirs could produce similar outcomes, though sometimes altered significantly by geometric effects. The difference in phase is altered by a voltage across the weak link, while the current is generated by a phase difference. This results in both the AC and DC Josephson effects listed below.
An SIS Josephson junction is formed between two superconductors with phases $\theta_1$ & $\theta_2$ separated by a thin insulating barrier.

$$V(t) = \frac{\hbar}{2e} \frac{\partial \delta}{\partial t} \quad (1.24)$$

$$I(t) = I_c \sin (\delta(t)) \quad (1.25)$$

$$\delta = \theta_1 - \theta - 2 \quad (1.26)$$

$$\quad (1.27)$$

- **DC:** Phase difference $\delta$ across junction creates a current across junction
- **AC:** Voltage across junction drives phase & AC current at $\nu = 2eV/h$

The Ambegaokar-Baratoff relation in Equation 1.28 is a general relation for tunnel barrier Josephson junctions [40]. The product $I_cR_n$ is invariant over junction shape and can be generalized to a wide variety of junction types since it deals with the number of conductance channels and not their arrangement. It is valid in cases where current is carried between superconductors via conductance channels that will only support a single Andreev bound state each [41]. Since resistance is the inverse of conductance, and the critical current through a barrier is directly related to the density of conductance channels we can see that the product of normal state resistance and critical current is sufficient to characterize a certain combination of superconductor and tunnel barrier [1].

$$I_cR_n = \left( \frac{\pi \Delta}{2e} \right) \tanh \left( \frac{\Delta(T)}{2kT} \right) = \frac{\pi \Delta(T = 0)}{2e} \quad (1.28)$$

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\[ L_J = \frac{\phi_0}{2\pi I_c} \]  

(1.29)

\[ E_J = \left( \frac{hI_{c0}}{2e} \right) \]  

(1.30)

\[ I_c(\phi) = I_c \left| \sin \frac{\pi \phi}{\phi_0} \right| \]  

(1.31)

\[ \phi = B w(h + \lambda_1 + \lambda_2) \]  

(1.32)

The behavior of a Josephson junction can change dramatically based on its geometry. Very small junctions can be considered point-like, defined by a single valued phase difference across them. Extended junctions can have a spatially varying phase, such that the local supercurrent depends on the local phase difference across that region of the junction. Long Josephson junctions are defined as being larger in any dimension than their Josephson penetration depth. The Josephson penetration depth characterizes how far into a junction an applied field can penetrate. So in long junctions the screening effects inside the junction are significant and must be accounted for in calculations of the critical current [1, 42]. In point-like short junctions the

![Figure 1.12: Fraunhofer interference pattern](image)

The characteristic shape of a Fraunhofer interference pattern is plotted. This shape is identical for both single slit experiments and flux biased Josephson junctions. X-axis: magnetic flux through the junction/distance along the single slit. Y-axis: critical current of the junction/light intensity. Plot is unitless.

phase can be modeled as only time dependent, but extended short junctions require a
spacial variable too because the phase difference across the junction will be different at various points along the length of the junction. Extended junctions can be thought of as a linear array of $N$ point-like junctions, each having critical current $I_c/N$ [1]. The flux through the junction is calculated as the applied field $B$, multiplied by the junction width $w$, and its effective height $h_{eff} = h + \lambda_1 + \lambda_2$, which includes the penetration depths of the superconductors on either side. Plotting the critical current as a function of magnetic field or flux will produce a Fraunhofer interference pattern that has the same functionality as the intensity of coherent light shining through a single slit (Equation 1.31 plotted in Figure 1.12). This results because the local Josephson current magnitude and direction will change depending on the local phase $\varphi$ across the junction (Equation 1.33). Since the phase also changes with applied voltage Equation 1.33 can be generalized to include both time and space dependence in Equation 1.35. We can combine Equations 1.27 & 1.33 to get the local current at any point $x$ in an extended junction (Equation 1.34. This current distribution and the resulting Josephson vortices are shown for varying values of $B$ in Figure 1.13 where the critical current at each magnetic field can be calculated from Equation 1.31 and the local current can be calculated from Equation 1.34.

$$\varphi(x) = 2\pi \frac{B x h_{eff}}{\phi_0} + \varphi(x = 0)$$

(1.33)

$$I(x) = I \sin(\varphi(x))$$

(1.34)

$$\varphi(x, t) = 2\pi \frac{B x h_{eff}}{\phi_0} + 2\pi \frac{V t}{\phi_0} + \varphi(x = 0, t = 0)$$

(1.35)

As shown in Figure 1.13, if the current through the junction starts at the critical current $I_c(B=0)$ in zero field, the critical current of the junction will decrease when a magnetic field is applied in either direction until zero net current is travelling across the junction, $I_c(B=\phi_0)=0$. This occurs because Josephson vortices form inside the junction carrying a flux quanta and zero net current. Note that Equation 1.31 uses the absolute value of the sine term, so the net current direction is dependent on the initial current and the critical currents are symmetric for an applied field in either direction. This process repeats again until another full flux quanta enters the junction. The formation of each Josephson vortex corresponds to one of the minima of the Fraunhofer interference pattern in Figure 1.12. Halfway between these minima the Fraunhofer pattern has a local maxima when the total flux is $\phi = (n+1/2)\phi_0$. At these points junction still has the same critical current density, but because the Josephson vortices carry zero net current these peaks will keep diminishing in magnitude. After $n=1, 2, 3, 4$ flux quanta are in the junction, only $1/3$, $1/5$, $1/7$, $1/9$ of the junction length will not be occupied by Josephson vortices and only that diminishing segment will carry a net current.
Figure 1.13: B-field effect on Josephson current
A Josephson junction starts with its critical current $I_c(B=0)$ flowing through it (top) and a magnetic field is applied through the junction directed into (out of) the page in the left (right) column. The distribution and local direction of current flowing through the junction, when the junction’s net current is equal to $I_c(B)$, will modulate with field. Josephson vortices (light blue rings) will form when and where a flux quantum is passing through the junction.
1.1.10 Superconducting Quantum Interference Devices

A Superconducting Quantum Interference Device (SQUID) is a superconducting loop interrupted by two (DC SQUID) Josephson junctions, for which the critical current of the system is dependent on the magnetic flux passing through the center of the loop [39]. In the same way that the critical current of a single Josephson junction in a varying magnetic field forms an interference pattern analogous to shining a coherent light source through a single slit, the magnetic field response of a SQUID is analogous to shining a coherent light source through a pair of slits. When magnetic flux enters a single junction, it adds to the total phase difference across the junction proportional to the magnetic flux quantum. The total shift in the phase difference across the junction is distributed in local phase differences along the width of the extended junction, and it is these local phase differences that tune the local Josephson current between $\pm J_c$, resulting in a total current throughout the junction between 0 and $I_c$. Changing the flux through a junction can tune the magnitude of the net current passing through by generating local currents in the opposing direction, but an application of magnetic flux will not switch the direction of the net current flowing through the junction. Like the hollow superconducting cylinder discussed at the beginning of the chapter, a SQUID operates on the property of flux quantization, such that the total flux through the loop of the SQUID must be an integer multiple of the flux quantum. If a magnetic field is applied to a SQUID that would pass $1/4\Phi_0$ of flux through the SQUID, a supercurrent will form to cancel that flux and keep the total at zero, as with the cylinder. If the a magnetic field is applied that would pass $3/4\Phi_0$ of flux through the squid, a supercurrent forms in the opposite direction to total $1\Phi_0$ through the SQUID loop. This is the same as would happen if the hollow cylinder were field cooled with the same $3/4\Phi_0$ flux passing through it. Where these object differ is in the case where the magnetic field is increased such that the flux goes from $1/4\Phi_0$ to $3/4\Phi_0$ applied, the junctions switch direction and add to the flux totalling $1\Phi_0$ [1]. This reversing of the Josephson current can only happen spontaneously if the phase across a junction jumps spontaneously, which happens when a flux quantum passes through the junction. So the junctions are acting as gates that allow flux quanta in and out of the SQUID loop so as to round the applied flux to the nearest integer number total of flux quanta. If we were to consider a SQUID built with junctions extended across the width of the SQUID loop, this action of opening of the gate and passing a flux quanta through would be seen as a Josephson vortex entering the Josephson junction.
from the exterior of the SQUID loop, then passing through the width of the junction, and exiting into the center of the SQUID. Rather than a spontaneous jump in phase and flux, it would occur over some short period of time.

\[ I_{\text{max}}(\phi) = 2I_c |\cos \pi \phi / \Phi_0| \]  \hspace{1cm} (1.36)

Figure 1.14: Schematic of a basic SQUID loop

A current is passed across a SQUID loop in a magnetic field. The direction of currents around the SQUID loop depends on the phase across the two Josephson junctions.

For the mathematical description, we will simplify it down to a SQUID built using identical point-like junctions with critical currents \( I_c \). Then the total current that can pass through the squid from one side of the loop to the other is \( 2I_c \). If we treat the two junctions as one dimensional junctions, they are each defined by the phase difference \( \delta \) across them, and this phase difference controls the current \( I_J \) with the usual \( \sin(\delta) \) functionality (maximized at \( \pi/2 \)). Remembering fluxoid quantization, we know that when there is a single flux passing through the SQUID loop, the phase around the SQUID loop must change by \( 2\pi \) \([1] \). The phase must be continuous in the superconducting wires on either side of the Josephson junctions; therefore the only locations a sudden phase difference can exist is in the \( \delta_{1,2} \) discontinuities across the junctions (measuring \( \delta_{1,2} \) starting from the same side of the loop for both). This can then be written as a condition that summing the phase around a closed contour of the loop requires \( \delta_1 - \delta_2 + \Phi_{\text{loop}} = 2\pi \phi / \Phi_0 (\text{mod}(2\pi)) \) so only when the flux is an integer multiple of \( \Phi_0 \) can \( \delta_1 = \delta_2 = \pi/2 \) and allow the maximum critical current \( 2I_c \) to pass across the SQUID loop. If the total flux is some \( (n+1/2)\Phi_0 \), then the total phase
around junctions in the loop is $\pi$, resulting in both junctions carrying the equal and opposite currents and zero net current passing across the SQUID loop. Any addition source of current will split between both junctions, and while it will cancel out some of the current in one junction, it would add an additional boost to the current through the other junction that is carrying the parallel current. Having started with both junctions at their critical current density, it is clear that this adding the new current will surpass the junction’s critical current and drive it into a normal state. This sudden resistance would then shunt all of the current in the circuit through the other junction and drive it normal too. This pattern of behavior can be functionalized to write the maximum supercurrent that can cross the SQUID loop at any applied flux in Equation 4.9 [1]. The same equation governs the distribution of bright and dark spots in the standard double-slit experiment. Essentially, the currents flowing around a SQUID loop and passing through the Josephson junctions interfere with themselves in the presence of magnetic flux, reducing the total current that can pass through the SQUID loop.

The ideas introduced in this chapter should provide a more than sufficient conceptual background to understand and appreciate the research work I present in the succeeding chapters.

### 1.2 Introduction to van der Waals Materials

van der Waals materials are crystals with covalent bonds between atoms in one plane forming an atomically thin layer, and weak van der Waals forces along the axis normal to the plane, holding the layers together [43, 44]. Unlike covalent or ionic bonds, the extraordinarily weaker van der Waals forces are not a form of chemical bonding, instead they result from dipole-dipole interactions between closely spaced atoms or molecules and die off extremely quickly with increasing separation. This allows the atomic planes in van der Waals materials to be cleaved from their adjacent planes with little or no damage to the in-plane atomic structure. With proper techniques, and much patience, it is possible to isolate single atomic layers of these crystals. This capability opens new directions of research in ultra-thin films that were previously limited by the ability to grow single atomic layers on substrates, which was limited in many cases by lattice mismatches and and stability [45]. This thinning process, commonly called exfoliation, lets us characterize materials by their layer number to better understand how their properties change as they transition from the three dimensional bulk, through an intermediate phase and into wholly two dimensional structures. As briefly discussed in Section 1.1.8 a reduction in dimensionality often results in phenomena, such as the quantum Hall effect, that either aren’t observed or behave very differently in three dimensional objects. Even 2D systems that had already been created using prior techniques, such as two-dimensional electron gases (2DEGs) at the interface of semiconductors (in which the quantum Hall effect has been studied for decades), can be studied and manipulated in new ways when they
exist in an atomically thin crystal. The atomic thinness provides direct access to the surfaces of the 2D state, enabling precise manipulation, tuning and coupling to other systems that couldn’t be done previously when the 2D system existed relatively deep inside a 3D system. Wolfgang Pauli has been quoted as saying, "God invented the bulk; surfaces were invented by the devil" [46]. So it is quite proper that 2D materials, which comprise only two surfaces, are tricky to work with yet produce fascinating physical phenomena.

Graphene

The modern era of studying and manipulating van der Waals materials began in 2004 with the exfoliation of atomically thin graphene from a bulk graphite source [43, 47, 48]. Graphene is a two dimensional hexagonal lattice of carbon atoms, with a unit cell of two atoms, corresponding to the two inequivalent graphene sublattices. The charge carriers in graphene form a 2DEG because no states with out-of-plane momenta are possible in the two dimensional system. Magnetotransport measurements of few-layer, and later monolayer, graphene showed the existence of a wide array of phenomena including quantized landau levels, half-integer quantum hall effect, and Shubnikov-de Haas oscillations. Graphene is ambipolar, able to be gated into having either of hole or electron charge carriers. Around the point where the conduction and valence bands touch it has a linear dispersion relation with zero charge carrier density at the zero dimensional, highly symmetric, K and K̄ crossing points [43, 47, 48]. The K and K̄ points are the reciprocal lattice vectors alternating around the corners of graphene’s hexagonal Brillouin zone, with each having threefold symmetry. The linear dispersion relation around this crossing point causes the electrons to function as massless particles following the Dirac equation, rather than the Schrödinger equation. At the Dirac point in high quality devices the minimum conductance is quantized at $4e^2/h$, corresponding to the conductance quantum of a single transport channel multiplied by the fourfold spin and valley degeneracy in graphene. Ballistic transport of electrons over 10s of microns shows the mean free path along certain edges can be extremely large before any scattering occurs [49–51]. In addition the these massive initial discoveries, graphene has become one of the most studied physical systems in the world over the last 15 years, leading to a steady tempo of new discoveries. Many groups have integrated graphene into planar or Josephson junctions, observing the proximity effect and multiple types of resonant effects [42, 49, 50, 52–57]. One of the most exciting graphene developments in the last few years is twisted bilayer graphene (TwBLG) which uses the unit cell size of a moiré pattern that forms through the overlap of two carefully misaligned monolayer graphene lattices to create flat rather than rounded bands in the bilayer system [58, 59]. This band engineering results in new highly correlated electron states in the graphene system, including superconducting states with rather low carrier density [60]. This superconducting structure is now being engineered to build superconducting circuit components [61,
Despite how exciting these advances are, my only use of graphite in the work presented herein is as an intermediary metallic interface between a van der Waals superconductor and a deposited metal contact lead.

**Boron Nitride**

Monolayer hexagonal boron nitride (h-BN or just BN, as the other polymorphs are not van der Waals materials), often known in its bulk powder form as white graphite, is also a single atom thick hexagonal lattice. It’s similarity in binding structure to graphene can be attributed to boron and nitrogen being carbon’s two closest neighbors on the periodic table. However, the similarities with graphene’s crystal structure do not lead to similar electronic properties. The two inequivalent sublattices of h-BN are each composed solely of one of the two elements, this breaks multiple symmetries in the system that are unbroken in graphene. One consequence of this is that hBN is a wide bandgap ($\sim 6\text{ eV}$) semiconductor that is often used as an insulator in combination with other vdW materials [63].

![Figure 1.15: Tunneling current density through BN by layer number](image)

The tunneling current density through few layer BN can vary by over 6 orders of magnitude for certain combinations of voltage and barrier thickness. Figure from [63].

One of the early problems face by graphene researchers was how to isolate the monolayer from its chaotic environment for the cleanest measurements. A standard
substrate, SiO$_2$, was unsuitable because of its spatially varying charge distribution, physical surface roughness, and disorder causing breakdown in the 2DEG [64]. While efforts to suspend the monolayer above a hole in a substrate led to more uniform and higher quality samples, the devices were also much more difficult to fabricate. When multilayer BN was used as an intermediary substrate on top of SiO$_2$, it smoothed out the surface roughness, screened charge defects, and enabled charge mobility in graphene on the order of suspended graphene [64–67].

The large bandgap of BN has also been used to create deep ultraviolet photodiodes as well as moiré patterns to tune the band structure of graphene [59, 68–70]. However one of the most common uses of BN is as an insulating protective cover for encapsulating air and moisture sensitive van der Waals materials. Especially for our work with superconductors, the insulating BN flakes do not interact with the superconducting materials, nor do they interfere with our measurements while they protect the sensitive materials from the environment [71]. BN can also serve as a top or bottom dielectric with a dielectric constant of $\sim 3.5$ perpendicular to the layers for electrostatic gating of samples [72, 73] Additionally, in the few layer limit, BN can be used as a tunnel barrier while still safely encapsulating a sensitive sample. As shown in Figure 1.15, the tunneling current density through BN is inversely proportional to layer number and is spread over 6 orders of magnitude for layer number 1-4 [59, 63, 72]. This opens up many possibilities for using thin BN to encapsulate air sensitive superconductors while fully encapsulating them.

### 1.2.1 The van der Waals "Zoo" & Heterostructures

In addition the graphene, there exist many other one mono-elemental 2D hexagonal crystals, including stanene, silicene, and phosphorene (black phosphorus) among others. Some of these have the one-atom-thick nature of graphene, while others such as phosphorene are corrugated. Bi-elemental one-atom-thick systems similar to boron nitride have also been studied. However, the variety of van der Waals materials expands tremendously when multi-atom-thick crystals are considered. While their monolayers are thicker than graphene, they still exhibit two dimensional properties and, most importantly, can be exfoliated into monolayers using similar methods.

Transition Metal Dicalcagenides (TMDs) are a class of van der Waals materials with three atom thick monolayers, as shown in Figure 1.16, and the transition metal trichalcogenides are five atoms thick. The family of TMDs consists of crystals with MX$_2$ unit cells, where M is a transition metal, and X is a chalcogen. Many TMDs have several polymorphs that are still van der Waals materials that result in different symmetries in the system. The two TMD’s that will be the main focus of later chapters are 2H$_a$-NbSe$_2$ and 2H$_a$-TaS$_2$ (henceforth: NbSe$_2$ and TaS$_2$), intrinsically superconducting crystals that both exhibit charge density waves at temperatures above their superconducting critical temperature, these materials will be discussed further in the next section [74–77]. The transition metal dichalcogenides are some
of the most numerous and well studied families of van der Waals materials, but researchers are constantly investigating new crystal types such as the 2D magnets CrI$_3$, CrCl$_3$, and RuCl$_3$ in the trihalide family.

Although many of these van der Waals materials are fascinating in their own right as they are thinned down to the monolayer limit, the most attractive property they have is re-stacking those monolayers back into multilayer van der Waals materials. After all the time and effort spent exfoliating a crystal down to a monolayer this may seem like a Sisyphean task, but the catch is, that they can be stacked with any other van der Waals material to build a van der Waals heterostructure. Unlike molecular beam epitaxy or other growth techniques that require lattice matching or have other constraints on which two materials can share an interface, the van der Waals forces will form an interface between any pair of van der Waals materials from the monolayer limit to the bulk (nonsensical stack shown in Figure 1.17). This stacking of arbitrary materials in an arbitrary order, and arbitrary orientation is an incredibly powerful tool. Proximity effects occur when two materials share an interface and one material gains a property like superconductivity, or magnetism from the other. With 3D materials, only a thin surface region can be proximitized, but with atomically thin van der Waals materials, the entire material is the surface, so its global properties can change based on what it is adjacent to in a stack. Coupling between materials can slightly or drastically alter a band structure. As has been done with twisted bilayer graphene, just stacking the same material on itself at a rotation can create new phenomena. Twisted bilayer semiconducting TMDs also form moiré patterns that will alter the band structure of the material [78, 79]. One group showed that stacking an NbSe$_2$ flake directly on another NbSe$_2$ flake with an unknown and unplanned relative
Although van der Waals materials are often compared with Lego’s for their ability to be stacked together, they actually have many more possible configurations since arbitrary materials can be combined in arbitrary order with arbitrary orientations. Figure from [44]

rotation, although predictably some rotation since they weren’t attempting to align it, created a Josephson junction between the two flakes of NbSe$_2$ [80]. Apparently the misalignment of crystal axes was sufficient to weaken the link between the two flakes’ superconducting wave functions. Current methods for exfoliating, stacking, and fabricating van der Waals heterostructure samples are adequate for single device experimentation, but unfortunately there are not yet good methods for scaling the process up to chip or wafer scale at the present.

**Intrinsic vdW superconductors**

Like other TMDs, NbSe$_2$ has been studied in its bulk form as a layered superconductor for many decades, but only relatively recently was it isolated and studied in the 2D limit [81–83]. The isolation of monolayer and few-layer NbSe$_2$ crystals brought new understanding the the nature of superconductivity in the material. For instance, in the bulk limit the $T_c$ of NbSe$_2$ is 7K, but when samples thinner than $\sim$ 7 layers are measured, a reduction in $T_c$ is observed, decreasing with layer number until the most dramatic drop to $T_c = 3K$ is seen in the monolayer limit (see Figure 1.18)[76]. This results from the interlayer Cooper pairing in NbSe$_2$ which, with an out of plane
coherence length of $\xi \approx 2.7\text{nm}$, can pair electrons up to 3 or 4 layers away and strengthen the superconducting state in the system [76].

Figure 1.18: Layer dependence of NbSe$_2$ critical temperature
The critical temperature of NbSe$_2$ is constant from bulk thicknesses down to 7 layers, below which the decrease in interlayer coupling reduces the critical temperature down to 3K in the monolayer limit. Figure from [76].

On the other hand, while TaS$_2$ has a $T_c = 0.7K$ in its bulk form, it shows clear increases in its critical temperature as it is thinned, and in our work presented in the next chapter, we show that in the monolayer limit $T_c = 3K$ (See Figure 3.14) [77]. These intrinsically superconducting 2D materials open new avenues of research into 2D superconductivity, while previous efforts have studied deposited atomic monolayers of superconductors, often these are somewhat disordered and in the dirty limit where the mean free path is shorter than the coherence length [37, 45, 84]. In contrast, superconductivity in crystalline NbSe$_2$, TaS$_2$, and other gated and intrinsic van der Waals superconductors appears to be far in the clean limit [76]. These superconductors are proposed to be good experimental systems for studying spin-triplet superconductivity, topological superconductivity in the monolayer limit and multi-band superconductivity (2-3L NbSe$_2$) [76, 85–87]. Our results on studying Ising superconductivity in few-layer and monolayer NbSe$_2$ and TaS$_2$ are the subject of Chapter 3.

Gated vdW Superconductors
The first published paper identifying Ising superconductivity used ionic liquid gates on thin, but not few-layer, MoS$_2$ flakes [31]. An ionic liquid gate consists of an electrolyte containing large, polarized and asymmetric ionic molecules that can move throughout the liquid and rearrange and self-assemble in response to applied voltages or light [88–91]. This first study on Ising superconductivity in ionic liquid gated MoS$_2$ used the electrolyte N,N-diethyl-N-(2- methoxyethyl)-N-methylammonium bis(trifluoromethylsulfonyl)imide (DEME-TFSI) for the ionic liquid top gate [31, 92]. Since 2015, Ising superconductivity has been observed by gating another van der Waals material, WS$_2$, also using ionic liquid gating, where the Ising protection is even stronger than in MoS$_2$ due to the greater SOC energy [26]
Figure 1.19: Ionic liquid gating schematics

(a) MoS$_2$ is double gated with a MOSFET-style backgate and an ionic liquid top gate, a drop of electrolyte on the sample that covers both the MoS$_2$ and a nearby metallic electrode. Figure from [92]. (b/c) Large, polarized and asymmetric ionic molecules self assemble at the interface of the electrolyte and the van der Waals material upon application of a voltage and/or light illumination. Figure from [90]
Figure 1.19a shows schematically how a droplet of the ionic liquid is deposited on top of the sample material and extends over to touch an additional metal contact used to apply a voltage to the ionic liquid gate [92]. When a voltage is applied to this electrode, the polarized ionic molecules in the electrolyte separate and polarize the droplet, with a layer of cation or anion molecules self assembling along the van der Waals material being gated, depending on the applied voltage being positive or negative, respectively, and a separate layer along the voltage contact forming electric double layers [90]. This separation is schematically shown in Figure 1.19a as the red and blue spheres clustering on the Liquid Gate and the MoS$_2$ hall bar, while in the top right pane of Figure 1.19c the self assembly of the ionic molecules into an electrical double layer at the interface of the ionic liquid and the van der Waals semiconductor is shown to occur with the application of a voltage and/or light. This layer of charges forms within a Debye length of the liquid/semiconductor interface, on the scale of several nanometers, and while the electric field is strongest between the two sides of the electrical double layer, it extends beyond the double layer to penetrate into the semiconductor as well, decreasing in strength with distance [90].

As the ionic liquid polarizes via the movement of these large, polarizable, ionic molecules, charge cannot transfer from the electrical double layer in the ionic liquid into the semiconductor layer. This allows a much stronger electric field to be applied to the semiconductor using an ionic liquid gate than with a MOSFET-style gate, which are limited by the oxide's dielectric breakdown voltage. This opens up a much broader range of carrier densities that can be accessed using an ionic liquid gate than with the more traditional MOSFET-style gate. However, because the electric field decreases sharply with distance from the ionic liquid, only the topmost layer of MoS$_2$ can be gated into the superconducting region, as shown by the left axis of Figure 1.20. Since these devices are studied at cryogenic temperatures, it is important to note that the ionic liquid polarization "freezes" at approximately 180-200K, locking in the applied electric field from the ionic liquid top gate during the cooldown process, resulting in a lower resolution probe of the superconducting dome when only an ionic liquid gate is used, as seen in the right side of Figure 1.20 [90, 92].

In order to tune the carrier density in the top layer of the van der Waals semiconductor flake at low temperature, a MOSFET-style backgate can be used to push the carrier density slightly above or below the setpoint created by the ionic liquid topgate [26]. Repeating these steps by warming to 200K and making coarse steps with the ionic liquid gate, then cooling down to make fine steps with the backgate, the full superconducting dome of monolayer WS$_2$ was accessed, as displayed in the top half of Figure 1.21, with a metallic region above the superconducting dome and insulating regions to either side. While ionic liquid gates are still in use, more materials are being worked with that don’t require an ionic liquid gate to be tuned into superconductivity. Ionic liquid gates were used to induce superconducting states SnSe$_2$, while more traditional MOSFET-style gates sufficed to induce superconductivity in WTe$_2$ as well as various heterostructures containing 'magic angle' twisted bilayer graphene.
Figure 1.20: Phase diagram of gated MoS$_2$

**Left axis:** When gated with an Ionic liquid gate, the topmost layer of the MoS$_2$ flake has it’s carrier density pushed high enough to enter the superconducting dome. **Right axis:** several gate voltages are used to set different critical temperatures and roughly define one side of the superconducting dome. Figure from [31]

While some of these materials do show enhanced upper critical fields well beyond the Pauli paramagnetic limit, they can not be attributed to Ising superconductivity as they are centrosymmetric, or lack in-plane mirror symmetry. Gated van der Waals superconductors offer advantages and disadvantages compared to intrinsic vdW superconductors. Many of them produce monolayer or bilayer superconductors without the greater difficulty of exfoliating flakes that thin. More importantly, the gating permits much more tunability of the superconducting states, providing more avenues of exploration. Lastly, the shape of the gates can be used to explicitly define superconducting regions in the midst of a larger flake, this was recently done using twisted bilayer graphene to form planar Josephson junctions. However, working with gated superconductors does add slightly more difficulty to designing and fabricating the more complex device geometry.
Figure 1.21: Phase diagram of gated WS\textsubscript{2}

Dual gates are used to fine tune the carrier density in WS\textsubscript{2}. The ionic liquid gate is used for coarse adjustments at high temperature, then frozen in place during the cooldown at which point a topgate is used to make smaller movements about the ionic liquid gate setpoint. This two step gating process enables the full superconducting dome and the metal-insulator transitions on either side to be probed. Figure from [26]

1.3 Thesis (hetero)Structure

In the following chapters I will describe my experimental work with 2D van der Waals superconductors. Chapter 2 will cover the experimental methods and techniques I have used in my measurements and sample fabrication. Chapter 3 reviews pair breaking in superconductors and first introduces Ising superconductivity by explaining the theory underpinning Ising pairing in monolayer TMD superconductors. I review the previously published work that motivated our experimental efforts. Chapter 3 concludes with our results on monolayer TaS\textsubscript{2} and comparisons between few-layer
TaS$_2$ and NbSe$_2$. At the beginning of Chapter 4 I introduce several common non-superconducting contact methods and briefly review the current state of the literature on integrating vdW materials into superconducting circuits. The remaining majority of Chapter 4 then turns to focus on our DC measurements of 2D-3D Josephson junctions formed between Al (the standard for superconducting quantum circuits) and NbSe$_2$, a 2D van der Waals superconductor. First I interpret the cross-sectional TEM images of our device interfaces to characterize our fabrication methods. This is followed by our DC measurements of critical temperature, field, and current in these samples. The magnetic flux dependence of critical currents in 2D-3D Josephson junctions and the quantum interference patterns that result are thoroughly explored experimentally and modelled with GL theory. Chapter 4 concludes with our experiments on two of these 2D-3D contacts in parallel forming SQUIDs. Chapter 5 contains our most recent work on integrating 2D van der Waals superconductors into hybrid superconducting RF resonators. First I discuss possible applications for 2D-3D hybrid RF superconducting circuits and contrast RF measurements with DC magnetotransport measurements. I then cover our schema for measuring and isolating the kinetic inductance of NbSe$_2$ (or any other van der Waals superconductor). Limited data analysis on the current state of our measurements is performed, and our next steps on this project are planned. Concluding the main text is Chapter 6, in which I discuss several possible directions of future work on these specific projects after which I extend my remarks to trends and directions I find interesting in the broader field of 2D materials.

Several appendices are attached to this thesis. Appendix A displays my work with 3D printing with examples of visual aids, functional prints, and prototypes for instrumentation. I provide instruction on how to use MATLAB and Mathematica to turn your data or plots into 3D printed visualizations, and show that 3D printing has matured as a technology to become an accessible and highly useful tool in the modern experimental research laboratory. Appendix B presents an odd but useful technique where an ultra-sharp needle is mounted to a micromanipulator and used to directly interact with micron scale structures on a sample substrate. Originally intended to assist with partially failed lithographic metal lift-off, it has now become useful for cutting and shaping exfoliated van der Waals materials before or after stacking a heterostructure. Lastly, Appendix C presents a PDF of the Mathematica code written by Dr. David Pekker to model the 2D-3D Josephson junctions (including my minor modifications and comments). This code mostly automates the modelling procedure discussed in Section 4.4.1 for arbitrarily shaped 2D superconductors.
Chapter 2

Methods, Techniques and Instrumentation

2.1 van der Waals Material Exfoliation & Stacking

To stack and encapsulate the NbSe$_2$ and TaS$_2$ flakes with hBN we used now standard exfoliation and dry transfer techniques inside our glovebox’s inert nitrogen atmosphere [93–97]. Exfoliated NbSe$_2$ is more difficult to pick up with a top hBN encapsulation layer than graphene, but over time my success rate has been greater than 50% (although some flakes are so strongly adhered to their substrate they will never pick, even after many attempts). I typically select top hBN flakes that are less than 10nm thick so it doesn’t take as long to etch through the top encapsulation into the TMD layer. However, I also do not use few-layer hBN flakes as they are much more difficult to see after being picked up on the transfer slide and make for significantly more difficult alignment to the vdW superconductor. Lastly, I choose even thicker hBN flakes for the bottom encapsulation that are broader than the top hBN. This provides a firm and stable vdW substrate for the top layers of the heterostructure and helps prevent the edges of the top layers from wrinkling badly. After the NbSe$_2$ or TaS$_2$ flakes are fully encapsulated, they can be removed from the inert environment for nanofabrication [98]. The samples we stacked for our study of Ising superconductivity in TaS$_2$ were stacked with a graphite flake touching the edge of the TaS$_2$ flake. This allowed us to evaporate metallic leads onto the graphene and etch it into channels to use it as an intermediary connection to the TaS$_2$.

2.2 Nanofabrication

Nanofabrication of samples discussed in this thesis was performed in three different nanofabrication cleanrooms. Our nanofabrication processes originally took place in the Carnegie Mellon Nanofabrication Facility. In this facility we performed electron
beam lithography (EBL), reactive ion etching (RIE), and evaporation of Cr, Pd, Au, and Ni. After several initial experimental processes using the dedicated Al qubit PLASSYS in Dr. Michael Hatridge’s lab, ion milling and in-situ Al evaporation processes in a PLASSYS occurred in the Nanoscale Fabrication & Characterization Facility (NFCF), part of the University of Pittsburgh’s Gertrude E. & John M. Peterson Institute of NanoScience and Engineering (PINSE). This machine is functionally identical to the one in Dr. Hatridge’s lab, but is used with a much wider variety of materials. After several years of work in the original Carnegie Mellon Nanofabrication Facility, CMU built a new nanofabrication facility, the Eden Hall Foundation cleanroom, which is part of the Claire & John Bertucci Nanotechnology Laboratory. The migration of cleanroom tools from the old nanofab to the new one took over a year, during which time my device fabrication process frequently took me to all three cleanrooms in the same day.

Our fabrication process for the 2D-3D superconducting contacts discussed in Chapter 4 is originally based off of the graphene edge contact procedure developed by Wang et al. [99]. As noted below, we modified several steps to adapt to the use of the air sensitive TMDs in place of graphene.

### 2.2.1 Lithography

For electron beam lithography we use a bilayer resist with a thicker bottom layer (900nm MMA EL-13) and a harder/thinner top layer (200nm 950 PMMA A4). After exposure to the e-beam and subsequent development, this resist stack forms a natural undercut where slightly broader regions of the bottom layer are exposed than the targeted channels in the top layer of PMMA. This is due to the lower dosage required to expose the bottom layer, a recipe and technique that was first developed as the Dolan bridge method using photolithography for creating Josephson junctions via double angle evaporation [100]. This bilayer resist stack with a natural undercut also helps immensely with successful lift-off of deposited metals by stopping any connections between the metal deposited on the substrate and the metal on top of the resist from forming (switching to this bilayer resist drastically limited, but did not eliminate, our use of the technique described in Appendix B). Additional details focusing on fabrication of our 2D/3D hybrid superconducting resonators can be found in Section 5.1.4

### 2.2.2 Etching

After lithographic exposure and development, the patterned samples were examined under an optical microscope for quality control and then taken back to the cleanroom to be etched. The sample is loaded face-up in a Plasmatherm 790 Reactive Ion Etcher (RIE) where we expose it to an anisotropically directed plasma composed of 40:4 CHF$_3$:O$_2$ with 50W power for $\sim$3 min depending on the total thickness of
the entire heterostructure. After removing the sample from the RIE, it is stored in a
sealed vacuum container for transport that is can be backfilled with nitrogen gas and
then evacuated several times to minimize the oxygen and water vapor content that
might degrade the now exposed NbSe$_2$ cross section.

### 2.2.3 Plassys in-situ ion milling and Al evaporation

After another optical inspection to ensure sufficient etching, the sample is transported
in the vacuum container to PINSE, approximately 1km away, using either ambulatory
methods, public transportation, or private vehicle for hire (depending on atmospheric
conditions such as precipitation necessitating one of the later two).

![Schematic of the sample in the RIE and PLASSYS vacuum chambers.](image)

- **(a)** represents the reactive ion etching and then Ar ion milling steps, followed by
  in situ Al evaporation from both positive **(b)** and/or negative **(c)** orientations, 30
  degrees from vertical (from the frame of reference of the sample).

At PINSE, the sample is loaded into a PLASSYS e-beam evaporator with in-situ
Ar ion mill. The sample substrate is carefully aligned on the PLASSYS sample holder
($\phi$) and held in place using wire clips or Kapton® tape so that the angled evaporation
Figure 2.2: Substrates on the PLASSYS sample holder

(a) Mounting of sample substrates using wire clips. (b) Shadow of the wire clip in the Al film on the substrate resulting from a single angle Al evaporation. (c) Sample substrates attached to the sample holder using Kapton tape on two sides, after evaporation. (d) Removal of Kapton tape leaves the deposited Al film on the active regions of the substrates. (e) Interior of the PLASSYS’s top vacuum chamber with the sample plate oriented toward the Ar ion mill at the rear of the chamber. (f) Sample attached to the sample plate with wire clips, oriented 30 degrees from horizontal prior to Al evaporation (sample shutter is visible at bottom, shielding the sample from evaporating metal.

\( \theta \) is oriented properly on the sample and the wires don’t cast an evaporation shadow over the active region of the substrate (Figure 2.2 a-d). The Plassys sample holder is then loaded into the Plassys’s top chamber and evacuated below \( 5 \times 10^{-7} \text{mbar} \), after which the sample holder is rotated to face the Ar ion mill at the rear of the vacuum.
Figure 2.3: Al flag at end of contact lead
45 degree tilted SEM image of an Al lead contacting an encapsulated NbSe\textsubscript{2} flake. the body of the lead is 100nm tall, while the flag at the end sticks up several times that height. The encapsulating hBN is everywhere else in the image (with some polymer residue strands on the surface of the hBN), and the NbSe\textsubscript{2} flake is visible under the hBN as a lighter color on the left two-thirds of the image.
chamber (shown in Figure 2.2e). We use a particularly strong ion mill recipe to clean the substrate for 3 minutes and expose a fresh cross-section of the encapsulated NbSe$_2$, as some degradation may have occurred after removing the sample from the RIE and transporting it to the Plassys. Ideally we would perform the entire etching process with the PLASSYS in-situ prior to evaporation, however, etch rate testing showed that even using the highest ion mill settings only the Ar ions only etch vertically through several nanometers of hBN ($\sim 10 - 20$ layers) over 3 minutes and we have concerns with damaging the resist over the extremely long etch times that would be necessary to expose a cross section of a 30-60nm thick heterostructure. This low etch rate is largely because Ar ion milling is an entirely physical etch process with the Ar ions sputtering atoms off the exposed surface of the sample, while the RIE, as described in the acronym, uses reactive ions which chemically etch the exposed surface of the heterostructure as well as physical etching. After the ion mill step we begin evaporating Ti in the chamber while the sample is blocked by a metal shutter, this process is known as a 'Ti sweep'. This further lowers the pressure in the vacuum chamber because evaporated Ti is a 'getter', meaning it adsorbs to other atomic and molecular species in the low pressure vacuum chamber and fixes them to the chamber walls or other surfaces they land on. In a previous version of this process, we deposited a thin layer of Ti (3-5nm) on the sample beneath the thicker Al lead as an adhesion layer with the belief that the bulk Al lead would proximitize the Ti layer between the Al and the NbSe$_2$. We discontinued this practice after several resistive samples (which we later discovered were due to the lack of filters). After the Ti sweep, we proceed to evaporate the $\sim 100$nm thick Al leads. The substrate is tilted at a 30 degree angle from horizontal such that the Al evaporating from below is incident on the substrate at 30 degrees from the normal direction (shown in Figure 2.2f).

Unlike the original graphene edge contact methodology, we evaporate the Al at an angle not only to ensure full coverage and encapsulation of the exposed NbSe$_2$ cross section, but also to show the compatibility of this contact method with the Dolan bridge technique used for standard Al/AlOx/Al Josephson junction fabrication processes in state-of-the-art superconducting qubits. To this end, we have shown that contact can be made from a single angle of evaporation, as well as double angle evaporation on opposing sides of a NbSe$_2$ flake as shown in Figure 2.1b,c. After evaporation, the re-encapsulated sample can be removed from inert environments for short periods of time. We then soak the substrate in near-boiling acetone (54°C) to dissolve the EBL resist bilayer and liftoff the excess Al. After optical examination the substrate is mounted on a chip carrier using silver paste to ensure quality thermalization. Au wirebonds are made between the pads of the chip carrier and the Al bond pads connected to the sample leads on the substrate. The sample is then ready to be loaded in the dilution refrigerator for cooling.

As represented in these schematic figures and shown in Figure 2.3, the angled evaporation causes some Al to deposit on the side of the resist stack undercut, creating 'flags' that can stick up 500-700nm above the substrate. However, because of the
undercut in the resist these flags are disconnected from the metal on top of the resist. So they do not impact the liftoff of the metal on top of the resist, nor do they affect our magnetotransport measurements. However, they could be problematic for any further attempts to place van der Waals heterostructures in their vicinity and they could have an impact on highly sensitive RF cavity device designs.

2.3 Magnetotransport Measurement Methods

2.3.1 RC and GHz Filters

The most important addition to our measurement setup has been the combination of low-pass filters and shielding the sample holder and measurement lines. Much of work on filter design has been borrowed from the superconducting qubit community, where high quality, multi-stage low-pass filters have been de rigueur for many years [101, 102]. In fact, a low-pass filter solution designed for the superconducting qubit community has been commercialized and is available for purchase (QDevil QFilters). While we have designed and built low-pass filters for our dilution refrigerator at CMU, we have utilised the QDevil Qfilters in our secondary DC measurement setup in a dilution refrigerator at HatLab. The purpose of low-pass filters is to dissipate high frequency noise into heat in the cryostat before the signal is incident with the device under test, and thus reduce the power being transmitted into the superconducting sample. Most of this high frequency noise we are concerned with has a thermal origin (Johnson-Nyquist noise) and is evenly distributed across the frequency spectrum (white noise) with power density $k_B T$ because it is frequency independent, so multiplying by a bandwidth gives you total power $P = k_B T \Delta f$ [9]. Much of the utility of performing sensitive measurements at cryogenic temperatures is lost if high temperature thermal radiation is incident on the sample. Even when the sample, sample holder, and measurement lines are well thermalized to the cryostat, such that none of these components produce thermal radiation at temperatures above that of the cryostat, measurement lines that connect to room temperature electronics can propagate some amount of room temperature thermal radiation in the form of high temperature electrons, which is to say high frequency noise, (this also includes $1/f$ noise and any other spurious high frequency noise) all the way to the sample [103, 104]. This is due to the reduction in coupling between electrons and phonons in the measurement lines at lower temperatures, well thermalized measurement lines cool the phonon bath in the metal wire, but this thermalization fails to cool the electron bath which transmits the hot electrons from room temperature electronics. When the hot electrons enter the superconducting device under test they dissipate their energy in the superconductor and alter its measured properties [105, 106]. The effect of cryogenic low-pass filters can then be understood as thermalizing the electron bath with the phonon bath at approximately the base temperature of the cryostat (in even the best setups the electrons still seem to be $\sim 10 mK$ hotter than the base temperature, but this is a
significant improvement)\cite{106, 107}. The reduction in power delivered to the sample in the form of high frequency noise can then be found approximately by integrating over the bandwidth of frequencies blocked by any stage of the filters (accounting for roll-off and total dB reduction), or by measuring the difference in the temperature of electrons incident on the sample using a sensitive system such as a single electron transistor \cite{106, 107}.

A well designed filter setup consists of multiple components. RC or LC low-pass filters with a cutoff frequency around 10kHz can be used to filter out noise in the kHz and MHz range, but higher frequency noise will pass through these lumped element RC filters once the wavelength of the noise is on the order of size of the filter elements. This necessitates the use of an extended dissipative element coupled to the measurement lines to kill off GHz and higher frequency noise. Some of the first designs for this dissipative coupling element routed a coiled measurement line through a copper container filled with fine (30 – 50µm diameter) metal powder, typically stainless steel or copper, with SMA connections to semi-rigid cables on either end \cite{108, 109}. Copper powder filters function by dissipating high frequency signals in the measurement line, coupling the small grain powder to the magnetic field surrounding a current carrying wire. The extremely large combined surface area of the powder grains leads to the skin effect dissipating the high frequency energy in eddy currents as a heat load on the cryostat. Because the skin depth of metals is smaller for higher frequency signals, copper powder filters are more effective as the noise approaches GHz frequencies and above. The next generation of filter designs used waveguides and micron-scale photolithographically patterned distributed RC filters, but standard powder filters continued to be the most effective at GHz frequencies \cite{110}. The measurement limitations of coaxial lines and large physical volume required to individually filter each coaxial line led to the development of copper tape filters using either superconducting or resistive twisted pair measurement lines \cite{111, 112}. Copper tape twisted pair filters work by adding distributed capacitances between the wires and the copper tape ground along the length of the copper tape filter (typically ∼ 1m), creating an extended RC low-pass filter, the dissipative properties of which increase with the length of the tape filter [111–113]. The copper tape must be pressed tightly around each twisted pair to maximize the capacitance, with a small separation between each twisted pair, as shown in Figure 2.4a. The copper tape also serves as a shield to block any photons from hitting the measurement lines, this necessitates a good seal with the sample holder which must also be light tight.

In our measurement setup (schematized in Figure 2.6) we use an 18 inch long copper tape filter tightly pressed around our 8 pairs of measurement lines connecting directly to our copper clam shell sample holder (as shown in Figure 2.4c & 2.4d). Inside the copper clam shell, which has an overlapping lip machined around the rim to block any light seepage, we have a single stage RC filter soldered between two DIP sockets that our sample chip carriers can plug directly into (see Figure 2.4c). Although this setup works, and has enabled all of the following DC measurements in
this thesis, this is non-ideal for several reasons. The DIP format RC filters take up the majority of the volume inside the copper clam shell, limiting the possible sample orientations or new methods of mounting samples inside the clam shell. Secondly, the RC filters are in direct thermal contact with the sample, and the sample itself is thermalized only through the measurement lines connecting through the RC filters. So when a larger current is sent through the RC filters they inevitably heat up beyond the base temperature cooling power of the dilution refrigerator. This warms up the entire experimental space of the probe including the sample (seen most clearly in the bottom of Figure 4.19). This is part of a more general issue with the heat load on a dilution refrigerator from Joule heating in RC filters when using large currents.
LC-π filters don’t have the same heating issues but have several other trade-offs. Our redesigned filter setup will continue using copper tape twisted pair filters leading into the sample holder, but between those components we will mount a new PCB design for RC filters. These filters will use lower resistances and higher capacitances to reduce their heating with larger currents. The location of the PCB outside of the clam shell sample holder should also better thermalize the filters and wires so that any heat produced is not funneled directly to the sample inside the clam shell.

### 2.3.2 Pseudo 4-pt resistance measurements

![Diagram of pseudo 4-pt measurement circuit]

The applied current travels down the red sections of each circuit diagram while the voltage is probed from either end of the blue sections. Voltage drops will only occur where these overlap in the purple sections. Unlike a standard 4-pt measurement circuit that excludes the contact resistances alongside the line resistances, we use this pseudo 4-pt measurement circuit to explicitly include the contact resistances with the device resistance since those are what we are trying to measure.
In a pseudo 4-pt measurement setup, an Al lead which contacts the NbSe$_2$ flake is connected to multiple wire bonds and the measurement lines they lead to. This can be done by designing the Al lead to split in a "Y" shape multiple times with each end leading to a separate bond pad, or by using a large Al bond pad that has sufficient room for multiple wire bonds. As in a standard 4-pt resistance measurement, the current travels from source to drain through 1 pair of measurement lines that connect from our room temperature measurement equipment (SR860 lock-in amplifiers and DC current sources), and the voltage is probed via the other pair of measurement lines. This measurement setup, which was originally developed by William Thomson (Baron Kelvin) and is now typically taught in the first week of undergraduate electronics classes, is so useful because it eliminates line resistances from the measurement. The voltage probe lines carry no current and thus contribute no voltage drop to the voltage measured. This allows us to include high resistance ($10^4 \Omega$) RC filters on our measurement lines without affecting our measurements of device resistance (so long as we have four contacts, see Figure 2.3.2). The length of Al lead between the Al/NbSe$_2$ contact and the "Y" carries a current and serves as part of the voltage probe, but it adds no additional line resistance to our measurement when the Al is in its superconducting state below 1K and 10mT and does not cause a drop in voltage along its length. This allows our pseudo 4-pt resistance measurement to include these sections of Al leads, the NbSe$_2$ flake, and the Al/NbSe$_2$ contacts. We are then confident that when the first two are in their superconducting regimes, any resistance we measure is attributable to either of the Al/NbSe$_2$ contacts in the measurement circuit.

The signal to noise ration of the measurement signal is further improved by measuring the voltage probes with a lock-in amplifier. We use the lock-in amplifier to current bias the sample at a set frequency and then measure the voltage signal at that same frequency. The lock-in functions as a single frequency band-pass filter by mixing a phase sensitive measurement of the voltage signal with a internal reference signal that is frequency matched with the excitation current. Mixing these signals produces sum and difference frequencies, with the difference between the desired voltage signal and the reference frequency being a DC voltage, allowing strong low-pass filters to cut off any AC voltages (including the sums and differences of any DC input signal with the reference), and outputting a measurement of the voltage signal at the reference frequency. By measuring this result with a time constant longer than the period (ideally several periods) of the excitation frequency, a time averaged result is output. Care must be taken when selecting an excitation frequency, because all noise in the input signal is blocked unless it has the same frequency as your excitation signal (60Hz = bad). While this is all done digitally with modern lock-in amplifiers which use high quality analog-digital converters on inputs, the concept is the same.
Figure 2.6: DC magnetotransport measurement schematic
Two wirebonds are connected to the Al leads on either side of the resonator are bonded twice to perform a pseudo 4-pt resistance measurement. All filters are used in these measurements.

2.3.3 Differential resistance measurements of critical currents

In a standard IV measurement of an ohmic sample, the slope of the IV curve is equal to the conductance of the sample, or, alternatively, the reciprocal of the slope is the sample’s resistance. In non-ohmic samples, the IV curve may be multi-valued (gate tuned transistors) or show negative resistance (amplifiers and diodes) [114]. A differential resistance measurement is equivalent to taking the derivative of an IV curve, but it can also be measured directly. For some samples it is advantageous to measure the differential resistance $\frac{dV}{dI}$ directly rather than differentiate the IV curve, as even small amounts of noise in the IV curve are compounded when taking its
derivative. We can set up a measurement of differential resistance by sourcing a DC current modulated by a small amplitude AC current, and then measuring the AC response with a lock-in amplifier. The measured voltage response to a DC current combined with a AC current can be expanded as in Equation 2.1 when the AC current is small compared to the DC current (note: when AC and DC currents are roughly equal, this no longer functions as a reliable measurement of differential resistance, so the AC current must be smaller than any critical currents you expect to measure).

\[
V(I_{DC} + I_{AC}\sin(\omega t)) = V(I_{DC}) + \frac{dV}{dI_{DC}} I_{AC}\sin(\omega t) + \cdots
\]  

(2.1)

This results in the lock-in measuring a voltage equal to \( \frac{dV}{dI_{DC}} I_{AC} \) (plus any noise at that frequency) which we can divide by the magnitude of our AC excitation current, \( I_{AC} \), to obtain the differential resistance. In measurements of a superconducting component’s critical current, the slope of the IV curve sharply bends to vertical at the critical current then bends back at a new slope, representing the increase in resistance as the superconducting component goes normal. So in a differential resistance measurement, where we see a zero resistance state before a critical current, a sharp spike in \( \frac{dV}{dI} \) occurs at the critical current as the derivative of a vertical slope goes to infinity. However, in our measurements, this spike is always of limited height due to the time averaging in the lock-in amplifier as we sweep thorough the critical current (See Figure 4.17. After this spike, the differential resistance curve levels off at a new value equal to the resistance of the sample with that component in the normal state.

### 2.4 Lab and Measurement Instrumentation

As the second graduate student to join the Hunt Lab, I have had the pleasure and opportunity to participate in the designing, building, and/or setup of most of our fabrication and measurement equipment.

#### 2.4.1 Sample Holders and the Measurement Setup

In addition to the RC low-pass, Cu tape twisted pair filters and Cu clam shell system discussed earlier, I also made several other generations of dilution refrigerator sample holders and filters.

I machined our fridge’s very first sample mount (Figure 2.7a from a block of oxygen free high conductivity (OFHC) copper in the Physics department student machine shop. I designed it to hold a dual in-line package (DIP) socket without shorting any of the pins to the frame. I then had to further machine it with a Dremel in our lab because I designed a rectangle to have one of it’s side lengths equal to the circumference of a hole.
Figure 2.7: Dilution refrigerator sample mounts v0.1 & v1.0

(a) Dismounted dilution refrigerator probe "ladder" for mounting samples, solenoid magnet center point is $\sim 80\%$ towards the bottom (left side in photo). Sample holder v0.1 at bottom (b) sample holder v1.0 mounted with two samples oriented perpendicular to the applied field. (c) Thermalizing sample holder used to heat mounted sample substrates for wire bonding.

Needless to say, I used AutoCad to design our sample holder version 1.0 and modeled the location it would be mounted to ensure a good fit before we sent it out to be machined by a professional machinist. A useful design upgrade to this sample holder allowed it to be mounted with the sample plane approximately perpendicular or parallel to the solenoid’s field. This sample holder served us well for several years, but provided no shielding around the sample.

The last sample holder I designed and built was for performing DC measurements in the fridges at HatLab, which do not have a large magnet inside. This necessitated wrapping our own superconducting magnet. A handwrapped magnet powered from
a smaller current source should also provide higher magnetic field resolution. The QDevil QFilter was mounted in the fridge and attached to the measurement lines immediately prior to this sample holder. So while we did not need to design our own filters for this sample holder, but it did still need to be fully shielded. I designed the sample holder to have a lid with a 500 turn superconducting magnet (2mT design) wound on it with an indium seal to the base of the sample holder. While we only used this sample holder several times, it performed well the few times we loaded samples in it. Although we have yet to calibrate the magnet, we could do so by measuring the quantum interference pattern in one of our samples in both this sample holder and our main measurement setup and use the periodicity of the interference pattern as our calibration.

One project that didn’t turn out as planned was a set of 5-pole RC low-pass filters that would be mounted on our fridge measurement lines at the 4K plate (Figure 2.9a). I used the CMU makerspace PCB milling machine to cut the boards I had designed based on reference [102] (Figure 2.4b). I used silver epoxy to glue the individual surface mount components to the PCBs as I was concerned that solder might crack due to the different thermal contraction coefficients of the PCB and filter components. I also designed a large copper box to fully enclose these filters and wrapped the braids of measurement wires in copper tape from the output of this filter box all the way to the sample space (Figure 2.9b). As discussed previously, the goal here was to create a Faraday shield around measurement lines EM radiation that may introduce high frequency noise into the measurement circuit. The 5-pole low-pass RC filter was designed with each successive pole having a higher cutoff frequency, increasing the
Figure 2.9: 5-pole RC low-pass filter box
(a) PCB with surface mount components. (b) Filter box mounted on the 4K plate of our dilution refrigerator with Cu tape shielded measurement lines. (c) Interior of filter box with separate section at top for higher cutoff frequency filters. (d) Cutoff frequencies of filters using various bias resistors. Our typical bias resistors are 1,10MΩ, resulting in far too low of a cutoff frequency for our measurements.

rolloff of the combined low-pass filter. The entire filter setup was designed to work in the large magnetic fields just 2 feet above a 13T solenoid. A catastrophic oversight in this design was neglecting to account for the large bias resistors we use on the output of the lock-in amplifier to current source our samples. Since the cutoff of an RC filter is proportional to $1/\sqrt{RC}$, adding in this bias resistor drastically dropped the cutoff frequency below the region we use for our lock-in measurements (Figure 2.9d. This filter setup could be updated with new resistor and capacitor values and would then work as hoped for.
2.4.2 Transfer Station

One of my last instrumentation projects is building a new van der Waals material transfer station. While the two converted probe stations that we have used for the past 4-5 years have worked well, there are several improvements that we wanted to make. With the intense interest in the highly correlated electron states of twisted bilayer graphene, as well as other moiré effects in misaligned van der Waals materials, we wanted to have a precision rotation capability on our microscope stage. This will enable us to cut a single flake, pick up one part and rotate the stage a desired angle and align it with the other portion with great rotational accuracy. We also thought that at least one more degree of freedom on the micromanipulator could help with trying new transfer techniques. Lastly, we wanted to upgrade the quality of the microscope itself since our current transfer station can only use up to the 25x objective during transfers.

This new van der Waals material transfer station has been designed with 7 independent degrees of freedom and duplicated XY motion between the transfer slide micromanipulator stage and the microscope stage (Figure 2.10a). An Olympus BXFM modular microscope has been integrated into our custom baseplate and stand with long working distance 5x, 10x, 20x, and 50x objectives that work in bright and dark field modes (Figure 2.10b). In addition to a brighter LED light source, it also has a 4K camera and accompanying 4K computer monitor that will provide much higher resolution images. We are using the same style of dual stage heating system that we currently use, equipped with a PID controlled thermoelectric heater (now thermally counterbalanced with pressurized N2 flow over radiator vanes in the stage), plus the rapid heating from a 150W cartridge heater backing the thermoelectric heaters. Our choice of a computer controlled stepper motor rotation stage will provide us with ±0.025 degree accuracy in our rotations within a 360 degree range. Our XYZ transfer slide stage uses high-resolution micrometers with 0.5 µm sensitivity for each axis and any combination of axes can be upgraded with drop-in piezo actuators that would provide 30 nm resolution. The whole system will sit on a vibration isolated metal plate, and is designed to fit inside our nitrogen glovebox.
Figure 2.10: Design and features of a homebrew 2D transfer station
(a) the 10 degrees of freedom on the two stages (the 10th degree of freedom is unlabelled). The entire left side can slide forward two inches in Y for easy access to transfer slides and to pull the transfer slide out of the microscope’s field of view temporarily without losing your prior XY alignment. (b) Mock-up of the new Olympus BXFM microscope with the micromanipulator stage and heater stage beneath it after the design was finalized but prior to machining parts. (c) Picture of the assembled transfer station.
Chapter 3

Ising Superconductivity

Ising superconductivity is a phenomenon in which the superconducting state of a 2D transition metal dichalcogenide (TMD) superconductor is protected from both spin and orbital pair breaking in an applied in-plane magnetic field. In this chapter I will first review the theory of Ising superconductivity and the prior experimental work published by other researchers. The second half of this chapter will discuss our experimental work on Ising superconductors. These efforts alongside those of our internal and external collaborators, led by Sergio de la Barrera and Benjamin Hunt, resulted in our paper "Tuning Ising superconductivity with layer and spin–orbit coupling in two-dimensional transition-metal dichalcogenides" being published in Nature Communications [115].

3.1 Ising Superconductivity background

3.1.1 Pair Breaking Effects

Superconducting states are destroyed by an applied magnetic field in two main ways, orbital pair breaking (leading to vortex crowding in type-II superconductors) and paramagnetic spin pair breaking. Respectively, these pair breaking effects are due to the Lorentz force and paramagnetism, as schematically displayed in Figure 3.1 [116, 117].

Orbital pair breaking

For Type-II superconductors, Figure 3.1 plots the Gibbs free energies of the normal state and superconducting state as functions of the applied magnetic field B. The free energy of the normal state (including Pauli paramagnetism) is in red, and it intersects the zero-field free energy of the superconducting state at \( H_P \) (\( B_P \) on plot) the Pauli paramagnetic limit. The Gibbs free energy of the superconducting state in a magnetic field is plotted in blue, and it intersects the red line at the standard \( H_{c2} \) (\( H_{c2}^P \)
Pauli paramagnetism decreases the Gibbs free energy in the normal state (red line) as field increases. In the absence of orbital effects, the Gibbs free energies of the normal and superconducting states intersect at the Pauli paramagnetic limit $B_P$. Including orbital effects, the Gibbs free energy of the superconducting state increases with the applied magnetic field until it crosses that of the normal state at $B_{c2}^P$ (including Pauli paramagnetism), or $B_{c2}^\ast$ (without Pauli paramagnetism). Figure from [117] on plot), and the zero-field normal state free energy at $B_{c2}^\ast$ on the plot (this being a relevant field for bipolarons, a proposed theory of high-$T_c$ superconductors)[118]. Though they are often interchanged freely in the treatment of superconductors, Fuchs et al. describe this figure as a plot of the Gibbs free energy rather than Helmholtz free energy due to the presence of the applied magnetic field (though they still use the labels $F_{N,S}$) [1, 10, 117, 119, 120]. In zero field the Gibbs (G) and Helmholtz (F) free energies of a superconductor are equivalent, which explains the earlier use of the Helmholtz free energy to calculate the critical field and in the development of the Ginzburg-Landau equation. Thermodynamically speaking, both free energies are appropriate when the system is in contact with a thermal reservoir (has constant $T$) and their magnetic energy terms can be written using the magnetic analogues of pressure (-P) % volume (V) which are magnetic field (H) & net magnetization (M) respectively (since the pair of -P,H are both intensive properties and the latter pair of V,M are extensive and depend on the size of the system) [10]. In accordance with their treatment of pressure and volume, the Gibbs free energy is of use in systems with constant H, while the Helmholtz free energy is applicable to systems with constant M, with an appropriate Legendre transform relating Equations 3.1,3.2.

$$dF = -SdT + HdM$$ \hfill (3.1)
$$dG = -SdT - MdH$$ \hfill (3.2)

Practically speaking, in an experimentally where we apply a magnetic field to a cold sample inside a solenoid, we are holding $T$ and $H$ constant, and a proper analysis of the system attributes its behavior to the minimization of the Gibbs free energy rather
Ising Superconductivity

than the Helmholtz free energy [10].

In type-I superconductors, the critical field has been found using Helmholtz free energy calculations, and modified to account for the magnetic penetration depth. These produce results that agree with the following thought process of depairing currents, but occur without letting any vortices form. In type-II superconductors, the expression in Equation 1.18 is conditioned on the superconducting state being destroyed when the local magnetic field \( H - H_c \) in a vortex of radius \( \xi \) causes a flux greater than or equal to the magnetic flux quantum, \( \Phi_0 \). If you combine this equation with the vortex lattice constant equation, at \( H_c \), we find that the lattice constant \( a \approx 2\xi \). This demonstrates an equivalence between local and global pair breaking conditions; the local magnetic field cannot cause more than a single flux quantum to penetrate a vortex until the vortices are already crowding and overlapping. One last and more fundamental, though equally equivalent approach to find this same upper critical field is to first consider the supercurrent surrounding a vortex. The supercurrent density is at a maximum at \( r = \xi \). Equation 1.9 says that the current density is the derivative of the local magnetic field, applying this to Equation 1.19 shows that current density is proportional to \( 1/r \) for \( r < \lambda \), if we take the limit as \( r \to 0 \) of this supercurrent around the vortex, it diverges and necessarily the kinetic energy of the charge carriers exceeds the BCS gap energy, breaking the Cooper pairs and destroying superconductivity in the region. At the radius of the vortex, \( r = \xi \), the maximum current is then \( \Phi_0/2\pi\lambda^2\xi \). This is the depairing current density at which the kinetic energy of the supercurrent is equal to the BCS gap energy. Once the applied magnetic field surpasses the upper critical field vortices crowd together and the supercurrent in those regions of the superconductor is pushed above the depairing current density, equivalent to vortex cores where \( \psi \to 0 \) overlapping, destroying the superconducting state everywhere. These chained approaches are all ways of describing the effect of orbital pair breaking, where the Lorentz force on electrons in a Cooper pair increases their momenta until they each have kinetic energy greater than the superconducting gap energy.

### Paramagnetism and diamagnetism

In any treatment of magnetism in materials it’s best to begin with the fundamental magnetic dipole moment, an infinitesimal loop of current. The magnetic moment will be \( d\mu = 1dS \), where \( dS \) is an area vector in a direction normal to the loop plane depending on the current direction via the right hand rule [121]. Any larger current loop can then be treated as an aggregate of \( d\mu \) magnetic moments by integrating over the area to get \( \mu = I\oint_S dS \). The Lorentz force on a charge moving through a magnetic field can be adapted to a current carrying wire, \( \vec{F} = q\vec{v} \times \vec{B} = \int_0^L I dl \times \vec{B} \). By definition a current loop is closed; so for a square loop with side length \( d \) in a uniform field the force on opposite sides will cancel resulting in zero net force in a uniform field due to symmetry [119, 121]. However, zero net force is not the same as zero force
on the loop, without loss of generality, we can consider the square loop oriented such that the force on one pair of opposing sides is in the plane of the loop and cancel, while the other pair of sides has canceling forces that are out of the plane of the loop. The later forces will have the form $F_1 = -F_3 = I dB$, resulting in a torque [119, 121].

$$
\tau = \vec{r} \times \vec{F} = \tau_1 + \tau_3 = 2 \frac{Id^2}{2B \sin \theta}
$$

(3.3)

Introducing the magnetic moment into this equation results in a torque $\tau = \mu \times B$. Since there is zero net force on the loop, the only work performed in the system is the rotation of the loop through an angle $\theta$ due to the torque, Equation 3.4 [119]. This torque on the magnetic moment is always perpendicular from the direction of the magnetic field, so rather than aligning the magnetic moment with the field, it precesses about the field’s vector.

$$
W = \int_0^\theta \tau d\theta = \int_0^\theta \mu B \sin \theta d\theta = \mu B (1 - \cos \theta)
$$

(3.4)

$$
U = -\mu B \cos \theta = -\mu \cdot \vec{B}
$$

(3.5)

From these expressions for the energy of (Equation 3.5), and torque on (Equation 3.3), a magnetic dipole moment in a magnetic field, we can proceed to treat the magnetic moment of an electron. In the classical picture, an orbital electron has both a magnetic moment $\mu$ and orbital angular momentum $L$ associated with its circular motion about the nucleus, and these can be related by the gyromagnetic ratio $\gamma = \mu / L$. Continuing on this classical path, we can treat the orbiting electron with radius $r$ and velocity $v$ as a current loop, where $I = -ev/2\pi r$ leads to $\mu = evr$ and the ground state angular momentum $L = m_e vr = \hbar$ leading to the Bohr magneton $\mu_B$ and gyromagnetic ration $\gamma$.

$$
\mu_B = \frac{e\hbar}{2m_e}
$$

(3.6)

$$
\gamma = \frac{-e}{2m_e}
$$

(3.7)

This points to the fundamental idea that a system’s magnetic moment and angular momentum are inextricably connected. That classical approach produces the Bohr magneton, a combination of several measurable constants. The spin magnetic moment of an electron $\mu_s = g\mu_B S/\hbar$ is proportional to both the Bohr magneton and its spin. However, due to anomalous magnetic moment of an electron with spin $1/2$, the dimensionless correction factor $g_s = 2(1 + \alpha) \approx 2$ (where $\alpha$ is the fine structure constant) must be included according to quantum electrodynamics to match experimental measurements [119]. So an electron with no orbital angular momentum ($L = 0$) in a magnetic field $H$ has an energy contribution $E = \mu_e B = \mu_s B = g_s \mu_B SB/\hbar$ [119].
While an electron with orbital angular momentum will have \( E = \mu_e B = g_J \mu_B J B / \hbar \) where \( g_J(J, L, S) \) is the spin & angular momentum dependent Landé g-factor and \( J=L+S \) is the total angular momentum [119].

Magnetic susceptibility \( \chi \) is defined as the relation between the magnetization \( M \) in a material and the magnetic field \( H \), as related by the vacuum permeability \( \mu_0 \), \( \chi = \mu_0 M / H \) [121]. The magnetic susceptibility of a material alters the material’s magnetic permeability linearly as \( \mu = \mu_0(1 + \chi) \) such that the magnetic flux \( B = \mu H = \mu_0 (1 + \chi) H = \mu_0 (H + M) \) is the superposition of the magnetic field in a material and its magnetization [121]. These relations implicitly average over some volume of the material in question. Materials with \( \chi > 0 \) are paramagnets with their magnetization aligned with the magnetic field (boosting the magnetic flux), while materials with \( \chi < 0 \) are diamagnets with a magnetization opposing that of the magnetic field (depressing the magnetic flux) [119, 120]. This connects back to the concept introduced in Section 1.1 of perfect diamagnetism, where \( \chi = -1 \), and the magnetization cancels the magnetic field resulting in zero magnetic flux. Of course, as we’ve shown, in superconductors perfect diamagnetism in the bulk results from supercurrents near the surface rather than a volumetrically dispersed diamagnetic susceptibility.

**Pauli paramagnetism**

Pauli paramagnetism results from an additional susceptibility term \( \chi_P \) that arises when spins in an electron gas gain or lose energy due to an applied magnetic field. Every momentum state in a normal metal can hold two electrons with opposite spin, due to the Pauli exclusion principle. When a magnetic field is applied upwards on a normal metal approximately half of all spins (spin down) will gain energy while the remaining half of opposing spins (spin up) will lose energy in the amount of \( \pm \mu_B B \). This creates two spin-polarized electron sub-bands that are separated by \( 2\mu_B B \). The shift in energy from this magnetic field will also result in a shift in spin populations such that there is a bias towards spin up electrons, as they are aligned with the field. The unbalanced spin populations create a magnetization in the metal. We can use the net magnetization to calculate \( \chi_P \) if we know more about the spin population dependence on the applied field. In the free electron model, in three dimensions, the density of states for electrons with energy \( E \) is:

\[
D(E) = \frac{3n}{2E_F} \sqrt{\frac{E}{E_F}} \quad (3.8)
\]

\[
E_F = \frac{\hbar^2 k_F^2}{2m_e} \quad (3.9)
\]

\[
(3.10)
\]

At the Fermi energy, \( E=E_F \), so \( D(E_F) = 3n/2E_F \). The splitting of spin pop-
lations with energy $2\mu_B B$ separating them results in an excess density of spin-up electrons \( n_\uparrow = 1/2D(E_F)\mu_B B \), and the equal and opposite change for spin down electrons \([119]\). Net magnetization is simply the net number of oriented spins, so:

\[
M = \mu_B(n_\uparrow - n_\downarrow) = D(E_F)\mu_B^2 B \tag{3.11}
\]

\[
\chi = \frac{M}{H} = \frac{\mu_0 M}{B} = \mu_0\mu_B^2 D(E_F) \tag{3.12}
\]

\[
\chi = \frac{3\mu_0 n\mu_B^2}{2E_F} \tag{3.13}
\]

From here, Clogston and Chandrasekhar make an argument from free energy. Going back to Equation 1.1, we will ignore all effects other than the Pauli spin susceptibility \( \chi_P \), which affects the normal metal free energy, but not the free energy of the superconducting state \([1, 76, 122, 123]\).

\[
f_N - 1/2\chi_P H^2 = f_S \rightarrow \mu_0\mu_B^2 D(E_F)H^2 = f_S - f_N = 1/2D(E_F)\Delta_0^2 \tag{3.14}
\]

\[
H^2 = \frac{\Delta_0^2}{2\mu_B^2} \tag{3.15}
\]

\[
H_P = \frac{\Delta_0}{\sqrt{2}\mu_B} \tag{3.16}
\]

\[
H_P = 1.84T_C(T/K) \tag{3.17}
\]

Solving for the magnetic field \( H \) produces the Pauli paramagnetic limit, \( H_P \). BCS theory can then be used to replace the superconducting gap, \( \Delta_0 = 1.76T_c \), and obtain the classic result \( H_P = 1.84(T/K)T_c \) \([1, 122, 123]\).

**Spin pair breaking**

Due to the component of the field parallel/antiparallel to the up/down spins of a Cooper pair, as shown in Figure 3.1, the Zeeman effect splits the energy of the two electrons until \( \Delta E = 2H \cdot \mu_e \) exceeds twice the superconducting gap. While components of a magnetic field perpendicular to the spin orientations cause a torque on the electron magnetic moments (anti-parallel to the spin) pulling them out of their opposing orientations. In an S-wave superconductor, spin pair breaking occurs (in the absence of orbital effects & spin-orbit scattering) at or below the Pauli paramagnetic limit given by Equation 3.17 and related to the critical temperature of the superconductor by the BCS gap equation \([1, 122, 123]\).

The superconducting state in Ising superconductors is protected from these deleterious mechanisms by their strong spin orbit coupling \([31]\). SOC in Ising superconductors produces a large effective Zeeman field pinning the electron spins of the Cooper pairs out-of-plane in the 2D superconductor, and inhibiting the spin pair breaking
effect of the applied in-plane magnetic field [31, 76, 124]. The orbital pair breaking mechanism is suppressed by the two dimensional geometry prohibiting out-of-plane electron momenta and negating any effects due to the Lorentz force. This 2D geometry therefore also inhibits vortex formation in the plane of a superconductor thinner than its coherence length [1]. Our primary motivation for studying Ising superconductivity in NbSe$_2$ and TaS$_2$ was to compare the strength of the Ising protection between two systems that have significantly different strengths of spin orbit coupling. An additional motivation of our focus on TaS$_2$ was to show that superconductivity persists down to the monolayer limit at which we expected the Ising protection to be maximal.
3.1.2 Ising protection

Orbital pair breaking with vortex formation is suppressed by the 2D nature of the superconductor, as the Lorentz force due to an in-plane field cannot push the in-plane momentum vectors of the paired electrons out of the plane of the superconductor. This effectively removes all contributions from orbital pair breaking effects from in-plane critical field considerations in superconductors thinner than their coherence length, because in-plane vortices cannot form [1, 117, 125]. The Josephson vortices that form in layered superconductors are also suppressed when the layered superconductor is thinner than the corresponding anisotropic coherence length (see Figure 1.9 and 1.8) [1].

However, the suppression of spin pair breaking (discussed in Section 3.1.1) is more complex. In Ising superconductors spins do not align with the applied in-plane magnetic field at lower fields because they experience an extremely large effective Zeeman field out-of-plane in the direction of their spin magnetic moment [76, 126, 127]. This alters the total field direction used in the calculation of the Pauli paramagnetic energy $\Delta E_\pm = 2H_{\text{total}} \cdot \mu_e$, which could also be seen as decreasing the effect of paramagnetic susceptibility on the free energy of the normal state dramatically increases the in-plane critical field by suppressing spin pair breaking (3.1.1). The origins of this effective field will be explained in the next section.

3.1.3 Ising Pairing

Figure 3.2: Brillouin zone of TaS$_2$ showing SOC valley splitting. Electrons in the K and K' valleys with spins pinned to the out-of-plane direction due to the effective field $B_{so} \propto E \times k$ resulting from planar crystal field and electron momenta. Straight black lines connect time-reversed pairs.

The out-of-plane effective Zeeman fields that suppress spin pair breaking due to the applied in-plane magnetic field result from strong antisymmetric spin orbit coupling in the Ising superconductor system. While Ising superconductivity has been observed
in multi-layer systems, the theoretical underpinnings are clearest in the monolayer limit. In TMDs the unit cell for the bulk system in the $2H_a$ phase contains 8 atoms in two layers and possesses inversion symmetry with the center of inversion located between the two layers. However, this unit cell can be split in half in the case of a single monolayer of the TMD, forming the $1H$ phase (Fig 1.16). The $1H$ phase lacks the inversion symmetry of the $2H_a$ phase, but instead has mirror symmetry about the plane of the monolayer, enabling an antisymmetric spin orbit coupling [128]. This mirror symmetry constrains the crystal electric field $\vec{E}$ to be in the plane of the monolayer, following from introductory physics examples of Coulomb’s law and electrostatics, no un-cancelled out-of-plane electric field components can remain in the monolayer crystal. The 2D nature of the monolayer also restricts the momenta of electrons to the plane of the crystal.

Figure 3.3: Spin-orbit field across the Brillouin zone.  
(a) The spin-split Fermi surface is projected on the Brillouin zone, with Ising pairings depicted in opposite valleys and on opposite sides of the $\Gamma$ point. Relative strength and direction of the spin-orbit field pinning the electrons out-of-plane is shown with the gray dashed lines.  
(b) Relative strength and direction of the spin-orbit field is shown across the entire Brillouin zone, valleys are separated by solid lines.  
(c) 3D model of the spin-orbit field ($z$-axis) across the Brillouin zone.

Electrons on opposite sides of the Brillouin zone, having opposing in-plane mo-
menta \(-k/k\), experience opposing out-of-plane effective Zeeman fields \(\pm \vec{B}_{so} \propto \pm \vec{k} \times \vec{E}\). The Zeeman fields break the spin degeneracy of the band structure in each of the valleys of the Brillouin zone with energy \(\Delta E_{so} = -g_s\mu_B B_{so}(\pm k)\). This energy is proportional to the strength of the SOC in the system, where \(g_s\) is the electron spin g-factor and \(\mu_B\) is the Bohr magneton introduced in Section 3.1.1. The spins parallel (antiparallel) to the Zeeman field will occupy a lower (higher) energy band in each valley of the Brillouin zone while spins with momenta along lines of symmetry (M \(\leftrightarrow \Gamma\) in Figure 3.4 c,d) between valleys remain in spin degenerate bands.

**Figure 3.4:** Electronic structure of monolayer TaS\(_2\) & NbSe\(_2\)

(a) Spin-projected Fermi surface of monolayer TaS\(_2\) and (b) NbSe\(_2\) computed by density functional theory (DFT). Red corresponds to one \(S_z\) projection and blue to the opposite (e.g. up and down, respectively). Variation in the shading and curve thickness indicates the magnitude of spin-splitting in the valence band \(\Delta_{vb}(k)\) due to spin-orbit coupling, with the color scale being shared between (a) and (b) to emphasize the difference in magnitudes. (c) Relevant bands around the Fermi level for monolayer TaS\(_2\) and (d) NbSe\(_2\) from DFT, with spin polarization corresponding to colors in (a), black bands being spin-degenerate.

At the Fermi level the spin split bands form spin polarized rings in each valley around the K (K') corner of the Brillouin zone with the lower energy spins closer to the corner (Figure 3.4 a,b). The momentum separating these rings is proportional to the energy separating the spin-split bands (compare Figure 3.4 a,c with b,d). These
spin polarized rings also form about the $\Gamma$ point in each valley, with the lower energy spins closer to the center of the Brillouin zone (Figure 3.4 a,b).

Cooper pairs then preferentially form between an electron in a spin polarized ring on the Fermi surface of one of the valleys and its time reversed partner with opposite spin and momentum on the opposite side of the Brillouin zone. These pairs of electrons, pinned out-of-plane by Ising SOC, are termed Ising pairs as they are akin to the spin relationships of the classic 2D Ising model [31]. These Ising pairs can form on either of the Fermi surfaces of the spin-split valleys, creating two distinct populations of Cooper pairs in the upper and lower split bands of the K and K’ valleys. Figure 3.4 shows the results of density functional theory (DFT) calculations performed by our CMU collaborators on this project, Dr. Nikhil Sivadas (overseen by Dr. Di Xiao), showing the difference in the spin splitting for TaS$_2$ and NbSe$_2$ monolayers. The former has stronger SOC and thus a larger $B_{so}$ pinning the spins out-of-plane than the latter. Spin orbit coupling originates from the movement of the magnetic dipole moments (Section 3.1.1) of electrons through the electrostatic field of the atomic nucleus (with relativistic corrections) [119]. An electron is partially shielded from the nuclear charge by any electrons in the same orbital and more strongly by those in orbitals between it and the nucleus, but not by any electrons in higher orbitals (Gauss’s law). This results in a distinct effective nuclear charge, $Z_{eff}$, and electrostatic potential for each electron orbital of each element [9]. $Z_{eff}$ for the valence electrons increases from left to right across each row of the periodic table since the shielding of each additional valence electron is less than the matching proton’s contribution to the nuclear charge. An exact solution for the spin orbit splitting energy is dependent on an electron’s spin, orbital and total angular momentum ($s, \ell, j$) as well as being proportional to $Z_{eff}^4/n^3$ [119]. So SOC increases in strength going from elements at the top to those at the bottom of each column in the periodic table. The heavier transition elements Tantalum and Niobium will dominate SOC contributions from Selenium and Sulfur in the crystals TaS$_2$ and NbSe$_2$. Since Tantalum is directly below Niobium in column 5 with double the atomic mass, and has 32 more protons contributing to its nuclear charge, each of its orbitals will have greater $Z_{eff}$ than the matching orbital in Niobium. This atomic mass and nuclear charge disparity causes the previously noted stronger SOC in TaS$_2$ than in NbSe$_2$. This marked difference drove our initial interest in experimentally confirming the stronger Ising protection in monolayer TaS$_2$ compared to monolayer NbSe$_2$ which had been previously studied [76].

### 3.1.4 Additional Perturbations to Ising Superconductivity

This initial picture of Ising superconductivity resulting from Cooper pairs pinned out-of-plane in the K and K’ valleys of monolayer TMD’s is complicated when additional features in the system are considered. One additional feature of interest are the split bands at the Fermi surface surrounding the $\Gamma$-point. These provide additional spin-
momenta pairings on the Fermi surface across the center of the Brillouin zone in which Cooper pairs can form. With lower momenta than either of the split valley bands, these $\Gamma$-point Cooper pairs will have a lower $B_{so}$ pinning the spins out-of-plane. This smaller $B_{so}$ will not boost the in-plane upper critical field for $\Gamma$-point Cooper pairs as high as the in-plane upper critical field of the K and K’ valley Cooper pairs. While our treatment of BCS theory in Section 1.1.4 was restricted to singlet Cooper pairs like those formed in the K and K’ valleys, strong SOC in this system also results in spin-triplet pairing.

![Figure 3.5: Bilayer TaS$_2$ Brillouin zones.](image)

Brillouin zones (neglecting interlayer coupling) for a bilayer of TaS$_2$ show opposite splitting in the K and K’ valleys, as the AB stacking of the layers results in the second layer having an inverted crystal structure from the first, with the bilayer system gaining inversion symmetry with an inversion point in space between the two layers.

Moving from monolayer systems to multilayer systems, we can see that odd-layer-number TMD superconductors with 2H structure will also lack inversion symmetry and have C-axis mirror symmetry with their mirror planes cutting through the center layer, while even-layer-number 2H-TMD’s lack mirror symmetry but gain inversion symmetry about a point between the layers (see Figure 3.5). This would seem to imply that even-layer-number samples will not exhibit Ising protection in large in-plane magnetic fields. However, in-plane critical fields above the Pauli paramagnetic limit are still observed. This can be attributed to the weak coupling between layers in layered superconductors, thus in the few layer limit they are better modeled as weakly coupled monolayers than as a thin bulk sample. Each monolayer will exhibit reduced Ising superconductivity where spin pair breaking protection is lessened since the effective Zeeman field in each layer is weakened by the coupling between that layer and all nearby layers, and orbital pair breaking protection lessens when Josephson vortices can form in the gaps between layers.
3.2 Prior experimental measurements of Ising Superconductivity

In late 2015 Lu et al. identified extremely high in-plane upper critical fields in the strongly gated semiconductor MoS$_2$ \[31\]. Spin-Orbit Coupling was identified as the mechanism responsible for these enhanced upper critical fields in both systems, with the lack of inversion centers and in-plane mirror symmetry being crucial to the formation of the effective Zeeman fields that pin the Ising pairs out-of-plane.

3.2.1 Ising SC in Gated systems

This first published paper identifying Ising superconductivity used ionic liquid gates on thin, but not few-layer, MoS$_2$ flakes \[31\]. As discussed in Section 1.1.8, ionic liquid gates were used because standard MOSFET-style backgates could not produce a large enough electric field to shift the carrier density of the MoS$_2$ flake into the superconducting dome region (see Figure ??). However, standard backgates were used in conjunction with ionic liquid gates to make smaller adjustments to the carrier density at low temperature when the ionic liquid gate polarization had frozen in place. This technique was used to show the entire superconducting dome of WS$_2$ (see Figure ?? several years later when Ising protection stronger than that of MoS$_2$ was observed and attributed to the greater SOC energy \[26\]).

![Figure 3.6: Magnetotransport data for monolayer MoS$_2$. Monolayer MoS$_2$ magnetotransport curves at constant perpendicular (A) and parallel (B) magnetic fields. (B) insets show the tight clustering of curves 0-11T parallel fields, as well as a schematic of the sample defining field angles. Figure from \[31\]](image)

The measurement setup for the MoS$_2$ samples was shown in Figure 1.19 (also shown in the inset of Figure 3.6 B), where a hall bar geometry is used for the magnetotransport measurements with the ability to gate the semiconductor electrostatically.
from above and below [31]. By placing the sample substrate on a rotating sample mount inside a cryostat, they performed magnetotransport measurements of the critical temperature at various magnetic field strengths with the sample’s plane oriented parallel and perpendicular to the axis of the applied magnetic field. These measurement curves, seen in Figure 3.6 A & B, show that the superconducting monolayer’s critical temperature drops significantly in increasing magnetic fields applied perpendicularly to the plane of the sample (A), but only decrease slightly in fields applied in the plane of the sample (B). Plotting these transition temperatures as a function of magnetic field in Figure 3.7 and fitting the data using 2D Ginzburg-Landau equations, Lu et al. show that in a perpendicular field the critical temperature decreases approximately linearly with field, while the expected $H_0(1 - \frac{T}{T_c})^{1/2}$ dependence holds for parallel field measurements [31, 129, 130].

![Figure 3.7: $H_{c2}$ vs $T$ for MoS$_2$.](image)

$H_{c2}^\parallel$ \& $H_{c2}^\perp$ of monolayer MoS$_2$ gated to $T_c$ = 7.3K. $H_{c2}^\perp$ is linearly fit, while $H_{c2}^\parallel$ is fit to a square root. Coherence length is extracted from the slope of $H_{c2}^\parallel$ near $T_c$. Figure from [31]

Figure 3.8 A-D schematically show MoS$_2$’s Brillouin zone oriented parallel and perpendicular to an applied field and the energetic effects of Zeeman SOC and Rashba SOC. In Figure 3.8 A,C the alignment of the Cooper pair spins by Zeeman and Rashba SOC (respectively) with the external field increases the Zeeman energy of each system and leads to pair breaking. While in Figure 3.8 B,D the Zeeman and Rashba SOC (respectively) align the spins normal to the externally applied $B$ field, minimizing the Zeeman energy of both systems and protecting the Cooper pair from this spin pair
breaking mechanism. The parallel field data from Figure 3.7 for the MoS$_2$ monolayer is also plotted (using temperatures and fields normalized by the critical temperature and Pauli field respectively) using blue filled circles in Figure 3.8E alongside data from a second sample at two different carrier densities (and therefore different critical temperatures and Pauli limits) showing even more enhanced critical fields for samples gated to have lower critical temperature. These measurements thus far show that MoS$_2$, when gated such that the topmost monolayer enters a superconducting dome region, exhibits an extremely enhanced parallel critical magnetic field. However, to attribute this enhancement to the previously described mechanism of Ising superconductivity due to Zeeman SOC, rather than the possibility of Rashba SOC suggested by Figure 3.8D, the authors proceeded to fit the data using models that include constant Zeeman SOC contributions with varying strengths of Rashba SOC. A model with no Rashba SOC contribution overshoots the 2.37K $T_c$ data, while adding a slight contribution of the Rashba SOC schematically represented in Figure 3.8C fits the data well. Further models with no Zeeman SOC included show that Rashba SOC will increase the critical field slightly above the Pauli limit, but not far enough to match the experimental data, and removing the Rashba SOC from the model recovers the bare Pauli limit.

![Figure 3.8: Fitting the effects of Rashba vs Zeeman SOC in MoS$_2$. A-D: schematic representation of the energy contributions of Zeeman and Rashba SOC oriented in an external magnetic field. E: Model fits to the data including various strengths of Zeeman and Rashba SOC. Axes are normalized by $T_c$ and the Pauli limit. Figure from [31]](image)

Lastly, this paper correctly predicted that Ising superconductivity would be observed in 2H-TMD superconductors as they approach the monolayer limit and the breaking of inversion symmetry results in similar intrinsic SOC to that in MoS$_2$ [31].
3.2.2 Ising SC in Intrinsic systems

Soon after the work on Ising superconductivity in a highly gated MoS$_2$ monolayer was published, Xi & Wang et al. published their results on Ising superconductivity in mono- and multilayer NbSe$_2$ [76]. They found enhancements of the in-plane upper critical field in few-layer samples as thick as 8 layers, inversely proportional to sample thickness. A secondary, but extremely useful, result of their work on few layer samples was to pin down the relationship between $T_c$ and layer number $N$ in NbSe$_2$ (as discussed in Section 1.2.1).

In their measurements, they used pre-patterned gold contacts in a Hall bar geometry onto which the exfoliated NbSe$_2$ flakes were stacked with a protective top layer of insulating hBN. The advantages of this contact scheme are producing samples ready to be measured immediately after stacking, and producing many pre-patterned substrates in parallel using standardized lithographic patterns. However, flakes must be of sufficient size to spread across the pre-patterned contacts and since the gold leads sit on top of the Si substrate and contact the bottom of the NbSe$_2$ flake, the stack tends to ‘tent’ over the leads with small gaps between the substrate and the van der Waals heterostructure adjacent to the leads. These flaws in the encapsulation of the air sensitive flakes permit oxygen and water vapor to enter and degrade the NbSe$_2$ over longer periods of time, but for materials that degrade slowly this is usually an acceptable trade-off for the ability to start measurements immediately after stacking.

Figure 3.9: $H_{c2}^{||}$ & $H_{c2}^{\perp}$ of NbSe$_2$

(a) $H_{c2}^{||}$ & $H_{c2}^{\perp}$ normalized by critical temperature and the Pauli paramagnetic limit of each sample thickness ($H_p/H_p = 1$ marked by dashed line) (b) shows more sample thicknesses and zooms in on the data in the bottom right corner of (a). Figures from [76].
Using this measurement setup, Xi & Wang et al. measured 1-4,8L and bulk thickness NbSe$_2$ samples in parallel and perpendicular magnetic fields, the R(T) data from which is shown in Figure ???. As the $T_c$ of NbSe$_2$ decreases with layer number, so does the Pauli paramagnetic limit. The critical temperatures they measured for each sample at assorted magnetic field setpoints are normalized by zero field $T_c$ and the respective Pauli limit, then plotted in Figure 3.9a and Figure 3.9b. When normalized by the respective Pauli limit $H^\perp_{c2}$ for each thickness is the same, showing that the perpendicular critical field is limited by orbital (vortex density) rather than spin mechanisms. The parallel field curves for the bulk sample show $H^\parallel_{c2} > H^\perp_{c2}$, $T_c$ decreases by about half in a 9T field applied in the plane of the sample, while a 2T field applied perpendicularly has a similar result. However, in the trilayer and monolayer parallel field data the critical fields are enhanced even more dramatically, requiring 31T to drop the trilayer $T_c$ by half, while the monolayer sample(s) were not measured in fields sufficient to see a similar reduction in $T_c$. The parallel field data is also plotted in Figure 3.9a, normalized by $T_c$ and the Pauli limit (marked by a dashed line). The parallel field bulk data follows a linear fit at the measured temperatures far above 0K, while the parallel field monolayer data is fit using the $(1 - \frac{T}{T_c})^{1/2}$ dependence discussed in the previous section, extrapolating to a zero temperature $H^\parallel_{c2}$ more than 6.5x greater than the Pauli limit of 5.5T for monolayer NbSe$_2$. The monolayer enhancement in critical field is greater than that of the bilayer or trilayer data, and close to $T_c$, the monolayer $H^\parallel_{c2}$ has a much greater slope. This is even more dramatically displayed in Figure 3.9b where 4L and 8L data is added to the plot. The enhancement seen in these multilayer (though not bulk) samples is further proof of the weak coupling between layers in NbSe$_2$, as well as evidence that in samples much thinner than the out-of-plane penetration depth (23nm) spin pair breaking mechanisms dominate orbital pair breaking effects (vortices).

### 3.3 Our Experimental Results

As discussed in the previous section, Ising superconductivity had been studied in NbSe$_2$ down to the monolayer limit, but the TaS$_2$ system had not been studied in samples thinner than 5 layers (in large part due to its greater sensitivity than NbSe$_2$ to degradation in atmosphere) [77]. Due of this limitation the strength of Ising protection in TaS$_2$ had not been fully explored. We set out to isolate and encapsulate a monolayer flake of TaS$_2$, as well as other few layer thick samples, both to study the degree of Ising protection in the TaS$_2$ system with strong SOC, as well as to demonstrate that TaS$_2$ retains its superconducting properties in the monolayer limit, which was expected, but had yet to be observed experimentally.
Figure 3.10: TaS$_2$ R(T) curves for TaS$_2$ characterization. 
(a) R(T) curves for two pairs of contacts (with different channels) on a few layer device with an anomalously high critical temperature, indicating likely intercalation of the TaS$_2$ flake. (b) R(T) for two bulk devices co-located on the substrates with our monolayer and trilayer samples. These bulk TaS$_2$ superconducting transition curves show critical temperatures in agreement with clean, non-intercalated, bulk TaS$_2$. 
3.3.1 TaS\textsubscript{2} Layer Characterization

As discussed in Section 1.2.1, the critical temperature of TaS\textsubscript{2} is layer dependent below the bulk limit, rising from a bulk T\textsubscript{c} of 0.7 K to 3 K in the monolayer limit [77]. Though with an opposite trend than that seen in NbSe\textsubscript{2}, this layer dependence of T\textsubscript{c} can again serve as a rather accurate sample thickness characterization method. However, for this characterization method to be valid, care must be taken to verify the stoichiometry of the sample and that the TaS\textsubscript{2} layers are not intercalated with any atomic or molecular species. TaS\textsubscript{2} samples with an excess of tantalum (though not samples with an excess of sulfur) have a slightly increased T\textsubscript{c} [131, 132]. Additional separation between layers reduces the interlayer coupling and increases the T\textsubscript{c} of an intercalated multilayer sample above that of a clean sample, meaning that either of these cases can confound an analysis of thickness based purely on critical temperature [131–133].

Energy-dispersive x-ray spectroscopy (EDX) was used to determine the stoichiometry of our two bulk source crystals used in our exfoliation of thin TaS\textsubscript{2} flakes. The EDX results found 67.2 % sulfur and 32.8 % tantalum for one bulk crystal and 69.6 % sulfur and 30.4% tantalum for the second bulk crystal, indicating a slight, but unimpactful, excess of sulfur. After seeing evidence of intercalation in a few layer TaS\textsubscript{2} sample with T\textsubscript{c} ≥ 3.5 K (see Figure 3.10a), we began creating simple two-terminal devices using bulk TaS\textsubscript{2} flakes attached to, or nearby, the few layer devices. We measured the R(T) of these bulk devices to ensure that their critical temperature matched the published value of 0.7 K for non-intercalated bulk TaS\textsubscript{2}. R(T) curves for the bulk devices adjacent to our monolayer and trilayer samples are shown in Figure 3.10b, displaying good agreement previous measurements of clean, bulk TaS\textsubscript{2} [76, 77].

Figure 3.11: AFM images of four TaS\textsubscript{2} devices.

Atomic force microscopy of TaS\textsubscript{2} devices. Height scans showing the lithographically defined TaS\textsubscript{2} channels (dotted region) using non-contact mode atomic force microscopy for (a) five-layer, (b) four-layer, (c) trilayer, and (d) monolayer devices. The total height of each channel is primarily composed of a relatively thick (∼20nm) h-BN encapsulating layer protecting the thin, underlying TaS\textsubscript{2} crystal. Scale bars denote 2 µm. Color scales correspond to height measured in nanometers.

Figure 3.11 shows atomic force microscopy (AFM) scans of the four TaS\textsubscript{2} devices featured in our paper.
Third harmonic generation of TaS\textsubscript{2} devices. (a) Polar plot of co-linear second harmonic generation (SHG) intensity (spectrally-integrated) as a function of incident polarization angle from monolayer 1H-TaS\textsubscript{2}. (b) SHG spectra for three odd-layer-number TaS\textsubscript{2} devices with h-BN spectrum for comparison. (c) SHG spectrum for an even-layer-number TaS\textsubscript{2} device with h-BN spectrum for comparison. Inset: maximum SHG intensity observed for the four samples of various thickness.

Lastly, after all magnetotransport measurements were complete, we sent our TaS\textsubscript{2} samples to our collaborators at the University of Washington (Kyle L. Seyler & Xi-aodong Xu) to perform second harmonic generation (SHG) optical characterization of our samples. In the supplemental information of our paper, we described the results of the SHG characterization as follows:

Second-harmonic generation (SHG) is a sensitive probe of inversion symmetry breaking, since the second-order nonlinear susceptibility is only nonzero for noncentrosymmetric crystals\cite{134}. In few-layer 2H-phase TMDs, strong SHG is only observed in samples with odd-layer-number, where inversion symmetry is broken\cite{135}. We studied the SHG from our TaS\textsubscript{2} samples to clearly distinguish between even and odd-layer-number, and thus further corroborate our sample thickness assignments. The samples were excited by a mode-locked Ti:sapphire laser (76 MHz repetition rate, 200 fs pulse duration, 1 mW average power) at 795 nm under normal incidence in reflection geometry and the SHG was detected by a spectrometer and Si charge-coupled device. The measurements were performed at room temperature under vacuum, and laser intensity was carefully tuned to prevent damage to the TMD material. In Supplementary Figure 4, we show the SHG polarization dependence and spectra from TaS\textsubscript{2} samples. The monolayer TaS\textsubscript{2} response to rotating the incident polarization forms a ‘rose’ pattern and is shown in Supplementary Figure 4a. The spectra of three odd-layer-number samples (1L, 3L, and 5L) are shown in Supplementary Figure 4b, while the spectrum of an even-layer-number (4L) sample is shown in Supplementary Figure 4c. It can clearly be seen that the SHG intensity of the odd-layer-number TaS\textsubscript{2} samples is significantly greater.
than that of the thin bulk h-BN that encapsulates them. On the other hand, the even-layer-number TaS2 sample produces an intensity nearly equivalent to that of the encapsulating h-BN layer, showing that the 4L TaS2 does not contribute significantly to the SHG response. The inset of Supplementary Figure 4c shows the maximum intensity observed for each of the four samples of varying thickness, demonstrating an oscillation in maximum intensity between odd- and even-layer-number samples, similar to other 2H-phase TMDs. Although a linear increasing trend is observed among the odd-layer-number samples, we draw no conclusion regarding this trend because of the small sample size. The even- and odd-layer-number assignments established by SHG are consistent with the thickness determined by transport and AFM.

### 3.3.2 National High Magnetic Field Laboratory

We made initial R(T) measurements on all of our samples in the BlueFors dilution refrigerator in our lab, sufficient to obtain an initial characterization of sample thickness. However, without a rotating sample mount, we could not precisely orient the samples parallel to the magnetic field of the superconducting solenoid magnet in the dilution refrigerator for magnetotransport measurements of the in-plane critical field. Additionally, with a maximum field of 13T, we would not have been able to measure the critical fields of a monolayer TaS2 device further than 5% below the critical temperature. The facilities at the National High Magnetic Field Laboratory in Tallahassee, Florida enabled us to measure our samples using a top loading probe in a He3 refrigerator down to a base temperature of 300 mK. This system in Cell 12 (Figure 3.13a) uses a resistive solenoid magnet to reach magnetic fields up to 34.5 Tesla. The top loading probe uses a linear actuator to control a sample rotator (Figure 3.13d) that generates very little heating at low temperatures. While this linear actuator can be driven using a stepper motor, in practice we found it better to manually adjust the linear actuator as the motor had some issues with backlash and led to an increase in the noise in our measurements. When aligning the sample parallel to the magnetic field for our measurements, we set the field close to the sample’s parallel critical field such that we saw a dip in resistance as the rotator passed through the parallel orientation. We then rotated back to the original orientation to minimize issues with backlash in the rotator (separate from the stepper motor backlash) and slowly rotated the sample until we had reached the minimum resistance measured in the angular sweep. This process was repeated as necessary to align the sample plane with the magnetic field with sub-degree accuracy.
Figure 3.13: National High Magnetic Field Laboratory
(a) Magnet cell 12 with 2 colleagues.  (b) Top loading probe system with linear actuator used to drive the sample rotator.  (c) Equipment racks holding Lock-in Amplifiers used in the measurements.  (d) Sample rotation mechanism built in our lab based on the system at the NHMFL.
Figure 3.14: R(T) for 1,3,5L TaS$_2$.

R(T) curves for the monolayer, trilayer, and five-layer TaS$_2$ samples, the increase in $T_c$ with decreasing layer number is clearly observed. Inset: optical image of the trilayer TaS$_2$ device with lithographically defined and etched leads and channel.

3.3.3 TaS$_2$ R(T) & R(B) Data

We began our magnetotransport measurement campaign for every sample with a 4-pt resistance measurement across the TMD flake as it cooled down to base temperature. From this R(T) data we could see if the leads we had chosen were working and if we saw a superconducting transition, the critical temperature would hint at the thickness of the TMD flake. Figure 3.14 shows R(T) data for three of our TaS$_2$ samples, normalized by normal state resistance, with the thicker samples having decreasing critical temperatures. Aside from the critical temperature, the shape of the R(T) curves imparts information as well. Looking at the three transition curves in Figure 3.14, the rounding at the top of the transition ($\geq 0.9R/R_n$) is explained by enhanced fluctuations in 2D superconductors and melting of the 2D vortex lattice resulting in vortex motion that produces a voltage by dissipating energy. These effects on the R(T) curve are well fit by Aslamazov-Larkin and Halperin-Nelson formulae [136, 137]. The enhanced fluctuations are due to the formation of isolated Cooper pairs forming above $T_c$ as a result of spatially varying amplitude fluctuations in the superconducting order parameter across the 2D channel. This can create small, well separated, and thus uncoupled, pockets of superconductivity with sizes on the order of a coherence length while the remainder of the channel is normal. As the temperature continues to drop, these pockets will merge and cohere as the channel goes fully superconducting.
Figure 3.15: Perpendicular and parallel magnetic field dependence.

(a) Temperature dependence of longitudinal resistance of trilayer (3L) TaS$_2$ in the presence of an applied magnetic field $H_\perp$ in the out-of-plane direction. (b) Magnetic field dependence of the TaS$_2$ resistance for a field $H_\parallel$ applied in an in-plane direction, for a few constant temperatures as indicated. The field value $H_{c2}$ at which the resistance transitions to a zero-resistance state at a fixed temperature is equivalent to the transition temperature $T_c$ of the superconducting state for a fixed field. (c) Temperature dependence of the bilayer (2L) NbSe$_2$ sample for a few perpendicular fields. (d) In-plane field dependence of the same NbSe$_2$ sample for a range of constant temperatures.

However, because the vortex formation energy in a 2D superconductor is of the order $k_B T$, vortices will spontaneously form throughout the channel in a lattice like configuration. At these relatively high temperatures the vortices can move freely throughout the 2D superconductor in a vortex liquid state that dissipates energy. Below $T_c$, the $R(T)$ curves will often have a resistive tail of various sizes that slowly trends to zero. The size and shape of this resistive tail varies from sample to sample because it arises from inhomogeneities in the channel and finite size effects. As discussed in Section 1.1.8, in small channels with dimensions on the order of the Pearl depth long range interactions will occur between vortices in the channel. This is clearly observable in by comparing the large resistive tail on the 1L data in Figure. 3.14 to the significantly smaller tail on the 3L data. This is expected, as the 1L sample (seen in Figure. 3.11 d) has a channel significantly smaller than that of the 3L
sample (shown in both Figure. 3.11 c and the inset of Figure. 3.14) [28, 45].

Figure 3.16: $H_{c2}$ vs $T$ for 3L TaS$_2$ & 2L NbSe$_2$.
Temperature dependence of the upper critical field $H_{c2}$ of both samples as extracted from the 50% normal state resistances from the data shown in Figure 3.15(a)–(d).

Perpendicular Field Data

Figure 3.15 presents some of our magnetotransport data on 3L TaS$_2$ and 2L NbSe$_2$ in parallel and perpendicular magnetic fields. The plots in Figure 3.15 a,c show R(T) curves taken at various constant magnetic fields, as would be expected the critical temperature decreases with increasing field strength. These transitions are then plotted in Figure 3.15 e, showing the perpendicular critical field, $H^{\perp}_{c2}$ (which corresponds with the condition that the area of the normal cores of the Pearl vortices in the sample is comparable to the total area of the sample), as a function of temperature. $H^{\perp}_{c2}$ is less than the Pauli paramagnetic limits of several Tesla for these flakes. The Ginzburg-Landau equation for these upper critical fields, $H^{\perp}_{c2}(T) = \frac{\Phi_0}{2\pi\xi_{GL}(0)}(1-T/T_c)$, provides an estimate of the samples’ coherence lengths: $\xi_{GL}(0) \sim 20$ nm for the 3L TaS$_2$ and $\sim 10$ nm for the 2L NbSe$_2$. 

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Finite Resistance State

Another feature of note in Figure 3.15 a & c is the finite resistance saturation of superconducting state in a perpendicular applied field. The existence of this state seems to run counter to the smooth superconductor-insulator transition in ground state 2D systems discussed in Section 1.1.8 [138]. After our work was published, Tamir et al. published an explanation of these finite resistance states, showing that in both crystalline (NbSe$_2$) and highly disordered (InO) superconducting systems these finite resistance states result from high frequency noise causing dissipation in the highly sensitive thin superconductor [139]. They further found that implementing a series of low-pass filters in the measurement circuit eliminated this finite resistance state in the thin superconductors with perpendicular applied magnetic fields. This result, in part, led to my own work using filters (Section 2.3.1) to observe fully superconducting interfaces between 2D NbSe$_2$ and 3D Al (Chapter 4). Later work in other systems with high quality filters implemented in the measurement setup has observed a finite resistance state in 2D superconductors in a magnetic field. For now this state remains an ongoing area of study in the field of 2D superconductors [140].

Figure 3.17: Parallel upper critical fields for TaS$_2$ and NbSe$_2$.

(a) Parallel upper critical field normalized to Pauli paramagnetic limit, $H_{c2}^\parallel / H_P$, as a function of reduced temperature $T/T_{c0}$ for monolayer (1L), trilayer (3L), four-layer (4L), and five-layer (5L) TaS$_2$ samples, and (b) monolayer (1L, from [76]) and bilayer (2L) NbSe$_2$. Dashed lines show the square-root fit described in the main text.
Parallel Field Data

Figure 3.15 b,d switch to data sweeps taken at constant temperature in a swept parallel field, as described above in Section 3.3.2. At the base temperature of 300mK in the He$_3$ refrigerator, we observed the superconducting state persist in fields of 25T for 3L TaS$_2$ and 28T for the 2L NbSe$_2$ sample. Figure 3.15 e shows that these parallel critical fields, $H_{c2}^\parallel$, are well above the Pauli paramagnetic limit, showing an anisotropic enhancement in critical field ($H_{c2}^\parallel/H_{c2}^\perp$) of 32x and 8x respectively.

The parallel field datapoints of 3L TaS$_2$ and 2L NbSe$_2$ from Figure 3.15 e are re-plotted in Figure 3.17 a,b alongside the data for 1L, 4L & 5L TaS$_2$ and 1L NbSe$_2$ (from Xi & Wang et al. [76]), normalized by the Pauli paramagnetic limit for every layer number. Both materials show a decrease in the enhancement of $H_{c2}^\parallel$ with increasing layer number, but the TaS$_2$ monolayer has a stronger enhancement than the NbSe$_2$ monolayer, as predicted based on the relative strengths of SOC in the two systems.

Figure 3.18: Removal of graphite magnetoresistance.
4L TaS$_2$ data obtained using a 3-pt measurement setup before (A) and after (B) the magnetoresistance of the graphite contact is removed.
The monolayer TaS$_2$ sample only had 3 working contacts, leaving a single lead of Au and graphite in series with the resistance of the monolayer TaS$_2$ flake. This required careful subtraction of the temperature and field dependent magnetoresistance of the graphite. Figure 3.18 shows similar 3-pt resistance data for our 4L TaS$_2$ sample before (a) and after (b) removing this magnetoresistance. In order to remove this temperature and field dependent magnetoresistance, we took measurements (shown in Figure 3.19) of the graphite while sweeping through the full range of the magnetic field at the base temperature and the $T_c$, then interpolated between the two curves to subtract from the 3-pt data. After processing, it is much clearer where the superconducting transition actually occurs, at which point the critical fields can be extracted and plotted, as in Figure 3.15a. The 1L TaS$_2$ data (after magnetoresistance subtraction) is shown in Figure 3.20, and then plotted separately for fitting in Figure 3.22.

By comparing the monolayer Ising protection for TaS$_2$ and NbSe$_2$, we can comment on the contribution of SOC to the enhancement of $H_{c2}$. The square root fit from GL theory (dashed lines) is valid near $T_c$, and as displayed in Figure 3.22, the square root dependence on temperature is scaled by a magnetic field parameter, $H_0$. By fitting the monolayer data, we can extract $H_0 = 65.6T$ for TaS$_2$ and $H_0 = 43.6T$ for NbSe$_2$. This yields a ratio of $H_{c2}^{TaS_2}/H_{c2}^{NbSe_2} \approx 1.50$. To compare these values to the SOC energies in the two systems we can calculate the effective Zeeman fields due to SOC that pin the spins in the Ising pairs out of plane, $B_{so}$. Xi & Wang et al. estimate that $H_0 \approx \sqrt{H_{so}H_p}$ where $H_{so} \sim B_{so}/\mu_0$ is proportional to the effective Zeeman field throughout the Brillouin zone. As the two monolayers both have $T_c=3K$, their Pauli paramagnetic limits are both $H_p=5.5T$, so the ratio between the parallel upper critical fields in the two systems should be approximately equal to the ratio of SOC energies, $\Delta_{so}$.

Looking back to the DFT calculations used to create Figure 3.4, we can estimate Fermi surface averages of $\Delta_{so}^{TaS_2} = 122$ meV, $\Delta_{so}^{NbSe_2} = 49.8$ meV and see that $H_{c2}^{TaS_2}/H_{c2}^{NbSe_2} = \sqrt{\Delta_{so}^{TaS_2}/\Delta_{so}^{NbSe_2}} = 1.57$ which is quite close to the ratio of parallel upper critical fields found above, $H_{c2}^{TaS_2}/H_{c2}^{NbSe_2} \approx 1.50$. This experimentally shows that the ratio of upper critical fields in these two Ising superconductors is roughly proportional to the square root of the ratio of spin splitting on their Fermi surfaces.

This result is clear in the monolayer case considered above, but it is interesting to consider the few layer TaS$_2$ samples that we have data on and compare them with the few layer NbSe$_2$ samples from Xi & Wang et al. by comparing SOC energies and interlayer coupling energies. As previously discussed, even-layer-number samples that are centrosymmetric shouldn’t exhibit Ising superconductivity, but because a bilayer sample appears to function more like two weakly coupled monolayers, we
still see significant Ising protection with the decrease in upper critical field from the monolayer attributable to the weak interlayer coupling. Using the values of $\Delta_{so}$ for TaS$_2$ and NbSe$_2$ from before, we can compare these energies with the interlayer coupling energy, $t_\perp$, extracted from DFT calculations of 2L, 3L and 4L TaS$_2$ and NbSe$_2$. This results in $t_\perp \sim 10$meV for TaS$_2$ and $t_\perp \sim 20$meV, which are both significantly smaller than the SOC energies in each system, but $t_\perp$ increases with each increase in layer number. Plotting the ratio of $t_\perp/\Delta_{so}$ for each layer number sample (starting with $t_\perp = 0$ for each monolayer) in Figure 3.21 a, we can see that interlayer coupling is a much more energetically important mechanism in NbSe$_2$ than in TaS$_2$. Comparing the upper critical fields of the multilayer samples (at 0.8 $T_c$), normalized by $H_{c2\parallel}$ of the monolayer, we can see in Figure 3.21 b that the enhancement of $H_{c2\parallel}$ in multilayer NbSe$_2$ dies off much faster with increasing layer number than in TaS$_2$. In fact, looking back to Figure 3.17 a & b, we can see that, normalized by their Pauli paramagnetic limits, 3L, 4L and 5L TaS$_2$ all have greater enhancements in their $H_{c2\parallel}$ than 2L NbSe$_2$. This highlights the importance of interlayer coupling in these two van der Waals layers superconductor systems and the different ways in which it works. Lastly, the role of interlayer coupling in these systems is also seen in their divergent $T_c(N)$ behavior. As discussed in Section 1.1.8, the $T_c$ of NbSe$_2$ samples decreases in thinner samples, showing that coupling between the layers serves to enhance the superconducting state by enabling interlayer Cooper pairing and boosting the $T_c$. Conversely, in TaS$_2$ interlayer coupling cannot be serving in the exact same role since the $T_c$ increases in thinner samples. Later work by Yang et al. showed that this is
Figure 3.20: Monolayer 3-pt TaS$_2$ data

3-pt magnetotransport data at various set temperatures for the 1L TaS$_2$ sample after the graphite lead’s magnetoresistance is removed.
Figure 3.21: Layer dependence of interlayer coupling in TaS$_2$ & NbSe$_2$.

(a) Ratio of interlayer coupling energies to spin-orbit coupling strength $t_\perp/\Delta_{so}$ as a function of the number of layers for TaS$_2$ and NbSe$_2$ extracted from DFT, with $\Delta_{so}^{TaS_2} = 122$ meV and $\Delta_{so}^{NbSe_2} = 49.8$ meV. Dashed lines are provided as guides to the eye.

(b) Dependence of the reduced upper critical field $h_{c2} \equiv H_{c2}^||/H_p$ (evaluated at $T/T_{c0} = 0.8$) on the number of TaS$_2$ or NbSe$_2$ layers, including NbSe$_2$ data from [76]. Data are normalized by the reduced upper critical field of a monolayer $h_{c2}^{(1L)}$ to enable direct comparison.
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Figure 3.22: Fitting of $H_{c2}$ in monolayer TaS$_2$. Parallel critical field of 1L TaS$_2$ (normalized by $T_c$) with fits by standard GL square root equation, Spin-Orbit-Scattering fit. The range of data points obtained is not sufficient to claim a better match with one fit over the other. Solid lines result from DFT models of the K valley and entire Fermi surface with the inset showing the full extent of the models’ overshoot.

related to the energetically competing phenomenon of charge density waves (CDW), which occur in multilayer TaS$_2$ at temperatures below 120K. When CDW are reduced in TaS$_2$, the density of states at the Fermi energy increases. This increase acts to strengthen the superconducting state. When the 2D limit is reached, CDW vanishes completely in the monolayer TaS$_2$ system. The resultant increase in carrier density is sufficient to account for the increase in $T_c$ in few-layer samples [141].

3.4 Future Directions and Applications of Ising Superconductivity

Ising superconductivity is an attractive property for future applications of 2D superconductors. Since we published our work on this topic, new results have been published identifying a Type-II Ising superconductivity in centrosymmetric systems such as few-layer stanene ($\alpha$Sn(111)) and PdTe$_2$ [140, 142]. As they lack mirror
symmetry have inversion symmetry in the monolayer case, they are unlike a bilayer of NbSe$_2$ or TaS$_2$ which behave as weakly coupled non-centrosymmetric monolayers. The mechanism behind Type-II Ising superconductivity appears to be due to Ising pairing in different orbital bands around the $\Gamma$ point, rather than in the K and K' valleys, resulting thus far in a smaller enhancement over the Pauli limit than in Type-I Ising superconductors [140]. This has enabled characterization of the in-plane critical field near $T=0$, a region inaccessible by the world’s largest persistent magnets in NbSe$_2$, TaS$_2$ and MoS$_2$. Additionally, stanene and PdTe$_2$ are persistently stable in ambient atmospheric conditions, so these materials could be more easily integrated into various spintronic or superconducting applications [140, 142, 143].

Figure 3.23: Integrating Ising Superconductors for nanowire Majorana modes. (a) The bands in the K and -K valleys of an Ising superconductor are split by strong SOC with opposite polarity, both with a Zeeman gap of $2\beta_{so}$. (b) A half-metal wire on top of a Ising superconductor monolayer TMD, the red dots signify Majorana fermions at the ends of the wire (or also at any defects in the wire) that exist when the half metal has an in-plane spin polarization due to an applied field. (c) Calculated energy spectrum for the device shown in (b), topological Majorana modes are shown in red. (d) In the topological regime (red line in (c)), a modeled ground state of the system shows excitations at the end of the wire, representing Majorana fermions. Figure from [144]

As discussed in Section 1.1, superconductors and magnetic fields have a love-hate relationship. Superconducting wires are used to build magnets that can reach high magnetic fields that use less energy and have a smaller footprint, but the magnitude of that magnetic field is then limited by the critical field of the superconductor used to
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make the wire. In Section 1.1 I discussed the applications of high-$T_c$ superconductors and how the applications for superconductors in general have broadened and become more common as the upper limits of their capabilities are pushed higher. As discussed above, the in-plane critical fields of Ising superconductors are much greater than critical fields for other superconductors. Although this is a narrow improvement since large applied fields are restricted to the plane of Ising superconductors, it does leave open many potential applications.

Many engineering challenges would need to be solved for vdW superconductors to be used as the superconducting current path for a solenoid. However, if those challenges could be solved Ising superconductors would be able to continue conducting supercurrents in the presence of magnetic fields an order of magnitude greater than the materials used today. An intermediate step towards this usage would be to create a much smaller Ising solenoid that would function inside, and locally boost the field of a standard solenoid magnet, such that the applied field is always in the plane of the layers of the Ising solenoid. One possible approach to these engineering challenges would be to grow a monolayer Ising superconductor on the outside of hollow cylinder, starting on one side and rotating the cylinder as the superconducting monolayer forms, and simultaneously growing an insulating capping layer on the opposite side of the cylinder, thus creating spiralling layers of the monolayer Ising superconductor, boosting the current density and packing the loops atomically close to each other [145].

Smaller scale applications for Ising superconductors that could be built with current techniques focus on their integration with superconducting circuits. This would enable components that can operate in extremely high parallel fields. One such setup would be to use an Ising superconductor to proximitize a half-metallic nanowire to create a topological superconductor in pursuit of Majorana fermions, the characteristic signals of which are observed in a parallel applied magnetic field [144, 146]. Figure 3.23 shows one proposed schematic for such a device, alongside an energy spectrum from a tight binding model calculation [144]. Lastly, most of these applications would likely require the use of intrinsic Ising superconductors, as the geometries of the circuits involved are prohibitive of the integration of electrostatic (ionic liquid and/or MOSFET-style) gates.
Chapter 4

2D-3D Hybrid Superconducting Devices

4.1 Motivation

The *sine qua non* of integrating 2D van der Waals superconductors with 3D conventional superconducting circuits is the ability to create a zero resistance interface between these two components. Forging quality connections between these systems enables the generations of hybrid components and hybrid circuits that follow. The same way our work has been enabled by the efforts of those who pushed this field forward to where we are now. In this chapter I will first discuss methods of contacting van der Waals superconductors that are resistive, and follow up with prior integrations of van der Waals materials with superconducting circuits. The remainder of the chapter then discusses our work developing and measuring 2D-3D superconducting contacts between deposited Al and exfoliated and encapsulated NbSe$_2$ that has been published in our paper, "Superconducting Edge Contact and Quantum Interference Between Two-Dimensional van der Waals and Three-Dimensional Conventional Superconductors" [147].

4.1.1 Previous Contact Schemes

Previous work on 2D TMD superconductors has focused on the superconducting properties of the TMD, such as the layer dependence of critical temperatures, currents, and fields [31, 76, 77, 97, 145, 148, 149]. Using standard 4-pt resistance measurements, the contact and lead resistances are removed from the measurement, enabling the use of a variety of resistive contact schemes using deposited top contacts, pre-patterned gold beneath the TMD, and graphene/graphite stacked with the TMD.
Figure 4.1: Top contact to TaS$_2$ with no encapsulation
AFM image of Cr/Au contacts patterned and evaporated on top of bare TaS$_2$. Figure from [77]

**Top Au contacts**

Figure 4.1 shows how Navarro et al. patterned and deposited Cr/Au contacts on top of freshly exfoliated and unencapsulated TaS$_2$ [77]. They report success with contacting and measuring TaS$_2$ flakes as thin as 3.5nm (5L). However, they were unable to contact and measure TaS$_2$ flakes thinner than five layers, hypothesizing that this was likely due to material degradation [77]. Using a similar top contact schema but substituting Al or another superconductor for gold would likely work for thicker flakes of TMD superconductors, but because many of the most interesting properties of TMD superconductors emerge as they approach the 2D limit, degradation during fabrication steps remains a limitation [97]. Lithographically defined top contacts to few layer thick air sensitive TMDs would likely require significant nanofabrication infrastructure inside an inert atmosphere or vacuum chamber, and would require an insulating capping layer to encapsulate the TMD device after lead fabrication.

**Pre-Patterned Au Contacts**

The use of pre-patterned Cr/Au or Ti/Au contacts was discussed briefly in Section 3.2.2. The possibility of using pre-patterned superconducting materials to create zero resistance contacts has not been explored. My main reason for not attempting this method is that Al, which is the superconductor most widely used for superconducting qubit technologies, forms a self-passivating oxide layer several nm’s thick, which would preclude any possibility of stacking with a superconducting TMD to cre-
Figure 4.2: TaS$_2$ on Au contacts
Optical image of TaS$_2$ flake with top hBN encapsulation on top of pre-patterned Cr/Au leads. Tenting of the flakes is clearly visible around and between the leads

MoRe is a deposited superconductor that only forms a surface oxide layer slowly, it could possibly be used for pre-patterned superconducting contacts if atmospheric exposure limiting precautions and an expedited fabrication process were to be used \[150\]. The issues with this approach for air sensitive TMDs outlined in Section 3.2.2 are still problematic: “tenting” of the TMD flake over the elevated leads (opens a channel for contaminants and this region is no longer parallel to the substrate), no full bottom encapsulation, and requires flakes sized to fit to the spacing of the pre-patterned leads. These issues are clearly visible in Figure 4.2 where a TaS$_2$ flake was placed on pre-patterned Cr/Au leads with hBN on top.

Graphite/Graphene Contacts
The samples discussed in Chapter 3 mostly used few-layer graphite contacts stacked on top of the TMD superconductor to interface between it and the deposited Cr/Au leads. These graphite flakes were then etched into several channels to create multiple contacts out of a single graphite/TMD stacked interface. This allowed us to keep the air sensitive TMD encapsulated during the initial nanofabrication steps, but did result in exposed bare edges of the TMD in the last step of etching, as the etch lines must extend into the body of the TMD flake to separate the graphite into multiple, independent leads. While the superconducting properties of the monolayer TaS$_2$ sample did not seem to be impacted when measuring immediately after fabrication, 2 months after fabrication we observed significant degradation of the TaS$_2$ flake, visible in the AFM image (Figure 4.3).

A second problem with using graphene or few-layer graphite to contact super-
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Figure 4.3: Graphite contacted TaS$_2$

AFM image of graphite-contacted monolayer TaS$_2$, degradation of the TaS$_2$ flake has spread from the etched incursions, between the graphite leads, across the entire body of the flake (monolayer region outlined with blue dashed line). Scale bar is 2 µm.

conducting TMDs for characterization measurements was elucidated by Sata et al. in 2018. They compared the critical current of an NbSe$_2$ flake contacted with both graphene (few layer graphite in other samples) and Cr/Au leads and found a dramatic decrease in Ic when the current is sourced through the graphene [151]. As shown in Figure 4.4a, they used the same many-layer thick flake of NbSe$_2$ with roughly the same channel region between both sources and the metallic drain.

In Figure 4.4b,c they illustrate how heat spreads from the graphene contact into the NbSe$_2$ flake, relative to the use of metal top contacts. This flow of heat is charted in subfigure (d) as a combination of electron-electron, electron-phonon, and phonon-phonon interactions in the materials. This heating then reduces the critical current they measure in the NbSe$_2$ flake (Figure 4.5a,b). Moreover, they show that they can gate the carrier density in the graphene contact and vary the observed critical current in the NbSe$_2$ flake, as the carrier density changes, the conductance of the graphene changes. The critical current is slightly asymmetric across the Dirac peak, as the resistance of the device is slightly different in p & n gated regimes. The authors do not discuss the proximity effect in their paper, but the region of graphene directly under (and extending ~ 100nm outwards) is proximitized by the NbSe$_2$ flake [53, 152]. This would mean that heating in the far regions of the graphene at low DC currents spreads inwards to push the graphene into a normal state prior to the heat spreading into the NbSe$_2$ flake.

It is important to note that this work uses Ti/Au top contacts as a null reference to compare the greater heating (and lower Ic’s) when using graphene contacts to a superconducting TMD. However, because Au is also resistive, there is likely some
heating of the NbSe$_2$ flake near the Au contacts with the heat being transferred to the NbSe$_2$ flake through the same electron-electron, electron-phonon, and phonon-phonon channels. Although I have not done a comparison experiment on the same flake, it is likely that the use of a superconducting contact with a critical current greater than that of the TMD (possibly MoRe, NbN, or NbTiN) would measure an even larger critical current. My work with Al contacts, which I discuss in the rest of this chapter, does not fit this criteria because 100nm thick Al has a lower critical current than the NbSe$_2$ flakes in all of the measurements I present.

**Graphene Edge Contact**

The creation of graphene edge contacts in 2013 transformed the field of study, in much the same way the usage of hBN substrates for graphene did in 2010, by decreasing contact resistances, while increasing electron mobility and ease of high quality sample fabrication [64, 69, 99]. The edge contact process developed by Wang et al. results in a one dimensional contact along the exposed edge of the two dimensional graphene sheet, as shown in the schematic view in Figure 4.6 A. The edge of an etched graphene sheet has dangling bonds, while the top of the sheet has none, enabling lower resistance contacts to the edge of a graphene sheet (or to the edge of defects in a sheet) [99, 153, 154].

The TEM and EELS map in subfigure B show a clean etch slope between the top/bottom hBN and graphene with the Cr/Pd/Au contact adhering along the slope. Actual contact is made between the graphene carbon atoms and the Cr adhesion layer,
Figure 4.5: Reduced $I_c$ in graphite contacted NbSe$_2$

(a) IV curves show the NbSe$_2$ critical current changing as a function of the graphene back gate voltage. (b) IV curves show the insensitivity of NbSe$_2$ critical current when sourcing current from a metal electrode. (c) Plot of NbSe$_2$ critical current vs back gate voltage. (d) Graphene/NbSe$_2$ contact resistance as a function of back gate voltage, Dirac peak is clearly visible. (e) NbSe$_2$ critical current is constant with back gate voltage when using metal electrode as a source. Figure from [151]

which results in a lower contact resistance than using other metals because the work function of Cr is lower than that of graphene. The authors prove this through modeling, as well as showing that a further reduction in resistance and increase in bonding is obtained by introduction of an oxygen plasma prior to metallization [99]. This work quickly spread through the field of graphene research and inspired our methods for contacting encapsulated TMD superconductors.

4.1.2 Prior vdW/Superconductor Integration

While intrinsically superconducting TMDs have not previously been integrated into superconducting circuits, their superconducting properties have been thoroughly studied using both normal metal contacts and tunnel contacts [76, 77, 86]. Many combinations of van der Waals materials with superconductors have been realized, including
both planar and vertical Josephson junctions with weak links between deposited superconducting leads made from graphene and semiconducting TMDs with the furthest progress made in planar graphene devices [55, 150]. Proceeding from earlier work on the quantum hall effects as well as the ballistic transport of electrons in monolayer graphene flakes, the transport properties of superconductor-graphene-superconductor (SGS) Josephson junctions have been thoroughly explored [42, 49, 50, 52, 53, 155–158]. Initial work focused on planar SGS Josephson junctions where a narrow strip of monolayer or few layer graphene was proximitized between two top contacting superconducting electrodes (Al, Ti/Al, W) [52, 155, 156, 158]. These groups showed that tuning the carrier density in graphene in the planar SGS junctions with a gate can alter the critical current, but asymmetrically in the electron and hole regimes. Multiple Andreev reflections between each pair of superconducting contacts were observed by the groups (as device geometry limited them to two terminal measurements) [52, 155, 156]. The two studies that used monolayer graphene each reported evidence of ballistic transport over ranges of 0.5-1 µm [52, 155]. One study observed Shapiro steps with their junction under RF exposure as well as interference patterns in the SGS junctions as they swept magnetic field, with periods roughly proportional to the proximitized region of graphene between the superconducting leads [155].

These previous results were built upon as new efforts using similar geometries experimented with different superconductors for the contacts (Pb, Nb, NbN, ) [50, 53, 159]. Other groups began adopting superconducting edge-contact geometries pioneered by Wang et al. using normal metal contacts [49]. The observation of Fraunhofer patterns has been repeated multiple times, mostly following the expected flux dependence for the Josephson junction area (Equation 1.31) [49, 53]. Fabry-Perot
oscillations were observed in the critical currents as a function of gate voltage only in the hole doped region by multiple groups [49, 50]. This is understood to be due n-type doping of the graphene in regions directly adjacent to the contacts, forming a n-p-n cavity region within the bounds of the graphene flake, but also reducing the critical current in this domain [49]. While many groups had been competing more with the diffusive conduction channels with with other researchers to produce the longest ballistic SGS junction, another group went in the other direction by evaporating Ti/Al/Au on a monolayer of graphene, before flipping it upside down and repeating the deposition process to fabricate a vertical SGS Josephson junction (vGJJ). The 8nm of Ti on each side was weakly proximitized by the Al, while the Au formed good contact with a non-oxidized Al surface. In comparison with a more conventional SIS style junction without graphene but having an oxidized layer of Ti to form a barrier, the vGJJ had a normal state resistance two orders of magnitude lower than the SIS, and showed transparency \( \tau = 0.98 \) just shy of perfect transmission. In comparison with a non-oxidized no-graphene junction, the Al/Ti/Al acted more like a continuous superconductor than a junction [55]. The vGJJ was integrated into a DC SQUID and its current phase relationship was studied, but the skew in magnetic field response could not be accounted for.

Zhu et al. showed the importance of edge states to conductance in gapped bilayer graphene where the bulk is insulating due to electron localization [160]. In large displacement fields produced by top and bottom gates they compared parallel contact SGS devices with Corbino geometry SGS devices in which contact is made from a central circular contact to an outer ring contact, a significantly different topology. In this Corbino geometry there are no edges, and at high displacement fields they showed that resistivity continued to increase exponentially, while the parallel contact devices plateaued at several times the resistance quantum [160]. They concluded that the edge conductance channels in the parallel contact geometry effectively short circuit the insulating bulk and limit the maximum measured resistance, while in the Corbino geometry the lack of edge conductance channels allows resistivity to be orders of magnitude greater [160]. Many of the previous published results used signatures of the quantum Hall effect in their planar superconductor-graphene-superconductor junctions either as characterization of the monolayer thickness, or as evidence of device quality based on the number of resolvable Landau levels. At very high magnetic fields in short ballistic SGS Josephson junctions, when the cyclotron orbit grows smaller than the separation between the contacts, all conductance channels other than edge states are suppressed as electrons in the bulk are localized [56, 161]. Drailos et al. constructed SGS junctions with one edge of the graphene sticking well out from the junction contacts [56]. This allowed them to show that conductance is suppressed in these extended graphene devices. Leading to their conclusion that rather than two independent edge supercurrent channels, the edge conductance channels are part of an Andreev bound state (ABS) that surrounds the perimeter of the graphene between parallel contacts. When an edge of the graphene extends out far beyond the
superconducting contacts the path that the ABS follows in a standard ballistic SGS junction no longer forms a conduction channel for the ABS along that extended edge [56]. The superconductor/graphene devices over the previous decade focus on the effects seen in the SGS devices, but in 2018 several groups showed that they can take these SGS devices and integrate them as components into superconducting circuits [51, 162, 163]. Using RF measurement techniques they observe many of the same phenomena as seen in DC measurements, such as the existence of a Fabry-Perot n-p-n resonator in the hole doped gated region of the device, ballistic transport, and the band dispersion of graphene with the clear presence of the charge neutrality point. The three groups take slightly different approaches to integrating short ballistic SGS junctions into microwave circuits, Schmidt et al. create a hybrid device that can be measured in RF and DC, while Wang et al. and Kroll et al. create fully functional transmon qubits tunable via backgate voltage [51, 162, 163]. A transmon qubit is a type of charge qubit where the Josephson junction has been shunted by a small capacitance to reduce its sensitivity to charge noise \( E_C \ll E_J \). As shown in Equation 1.30, the Josephson energy is proportional to the critical current of the junction, so the frequency of the qubit is tunable by altering the junction’s critical current via the backgate. One of the advantages of an SGS transmon highlighted by Kroll et al. is its ability to operate in large in-plane magnetic fields up to 1 T, an order of magnitude higher than previous studies on other qubit systems [163]. Wang et al. highlight their ability to coherently control their SGS transmon by measuring the Rabi oscillations as it rotates continuously between the |0\rangle and |1\rangle states, and then using those measurements as calibration for their gate pulses to control the state of the qubit [162]. Lastly, using this coherent control of their qubit they were able to measure the decoherence times in the system, an energy relaxation lifetime \( T_1 \approx 36 \text{ ns} \) and a dephasing lifetime \( T_2 \approx 51 \text{ ns} \) [162]. In comparison, these are about four orders of magnitude below the current state of the art, but approximately equal to where that state was 15 years prior [164]. Various methods have been used to proximitize graphene into superconductivity over many micron long channels utilizing deposited superconducting films as well as arrays of superconducting nanodots [165]. Beyond the proximity effect in SGS Josephson junctions and graphene sheets, one of the biggest advances in graphene in recent years has been the realization of superconductivity in magic angle twisted bilayer graphene (TwBLG) [58, 60]. Unlike SGS junctions where the graphene is being proximitized by an edge contact and supercurrents cross the device via ABS edge channels, TBG is gated into being superconducting in and of itself. Alongside the other highly correlated electron states that can be found in gated TBG, the discovery of unconventional superconductivity which is as yet unexplained, has driven intense interest and fervorous experimental work in this system over the past 2 years [166–172]. Building upon this discovery and its subsequent verification, during the writing of this thesis two groups posted pre-prints on back-to-back days regarding their independent fabrications of gate-defined 2D planar Josephson junctions in twisted bilayer graphene. The results from the two groups are in excellent
agreement, and their observations of quantum interference patterns in the 2D planar Josephson junctions follow the same principles detailed later in this chapter [61, 62]. The potential integration of this system with conventional superconducting circuits is yet untried and unknown, but could be quite promising based on the tunability already demonstrated in this system.

### 4.2 TEM Characterization of Al/NbSe$_2$ contacts

We collaborated with Dr. Susheng Tan at PINSE, who specializes in cross-sectional Scanning Transmission Electron Microscopy (STEM) of nano-scale structures, to examine the Al/NbSe$_2$ interfaces in both our working and non-working devices. We hoped to gain a better understanding of how this interface works in our functioning devices to better understand the 2D-3D Josephson physics, as well as our nanofabrication process results. We also hoped to find out why our non-functioning devices were failing so we could alter our fabrication processes and increase our low yields.

Using an FEI (now Thermo Fisher Scientific) Scios focused-ion beam (FIB)/scanning electron microscope (SEM) dual beam system, in the process shown in Figure 5.10, Dr. Tan located the heterostructure (a) and began by depositing 100nm of amorphous carbon followed by 2 μm platinum capping layer on top of the devices on the substrate (b). This capping layer supports the structures as a 30kV focused ion beam is used to cut trenches on either side of the structure to isolate a thin cross section slice (c). This lamella is removed from the original substrate using the finger attached to the Pt capping layer (d) and placed on a Cu TEM grid which will be used during the STEM measurements (e). Using a lower acceleration voltage, the face of the cross section is polished using the FIB to create a more uniform surface. The final thinning of the cross section is performed using the FIB on the reverse face, such that the entire cross section is transparent to the electron beam (f). After this, Dr. Tan transferred the sample holder from the Scios system into the Thermo Fisher Scientific field-emission TEM. The STEM system is equipped with an X-ray energy dispersive spectrometer (EDS) and a high-angle annular dark-field (HAADF) STEM detector.

While our magnetotransport data provides indirect evidence of sample quality, STEM imaging of the sample with atomic scale resolution directly shows us the sample’s pristine structure. Figure 4.8a shows the NbSe$_2$ flake at the highest resolution, showing 6 layers of NbSe$_2$ in sample G with no substituted atoms, atomic vacancies, or intercalation between the layers, the lack of NbSe$_2$ degradation is good evidence of our encapsulation and protection techniques working as hoped. Zooming out, we can see the entire thickness of NbSe$_2$ and its interfaces with the top and bottom h-BN layers in Figure 4.8b. In this image the layers are atomically flat and clean, although in other devices we did see locations where the heterostructure interfaces were bubbled over dirt, or separated completely. In one non-working device a TEM scan (Figure 4.9) showed us that the NbSe$_2$ flake had been cut completely (or at least along this cross section), resulting in no observed resonances in RF, or super-
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(a) Device location
(b) Carbon & platinum protective cover
(c) FIB trenching and finger attachment
(d) removal of lamella for mounting
(e) Lamella mounted on Cu TEM grid
(f) Final thinning of cross section

Figure 4.7: Preparation for cross-sectional STEM
(a) The heterostructure is located using an SEM. (b) An amorphous carbon (100 nm) and Pt (2 µm) protective cap is deposited over the cross section. (c) Trenches define the cross section using a focused ion beam, and a finger is attached to the Pt cap. (d) The lamella is removed using the attached finger. (e) On the Cu TEM sample holder, the sample is polished thinner using lower FIB accelerating voltages. (f) The cross section is thinned to electron transparency.

conducting transitions in DC related to the flake or contacts, despite having a room temperature resistance below 1 kΩ. In comparison, most non-working devices showed room temperature resistances 20-60x greater, caused by the measurement current passing through the silicon substrate.
Figure 4.8: TEM of atomic layers and layer interfaces
Atomic resolution of NbSe$_2$ atoms and layer resolution of heterostructure interfaces in device G

Figure 4.9: TEM image of break in NbSe$_2$ flake
The red oval surrounds the region in which the NbSe$_2$ flake is broken off, with h-BN on top and a bubble of dirt beneath. The blue arrow points at the splayed and frayed layers at the very edge of the NbSe$_2$. The green arrow points to a cluster of crumpled layers a small distance from the break, and the purple arrow point to where the top h-BN has broken off. Black scale bar is 50nm.

**Etch profile**

TEM images of our functional contacts on two devices (Figure 4.10) surprised us by showing the lateral extension of the Al/NbSe$_2$ interface ranges between 79-130 nm in the four contacts. This seems to be a result of our etching process in which the NbSe$_2$ is apparently slower to etch in this region than our initial etch rate tests suggested.
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Figure 4.10: TEM scans of sample F&G Al/NbSe$_2$ contacts
TEM scans of the contacts in sample F with critical currents (a) 56.5 $\mu$A and (b) 78.5 $\mu$A and the contacts in sample G with critical currents (c) 128 $\mu$A and (d) 108 $\mu$A (e)/(f) Detail images of the Al/NbSe$_2$ contact regions indicated in (c)/(d) of sample G.

The right side of Figure 4.11 shows that the NbSe$_2$ is etched completely through in regions farther from the front of the lead. This could be explained by our ideally anisotropic vertical etches, that should stop etching at a sharp boundary delimited by our resist mask, scattering beneath the undercut of our resist mask and etching that region at lower etch rates. If so, we would expect the etch rate to decrease in
regions deeper inside the resist undercut. This could produce the features we see in the TEM images where we have a shallow sloped etch profile in one region and a deeper etch in the regions fully exposed by the mask. While the etch was performed normal to the substrate, the evaporation was angled to cover a region beneath the resist undercut. The etch profile extends almost to the front of the Al lead, providing further confirmation that etching occurred beneath the resist undercut. Our intention

![Figure 4.11: Labelled TEM scan of Al/NbSe$_2$ contact in sample G](image)

with the etch was to create a steep continuous slope from the top BN down through the NbSe$_2$ into the bottom BN that would expose just the edges of the NbSe$_2$ flake’s layers. This is still likely to happen for a monolayer TMD superconductor using our current process, and few layer samples should also be closer to this ideal etch profile. Another route to a steeper etch profile would be to use a different resist stack. A single layer resist does not have an undercut that could etch at a slower rate, but it would likely cause lift-off problems after Al deposition. A resist stack with a shorter bottom layer could be the middle path between a single resist layer and the status quo. A shorter undercut would limit the lateral spread of the etching plasma. So while it may not result in an ideally steep etch profile, it would likely be an improvement over our current results.

While our process has succeeded wonderfully in creating zero resistance 2D-3D superconducting contacts, the contacts that we made are somewhat of a hybridization between top contacts and edge contacts. This is still a success, because our contact method has produced this interface while keeping it safely encapsulated from the environment throughout the vast majority of our fabrication process. The other contact methods discussed at the beginning of this chapter did not have that capability.
X-ray energy dispersive spectrometry and HAADF detectors are used in parallel inside the TEM and are sensitive to atomic number, allowing elemental mapping of the sample. HAADF sensors detect scattered electrons, which scatter at shallower or sharper angles depending on the weight of the element they scatter from. The EDS detector measures the X-rays that are emitted by the elements in the sample when the electron beam causes their electrons to jump energy levels, each element having a unique emission spectrum. Figure 4.13 shows the results of scanning a single contact for six different elements (N,O,Si,Nb,Se,Al). We see high concentrations on nitrogen in the encapsulating BN layers above and below the NbSe$_2$ flake, with a slight signal in the amorphous carbon region above the BN and thankfully none in the contact region. The niobium is seen only in the NbSe$_2$ flake, but while the selenium signal is just as high as niobium in the flake, there is a dilute signal above the top BN flake where the amorphous carbon was deposited as well. This Se migration could have occurred during our etch process, but this region was covered with resist polymer throughout the etching and evaporation process, so it is much more likely to have happened during the FIB cutting and polishing during preparation for these TEM scans. Perhaps the niobium/selenium discrepancy in this region can be explained by a preferential bond to the amorphous carbon. The Si is solely in the substrate as expected (our etch did not hit the substrate in the near vicinity of the sample). Al is of course seen in the Al contact, but unexpectedly a faint Al signal is also seen along the top length of the NbSe$_2$ flake. It may be possible that aluminum atoms intercalated into the NbSe$_2$ layers, but no prior evidence of this could be found in the literature where purposeful intercalation of NbSe$_2$ is performed with a wet electrochemical process [173]. A more likely explanation includes the EDS oxygen data, which shows faint oxygen signatures around the rim of the Al lead, as well as in this same region at the top of the NbSe$_2$ flake. As we have taken strong precautions to etch away any region of the sample that was exposed to atmosphere before Al evaporation, the only exposure to atmosphere this region of the sample had was after FIB preparation as it was loaded into the TEM. It may then be possible that Al redeposited in this region during the FIB polishing process, and bonded to oxygen during the short window
between vacuum chambers, but this cannot be proven. However, the most important region of this device is the Al/NbSe$_2$ interface, and though it is a more extended length than we expected, it appears to be a rather clean and direct contact between the two materials. This shows that both our encapsulation during stacking and our etch process (RIE followed by in situ ion milling prior to evap) are working as planned to produce a clean 2D superconductor to 3D superconductor interface.

Figure 4.13: EDS elemental scans of an Al/NbSe$_2$ contact

EDS element sensitive scan for: (A) Nitrogen (B) Oxygen (C) Silicon (D) Niobium (E) Selenium (F) Aluminum.

4.3 Magnetotransport Measurements

As with our Ising superconductivity work, our primary experimental measurement technique for this project is low temperature magnetotransport measurements. All of my measurements for this project occurred in Pittsburgh in our lab at CMU or in one of the two dilution refrigerators at HatLab. Unlike the Ising superconductivity measurements, this project did not require magnetic fields greater than 5 Tesla. So we did not need the facilities available at the National High Magnetic Field Lab. My DC magnetotransport measurements focus on the properties of the Al/NbSe$_2$ contacts, rather than the NbSe$_2$ flakes themselves. To this end, rather than using a 4-pt resistance measurement setup with four contacts to the NbSe$_2$ flake, which would only measure the superconducting transition and critical current of the flake channel, I used what we call a pseudo 4-pt measurement setup. As described in more detail in Section 2.3.2, the Al leads split in a "Y" as they travel away from the Al/NbSe$_2$ contact (see inset, Figure 4.15), adding no line resistance at $T < 1K$ and $B < 10$ mT. Thus, when both the Al leads and NbSe$_2$ flake are superconducting and adding no resistance to the measurement circuit, the only resistance we could be measuring.
is the resistance of the Al/NbSe$_2$ contacts on either end of the flake measurement channel.

### 4.3.1 R(T) and our Noise Floor

As briefly discussed in Section 3.3.3, 2D superconductors in perpendicular magnetic fields are highly sensitive to high frequency noise which transmits significant power into the sample, and low pass filters must be added to the measurement lines to regain a zero resistance measurement[139]. These filters have not traditionally been used in the superconducting materials community, as evidenced by the long history of studies on the "quantum metal" finite resistance state in superconducting thin films [174–178]. While subsequent studies have found evidence of these finite resistance states, NbSe$_2$ regains its zero resistance state in a perpendicular magnetic field when the measurement lines are sufficiently filtered [179].

In our initial measurements of samples with Al/Ti/NbSe$_2$ contacts, we persistently measured a remnant resistance of $\sim 20–50\Omega$. We performed standard 4-pt resistance measurements on the NbSe$_2$ and Al separately to confirm that they each showed zero resistance states, which they did. So in our pseudo 4-pt resistance measurements we can associate any remnant resistance, after seeing both NbSe$_2$ and Al superconducting transitions in our R(T) measurements, with the 2D-3D contacts. The same pattern held true for an early device in which Al leads were evaporated directly on top of few-layer graphene encapsulated NbSe$_2$. After initially hypothesizing that this finite remnant resistance was due to fabrication flaws when we made the samples, we increased the RIE etch and in-situ ion milling times to ensure a clean exposed cross section, and stopped depositing the 3-5nm Ti adhesion layer below the Al. Neither of these changes affected the remnant resistances we were observing. Around this time period Dr. Hatridge raised the idea of adding filters to our measurement lines, as this was a standard procedure in the superconducting qubit community. We then upgraded our measurement setup with RC low-pass filters (cutoff frequency $\sim 10$ kHz) in series with a copper tape GHz frequency low-pass filter and a new Cu sample holder that fully enclosed and shielded our samples from any other sources of thermal radiation.

The dramatic effect of adding these filters is seen in Figure 4.14, where the R(T) curves of the contact resistances between Al and NbSe$_2$ are plotted for three samples with resistance on a log scale (Most samples discussed in this chapter have their characteristics summarized in Table 4.1). Sample A in this plot is the first sample we measured after implementing these changes. With both RC and Cu tape filters, it shows zero remnant resistance down to the noise floor of our measurement setup ($V_{RMS} = 0.8nV$ with a 100nA excitation current and 3s integration time). The noise floor we see here is symmetric about zero, giving us high confidence that this truly is a zero resistance superconducting state of the Al/NbSe$_2$ contacts. The bottom right inset plot of Figure 4.15 show the critical temperatures of NbSe$_2$ and Al in sample
Figure 4.14: Effect of low-pass filters on $R(T)$ of several devices
Sample A was measured both a complete filter system (blue) and without the RC filters removed (green). Sample B (yellow) was measured with the complete filter system, but still had a small remnant resistance. Sample J (red) was measured prior to our filter system being built.

$F$ on a linear plot. The main part of the figure displays log resistance down to the measurement’s symmetric noise floor, which is approximately an order of magnitude higher than that of sample A ($V_{RMS} = 6.7nV$ with a 100nA excitation current and 1s integration time). Sample F was measured approximately 1 year after sample A, so it is unclear if the difference in integration time fully accounts for the greater noise floor or if there was any other difference in the measurement setup that contributed.

When we remove the RC low-pass filters and measure sample A again we see a small (but non-zero) resistance, proving that these 2D-3D superconducting contacts are highly sensitive to noise in the kHz-MHz frequency range. The sensitivity of these 2D-3D superconducting contacts to noise in the GHz range is evident in Figure 4.14’s
Figure 4.15: Log(R) vs T from sample F

R(T) data from sample F plotted on a log resistance scale to better observe the noise floor. Top left inset is a schematic of our pseudo 4-pt measurement circuit, bottom right inset is the same R(T) data on a linear scale that includes the NbSe$_2$ transition at 7K.

R(T) curve for sample J, a similar sample that we had measured prior to installing the filters. Sample J shows a substantially larger remnant resistance ($\sim 20\Omega$) after the Al superconducting transition at 1K, which was typical for our samples measured without filters. The $\sim 0.6\Omega$ remnant resistance in sample A when exposing it to kHz and MHz frequency noise by removing the RC low-pass filters (measuring with only Cu tape GHz filters connected to the Cu clamshell sample holder), is overshadowed by the $\sim 20\Omega$ remnant resistance in sample J, which was exposed to an unfiltered spectrum of noise. This shows the relative effects of noise in GHz frequencies vs. kHz and MHz frequencies. The underlying mechanism behind this high frequency noise sensitivity is the decoupling of electron temperature from phonon temperature in the thermalized measurement lines inside the cryostat [103, 104]. Without filters, the electrons propagate high frequency thermal white noise from room temperature electronics by remaining at a higher temperature than the wires they pass through, and eventually dissipating this energy in the superconducting device being measured.
This system of low-pass filters dissipates high frequency noise as heat into the cryostat, reducing the electrons effective temperature close to that of the cryostat. The measurement of sample A with a remnant resistance of $\sim 0.6 \Omega$ shows that Cu tape GHz filters do the majority of the electron thermalization, but not 100%. The RC low-pass filters are essential for the best possible thermalization of electrons in the measurement lines. As a sanity check, we know that higher temperatures are associated with higher frequencies, so the Cu tape GHz filters allow electrons with lower, but still elevated, temperatures to pass. This setup was discussed in further depth in Section 2.3.1.

4.3.2 R(B)

![Figure 4.16: R(B) of sample A](image)

Semi-log plot of resistance vs. magnetic field in sample A. The magnetic field is presented on a log scale to show the critical field transitions of Al and NbSe$_2$, which are separated by 2+ orders of magnitude. Multiple critical fields are associated with various regions of Al. While the critical field of bulk Al is just 10mT, narrow Al leads will partially suppress orbital pair breaking, increasing their critical field by $\sim 10x$.

Our second measurement for any superconducting sample is measuring the resistance during a magnetic field sweep, R(B), using the same pseudo 4-pt measurement setup as with R(T). Aluminum, in the bulk, has a critical field of 10mT, but we see in Figure 4.16 that a second critical field is observed. This split occurs because our very narrow Al leads suppress orbital pair breaking effects (as described in Section 3.1.1) increasing their critical field by an order of magnitude. NbSe$_2$ has a perpendicular critical field that varies with thickness, for 10nm thick sample A the critical field is around 4.5T.

4.3.3 Critical Currents

After observing zero resistance states in our 2D-3D superconducting contacts and measuring the critical temperatures and fields of our sample’s components, the natural followup measurement is to measure the critical currents. As discussed in Section 1.1.9, interfaces between superconductors are Josephson junctions, weak links
between superconducting condensates. Technologically, the critical current we can pass between 3D and 2D superconductors will limit the types of 2D superconducting components we can integrate into superconducting circuits. If a 2D superconducting circuit component is reliant on using a current greater than that of the 2D-3D interface’s critical current, the junction will be driven into a resistive state, creating resistance in the formerly superconducting circuit. As physicists, we are interested in measuring the critical current of the 2D-3D Josephson junction to explore the Josephson dynamics of this novel superconducting interface by probing the current-phase relationship of the junction at various magnetic fields.

\( I_c - I_r \) Hysteresis in Al/NbSe\(_2\) junctions

![Figure 4.17: Critical current hysteresis with sweep direction](image)

We observe a small hysteresis of the spikes in the dV/dI curve of sample F related to the direction of the current sweep. Here, the green curve was measured from positive to negative, while the red curve was measured from negative to positive DC currents. Red spikes are critical currents (\( I_c \)) and green spikes are retrapping currents (\( I_r \)).

We determine the critical currents of a junction by measuring the differential resistance, dV/dI, using the same pseudo 4-pt measurement setup described above. The single addition to this setup is the inclusion of a DC current source spliced into the same measurement line as the lock-in amplifier AC excitation current source. When looking at differential resistance curves of superconducting samples, a sharp spike in the curve that then levels off at a higher resistance indicates a component’s critical current, while the jump in resistance from before to after the spike is the normal state resistance of that component. Section 2.3.3 describes the differential resistance measurement procedure in more detail.

The measured differential resistance curve of a superconductor will display hysteresis of the critical currents depending on the direction DC current is swept, as seen in Figure 4.17. When sweeping a DC current from the normal state down through a
critical current into a superconducting state, Joule heating occurs in the sample above the critical current, elevating the sample’s temperature and depressing the magnitude of the critical current [1, 116, 180]. In the other direction, the sample will remain at base temperature while the sourced DC current is below the critical current, maximizing the measured critical temperature. The spike in differential resistance observed when decreasing the magnitude of sourced DC current from above the transition point is called a retrapping current, to differentiate it from the critical current. We have observed 5-25% drops in retrapping currents compared to the critical currents in our various samples.

Much of the hysteretic behavior seen in the Al leads and the NbSe₂ flake (not shown in Figure 4.17) is due to Joule heating in our RC filters at their large values of I_c and I_r. As discussed in Section 2.3.1 at currents over 50 µA the RC filters heat the entire sample space significantly, increasing the base temperature by 50 mK at 80 µA and 250 mK at 150 µA. It is likely that a major contribution to hysteresis in the Al/NbSe₂ Josephson junctions can be attributed to heating in both the RC filters and possibly the Al leads. These dV/dI data sweeps were performed over approximately 3 minutes, so the time between the current bias I_r of the Al leads, and then subsequently passing through I_c of the contacts was about 20-30 seconds, with another 20 seconds pause between data runs for temperature stabilization, but from our present measurement setup and procedure, it is unclear what the relative contributions are to the heating of the sample. Since we are planning to replace our RC filters with a new design that will produce less heating at even larger currents, it’s worth investigating other possible causes of this hysteresis.

A possibility that Tinkham discusses as part of the RCSJ (resistively and capacitively shunted junction) model is that similar I_c-I_r hysteresis occurs in underdamped Josephson junctions with large shunt capacitances (Q>1, see Section 5.1.1 for an introduction to Q factors) [1, 116]. Looking to the literature for reported observations of I_c-I_r hysteresis due to underdamped Josephson junctions in similar systems, one group presented evidence of this occurring in proximity SGS Josephson junctions in both the short and long limits [159]. In this situation, an underdamped junction has been driven into the resistive state by a bias current exceeding the critical current. The bias current across the resistive junction creates a voltage, which drives the phase around continuously according to the second Josephson equation (Equation 1.27). The current then adds a constant amount of energy (IV=I²R) per 2π rotation of the phase, if the junction has Q>1, then for I ≥ I_r the damping doesn’t dissipate the full energy input, and the junction continues to be driven. The bias current must fall to some value I_r (dependent on Q) below I_c such that the entire IV energy input is damped each cycle, allowing the junction to return to a superconducting state with no voltage across the cycle that drives the phase [1]. This possibility could be relevant to many of our samples that are now integrated into superconducting LC resonators where the Al/NbSe₂ junctions are shunted by finger capacitors and Q≈ 10³ (See Chapter 5). However, those Q values were measured with RF signals using the transmission line
with no connections to the DC bond pads. In another paper on SGS junctions, 4 years later, the same authors attribute the hysteresis in their new assortment of long and short SGS junction samples to self heating effects after considering the underdamped junction scenario again, but this time rejecting it \cite{42}. So while we should be aware of this phenomenon, until we have any evidence that this process is causing hysteresis in our samples, we should first look to other potential causes.

It is also possible that hysteresis would result from heating in the junction itself, as the SGS junction authors concluded for their second set of samples \cite{42,181}. After the Al has returned to a superconducting state, the supercurrents flowing through the Al leads and NbSe$_2$ flake are larger than the junction critical current (as well as its retrapping current). So it cannot all tunnel coherently through the Al/NbSe$_2$ junction. At voltages below $2\Delta_0$, the current through the junction can be an admixture of tunneling supercurrent and a normal current \cite{182}. Because the currents in the Al and NbSe$_2$ are supercurrents, the normal component of the current must result in pair breaking as it crosses the junction, resulting in quasiparticle excitations (excitations of a matched hole and particle) out of equilibrium with the surrounding phonon bath \cite{1,86,106,182–184}. Although our current measurement circuit does not measure electron temperature in our samples, we can consider if it contributes to the difference between $I_c$ and $I_r$ \cite{103,104,185}. As discussed in Section 2.3.1, the low-pass filters on our measurement lines dissipate energy from hot electrons carrying room temperature thermal radiation so they don’t drive the Al/NbSe$_2$ Josephson junctions out of their zero resistance state. Pair breaking tunneling from NbSe$_2$ into Al would then be expected to generate quasiparticle excitations, also called Bogoliubov quasiparticles, or bogoliubons, further from equilibrium in the Al than the reverse, as $\sim 7\Delta_0^{Al} \approx \Delta_0^{NbSe_2} \approx 1.2\text{meV} \ (\Delta_0 = 1.764k_BT_c$ as discussed in Section 1.1.4) \cite{1}. Measurements in narrow aluminum wires show that hot quasiparticles will diffuse over $> 60\mu m$ through the superconductor as they interact with and lose energy to phonons and lower energy quasiparticles on nano- to micro-second timescales \cite{181}. Measurements were performed from a base temperature of 400 mK up to 800 mK and effects would be expected to be enhanced at lower temperatures. Lastly, a direct measurement of electron temperature in long SNS Josephson junctions supported the conclusion that self heating of electrons in the normal metal component suppressed retrapping current \cite{106}. They measured the electron temperature using the electron temperature dependent tunneling rate of a co-located SINIS junction that shared the normal metal component with the long SNS junction. In their conclusions, based on the $2pW/\mu m^3 = 1nW/\mu m^3$ power generated in their devices, they believe these results will hold for short SNS junctions as well as Josephson junctions based on nanowires, 2DEGs, nanotubes, which they estimate will generate $\geq 1nW/\mu m^3$ \cite{106}. 

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Critical current identification

When performing a differential resistance measurement at base temperature (< 100 mK), it may not be clear which critical currents are associated with the different superconducting components in the sample. For instance, in the differential resistance curve for sample A in Figure 4.18a we see five distinct peaks marking five critical currents, corresponding to five superconducting components in the sample. However, from just this plot, we can’t claim much, if any, knowledge of which components these are. At most, we can say that the Al/NbSe$_2$ Josephson junctions must have critical currents lower than the NbSe$_2$ flake and the portion of the Al lead directly adjacent to the interface. We have no firm knowledge based on this single plot of whether Al or NbSe$_2$ has the higher critical current.

One way to gain more characterization information to aid our identification of critical currents with superconducting components is to measure dV/dI at multiple temperatures and observe the behavior of the critical currents. Since we are already familiar with the critical temperatures of Al and NbSe$_2$ from our R(T) data, the temperature dependence of the critical currents near each $T_c$ is very informative. We do this in Figure 4.18b by taking a dV/dI sweep at base temperature (Figure 4.18a), then slowly increasing the sample temperature using a heater in the cryostat, and performing differential resistance measurements (always sweeping current up from zero in the same direction, raster) repeatedly, then finishing off with one final dV/dI at max T. The resulting data from this method is not quite as clean as if we were to stop and stabilize the temperature at a setpoint before taking a dV/dI measurements, but it is significantly faster (and orders of magnitude faster than sweeping the sample temperature at fixed DC current setpoints). The biggest difference between these two methods is the resulting data points in Figure 4.18(b) lay on diagonal lines with positive slope stretching across the plot, rather than a truly horizontal raster scan. We can learn much more from this dV/dI data with temperature dependence than we could from sweeping the current at one single temperature. We see that the five critical currents observed in Figure 4.18a all vanish above $T_c^{Al} \sim 1$K, which along with the appearance of a critical current that vanishes at $T_c^{NbSe_2} \sim 7$K, tells us that none of those five critical currents belong to the NbSe$_2$ flake, and are all associated with the Al leads or the Al/NbSe$_2$ Josephson junctions. Our fabrication process for this sample used 40 nm of Al evaporated at ±30 degrees for two opposing contacts, resulting in small regions of Al near the flake that are only 40 nm thick, while the majority of the Al leads elsewhere are 80 nm thick with 40 nm edges. Knowing that the Josephson junction critical currents must be smaller than the adjacent 40 nm Al leads, and thin Al should have a smaller critical current than thicker Al, we can tentatively identify $I^1_c$ & $I^2_c$ as belonging to the two Al/NbSe$_2$ Josephson junctions and the larger three critical currents to the various sections of Al leads and bond pads in order of increasing cross-sectional area. There are several less prominent shifts in shading in the same region as $I^3_c, I^4_c, I^5_c$ that are also likely related to the Al leads, but we will restrict our discussion to the most prominent Al critical currents for clarity.
Figure 4.18: $dV/dI$ vs. $I_{DC}$ and $dV/dI$ vs. $T$ and $I_{DC}$ for sample A

(a) Differential resistance ($dV/dI$) vs. DC current $I_{DC}$ of same device, showing five DC critical currents 1, 2, 3, 4, 5 with $I_c \approx 12, 26, 35, 45, 49 \mu A$. The temperature dependence of these critical currents in b associates them with aluminum and the Al-NbSe$_2$ contacts instead of the NbSe$_2$ flake, the critical current of which is not shown.

(b) $I_{DC}$ and $T$ vs. $dV/dI$ shows that all five critical currents observed in B are associated with the Al/NbSe$_2$ contacts and Al leads, as evidenced by $I_c^{(1-5)} \to 0$ at $T_{cAl} = 1.2K$, while $I_{cNbSe_2} \to 0$ at bulk $T_{cNbSe_2} = 7K$.

One further detail to examine is the normal state resistance, $R_n$, of the Al/NbSe$_2$ junctions. Using the Ambegaokar-Baratoff relation, Equation 1.28, we can multiply each $R_n$ by its respective critical current to see if our junctions of different sizes are invariant to scaling \[40, 186\]. With further knowledge of the nature of the junction, we could also use this equation as a sign of the quality of the junctions \[187\].

Sample F was fabricated using only a single angle of evaporation, so the Al leads and bond pads are of uniform thickness, this simplifies the process of matching critical currents with superconducting components in the sample. Additionally, we have cross sectional STEM images of sample F’s Al/NbSe$_2$ Josephson junctions (Figure 4.10 a,b), allowing us to calculate critical current densities, $J_c$, after we have identified the
Figure 4.19: $dV/dI$ vs. $T$ and $I_{DC}$ for sample F at 0mT & 3mT

(a) $dV/dI$ vs. $T$ and $I_{DC}$ at 0 mT (Device F). The critical currents associated with the contacts ($I_c^{(1)}$ & $I_c^{(2)}$) are well below their maximum at zero flux, indicating that this measurement with zero applied field is measuring a finite amount of trapped flux through the NbSe$_2$ flake in the areas associated with each junction. (b) $dV/dI$ vs. $T$ and $I_{DC}$ at 3 mT. The smaller of the critical currents (associated with the narrower of the 2 contacts) exhibits hopping behavior between two discrete flux states. This suggests that a single vortex is moving in and out of the area of the NbSe$_2$ flake measured by this contact. The shift in $I_c$ between the two levels is significant. In both plots, the $T_c$ of all critical currents associated with the aluminum leads and Al/NbSe$_2$ contacts is 1.1 K. Above 5.5 K the NbSe$_2$ critical current splits into two critical currents with $T_c = 6.5$ K, 7 K.
critical currents with $T_c = 6.5\,\text{K} \& 7\,\text{K}$ (perhaps due to a small section of NbSe$_2$ being slightly thinner). Comparing these zero field critical currents with those measured at 3mT, we see that the Al critical current, $I_{c}^{(3)}$, which was previously stepped over a small range, has split into two distinct levels corresponding to the bulk Al and the narrow leads where orbital pair breaking is slightly suppressed (as in Figure 4.16 and Section 3.1.1). The NbSe$_2$ flake’s critical current, $I_{c}^{(4)}$, remains much the same at $< 0.1\%$ of its critical field. Most interesting, however, are the critical currents of the Al/NbSe$_2$ Josephson junctions, both of which are larger than measured at zero field, with the smaller of them showing 19 intermittent jumps between two (or more) states (the larger one follows a smooth curve with no jumps, aside from a single $dV/dI$ curve at the lowest temperature). Measuring larger critical currents at a finite field than at zero applied field implies that the critical currents of the Josephson junctions are in some way dependent on magnetic field. As discussed in Section 1.1.9, we know that Josephson junctions produce quantum interference patterns as magnetic flux is threaded through the cross section of the junction with period $B*\Delta_{eff}/\Phi_0$ (magnetic field $B$, effective cross sectional area $A$, and flux quantum as in Equation 1.31). However, in typical Al/AlOx/Al Josephson junctions the period is greater than the critical field of Al, so significant modulation is not observed. Lastly, we seek to explain the critical current jumps between several states. As the applied magnetic field was held constant throughout the measurements used for Figure 4.19b, there must be some local phenomena affecting the flux through the Josephson junctions. We will explore both of these features in further depth in the next section.

The last dimension we can explore critical currents along in our measurement setup is magnetic field. As with the above measurements of the critical currents’ dependence on temperature, our knowledge of the critical fields of the superconducting components can also help us match critical currents with components. Figure 4.20a is an amalgamation of three separate data sets that each have different parameter windows. Each data set can take 12-24 hours (and sometimes significantly more) to capture, so we tune the parameter space for each data set to capture specific features of the device. In the amalgamation, we can see the critical current of the NbSe$_2$ flake at the top, with little variance at these small magnetic fields, and the cluster of Al and critical currents in the bottom left, with the critical current of the narrow Al leads extending out to higher fields in the bottom right. If we look at the higher resolution data set that focuses on the Josephson junction and bulk Al critical currents in Figure 4.20b, we can see that the peak of the currents is slightly offset from 0 mT. This can be attributed to either flux trapping or a slight (0.03%) offset in the calibration of our 13 T superconducting magnet used to apply the magnetic field to the sample. While this zero field offset is approximately equal to the 3 mT change between Figure 4.19a,b that caused the Al/NbSe$_2$ critical currents to increase above, those measurements were taken over a year after the measurements in Figure 4.20b, and we can tell that there was not an equivalent field offset then because the Al critical currents decreased in the 3 mT, while the Josephson junction critical currents
Figure 4.20: $dV/dI$ vs. $B$ and $I_{DC}$ data from sample A

(a) Three data sets covering partially overlapping regions are combined to show the critical currents of the Al leads, Al/NbSe$_2$ contacts and the NbSe$_2$ flake. (b) The central data set from (a) has the highest resolution (0.5 mT/scan) of the Al/NbSe$_2$ Josephson junction interference patterns.

increased. In measurements over several years we have seen the measured zero field shift by $\pm 7$ mT from the zero field/current setpoint of the magnet, so this is not
particularly unusual. In the range of $0-10 \text{ mT}$ the critical currents associated with the Al/NbSe$_2$ Josephson junctions are mostly indistinguishable due to the low resolution, but it does appear that they modulate non-monotonically with magnetic field. When this data was taken, we ascribed this complex and uninterpretable behavior to the presence of 5 or more critical currents resulting from double angle evaporation. We decided to primarily use single angle evaporation in the future to, in part, reduce the complexity of these plots. If we had taken another data set with higher magnetic field resolution, it's possible that we could have recognized the quantum interference pattern causing a modulation of critical current as we change the magnetic field. If we had taken further data and consulted with colleagues, we could have understood the nature and behavior of our samples over a year earlier when we finally did.

A note on pausing between data sets

The several Al critical currents in this plot with critical fields within $\pm 10 - 20 \text{ mT}$ of the center of symmetry have a non-monotonically decreasing critical field that is "pinched in" below $5 \mu\text{A}$. This feature appears to be an artifact from the precise way we set up the measurement run, as it occurs in no other sample we measured, nor one of the other data sets on this sample. We swept the DC current up to $40 \mu\text{A}$ at a set field, then stepped the field to the next setpoint and immediately started the next DC current sweep. Because our code executed these steps one immediately after the next, there was no settling time for the sample to cool from the Joule heating regime it was in at the end of the previous sweep. So at the beginning of each sweep, the Al leads were still cooling, and it took several seconds for them to cool sufficiently to be within their critical current at that temperature. This behavior is not seen in the data set in Figure 4.20a that encompasses $\pm 50 \mu\text{A}$ and $0-50 \text{ mT}$, where this transition is observed as a slightly reduced retrapping current below the X-axis. One of the critical currents does not seem to exhibit this same heating/retrapping current behavior, instead that critical current extends relatively smoothly out to both positive and negative fields. It appears to survive past $\pm 10 \text{ mT}$, so it is unlikely to be bulk aluminum. However, based on this data set, we can’t say anything further with confidence. In all future measurement campaigns, we coded in a wait time between all data sweeps, with the time being varied as needed in that parameter space. Although this particular data set wasn’t the sole cause for our change in practice, it was a good lesson to respect the characteristic times of your sample and measurement setup.

4.4 Quantum Interference Patterns

In Section 1.1.9 we discussed the dependence of the Josephson current in a short Josephson junction on an applied magnetic field aligned with the cross section of that junction (See Figure 1.13 and 1.12). After seeing hints of a quantum interference
pattern in the data we have already presented and discussed, we will now focus on the primary data sets and analyzing the quantum interference patterns we find.

Measurements

![Figure 4.21: $dV/dI$ vs. $B$ and $I_{DC}$ data from sample F](image)

$dV/dI$ vs. $B$ and $I_{DC}$ data were taken by sweeping DC current from negative to positive, resulting in the top/bottom asymmetry of retrapping and critical currents. Two quantum interference patterns are evident within the envelope of Al critical currents. The centers of the two interference patterns are offset slightly in magnetic field, likely due to trapped flux.

When measuring sample F, I repeated the same type of $dV/dI$ vs. $B$ and $I_{DC}$ measurements that I had performed on sample A the previous year, but with a smaller magnetic field step size, resulting in the higher resolution plot shown in Figure 4.21. The bulk and narrow Al critical currents are clearly visible, splitting at $\pm2\,\text{mT}$ with the narrow Al persisting at much higher fields and the bulk Al vanishing near $10\,\text{mT}$, while the NbSe$_2$ critical current is far above this scale. Inside the envelope formed by the bulk Al critical currents, we see the two critical currents associated with the Al/NbSe$_2$ Josephson junctions modulate with changing magnetic field, forming two overlapping quantum interference patterns with periods of $\sim2.4\,\text{mT}$. In our measurement, we only see a zero resistance state when both contacts are each in a zero resistance state. So it is interesting to note that the two patterns appear to be offset by $\sim1\,\text{mT}$. Since they are in a uniform applied field, and the entire pattern is offset, not just a single peak, the one contact must have flux $\phi_1$, while the other contact has flux $\phi_2 \neq \phi_1$. From our discussion of vortices in Section 1.1.7, we know that they can be pinned on defects, impurities or external influences on a superconductor. So the best explanation for the offset between these two quantum interference patterns...
is that a vortex carrying a flux quantum is near one of the contacts, and was pinned there with a high enough pinning energy that it did not become unpinned throughout the overnight data run that swept DC current ±150 µA and -12 mT up to 12 mT. However, if this vortex carrying a flux quantum was inside the junction we would see a full one period offset between the two patterns. Instead we see an offset of only one quarter of the larger period pattern, leaving this offset unexplained by the presence of a Josephson vortex carrying one flux quantum.

Returning to the interference pattern periodicity question, we can use the magnetic flux quantum to convert from magnetic field period to physical area ($\phi_0 = \hbar/2e = 2.06 \times 10^{-15}$ Tm$^2$ in SI units). Doing so, we see that these periods correspond to Josephson junctions with cross sectional areas of $0.5 \mu m^2$ & $1 \mu m^2$.

A standard Al/AlOx/Al Josephson junction (d=1.7nm, $\lambda = 16nm$) would need to be 15-30 µm long to have equivalent cross-sectional areas [188]. From our TEM images in the previous section (Figure 4.10) we can measure the length of the interface.
between the etched NbSe\textsubscript{2} slope and the aluminum deposited along it. Our two Al/NbSe\textsubscript{2} interfaces on sample F are 92 nm and 79 nm long and 1.4 \mu m and 2.0 \mu m wide (See Table 4.1 for characteristic data on all samples discussed in this chapter). So the interfaces of the two contacts are 0.128 \mu m\textsuperscript{2} and 0.158 \mu m\textsuperscript{2}. This shows that the effective area of each junction is many times larger than the physical interface region. In fact, the total area of the NbSe\textsubscript{2} flake used in sample F is only \sim 5 \mu m\textsuperscript{2}, so the effective areas of these 2D/3D Josephson junctions are 10-20\% of the total area of the 2D superconductor.

Figure 4.23 shows that the periodicity of this quantum interference pattern has no temperature dependence (100 mK data is reproduced from Figure 4.21). After the 100 mK data was taken, the NbSe\textsubscript{2} flake was driven into the normal state before the measurements for the five plots at elevated set temperatures, so the vortex that caused the offset between the two interference patterns in Figure 4.21 is no longer present. As temperature is increased, the diamond shaped window of the Al critical current is narrowed in both field and current.

Having previously identified the origins of each critical current, we are now able to find the normal state resistance of each contact independent of the other and use those values in the Ambegaokar-Baratoff relation. If we look closely at different regions of the superposed quantum interference patterns in Figure 4.21 we see the normal state resistance of each contact while the other contact remains superconducting. As shown in Table 4.1, the two contacts with critical currents 56.5 \mu A \& 78.5 \mu A have normal state resistances of 2.06 \Omega \& 1.31 \Omega respectively, resulting in I\textsubscript{c}R\textsubscript{n} values of 116.4 \mu V \& 102.8 \mu V. These values are reasonably close to one another, such that we could start off by working under the assumption that the Ambegaokar-Baratoff relation is valid for our system and the junctions are invariant under scaling. Unfortunately, the right hand side of the equation is more complicated than was presented in Equation 1.28 because these are two dissimilar superconductors with unequal superconducting gaps (\Delta_{\text{NbSe}\textsubscript{2}} = 1.764k_B7K = 1.064 meV \& \Delta_{\text{Al}} = 1.764k_B1.1K = 0.1672 meV). Golubov et al., among others present modifications to the Ambegaokar-Baratoff relation to handle the case of dissimilar superconductors [40, 186, 189]. Ambegaokar and Baratoff suggest a method of using the smaller gap weighted by an elliptic integral of the ratio of the gaps squared (Equation 4.1 [40]. Evaluating this in the zero temperature limit, since our data was taken at \text{T} \ll \text{T}_{\text{c}}^{\text{Al}}, results in the value of I\textsubscript{c}R\textsubscript{n} = 967 \mu V significantly larger than our measured value for our junctions. Lee et al., in their study of SGS vertical junctions, use a weighting from Böttcher et al. of the two superconducting gaps for the top and bottom Al leads (Equation 4.2) In their case, the difference in thickness was sufficient to alter the critical temperature and thus the superconducting gap of the bottom lead [41, 55]. Originally formulated for a generic S\textsuperscript{1}NS\textsuperscript{3} junction, it doesn’t exactly match our S\textsuperscript{1}S\textsuperscript{2} style junction, not to mention that one of the superconductors is in the two dimensional limit, so this specific application is certainly not its intended use-case either [41, 55, 189]. This results in I\textsubscript{c}R\textsubscript{n} = 227 \mu V, which is slightly lower
Figure 4.23: $dV/dI$ vs. $B$ and $I_{DC}$ at 6 temperature setpoints
Performing the same measurement as in Figure 4.21 at an additional 5 higher temperature setpoints shows the interference pattern periods have no temperature dependence. Instead, they are cut off as the critical current of aluminum shrinks. The offset between interference patterns does not reoccur after 100mK, however, that data set was taken several days before the other 5 data sets.

than the 262mV obtained by plugging the superconducting gap of Al into the standard Ambegaokar-Baratoff Equation 1.28, but still more than twice as large as our experimental values.
A further complication to these calculations that explains our poor results thus far is the fact that NbSe$_2$ is a multiband superconductor with two superconducting gaps, so unlike aluminum it is not a simple s-wave BCS superconductor [86, 190–193]. Noat et al. characterize NbSe$_2$ as having three sets of bands, bonding and antibonding Nb associated bands and a Se band [190, 193]. Only the Nb band that surrounds the K points of the Brillouin zone is inherently superconducting. That Nb band has the larger gap, while the Nb band around the $\Gamma$ point is proximitized into having a smaller band gap[190, 193]. The Se band is strongly coupled to the K point Nb band. The larger gap is observed when tunnelling spectroscopy is performed on a flat top or bottom surface such that tunneling is aligned with the crystal’s c-axis [193]. The large gap is observed because it is coupled to the Se band that dominates current transport in the out-of-plane direction[190]. Conversely, the smaller superconducting gap is observed when tunneling spectroscopy is performed edge on to the plane of the NbSe$_2$ flake [190, 193]. Although the two gaps are seemingly anisotropic, the phenomena of two gap superconductivity is distinctly different from a superconductor having an anisotropic gap. The multiple scanning tunneling spectroscopy studies of NbSe$_2$ have produced an array of large/small gap values. Most agree that $\Delta_L^{\text{NbSe}_2} = 1.2 - 1.4$ meV while the smaller gap $\Delta_S^{\text{NbSe}_2} \leq 0.5$ meV, but the smaller gap has much wider spread of estimates. However, knowing that NbSe$_2$ is a multiband superconductor still does not enable us to use a standard form of the Ambegaokar-Baratoff relations to evaluate $I_c R_n$. While Golubov et al. present a wonderful compendium of current phase relationships in a myriad of superconducting weak links, none of them fit the situation we have here of a multiband-single band 2DS-3DS' junction [187, 189].

\[
I_c R_n = \left( \frac{\pi \Delta_1}{2e} \right) K \left( \sqrt{1 - \frac{\Delta_1^2}{\Delta_2^2}} \right) \quad (4.1)
\]

\[
I_c R_n = \left( \frac{\pi \Delta_1 \Delta_2}{2e(\Delta_1 + \Delta_2)} \right) \quad (4.2)
\]

If we approach this relation from the opposite end of things, we can use our experimental values of $I_c R_n$ to solve for the band gap, or in this case for an effective band that we can’t calculate in the standard way with a quick and easy corrective term. For $I_c R_n = 116 \mu V$, the associated band gap for a BCS superconductor would be $\Delta_{\text{eff}} = 0.0738$ meV, less than half that of Al.

### 4.4.1 Theory of 2D-3D Josephson Junctions

From Section 1.1.8, we know that superconductors with thickness $d \ll \lambda$ fall into the Pearl limit, where their effective penetration depth is $\lambda_{\text{Pearl}} = 2\lambda^2/d$ and unlike Abrikosov vortices, the magnetic field associated with each Pearl vortex falls off as
For sufficiently thin samples, $\lambda_{\text{Pearl}}$ can be many microns or even millimeters long. The presence of multiple Pearl vortices in a sample, which will spread out due to long range repulsive forces, results in the 2D superconductor being nearly uniformly penetrated by the applied magnetic field (discounting the normal vortex cores themselves). The London equations then tell us that a sheet current will flow throughout its extent which will slightly, but by no means fully, counter the applied field. In a 3D-3D Josephson junction it is always possible to use flux quantization to draw a contour (and its enclosed surface) within some connected region of current-free bulk around which the phase will wind by $2\pi$ due to a single flux quantum, in 2D superconductors the more general fluxoid quantization condition that integrates over the supercurrents on the contour is necessary (Section 1.1.6). Looking at Figure 4.24(a), we can see that in a 3D-3D SIS junction the field only penetrates within $\lambda$ of the tunnel barrier, letting us draw a contour using points P, Q and P', Q' exterior to the flux region. Fully enclosing the flux, we know that the supercurrent along this contour will be zero. This is the case described by the definition of $\phi$ in Equation 1.31.

Figure 4.24: 3D-3D vs 3D-2D Josephson junctions

(a) Effective flux area of a 3D-3D Josephson junction includes the width $L$ of the barrier, plus a penetration depth into the superconductors on either side. (b) Effective flux area of a 3D-2D Josephson junction includes a large region within the body of the flake (an idealized circular 2D superconductor with radial symmetry simplifies this example).

In the case of our 2D-3D junctions, the field will penetrate a depth $\lambda_1$ into the 3D superconductor as before, but this is negligible compared to the near uniform penetration of the entire 2D superconductor. If we take the case where the 2D-3D junction has one flux quanta through it and apply fluxoid quantization, as the 2D superconductor has supercurrents flowing everywhere, we need to draw a contour to fulfill the condition that the phase changes by $2\pi$ around the contour. This is necessary because the superconducting phase is a continuous variable within a superconductor, and can only be discontinuous across a boundary like a Josephson junction. Along the boundary of the Josephson junction (P-Q) in Figure 4.24(b), when one flux quanta
is within the junction’s effective area, the phase difference $\delta$ across the junction must change continuously (though not necessarily uniformly) along the length of the junction ($\delta_P = 0$ to $\delta_Q = 2\pi$). In Figure 1.13 zero net current passes through the junction when one flux quanta (one Josephson vortex) is threaded through it. So if we draw our contour starting at point P inside the 2D superconductor, cross the junction and then pass through the bulk region of the 3D superconductor such that there is no current and no phase change and return to the junction at point Q, we then cross the junction at point Q and have gained a full $2\pi$ shift in phase. To complete our contour, we then have to find a path through the body of the 2D superconductor on which there is no phase change from Q to P. Recalling the Ginzburg-Landau supercurrent Equation 1.14, we can see that the current density is dependent on the gradient of the phase, so we know that conversely, the phase must change along the path of the current. This allows us to select a path from Q to P that is transverse to the supercurrent everywhere, adding zero change in phase to our total. For the circular 2D superconductor with supercurrent flowing in concentric circles in Figure 4.24(b), the current has no radial components ($\mathbf{J} = J \hat{\theta} + 0 \hat{r}$). So we can choose the radial paths Q-O and O-P to close our original contour with a total phase change of $2\pi$. This defines the region PQO as the effective flux region of this 2D-3D Josephson junction. Looking back at the offset in the two quantum interference patterns that we noted in Figure 4.21) we had concluded that because they were only offset by a fraction of a period, there could not be a Josephson vortex carrying a whole flux quanta in the one contact to cause the offset. The same would hold true for these effective flux regions if this were a 3D superconductor and an Abrikosov vortex was inside the region. Since the vast majority of the flux of an Abrikosov vortex is within the normal core and a penetration depth radius around the core, the presence of an Abrikosov vortex within this region would cause a larger offset between the patterns than we observe here. However, Pearl vortices have their magnetic flux spread over a much larger region. So a Pearl vortex could be right near the boundary of this effective flux region with a significant fraction of its flux passing through the contact’s effective flux region, without contributing a full flux quantum. In fact, if you were to take a symmetric pie slice on the opposite side of the circular 2D superconductor in Figure 4.24(b), call it some RSO region of equal size and opposite position to PQO. Then a Pearl vortex could be pinned in the 2D superconductor somewhere outside of these two regions such that magnetic flux associated with the vortex is passing through both contacts’ effective flux regions, but in different amounts. In fact, in a 2D superconductor with dimensions on the order of a Pearl length $\lambda_{Pearl}$, a Pearl vortex anywhere in the sample will contribute magnetic flux to both contacts’ flux regions, even in a non-circular sample. We can compare this to another vortex we detected in Figure 4.19(b), where we see many discrete jumps in one contact between flux states with dramatically different Josephson currents, while the other contact shows no jumping at all. This would mean that the flux through one contacts effective flux area is changing dramatically, while the other is not changing much if at all. This could perhaps be due to the
normal core of a vortex, which even in a Pearl vortex contains the highest density of flux, moving between two or more pinning sites, one of which was inside the effective area of the contact and all of which were far away and approximately equidistant from the other contacts effective flux area.

The case of a non-circular 2D superconductor is, of course, more complicated than what we sketched out above. Using the NbSe$_2$ flake in sample F, shown in the SEM image in Figure 4.25(a), its not possible to just look at this flake at define an effective flux region because of its irregular and non-symmetric shape. The Ginzburg-Landau supercurrent equation for such a shape cannot be solved analytically, instead we undertake to solve it numerically with boundary conditions. We know that our 2D flake is nearly uniformly penetrated by the applied magnetic field, because the sample’s dimensions are of the same order of magnitude as the Pearl length, which lets us treat the magnitude of the order parameter as a constant $|\psi(\vec{r})| = \psi_0$ such that our order parameter is only a function of the position dependent phase $\phi(\vec{r})$. Starting from the Ginzburg-Landau equation as written in Equation 1.13, we can rewrite it as below using this condition.

\[
\alpha \psi + \beta |\psi|^2 \psi + \frac{1}{2m^*} \left( \frac{\hbar}{i} \nabla - \frac{e^*}{c} \vec{A} \right)^2 \psi = 0 \quad (4.3)
\]

\[
\nabla \phi(\vec{r}) - \frac{2e}{\hbar c} \vec{A}(\vec{r}) = 0 \quad (4.4)
\]

Equation 4.4 is then solved numerically with the boundary condition that at the edge of the 2D superconductor, the supercurrent is parallel to that edge. In other words, there is no supercurrent passing through the boundary of the flake, so the component of the supercurrent perpendicular to the boundary is zero at all points on the boundary (ignoring Josephson currents through the contacts on the assumption that they are small in comparison). Our only input to this model is the shape of the 2D superconductor with a known physical scale. Our theory collaborator, Dr. David Pekker, wrote this first-principles model in Mathematica. After we provide our geometric input and define which edges of the polygon are the Al/NbSe$_2$ contacts, the Mathematica model converts the shape to a partial differential equation for $\phi(\vec{r})$. Using the Landau gauge we can write the vector potential $\vec{A}(\vec{r}) = B_z \times \hat{j}$, which the program uses to solve the partial differential for $\phi(\vec{r})$ in our defined shape using Neumann boundary conditions, which are equivalent to our statement above that the component normal to the boundary is zero everywhere, and the phase is continuous and smooth around the boundary so that it has a derivative everywhere. Physically, this means that the model has to solve the partial differential equation such that there are supercurrents everywhere in the flake with no discontinuities.

\[
\vec{J}(\vec{r}) = \frac{e^* \hbar}{m^* \psi_0^2} \left( \nabla \phi(\vec{r}) - \frac{e^*}{\hbar c} \vec{A}(\vec{r}) \right) \quad (4.5)
\]
Using the phase \( \phi(\vec{r}) \), the GL supercurrent Equation 4.5 can be solved everywhere inside the boundaries of the 2D superconductor, allowing us to plot the vectors of the supercurrent density in Figure 4.25(b). We can see that although we assumed the order parameter’s magnitude is constant throughout the flake, the supercurrent is not of constant magnitude because the gradient of the phase is non-uniform. Given our definition of the vector potential in the Landau gauge, Equation 4.5 is linearly proportional to \( B_z \), the perpendicular applied field, we can take our solution for the zero field case and then scale the solution linearly with field. The effective flux regions for the two contacts on either side of the 2D superconductor are found by starting at each corner, and numerically taking discrete steps of length \( d\vec{r} \) in the direction transverse to the current density \( J(\vec{r}) \) at the present location. Repeating this process for both corners of the contact eventually stops when the two paths are within some value \( \epsilon \) of each other. Of course, this being a numerical solution, it isn’t exact, but it is very close.

Figure 4.25: SEM of flake and GL model outputs
(a) SEM image of h-BN encapsulated NbSe\(_2\) flake between Al leads. (b) Ginzburg-Landau model sheet current density from numeric solution of flake boundary conditions. (c) Effective flux regions for each of the contacts on the sides of the NbSe\(_2\) flake.

These effective flux regions are filled in purple in Figure 4.25(c), and we can use
the model calculate their areas as well as the area of the entire 2D superconductor via numerical integration. It is important to note that these regions are modeled for zero transport current flowing through the 3D-2D-3D device. The superposition of a transport current with the circulating screening currents will result in a drastically different phase \( \Phi(\mathbf{r}) \) and its resulting gradient. Because our interference pattern periods are consistent throughout, it appears that the area of these effective flux regions will be constant, but that the borders defining them are liable to change with the applied current or movement of a vortex shifting the gradients of the superconducting phase. Lastly, we can use our solution for \( \Phi(\mathbf{r}) \) inside the boundaries to solve for the Josephson current through each contact by integrating the phase difference across the Al/NbSe\(_2\) junction along the junction. If we integrate the reduced Ginzburg-Landau Equation 4.4 around the entire boundary of the 2D superconductor, the result is an integer multiple of \( 2\pi \). So if we define the phase difference across junction \( i \in [L, R] \) as \( \delta_i = \phi_i - \chi \), where \( \phi_i \) is the phase of the Al contact (constant across the width of the contact) and \( \chi \) is the local phase of the flake at some region on the boundary as defined by Equation 4.6 integrated from the corner of the flake’s interface with the Al contact (where the flake has phase \( \varphi \)), to the location at which you want to obtain \( \chi \) (typically along the width of the junction to the other corner).

\[
\chi = \varphi + \int \left( \nabla \cdot \Phi(\mathbf{r}) - \frac{e^*}{\hbar c} A(\mathbf{r}) \right) \, dl \tag{4.6}
\]

\[
I_j = J_c \int_{\text{contact}} \sin(\delta_i) \, dl \tag{4.7}
\]

\[
\delta_i = \phi_i - \chi \tag{4.8}
\]

Then, following from Equation 4.6 we can integrate Equation 4.7 along the length of the contact interface to obtain the Josephson current for lead \( i \in [L, R] \). As discussed earlier, the integrand of Equation 4.6 scales linearly with \( B \), so we can plot the Josephson current as a function of magnetic field for each contact. Doing so, we obtain a interference pattern roughly of the form in Equation 1.31. We have plotted the outputs for this model on top of one of our data sets in Figure 4.26. Note that the absolute height of the central peak is controlled by \( J_c \), which the model does not calculate, so we scale the outputs to fit the central peak of our data set. However, from that absolute scale, the model has done a rather good job at predicting the relative heights of the side peaks in comparison to the central peak. Another point to note is that the model correctly predicts that the minima between peaks in the interference patterns will not go all the way to zero. This is more clear on the red-dashed line than the white, but the minima in the data of that interference pattern are larger too. This non-zero minima can be explained in contrast to the ideal case illustrated in Figure 1.13 where a perfectly symmetrical junction produces equal and
The Ginzburg-Landau model output using the SEM image to outline the flake is plotted on top of a quantum interference data set with no horizontal scaling. The Mathematica code for this model of sample F is contained in Appendix C.

opposite Josephson currents along its length at integer flux quanta. Our fabricated 2D-3D junctions are not symmetrical, especially with regard to the shape of the flake. Looking at the effective flux regions in Figure 4.24(c), we can see that $A_R$ is much more symmetrical across a line normal to the midpoint of the junction than $A_L$ is. This is indicative, rather than causal, of the asymmetry in flux gradient in these regions along the length of the junction. This matches with what we see in Figure 4.26, where the interference pattern with the smaller central peak critical current (the red-dashed line, matching the narrower interface, the left contact) has a slightly larger minima between peaks of the interference pattern.

The primary result we wanted from this model is the periodicity of the quantum interference patterns. Comparing the model output to the data, we see that it slightly over predicts the periods by $\approx 8\%$, which corresponds to an under prediction of the effective flux areas by about the same amount. This inaccuracy is likely limited by how closely we can match our geometric input to the model with the actual size and shape of the flake. However, we can note that the model explicitly only accounts for the region of the 2D superconducting flake between the Al contacts and the phase change along the inside boundary of the 2D superconductor. The under prediction of area is an error in the proper direction that an addition to the model.
that adds some additional area to account for the region of the NbSe$_2$ seen under the aluminum contact in the TEM images as well as accounting for the phase change in the Al contact due to the magnetic field penetrating it a penetration depth in from the contact would push the model’s predictions in the correct direction. The model might also be incorrect in the presumption of uniform coupling across the width of the junctions, but even with a TEM cross section, we don’t have a good way of modeling this any differently.

As mentioned in Section 4.1.2, the interference patterns measured in fully planar TBG Josephson junctions are quite similar to what we have seen in 2D-3D Josephson junctions. Of course, the planar TBG junctions have a bilateral symmetry that we do not have here, but I would be interested in seeing how we could adapt this model to that geometry and how accurate it could be in such cases. In some ways it may be easier to model, since the junction interface itself is gate defined and not a 2D-3D sloped interface. On the other hand, perhaps the nature of the correlated insulated tunnel barrier they create could be harder to model accurately. Currently they are using the calculations of Moshe et al. for edge-type Josephson junctions in narrow thin film strips, which agree with our model in several respects [61, 62, 194]. Those calculations agree that the phase difference along the junction interface is dependent on field, and junction geometry, but universal and independent of Josephson critical current density, as is ours. Lastly they found that the periodicity is nonuniform at low fields, but attains regularity at higher fields proportional to $1/w^2$, where $w$ is the width of the planar junction. It’s possible that a rework of our model that accounted for changing phases on both sides of a planar junction could match this prediction.

![Figure 4.27: SQUID measurement circuit](image)

(a) Optical image of Sample C with measurement circuit schematic. contacts 1 & 2 did not work. (b) Tilted SEM image of contact 3, with components labeled.
4.4.2 2D/3D SQUID

Soon after measuring our first functioning 2D-3D zero resistance contact we decided to make the logical next step and create a SQUID loop out of two connected Al/NbSe$_2$ contacts. Designed with a physical loop area in the Al leads between the two contacts, we were interested in seeing if the measured interference patterns reflected the physical loop area, or some larger effective area.

Our measurement circuit is schematized in Figure 4.27, showing our use of the SQUID contact to the NbSe$_2$ as a source, and the bottom contact as our drain. Our measurements of $R(T)$ and $R(B)$ proceeded with similar results as above, but our observation of interference patterns in the $dV/dI$ vs. $B$ and $I_{DC}$ data sweeps was at the time a completely new observation for us, this being 9+ months before we would measure sample F.

Figure 4.28a shows several distinctive features. The sharp transition of the Al leads at low fields does not show splitting of narrower leads until 5 or 6 mT, 2-3x higher than on the previous samples. Inside the Al current envelope, we see a dark interference pattern which I have outlined with red curves, while a fainter critical current is modulated with field just below the Al critical current (indicated with red arrows). Noticeably, this critical current modulation appears to stretch out past the critical field of bulk Al (rightmost red arrow) at 10 mT (marked with a black dotted line). This had not been seen before, and is unclear why it is occurring here. We believe the Al critical currents to split into bulk critical field and higher critical field traces based on their width, as Al leads narrower than a penetration depth will see a slight suppression of orbital pair breaking. We identify the smaller critical current as belonging to the SQUID contacts which are 1 µm wide, while the larger critical current belongs to the large drain contact which is ≈ 8 µm wide. The SQUID interference pattern stops at 10 mT. Below that, Figure 4.28b shows both positive and negative magnetic field regions, but was taken with B-field sweeps at constant current, which is the inverse of all previous plots of this type. In this figure we have higher B-field resolution, but lower $I_{DC}$ resolution. In particular, we see more of the fine structure of the drain contact interference pattern which appears to show a slight skew. Extracting the critical currents and normal state resistances we see that the two SQUID contacts have a critical current of \( \sim 10 \mu\text{A} \) while the drain contact has a critical current of 40 µA. Their associated normal state resistances are 2 $\Omega$ & 1 $\Omega$ respectively. However, the Ambegaokar-Baratoff relation is relevant to Josephson junctions, not the combined SQUID, so if we make the reasonable assumption that the two junctions forming the SQUID are identical, then with a parallel resistance of 2 $\Omega$, they each would have a resistance of 4 $\Omega$ and a critical current of \( \sim 5 \mu\text{A} \), resulting in $I_{DC}R_n$ values of 20 µV, 20 µV & 40 µV. Because we assumed the SQUID junctions are identical, the $I_{DC}R_n$ values came out to be the same. It is unclear why these values differ by a factor of two from that of the drain contact, as well as why they are so much smaller than the values found for sample F.

After these wide range data sweeps, we focused in on some of the oscillations in
Figure 4.28: \( \frac{dV}{dI} \) vs. \( B \) and \( I_{DC} \) on sample B SQUID

(a) (b) The current is swept beyond the critical current of the Al leads for this SQUID sample at positive magnetic fields up to 11 mT.

the smaller critical current, using higher resolution in B field setpoints to observe them. Figure 4.29 shows two versions of the same data, the left side plots \( dV/dI \) vs. \( B_{\text{measured}} \) and \( I_{DC} \), while the right side plots \( dV/dI \) vs. \( B_{\text{setpoint}} \) and \( I_{DC} \). The left plot is much noisier and indistinct than the right plot, this stems from the difference between \( B_{\text{measured}} \) and \( B_{\text{setpoint}} \). \( B_{\text{measured}} \) is not a direct measurement of magnetic
field from a Hall sensor or anything else inside the center of the solenoid. Instead, it is calculated by the magnet power controller based on a current it measures and a known calibration in units of Tesla/Amps.

![Figure 4.29: Quantum interference in a 2D-3D SQUID](image)

Quantum interference data from sample B, a 2D-3D SQUID, is presented as taken (left), with approximately ±50 µT B-field noise, and plotted against field setpoints so each datasweep is an individual vertical line (right). Data was taken at the highest field resolution possible with our magnet power supply: 0.01mT stepsize. Four well-defined lobes are seen between -0.8mT and -0.2mT, while multiple sudden jumps that cut lobes in half (associated with vortex motion) are seen between -1mT and -1.5mT. Interference pattern shows periodicities of 0.07mT and 0.14mT.

Even in a steady state where the magnet is holding at a constant field setpoint, the current measurement appears to have noise equivalent to ±50 µT, which shows up in our measurements like the left side of Figure 4.29. However, this current noise appears to be somewhat unrelated to any actual noise in the magnitude of the magnetic field. Based on the clarity of the signal in the right plot of Figure 4.29, the magnetic field appears to be very stable and precise at any given setpoint, as well as any series of consecutive setpoints. Its accuracy is less laudable, as we have seen in multiple plots so far where the zero field setpoint is several mT away from the zero field signal in a sample. For our purposes of measuring interference patterns though, precision is more important than accuracy, and because of this we are able to re-plot noisy data in a much sharper and clearer form.

Analyzing the data itself in Figure 4.29, we can see on the right side plot that between −0.8 mT and −0.2 mT there are 4 clearly defined and fully formed oscillations of the SQUID critical current. Below −0.8 mT we see multiple oscillations, but there are sudden jumps that cut almost all of them into fractions of a full oscil-
The period of oscillation for the four clearest lobes is \( \sim 0.14 \text{mT} \), and a second period of \( \sim 0.07 \text{mT} \), which we convert to areas of 14.8 \( \mu \text{m}^2 \) \& 7.4 \( \mu \text{m}^2 \) using the magnetic flux quantum. Sample B was fabricated with a 4 \( \mu \text{m}^2 \) Al loop that did not overlap the NbSe\(_2\) in this area. This sample shows a factor of 3.5x between the physical area of the SQUID loop and the effective area of the SQUID loop based on its quantum interference pattern.

For the same reasons we switched to fluxoid quantization from flux quantization when we moved from a 3D-3D junction to a 2D-3D junction, we must do the same when we are discussing the operation of a 2D-3D SQUID. Equation 4.9 uses flux quantization to relate the maximum supercurrent that can pass through a SQUID loop at any flux \( \phi \), but it is predicated on having single valued phases in the superconducting electrodes on either side of the junctions in the SQUID. A shown in Figure ??This can be accomplished by drawing the contour of integration deep inside the bulk of these electrodes, where the phase is single valued because there is no magnetic field or supercurrents along that contour. Just as with the 2D-3D junction though, we can’t draw such a contour on the 2D side of a 2D-3D SQUID. Working from Equation 4.9, where the inside of the cosine term is essentially adding up the phase discontinuities across the Josephson junctions. Since we’ve seen that those are related to the total applied flux, we have to add a term as in Equation 1.15 that integrated the vector supercurrent around a contour to add up the change in phase on the contour due to that supercurrent. Using London’s \( \Lambda = m/(n_se) \) constant we can write the combination of the total flux plus the total phase change around the contour as the term inside the cosine.

\[
I_{\text{max}} = 2I_c \cos \pi \phi / \Phi_0 + \Lambda \oint_{\gamma} (\vec{J}(\vec{r})) \cdot d\vec{l} \]

\[(4.9)\]
For a 2D-3D SQUID the contour C will then include some path inside the 2D superconductor, skip the junctions, but include a path through the bulk of the 3D superconductor on which there is no current and no phase change. As usual with fluxoid quantization, if you apply it to a 3D-3D SQUID with the correct choice of contours, it collapses down to flux quantization where $I_{max}$ depends solely on $\phi$.

Our second 2D-3D SQUID sample (optical image in Figure 4.27(a)) exhibited some more complex behavior in the data shown in Figure 4.31. Unlike the previous samples, this device had a rather large remnant resistance at base temperature of $81 \Omega$ that we subtracted out for clarity. Additionally, the critical currents in this device are two orders of magnitude lower than in the other samples. Rather than picking out the interference pattern periods by eye, we resort to taking the Fourier transform of a horizontal linecut at $I_{DC}=0$. The Fourier transform has three distinct peaks at $\Delta B_i = 2.7, 6.8, \text{and} 9.5 \text{mT}^{-1}$. Again using the flux quantum to convert these to areas, we get $5.4 \mu m^2, 13.6 \mu m^2, \text{and} 19.1 \mu m^2$. The physical area inside the Al SQUID loop for contact 3 on this sample is $7 \mu m^2$, which is 2-3x smaller than the larger flux areas measured, and larger than the smallest, which we can rule out as corresponding to the SQUID loop immediately since it is smaller than the physical area.

With a SQUID loop of $\gg 7 \mu m^2$, and the $1 \mu m$ wide Josephson junction which likely has an effective area of a $1-3 \mu m^2$, function o Using the Ginzburg-Landau model in Mathematica to simulate the circulating supercurrents screening this NbSe$_2$ flake, we use the model to perform the same analysis as before, but this time using the two opposing corners of the SQUID Josephson junctions as the bounds of our "contact". From these corners, the effective flux region of the SQUID loop "contact" proceeds in the same way to define a boundary along which the phase is constant, so it is drawn transverse to the supercurrent flow. In doing this, we obtain a result of $19.7 \mu m^2$, an extremely close match for the value we extracted from the interference pattern’s $9.5 \text{mT}^{-1}$ frequency (which is the smallest period at $0.11 \text{mT}$). We expect the drain, contact 4, to also function similarly to the Josephson junctions previously studied, and the model predicts an effective area of $6.3 \mu m^2$, which we match to the $5.4 \mu m^2$ measured area. This corresponds to the $0.37 \text{mT}$ period in the data. Lastly, we seem to have run out of components that the $13.6 \mu m^2$ effective area could correspond to. Lacking a physical component to tack this area onto, we notice that $13.6 \mu m^2$ is approximately the difference between our other two measured areas, $19.1 \mu m^2 - 5.4 \mu m^2$. This seeming coincidence points towards the idea of coupling between the SQUID and the drain contact. In the RCSJ model, resistances measured across junctions can be due to dissipation of energy in an underdamped Josephson junction (previously discussed in Section 4.3), where the phase of a junction continuously rotates and creates a voltage because the damping in the system is insufficient to dissipate the energy input by the current. These phase could be coupling with the drain contact junction, creating sum and difference frequencies. We might then see a difference frequency (specifically $9.5\text{mT}^{-1} - 2.7\text{mT}^{-1} = 6.8 \text{mT}^{-1}$) as a period in the data corresponding to an intermediate flux area with no matching physical
component. The one biggest question about the explanation is then, where is the sum frequency? At 12.2 mT$^{-1}$ corresponding to a period of 0.08 mT and an area of 25.8 $\mu$m$^2$, it isn’t physically impossible for us to see with the resolution of our measurement setup, yet we found no sign of it.

Figure 4.31: Interference pattern of Sample C
The interference pattern from sample C shows a significantly smaller critical current, with more complicated overlapping periods. Inset shows Fourier transform of $I_{DC}=0$ linecut.
<table>
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<th>Device</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>F</th>
<th>G</th>
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<td>SQUID</td>
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<td>1/1.5.2</td>
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<td>1.2,1.4</td>
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<td>-</td>
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<td>2.7</td>
<td>7.10</td>
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Table 4.1: Properties of 7 devices exhibiting superconducting contacts. Lateral dimensions are obtained from optical and AFM images, Thicknesses are obtained by AFM topography or cross-sectional STEM. Critical current densities are calculated from these dimensions. $R_{contact}^{normal}$ is measured in the critical current measurements where the contacts have gone normal, but while the Al and NbSe₂ flake are still superconducting. $R_{SC}$ is measured as $T \rightarrow 0$ with no applied DC current or magnetic field. Contact lengths for devices F and G were measured from STEM images of a sample cross section. $J_C$ entries marked with a † are calculated using a nominal contact length of 100nm.
4.5 Future Directions

Although our technique for fabricating 2D-3D superconducting contacts was developed using NbSe$_2$, there are no fundamental or technical reasons why it would not work with all other 2D van der Waals superconductors (intrinsic or gated). The next step for this project is to fabricate samples that prove this universality. Gated van der Waals superconductors (Section 1.2.1) would need their electrostatic gates to cover the full region of the 2D-3D contact so the superconducting state is uniform in the 2D material. This geometric constraint on the gates and the need to avoid electrical shorts between the contacts and gates could add some degree of difficulty to a device’s design or nanofabrication, but it is certainly not an insurmountable problem. However, gated superconductors would have yet another minor constraint if they are to be integrated into hybrid superconducting resonators (as we show with intrinsic vdW superconductors in Chapter 5). The electrostatic gate cannot be made of a normal metal. If it were fabricated from a normal metal it would capacitively couple to the superconducting circuit and dissipate energy from the resonator. These constraints on integrating gated van der Waals superconductors into DC and RF hybrid superconducting circuits would hold true for any other future methods of contacting the 2D superconductor, not just the method we presented above.

Our method is the first to show fully superconducting contact between 3D deposited superconductors and 2D superconductors, but we do not expect it to remain the only such method. Prior to adding the low-pass filters to our measurement setup (Section 2.3.1) I fabricated and measured a sample with Al leads deposited on top of few-layer graphene encapsulated NbSe$_2$. Using all four leads in a 4-pt measurement circuit I was able to measure the superconducting transition of the NbSe$_2$ flake and see a zero resistance state, but in a pseudo 4-pt measurement circuit a $40 \, \Omega$ resistance remained at base temperature. I did not further pursue this method after achieving success with our etched side contacts, but it should be further explored and measured using low-pass filters. The same could be attempted with semiconducting TMDs. Another similar method is to deposit Al on top of mono-, bi- or trilayer hBN to form an SIS Josephson junction contact to a van der Waals superconductor. The critical current density for each of these methods could be varied by changing the number of layers in the encapsulating tunnel layer. These methods would need to be tested to see what their benefits and challenges are. The last style of contact that I can currently conceive of is a superconducting via contact based on those constructed by Telfore et al. in reference [195]. However, just as we adapted the edge contacts from Wang et al. to be used in conjunction with superconductors, a similar process would be necessary with hBN embedded via contacts. As mentioned previously, many deposited superconductors will form oxides, nitrides or other surface layers in atmosphere. If these inhibited a superconducting interface with the van der Waals superconductors then either a different deposited superconductor would need to be used, or the via contacts would need to be sealed off from atmosphere until immediately prior to usage. One
possible issue with these proposed contact methods is their approach to a van der Waals superconductor from a top (or bottom) surface rather than the edge. Wang et al. discuss the benefit of contacting graphene from the edge of the plane where it has sp$^2$ hybrid orbitals that form short and strong bonds [99]. The $p_z$ orbitals on both surfaces of the graphene hybridize together and result in graphene’s unique electronic structure, but they cannot form as strong of bonds as those at the edge of a graphene sheet [99, 153, 154].

Analogously, in Chapter 3 we looked at DFT calculations of each Fermi surface in the Brillouin zones of NbSe$_2$ and TaS$_2$. The split-bands we focused on were those associated with Nb and Ta, where stronger SOC occurs. However, as discussed earlier during the exploration of Ambegaokar-Baratoff relations we know that these materials also have a third band at the Fermi surface that is associated with their lighter elemental components [190, 193]. In NbSe$_2$, the Se Fermi pocket around the $\gamma$ point was found to contain less than 5% of the total density of states and carry a very small minority of all Cooper pairs in the system. This pocket in the Fermi surface does not contribute significantly to the formation of superconductivity or the Ising superconductivity phenomenon thought it will couple to the the Nb band that causes superconductivity to appear. Yet, when NbSe$_2$ is contacted on the top or bottom surface, this Se band carries 75% of the transverse currents in the system. In other words, the interlayer coupling that strengthens the superconducting state and increases $T_c$ in multilayer NbSe$_2$ is reliant on the small, sparse, and non-superconducting Se band to carry currents between adjacent layers or surface contacts [190, 191, 193]. The Se channel dominates all other contributions to perpendicular conductance and carries the majority of the out-of-plane currents [193]. So tunneling spectroscopy on the surface of NbSe$_2$ as performed by Dvir et al., will in large part be probing the Se Fermi pocket, but because it couples strongly with the large superconducting gap K point Nb band surface contacts might work better than edge contacts in superconducting circuits. However, some evidence has shown that the exfoliation atmosphere conditions of a crystal can alter the Se band and possible cut off the flow of transverse currents [190]. As we showed in Section 4.2, our Al/NbSe$_2$ contacts have an etch slope that stretches out for $\sim$ 100 nm. Over that extended distance the deposited Al lead conforms closely to the exposed NbSe$_2$, making contact to both the top surface as well as the step edges. So it is likely that this version of our 2D-3D contacts is rather hybridized between interfacing with the Se and Nb bands of the Fermi surface, and our 2D-3D Josephson junction may well depend on both superconducting gaps. Multiband tunneling If these curiosities in the NbSe$_2$ system aren’t sufficient to motivate further exploration of these properties, then perhaps the broader world of 2D superconductivity is a sufficient incentive. MgB$_2$ was discovered to be a two-gap superconductor long before NbSe$_2$ [190, 196]. NbS$_2$ and TaS$_2$ are also two gap superconductors (in the thin limit for TaS$_2$) along with several more van der Waals materials like proximitized single layer graphene and Bi$_2$Se$_3$ [197]. Talantsev et al. claim that all atomically thin superconductors that have an enhancement in $T_c$ will
have a second gap open when the out-of-plane coherence length exceeds the sample's thickness [197, 198]. While not conclusive, several groups have put forward models of two gap superconductivity in TwBLG driven by both intralayer and interlayer phonon modes [197].

Experimentally, I believe that parallel efforts to improve the 2D-3D side etched contact fabrication method while exploring other methods of fabricating 2D-3D superconducting contacts is worthwhile. Further development of our current contact method as well as trials with other methods could synergistically accompany the types of experiments needed to learn more about two gap superconductors including any technological advantages or disadvantages they might have. The individual bands in multiband superconductors can couple to each other, and unusual phenomena like fractional quantum vortices can appear, where a fraction of a vortex is associated with each band in the superconductor [196]. There is no reason to believe that our 2D-3D contacts would not still show zero resistance, but depending on their geometry and the band structure of the superconductor, the critical current could be affected.

Something to keep in mind for future samples on potential two gap superconductors is gathering temperature dependent data of critical currents and fields, as this can be used to better understand the superconductors internal dynamics. It may also enable us to use multiband tunneling models developed by Brinkman et al. and Ota et al. that essentially generalize the Ambegaokar-Baratoff relation by summing over N bands [186, 196, 199]. Ota also discusses how the generalized AB method can be used to identify the type of pairing in an unknown iron based superconductor that may be s-wave or

Lastly, beyond these new ideas for experiments, whether our current fabrication process persists, is updated/modified, or even if it is replaced wholesale, I would like to see and do more pre-fabrication modeling of samples. David Pekker’s GL model for the effective flux areas of 2D-3D Josephson junctions is a great example of being able to turn a retrospective analysis tool into a diagnostic and preparatory tool. That analysis of 2D-3D Josephson junctions followed directly from decades old theory and agrees exceptionally well with our experimental data. Looking at the preprints of the 2D-2D planar JJ in TwBLG, I think that the adaptation of our Ginzburg-Landau model to handle 2D-2D Josephson junctions would be a forward thinking project, especially if a method was found to include gate tuning effects as well as handling more complex geometries.
Chapter 5

2D/3D Hybrid Superconducting Resonators

5.1 Introduction to Superconducting Resonators

Superconducting resonant circuits have grown over the last decade to be a dominant thrust in the quest for a scalable quantum computer. In pursuit of this, many RF techniques have been honed towards modeling and controlling the behavior of these sensitive circuits [101, 185, 200–206]. This knowledge and technological base provides a well developed platform that we can use to study and characterize the properties of 2D van der Waals materials, with a focus on the 2D vdW superconductors, utilizing capabilities and techniques distinctly different from standard low temperature transport measurements [51, 162, 163]. RF measurement techniques for superconducting circuits are able to measuring some properties of superconductors and Josephson junctions that are inaccessible parameters, or just very difficult to measure, using standard magnetotransport measurements at pseudo-DC frequencies. In devices with tunable critical currents, the current phase relation (CPR) is accessible via RF resonance measurements that probe the Josephson inductance, which can then be compared with DC measurements of the critical current and the calculations of the Josephson inductance based on an appropriate CPR model or generic sinusoidal CPR [51]. Tunnel barrier Josephson junctions can be probed using microwave loss spectroscopy to obtain the sub-gap resistance, a characteristic parameter of the tunnel barrier material. The sub-gap resistance is a measure of how a material will perform as a tunnel barrier based on the maximum leakage current in DC measurements, and the dissipation it will cause in RF measurements. Materials with larger sub-gap resistances produce better tunnel barriers [51]. A microwave circuit that incorporates a vdW tunnel barrier Josephson junction using hBN, with either deposited superconducting electrodes or stacked with van der Waals superconductors for the best interface uniformity, could measure the sub-gap resistance of hBN to characterize its performance as a tunnel barrier in a manner difficult to access in DC measurements.
In DC, it can only be found by measuring the temperature dependence of the conductance with applied voltages above and below $2\Delta(T)/e$. Larger voltages will result in conductance being inversely proportional to the normal state resistance $R_n$, but for voltages below the gap, conductance will be inversely proportional to $R_{sq}(T)$ which is related to the number of thermally excited quasiparticles [182–184].

In addition to characterizing van der Waals superconductors using RF techniques, we are also searching for potentially advantageous use cases where vdW superconductors could be integrated into superconducting circuit components used in the field of superconducting qubits and quantum information [51, 162, 163]. 2D van der Waals materials may provide some advantages over traditionally used materials. They are able to form atomically flat, clean and uniform interfaces with other van der Waals materials. This allows Josephson junctions with uniform current densities across very large areas to be made [207]. Monolayer and few-layer TMD superconductors are Ising superconductors that can function in extremely large in-plane magnetic fields [31, 76, 115]. The kinetic inductance ($L_k$) of superconducting van der Waals materials can be measured in RF resonator circuits. This property is inaccessible to direct DC measurements. Equation 5.1 shows the inverse dependence of kinetic inductance on superfluid density, and cross sectional area, which can be used to transform the equation to the 2D limiting case using the 2D superfluid density and the sheet’s width to replace cross sectional area. Superfluid density, in both 2D and 3D, is rather inaccessible experimentally. Annunziata et al. show how BCS and GL theory can be used to instead write the kinetic inductance of a superconductor at finite T in terms of its superconducting gap and $R_{sq}$, the normal state sheet resistance [208]. The sheet resistance isn’t a standard measurement we perform, but it can be easily obtained from the normal state resistance and the sample’s dimensions. One issue with using Equation 5.2 after we have performed our measurements are the limits on its validity. They used BCS theory to write the complex conductivity of a superconductor as a function of its gap and the measurement frequency. Unfortunately, the expansion used is only valid in the low frequency limit ($hf \ll k_B T$) [208]. Our RF measurements occurred at the dilution refrigerator’s base temp, approximately 20 mK, which would limit our measurements to less than 0.5 GHz. Unfortunately our measurements were performed at around 3GHz and there is no good method of up or down conversion, so we can try the calculation for the samples, but its unlikely to be highly accurate.

\[
L_k = \left( \frac{m_e}{2n e^2} \right) \left( \frac{l}{A} \right) = \left( \frac{m_e}{2n_{2D} e^2} \right) \left( \frac{l}{w} \right) \tag{5.1}
\]

\[
L_k = \left( \frac{l}{w} \right) \left( \frac{R_{sq} h}{2\pi^2 \Delta(T)} \right) \left( \frac{1}{\tanh \frac{\Delta(T)}{2k_B T}} \right) \tag{5.2}
\]

As the atomically thin limit is approached in van der Waals superconductors, the kinetic inductance will increase inversely proportional to thickness, Equation 5.1.

\[
L_k = \left( \frac{l}{w} \right) \left( \frac{R_{sq} h}{2\pi^2 \Delta(T)} \right) \left( \frac{1}{\tanh \frac{\Delta(T)}{2k_B T}} \right) \tag{5.2}
\]
Additionally, the same equation shows that in vdW systems with gated superconductivity (Section 1.2.1) the kinetic inductance could be gate tuned by changing the carrier density in the vdW superconductor [51]. Kinetic inductance is used in superconducting circuits as another source of inductance in addition to the geometric inductance, reducing the need for circuitous meanders that can cause undesirable parasitic inductances [203, 209–212]. This could be particularly useful in circuits with constrained geometries. Implementation of a kinetic inductance component requires a measurement of the kinetic inductance boost to calibrate the components prior to circuit design and fabrication. In order to measure the kinetic inductance of NbSe$_2$ we have integrated heterostructures of BN encapsulated NbSe$_2$, using the techniques discussed in Chapter 2, into a superconducting resonator. We proceed to measure the shift in resonant frequency that occurs in the hybrid resonators compared to their matching control resonators. The change in resonant frequency compared to the control is proportional to the change in inductance compared to the control. When unwanted inductive components (geometric, Josephson) are accounted for, the remaining shift in inductance will be equal to the NbSe$_2$ flake’s kinetic inductance.

5.1.1 LC Circuits

Circuits containing capacitive (C) and inductive (L) components resonate at a specific resonant frequency $f_{\text{res}} = \frac{1}{\sqrt{LC}}$ at which energy is stored in the resonant circuit by continually oscillating out of phase between the capacitor and inductor. A normal circuit will also include a non-negligible resistance that will dissipate energy from the resonator. The relation between energy storage and dissipation in a resonator is the quality factor (Q-factor) where $Q = \frac{f_{\text{res}}}{\Delta f}$.

Superconducting resonators are also LC circuits, but as they are fabricated from superconducting materials, they do not have an intrinsic R component that causes energy loss within the resonant circuit. Nevertheless, some energy will be lost from the superconducting resonator through coupling to the surrounding environment. This enables the creation of resonators with extremely large, but finite, Q.

5.1.2 Hanger Resonators

Hanger resonators are a type of resonant circuit that does not physically contact the input/output signal line. Instead, as shown in Figure 5.2, a superconducting microwave stripline runs the length of the sample chip with signal input on one end and output on the other end connected to the sample carrier PCB using Al wirebonds. We designed each of the 5 resonators to have resonant frequencies spaced out in frequency space so each physical resonator is easily matched to an observed resonance curve (originally designed to be 4.5, 5.0, 6.1, 6.7, and 8.0 GHz ± 100 MHz). The hanger resonators are positioned equidistantly along the length of the transmission line and are capacitively coupled to it, allowing multiple resonators to be excited.
The shape of a resonance peak relates to the Q-factor of the resonator. Sharper peaks have higher Q-factors and broader peaks have lower Q-factors. Image source: https://reviseomatic.org

using a single input/output pair. As written in Equation 5.3, the capacitive coupling $C_c$ charges the hanger resonator’s capacitor and pumps energy into the LC resonator at the frequency of the signal passed through the transmission line. The resonator stores more energy at frequencies closer to $f_{res}$ and no energy is dissipated in the superconducting resonator. Energy that leaves the hanger resonator is back-scattered along the transmission line towards the input port, leaving a dip in the magnitude of the signal measured at the output port around $f_{res}$. The width of this dip, $\Delta f$, known as the bandwidth of the resonator, determines the Q-factor of the resonator. Additionally, the magnitude of the capacitance between the hanger resonator and the transmission line, controlled by their spacing, determines the strength of the coupling Q-factor (Eq. 5.3) alongside the impedance matching between the transmission line ($Z_0$) and the resonator ($Z_{char}$). In a hanger resonator measurement the Q-factor of the observed resonance dip in $S_{21}$ (see Table 5.1) is not that of the resonator alone, but instead the combination of the resonator’s internal and coupling Q-factors as combined in Eq. 5.4.

$$Q_{coupling} \approx \frac{1}{C_c^2} \left( \frac{Z_o}{Z_{char}} \right)^2$$  \hspace{1cm} (5.3)

$$\frac{1}{Q_{total}} = \frac{1}{Q_{internal}} + \frac{1}{Q_{coupling}}$$  \hspace{1cm} (5.4)

By examining this inverse addition of Q-factors, we can see that if the mismatch between the internal and coupling Q-factors is too great, then the smaller of the two Q-factors will dominate $Q_{total}$. In the case of $Q_{coupling} \gg Q_{internal}$ the resonator’s

Figure 5.1: Q-factor illustration

The shape of a resonance peak relates to the Q-factor of the resonator. Sharper peaks have higher Q-factors and broader peaks have lower Q-factors. Image source: https://reviseomatic.org
Table 5.1: 2-port scattering matrix
Scattering matrix for 2-port VNA measurements. In the case of hanger resonators along a transmission line we measure $S_{21}$, the signal transmitted from port 1 to port 2. For our second generation resonators with only one signal line, we will measure $S_{11}$, the signal reflected back to the input port.

<table>
<thead>
<tr>
<th>Input</th>
<th>Output</th>
<th>Port 1</th>
<th>Port 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Port 1</td>
<td></td>
<td>$S_{11}$ (reflection)</td>
<td>$S_{21}$ (transmission)</td>
</tr>
<tr>
<td>Port 2</td>
<td></td>
<td>$S_{12}$ (transmission)</td>
<td>$S_{22}$ (reflection)</td>
</tr>
</tbody>
</table>

Table 5.1: 2-port scattering matrix

Scattering matrix for 2-port VNA measurements. In the case of hanger resonators along a transmission line we measure $S_{21}$, the signal transmitted from port 1 to port 2. For our second generation resonators with only one signal line, we will measure $S_{11}$, the signal reflected back to the input port.

internal Q dominates and the coupling is negligible, so no energy is stored and subsequently backscattered by the resonator, resulting in no observed dip in $S_{21}$. In the opposite case of $Q_{\text{internal}} \gg Q_{\text{coupling}}$ the coupling between the transmission line and the resonator dominates the resonator’s internal Q, resulting in a dip due solely to the coupling that provides no information about the internal workings of the resonator. Both of these cases will inhibit our study of hanger resonators that contain superconducting van der Waals materials. After several initial sets of samples did not exhibit any evidence of resonant dips in our measurements, we shifted the positioning of the resonators on the chip so that the finger capacitors, which were 200 $\mu$m from the transmission line in the original design, to 20 $\mu$m from the transmission line. This addressed our hypothesis that $Q_{\text{coupling}} \gg Q_{\text{internal}}$, leading the internal Q factor to dominate the coupling Q, resulting in no observed resonances. This design change increased the coupling capacitance between the transmission line and the finger capacitor by a factor of 10x, and thus dropping $Q_{\text{coupling}}$ by two orders of magnitude (see Equation 5.3) to approximately match the internal and coupling Q-factors near $Q=4000$.

5.1.3 Kinetic Inductance Measurement Schema

To isolate the kinetic inductance of the 2D superconductor integrated into a superconducting resonator, we will need to perform both RF and DC measurements. Due to the measurement setups of the various dilution refrigerators available for us to use, this will require us to measure the samples in two separate dilution refrigerators, one with RF measurement capabilities, and the other with DC measurement capabilities. The primary data for a sample, as explained above, is the downshift in resonant frequency of a hybrid resonator compared to that of a matching control resonator as shown in Figure 5.3. This shift in frequency is due to the multiple sources of added inductance in the hybrid resonator totaling $\Delta L$. We can convert from the frequency downshift in MHz to the additional lumped inductance in pH using simulations of the resonator circuit, but to tease apart the lumped inductance and ascribe its com-
Diagram of resonator chip with inset zoom of a single resonator. Transmission line, finger capacitor and inductive meander are patterned optically and deposited as NbTiN while purple regions are patterned via EBL and deposited as Al to make contact between NbTiN and TMD heterostructure. Bondpad regions are modelled but do not significantly change resonator characteristics. Finger capacitor is spaced $20 \mu m$ from the transmission line to decrease coupling Q.

Components to their respective origins requires an additional measurement. Beyond the lithographically patterned finger capacitor and Al meanders, the combined sources of inductive shift in the hybrid resonator are:

1. Geometric inductance of exfoliated NbSe$_2$ flake and leads ($L_{geo}$)

2. Josephson inductance of each Al/NbSe$_2$ contact ($L_{j1,2}^{1,2}$)

3. Kinetic inductance of exfoliated NbSe$_2$ flake ($L_{k}^{NbSe2}$)

We control for the geometric inductance of the flake by patterning the control sample with leads that precisely match those of the hybrid resonator. Furthermore, we pattern an Al bridge between those leads with the same shape as the exfoliated flake, this excludes the geometric inductance from contributing to the downshift or being included in the simulation’s lumped inductance output. However, this means that our end result is not simply the kinetic inductance of NbSe$_2$, instead it is the boost in kinetic inductance of NbSe$_2$ over the kinetic inductance of Al. The lumped inductance
The Hybrid resonator is downshifted in frequency, and has a shallower dip in power.

The Josephson inductance of the contacts can be calculated by performing DC measurements of the contacts’ critical currents. Assuming the current phase relationship of our Al/NbSe$_2$ Josephson junctions doesn’t veer far from a generalized sinusoidal function, then we can make a direct connection between the critical currents we measure for a Josephson junction and its Josephson inductance (see Equation 1.29).

Subtracting the two Josephson inductances from the lumped inductance $\Delta L$ leaves only the kinetic inductance of the NbSe$_2$ remaining. We can then compare this value between multiple samples to examine its dependence on flake thickness and aspect ratio.
5.1.4 Fabrication

Initial design and proof of concept work on a pure Al resonator design was done by Olivia Lanes. She designed the five hanger resonators along the length of the transmission line to have resonant frequencies equally spaced between 4-8GHz. The original fabrication process for resonators including TMD heterostructures starts with a silicon wafer on which transmission lines, EBL and optical alignment marks and dicing saw marks are patterned using optical lithography. The dimensions of the chips and transmission lines are matched to the Josephson Parametric Converters (JPC) sample holders used by HatLab for their own samples. These sample holders were repurposed for measuring the resonator samples because they were already used in the HatLab dilution refrigerator, and they had sufficient input/output signal line connections. After the chips are diced apart, encapsulated TMD heterostructures are set down within the optical alignment marks using standard dry transfer techniques. Optical microscope images are imported into the EBL CAD designs for the hanger resonators so I can align the lithographically patterned resonator leads with the location of the deposited TMD stack (as it is not feasible to place every stack in the same location for every sample chip and all stacks inherently have a unique geometry), and written in a bilayer of MMA/PMMA EBL resist. Initial attempts to write the entire resonator with EBL failed at the finger capacitor, with various avenues of failure such as shorting between fingers, incomplete lift off of excess metal, incompletely written fingers, and gaps in the stitching of the pattern between adjacent write windows.

After several chips with similar failure modes, we altered our fabrication protocol to use optical lithography to mass produce resonators on a 3-inch wafer. Similar to our EBL resist bilayer, we use a bilayer of optical resist (LOR 5B/S1805) to pattern the finger capacitor and inductive meanders of the resonators as well as the transmission line, alignment marks and dicing saw marks. NbTiN, a superconductor with $T_c = 15$ K, is deposited on the pattern via sputtering. Our stacking and fabrication process then proceeds as before except the Al leads just form connections between the NbSe$_2$ flake and the NbTiN resonator. This new process resulted in a 30-40% yield of chips from the wafer that each had 4 or 5 functional capacitors. In comparison, our yield when patterning finger capacitors via EBL with heterostructures on the substrate was zero. Failure modes in the remaining 60-70% of chips still typically involved the finger capacitors, including dust or particulate above or below the resist cutting off individual fingers or shorting between opposing fingers. Slight variations in optical dosage across the chip also caused problems in which our standard development time would not fully develop some regions while in other regions the capacitor fingers would start to overdevelop.

By patterning an entire 3-inch silicon wafer with dozens of individual resonator chips we can postselect for individual chips with the best resonators for TMD stack placement. NbTiN works well for this initial deposition because it does not form a robust insulating oxide layer, unlike evaporated Al. Our etch steps enable a clean
Figure 5.4: Comparison of EBL vs photolithographic patterning of resonators

(A)/(B) EBL writing and aluminum deposition of the entire resonator and TMD contacts resulted in finger capacitors with both fingers cut off and shorts between fingers. (C)/(D) Resonators incorporating NbTiN finger capacitors and meanders written using optical lithography are connected to the TMD using EBL written aluminum leads. This allows the finger capacitor to be inspected before transferring TMD heterostructures and increases device yield. See 5.5 for details on photolithography and NbTiN deposition.

interface to form during the second deposition when Al is deposited to contact the NbTiN components and connect them to the TMD stack as shown in Figure 5.4 C,D. Resonators integrating NbTiN and Al performed well, confirming the quality of the interface between the two materials, but with lower Q factors than pure Al resonators. This method of depositing NbTiN onto a lithographic mask consistently results in lower Q factors for resonators than deposit-first method. A uniform NbTiN layer is deposited over the entire wafer, and then resonators are lithographically patterned and the excess NbTiN is etched away. A possible explanation for this disparity could
Figure 5.5: Failed photolithography finger capacitors

(A) Finger capacitor and inductive meander of a resonator after NbTiN liftoff. (B) Scrambled finger capacitor with shorts between fingers due to overdevelopment. (C) Finger capacitor with cut fingers due to a $\sim 30\mu m$ particle on top of the resist blocking the write. (D) Overdeveloped finger capacitor with a small skew in the fingers and a cut in the inductive meander. (E) A cut finger tip will lower the resonator capacitance. (F) 3-inch wafer during development of resonator chip arrays.

be the presence of hydrocarbon resist contaminants in the NbTiN as it is deposited, but this is unconfirmed. We used the lithography first method in large part because the technique was previously well developed by members of HatLab, and it enabled
Table 5.2: DC resistance probing of resonators
Probe station 2-pt resistances with 10mV bias across the flake and contacts using probes on the Al bond pads or leads.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_{\text{initial \ probe}}$ (Ω)</th>
<th>$R_{\text{post-\ RF \ probe}}$ (Ω)</th>
<th>Resonance</th>
</tr>
</thead>
<tbody>
<tr>
<td>006-1</td>
<td>920</td>
<td>590</td>
<td></td>
</tr>
<tr>
<td>006-2</td>
<td>800</td>
<td>830</td>
<td>✓</td>
</tr>
<tr>
<td>006-3</td>
<td>812</td>
<td>950</td>
<td></td>
</tr>
<tr>
<td>006-4</td>
<td>14.2k</td>
<td>disconnected</td>
<td></td>
</tr>
<tr>
<td>006-5</td>
<td>1.33k</td>
<td>1.67k</td>
<td></td>
</tr>
<tr>
<td>007-1</td>
<td>11.8k</td>
<td>16.7k</td>
<td></td>
</tr>
<tr>
<td>007-2</td>
<td>11.4k</td>
<td>19.2k</td>
<td></td>
</tr>
<tr>
<td>007-3</td>
<td>2.65k</td>
<td>2.5k</td>
<td></td>
</tr>
<tr>
<td>007-4</td>
<td>170</td>
<td>disconnected</td>
<td></td>
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<tr>
<td>007-5</td>
<td>194</td>
<td>21.8k</td>
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<tr>
<td>008-1</td>
<td>36.5k</td>
<td>59k</td>
<td></td>
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<td>38.1k</td>
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<td>009-1</td>
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<td>710</td>
<td></td>
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<td>009-2</td>
<td>303</td>
<td>303</td>
<td>✓</td>
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<tr>
<td>009-3</td>
<td>61k</td>
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<tr>
<td>009-5</td>
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</tr>
<tr>
<td>010-2</td>
<td>1.8k</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>010-3</td>
<td>2.4k</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>010-4</td>
<td>9.8k</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>010-5</td>
<td>12.6k</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>011-2</td>
<td>320</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>011-3</td>
<td>3.95k</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>011-4</td>
<td>1.38k</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>011-5</td>
<td>900</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>013-2</td>
<td>1.33k</td>
<td>1.14k</td>
<td></td>
</tr>
<tr>
<td>013-3</td>
<td>3.28k</td>
<td>3.85k</td>
<td>✓</td>
</tr>
</tbody>
</table>

Probe station 2-pt resistances with 10mV bias across the flake and contacts using probes on the Al bond pads or leads.

the speedy resumption of sample fabrication and measurement, however, switching to a deposition and etching method may improve the Q factors for future resonators.
Bond pads were added to the design to enable wire bonding for DC measurement of the 2D-3D contacts’ critical currents and for more convenient probing of device resistances prior to RF measurement. Using a homebrew probe station connected to a Keithley 2400 source measurement unit I found that hybrid resonators with 2-pt resistances across the NbSe₂ flake below 4 kΩ could produce observable resonances, but that resonators with contact resistances above that never had an observable resonance. When a large contact resistance was measured in the range of 20 - 60 kΩ, we discovered that the patterned circuit was broken and we were measuring a small current passing through the Si substrate. At cryogenic temperatures the undoped Si substrate is highly insulating, but at room temperature it is a much worse insulator.

5.2 Resonator Measurements

5.2.1 RF Measurements

After fabrication and initial probe station contact resistance measurements, we glue the resonator chip into a re-purposed 4-port JPC sample holder using a silver
epoxy and allow it to set overnight (our transmission line format only uses two opposing RF ports). We connect the transmission line to the input/output connectors of the sample holder by making several aluminum wirebonds between the ends of the transmission line and the matching traces on the sample holder PCB which are soldered to the pins of the SMA RF connectors. The sample holder is closed and the SMAs are attached to the measurement lines in the dilution refrigerator while the body of the sample holder is attached to a thermalization point on the base temperature region of the refrigerator. The measurement circuit is detailed in Figure 5.6, showing various size attenuators mounted several different temperature plates on the input line, and an isolator and a High Electron Mobility Transistor (HEMT) on the output lines. These discrete components are used to thermalize the signal coming from the room-temperature VNA and kill off most of the attendant thermal noise on the input line, and to then amplify the output signal back up to a level usable by the VNA.

After the dilution refrigerator has cooled down (approximately 36 hours) we use a vector network analyzer (VNA) to send a signal through the transmission line passing by each of the resonators. We sweep the frequency of this signal in 100MHz steps between 2.5-8GHz at constant power looking for dips in the transmitted signal $S_{21}$ (see Figure 5.3) that are characteristic of a working resonator. After we identify a resonance dip, we narrow the frequency range of the sweep to increase the resolution of the curve. We then save the data and fit it to Equation 5.6 using a Python script. This fit extracts parameters such as center frequency, internal Q, coupling/external Q and total Q, as well as several other parameters (A,B,E,Δ) required to fit each resonance. The fitting parameters for a hybrid resonator and its matching control are shown in Table 5.3 and the resulting fit curves for the resonances in Figure 5.3 are shown in Figure 5.7.

$$\text{Magnitude} = A \left[ \frac{Q_{\text{ext}} + iQ_{\text{ext}}Q_{\text{int}} \left[ \frac{-4(\omega - \omega_0 - \Delta)(\Delta)}{(\omega_0 + \Delta)(\omega_0 + \Delta)} \right]}{Q_{\text{int}} + Q_{\text{ext}} + 2iQ_{\text{int}}Q_{\text{ext}} \frac{(\omega - \omega_0 - \Delta)}{(\omega_0 + \Delta)}} \right]^* e^{i(E\omega + B)} \quad (5.6)$$

After a resonance was observed in a sample we would proceed to test the sample’s response to different levels of input power in search of nonlinear behavior. We only observed a power response in one sample, 013-3, which unfortunately did not survive to be fully measured in DC (further discussion in subsection 5.2.5 below). One of the two contacts on that sample did not exhibit an interference pattern characteristic of a Josephson junction during magnetotransport measurements, and its critical current appeared to be 10x lower than its matching contact.

Our next step is to compare the hybrid hanger resonator with its matching control hanger resonator. Olivia Lanes or another student at Hatlab use HFSS to model the resonators with increasingly to extract the downshift in resonant frequency due to the presence of the van der Waals superconductor and the attendant 2D-3D junctions.
Table 5.3: Fitting parameters for a hybrid resonator and its matching control resonator.

<table>
<thead>
<tr>
<th>Fitting parameter</th>
<th>Hybrid resonance</th>
<th>Control Resonance</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-3.003436x10^{-3}</td>
<td>3.506474x10^{-3}</td>
</tr>
<tr>
<td>B</td>
<td>-5.558947x10^{-1}</td>
<td>-1.725589x10^{-1}</td>
</tr>
<tr>
<td>E</td>
<td>-3x10^{-8}</td>
<td>2.282969x10^{-8}</td>
</tr>
<tr>
<td>$\omega_0$</td>
<td>3.24021 GHz</td>
<td>3.292935 GHz</td>
</tr>
<tr>
<td>$Q_{ext}$</td>
<td>1,000</td>
<td>7,000</td>
</tr>
<tr>
<td>$Q_{int}$</td>
<td>1,473</td>
<td>2,600</td>
</tr>
<tr>
<td>delta</td>
<td>-7871</td>
<td>-12,336</td>
</tr>
</tbody>
</table>

increasing the circuit inductance. While the Q factors of the resonator provide some information about the quality of the resonator, the magnitude of this downshift in resonator frequency between the control and flake resonators is the main data point used for calculating kinetic inductance.

After all RF measurements have been completed in the dilution refrigerator at HatLab, the fridge is warmed up and the sample holder is removed and the sample
Figure 5.8: 5 hybrid resonators and their matching controls
The five hybrid resonances we have observed and their matching control resonators. The green dotted line is the fit on each resonance.

The sample chip is carefully dismounted. The sample chip is stored in a vacuum desiccator at all times after fabrication is complete except for when it is loaded in one of the dilution refrigerators for measurements.
Table 5.4: Q factors of each working hybrid resonator and control

<table>
<thead>
<tr>
<th>Sample</th>
<th>$Q_{int}$</th>
<th>$Q_{ext}$</th>
<th>$Q_{tot}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D:006-2 flake</td>
<td>4,000</td>
<td>3,700</td>
<td>1,922</td>
</tr>
<tr>
<td>006-2 control</td>
<td>4,720</td>
<td>5,720</td>
<td>2,587</td>
</tr>
<tr>
<td>E:007-5 flake</td>
<td>2,000</td>
<td>6,000</td>
<td>462</td>
</tr>
<tr>
<td>007-5 control</td>
<td>1,500</td>
<td>3,000</td>
<td>2,500</td>
</tr>
<tr>
<td>F:009-2 flake</td>
<td>1,473</td>
<td>1,000</td>
<td>5,951</td>
</tr>
<tr>
<td>009-2 control</td>
<td>2,600</td>
<td>7,000</td>
<td>5,515</td>
</tr>
<tr>
<td>G:009-4 flake</td>
<td>3,500</td>
<td>4,000</td>
<td>1,867</td>
</tr>
<tr>
<td>009-4 control</td>
<td>1,500</td>
<td>3,000</td>
<td>2,500</td>
</tr>
<tr>
<td>013-3 flake</td>
<td>1,400</td>
<td>4,520</td>
<td>1,068</td>
</tr>
<tr>
<td>013-3 control</td>
<td>7,790</td>
<td>8,200</td>
<td>3,995</td>
</tr>
</tbody>
</table>

The Q factors of each working pair of hybrid and control resonators. While there is a spread across an order of magnitude, in general, the control resonators have higher Q values. This suggests that the integration of NbSe$_2$ into the resonator does cause some additional energy losses in the resonator. The resonators with capital letters in the first column are samples that were characterized in Table 4.1.

5.2.2 DC Measurements

After RF measurements are complete, the sample is remounted in a large chip adapter 16-pin DIP socket for wirebonding. Two bonds are made from separate pins on the socket to each bondpad on either side of the flake in the resonator, this enables the pseudo 4-pt resistance measurement we used previously (see Section 2.3.2). When possible, two twisted pair connections are used with one side of each pair connected to each bondpad, enabling a twisted pair measurement configuration wherein current travels along one twisted pair of wires, and voltage signals are carried along the other, reducing any possible inductive loop noise in the measurement.

This measurement setup is functionally equivalent to those described in the previous chapter and is used to measure the critical current of the two Al/NbSe$_2$ junctions as well as the critical currents of the Al leads and the NbSe$_2$ flake itself (see Figure 2.6).

5.2.3 Kinetic Inductance Data Analysis

As discussed in the measurement schema section 5.1.3, we simulate the frequency shift between the hybrid resonator and the control resonator using high-frequency structure simulator (HFSS) software. HFSS takes the klayout CAD design of the resonator and simulates the resonant frequency of that design. In subsequent simulations, lumped element inductors are added to the resonator in the location of the NbSe$_2$ flake until the additional lumped inductance shifts the resonant frequency proportionately to
The forgiving distribution of bond pads on the resonator chips allows me to bond them using twisted pairs for voltage/current lines.

| Sample | $F_{\text{res}}$ (GHz) | $|\Delta f|$ (MHz) | $I_c$ (µA) | aspect (L/W) | thickness (nm) | $R_N^{\text{NbSe}_2}$ (Ω) |
|--------|----------------|----------------|-------|--------|------------|----------------|
| D:006-2 | 3.27 | 45.75 | 71.7 | 9 | 12* | 76.2 |
| E:007-5 | 4.917 | 235.5 | - | 4 | 6.2* | - |
| F:009-2 | 3.24 | 52.7 | 56.5,78.5 | 2.33 | 11.9 | 19.3 |
| G:009-4 | 4.287 | 62.6 | 108,128 | 3.8 | 8.8 | - |
| 013-3 | 3.6966 | 66.8 | 20,2 | 1.94 | 4* | 13.8 |

Table 5.5: Hybrid resonator RF and DC data

Data and parameters for each device exhibiting a resonance. Device 007-5 died after the RF measurements were performed, but before DC measurements of critical current could be made. Letters correspond to the same device in Table 4.1.

our observed shift in the hybrid resonator from the control. A list of the simulation results with the size of the lumped inductance and the percent downshift is given in Table 5.6.

After we have ascertained the inductance that causes the most proportionate shift, we declare that to be equal to our total inductive shift $\Delta L$ from Equation 5.5. We can then use the critical currents $I_{1,2}^c$ from our DC measurements to calculate the two Josephson inductances using Equation 1.29. These values have been put in Table 5.7. Unfortunately, due to limited device longevity, we only have full measurements for
Table 5.6: Frequency shifts due to lumped inductance
HFSS simulation values of the hanger resonator frequency shift as a lumped inductor value is increased.

<table>
<thead>
<tr>
<th>$F_{res}^{sim}$ (GHz)</th>
<th>$L_{lumped}$</th>
<th>Downshift (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5651</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4.5536</td>
<td>10</td>
<td>0.2519</td>
</tr>
<tr>
<td>4.5425</td>
<td>20</td>
<td>0.4951</td>
</tr>
<tr>
<td>4.5323</td>
<td>30</td>
<td>0.7185</td>
</tr>
<tr>
<td>4.5214</td>
<td>40</td>
<td>0.9573</td>
</tr>
<tr>
<td>4.5004</td>
<td>60</td>
<td>1.4173</td>
</tr>
</tbody>
</table>

Table 5.7: Hybrid resonator kinetic inductance analysis
Data and parameters for each device exhibiting a resonance. Device 007-5 died after the RF measurements were performed, but before DC measurements of critical current could be made. The second contact on device 013-3 seemed to have died at some point between RF and DC measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta f$ (MHz)</th>
<th>$\Delta L$ (pH)</th>
<th>$I_c$ ($\mu$A)</th>
<th>$L_{T}^{12}$ (pH)</th>
<th>$L_k$ (pH)</th>
<th>(L/W)</th>
<th>thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D:006-2</td>
<td>45.75</td>
<td>53</td>
<td>71.7</td>
<td>9.27</td>
<td>43.73</td>
<td>9</td>
<td>12*</td>
</tr>
<tr>
<td>E:007-5</td>
<td>235.5</td>
<td>125</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>6.2*</td>
</tr>
<tr>
<td>F:009-2</td>
<td>52.7</td>
<td>42</td>
<td>56.5,78.5</td>
<td>10.02</td>
<td>31.98</td>
<td>2.33</td>
<td>11.9</td>
</tr>
<tr>
<td>G:009-4</td>
<td>62.6</td>
<td>31</td>
<td>108,128</td>
<td>5.62</td>
<td>25.4</td>
<td>3.8</td>
<td>8.8</td>
</tr>
<tr>
<td>013-3</td>
<td>66.8</td>
<td>42</td>
<td>20, x2x</td>
<td>181.1</td>
<td>X</td>
<td>1.94</td>
<td>4*</td>
</tr>
</tbody>
</table>

5.2.4 Calculations of $L_k$

If we try to calculate values for $L_k$ using Equation 5.1, we can plug the mass and charge of the electron, the aspect ratios and thicknesses we have collected in the previous tables, and a value of $n_{2D} = 1.9 \times 10^{15} cm^{-2}$ from [213]. Listed in column 3 of Table 5.8 (experimental results are reprinted in column 2), these values are approximately two orders of magnitude lower than the values we extracted from our experimental data. This is quite difference between values extracted from experiment and a basic calculation. The carrier density has been measured quite thoroughly, so it is unlikely to be the source of much error [213]. Certainly a fraction of a micron error due to incorrect measurements of the NbSe$_2$ flake’s dimensions is possible if not likely, but spatial measurement errors could not have contributed more than a small
fraction of total error. Instead, larger source of error is likely our use of the rest mass of an electron \((m_e)\), rather than the effective mass \((m_{eff})\). The effective mass of an electron in a band structure, as discussed in Section 1.1.3, can vary above or below the rest mass by several orders of magnitude in extreme cases. So the use of the rest mass of an electron could have caused this large of an error in our calculation if the band structure’s effective electron mass is on the order of 80-200\(m_e\). To account for this source of error we would need either a theoretical model that predicts the effective mass or measurements of the effective mass. The only published values of \(m_{eff}\) that I could find are mostly for monolayers and their values vary from 0.5-5\(m_e\), so this could be a significant error in the calculation, but is not sufficient to account for the entire error. After the measured dimensions of the NbSe\(_2\) flake and the effective mass of its electrons the values we calculated are still much lower than our experimental results. Superconducting systems that are highly disordered are still be dissipationless, but they will have a much larger kinetic inductance \([214]\). This can be seen in the direct relation between kinetic inductance and the normal state sheet resistance of a superconductor in Equation 5.2 \([208]\). Disorder in any (non-superconducting) system will increase the electrical resistance because the mean free path of charge carriers has decreased. The NbSe\(_2\) flake could contribute to our measurements of kinetic inductance being larger than our calculations, but crystalline superconductors like NbSe\(_2\) are typically considered to be in the far clean limit, especially when they have been exfoliated and encapsulated \([19, 215, 216]\). Especially after our cross-sectional TEM images in Section 4.2 showed pristine NbSe\(_2\) crystal structure down to the atomic limit with the exception of single mesoscopic break in one of the devices. So we should not look to disorder for an explanation of the remaining discrepancy between our calculations from Equation 5.1 and our experimental results.

\[
R_{N}^{\text{NbSe}_2} = \frac{\rho L}{(wt)} \quad (5.7)
\]

\[
R_{sq} = \frac{\rho}{t} = \left(\frac{w}{L}\right) R_{N}^{\text{NbSe}_2} \quad (5.8)
\]

\[
L_K = \frac{R_{N}^{\text{NbSe}_2} h}{2\pi^2 \Delta_0} \quad (5.9)
\]

The expansion used by Annunziata et al. to derive Equation 5.2 from the Mattis-Bardeen formula for complex conductivity is only valid for \(hf \ll k_B T\) \([208]\). Since our RF measurements were performed at \(\approx 20\) mK, our measurement frequency would have had to be well below 500 MHz to comply. Our measurements actually occurred in the range of 3.2-3.7 GHz, several times greater than permitted by this criterion. While we should harbor some concerns regarding the validity and predictivity of Equation 5.2 due to our high frequency measurements, the previous calculations had such a large error that we may still learn something from this calculation. The equation for kinetic inductance was transformed to replace parameters like carrier density as well as the mass and charge of an electron with the temperature dependent
Table 5.8: Theory calculations of $L_k$ for our hybrid resonators
Two methods of calculating $L_k$ produce drastically different results that still don’t match our samples.
superconducting gap and the sheet resistance of the NbSe$_2$ flake [208]. We can rewrite Equation 5.2 in Equation 5.9 by replacing the sheet resistance with the normal state resistance, since $R_n = R_{sq}(l/w)$. The temperature dependent superconducting gap can be replaced by the zero temperature gap value since measurements occurred at $\approx 20$ mK, which is 0.2% of NbSe$_2$’s critical temperature. Lastly, the hyperbolic tangent term can also be discarded, due to the low measurement temperature it is almost equivalent to unity. The normal state resistance of the NbSe$_2$ flake was not previously something I set out to measure, but I was able to find it in my datasets for three of the hybrid resonators. The NbSe$_2$ flake, despite being the smallest component of the sample, has a higher critical temperature, critical field and critical current than the Al contacting it. This provides a very precise measurement of the contact resistances and the Al lead resistances as they each go normal, but to obtain $R_n^{\text{NbSe}_2}$ I had to take the total resistance of the sample and then subtract off the contact and lead resistances obtained via $R(T)$, $R(B)$ and $dV/dI$ measurements. This is not quite as precise as it could be if it were included as part of my standard measurement campaign, yet the normal state resistances should be rather close to the true values. As a sanity check on this methodology, the resistivity is obtained by dividing $R_n$ by the flake length and multiplying by the cross-sectional area. The resistivities for these three samples are all within about 16% of each other. So my process to obtain $R_n$ for these three samples appears to work sufficiently well. These $R_n^{\text{NbSe}_2}$ estimates (for the samples we have sufficient measurements on) are given in the final column of Table 5.5.

The greater difficulty lies with choosing an appropriate superconducting gap energy to use in the calculation since NbSe$_2$ is a multiband superconductor with two unequal gaps [190]. Noat et al. review many prior models of the NbSe$_2$ two gap system in addition to presenting their own work. As briefly discussed last chapter the larger of the superconducting gaps is inherent to its band and it proximitizes the other gap into existence on the other Nb band. The sizes for these gaps vary from model to model and fit to fit. However, the larger one is consistently around 1.3 meV, while the smaller gap is often around 0.5 meV, so we will perform the calculation with both of these options. The results are presented on the right side of Table 5.8. Unfortunately the overlap between resonators that were fully measured in RF + DC and the NbSe$_2$ flakes that I had normal state resistance measurements of is $N=2$.

Despite our measurements being performed at to high of an RF frequency for the temperature of our sample, this equation has produced better results than our prior calculation. There is still plenty of room for improvement though. Based simply on the functionality of Equation 5.9 the smaller superconducting gap value resulted in larger kinetic inductances than the larger gap value. The closest match of calculations to experimental values is then only 25% below experiment rather than 98.7% below the experiment. The largest possible source of error in this calculation is without a doubt the choice of what superconducting gap energy we plug into the equation, and its also the variable that has the least evidence motivating the decision since different
theory groups that have worked on this problem all have slightly different results.

For instance, the two gaps are partially anisotropic, but not fully. The larger gap is heavily dominant for perpendicular currents due to its strong coupling with the Se band. However, in-plane currents are split in favor of the smaller gap Nb band, though neither orientation is fully polarized the two Nb bands [190, 193] This isn’t a Josephson junction with an Ambegaokar-Bartoff relation we can we wanted to use an admixture of the two gap energies, as in Equation 4.2, our result would be $\Delta_{1,2} = 0.361 \text{meV}.$ If we then used this value in the calculation of kinetic inductance for sample 006-2 our output would be $L_k = 44.2 \text{pH},$ a 99% match. However, these gaps are not on either side of an SNS Josephson junction, which was the intended use of Equation 4.2. I am aware of no scientifically compelling reason to mix the gap energies in that manner other than "it worked for that one sample". And at the same time, the exact same method would only result in a minuscule improvement for Sample 009-2. We will need measurements on at least several more successful samples before we can start making firm conclusions about these samples and our measurements of them.
5.2.5 Hybrid resonator power response

Our project plan and measurement schema for determining the kinetic inductance of NbSe$_2$ focuses solely on shifts in resonant frequency. While we have made attempts to fabricate resonators with high quality factors, the profile of the resonance dips in Figure 5.8 hasn’t been discussed up to this point, nor has there been much reason to do so. As we start looking to build superconducting circuit components out of 2D superconductors, we will need to further characterize the properties of various 2D superconductors. One way to do that is to probe hybrid resonators with off-resonance signals as well as varying signal strengths. While previous hybrid resonators have been probed with varying power levels, sample 013-3 was the first to show the resonance shifting in frequency space at increasing powers (Figure 5.10a & 5.10b). This was the first sign in any of our resonator samples of bifurcation occurring. Unfortunately, in follow up measurements no hysteresis was observed (Figure 4.17). However, bifurcation was later confirmed by using the hybrid resonator as an amplifier (Figure 5.10d) [217]. This sample was then removed and taken for DC measurements of it’s critical current, where we discovered that one contact did not seem to be behaving like a Josephson junction, and had a highly reduced critical current. So we believe that most of the odd and interesting RF behavior in these measurements was due to a malfunctioning contact. Eventually, our goal for this type of measurement is to use the off-resonance power response from van der Waals superconducting circuit components to better understand and back out higher order terms of their Hamiltonian. This would then help us understand how the component will behave as part of the larger system, and possibly provide feedback to influence future component designs.
Figure 5.10: Power response in sample 013-3

Results of probing resonator 013-3 with additional frequency generators and varying signal powers. (a) frequency sweeps at varying powers give the first hint of bifurcation. (b) A higher resolution colormap of the same parameter space shows a downshift in frequency as power goes up. (c) The search for left-right hysteresis in these frequency sweeps produced two almost entirely identical plots with no sign of hysteresis. A jump between two states should have been visible. (d) Around 20dbm gain can be produced using this device right near it’s center frequency.
While we were delighted to have a measurable shift in resonant frequency due to the addition of NbSe$_2$ flakes in a resonator, the shift was rather small in comparison. This new resonator design should amplify an equivalent change in inductance into a much large change in resonant frequency because the resonator is designed to have no additional inductive meanders or other sources.

5.3 Immediate plans through Spring 2021 Postdoc

Based on our successes and failures with NbSe$_2$ in hanger style resonators, we have planned two paths forward. First, although the shift in resonant frequency was measurable, it was only a few percent. We have designed and fabricated a completely new resonator chip that has very low built-in inductance, mostly consisting of two large vertical capacitors on either side of our NbSe$_2$ flakes. Because they are mostly capacitive devices, any inductance from our 2D superconductors will cause a much greater shift in resonance than it did in the hanger geometry. Our second direction forward is to work with new materials in the hanger resonator chips. Tantalum has been identified within the superconducting qubit community as producing significantly higher qubit lifetimes. We had previously believed that our implementation of NbTiN, and especially the deposition process, were causing some of the problems in our samples. Just in the past few days we have collaborated with HatLab on designing and fabricating tantalum substrates to test stacking for DC devices, with the thought process being that DC devices will have fewer surprise difficulties, and we will be able to ramp up to resonator samples on this new substrate in the near future.
Chapter 6

Concluding Remarks and Future Work

6.1 Concluding Remarks

Prior to and during this work, many exciting results have encouraged the further development of methods to integrate superconducting circuit components composed of 2D van der Waals materials into conventional superconducting circuits. The superconducting proximity effect has been studied in multiple van der Waals systems where the 2D nature of the materials enable surface proximity effects to alter the properties of the entire 2D system [156, 157, 165]. Superconductor-graphene-superconductor Josephson junctions have been studied for over a decade at a wide range of scales and using a plethora of deposited superconductors [42, 50–53, 152, 165]. Fully van der Waals Josephson junctions have been built using crystal misalignment to form a weak link between bulk NbSe$_2$ flakes, while another group inserted graphene as a normal metal tunnel barrier between bulk NbSe$_2$ [80, 218]. Other groups have used van der Waals materials as tunnel barriers between deposited superconductors [55, 150, 162, 219]. Most recently, magic angle twisted bilayer graphene has emerged as a prominent gated superconductor that can be gate tuned into a bewildering variety of states [58, 58]. Careful design of gate geometries has even enabled two independent groups to create fully 2D planar TwBLG Josephson junctions that replicate and enlarge the large effective areas we find in 2D-3D Josephson junctions due to uniform magnetic field penetration of the 2D superconductor (discussed in Chapter 4), but with bilateral symmetry and the ability to tune their properties via gating [61, 62].

In DC superconducting circuits, patterning of 2D van der Waals superconductors could improve upon the function of devices like the "nanocryotron", which functions as a superconducting transistor patterned from a continuous superconductor with no Josephson junctions [220]. The three terminal device uses a constriction (though not a "weak link") connecting one "gate" arm to a superconducting wire connecting the "source" and "drain". Increasing the current from the gate beyond the critical cur-
rent of the constriction causes heating that will decrease the current from source to drain, enabling off and on states as well as gain. Another geometry based DC superconducting device from the same group is the "yTron", which uses current crowding at a sharp Y in the superconductor to enable a user’s measurement of the critical current in one arm of the Y to determine the current flowing from the other arm of the Y through the base and requires the use of a superconductor thinner than its penetration depth to function as designed, a natural fit for atomically thin van der Waals superconductors\cite{221}. TMD Ising superconductors in the few layer limit could enable these devices to operate in very large in-plane fields, while the superconducting contacts I discuss in Chapter 4 would enable the integration of such devices into conventional superconducting circuits. These superconducting DC devices have been something I’ve wanted to do for a long time. The use of current crowding and geometric effects to sense and control supercurrents is just so intriguing to me.

I’m really excited for the next era of scaleable 2D heterostructures that we can see hints of on the horizon. Not just the idea that you can layer anything you want together to tailor the hetero structure’s properties, when in fact its going to take a grad student half a year to get halfway towards that designed heterostructure. Rather, within a decade or two I bet we will have fully automated growth and stacking robotic assembly lines working in inert atmosphere and stacking structures dozens or hundreds of layers thick.

### 6.2 Future Work

I’m really looking forward to seeing where this field will be in another 5-10 years. I hope so much of what we’ve struggled with will become routine or automated (exfoliation, searching, stacking), and I can’t wait to see what new combinations of 2D superconductors someone will come up with next. I’m hopeful that we have some success with out plans for research over the next semester, I think integrating TwBLG into a superconducting resonator is a great next step,

In terms of the work that I’ve spent so much time on during this degree, I’m really excited to see what other 2D superconducting materials and components can be hacked into resonators for HatLab to study. Kinetic inductance has only ever been the intended starting point for this project, and I think there is lots and lots of room to expand with various types of junctions and gate tunable superconductors.

Looking back to the discussion of proximitized superconductivity in graphene in Section 4.1.2, a clear research and development path is visible (a similar path seems to be followed for many superconducting systems such as nanotubes, nanodots, 2DEGs, etc). First the properties of a superconducting system are studied and characterized. Next, those properties are utilized in the creation of high quality Josephson junctions and superconducting circuit components, and then those components are integrated into qubit circuits so they can be optimized and utilized for what they do best. SGS junctions were used in a superconducting circuit to build a superconducting qubit.
three years ago after almost a decade of sustained research. I hope that my work these past 5 years has helped 2D van der Waals superconductors as a system take a few more steps along this pathway that every new technology proceeds down.
Bibliography


Concluding Remarks and Future Work


Concluding Remarks and Future Work  

M.R. Sinko


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Concluding Remarks and Future Work


Concluding Remarks and Future Work

M.R. Sinko


Concluding Remarks and Future Work

M.R. Sinko


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Concluding Remarks and Future Work

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Appendices
Appendix A

3D Printing: Prototyping, Data Visualization & Utility

Figure A.1: Model and Print of 2H-TMD crystal structure
A.1 Introduction to 3D Printing

3D printing, also called additive manufacturing, has been developing over more than four decades. Advances in 3D printing technology have occurred along several axes in parallel: printing technologies (stereolithography, extrusion, sinter or adhesive powder bed fusion), printable materials (photo-polymers, thermoplastics, metals, concrete, etc), print resolution (10’s-100’s of microns) and print speed. While each printing method is only capable of printing certain materials, the final results can be structures that are impossible to fabricate any other method. For the first two decades the technology was rather inaccessible outside of industrial and academic R&D, but in the early to mid 2000’s 3D printing with homebrew equipment increased in popularity amongst the growing open source community. The expiration of the earliest 3D printing patents around this same time led to the broader commercialization of multiple 3D printing technologies as well as widely available consumer products in the past decade (primarily plastic filament extrusion printers). 3D printing provides the capability to quickly iterate a design at much lower price points than injection molding or machining, and cheaper plastic prints can be used to prototype for more expensive professional metal prints.

The ever lower cost of entry to plastic and resin 3D printing, both in dollars and in technical skills, now enables researchers to routinely use the technology in support of their primary research focus. New instrument and component designs can be printed multiple times to iterate a design in the same amount of time it would take to get an initial design prototype from an external machine shop. Being able to fit a printed component into place to verify the design prior to commissioning the final product is a much truer test than using a 3D CAD render. Most CAD programs used for 3D design and modeling are able to export the 3D model to the .stl (coming from stereolithography) file format that is most frequently used for 3D printing. The .stl file is then "sliced" using one of an assortment of programs (I used Cura) that output a .gcode file containing every individual X,Y,Z step, temperature setting, and material flow rate for the entire printing process. These g-code instructions are customized for the specific 3D printer model you are using, but they also add components such as material infill or external support structures that were not in the original .stl file. The .gcode file is transferred to your printer which then starts the 3D printing process. Small parts may take only minutes to print, but large and complex designs can take multiple days of continuous printing to finish.

I used Autodesk Inventor and Autodesk Fusion to create component prototypes and van der Waals crystal models. For the crystals, I would start with a stick and ball unit cell, then use mirror planes and rotations to fill out a larger model of the crystal as shown in Figure A.1 (compare with Figure 1.16). Structures like this will have large amounts of support structure that must be removed after printing, but some printers with dual extruders are capable of printing the support structure with a water soluble material that can be rinsed off rather than cut away. Other structural
models are easier to make using CAD design techniques. I was able to put together this design for a cutaway model of the 2D-3D superconducting contact shown in Figure A.3 based on the SEM image in Figure 2.3 in less than half an hour.

![Fig A.2: 1T TMD crystal structure](image)

Designs for functional components usually start with a set of measurements and a rough sketch of the part. During your design process it is helpful to keep in mind the layered deposition of 3D printing and how this can produce anisotropic strengths in your component. The nature of the 3D printing method you are using should also influence your design, just as standard fabrication methods influence their designs. Support structures must be removed, curves are smoother when printed in the plane of the print rather than across multiple layers, and the resolution/tolerance of a printer can limit your design as well. Most CAD software provides sufficient usage tutorials,
Figure A.3: Cutaway model of Al/NbSe$_2$ side contact with Al flag
This model shows an representation of the 2D-3D superconducting contacts discussed in Chapter 4. Printed in white PLA plastic, I added color with nail polish to distinguish the SiO$_2$ (light green), hBN (teal), NbSe$_2$ (purple) and Al (white).

so I won’t discuss the mechanics of the design process further.

For our lab I have designed several functional 3D prints. Figure A.5 shows an adapter I designed and printed for refilling a liquid nitrogen dewar that holds our dilution refrigerator’s cold trap. My design includes a way of attaching a filling hose and venting the boiled off gaseous nitrogen to the side away from the vacuum connections above while not removing the cold trap from the dewar. While this design did work, the tube inserted inside the filling hose significantly reduced the fill rate. A new version might fix this by holding the fill hose around its exterior. More successfully, I designed a mount for holding our PPMS probe vertically on the side of an equipment rack (Figure A.4). I printed this with a high infill percentage so it would be structurally stronger, and I designed a latching mechanism so the probe could not be accidentally knocked off the mount. It is attached to the equipment rack with several bolts that pass through holes I designed in the printed object.
A.2 3D printing visualizations

A.2.1 Printing Data from MATLAB

While Autodesk and other CAD products are excellent for designing new components, other programs can be used to plot 3D models of your original data. I wrote the short MATLAB code shown in Figure A.6 which uses the two open source methods written by Sven Holcombe to transform my XYZ data from Figure 4.26 into a closed surface .stl file that I could print (surf2solid & stlwrite available at these sites: https://www.mathworks.com/matlabcentral/fileexchange/42876-surf2solid-make-a-solid-volume-from-a-surface-for-3d-printing & https://www.mathworks.com/matlabcentral/fileexchange/stlwrite-write-ascii-or-binary-stl-files). Due to the signal to noise ratio of my data, and the resolution of my 3D printer, I removed some outlier data points and slightly
smoothed the Z data along both X and Y axes to make it easier to print. Lastly, I sectioned the data set into six separate blocks (Figures A.7a & A.7b) so that the final model could be held together at the bottom and folded to display linecuts of the data set (Figures A.7c & A.7d, compare with Figure 4.17) & 4.18.

While a printed 3D visualization of data may be helpful in monochrome, I took
advantage of color changing filament that has a rainbow of roughly equal length colored segments to loosely replicate the colormap on my 3D data visualization. It would be difficult to be precise with the locations of color changes in such a model because the colored segments of the filament are not precisely equal in length, and the printed data visualization varies in density along the vertical axis, so at the bottom of the model a color will only print 3-5 layers of the design, but in the sparser regions near the top of the design a color will last through 20-30 layers. If sharp changes in color are desired, single color filaments can be swapped out at predetermined print heights as I did in my 2H crystal model shown in Figure A.1b. Most 3D printing materials can be painted after the print is complete, for PLA plastic I have found that standard nail polish colors adhere well and produce a fine finish (see Figures ??). Lastly, some commercially available 3D printers now allow for multiple plastic filament colors to be melted together creating an RGB colorspace for printing. However, these printers are substantially more expensive than the lowest price point printers.

```
X3d=X(21:201,300:601)*8;
Y3d=Y(21:201,300:601);
Z3d=Z(21:201,300:601)*2;

Z3d = filloutliers(Z3d,'clip','percentiles',[0,97])
Z3d = filloutliers(Z3d,'clip','percentiles',[0,97],2)

[Z3d,window] = smoothdata(Z3d, 1,'movmedian',5);
[Z3d,window] = smoothdata(Z3d, 2,'movmedian',5);

solidd = surf2solid(X3d,Y3d,Z3d,'elevation',-4);
stlwriter('3DPoshalfFraun.stl',solidd)
```

Figure A.6: Matlab code for plotting XYZ data

A.2.2 3D printing from Mathematica

Mathematica can also be used to create .stl files for 3D printing. Here I use its built in functions to print a representation of the spin orbit field in an Ising superconductor’s Brillouin zone rather than experimental data (compare Figure A.8 & 3.3 b,c).
Figure A.7: MATLAB generated design from experimental data
Figure A.8: Mathematica generated model
A.3 Open source 3D printing

One of the best resources for 3D printing is the open source community that has embraced it. Thousands of designs for useful gadgets and components as well as some basic scientific instruments and instructional models are freely shared and available on websites such as thingiverse.com where you can download the .stl file and learn from other users what printer settings to use. Some of my own original designs are available on my profile page: https://www.thingiverse.com/sinkomr/designs. I have printed many open source objects for our lab, from functional modular organizers (Figure A.9a) to models of atomic orbitals (Figure A.9b) and the band structure of graphene (Figure A.9c).

![Open source designs](image)

(a) (b) (c) (d)

Figure A.9: Open source designs

In conclusion, 3D printing has been developed into an extremely accessible tool that has a wide array of uses in the modern experimental research lab. New designs
can be prototyped and iterated many times prior to being finalized for an expensive order. Visual aids of sample structures or experimental data can be produced for presentations (though this works better for in-person presentations than for virtual presentations), and useful gadgets can be printed for regular usage in the lab environment.
Appendix B

Precision Oriented Kinetic Extraction (POKE)

We present a novel method for removing unwanted evaporated metal from a failed resist liftoff. This technique is capable of removing flags of metal from along the edges of features, as well as areas of metal that are connected to features on one or more sides including regions that are fully surrounded and connected to features. Working under a long working distance microscope lens, a fine probe mounted on a micromanipulator allows the user to carefully approach regions of trapped metal and use the tip of the needle to separate the unwanted material from the features.

Nanoscale lithography of metal electrodes is at the heart of modern device fabrication processes. The final step in this procedure is the removal of excess metal, which is on top of undeveloped e-beam resist. This "lift-off" technique involves soaking the device in acetone to dissolve away the resist and lift off the extra metal from the surface. At times however, the lift-off technique can fail resulting in unwanted excess metal around the device. This problem can be mitigated to a large extent by careful preparation of the sample, sensible pattern design and appropriately choosing the resist stack, including the spin & bake recipes. Failed liftoffs can occur occasionally in spite of these precautions. The problem is even more frequent when working with particularly chemically sensitive samples, as that puts a limit on the the choice of resists, baking temperature etc. so as to not degrade the sample. While an obvious technique to solve the problem of failed lift-offs might be to sonicate the device in an acetone bath, this technique cannot be applied to layered two dimensional (2D) materials and vertical van der Waals (vdW) heterostructures. The vibrations of the sonicator are strong enough to dissociate the 2D flakes and move them around randomly, destroying the device in the process, as shown in (Fig. B.1a,b). Here we present a precise, non invasive technique to remove any excess metal layers and salvage failed lift-offs. Our setup consists of a sharp probe that is attached to an X-Y-Z micromanipulator. This apparatus, along with the device is placed under a long working distance optical microscope. The setup allows us to precisely poke away any excess metal, causing it
to detach from the surface. The real time observation ensures that the probe is at a safe distance from the actual device, and the micromanipulator provides us precise control over the excess metal removal. Using this technique, we are able to remove excess metal features that have sub-micron lateral widths, demonstrating that our technique works to high resolutions.

Figure B.1: Sonication can destroy van der Waals materials
Before and after comparison of sonication and kinetic extraction methods
(A) Optical microscopy image of multiple flakes of VSe$_2$, a 2D vdW material, adhered to a substrate (B) Optical microscopy image of the same region as 1.A, after sonication (C)

Lithographic patterning of metallic leads is a common nanofabrication technique used in a wide array of applications. One persistent issue is in this process is difficulty in the removal of excess evaporated metal around the features of the mask. This problem can be mitigated to a great extent by careful preparation of the sample before lithographic patterning by the choice of mask/resist materials/layers, better design of lithographic features, and liftoff process. In cases where these steps have not worked, or have not been taken, the most common step to complete the liftoff
of undesired regions is to ultrasonicate the sample in a container of acetone. This method is viable for samples that are not sensitive to such vibrations, but would be inadvisable for other samples, such as ones that contain layered 2D materials or stacks of 2D materials forming van der Waals (vdW) heterostructures. We present a method for removing loosely flagging metal, peninsulas, isthmuses, and trapped islands of metal resulting from a poor liftoff. Our technique, as shown in (Fig. ??a), uses a fine needle mounted to a micromanipulator with \( \sim 1 \mu m \) control. The specific mounting method is used for a micromanipulator adapted to holding glass slides in a standard 2D material dry transfer setup. A fine needle is inserted in reverse (to preserve the fine tip) through the corner of a small block of PDMS (poly dimethylsilicane?) at an angle between 30 and 45 degrees below horizontal (1cm x 1cm x 4mm?) that is adhered along the edge of standard glass slide. The glass slide is then mounted to a micromanipulator, while the substrate remains in an acetone bath in a shallow walled dish (we used a watch glass) to be placed under a long working distance lens of a microscope. After the sample area with poor liftoff is located in the objective area, the micromanipulator is used to bring the needle into contact with the substrate away from sensitive written features. At this point, a few strategies can be used which will be discussed later. This technique has been used with success to remove flags from between features with sub-micron separations.

### B.1 Methods

A schematic of the lift-off apparatus is shown in Fig. 2X. A square stamp of polydimethylsiloxane (PDMS) (5 x 5 x 3 mm) is placed near the edge on a microscopic glass slide (75 x 25 x 1 mm). A catwhisker needle (\( \sim 1 \mu m \) tip diameter) is suspended downwards from the PDMS stamp at an angle. This glass slide is then attached to an X-Y-Z micromanipulator. For liftoff, the device is submerged in acetone inside a watch glass and placed under a long working distance microscope. For coarse metal features greater than 50 um, a sharp metal tweezer is used to scratch away the excess metal. After all the unwanted coarse metal features are removed, the lift-off apparatus is brought next to the device to remove the finer features. Using the X-Y-Z micromanipulator, the position of the needle is precisely controlled. The needle is brought right next to an excess metal feature and lowered enough that it touches the Si substrate and exerts a downward force. The needle is then laterally dragged on the substrate in the direction of the excess metal, poking its way underneath the metal and lifting it off of the surface. Repeating this procedure a few times causes the unwanted metal feature to completely detach from the surface and float away. The metal features that are part of the actual device have no ebeam resist underneath, and hence adhere much more strongly to the surface. As a result, they do not detach from the surface, even if they are accidentally scratched by the lift-off apparatus.

The role of the PDMS in the mounting of the needle to the micromanipulator is twofold. First, it allows for the angle of the needle relative to the substrate to be
changed by inserting the back of the needle into the corner of the PDMS block at a different angle; secondly, the PDMS applies a spring force to the needle as it is pushed down slightly onto the substrate. The tip of the needle should glide smoothly forward after it is lowered and touches the surface, and bending the PDMS slightly. Caution should be used when retracting the needle, as the tip will pull backwards along the substrate the same distance it was pushed forward by pushing down on the substrate with the PDMS as the tip was lowered. The needle’s fine tip allows for easy movement along the sides of large features (10+ µm) that are separated by a similar distance, in these instances, the needle can be pushed along the edge of the large feature, with the length of the needle parallel to the edge of the feature, this will serve to shear the flagging metal off of the feature’s side. This can be repeated as necessary to remove flags of metal from large features by reorienting the needle or the substrate to parallel each edge. Trapped islands of metal that are fully enclosed or nearly fully enclosed with only a thin isthmus connecting it to a bulk flag should be approached differently. Regions with diameters larger than the diameter of the needle’s tip should be accessible, with larger regions being easier than smaller regions. Here, the tip of the needle can be brought down near the middle of the region and dragged around slightly until a tear at the edge of the enclosing feature can be formed and exploited. Many times, the small flag of metal will stick to the tip of the needle after it is removed from its connected feature. Typically, this can be due to part of the flag being held down by the needle, lifting the needle from the surface of the substrate can allow the flag to float away.

Figure B.2: Mounting and orientation of catwhisker needle on a micromanipulator
Images show the setup of the slide mounted needle attached to a micromanipulator (B) Closeup image showing how the needle is attached to the glass slide using a PDMS block (C) Optical microscope image of the tip of the needle.

In conclusion, we present a novel, non invasive technique to remedy failed lift-off procedures. The technique is particularly useful for chemically sensitive 2D materials
which have implicit restrictions on their nanofabrication recipes and hence, are more susceptible to failed lift-offs. Our technique should allow for a greater success in fabrication of devices comprising such materials.
Appendix C

2D/3D JJ Ginzburg-Landau Model
Mathematica Code
combined analysis

scan image

In[226]:= img = Import[
"/Users/michaelsinko/Dropbox/Sinko/Papers;write/Superconducting contacts/TEM stuff/Picture1.png"];

In[227]:= imgScale = 

Out[227]=


Out[228]=

In[ ]=
choose points starting in top left corner
and go counter clockwise (this is important later for how
TraceCurve selects which pair of points define the contact edges)

```
In[379]:= pts = {{282.91726007887814`, 302.76087313759865`},
    {290.23505970639786`, 271.8720557624891`}, {313.2915205959684`,
        270.8521858282213`}, {321.9434706397896`, 257.5856567703769`},
    {332.7871658632778`, 252.34046340929012`}, {351.9058802585451`,
        245.0842873575811`}, {368.2207219544259`, 286.2385654031552`},
    {343.6113469544259`, 300.2281441717792`}, {325.16432953549514`,
        302.8543355609115`}, {282.91726007887814`, 302.76087313759865`}};
DynamicModule[{}, ClickPane[Dynamic[Show[img, Graphics[Line[pts]]]],
    AppendTo[pts, #] &]]
```

```
(* sets last point equal to first point to close the polygon *)
```
Solve for phase & current distribution
\begin{align*}
\text{boundaries} &= \text{Table[getEqn[pts2[[k]], pts2[[k+1]], \{k, Length[pts2] - 1\}]}; \\
\Omega &= \text{ImplicitRegion[And@@\{# \geq 0 \&/@boundaries\}, \{x, y\}];} \\
\end{align*}

\begin{align*}
\text{Out[246]} &= \{1 + 0.0304747 x + 0.0072197 y, 1 + 0.00504963 x + 0.114158 y, \\
& 1 + 0.0741307 x + 0.0483454 y, 1 + 0.022645 x + 0.0468153 y, 1 + 0.0168253 x + 0.0443315 y, \\
& 1 - 0.00589577 x - 0.0423944 y, 1 - 0.0000937883 x - 0.0423944 y\} \\
\text{Out[248]} &= \{1. \times (x \to 0, y \to 0) \} \&/@\text{boundaries} \\
\text{Out[249]} &= \{1., 1., 1., 1., 1., 1., 1., 1., 1.\}
\end{align*}
xMS = Table[\(\text{pts2}[[i, 1]] + \text{pts2}[[i + 1, 1]]\) \(\frac{1}{2}\), \(i, \text{Length}[\text{pts2} - 1]\)]
sgn = \{1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1\};(* must have more 1's than number of edges *)


getN\[x\_, y\_] := Module\[\{\epsilon, a, b, c, d, \theta1, \theta2, dx, dy\},
\epsilon = 0.001;
a = RegionDistance\[r1, \{x + \epsilon, y\}\];
b = RegionDistance\[r1, \{x - \epsilon, y\}\];
c = RegionDistance\[r1, \{x, y + \epsilon\}\];
d = RegionDistance\[r1, \{x, y - \epsilon\}\];
\theta1 = ArcCos\[\text{Max}\[a, b\] \epsilon\];
\theta2 = \(\pi/2 - \text{ArcCos}\[\text{Max}\[c, d\] \epsilon\]\);
If\[a > 0, dx = \text{Cos}\[\theta1\], dx = -\text{Cos}\[\theta1\]\];
If\[c > 0, dy = \text{Sin}\[\theta1\], dy = -\text{Sin}\[\theta1\]\];
Return\[\{dx, dy\}\]
]

getA\[x\_, y\_] := Module\[\{dx, dy\},
Print\[\{x, y\}\];
\{dx, dy\} = getN\[x, y\];
Return\[y \times dx\];
]

pl = Table[
x0 = xMS[[nr]];\(\{x0, y0\} = \{x0, y \}/. \text{Solve}[\{(\text{boundaries}[[nr]] \/. x -> x0) = 0, y\}[[1, 1]]]\};
g1 = Graphics\[\text{Line}[\text{pts2}]\];
g2 = ListPlot\[\{(\text{x0}, \text{y0})\}, \text{PlotMarkers} \rightarrow \text{Automatic}\];
g3 = ListPlot\[\{(\text{x0}, \text{y0}) + 30 \text{getN}[\text{x0}, \text{y0}]\}, \text{Joined} \rightarrow \text{True}\];
nv = sgn[[nr]] \sqrt\[\text{boundaries}[[nr, 2, 1]]^2 + \text{boundaries}[[nr, 3, 1]]^2\];
p2 = ListPlot\[\{(\text{x0}, \text{y0}) + 25 \text{nv}\}, \text{Joined} \rightarrow \text{True}, \text{PlotStyle} \rightarrow \text{ColorData}[97][2]\];
\{getA[x0, y0], \text{n}, \text{y0, 0}\}, \text{Show}[g1, g2, g3, p2]\]
, \{nr, \text{Length}[[\text{boundaries}]\}];
Show\[\text{pl}[[\text{All}, 3]]\]

SampleFsem.nb
\{ -34.7232, 8.05872 \}
\{ -19.5361, -7.89562 \}
\{ -3.68191, -15.0388 \}
\{ 6.06592, -24.2947 \}
\{ 21.0471, -30.5454 \}
\{ 38.7639, -13.5963 \}
\{ 34.6166, 13.9756 \}
\{ 13.0884, 22.2835 \}
\{ -17.2586, 23.5499 \}
\begin{align*}
\text{nbt} &= \text{Sum}[
\left(\text{ boundaries}[[\text{nr}, 2, 1]], \text{ boundaries}[[\text{nr}, 3, 1]]\right) \cdot \\
\sqrt{\text{ boundaries}[[\text{nr}, 2, 1]]^2 + \text{ boundaries}[[\text{nr}, 3, 1]]^2};
\end{align*}

\text{NeumannValue}[\text{nv}.\{y, 0\}, \text{ boundaries}[[\text{nr}]] = 0]
,\{\text{nr}, \text{Length}[	ext{ boundaries}]\}]

\begin{align*}
\text{Out}[257]= & \ \text{NeumannValue}[0. - 0.973066 y, 1 + 0.0304747 x + 0.0072197 y \approx 0] + \\
& \ \text{NeumannValue}[0. - 0.837614 y, 1 + 0.0741307 x + 0.0483454 y \approx 0] + \\
& \ \text{NeumannValue}[0. - 0.435443 y, 1 + 0.022645 x + 0.0468153 y \approx 0] + \\
& \ \text{NeumannValue}[0. - 0.354836 y, 1 + 0.0168253 x + 0.043315 y \approx 0] + \\
& \ \text{NeumannValue}[0. - 0.0441904 y, 1 + 0.00504963 x + 0.114158 y \approx 0] + \\
& \ \text{NeumannValue}[0. - 0.00221228 y, 1 + 0.0000937883 x - 0.0423944 y \approx 0] + \\
& \ \text{NeumannValue}[0. + 0.140943 y, 1 - 0.00589577 x - 0.0414133 y \approx 0] + \\
& \ \text{NeumannValue}[0. + 0.494196 y, 1 - 0.0168915 x - 0.0297142 y \approx 0] + \\
& \ \text{NeumannValue}[0. + 0.929616 y, 1 - 0.0226481 x + 0.0089784 y \approx 0]
\end{align*}

\begin{align*}
\text{Out}[258]= & \ \text{res} = \text{NDSolveValue}[\{\text{D}[u[x, y], \{x, 2\}] + \text{D}[u[x, y], \{y, 2\}] = \text{nbt}, \\
& \ \text{DirichletCondition}[u[x, y] = 0, x \leq \text{pts2[[1, 1]]}], u, \{x, y\} \in r1, \\
& \ \text{MaxSteps} \to 1000000, \text{MaxStepSize} \to 0.0001, \text{AccuracyGoal} \to 15]
\end{align*}

\begin{align*}
\text{Out}[258]= & \ \text{InterpolatingFunction}[\text{Domain: \{\{-38.4, 46.9\}, \{-34.2, 23.6\}\}}, \text{Output: scalar}]
\end{align*}
pl1 = ContourPlot[res[x, y], {x, Min[pts2[[All, 1]]], Max[pts2[[All, 1]]]}, {y, Min[pts2[[All, 2]]], Max[pts2[[All, 2]]]}, AspectRatio -> (Max[pts2[[All, 2]]] - Min[pts2[[All, 2]]])/(Max[pts2[[All, 1]]] - Min[pts2[[All, 1]]]), Frame -> True, ImageSize -> Large, PlotRange -> All]

xSpan = 200;
ySpan = 300;
t1 = Table[
   If[RegionMember[r1, {x1, y1}],
   {{x, y}, {D[res[x, y], x] + y, D[res[x, y], y]}} /. {x -> x1, y -> y1}
   , {{x1, y1}, {0, 0}}
   ], {x1, -xSpan, xSpan, 2}, {y1, -ySpan, ySpan, 2}];
t2 = Select[Flatten[t1, 1], #[[2]] != {0, 0} &];
t3 = (#[[1]], #[[2]], Norm[#[[2]]]) & /@ t2;
nf = Max[t3[[All, 3]]];
t4 = (#[[1]], #[[2]]/nf, #[[3]]/nf) & /@ t3;
pl1 = ListPlot[(# + mpts) & /@ pts2, 
  Joined -> True, PlotStyle -> {Thickness[0.001], Black}];
pl2 = Graphics[{Hue[#[[3]]], Thickness[0.001], Arrowheads[Small],
  Opacity[0.7], Arrow[{#[[1]] + mpts, #[[1]] + 5#[[2]] + mpts}] & /@ t4};
Show[img, pl1, pl2, PlotRange -> {mpts[[1]] + {-100, 100}, mpts[[2]] + {-100, 100}}]

(* make sure arrows in above image form a closed loop, 
if they diverge at an edge of the flake, the program will fail later *)
In[269]:= \( t4 \)

\[
\{ \{-38, 22\}, \{-0.0122433, 0.094604\}, 0.095393\}, \\
\{\{-36, 14\}, \{-0.0882709, 0.391467\}, 0.401296\}, \\
\{\{-36, 16\}, \{-0.0540253, 0.318435\}, 0.322985\}, \\
\{\{376\}, \{44, 6\}, \{0.084592, -0.23382\}, 0.248652\}, \\
\{\{44, 8\}, \{0.214661, -0.177547\}, 0.278572\}, \\
\{\{46, 6\}, \{-0.0119347, -0.171668\}, 0.172083\}\}
\]

Out[269]=

Export["/Users/michaelsinko/Dropbox/Sinko/Papers;write/Superconducting
contacts/ Figures/ Main3 stuff/Fig2/ arrows.pdf", pl2]

contacts/ Figures/ Main3 stuff/Fig2/ arrows.pdf

**Effective contour**

In[270]:= \( \text{traceCurve[}p0\text{, maxStep\_, dir\_] := Module[}\{p, \epsilon, j, \text{perp, } x, y\}, \)

\[
p = p0;  \\
\epsilon = 0.1; \\
nn\text{tt1 = Table[} \\
j = \{(x, y), (D[\text{res}[x, y], x] + y, D[\text{res}[x, y], y])\} /. \{x \rightarrow p[[1]], y \rightarrow p[[2]]\}; \\
\text{perp = Cross[}\{0, 0, -1\}, \{j[[2, 1]], j[[2, 2]], 0\}\}[[\; ; 2]]; \\
p += \text{dir} \star \epsilon \star \text{perp}; \\
(*\text{Print[}\{j[[1]], \text{perp, } p\}\};*) \\
\{j[[1]], \text{perp, } p\} \\
, \{\text{step, maxStep}\}\}; \\
\text{Return[tt1];}\]

(*my \text{Problem occured below,} \\
\text{this functions traces out the curves enclosing the contact. the indices of } \text{pts2} \\
in \text{traceCurve should correspond to the corner points of each contact. got this} \\
\text{working by changing indices and increasing maxStep due to the larger image*})
```math
\textbf{c1} = \text{traceCurve}[\text{pts2}[\{1\}] + \{0.1, -0.1\}, 300, 1];
\textbf{c2} = \text{traceCurve}[\text{pts2}[\{2\}] + \{0.1, 0.1\}, 300, 1];
\textbf{c3} = \text{traceCurve}[\text{pts2}[\{6\}] + \{-0.1, 0.1\}, 300, 1];
\textbf{c4} = \text{traceCurve}[\text{pts2}[\{7\}] + \{-0.1, -0.1\}, 300, 1];
\textbf{areas} = \text{ListPlot}[[\text{pts2}, \text{c1}[\text{All}, 1]], \text{c2}[\text{All}, 1]], \text{c3}[\text{All}, 1]], \text{c4}[\text{All}, 1])],
\quad \text{Joined} \rightarrow \text{True}, \text{PlotRange} \rightarrow \text{All}, \text{PlotStyle} \rightarrow
\quad \{\text{Black, ColorData}[97][1], \text{ColorData}[97][1], \text{ColorData}[97][2], \text{ColorData}[97][2])}
```
Scale

\[ sc = \frac{10}{203} \]

\[ \text{ListPlot}[(sc \times #) \& /@ pts2, (sc \times #) \& /@ c1[[All, 1]], (sc \times #) \& /@ c2[[All, 1]], (sc \times #) \& /@ c3[[All, 1]], (sc \times #) \& /@ c4[[All, 1]]], Joined \rightarrow \text{True}, \text{PlotRange} \rightarrow \text{All}, \text{PlotStyle} \rightarrow \{\text{Black, ColorData[97][1], ColorData[97][1], ColorData[97][2], ColorData[97][2]}\}, \text{Frame} \rightarrow \text{True}, \text{FrameLabel} \rightarrow \{"x \ [\mu m]", "y \ [\mu m]"\}, \text{Axes} \rightarrow \text{False}] \]
(* used this mesh region to measure the area of the flake in pixels,
then convert output using scale,
numbers of Polygon should equal number of pts in pts and pts2*)
flake = MeshRegion[pts2, Polygon[{{1, 2, 3, 4, 5, 6, 7, 8, 9, 10}}]]

Area[flake] \ast (sc^2) (*in pixels, convert to um using sc^2*)

7.45553

Fraunhofer patterns

nSeg = 50;
In[386]:= edgeList = {1};

A1 = Table[
    eq = FullSimplify[x /. Solve[boundaries[[edgeList[[i]]]] == 0, x]][[1]];  
    slope = D[eq, y];

    Print["eq=>", eq, ", slope=" , slope];
    
    ya = pts2[[edgeList[[i]], 2]];  
    yb = pts2[[edgeList[[i]] + 1, 2]];  

    pl = ListPlot[pts2, Joined -> True, AspectRatio -> Automatic];  
    p2 = ParametricPlot[{eq, y}, {y, ya, yb}, PlotStyle -> Red];  
    Print[Show[p1, p2]];  

    f = ((D[res[x, y], x] + y, D[res[x, y], y]) /. x -> eq;  
    Table[
        y1 = ya + (seg - 1) * (yb - ya) / nSeg;  
        y2 = ya + (seg) * (yb - ya) / nSeg;

        l = Norm[Integrate[{slope, 1}, {y, y1, y2}]];  
        A = NIntegrate[{slope, 1}.f, {y, y1, y2}];
        {l, A}
    , {seg, nSeg}];

    Table[
        eq = -32.8141 - 0.236908 y slope = -0.236908
\textbf{Out[387]= } \{\{0.634876, -0.448565\}, \{0.634876, -0.947976\}, \\
\{0.634876, -1.44739\}, \{0.634876, -1.9468\}, \{0.634876, -2.44621\}, \\
\{0.634876, -2.94562\}, \{0.634876, -3.40041\}, \{0.634876, -3.74063\}, \\
\{0.634876, -4.07511\}, \{0.634876, -4.40958\}, \{0.634876, -4.74405\}, \\
\{0.634876, -5.07853\}, \{0.634876, -5.37667\}, \{0.634876, -5.59099\}, \\
\{0.634876, -5.8137\}, \{0.634876, -6.03641\}, \{0.634876, -6.25912\}, \\
\{0.634876, -6.48183\}, \{0.634876, -6.70641\}, \{0.634876, -6.87361\}
\}

\textbf{In[388]= } l = 0;
\textbf{In[389]= } jt = 0;
\textbf{In[390]= } r1 = \{\#[[1]] \text{ sc}, l++ \#[[1]] \text{ sc}, jt++ \#[[2]] \text{ sc}^2\} \& @ Flatten[A1, 1];

\textbf{In[391]= } Print["Length=", r1[-1, 2], " \mu m"]
\textbf{In[392]= } Print["Area=", -r1[-1, 3], " \mu m^2"]

Length=1.56373 \mu m
Area=0.67683 \mu m^2

\textbf{In[393]= } ListPlot[r1[[All, {2, 3}]], Frame -> True, FrameLabel -> {"x [\mu m]", "phase"}]
\( (* \text{ Flux quantum in mT} \times \mu\text{m}^2*) \)

\[
\text{UnitConvert}\left[\text{Quantity}\left[\text{"MagneticFluxQuantum"}, \text{"miliTesla}\times\text{Micron}^2\right]\right]
\]

\[
\frac{1104345025}{534058878} \text{ micron}^2\text{mT}
\]

\[
\frac{1104345025}{534058878} \text{ micron}^2\text{mT}
\]

\[
\frac{1104345025}{534058878} \text{ micron}^2\text{mT}
\]

\[
\text{N}\left[\text{Quantity}\left[\frac{1104345025}{534058878}, \text{"Microns}^2 \text{"Milliteslas"}\right], 8\right]
\]

\[
2.0678338 \text{ micron}^2\text{mT}
\]

\[
\text{fp1} = \text{Table}\left[
\begin{array}{c}
j = \text{Total}[\text{[[1]]}] \sin[\phi + 2 \pi \frac{\text{B}\times\text{[[3]]]}{2.068}] \& /@ \text{r1}];
\end{array}
\right]
\]

\[
\{\text{B}, \text{FindMaximum}[j, \{\phi, -5 \text{B}\}][[1]]
\]

\[
, \{\text{B}, -10, 10, 0.05\}\};
\]

\[
\text{... FindMaximum}: \text{The line search decreased the step size to within the tolerance specified by AccuracyGoal and PrecisionGoal but was unable to find a sufficient increase in the function. You may need more than MachinePrecision digits of working precision to meet these tolerances.}
\]

\[
\text{... FindMaximum}: \text{The line search decreased the step size to within the tolerance specified by AccuracyGoal and PrecisionGoal but was unable to find a sufficient increase in the function. You may need more than MachinePrecision digits of working precision to meet these tolerances.}
\]

\[
\text{... FindMaximum}: \text{The line search decreased the step size to within the tolerance specified by AccuracyGoal and PrecisionGoal but was unable to find a sufficient increase in the function. You may need more than MachinePrecision digits of working precision to meet these tolerances.}
\]

\[
\text{... General}: \text{Further output of FindMaximum::lstol will be suppressed during this calculation.}
\]

\[
\text{ListPlot}[\text{fp1}, \text{PlotRange} \to \text{All}, \text{Frame} \to \text{True},
\]

\[
\text{FrameLabel} \to \{\text{"Magnetic field mT"}, \text{"Critical current [au]"}\}]
\]
In[400]=  
edgeList = {6};  

A1 = Table[
  eq = FullSimplify[x /. Solve[boundaries[[edgeList[[i]]]] == 0, x]][[1]];  
slope = D[eq, y];

  Print["eq=>", eq, " slope=", slope];

  ya = pts2[[edgeList[[i]], 2]];  
  yb = pts2[[edgeList[[i]] + 1, 2]];  

  p1 = ListPlot[pts2, Joined -> True, AspectRatio -> Automatic];  
  p2 = ParametricPlot[{eq, y}, {y, ya, yb}, PlotStyle -> Red];  
  Print[Show[p1, p2]];

  f = ((D[res[x, y], x] + y, D[res[x, y], y]]) /. x -> eq;
  Table[
    y1 = ya + (seg - 1) * (yb - ya) / nSeg;  
    y2 = ya + (seg) * (yb - ya) / nSeg;

    l = Norm[Integrate[{slope, 1}, {y, y1, y2}]];  
    A = NIntegrate[{slope, 1}.f, {y, y1, y2}];  
    {l, A}
      , {seg, nSeg}]
      , {i, Length[edgeList]}]

eq=>44.1539 + 0.396431 y  slope=0.396431
\begin{verbatim}
Out[401]= {{0.885404, -1.79302}, {0.885404, -2.96368},
{0.885404, -4.13434}, {0.885404, -5.30499}, {0.885404, -6.47565},
{0.885404, -7.64631}, {0.885404, -8.50377}, {0.885404, -9.04224},
{0.885404, -9.60972}, {0.885404, -10.1772}, {0.885404, -10.7447},
{0.885404, -11.3121}, {0.885404, -11.8324}, {0.885404, -12.16},
{0.885404, -12.4706}, {0.885404, -12.7812}, {0.885404, -13.0918},
{0.885404, -13.4024}, {0.885404, -13.7015}, {0.885404, -13.8599},
{0.885404, -13.9821}, {0.885404, -14.1043}, {0.885404, -14.2265},
{0.885404, -14.3487}, {0.885404, -14.4709}, {0.885404, -14.4951},
{0.885404, -14.4403}, {0.885404, -14.3854}, {0.885404, -14.3306},
{0.885404, -14.2758}, {0.885404, -14.2209}, {0.885404, -14.142},
{0.885404, -13.9035}, {0.885404, -13.6478}, {0.885404, -13.3922},
{0.885404, -13.1366}, {0.885404, -12.881}, {0.885404, -12.6268},
{0.885404, -12.1633}, {0.885404, -11.6287}, {0.885404, -11.094},
{0.885404, -10.5594}, {0.885404, -10.0248}, {0.885404, -9.43764},
{0.885404, -8.50333}, {0.885404, -7.58114}, {0.885404, -6.64388},
{0.885404, -5.21694}, {0.885404, -3.58493}, {0.885404, -1.95293}}
\end{verbatim}

\begin{verbatim}
l = 0;
jt = 0;
r1 = {#[[1]] sc, l += #[[1]] sc, jt += #[[2]] sc^2} & /@ Flatten[A1, 1];
\end{verbatim}

\begin{verbatim}
In[405]:= Print["Length=" , r1[[-1, 2]], " μm"]
Print["Area=" , -r1[[-1, 3]], " μm^2"]
\end{verbatim}

\begin{verbatim}
Length=2.1808 μm
Area=1.31139 μm^2
\end{verbatim}

\begin{verbatim}
In[343]:= ListPlot[r1[[All, {2, 3}]], Frame -> True, FrameLabel -> {"x [μm]", "phase"}]
\end{verbatim}

\begin{center}
\includegraphics[width=0.5\textwidth]{SampleFsem.nb}
\end{center}
\textbf{fp2 = Table[}
\begin{align*}
 j &= \text{Total}[[1]] \sin(\phi + 2 \pi \text{\#3}) /@ (r1); \\
&\{B, \text{FindMaximum}[j, \{\phi, -5B\}][[1]]\}
\text{, \{B, -10, 10, 0.05\}}; \\
\end{align*}
\textbf{]}
\textbf{}}

\textbf{FindMaximum}: The line search decreased the step size to within the tolerance specified by \text{AccuracyGoal} and \text{PrecisionGoal}
but was unable to find a sufficient increase in the function. You may need more than \text{MachinePrecision} digits of working
precision to meet these tolerances.

\textbf{FindMaximum}: The line search decreased the step size to within the tolerance specified by \text{AccuracyGoal} and \text{PrecisionGoal}
but was unable to find a sufficient increase in the function. You may need more than \text{MachinePrecision} digits of working
precision to meet these tolerances.

\textbf{FindMaximum}: The line search decreased the step size to within the tolerance specified by \text{AccuracyGoal} and \text{PrecisionGoal}
but was unable to find a sufficient increase in the function. You may need more than \text{MachinePrecision} digits of working
precision to meet these tolerances.

\textbf{General}: Further output of \text{FindMaximum}:.\text{lsto} will be suppressed during this calculation.
In[409]:= Export["/Users/michaelsinko/Dropbox/Sinko/measurements/Measure
2019 -10-8 Lk-NbSe2-009/MathematicaOutput1SEM.csv", fp1]
Out[409]= /Users/michaelsinko/Dropbox/Sinko/measurements/Measure
2019 -10-8 Lk-NbSe2-009/MathematicaOutput1SEM.csv

In[410]:= Export["/Users/michaelsinko/Dropbox/Sinko/measurements/Measure
2019 -10-8 Lk-NbSe2-009/MathematicaOutput2SEM.csv", fp2]
Out[410]= /Users/michaelsinko/Dropbox/Sinko/measurements/Measure
2019 -10-8 Lk-NbSe2-009/MathematicaOutput2SEM.csv