Experimental Confirmation of Ballistic Nanofriction and Quasiparticle Interference in Dirac Materials.

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EXPERIMENTAL CONFIRMATION OF BALLISTIC NANOFRICTION AND QUASIPARTICLE INTERFERENCE IN DIRAC MATERIALS

by

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B.S. University of Central Florida, 2010

A dissertation submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Department of Physics in the College of Sciences at the University of Central Florida Orlando, Florida

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Major Professor: Masahiro Ishigami
This dissertation is broadly divided into two parts. The first part details the development and usage of an experimental apparatus to measure the dry nanofriction for a well-defined interface at high sliding speeds. I leverage the sensitivity of a quartz crystal microbalance (QCM) to determine the drag coefficient of an ensemble of gold nanocrystals sliding on graphene at speeds up to \( \sim 11 \text{ cm/s} \). I discuss the theories of velocity-dependent friction, especially at high sliding speeds, and QCM modeling. I also discuss our synthesis protocols for graphene and molybdenum disulfide, as well as our protocol for fabricating a clean, graphene-laminated QCM device and nanocrystal ensemble. The design and fabrication of our QCM oscillator circuit is presented in detail. The quantitatively-measured the drag coefficient is compared against molecular dynamics simulations at both low and high sliding speeds. We show evidence of a predicted ultra-low friction regime and find that the interaction energy between gold nanocrystals and graphene is lower than previously assumed. In the second part of this dissertation, I detail the band structure measurement of a novel semimetal using scanning tunneling microscopy. In particular, I measured the energy-dependence of quasiparticle interference patterns at the surface of zirconium silicon sulfide (ZrSiS), a topological nodal line semimetal whose charge carrier quasiparticles possess a pseudospin degree of freedom. The aims of this study were to (1) discover the shape of the band structure above the Fermi level along a high-symmetry direction, (2) discover the energetic location of the line node in the same high-symmetry direction, and (3) discover the selection rules for \( k \) transitions. This study confirms the predicted linearity in \( E(k) \) of the band structure above the Fermi level. Additionally, we observe an energy-dependent mechanism for pseudospin scattering. This study also provides the first experimentally-derived estimation of the line node position in \( E(k) \).
This dissertation is dedicated to my parents, Michael and Nancy Lodge.
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CHAPTER 1: INTRODUCTION TO FRICTION

1.1 Friction: Ubiquity at many size scales and velocities

Friction, the force that resists relative motion between two bodies in contact with one another,\(^1\) is present at every macroscopic interface. It is largely responsible for keeping everyday objects in place, preventing Newton’s first law of motion from being terribly inconvenient. Indeed, we have leveraged its effects in order to make our lives easier. However, its effects are also responsible for reductions in efficiency and for the wearing down of mechanical parts in machinery, which has associated costs of replacement as well as certain safety hazards. As friction is a very old issue, advances in engineering to either leverage or reduce friction will precipitate from improvements in our understanding of friction at a fundamental level. The advent of ultra-high vacuum systems, scanning probe microscopies, and piezoelectric sensors have led to the development of experimental apparatuses capable of measuring friction in clean, controlled environments with extremely high sensitivity such that fundamental theories about friction can be tested. These developments enabled experimentalists to measure the velocity dependence of friction at sliding speeds ranging from \(\sim 3\) nm/s to \(\sim 10\) mm/s for a single asperity sliding on various substrates.\(^2\text{–}^6\)

These experiments helped to reveal that friction at the nanometer size scale is vastly different than friction at the macroscopic scale.

Nanofriction is complicated and not well understood. Low-speed nanofriction has been intensely studied both experimentally and theoretically in both force-added,\(^2\text{–}^{20}\) meaning that an external force is applied to an asperity in order to move along a surface, and force-free\(^{21}\text{–}^{27}\) configurations that lack an external applied force. Low-speed nanofriction in the force-added configuration is generally characterized by stick-slip motion, wherein the asperity sticks in a potential well until it is compelled to abruptly jump out of the well and slide until it becomes stuck in another potential well. Except at very low velocities\(^9\) in which \(F_{\text{fric}} \propto v\), studies of force-added,
low-speed friction show $F_{\text{fric}} \propto \ln(v)$ and $F_{\text{fric}} = C_1 - C_2 T^{2/3}$, where $v$ is the sliding velocity and $T$ is temperature. In force-free configurations, such as isolated metal nanocrystals on graphite, low-speed nanocrystals exhibit thermally-activated drift-diffusion behavior, and $F_{\text{fric}} \propto v$ and $F_{\text{fric}} \propto kT \times \exp E_0/kT$. However, vastly different physics were observed in a force-free simulation when sliding speeds were high enough for the asperity to have insufficient time to relax into potential wells. In this previously-unobserved “ballistic” sliding regime, the simulation showed that $F_{\text{fric}} \propto T^{-0.82}$, indicating that thermal fluctuations did not assist the nanocrystal in hopping from site to site. Instead, they actively impeded motion. In addition, $F_{\text{fric}} v$ is expected, which is similar to the velocity dependence in drift-diffusion. Most interestingly, friction in the ”ballistic” simulation was observed to be two orders of magnitude smaller than in the diffusive simulation in a comparison of both at room temperature. Ballistic speeds are predicted to be 3 orders of magnitude higher than those accessible to previous experiment techniques, which were 10 mm/s. The sliding speeds involved in the ballistic nanofriction simulations are readily comparable to sliding speeds considered ideal for molecular dynamics simulation. Therefore, realizing an experimental apparatus capable of measuring nanofriction at comparable sliding speeds can help to quantitatively refine simulation techniques. It is this new ballistic nanofriction regime that I aimed to observe experimentally. As such, accessing ballistic sliding speeds via experiment requires the development of a new experimental apparatus.

The first three chapters of this dissertation focus on the fundamental physics of velocity-dependent nanofriction. The design and implementation of an experimental apparatus capable of measuring force-free nanofriction are emphasized. The primary questions that will be addressed are:

1. How can we realize an experimental apparatus to measure force-free nanofriction?

2. How can we distinguish ballistic nanofriction from drift-diffusion nanofriction in experiment?
3. Can we quantify the interaction strength of gold nanocrystals on graphene?

The main conclusions drawn from this work are that force-free nanofriction can be measured by leveraging the high quality factor of a piezoelectric resonator, we must appeal to a direct comparison of experimental data with molecular dynamics simulations in the absence of a temperature dependence measurement in order to distinguish ballistic nanofriction from drift-diffusion nanofriction, and that the interaction strength of gold nanocrystals on graphene is weaker than previously thought.

The first chapter of this dissertation primarily serves to give an overview of the friction section of the dissertation. I also give an overview of what is known about friction at the macroscopic size scale, which is then contrasted with the physics of nanofriction. I describe the velocity and temperature dependencies of the Prandtl-Tomlinson model, which is frequently used in the context of nanofriction experiments. I then describe "slip time," which is a way to parameterize nanofriction and is related to the drag coefficient. Slip time is a parameter that I frequently use in order to quantify nanofriction in my experiments.

In the second chapter, I describe some of the physics of two different two-dimensional materials: graphene and molybdenum disulfide. Synthesis protocols, adapted from other publications, that I developed for the Ishigami laboratory are presented for both materials. Synthesis results of both materials are also shown. Graphene synthesized in the manner presented in this dissertation can be easily transferred to another substrate. As such, a method to transfer graphene onto a target substrate is presented. The synthesized graphene was used in the fabrication of my experimental apparatus for measuring nanofriction.

In the third chapter, I detail the development, fabrication, and usage of an experimental apparatus to measure force-free nanofriction. I first I describe the ballistic nanofriction simulation and compare it with drift-diffusion simulations. Then, I describe the properties of the quartz crystal microbalance (QCM) and how it can be used to measure friction properties. The fabrication of the
nanofriction QCM is presented in great detail, in addition to the design and fabrication of the QCM oscillator circuit. I describe how one may interpret the response of a QCM to adsorbates and infer the particulars of how adsorbates stick to the QCM surface. I show that the results of our measurement produce slip times that are very close to the slip times observed in ballistic nanofriction simulations.

### 1.1.1 Macroscopic friction

The most accessible laws of friction at the macroscopic level were described mathematically centuries ago by Guillaume Amontons and Charles-Augustin Coulomb for dry friction. These laws are:

1. **Amontons’ 1st Law:** \( F = \mu N \)
2. **Amontons’ 2nd Law:** \( F \neq F(A) \), where \( A \) is the apparent contact area
3. **Coulomb’s Law:** \( F \neq F(v) \), where \( v \) is the sliding velocity

where the force of friction, \( F \), is given by the product of the coefficient of friction, \( \mu \), and the normal force \( N \), which is the reactionary force exerted from pressing the two objects against one another. The longevity of Amontons’ 1st Law is a testament to its usefulness. Charles-Augustin de Coulomb considered the apparent contact area, differences in surface particularities (coatings, for example), the normal force, and the effect of contact aging. Coulomb famously ruled out the possibility that friction could be determined by surface roughness, reasoning that the energy gained by moving an asperity over a surface is reversibly lost once the surface interlocks again. Additionally, he posited that the force of friction was independent of sliding velocity.

### 1.1.2 Coefficient of friction: kinetic and static friction

Friction is governed by the atomic-scale asperities that form the real contact area between two surfaces. The coefficient of friction is a dimensionless proportionality constant describing the
complicated interaction between the two surfaces. This empirical quantity is dependent on not only the particular materials in contact, but also on the binary case of whether the contacting materials are in motion or are static relative to one another. We can disambiguate between the two cases of static and kinetic friction using Amontons’ Law.

For the case of contacted, static surfaces, we let $\mu = \mu_s$ and rewrite Amontons’ Law as

$$F_s = \mu_s N,$$  \hspace{1cm} (1.1)

where $F_s$ is the static friction force. When two contacting surfaces are at rest, their surfaces are able to deform under the applied normal force and form some maximal number of chemical bonds and van der Waals interactions. In addition to the amount of each surface’s deformation, governed by the properties of the material itself, due to the normal force, the surface roughness also plays a role in the quantity of chemical bonds that occur between the contacting surfaces.

The true contact area of a static surface increases with time, increasing friction of a static surface. Shearing the two surfaces at the interface, setting them in relative motion, keeps the true area of contact low. In addition, the inertia of the moving surface helps in overcoming friction. This causes the two surfaces to experience a reduced amount of friction force as long as they stay in relative motion. In this situation, we let $\mu = \mu_k$ and rewrite Amontons’ Law as

$$F_k = \mu_k N,$$  \hspace{1cm} (1.2)

where $F_k$ is for force of kinetic friction.

1.1.3 Viscous friction

Viscosity is the motional resistance of a fluid to deformation by shear or tensile stress. In liquids, the level of interaction between neighboring constituent particles is non-negligible, and
can be quite high, due to their close proximity to one another. The strength of intermolecular forces
governs a liquid’s ability to deform under an applied force, as the bonds formed by the forces must
be broken. As a result, liquids with relatively large intermolecular forces, like honey, are much
more resistant to flow than fluids with relatively small intermolecular forces, like acetone.

Figure 1.1: **Viscous friction during laminar flow.** Force must be applied to the moving plate in
order to shear the layered, viscous liquid ”sheets” and keep the plate moving with constant velocity.
The necessary shear force is a direct measurement of the viscosity.

If we consider the case of a homogeneous, viscous liquid trapped between two parallel
plates, we can consider a scenario in which we move one plate relative to the other such that the
plates remain parallel to one another. In this situation, shown in Figure 1.1, the liquid is in ”true”
contact with each plate over an area $A$ and the plates’ resistance to motion is mediated by the
chemical properties of the liquid. This is in stark contrast with the case of dry friction where
the relative motion is mediated by the statistics of contacting asperities that make up the relatively
small, true area of contact. Here, if we assume the velocity of the plate to be sufficiently low, then
we can approximate the liquid as a stack of constituent layers in which each layer glides parallel
to its neighbors with a different velocity. This phenomena is called **laminar flow.** Each layer
will resist the motion of its neighboring layers via friction forces that are exerted in the direction
opposite that of the motion; the strength of the interlayer interaction is the *viscosity*. The force required to overcome the total friction originating from the liquid and maintain a constant velocity can be described by\(^\text{31}\)

\[
F = \eta A \frac{v}{y},
\]

(1.3)

where \(\eta\) is the viscosity of the liquid, \(A\) is the area of contact, \(v\) is the velocity of one plate relative to the other, and \(y\) is the separation distance of the plates. Viscosity, \(\eta\), which has units of Pa·s, describes the strength of the interaction between neighboring layers.

### 1.1.4 Nanofriction

With, perhaps, the exception of drag force, the macroscopic laws of friction are largely empirical. The phenomenology that leads to Amontons’ laws and Coulomb’s law is a manifestation of the much more complicated, and very numerous, nanoscopic interactions that ultimately make up the real contact between macroscopic contacting bodies. The complexity arises from the many degrees of freedom involved in the contacting surfaces, including, but not limited to, the amount of pressure at a contact site, the atomic structure at the interface, the rigidity of the constituent materials and of the contact, sliding velocity, and temperature. The complex, statistical nature of the interaction means that we should not necessarily expect macroscopic friction laws to offer much insight into the nature of friction at the nanometer scale.

In contrast to Coulomb’s Law, velocity plays a very important role in nanofriction\(^\text{29,33}\). Sliding friction between a nanoscopic surface, or a thin film, and another surface looks very much like laminar flow since the entirety of the nanoscopic surface or the thin film is in contact with the other surface. As such, the friction force should exhibit strong velocity dependence, like the case of viscous friction. In particular, low-speed friction is expected to behave much differently than high-speed friction. This is especially true for isolated nanocrystals physisorbed on a substrate that may undergo diffusive transport at very low sliding speeds, similar to Brownian motion. While the slow
drift of a nanoisland on a surface is well characterized theoretically, and experimental techniques exist that can quantify diffusive transport, there are comparatively few theoretical treatments at high speeds.\textsuperscript{9,26,34} This seems to result from the lack of a good experimental technique. It is the high-speed sliding regime that we wish to explore here.

1.2 Nanotribology

1.2.1 Phononic and electronic energy dissipation

At the atomic and nanoscopic size scales, energy dissipation pathways can be broadly categorized as either phononic or electronic. Since atomic bonds are not perfectly rigid, atoms can be elastically displaced by vibrations. Sound waves through solid media are the coordinated vibrations of atoms within the material. Each quantum of vibration is called a phonon. At or near the interface of sliding surfaces, phonons in one surface can be set into vibration via the interaction with the opposite surface. These phononic excitations provide a crucial route for energy dissipation in friction processes.\textsuperscript{35,36}

As long as the time scale for adsorbate motion are much smaller than the time scale for phonon excitations (and, for a metallic substrate, the Fermi frequency) in the substrate, then the friction force $\vec{F} = -m\eta \vec{v}$, where $m$ is the adsorbate’s mass and $\vec{v}$ is its center-of-mass velocity.\textsuperscript{37} Phononic and electronic contributions to friction are expressed in terms of a drag coefficient $\eta$ as

$$\eta = \eta_{ph} + \eta_{el},$$

where $\eta_{ph}$ and $\eta_{el}$ are the coefficients of phononic and electronic drag, respectively. It is important to note that $\eta$ is not isotropic; it can vary depending on the direction of motion, as will be discussed later. The phononic contribution to friction is expected to dominate over the electronic energy pathways except at low temperature.\textsuperscript{38} As such, phononic dissipation is excepted to dominate in
the nanofriction experiments I describe in this dissertation.

1.2.2 Structural lubricity

A very important aspect of nanofriction is the arrangement of atoms in the respective surfaces of an interface. The registry of atoms between the two interfacing surfaces can sensitively modulate the friction force. Interfacing surfaces that have regular, periodic atomic corrugations, like crystals, at the respective surfaces interact more strongly when the surfaces are brought into commensurate contact with one another, leading to increased friction. Conversely, rotating one surface relative to the other can bring the surfaces into incommensurate contact, drastically reducing friction. This particular phenomenon is called structural lubricity. This phenomenon is one route to superlubricity, in which friction force drops, by some means, abruptly below the noise level of the measuring device. Structural lubricity is most easily observed in crystalline materials, where the atomic arrangements are highly periodic, especially when the interacting surfaces are made of the same material. Dienwiebel, et al. showed that graphite sliding on graphite exhibited approximately zero measurable friction when the two surfaces were more than approximately 7° out of atomic registry, with friction peaking in 60° intervals corresponding to the in-plane rotational symmetry of graphite.

1.2.3 Prandtl-Tomlinson (PT) model of friction

In the PT model, one considers the relative motion of two crystalline solids held at a fixed distance apart from one another. The atoms in one surface are taken to be immobile and serve as a periodic potential through which the atoms in the other surface move. The atoms in the mobile surface are affixed to a mobile sled via springs. A single spring connects each constituent atom to the mobile surface, and the atoms do not interact with one another. Hence, the PT model is sometimes called the independent oscillator model. The mobile surface is taken to move at some constant velocity. As the sled moves parallel to the immobile surface, the springs stretch
and contract depending on the particular contact geometry with the immobile surface. Energy is
dissipated into the mobile surface via the damping of the springs.\textsuperscript{38} The equation of motion for a
single mobile atom in one dimension is\textsuperscript{7,18}
\begin{equation}
m\ddot{x} = k(v_0 t - x) - \eta \dot{x} - N_0 \sin \left( \frac{2\pi x}{a} \right), \tag{1.5}
\end{equation}
where $x$ is the lateral position of the atom, $m$ is the mass of the atom, $k$ is the stiffness of the
spring attaching the mass to the moving sled, $v_0$ is the velocity of the moving sled, $t$ is time, $\eta$ is
the damping coefficient of the spring, $N$ is the amplitude of the periodic force, and $a$ is the spatial
period of the potential.\textsuperscript{7,18}

The behavior of the oscillators as the mobile surface slides can vary drastically depending
on the periodicity and amplitude of the periodic potential and on the stiffnesses of the springs.\textsuperscript{7,18,38}
If $k > N 2\pi / a$, then the atoms move smoothly and commensurably with the immobile surface.
However, if $k < N 2\pi / a$, the atoms will exhibit instabilities and abruptly jump from one position
to another,\textsuperscript{38} which is referred to as stick-slip motion. The abrupt jumps produce mechanical vibra-
tions, whose energy is dissipated by thermal vibrations.\textsuperscript{38} In reality, the dissipation mechanisms
can include excitations of vibration modes, coupling to a phonon bath, excitations of electron-hole
pairs, and fluctuations of electric fields acting on charges.\textsuperscript{29} These dissipation mechanisms also
have velocity dependencies, which will be discussed later in Section 1.2.5.

The PT model serves as a starting point for describing friction at the atomic or nanoscopic
size scale. However, it is by no means complete. Advancing beyond the PT model involves
increasing the number of degrees of freedom of each oscillator, as well as the degree of connectivity
of each oscillator to its neighbors. One should also allow for additional degrees of freedom for
motion in the corrugated potential. Thermal fluctuations should be considered as well as electronic
contributions to friction. However, one should note that the PT model has not been used to predict
for ballistic nanofriction. Sokoloff has applied an extended PT model to analyze the high-speed
behavior of an interconnected spring-mass. In his paper, he states that at sufficiently high sliding speeds the periodic potential causes surface atoms to displace by a negligible amount due to the short time scale in which the two surfaces interact. This is consistent with the explanation offered from the ballistic nanofriction article. However, Sokoloff seems to predict a different velocity dependence of friction than what is found via ballistic nanofriction simulation.

1.2.4 Temperature dependence

The simplest considerations of friction force, as in the Prandtl-Tomlinson model above, are at zero temperature in order to negate the effects of thermal fluctuations. However, thermal fluctuations will contribute to the friction force. As such, it is necessary to consider the effects of temperature on friction. Thermal fluctuations in the substrate will exhibit a stochastic force $f$ on a particular adsorbate. The components of $f_i$ satisfy the fluctuation-dissipation theorem and are related to $\eta$ through

$$\langle f_\alpha^\alpha(t) f_\beta^\beta(0) \rangle = 2mk_B T \eta_{\alpha\beta} \delta_{ij} \delta(t).$$

Thermal fluctuations can assist a nanocontact in overcoming a potential barrier, reducing friction. By adding thermal fluctuations to his model, Prandtl showed that the friction force $F_{\text{fric}}$ depends on substrate temperature, $T$, as

$$F_{\text{fric}} = C_1 - C_2 T^{2/3},$$

where $C_1$ and $C_2$ are constants, which is in agreement with molecular dynamics simulations for roughly three decades in temperature, and has been observed experimentally with AFM. In addition, it has been shown that stick-slip behavior can be completely destroyed by thermal effects, with an overall reduction in friction. This effect is termed thermolubricity.
1.2.5 Velocity dependence

From Coulomb’s Law, friction force is independent of sliding velocity at the macroscopic scale. Narrowing the scale of the sliding interface to individual atoms, the stick-slip motion of the atoms offers an explanation for the velocity independence of friction. In stick-slip motion, the atoms quickly accelerate to high speeds as they slip from one potential minimum to the next, dissipating energy as they do so. While the dissipation mechanisms (mentioned in Section 1.2.4) vary linearly with velocity for sufficiently small sliding velocities, the macroscopic sliding velocities are typically much slower than the time scales for which the elementary processes involved in the dissipation mechanisms become damped. For example, macroscopic sliding velocities may be on the order of 1 m/s, but the typical velocity of a vibrating atom is on the order of 10 km/s. Further, vibrating atoms couple to vibrations that dissipate energy into the bulk on the order of picoseconds. The independence of friction force on sliding velocity holds as long as sliding velocity is much smaller than the "slip" velocity of the atoms at the interface.

Temperature plays a significant role in the velocity dependence of friction. As mentioned previously, thermal excitations can reduce the overall friction such that thermally-excited atoms can slip between neighboring potential minima on times scales that are comparable to the sliding velocity. This imparts a dependence of friction force on sliding velocity.

In the ultra-low velocity limit where an is object undergoing Brownian-like motion, such as a true random walk or when drifting under a weak applied force, friction force is expected to exhibit a linear dependence on sliding velocity. A rigorous derivation the linear velocity dependence for a particle undergoing Brownian motion is given by Lebowitz and Révész. The linear dependence was also derived by Prandtl via analysis of his model as long as $Fa/2 \ll kT$, where $F$ is a constant force applied to the particle in motion and $a$ is the spatial period of the potential corrugation. For very small velocities, Prandtl concluded that this force is proportional to the deformation rate, so "a resistance of the same type of drag in a fluid exists." Thus, one
should expect the behavior of a very slow moving interface to experience a viscous-like friction force.

For slightly larger velocities, a logarithmic dependence on sliding velocity is expected. A logarithmic dependence was predicted for several decades in velocity by Muser, and observed experimentally for a single asperity on the surface of NaCl(100) for velocities in the range of 5 nm/s to 1 µ/s of the form $F \propto C + \ln(v)$, where $C$ is a constant. This kind of dependence was ascribed to thermal activation with the jumps in equilibrium position biased in one direction.

The velocity dependence of friction at the atomic scale at high speeds is less studied. However, several theoretical treatments of this kind of system do exist. For even higher speeds than those accessible to the previously-aluded experimentalists, first principles calculations posit that thermal fluctuations are less relevant for friction force, and that friction force will depend on sliding velocity, $v$, as $F_{fric} \propto v^\beta$, where $0 < \beta < 1$. Additionally, force of friction was predicted to be higher than that of that at slower velocities.

However, if sliding velocity is so large that atoms cannot relax into equilibrium sites sufficiently quickly, then one may expect the displacement of interfacial atoms due to the interaction with the potential corrugation during sliding to be negligible. Sokoloff predicted the force of friction in a crystalline system to behave as $F_{fric} \propto 1/v$ in this regime using the framework of coupled oscillators, assuming that (1) dislocations in atomic positions exist in the crystal prior to motion, and (2) that the thickness of each interfacing materials was infinitely large. In the limit of an atomically-thin sliding film, he predicted that friction force is independent of sliding velocity. Interestingly, the shear stress he calculates for the high-speed interface with infinitely-thick materials was smaller than that of the same system at slow speeds by a factor of approximately $10^2$. In addition, the shear stress of the high-speed, atomically-thin system was calculated to be smaller than the low-speed bulk system a factor of $10^6$. Therefore, the friction force at very high speeds is expected to be lower than in the low-speed regime. Recently, a molecular dynamics simulation by Guerra, et al. of thermalized gold nanocrystals sliding on graphite at speeds of $v = 100$ m/s
observed slip time to be approximately 100 times larger than the slip time of the same system calculated from the thermally-activated Einstein relation $D = \mu kT = D_0 \exp(-E_d/kT)$ and experimental diffusivity values $D_0 = 10^3$ and $E_d = 0.5$ eV.$^{21,26}$ The authors refer to this high-speed friction as *ballistic nanofriction*, and they argue that it results from the inability of atoms in the sliding nanocrystal to relax into potential minima due to the rapid sliding velocity.

### 1.2.6 Slip time

In sliding nanosystems where viscoelasticity can be neglected, including sliding thin films, sliding objects are expected$^{38}$ to experience a drag force $F_{drag}$ equal to

$$F_{drag} = -\xi v,$$  \hspace{1cm} (1.8)

where $\xi$ is a drag coefficient and $v$ is the sliding velocity. The drag coefficient can be expressed in terms of a characteristic momentum relaxation time, $\tau_s$, or ”slip time,” via the relationship

$$\xi = \frac{m}{\tau_s},$$  \hspace{1cm} (1.9)

where $m$ is the mass of the sliding object.$^{38,46}$ Slip time is a useful quantity to parameterize drag in a viscous friction system, especially when friction force is not directly measurable. In our experiments, we measure slip time.
CHAPTER 2: TWO-DIMENSIONAL MATERIALS

In the ballistic nanofriction simulation by Guerra et al., gold nanocrystals were simulated to slide on graphite. In my experiments, I utilize a graphene-laminated QCM in order to approximate the graphite surface from the simulation. In this chapter, I detail our group’s method to synthesize, characterize, and transfer graphene onto an arbitrary substrate. In addition, I also describe our group’s method to synthesize and characterize single-layer molybdenum disulfide.

2.1 Graphene

A single layer of graphite isolated from the bulk material is called graphene. Being only a single atom in thickness, it is a truly two-dimensional material. Its atomic structure can be thought of as two interpenetrating hexagonal lattices offset by the C-C bond length of $a_{C-C} \approx 1.42\text{Å}$, forming a honeycomb structure depicted in Figure 2.1.

In graphene, the $s$ and $p_{x,y}$ orbitals of each carbon atom hybridize into $sp^2$ orbitals, forming extraordinarily strong $\sigma$ bonds with one another. These bonds give rise to graphene’s equally
extraordinary Young’s modulus, measured to be 1 TPa,\textsuperscript{48} which is roughly 30-40\% higher than that of tungsten carbide.\textsuperscript{49} The out of plane $p_z$ orbitals hybridize into a network of $\pi$ bonding and $\pi^*$ anti-bonding orbitals, which, respectively, form graphene’s valence and conduction bands. These orbitals are also responsible for the van der Waals forces that hold together neighboring layers.

Graphene’s remarkable strength and electron configuration make it an intriguing material for tribological applications for many of the same reasons as its 3D analog, graphite. Graphene, like graphite, enjoys a high thermal stability up to 1000°F without significant mass loss\textsuperscript{50} thanks to its extremely stable $\sigma$ bonds. In addition, graphene can be used as a durable, dry lubricant coating.\textsuperscript{51–53} Graphene films ranging in thickness from from 1 to multiple layers between steel contacts were shown to reduce friction and wear drastically.\textsuperscript{51} Adding a thin coating of graphene flakes onto a steel surface was shown to reduce the coefficient of friction from $\sim$1 to $\sim$0.15 for thousands of sliding passes, and reduced the wear rate of steel by as much as two orders of magnitude.\textsuperscript{52} This drastic reduction in friction and wear rate was attributed to the low shear stress of the sliding contact from the two-dimensional graphene.

2.2 Molybdenum Disulfide

Following the realization of graphene, other two-dimensional materials were realized from their parent 3D van der Waals structures. The transition metal dichalcogenides, which have the chemical structure MX$_2$, where M is transition metal and X is a chalcogen. One of the transition metal dichalcogenides, molybdenum disulfide is a van der Waals material that is primarily found in one of two phases: the semiconducting 2H phase and the metallic 1T phase. In the 2H phase, each molybdenum atom is coordinated with six sulfur atoms with trigonal prismatic symmetry. The 1T phase differs by having tetragonal symmetry, instead. The 2H phase, notably, has an indirect band gap of 1.29 eV,\textsuperscript{54} whereas a single monolayer of MoS$_2$ about 1.8 eV.\textsuperscript{55,56} The structure of
2H-MoS$_2$ is shown in Figure 2.2. The lattice parameters are $a = b = 3.15$ Å and $c = 12.99$ Å. As a dry lubricant, MoS$_2$ powder is widely commercially available. In single-layer form in air, MoS$_2$ does not appear to be a suitable lubricant due to its apparent instability in air. As an additive in oil, ultra-thin MoS$_2$ nanosheets appear to act as a protective layer between contacting surfaces, preventing them from coming into direct contact and seizing up.$^{57}$

![Atomic structure of 2H-MoS$_2$.](image)

Figure 2.2: **The atomic structure of 2H-MoS$_2$.** Each molybdenum atom (purple) has trigonal prismatic coordination with six sulfur atoms (yellow). Graphic produced with VESTA 3.$^{47}$

Synthesizing materials in two dimensions can be accomplished in essentially two ways. The first is by exfoliation from the bulk material through either mechanical or chemical means. Mechanical exfoliation of layered materials, such as with adhesive tape, can result in single crystal monolayers of reasonably high-quality, but the technique is not scalable and it is not always possi-
ble to achieve monolayer film thickness. To overcome this limitation, various methods have been investigated to directly synthesize two dimensional materials.\textsuperscript{56,58–61} Here, I describe the synthesis of two thin-film, van der Waals materials via chemical vapor deposition (CVD). Our synthesis protocol of graphene is adapted from Li \textit{et al.},\textsuperscript{58} and the protocol for synthesizing molybdenum disulfide is adapted from van der Zande \textit{et al.}\textsuperscript{56} and Ling \textit{et al.}\textsuperscript{60}

2.3 Synthesis of two-dimensional materials

2.3.1 \textit{Chemical vapor deposition of graphene on Cu foil}

We synthesize monolayer graphene directly on copper foil following the pioneering recipe of Li, \textit{et al.}\textsuperscript{58} In this method, one forms a monatomically-thick residue of carbon on copper foil by thermally decomposing methane on copper at low pressure in a non-oxidizing environment. As the film thickness is self limited to monolayer, this method results in high-quality, polycrystalline graphene films that are more than 90\% monolayer across the sample. The areal size of the films is limited by the physical dimensions of the furnace and the physical extent over which its hot zone’s temperature is constant. I adapted this recipe for the Ishigami group at the University of Central Florida.

We first cut copper foil (\textit{Alfa Aesar} #46986, 99.8\% purity, 25 \textmu m thickness) into a sheet of size $\sim 4 \times 0.75$ in\textsuperscript{2}. The sheet is then flattened by sandwiching it between two glass microscope slides and applying pressure. Creased foil will retain the creases as wrinkles post-flattening that result in poor quality graphene films at the crease sites. As such, it is important to start with copper foil that has, ideally, no creases. The flattened copper is then immersed in a solution of 1:1 v/v glacial acetic acid:deionized (DI) water for 10 minutes to expose fresh copper at the surface, ensuring uniform cleanliness. Following the acid etch, the foil is rinsed by immersing into 3 separate DI water baths, spraying with DI water in between each bath, and then blow dried with N\textsubscript{2}. Oxidation of the copper surface during rinsing can occur, but it is not detrimental to graphene.
growth.

Next, the foil is slid into the center of a 1” quartz tube furnace on a quartz boat using a poly-tetrafluoroethylene (PTFE) push rod. The quartz tube is evacuated to a terminal pressure $\leq 30$ mTorr using a roughing pump. Each gas line has a physical volume of approximately $15 \text{ cm}^3$ before its mass flow controller that does not get pumped. First, the gas lines are flushed thoroughly by opening the flow of $\text{H}_2$ to 7 sccm and the flow rate of $\text{CH}_4$ to 25.4 sccm and waiting ten minutes. Using these parameters, the hydrogen foreline has its volume refreshed approximately 4.6 times, and the methane foreline is refreshed approximately 17 times.

The graphene synthesis protocol is illustrated in Figure 2.3, which shows the temperature schedule and gas flow rates, as well as a schematic of the setup. Following flushing the gas lines, the $\text{H}_2$ flow rate is reduced to 2 sccm and the $\text{CH}_4$ flow is shut off. Note that the growth chamber is under vacuum the entire time. After pressure stabilizes to about 70 mTorr for 5 minutes, temperature is ramped to 500$^\circ\text{C}$ over 10 minutes, then immediately ramped again to 750$^\circ\text{C}$ over 10 minutes, then from 750$^\circ\text{C}$ to 950$^\circ\text{C}$ over 20 minutes, and then to the final temperature of 1000$^\circ\text{C}$ over 15 minutes. Staggering the temperature ramp-up prevents the furnace from overshooting the temperature too much and melting the foil ($T \geq 1080^\circ\text{C}$). Due to temperature overshoot, the real, final temperature after ramp-up is about 1050$^\circ\text{C}$ as measured with an external thermocouple (type K) inserted into the furnace and touching the outside of the quartz tube. To improve surface cleanliness of the copper, it is allowed to anneal under $\text{H}_2$ flow for one hour. During this time, temperature settles to about 1035$^\circ\text{C}$. Methane flow is then set to 25.4 sccm for one hour. Methane flow, along with power to the furnace, are then quickly shut off and the furnace is slid to the other end of the quartz tube such that the copper is no longer in the furnace’s hot zone and can rapidly cool. Note that the flow rates of the gases were in volumetric flow instead of mass flow on the mass flow controllers at the time these recipes were developed.
2.3.2 Polymer-mediated wet transfer

The strategy for isolating graphene film from the copper foil is as follows: (1) coat the graphene film with a thermal-setting polymer, (2) remove the copper from the graphene, (3) transfer the graphene onto a target substrate, and then (4) remove the supporting polymer off the graphene. In principle, one may transfer graphene to any solid substrate, including plastic. However, one must be mindful of the temperature range and the solvents that are compatible with...
the target substrate so as not to destroy it when processing the thermal-setting support polymer or removing the copper. Our transfer protocol is outlined in Figure 2.4.

![Figure 2.4: Polymer-assisted, wet transfer process of CVD graphene. (a) Cartoon depicting the two-step PMMA coating process and subsequent transfer of a graphene layer. (b) CVD-grown graphene transferred onto SiO$_2$ (280nm)/Si wafer.](image)

First, one cuts the graphene-on-copper (Gr/Cu) sample to an appropriate size. Then, the Gr/Cu is carefully taped at the corners of the sample to a glass slide such that there is minimal tape coverage. The glass slide serves to protect the graphene-on-copper from the vacuum chuck of the spin-coater. We spin-coat one side of the Gr/Au sample with poly-methyl methacrylate (PMMA, MicroChem 495 PMMA A4) in order to support the graphene film during and after removal of the copper foil. The rigidity of the microscope slide prevents the copper from deforming under pressure from the spin coater’s vacuum chuck, which can strain or rupture the graphene in the process. One must be careful to ensure (1) the foil lays flat against the glass slide and (2) that one does not drop too much PMMA onto the sample so that it does not spill off of the foil and creep
between the sample and slide. PMMA is carefully dropped onto the sample and then spun on at 6000 rpm for 1 minute followed by a pre-bake at 120°C for 5 minutes. Then, PMMA is spun on again at 4000 rpm for 1 minute, then hard baked at 180°C for 10 minutes. The overall thickness of the PMMA film is about 380 nm. PMMA is baked at such a high temperature to reflow the PMMA and promote better conformal contact to the graphene.

The next step is to remove the graphene on the back side of the Cu foil using oxygen plasma. First, the adhesive tape is carefully peeled away from the sample and the sample is retaped onto the glass slide PMMA side down. The slide is then placed into the center of a reactive ion etcher. The back side of the sample is etched in oxygen plasma for 30 seconds at 50W with an O₂ flow rate of 5 sccm. We then cut away the area of PMMA/Cu/Gr stack that is coated with adhesive tape from the rest of the sample and discard it so that tape residues, which are difficult to remove, do not contaminate the sample in further processing steps.

Copper is then removed from the graphene by dissolving it in a solution ammonium persulfate (APS). APS is diluted with deionized (DI) water to a final concentration of 1% w/v. The sample is floated on the APS solution, copper side down, until copper is no longer visible (typically overnight). Then, the PMMA/Gr is transferred to another 1% APS bath for 8 hours to finish removing residual copper. The film is then transferred to a series of three DI water baths and left to float for 1 hour on each.

The PMMA/Gr stack can then be removed from the DI water bath using one’s target substrate and then placed onto a cold hotplate. The hotplate is then warmed to a temperature of about 50°C until the sample is visibly dry. This gentle drying method prevents the film from wrinkling as it dries. Then, the temperature can be safely raised to 110°C for 5 minutes to finish drying the sample.

Finally, PMMA is removed by immersing the sample in acetone for 20 minutes, followed by a rinse in isopropyl alcohol (IPA) to remove residual acetone. The sample is carefully dried under a flow of dry nitrogen gas. Generally, there is a very thin residue of PMMA left on the
graphene. This can be removed by annealing the sample at 350°C under a flow of H\textsubscript{2} and Ar for three hours.\textsuperscript{62}

![Raman spectroscopy of CVD-grown graphene](image)

Figure 2.5: **Raman spectroscopy of CVD-grown graphene.** (a) Typical Raman spectrum of our single-layer graphene synthesized via CVD with spectral features labeled. The red curve over the 2D peak is a Lorentz fit of the peak. (b) The 2D peak of a good quality sample. A Lorentzian fit is shown in red.

The quality and thickness of graphene can be determined by Raman spectroscopy,\textsuperscript{63,64} in which photons from a laser source inelastically scatter from the graphene and are collected by a spectrometer. Raman spectroscopy probes vibrational modes in the sample, providing chemical and structural information. A typical Raman spectrum of our as-transferred, CVD-grown graphene is shown in Figure 2.5. The primary features of the spectrum are the D peak at \( \sim 1360 \text{ cm}^{-1} \), the G peak at \( \sim 1560 \text{ cm}^{-1} \), and the 2D peak at \( \sim 2700 \text{ cm}^{-1} \). The D peak is a breathing mode that results from defects in the graphene and can be used to determine the defect density.\textsuperscript{64,65} The G peak results from the \( \text{E}_{2g} \) phonon mode in which all the sp\textsuperscript{2} bonds stretch. The 2D peak is a second order mode of the D peak. For pristine monolayer graphene, the 2D peak has been shown to have a Lorentzian peak shape with a full width at half maximum (FWHM) of about 23
For our CVD graphene, the 2D FWHM ranges from 23 to 32 cm\(^{-1}\) and can shift position slightly. The reason for the broadening and shifting appears to result from doping.\(^{65}\) The 2D peak in Figure 2.5(a) had a FWHM of \(\sim 32\) cm\(^{-1}\), and the 2D peak in Figure 2.5(b) had a FWHM of \(\sim 23\) cm\(^{-1}\). Both spectra were acquired from the same sample.

2.4 CVD synthesis of molybdenum disulfide

2.4.1 Substrate preparation

First, silicon wafers having 285-300 nm thermally grown oxide are cleaved to dimensions to an appropriate dimension. The dimensions of the wafers should be large enough to not slip off the ceramic boat on top of which they will later be placed, but not so large as to get stuck on the interior of the quartz tube. For our 1” tube furnace, this translates to about 0.7 x 0.7 in\(^2\) and up to three such wafers can be inserted into the furnace at once. The wafers are then sonicated for two minutes each in acetone and isopropyl alcohol to remove organic residues and debris from cleaving. Then, the surfaces of the wafers are further cleaned and made hydrophilic by O\(_2\) plasma generated in a Samco RIE. Plasma is generated with an RF power of 50V under a flow of 5 sccm of O\(_2\) for 10 minutes.

Next, a seeding promoter is deposited onto the wafers using a procedure adapted from Ling et al.\(^{60}\) Each wafer is taped to the lid of a glass petri dish with a small piece of Kapton tape at a single corner of each wafer. If more than one wafer is being prepared at once, they should be arranged symmetrically around the center of the lid. Care should be taken to minimize the area of contact the tape makes with each wafer. A very small amount of F16CuPc (Sigma-Aldrich 446653) is placed in the center of the petri dish bottom, which is then covered with the petri dish lid. The petri dish is then moved to a hotplate (if it is not already on one) to 350°C with the petri dish centered near a corner of the hotplate. Once the hotplate is at temperature, the petri dish should be carefully moved to the center of the hotplate using a burn-proof utensil (the petri dish will be
hot!). The petri dish should be left at the center of the hotplate for 10 seconds before it is moved back to a corner of the hotplate (it is still hot!). The hotplate is then shut off and allowed to cool.

2.4.2 Synthesis

The wafers can then be loaded into the tube furnace. As this synthesis protocol uses vaporized sulfur, it is important that the synthesis be carried out in a system that will not allow cross contamination with the graphene synthesis. One begins by placing 20 mg of MoO$_3$ powder (99.95%, Alfa Aesar 11837) into an alumina crucible and 100 mg of sulfur into a separate glass crucible. The MoO$_3$ crucible is then set into an open end of the tube. The wafers are placed side-by-side, but not butting against each other, on top of the ceramic boat with promoter side facing the MoO$_3$ powder. Then, the MoO$_3$ crucible is very carefully pushed into the center of the tube furnace using a polytetrafluoroethylene (PTFE) rod. The sulfur boat is placed upstream from the MoO$_3$ crucible such that it is near the end of the insulation material furthest from the furnace center. The remainder of the plumbing can then be assembled. A schematic of the system is shown in Figure 2.6.
Figure 2.6: **Chemical vapor deposition synthesis of MoS$_2$.** Illustration of the flow system: (1) a low-flow (left) and high-flow (right, valved) set of rotameters to regulate the flow of ultra-high purity N$_2$ gas; (2) DRIERITE gas drying column to remove moisture from the incoming N$_2$; (3) sulfur crucible (glass); (4) 300 nm SiO$_2$/Si wafer with F16CuPc promoter placed promoter-side down on (5) the alumina crucible containing MoO$_3$ powder; (6) tube furnace containing a 1” quartz tube.

Once the wafers and crucibles are in the furnace and the plumbing is secured, the system is flushed with N$_2$ gas at a flow rate of 2600 sccm for 10 minutes. This is accomplished with a 2 hour dehydration bake at 105°C with 500 sccm N$_2$ immediately following the N$_2$ system purge. The N$_2$ flow is then reduced to 10 sccm by closing the valve to the high-flow rotameter, and the temperature is then ramped to 700°C at a rate of 12°C/min. The temperature is kept at 700°C for 3 minutes and then is cooled without feedback for 20 minutes. Then, the N$_2$ flow is returned to 500 sccm and the furnace is opened and cooled rapidly. The temperature and flow programs are illustrated in Figure 2.7.
Figure 2.7: **Temperature and flow rate programs for CVD MoS$_2$ synthesis.** The dehydration bake is done at 105°C for 2 hours with 500 sccm of N$_2$ flowing. Synthesis and Cooldown occur in 4 steps: (1) Adjust N$_2$ flow to 10 sccm and ramp temperature to 700°C over 50 minutes. (2) Hold temperature at 700°C for 5 minutes. (3) Stop power to the furnace and allow it to cool without feedback for 20 minutes. (4) Adjust N$_2$ flow to 500 sccm and open the furnace clamshell until the furnace cools completely.

This recipe consistently produces single-grain, monolayer and bilayer MoS$_2$ crystals. However, the yield is typically < 1% of the wafer area and grows in isolated patches with grain sizes ranging from 5 to 10 µm. This recipe also produces thin films of MoS$_2$ whose thickness ranges from monolayer to, likely, hundreds of nanometers, with a yield of about 40% of the wafer area. An optical micrograph of an example result from our synthesis technique is shown in Figure 2.8(a) with typical photoluminescence signals shown in Figure 2.8(b) (Renishaw inVia confocal Raman Microscope, 532 nm laser, 0.05 mW, 100 second acquisition). The optical band gap is observed to be at about 1.87eV, which is consistent with previous measurements.$^{55,56}$
Figure 2.8: Results of CVD MoS$_2$ synthesis. (a) Optical microscopy of CVD-grown MoS$_2$ on SiO$_2$ (300nm)/Si wafer. (b) Photoluminescence spectra of CVD-grown MoS$_2$.

Note that this recipe, which follows the recipe of Van der Zande, et al.,$^{56}$ thoroughly dehydrates the wafer and MoO$_3$ prior to synthesis. However, recent evidence indicates that humidity aides in volatilization of precursor materials.$^{66}$ Therefore, our recipe may be refined by carefully controlling the humidity to achieve consistent, high-quality synthesis of transition metal dichalcogenides.
CHAPTER 3: BALLISTIC NANOFRICTION

3.1 Background

The study of high-speed friction at the nanometer scale suffers from the lack of a good experimental technique. Additionally, there are few theoretical investigations into this sliding regime. Atomic force microscopy (AFM) is the primary tool for measuring friction in the experiments described in Chapter 1. Essentially, this technique relies on measuring the deflection of a sharp tip as it is dragged across a substrate at a known velocity. The velocity at which the tip is dragged ranges from several nm/s up to $\sim 1$ mm/s, and, in novel configurations, can reach velocities up to 10 mm/s by oscillating the substrate rather than the AFM tip. In these higher-speed configurations, it is impossible to elucidate the velocity dependence of a single force due to the complicated and unknown contact geometry between tip and sample. The tip contact geometry issue is persistent in all AFM friction measurements and is a detriment to gaining deeper fundamental insight into the physics of high-speed, nanoscopic friction. One way to overcome the issue of unknown contact geometry is to consider the motion of a system in which both contacting surfaces are crystalline. The workhorse system of this type considered here is an ensemble of thermalized gold nanocrystals on a crystalline substrate (graphite).

Before discussing the behavior of high-speed friction, I first discuss friction in the limit of drift-diffusion. Bardotti et al. experimentally examined the formation of clusters from $\sim 250$ and $\sim 2300$ atom antimony crystals, as well as clusters of $\sim 250$ atom gold crystals, deposited on graphite via low-energy cluster beam deposition as a function of substrate temperature from $T = 263$ K to $T = 473$ K. The authors qualitatively compare TEM and STM images of aggregated crystals to simulation results of their own deposition-diffusion-aggregation model and concluded
that the motion of the crystals is Brownian, and that the diffusion coefficient $D$ may be given by

$$D = \frac{D_m^2}{4t} \quad (3.1)$$

where $t$ is the time needed for the crystal to move in a random direction by one diameter $D_m$. From their temperature dependence measurements, they found that $D$ is thermally-activated and can be expressed as a function of temperature according to

$$D = D_0 \exp \left(-\frac{E_d}{kT}\right), \quad (3.2)$$

where $D_0 = 10^3$ cm$^2$/s and $E_d = 0.5\pm0.1$ eV for gold. For nanocrystal of 250 Au atoms, $m \approx 8.18 \times 10^{-22}$ kg, and the authors find that $D \approx 4 \times 10^{-6}$ cm$^2$/s at $T = 300$ K, with $D$ increasing with temperature up to the maximum temperature considered ($T = 473$ K). The authors note$^{21}$ that their value for the prefactor $D_0 = 10^3$ cm$^2$/s is probably too high by $\sim 6$ orders of magnitude, which is echoed by other authors.$^{23,24,26}$ Maruyama$^{24}$ notes that the diffusion time scales involved in Bardotti’s model can be, at certain temperatures, an order of magnitude smaller than time scale at the thermodynamic limit $t_{th} \sim D_m \sqrt{m/kT}$, which is not physically possible. Since the diffusing nanocrystals cannot violate energy equipartition, Bardotti’s model likely makes some bad assumptions or is incomplete.

No matter the value of $D_0$, one may use the Einstein-Smoluchowski relation, given by

$$D = \mu kT, \quad (3.3)$$

where $\mu$ is the positional drift mobility, to quantify the temperature-dependent slip time for this system as long as the value of $D$ is accurate.$^{26}$ Noting that the drift mobility $\mu = \tau/m$, where $m$ is
the nanocrystal mass, the temperature-dependent $\tau$ can be expressed as

$$\tau(T) = \frac{mD_0}{kT} \exp \left(-\frac{E_0}{kT}\right).$$ (3.4)

At 300 K, $\tau \approx 8 \times 10^{-12}$ s using the values obtained by Bardotti et al for Au_{250}. This is consistent with the value of $\tau \approx 1.5 \times 10^{-12}$ s that I calculate from Maruyama’s $E_0 = 0.103$ eV and $D_0 = 1.83 \times 10^{-4}$ cm$^2$/s found from simulation.\textsuperscript{24} In contrast, the slip time from Guerra’s simulation\textsuperscript{26} is about $\tau \approx 5 \times 10^{-14}$ s, with $E_0 = 0.351$ eV and $D_0 = 0.02$ cm$^2$/s for positional diffusion. The slip time for diffusion in this system appears to be in the range of $\tau \sim 10^{-14}$ to $10^{-11}$ s.

The measurement by Bardotti et al, while likely producing the wrong value of $D_0$, seems to represent the only measurement of thermally-activated diffusion of metal nanocrystals on graphite. However, from their measurement\textsuperscript{21} and from molecular dynamics simulations,\textsuperscript{22–24, 26} one may draw several conclusions about this system. First, the diffusion coefficient $D$ is thermally activated and follows $D = D_0 \exp \left(-\frac{E_d}{kT}\right)$. Second, the slip time $\tau$ is, at the highest, on the order of $\sim 10$ ps at room temperature. An interesting result from Guerra et al.\textsuperscript{26} and Luedtke et al\textsuperscript{22} is the high correlation between rotations and translations in this system, indicating that thermal depinning that coincides with rotation of the nanocrystal out of registry with the substrate allows the nanocrystal to translate along the surface. Therefore, one may expect angular and positional jumps and stops to be highly correlated in the diffusive limit.\textsuperscript{26}

However, significantly different behavior is observed for nanocrystals kicked to high velocities of 100 m s$^{-1}$. At these speeds, nanocrystals do not have sufficient time to settle into the atomic corrugations of the substrate’s surface and become pinned. With the corrugation potential effectively lowered, kinetic energy of the nanocrystals is lost through a series of collisions with thermal fluctuations in the substrate until motion crosses over into the diffusive regime.\textsuperscript{26} This is a drastic change in behavior from the diffusive case because the motion is no longer thermally activated, which is expected for sufficiently high sliding velocities.\textsuperscript{9} From the simulations of Guerra
et al., angular and translational position become anticorrelated in this regime, contrasting from the highly-correlated motion in the diffusive limit. They observe off-center collisions with thermal fluctuations initiating rotational speed-up, and near-center collisions during fast rotational motion causing translational speed-up and rotational slow-down. Thus, higher temperatures serve to increase the number of thermal "bumps" experienced by the sliding nanocrystal and contribute to the drag force. As a result, drag force is observed to increase with temperature. The number of thermal bumps encountered by the sliding nanocrystal is expected to increase linearly with its sliding speed, and friction force, therefore, should have a linear dependence on sliding velocity. Thus, the drag force $F_{\text{drag}}$, likely maintains the same linear dependence on sliding velocity, $v$, as in drift motion, but it now originates largely from thermal fluctuations instead of the corrugated atomic lattice. This high-speed friction regime is referred to as "ballistic nanofriction." The slip time in the ballistic regime takes on a slightly different definition than in the diffusive regime. First, it does not make sense to talk about the drift mobility $\mu$ because the nanocrystals are no longer drifting. Second, the temperature-dependence slip time can no longer be found from the Einstein-Smoluchowski relation. However, we may still go back to our original definition from Sec. 1.2.6 and parameterize slip time with the drag coefficient $\xi$ as $\tau = m/\xi$, which will apply equally well in both diffusive and ballistic limits since we have $F_{\text{drag}} = \xi v$ in both cases. The slip time for a 459 atom Au nanocrystal in the "ballistic" limit is found to be $\tau \approx 750$ ps at room temperature. If we take the slip time value of $\tau \approx 8$ ps from Bardotti’s diffusion data to be accurate, which is evidently the lowest-friction scenario, then the slip time in the ballistic limit is larger by a factor of $\sim 100$ at room temperature. Comparing directly between Guerra’s own simulations, the ballistic slip time is larger by a factor of $\sim 15000$ at room temperature. One cannot account for the large difference in slip times between the two regimes by the difference in masses (250 atoms vs 459 atoms). The difference must come from a drastic reduction in $\xi$ in the ballistic case.
3.2 Quartz Crystal Microbalance (QCM) Technique

There is an experimental technique to measure friction called the "quartz crystal microbalance (QCM) technique" that operates on a fundamentally different principle than the AFM described above. In the QCM technique, the interaction dynamics between an ensemble of adsorbates and a substrate are inferred from the response of a mechanical resonator. Broadly, the surface of a resonator serves as a substrate that, as it oscillates, experiences some mechanical stress via tribological interactions with added adsorbates. With certain assumptions, one may experimentally determine the ensemble-averaged drag coefficient of adsorbates on the resonator, as well as its temperature and velocity dependences.\textsuperscript{38,46}

The QCM technique offers a few advantages over AFM. First, it can potentially access sliding velocities on the order of 100 cm/s, which is two orders of magnitude higher than the fastest sliding speeds accessible to AFM. Secondly, the resonator surface and the adsorbates can be highly crystalline materials. As such, the substrate-adsorbate contact geometry is greatly simplified compared to that of AFM. In a vacuum, this experimental platform should, therefore, be able to isolate the drag force for much higher sliding velocities.

3.2.1 The quartz crystal microbalance

3.2.1.1 Quartz as a highly-efficient piezoelectric resonator

Piezoelectric materials have the unique property of reversibly generating a macroscopic electric pole under an applied physical stress. The converse of this effect is also possible; a piezoelectric material can reversibly deform due to strain induced by an external electric field. The piezoelectric effect is exhibited by a large number of crystals, and even by certain polymers as well as biological materials.\textsuperscript{68,69} A lack of inversion symmetry is required in order for this phenomenon to be observed in crystalline materials. Additionally, materials are only piezoelectric below a certain, material-dependent critical temperature $T_C$, called the "Curie temperature," above which the
material undergoes a semi-reversible phase change that destroys the microscopic polarizability of the crystal. Cooling the crystal below $T_C$ recrystallizes the crystal into a polycrystalline form in which each domain exhibits piezoelectricity, but the macroscopic piezoelectric effect is destroyed due to the random orientation of the domains.

Figure 3.1: $\alpha$-Quartz used for QCMs. (a) The atomic structure of quartz. Graphic produced with VESTA 3.47 (b) The macroscopic structure of quartz. (c) Illustration showing the cutting angle for AT-cut quartz.

One such piezoelectric material that is widely used in technological applications is quartz, which consists of silicon and oxygen and has an overall chemical formula $\text{SiO}_2$. While quartz may be found in different crystalline structures, the one used for piezoelectric applications is $\alpha$-quartz. It has a trigonal structure belonging to the $\text{P}3_21$ space group (No. 154), which notably lacks
inversion symmetry. The crystal structure is depicted in Figure 3.1a. The Curie temperature of α-quartz at atmospheric pressure is 573°C.

Piezoelectric materials, like quartz, may be cut into shapes that leverage the piezoelectric property to create mechanical oscillators. Once the crystal is cut into a particular form, the interplay of mechanical deformation and voltage buildup is analogous to the interplay of an inductor and capacitor in an LC circuit. As such, the transduction of mechanical and electrical energies can exhibit harmonic motion at resonance. In fact, the mechanical motion and charging-discharging behavior of crystal resonators are often represented in terms of an equivalent RLC circuit, which will be discussed in detail later. Both parallel and series resonances are defined for crystal oscillators, and the mode of operation can be tuned via an external circuit.

The most common cut of quartz is the AT-cut, which is cut at 35° relative to the z-axis, parallel to the x-axis (refer to Figure 3.1b,c). Cutting thin, circular disks whose faces are cut along the AT direction produces a crystal oscillator that oscillates in thickness shear mode. Motion occurs parallel to the crystal faces along a particular linear direction. Along the thickness direction, the crystal oscillates sinusoidally. It has a node at the center plane, and antinodes at each crystal face. The fundamental frequency of oscillators of this type, which is typically 4-8 MHz, can be set by the crystal thickness. Surface displacement amplitudes for these crystals is in the range of 1-10 nm. This particular cut also offers good thermal stability, having near zero shifts in frequency and Q factor near room temperature.

The quality factor, Q, of an oscillator is defined as

\[ Q \equiv \frac{2\pi E_{\text{stored}}}{E_{\text{diss}}}, \tag{3.5} \]

where \( E_{\text{stored}} \) is the energy stored in the resonator and \( E_{\text{diss}} \) is the energy dissipated per cycle.\(^{70}\) QCMs possess an extraordinarily high quality factor on the order of \( 10^5 \).\(^{27,38,70}\) Typically, the oscillation amplitude, \( A \), of a QCM decays to \( Ae^{-1} \) on the order of a few milliseconds, wherein
the oscillator can cycle 1000 times or more due to its exceptionally high efficiency.\textsuperscript{27,38} Their high oscillation efficiency makes them extremely sensitive to dissipative phenomena at their surface, like friction.\textsuperscript{38,46}

Another useful quantity when discussing the efficiency of a QCM is the inverse quality factor, 1/Q. By inspection of equation (3.1), the quantity 1/Q is proportional to the energy dissipated by the oscillator per cycle. In this dissertation, 1/Q is referred to as \textit{dissipation}.

### 3.2.1.2 Energy trapping and surface velocity profile

Crystals must be driven by large electrode pads that cover their faces in order to overcome internal losses and continue oscillating. For stability, QCMs are mounted in a holder, being held in place at the edges. Holding a crystal this manner would impede its ability to oscillate if the crystal simply had a uniform thickness everywhere. This problem is usually overcome by beveling the QCM to be thinner at the edges. This keeps the QCM’s vibrational energy located at its center and suppressed at the edges, but it reduces the overall active area. "Energy trapping” in this manner results in a crystal that can be held in place along its periphery and maintains a high Q factor; however, it does alter the uniformity with which the active area of the crystal oscillates.

![Velocity Profile](image)

**Figure 3.2:** \textbf{Thickness shear oscillation of AT-cut quartz.} The velocity profile of a QCM is Gaussian.
Sensitivity, which follows the surface velocity, is highest at the center of the electrode.\textsuperscript{70,71} Surface velocity closely follows a Gaussian profile along the diameter of the electrode.\textsuperscript{70,71} This is illustrated in Figure 3.2. The combination of a nonuniform velocity profile and thickness shear oscillations mean that there is actually a time and location dependent divergence in material buildup due to the "flow" of neighboring atoms, which can be positive or negative. This causes some time and location dependent thickness variations in the crystal. These variations are assumed to be negligible.\textsuperscript{38,46}

The amplitude of oscillation is measured in units of volts, V. However, for our experiment, we are interested in the actual lateral displacement of the QCM surface (at its center) because this will later inform us of the distance that our adsorbate nanocrystals slide. One can calculate the motional oscillation amplitude, $A_{osc}$, using a simple formula

$$A_{osc} = \left(\frac{2}{\pi n}\right)^2 d Q A_{el}, \quad (3.6)$$

where $n = 1$ is the fundamental mode of oscillation, $d = 3.1 \text{ pm/V}$ is the piezoelectric strain coefficient for AT-cut quartz, $Q$ is the quality factor, and $A_{el}$ is the measured electronic amplitude.\textsuperscript{72} In the fundamental mode, $(2/\pi n)^2 d \approx 1.25 \text{ pm/V}$, which compares well with Borovský’s measured value of 1.4 pm/V.\textsuperscript{73}

3.2.1.3 \textit{Butterworth van Dyke circuit}

The electromechanical properties of a QCM can be modeled, at resonance, with a relatively simple equivalent circuit that can be used to make predictions about the behavior of the QCM when under load. Mathematically, the equivalent circuit is the same as a continuum mechanics model.\textsuperscript{74} The Butterworth van Dyke model is an RLC circuit approximation of the QCM, shown in Figure 3.3, which treats the electromechanical response of the QCM as that of a dissipative mass-spring system. The BvD model consists of two branches: (1) the acoustic branch that simulates the
motion of the QCM, and (2) the electrical branch that characterizes the parallel plate capacitance across the QCM, consisting of a single capacitor, called the "parasitic capacitance," that is denoted by $C_0$.

![Butterworth van Dyke model of a QCM figure]

Figure 3.3: **Butterworth van Dyke model of a QCM.** The top branch shows the "motional arm" which describes the properties of the quartz, while the bottom branch is the shunt capacitance from the parallel plates and the mounting structure.

The static parasitic capacitance, $C_0$ consists of capacitances from the mounting structure, and charge buildup on the parallel plates, and from the connector that connects to the rest of the electronics.\(^{46,75}\) This capacitance can detrimental to the operation of the QCM as it shunts activity from the acoustic branch by injecting a leading current into the acoustic branch of the QCM, changing the overall phase.\(^{75}\) Cancellation of $C_0$ is particularly important when measuring the properties of liquids or other soft media,\(^{75}\) and can typically be trimmed away with some external circuitry. However, when the QCM is operated in vacuum, $C_0$ increases admittance slightly and does not affect the conductance at all.\(^{46}\) In any case, the circuit should, therefore, be operated above its resonance frequency such that the reactance of the acoustic branch is inductive and will supply a lagging current into the acoustic branch to cancel the leading one and ensure the phase is $0^\circ$ and the circuit will operate at series resonance.\(^{75}\)
The motional arm of the BvD circuit consists of three series-connected components that have mechanical counterparts.\textsuperscript{46,75} In the figure, we have included an additional element in the motional arm, X, that denotes an external load on the QCM (like adsorbates). For simplicity, we ignore the effect of X as its motional impedance may be complicated. Energy dissipation phenomena resulting from the crystal’s mounting structure and the internal motion of the crystal are captured by the crystal’s motional resistance \( R_m \), which is equated with a drag coefficient \( \xi_p \).

The inertia of the system is quantified by a motional inductor \( L_m \), and is equated with a mass \( m_p \). The motional capacitance, \( C_m \), characterizes energy stored in the oscillator, and is equated to a spring constant \( k_p \). These quantities describe an unloaded QCM. We can also load the crystal with something, like an atomic layer of noble gas atoms, which introduces a load impedance, \( Z_L \), in the acoustic branch that arises from interfacial interaction with the crystal. Its particular form will be determined by the loading regime (inertial, dissipative, etc.). The resonance conditions and complex frequencies are found using the formalisms for both the series RLC circuit and the damped, forced spring-mass oscillator system, which each require expressions for the respective circuit or mechanical elements involved. The reader is referred to Johannsmann\textsuperscript{46} for a complete derivation. The equivalent circuit approach to determining the behavior of the load relies on the stress and strain are linearly related.\textsuperscript{46} Otherwise, nonlinear mechanics analysis is required.

\subsection{3.2.1.4 Clapp oscillator driving circuit}

Since the QCM is, essentially, an RLC oscillator with a set resonance frequency, we can look to LC oscillator circuits to drive the crystal. The Clapp oscillator is type of tuned LC oscillator circuit that has active, positive feedback to prevent amplitude decay.\textsuperscript{76} Active feedback on the LC portion of the circuit can be provided by amplifier, such as an operational amplifier (op-amp) or a bipolar junction transistor (BJT) linked to a capacitive voltage divider.\textsuperscript{76} In our circuit, we use an NPN BJT (2N918) in a common-base configuration to feed energy back into the emitter by the capacitive voltage divider.\textsuperscript{76}
Figure 3.4: **Common-base BJT amplifier.** This circuit amplifies the voltage of an AC signal, but produces unitary current gain. The input and output signals are in phase with each other. Figure adapted from Floyd.\(^7\)

A diagram of a typical common-base BJT amplifier is shown in Figure 3.4 (adapted from Floyd\(^7\)). In this configuration, positive DC voltage is applied to the base and collector via a voltage divider network such that the emitter is forward biased with respect to the base, and the collector is reverse biased with respect to the base. The common-base configuration provides high voltage gain, but not current gain, which is desirable in order to maintain the AC oscillation amplitude of the LC circuit that we connect to the capacitive voltage divider network that will be connected to the input/output terminals.\(^7\) That is to say, we do not simply connect the input/output terminals from Figure 3.4 to the crystal terminals. Instead, we connect the crystal to the amplifier in the way shown in Figure 3.5. Note that one terminal of the QCM is grounded and that the signal is measured between \(C_2\) and \(R_4\). Grounding one electrode of the QCM gives the Clapp circuit the advantage of making it suitable for future scanning probe microscopy experiments where a charge-neutral surface would be beneficial. Additionally, the phase angle between the input and output
signals for this configuration is $0^\circ$.\footnote{76, 77}

Analysis of the circuit by substituting the crystal in Figure 3.5 with resistor $R_q$, capacitor $C_C$, and inductor $L$ connected in series. The feedback of the system should be such that the relationship between the gain, $A$, and the input and output voltages, $V_{in}$ and $V_{out}$, of the transistor is

$$A \geq \frac{V_{out}}{V_{in}}, \quad (3.7)$$

which is the gain criterion. Useful relationships between the circuit elements can be found after making a few simplifications.\footnote{76} First, one combines the emitter-base capacitance with $C_4$, and the collector-emitter capacitance with parallel capacitors $C_3$ and $C_v$ into an equivalent capacitance $C_{3eq}$. Let the total reactance $X_q \equiv X_L + X_C$. Then, for a Clapp oscillator, one may assume $R_q \ll X_q$ and $g_mX_4X_{3eq} \ll X_q$ (the latter is equivalent to $g_mX_4X_{3eq} \ll |X_4 + X_{3eq}|$ from the resonance criterion $X_4 + X_{3eq} + X_q = 0$).

![Circuit diagram of the Clapp crystal oscillator.](image)

Figure 3.5: Circuit diagram of the Clapp crystal oscillator.
Then, we define the amplifier gain, $A$ to be

$$A \equiv Z_L/ \frac{1}{g_m} = Z_L g_m,$$

(3.8)

where $g_m$ is the mutual transconductance, $1/g_m$ is the input impedance of the common-base amplifier, and $Z_L$ is the collector load impedance approximated by

$$Z_L \approx \frac{(X_4 + X_{3eq})^2}{R_q + g_m X_4^2}.$$

(3.9)

The voltage ratio $V_{out}/V_{in}$ can be approximated as

$$\frac{V_{in}}{V_{out}} \approx \frac{X_4}{X_4 + X_{3eq}}.$$

(3.10)

Substituting these expressions into the gain criterion (3.7), we get

$$\frac{g_m (X_4 + X_{3eq})^2}{R_q + g_m X_4^2} \geq \frac{X_4 + X_{3eq}}{X_4},$$

(3.11)

which simplifies to

$$g_m X_4 X_{3eq} \geq R_q.$$

(3.12)

The series resonance frequency, $f_S$, of this oscillator is set by the series elements $C_4$, $C_{3eq}$, $C_C$, and $L$, and is given by

$$f_S = \frac{1}{2\pi} \sqrt{\frac{1}{L} \left( \frac{1}{C_4} + \frac{1}{C_{3eq}} + \frac{1}{C_C} \right)}.$$

(3.13)

The resonance frequency of the Clapp circuit can be tuned by the capacitance $C_C$. When designing a Clapp circuit, $C_4$ and $C_{3eq}$ should be chosen to be as large as possible with the restriction that the circuit should be able to oscillate even if $R_q$ is at least twice the maximum permissible
value. One may empirically find this value by simply putting resistances in series with the inductor until the circuit will no longer oscillate. If this causes $X_q$ to be too small for the required load capacitance, then one can put an additional capacitor in series with the inductor.

To make a crystal oscillator circuit, one can simply replace $L$, $C_C$, and $R_q$ with a QCM. The QCM will have its own $R$, $L$, and $C$ at resonance, but the analysis is the same as the above. The oscillator circuit used for my measurements is shown in Figure 3.5. This design is based on Figure 7-17 in Frerking,76 but with two differences. Frerking’s capacitor labeled $C_5$ is 20 pF, which gives a voltage ratio $V_{out}/V_{in}$ of about 1.06. In my circuit, I use a capacitance of 220 pF, resulting in a voltage ratio of 1.67. Despite the boosted voltage, this configuration does not break our initial assumption that $g_m X_4 X_{3eq} \ll X_q$, and also maintains $g_m X_4 X_{3eq} \geq R_q$, because we observe stable oscillations. The other difference is that I use a 0.01 pF capacitor between the base terminal of the BJT and ground instead of 0.1 µF. This is an issue because this is a decoupling capacitor designed to shunt AC signal at the base to ground. Since a capacitor’s impedance $Z_C = 1/\omega C$, this capacitor should have a high capacitance to shunt effectively. Our use of the 0.01 pF capacitor is not correct. However, our circuit oscillates stably despite this capacitance being 6 orders to magnitude smaller than recommended. This capacitor should be replaced for future experiments.

In our Clapp circuit, frequency is measured at the low-pass filter on the emitter between $R_4$ and $C_2$. This junction gives moderate voltage signal and has reasonably low impedance.76 Our Clapp circuit also has a single-pole, double-throw reed relay (Coto 2341-05-020) that decouples the QCM from the Clapp circuit and outputs the crystal directly to an oscilloscope for ring-down measurement. The pinout and connections to the relay are shown in Figure 3.6. A voltage pulse applied to pin 3 causes the reed in the relay to open the connection between pins 4 and 8 and close on pins 5 and 8, so that the QCM output is completely isolated except for its connection to an oscilloscope that reads the ringing response. Note that the QCM is not connected to capacitors $C_v$, $C_3$, or $C_4$, so the resonance frequency is that of the isolated crystal and, therefore, is slightly different than what we measure in the steady-state response.
Figure 3.6: **2341 SPDT reed relay pinout.** Connections and pinout of the Coto 2341-05-020 reed relay (Digikey).

A custom printed circuit board (pcb) design is shown in Figure 3.7 (ExpressPCB), which realizes the Clapp oscillator diagram from Figure 3.5. The pcb supports traces on both the front and back sides of the board. Green traces are on the back side of the pcb, whereas red traces are on the front. Open red circles are conducting through-holes to the back side of the pcb. Through-holes that overlap intersecting red and green traces are connected to each other via the through-hole. Note that the red square in the 2341 trace denotes pin 1 of the reed relay in Figure 3.6. The front and back sides of an assembled board (ExpressPCB) is shown in Figure 3.8. Two such boards were fabricated for use with two QCMs simultaneously.
Figure 3.7: **Diagram showing the design of a real Clapp oscillator circuit.** Red and green traces are on two different layers.
Figure 3.8: The Clapp oscillator circuit board. (a) Front side of the board with elements soldered in places. (b) Back side of the board. The red square in the 2341 trace indicates pin 1 of the reed relay.

3.2.1.5 Procedure for QCM measurement

In order to create an experimental device that can potentially measure high-speed, nanometer-scale friction at the interface of two crystals, we laminate the surface of a quartz crystal microbalance with large-area graphene. Then, we may deposit crystalline adsorbates onto the graphene in a controlled environment and leverage the properties of the QCM to measure ensemble-averaged dissipation phenomena at the graphene/nanocrystal interface. In this subsection, I give an overview
of the measurement procedure.

Two QCMs were utilized for a single experiment: one with graphene laminating one surface, and the another without graphene to serve as both a control device and as a thickness monitor. Prior to experimentation, both QCMs were cleaned down to the atomic level using a two-step annealing process involving both *ex situ* annealing in H$_2$/Ar and *in situ* vacuum annealing, both of which are described in Sec. 3.2.4.3. After the H$_2$/Ar annealing, QCMs were tested for functionality. Typically, the oscillation amplitude and quality factor improved significantly after this annealing step when compared to their performance immediately after metallization or graphene lamination. This is attributed to the reduction of impurities on the QCM surface. The removal of impurities has the additional effect of increasing the frequency of each QCM, consistent with the Sauerbrey relationship (see Section 3.2.3.1).

Next, the QCMs were pumped into an ultra-high vacuum system and outgassed completely in order to carefully control impurities on the QCMs. The bakeout procedure is detailed in APPENDIX A. The QCMs were then oscillated and allowed to stabilize at room temperature for several hours. The reduced pressure in UHV system causes the frequency of the QCMs to increase slightly ($Q$ is less sensitive to the change in pressure; the change is difficult to detect). Throughout the experiment, QCM frequency and oscillation amplitude, as well as quality factor and temperature are continually measured in certain time intervals. Once stabilized, we sweep driving voltage to the QCMs and measure the frequency and oscillation amplitude responses. For the Clapp oscillator circuits here, the minimum input voltage that result in measurable QCM responses was about 8.8V, yielding an electronic amplitude of 24 mV, and the maximum voltage supplied was 32V, yielding an electronic amplitude of 255 mV (both values are for the graphene-laminated QCM). Experimental values for the measurements reported here correspond to $V_{supply} = 30$ V.

Quality factor was determined by measuring the ring-down response of the QCMs. The electronic amplitude, $A_{el}$, of the QCMs exhibit damped harmonic motion and decay exponentially.
A damped sine function can be fit to the graph of $A_{el}$ vs. time plot, which has the form

$$A_{el} = A_0 e^{-t/\tau} \sin(2\pi f' t + \alpha),$$  \hspace{1cm} (3.14)$$

where $A_0$ is the initial oscillation amplitude, $t$ is time, $\tau$ is the decay time constant, $f'$ is the damped frequency of the QCM in Hz, and $\alpha$ is the phase. In reality, our measurement hardware cannot sample the QCM signal quickly enough to accurately capture $f'$, so the frequency that we extract from the fit is aliased and appears to be in the range of kHz instead of MHz. Fortunately, the frequency aliasing does not matter because it does not affect the parameter of interest, $\tau$. For a damped oscillator, $f' = f_0 \sqrt{1 - 1/(2Q^2)}$. Since $Q \sim 10^5$, we can approximate $f' \approx f_0$. Quality factor, $Q$, is equal to half the ratio of the natural frequency, $f_0$, to the decay rate, $1/\tau$, according to

$$Q = \frac{1}{2} \frac{2\pi f'}{\frac{1}{\tau}} = \pi f_0 \tau.$$  \hspace{1cm} (3.15)$$

A typical ring down response is show in Figure 3.9.
Figure 3.9: **Ring-down measurement of a QCM.** Oscillation amplitude is plotted as a function of time for a crystal that has been disconnected from the oscillator circuit. The decay time constant is extracted from the best fit of a damped sine wave.

Gold nanocrystals are formed by evaporating gold onto the QCMs for a predetermined amount of time that is well below the time required for monolayer gold coverage. For typical metallization processes, the target device is initially protected from the evaporation source by a shutter.
so that an evaporation rate, as determined by a thickness monitor, can be set. However, QCMs in this experiment could not be shuttered separately, so initial trial runs with certain evaporation parameters were done in order to determine an appropriate evaporation rate of gold. Thus, the target evaporation time was determined empirically based on initial evaporation experiments.

Gold was evaporated from the e-beam source at a rate of $1.6 \text{ ng/(cm}^2 \text{ sec)}$, as determined by the control QCM using the Sauerbrey equation (see Sec. 3.2.3.1), for 605 seconds. Note that this does not necessarily mean we should expect the graphene-laminated QCM to be coated with the same amount of gold as the control QCM/thickness monitor, despite the two QCMs seeing the same amount of gold flux. This is due to the probable difference in sticking coefficients between the gold and the graphene surfaces, which will be discussed further later. This was found to give sub-monolayer Au coverage such that Au forms nanometer-size islands with sufficient space between them so that they do not interact with each other, on average, while the QCM oscillates.

Following evaporation, the QCMs were allowed to thermally stabilize, as they tend to heat slightly from the Au deposition process, which causes their frequencies and quality factors to shift. These shifts were compared to their pre-evaporation values in order to isolate the response from the added gold. Finally, the driving voltage was swept again and the QCM responses were subsequently compared to their values from the previous measurement without added gold. The LabVIEW code to acquire the QCM ring down, frequency, amplitude, and temperature data is shown in APPENDIX B.

### 3.2.2 Small-load approximation: relating frequency shift to the load impedance at resonance

The load impedance is defined as

$$Z_L = \frac{\sigma}{\dot{u}},$$

(3.16)
where $\sigma$ is the interfacial shear stress and $\dot{u}$ is the velocity of the added layer relative to the crystal’s surface. The resonance condition\textsuperscript{46} of the loaded QCM is

$$0 = i\tilde{\omega}_r m_p + \frac{k_p}{i\tilde{\omega}_r} + AZ_L$$

$$\approx i\sqrt{\tilde{k}_p m_p}\frac{2(\tilde{\omega}_r - \tilde{\omega}_0)}{\tilde{\omega}_0},$$

where we let $\tilde{k}_p = k_p + i\omega_r \xi_p$ be a complex spring constant and $\tilde{\omega}_0 = \sqrt{\tilde{k}_p / m_p}$ be the complex resonance frequency. Since we expect the load to be small, the added inertia should not shift the resonance frequency much. Hence, we used the approximation $\tilde{\omega}_0 + \tilde{\omega}_r \approx 2\tilde{\omega}_0$. We can further simplify Eq. 3.17 by letting $\sqrt{\tilde{k}_p m_p} \approx n\pi A\tilde{Z}_q/2$, where $\tilde{Z}_q$ is the complex acoustic impedance of quartz, and letting $n = 1$ since we are intending to operate in fundamental mode.\textsuperscript{46} We then have

$$0 = i\pi A\tilde{Z}_q\frac{\tilde{\omega}_r - \tilde{\omega}_0}{\tilde{\omega}_0} + AZ_L,$$

which gives

$$\frac{\Delta f + i\Delta \Gamma}{f_0} = \frac{i}{\pi} \frac{Z_L}{Z_q},$$

where we dropped the tilde from $Z_q$ and $f_0$, since they are in phase, and we expanded the complex frequency shift in terms of its real and imaginary components. The real part, $\Delta f$, is the measured shift in resonance frequency of the crystal and the imaginary part, $\Delta \Gamma$, is the shift in the half-band-half-width, which is related to the quality factor, $Q$, via the relationship $Q = f_0/2\Gamma$.\textsuperscript{46} The acoustic impedance of AT-cut quartz is simply a number equal to $Z_q = 8.8 \times 10^6 \text{ kg/m}^2 \text{ s}$. Now, one needs only to find the form of $Z_L$, which can be determined by the complex frequency shift of the QCM to a load. Equation 3.19 is referred to as the small-load approximation and holds true as long as the frequency shift is small.\textsuperscript{46}
3.2.3 Interpreting the QCM response: mass loading within the SLA using discrete mechanical elements

The way in which the load interacts with the QCM’s surface manifests in the complex frequency shift of the QCM. Analysis proceeds by first measuring the QCM response to a particular load and then comparing the result to the complex frequency shifts predicted by Eq. 3.17 for a given $Z_L$. The form of $Z_L$ is specific to the way in which the load interacts with the crystal. There are at least six limiting cases for $Z_L$ that lead to rather unique complex frequency shifts. Two limiting cases are discussed below that are consistent with our measurements, which will be discussed later.

3.2.3.1 Purely inertial loading

Assume the load is some mass $m_L$ that is rigidly attached to, and uniformly distributed over, the active area $A$ of the crystal. Assume, also, that $m_L$ is, itself, rigid. In the BvD analogy, this amounts to increasing the mass of the spring-mass oscillator by $\Delta m = m_L$ so that the total mass is $m_p + \Delta m = m_p + m_L$. Since there is no dissipation term, we only need to consider the real frequency shift $\Delta \omega$, which is

$$\Delta \omega = \omega_r - \omega_0 = \sqrt{\frac{k_p}{m_p + m_L}} - \sqrt{\frac{k_p}{m_p}} = \sqrt{\frac{k_p}{m_p}} \left( \sqrt{\frac{1}{1 + \frac{m_L}{m_p}}} - 1 \right).$$

(3.20)
Assuming $m_L \ll m_p$ and noting that $\omega_0 = \sqrt{k_p/m_p}$, Eq. 3.20 becomes

$$\approx \omega_0 \left(1 - \frac{1}{2} \frac{m_L}{m_p} - 1\right)$$

$$= -\frac{\omega_0 m_L}{2 m_p}$$

$$= -\frac{\omega_0 2m_L}{2 A \rho q d_q}$$

$$= -\omega_0 \frac{\sigma_L}{\sigma_q},$$

(3.21)

where $m_p = \rho q d_q / 2$ is half the mass of the quartz crystal between the electrodes, $\rho q$ is the volumetric density of quartz, $d_q$ is the thickness of the quartz crystal, $\sigma_L = m_L / A$ is the area density of the load, and $\sigma_q = \rho q d_q$ is the area density of quartz. This relationship is equivalent to the Sauerbrey equation and it can be used to estimate the thickness of the loaded material, $h$, called the "Sauerbrey thickness." In this loading regime, we expect to observe a strictly negative frequency shift. Because the film is rigidly attached, we expect no dissipation, so $\Delta Q = 0$, and the slip time $\tau_s = 0$.

### 3.2.3.2 Dissipative inertial loading

If the loaded mass $m_L$ is itself rigid, but is allowed to slide with respect to the crystal’s surface such that there is a linear relationship between friction force and sliding speed, and there is no restoring force between the mass and the crystal, then we can approximate the load as a mass in series with a dashpot. This situation can happen if the load mass is creeping along the surface, and, evidently, if it is sliding ballistically. Assuming the ratio of shear stress from the drag force to the sliding velocity, or $Z_L$, is much smaller than $Z_q$, we can use the small load approximation to find the complex frequency shift. Therefore, we need to find the form of $Z_L$ for this configuration. Instead of a thin, continuous film, we will assume there are $N_s$ individual, sliding masses each having mass $m_s$ that are uniformly distributed over $A$. $Z_m = i \omega m_s$ to be the mechanical impedance

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of an individual mass, and $Z_\xi = \xi$ is the mechanical impedance of the dashpot. Then,

$$Z_L = \frac{N_s}{A} \left( \frac{1}{Z_m} + \frac{1}{Z_\xi} \right)^{-1} = \frac{N_s}{A} \left( \frac{1}{i \omega m_s} + \frac{1}{\xi} \right)^{-1} = \frac{N_s}{A} \frac{i \omega m_s \xi}{\xi + i \omega m_s} = \frac{N_s}{A} \frac{i \omega m_s}{1 + i \omega m_s / \xi}. \quad (3.22)$$

Let $\tau_s = m_s / \xi$ be the slip time. Then, we can rewrite Eq. 3.22 as

$$Z_L = \frac{N_s}{A} \frac{i \omega m_s}{1 + i \omega \tau_s} \frac{1}{1 - i \omega \tau_s} \left( \frac{1 - i \omega \tau_s}{1 - i \omega \tau_s} \right) = \frac{i N_s m_s \omega}{A} \frac{1 - i \omega \tau_s}{1 + \omega^2 \tau_s^2}. \quad (3.23)$$

Substituting Eq. 3.23 into Eq. 3.19 yields

$$\frac{\Delta f + i \Delta \Gamma}{f_0} = -\frac{N_s m_s \omega}{A \pi Z_q} \frac{1 - i \omega \tau_s}{1 + \omega^2 \tau_s^2}. \quad (3.24)$$

The real and imaginary components of Eq. 3.24 are, respectively,

$$\frac{\Delta f}{f_0} = -\frac{N_s m_s \omega}{A \pi Z_q} \left( \frac{1}{1 + i \omega^2 \tau_s^2} \right) \quad (3.25)$$

and

$$\frac{\Delta \Gamma}{f_0} = \frac{N_s m_s \omega}{A \pi Z_q} \left( \frac{\omega \tau_s}{1 + \omega^2 \tau_s^2} \right). \quad (3.26)$$

Inspection of Eq. 3.25 shows that setting slip time $\tau_s = 0$ recovers the Sauerbrey relation that we found previously. Noting that $\Gamma = f_0 / 2Q$, where $Q$ is the quality factor, we can estimate
\[ \Delta 1/Q = 2 \Delta \Gamma / f_0 \] and rewrite the above equation as

\[
\frac{\Delta (1/Q)}{f_0} = \frac{2 N_s m_s \omega}{A \pi Z_q f_0} \left( \frac{\omega \tau_s}{1 + \omega^2 \tau_s^2} \right) = \frac{4 \pi N_s m_s}{A \pi Z_q} \left( \frac{\omega \tau_s}{1 + \omega^2 \tau_s^2} \right).
\]

By inspection, change in dissipation is always positive.

We can get an explicit expression of the slip time \( \tau_s \) by dividing Eq. 3.27 by Eq. 3.25. This gives

\[
\tau_s = 4 \pi \frac{\Delta (1/Q)}{\Delta f}
\]

which is consistent with other analysis methods.\(^7^9\) Therefore, we can determine slip time by measuring the shifts in quality factor and resonance frequency of the QCM.

3.2.4 QCM preparation

Two kinds of QCMs were prepared for experimentation: (1) graphene-laminated QCMs to serve as the experimental devices, and (2) QCMs without graphene to serve as controls. QCMs used for the experiments described here began as 0.538 in diameter blanks with 5 MHz fundamental frequency and were made from AT-cut quartz (ICM Mfg.). Both kinds of QCMs were prepared simultaneously and saw the same treatments, except the graphene lamination step was skipped for the control QCMs.

QCMs were initially cleaned by sonicating in acetone, isopropyl alcohol, and deionized water for 2 minutes each and then blown dry under a flow of dry, filtered air. Additionally, the QCMs were carefully handled by their edges with wide-tipped tweezers to prevent contaminating the crystal’s surface. One must handle crystals like these very carefully so as not to chip or crack them, as they are only 330 \( \mu \)m thick in the center (they are even thinner at the edges).
3.2.4.1 Metallization

The cleaned QCMs were mounted into a keyhole electrode mask, shown in Figure 3.10 with a metallized QCM, and loaded into a physical vapor deposition (PVD) system that was evacuated to a pressure of about $5 \times 10^{-7}$ Torr. First, a 10 nm chromium adhesion layer was deposited, followed by 100 nm of copper and 80 nm of gold via thermal evaporation. The ion gauge and evaporators were then completely powered off and the PVD system was allowed to cool for one hour. Then, the vacuum chamber was vented and the QCMs were manually flipped over so that the observe side could be metallized.

Figure 3.10: **Evaporator mask for QCM metallization.** A metallized QCM is shown in the top left seat.
Metallized QCMs were then removed from the PVD system and operated in air to measure their oscillation amplitude and quality factor. Crystals whose peak-to-peak oscillation amplitude was lower than 300 meV, or whose quality factor was lower than 100,000, were rejected for further processing. QCMs that did not crack or chip, but whose processing failed (usually due to crystals rotating inside the keyhole electrode mask during pump down of the PVD chamber), could be stripped of their metals (20 minutes in Transene GOLD ETCHANT TFA for both Au and Cu, and 5 minutes in Transene CHROMIUM ETCHANT 1020 for Cr) and metallized again after a thorough rinsing.

3.2.4.2 Graphene lamination

Sheets of graphene-on-copper, grown by low-pressure chemical vapor deposition (see Section 2.1.1), are cut into squares of 0.25 in edge length. This size is just large enough so that the graphene, one transferred, will completely cover one QCM electrode. Following the procedure in Sec. 2.1.2, after spinning on PMMA and etching away the copper, the PMMA/graphene stack is thoroughly rinsed by floating the sample, graphene side down, in several deionized water baths.

Once rinsed, each film was transferred onto an electrode on one side of a QCM. This is accomplished by immersing the as-metallized QCM into the water bath, carefully aligning the electrode directly beneath the graphene, and slowly lifting the QCM out of the water. The QCM’s face is held at an approximately 20 degree angle with respect to the water’s surface and slowly lifted upwards towards the graphene until it makes physical contact. Then, the QCM is pulled in its tilt direction out of the water so that the surface tension of water continuously pulls the PMMA/graphene into contact with the QCM. Occasionally, during lift-out, the film will slide on the QCM surface such that it does not completely cover the electrode. Slowly reinserting the QCM into the water in the tilt direction will force the film to delaminate so that one may try lamination again. If the film drifts into contact with the tweezers that are holding the QCM, it very likely cannot be recovered. One must take great care to not let the film touch the experimenter’s tweezers.
Due to the way in which the QCMs are removed from the water, they should be mostly dry, except for some water buildup at the QCM edge that last left the water and the end of the tweezers. The majority of water can be removed from the QCM by simply laying it onto a delicate task wiper (Kimwipe).

The laminated QCMs are placed into the bottom of a glass petri dish with one edge of the QCM elevated on a glass microscope slide. This prevents the QCM’s face from coming into complete contact with the petri dish, where it may then stick after drying. The petri dish was set in the center of a room-temperature hot plate. The hot plate was then set to 60°C and left for about one hour. The water between the QCM and graphene/PMMA is gently removed by the process. One may see the difference in contrast for the “wet” film versus the dried film by simple inspection. Following this step, the temperature is raised to 120°C and the film baked for 5 minutes.

The PMMA was stripped from the QCMs by immersing them in 50°C acetone for 20 minutes. The QCMs were then gently immersed into an isopropyl alcohol bath and gingerly agitated. Finally, the QCMs were transferred to a deionized water bath to remove the organic solvent residue. The QCMs were then placed onto the center of a Kimwipe and gently blown dry under a flow of dry nitrogen. Using dry tweezers to pick up the QCMs, the flow of nitrogen is redirected to flow edge-on and dry the obverse side.

3.2.4.3 Annealing

Although PMMA was stripped with heated, liquid acetone, the graphene is not clean at the atomic scale; a very thin film of PMMA residue persists on the graphene surface during this process. However, we want to utilize the graphene’s crystallinity for friction experiments. Therefore, atomic-level cleanliness of the graphene is imperative. We use the annealing procedure for graphene described in Section 2.1.2 in order to remove residual PMMA from the QCMs.62 The control QCMs are annealed alongside the graphene laminated ones for both improved cleanliness and for consistency among control and experimental device.
After \( \text{H}_2/\text{Ar} \) annealing, a control QCM without graphene and an experimental QCM with graphene were loaded into the vacuum system that was subsequently evacuated to a base pressure of \( 2 \times 10^{-9} \text{Torr} \). Once terminal pressure was achieved, the QCMs were annealed at a temperature of 180\(^\circ\text{C}\) for 8 hours for improved cleanliness.

![Diagram of experimental setup for QCM measurements](image)

**Figure 3.11:** Diagram of the experimental setup for the QCM measurements.

### 3.3 Experimental setup for high-speed nanofriction measurement

The diagram of the experimental apparatus is shown in 3.11. It consists of two QCMs mounted side-by-side at the top of the vacuum chamber, and each sits in a custom QCM holder. The QCM holder bodies were machined from high-purity aluminum and machinable ceramic (Macor), and are shown in Figure 3.12. Temperature is monitored by a type K thermocouple located approximately 3 mm away from the graphene QCM, and is attached to the QCM holder with a single screw. The thermocouple is electrically isolated from the QCM holder by sandwiching it between two ceramic washers. Located 11 inches below, and centered between, the two QCM holders is an electron-beam (e-beam) evaporator source containing 99.999\% pure gold pellets (Kurt J. Lesker).
The e-beam source can be shuttered in order to accurately control the Au deposition time.

Figure 3.12: **Side-by-side QCM holders for two independent QCM measurements.** (a) Side-by-side of the two QCM holders showing the placement of the QCM. The "top" plate shown on the left sits directly on top of the QCM shown on the right. A type K thermocouple is mounted between the two ceramic washers shown on the far left side of the top plate. (b) Gold-plated QCM-facing side of the grounded top plate in which the QCM sits, showing the ceramic isolation washer. (c) Evaporator-facing side of the top plate. (d) Exploded view of the bottom plate showing the wiring for the isolated AC signal. (e) The QCM-facing side of the bottom plate showing the gold-plated, steel spring electrode. (f) Chamber-mounted side of the bottom plate.

Measurements are performed in UHV at a pressure of $2 \times 10^{-9}$ Torr. This is important for controlling maintaining cleanliness of the graphene surface and for depositing the gold nanocrystals, which require a large mean-free path as they are formed spontaneously from a flux of hot gold atoms. We may estimate the coverage time due to exposure from the low pressure environment.
Additionally, we may also estimate the mean free path of gaseous particles.

The incident flux density of gas particles $F$ is

$$F = \frac{1}{4} n \bar{c},$$

(3.29)

where $n$ is gas particle density, $\bar{c}$ is the mean molecular speed, and $F$ is given in units of molecules/m$^2$s. We assume the particles are noninteracting, and, thus, $n = P/kT$, where $P$ is the pressure in N/m$^2$, $k$ is the Boltzmann constant, and $T$ is the gas temperature in K. Additionally, we take $\bar{c}$ to obey Maxwell-Boltzmann statistics, giving

$$\bar{c} = \sqrt{\frac{8kT}{m\pi}},$$

(3.30)

where $m$ is the molecular mass in kg. We may then express $F$ as

$$F = \frac{P}{\sqrt{2\pi mkT}}.$$

(3.31)

The molecular mean free path $\lambda$ is taken to be

$$\lambda = \frac{kT}{\sqrt{2P\sigma}},$$

(3.32)

where $\sigma$ is the collision cross section in units of m$^2$, and $\lambda$ is in units of m. For our estimations of $\lambda$ and $F$, we assume $T = 293K$, $P = 2 \times 10^{-9}$, and that all gas particles are neutrally charged and become stuck when they collide with the chamber. Then, in our system, the coverage time for one monolayer of adsorbates is about $10^3$ seconds, and the mean free path is about $2 \times 10^4$ meters.

The QCM electrodes facing the e-beam source are grounded via the QCM holders which are directly mounted to the vacuum chamber. The obverse electrode of each QCM is wired to its own Clapp oscillator circuit and can be oscillated independently. Both Clapp circuits are powered
by a single programmable DC power supply (UNI PS-3305U), with each Clapp circuit connected to a separate power channel. Frequency is measured from each Clapp circuit by a frequency counter that has two input channels and 100 ps time interval resolution (Agilent 53220A). Each Clapp circuit also has a switch that removes the input power from the circuit and simply shorts each circuit to a channel on an oscilloscope (Tektronix TDS 2024B) in order to measure crystal ring down. Switching power is provided by a second programmable DC power supply (UNI PS-3305U). Measurements are automated via a computer running custom LabVIEW code.

3.4 Results

3.4.1 Graphene coverage on QCM

Graphene coverage on the QCM electrode is evaluated via visual inspection aided by an optical microscope. In general, because graphene is only one atom thick, one “sees” graphene by observing very faint differences in optical contrast between areas that are and are not covered with graphene. This predominantly occurs at two locations: (1) at voids in the graphene that result from tearing during transfer, and (2) at the ”connecting strip” of metal on the keyhole electrode that connects the large, circular pad at the center of the QCM to the crescent-shaped part of the electrode at the QCM periphery. Continuous graphene containing no voids is essentially invisible to visual inspection on the circular gold pad and is ideal for experimentation (it can still be observed on the connecting strip of the keyhole pattern). However, one must be careful to ensure that graphene is actually present on the QCM’s electrode, which can be done via Raman microscopy.

For the case of highly continuous graphene containing no, or very few, voids, the presence of graphene can be verified in two ways. First, the connecting strip of the keyhole electrode is inspected visually. With some effort, one can observe the relative difference in optical contrast between the presence and absence of graphene under a microscope, which can be observed in a graphene tear, for example. For the tribology experiments described in this dissertation, no voids in
the graphene could be identified. The second detection method is to simply perform micro-Raman spectroscopy on the graphene-covered electrode. Weak Raman signals consistent with the major spectral features of graphene from 532 nm laser excitation can easily be observed, as shown in Figure 3.13.

![Raman spectra of graphene transferred onto copper.](image)

**Figure 3.13: Raman spectra of graphene transferred onto copper.** Spectra were acquired at three different locations on the same copper electrode. Spectra show strong fluorescence background signal from the copper substrate and weak 2D Raman peaks from the graphene appear at \( \sim 2700 \text{ cm}^{-1} \). All spectra are unusually noisy from an undiagnosed issue with the instrument.

To gain experience with transferring graphene onto a metal substrate, I transferred graphene onto QCMs that had been metallized with 10 nm of Cr and 100 nm of Cu on each side. Copper was chosen as the terminal metal because it oxidizes slightly during the dehydration bake after lamination with the graphene/PMMA stack. In particular, copper will oxidize more in the areas
beneath wrinkles in the cvd graphene where water can get trapped. Thus, after stripping the PMMA from graphene with acetone, but before annealing in H₂/Ar, one can easily identify continuous graphene on copper by visual inspection under an optical microscope, as shown in Figure 3.14. Oxidation patterns commensurate with graphene wrinkles can occasionally be observed, as well, though this happens when the underlying substrate is copper. After Ar/H₂ annealing, all visible traces of oxidation were completely gone and the electrode became very lustrous. In the real device, an 80 nm layer of gold is evaporated on top of copper to provide a completely inert surface for the graphene. With graphene on gold, one can spot rips in graphene with relative ease, but it is more difficult that on copper.

Figure 3.14: **Optical microscopy of graphene transferred onto copper.** The presence of graphene facilitates oxidation of the underlying copper during the transfer process and has a darker optical contrast. The dashed white line demarcates a void in the graphene sheet. White arrows point to areas in which loose graphene from the tear has bunched together.
Figure 3.15: **Morphology of gold nanocrystals.** (a) AFM topograph showing gold nanocrystals on graphene. (b) TEM of a gold nanocrystal on graphene. The nanocrystal is about 4.5 nm in diameter. (Inset) Diffraction pattern of the crystals are consistent with an fcc lattice.

### 3.4.2 Morphology of evaporated Au on graphene

The shapes, sizes, and distribution of gold nanocrystals were evaluated using both atomic force microscopy and transmission electron microscopy. A typical AFM topograph (Digital Instruments D5000), acquired in tapping mode and in air, of Au evaporated onto a graphene-laminated QCM is shown in Figure 3.15a. The flux of hot gold atoms is observed to spontaneously coalesce into nanometer-sized islands on the graphene surface, consistent with previous experiments involving similarly deposited gold. For the data shown in the figure, sharp AFM tips (NanoWorld PointProbe SuperSharpSilicon SSS-NCH) having a radius of curvature < 5 nm at the apex were used to measure the gold islands. Because the radius of curvature is on the order of the size of the gold islands, the islands appear to be pancake shaped. In reality, their shape in the lateral direc-
tions is due to the finite width of the AFM tip. Gold islands were measured with AFM to be 2.8 nm to 4 nm in height in selected areas. In addition, the average area density of the nanoislands was measured to be \(1.01 \pm 0.02 \times 10^{12}\) crystals/cm\(^2\) near the center of the QCM electrode. This was determined by counting the number of crystals in a 1 \(\mu\)m\(^2\) AFM topograph and dividing by the scan area. The average density of three topographs is reported. The mean distance between gold nanocrystals is estimated to be 10 nm, which will be important later when determining the likelihood of collisions between sliding nanocrystals.

The nanocrystal size and polyhedral shape, consistent with an FCC lattice, was verified in a separate experiment with TEM (FEI Titan 80-300 FEG S/TEM) at 300 kV and low beam current. Shown in Figure 3.15b is the morphology of a single gold nanocrystal on a graphene-laminated, 16 nm-thick Si\(_3\)N\(_4\) membrane in which gold was evaporated using the same parameters as on the QCMs. The selected-area diffraction pattern is also shown, and is consistent with the FCC lattice of gold. The size of the nanocrystal shown in the TEM image is 4.5 nm, while the size distribution was about 4.2\(\pm\)1 nm, consistent with AFM measurements.

### 3.4.3 QCM response to Au nanocrystals

The frequency and 1/Q responses of both the control QCM and the graphene QCM to the gold deposition are shown in Figure 3.16. In the figure, the evaporator’s shutter is opened at time \(t \approx 5.2 \times 10^4\) s, and it is closed 605 seconds later. The frequency of both QCMs initially rises with temperature from the hot evaporator source for about 2,000 seconds prior to opening the shutter. Upon opening the shutter, the QCMs exhibit monotonic decreases in frequency until the shutter was closed again. However, the magnitude of the frequency shifts, as well as the behaviors of 1/Q for the respective oscillators, are markedly different between the two crystals. Note that the respective frequencies of each crystal continues to decrease for about 2000 seconds after the shutter is closed and the evaporator power is turned off. This is due to the thermal stabilization of the QCMs, and the ”final” responses of the QCMs are considered to be after they have completely
First, we examine the behavior of the control QCM. The inverse quality factor of the control QCM increases slightly during gold deposition. This is attributed to the combined temperature rise of the QCM, along with increased dissipation due to the interaction with hot gold atoms. However, once the shutter is closed, the $1/Q$ value returns to its initial value prior to deposition. Thus, the added gold does not contribute to the overall dissipation of the control QCM. In addition, the control QCM’s frequency decreases by 53.9 Hz. This is completely consistent with purely inertial loading of the QCM, which makes sense because we are simply adding slightly more gold to the thermally stabilized.

Figure 3.16: QCM response to Au deposition. Shifts in (a) inverse quality factor and (b) resonance frequency for the control and graphene-coated QCMs as a function of time.
gold electrode. Because the frequency shift is >2 % of the initial frequency, we are justified in using the Sauerbrey equation to determine the mass density of deposited gold. The frequency shift corresponds to an added mass density of 968 ng/cm². Since we evaporated for a total of 605 seconds, this corresponds to a flux density of 1.6 ng/(sec cm²).

The inverse quality factor of the graphene QCM increases monotonically with gold coverage and persists after the evaporator is shut off, indicating a persistent dissipation mechanism rather than a transient one like a temperature or pressure effect from the evaporator. Like the control QCM, the frequency shift is monotonically negative; however, it decreased only by 41.3 Hz. Both the enhanced energy dissipation and the fact that the frequency shift is only about 77 % of the control QCM indicates that the added gold on the graphene QCM is not loaded in the purely inertial regime.

\subsection*{3.4.4 Dependence of the QCM response on oscillation amplitude}

Driving the Clapp oscillator circuits at a range of voltages changes the QCMs’ amplitude of oscillation. Amplitude, $A_{\text{osc}}$, is intimately related to the peak velocity, $v_s$, of the QCM surface through the relation $v_s = \omega A_{\text{osc}}$, where $\omega$ is the natural frequency of the QCM. Since certain dissipative phenomena are dependent on the sliding velocity, like viscous friction, it is crucial to understand the dependence of the QCM’s shifts in resonant frequency, $\Delta f$, and dissipation, $\Delta (1/Q)$, on the QCM’s oscillation amplitude.

\subsection*{3.4.5 Evaluation of slip time and nanocrystal mass}

The graphene QCM’s response to gold deposition, in particular $\Delta f < 0$ and $\Delta (1/Q) > 0$, indicate that there is no detectible restoring force between the graphene and the nanocrystals. If, instead, we had observed $\Delta f > 0$, we would treat the nanocrystals as if they had some effective restoring force, $F_R = -k x_{nc}$, where $k$ would be an effective, mean spring constant and $x_{nc}$ would be the mean, lateral displacement of the nanocrystals with respect to the graphene surface. Since
the sign of the frequency shift is negative and nearly the same as the control QCM, we neglect the existence of $F_R$. Additionally, since $\Delta(1/Q) > 0$ persists indefinitely after the gold evaporator was shutoff, we conclude that the effect of the nanocrystals on the graphene is purely dissipative. To first order, we assume that the nanocrystals are rigid and that they do not roll, which seems safe based on previous molecular dynamics simulations.\textsuperscript{26} Thus, we analyze the nanocrystals in the framework of sliding adsorbates on QCM, which has been used previously to analyze the behavior of sliding noble gas monolayers.\textsuperscript{82,83}

Figure 3.17: **Response of graphene-QCM as a function of surface oscillation amplitude.** Shifts in (a) resonance frequency, (b) inverse quality factor, and (c) slip time as a function of QCM surface amplitude.

The mean slip time, $\tau_s$, of the nanocrystals is related to the gold nanocrystal-induced shifts in both the resonant frequency, $\Delta f$, and the dissipation, $\Delta(1/Q)$ of the graphene QCM according to the relationship

$$\tau_s = -\frac{1}{4\pi} \frac{\Delta(1/Q)}{\Delta f}.$$  (3.33)

Evaluating $\tau_s$ using the values $\Delta f = -41.3$ Hz and $\Delta(1/Q) = 4.61 \times 10^{-6}$ gives $\tau_s = 8.9$ ns. Note that this is the slip time at room temperature for $A_{osc} = 11.4$nm and $v_s = 35.6$ cm/s. However, we
may also calculate the slip time as a function of oscillation amplitude using the formula above, as shown in Figure 3.17. Slip time decreases slightly with the oscillation amplitude, but not more than 11% over the value at $A_{osc} \approx 1.5$ nm. Thus, there is not a distinct transition to a different dissipative regime.

With the slip time now determined for the complete range of accessible QCM surface amplitudes, we may now determine the average mass, $m_s$, of the nanocrystals. Recall that we may express the adsorbate-induced frequency shift of the graphene QCM as

$$\frac{\Delta f}{f} = -\frac{N\omega m_s}{A\pi Z_q} \left( \frac{1}{1 + \omega^2 \tau_s^2} \right).$$

(3.34)

If we assume that all nanocrystals participate in sliding, then the quantity $\frac{N}{A} = 1.01 \pm 0.02 \times 10^{12}$ crystals/cm$^2$ is the areal nanocrystal density we found with AFM. Solving the equation for $m_s$, the average nanocrystal mass is found to be $m_s = 7.8 \pm 0.15 \times 10^{-22}$ kg. We can also calculate the deposited mass density on the graphene QCM, $\sigma_{Au} = m_s \times \frac{N}{A} \approx 7.9 \times 10^2$ ng/cm$^2$, which is about 18% smaller than the density measured by the control QCM. There are several possibilities that can explain the mass discrepancy between the two QCMs. It is possible that we have made an error in our relationship between $\Delta f$ and $m_s$. If we did, then it likely stems from our assumption that all nanocrystals participate in sliding. However, it is more likely that some of the incident gold did not stick to the graphene surface as well as it did to the control QCM’s gold surface. This is not unusual, as this phenomenon has been observed in other experiments for gold on graphite at room temperature.$^{84}$ The error may also simply stem from the evaporator being tilted slightly to favor the control QCM side. However, the other errors seem more likely since the difference in lateral position of the two QCM with respect to the gold source is negligible.

The slip time and nanocrystal mass compare favorably with previous molecular dynamics simulations on this kind of system.$^{26}$ Guerra et al. simulate the interaction of nanocrystals having mass of $1.5 \times 10^{-22}$ kg on graphene, and find their slip time to be approximately 0.75 ns if they are
sliding in the ballistic regime. While the average mass of the nanocrystals in our experiment is about $5.2 \times$ as large as those considered in the simulation, our slip time is about $12 \times$ as large as in the simulation. Note that the surface velocity of our QCM is on the order of 35 cm/s, placing an upper limit on the maximum sliding velocity of the nanocrystals, while the ballistic nanofriction simulations were done at a sliding velocity of 10,000 cm/s. We conclude that an ultra-low friction regime exists for this contact morphology and that it is attainable at velocities accessible to a QCM at room temperature.

3.5 Interpretation

3.5.1 Critical assumptions and failure analysis

In order to apply our purely-dissipating, finite-element model to our QCM system, we must make assumptions about our system that we were not able to directly verify given the large quantity of nanocrystals in the ensemble. A thorough analysis of these assumptions, and the ways in which our model can fail as a result of bad assumptions, is necessary in order to understand the limitations of the model. The four assumptions we make for our model are:

1. All of the nanocrystals are rigid and do not deform during oscillation.

2. The nanocrystals are monodisperse.

3. All $N$ nanocrystals participate in sliding.

4. The nanocrystals do not interact with one another.

5. The friction force is viscous and linearly proportional to sliding velocity.

6. Graphene is rigidly and uniformly attached to the underlying gold electrode

   Significant deformation of the nanocrystals during QCM oscillation can change the contact geometry and, therefore, the friction interaction since it depends on surface area. We can estimate
the shear strain, $\gamma$, of a nanocrystal under the shear stress, $\sigma$, applied by our viscous drag force, $F_d$, over the contact area $A$, provided we know the shear modulus of gold. Assuming the shear modulus of gold to be $G_e = 27$ GPa, we estimate the lateral deformation, $\Delta x$, using the relation

$$G_e = \frac{\sigma}{\gamma} = \left( \frac{F_d}{A} \right) / \left( \frac{\Delta x}{L} \right),$$

(3.35)

where $\sigma = F_d/A$, $\gamma = \Delta x/L$, $F_d = \xi v_s$ is the drag force, $A$ is the contact area of one icosahedral facet, and $L$ is the nanocrystal height. Taking $F_d = 8.61 \times 10^{-14}$ kg/s $\times$ 0.356 m/s $= 3.07 \times 10^{-14}$ N (assuming maximum possible sliding speed to get the highest shear stress), $A = \frac{1}{2}(2.9\text{nm})^2$, and $L = 5\text{nm}$, the nanocrystal should see a shear stress of about $\sigma \approx 7.3$ kPa. Then, the total lateral deformation of the nanocrystal is about $\Delta x \approx 1.3 \times 10^{-6}$ nm. Thus, the deformation is negligible. Negligible deformation is also observed in molecular dynamics simulations that modeled the internal Au interactions using an embedded atom model (EAM) and the gold-graphene interaction with a Lennard-Jones potential.$^{26,27}$

The size distribution of nanocrystals seems to have a range of $4.2 \pm 1$ nm based on our measurements. The linear size difference between the smallest and largest nanocrystals is about $100\%(1 - 3.2\text{nm}/5.2\text{nm}) = 40\%$. This means there is a distribution in the contact contact area between the individual nanocrystals with the graphene, which will impart a dispersion in the shear stress exerted by the individual nanocrystals on the graphene. The difference in contact area should, then, vary by about 60% between the largest and smallest nanocrystals. The shear stress should have a similar range, but the smallest and largest values should be on the same order of magnitude.

Nanocrystals can become pinned to the graphene at defect sites. To evaluate the validity of assumption 3, we characterize the defect density in our graphene using Raman microscopy.$^{64}$ We find that the defect density in our graphene is about $1.9 \times 10^{10}$ defects/cm$^2$. This is two orders of magnitude lower than the areal density of nanocrystals, $N = 1.01 \pm 0.02 \times 10^{12}$ crystals/cm$^2$, so most of the nanocrystals should be away from defect sites.
Analysis of assumptions 4 and 5 are addressed in the Sec’s. 3.5.2 and 3.5.3. However, they appear to be reasonable. Fortuitously colliding nanocrystals at this size scale were observed in TEM to stick together. Large-scale collisions would result in not only an additional source of dissipation, but may cause large-scale coalescing of nanocrystals that would change both the physical dimensions and the areal density of sliding objects. Nanocrystals are estimated to be spaced about 10 nm apart, on average, and slide for about 3.1 nm. We do not expect them to collide with one another, on average. In addition, one may inspect the behavior of the $\Delta(1/Q)$ with respect to sliding amplitude $A_s$ to determine the dependence of drag force on sliding velocity. Our analysis shows that this relationship is, indeed, linear.

Assumption 6 is the weakest assumption. Graphene is known to adhere nonuniformly to substrates like SiO$_2$ on size scales on the order of 200 nm.$^{62}$ While neither the roughness nor the height-height correlation of our electrode with and without graphene were characterized, the electrode metal was not grown in a way that would make it atomically flat, and CVD graphene was clearly observed to contain wrinkles. Therefore, we certainly do not expect either the graphene or the electrode to be atomically flat, nor for the graphene to be in complete conformal contact with the underlying electrode over the $\sim$1 cm$^2$ coverage area. We anticipate the high density of contacting regions between the graphene and electrode to anchor the graphene film in place reasonably well in comparison to the nanocrystals. In addition, if we assume that the RMS roughness of graphene on gold is comparable to that of graphene on SiO$_2$, which is 1.9 Å, then we expect most of the deformation of graphene, if any, to be in the plane of graphene itself. However, graphene is known to have an extremely high shear modulus on the order of 300 GPa,$^{85}$ so motion likely occurs mostly between the nanocrystal and graphene. Further work needs to be done to validate this assumption.
3.5.2 Determination of the velocity dependence of drag force

The small load approximation we used to interpret $\Delta f$ and $\Delta(1/Q)$ only works as long as the drag force is linearly proportional to sliding velocity. We may employ a check that was originally developed by Sokoloff et al. to determine whether we are in this sliding regime.\textsuperscript{86} If the drag force, $F_{\text{drag}}$, is assumed to take the form

$$F_{\text{drag}} = -\xi |v|^n \text{sgn}(v),$$  \hspace{1cm} (3.36)

where $v$ is the relative velocity of the nanocrystal and the graphene and $\text{sgn}(v)$ simply returns the sign of $v$, then $Q \propto A^{1-1/n}$. One may plot $\Delta(1/Q)$ as a function of QCM oscillation amplitude, $A$, and examine the relationship. For a linear $F_{\text{drag}}$ vs. $v$ dependence, $n = 1$ and $\Delta(1/Q)$ is expected to be independent of $A$. Indeed, in Figure 3.17(b), $\Delta(1/Q)$ for our system is independent of $A$ over a decade in oscillation amplitude. We conclude that $F_{\text{drag}}$ in our system is linearly proportional to $v$.

3.5.3 Amplitude of motion and possibility of nanocrystal collisions

Our analysis also depends on the nanocrystals interacting with only the graphene substrate and not with each other. We may estimate the amount by which the nanocrystals move relative to the graphene surface to determine the likelihood of the majority nanocrystals colliding with each other. Let the motion of the nanocrystals be described by\textsuperscript{27,86}

$$m \frac{dv_2}{dt} = -\xi |v_2 - v_1| \text{sgn}(v_2 - v_1),$$  \hspace{1cm} (3.37)

where $m$ is the mass of a nanocrystal, and $v_1$ and $v_2$ are the velocities of the graphene QCM surface and the gold nanocrystal, respectively, in the lab frame. We let $v_1 = v_0 \cos(\omega t)$, where $v_0$ is the
amplitude of the QCM’s surface velocity. The solution to this differential equation is

\[ v_2 = \frac{1}{\omega^2 m^2 + \xi^2} \left[ \xi^2 v_0 \cos (\omega t) + \xi \omega m v_0 \sin (\omega t) \right]. \quad (3.38) \]

Then, the relative velocity, \( v \), is given by

\[ v = v_2 - v_1 = \frac{1}{\omega^2 m^2 + \xi^2} \left[ -\omega^2 m^2 v_0 \cos (\omega t) + \xi \omega m v_0 \sin (\omega t) \right]. \quad (3.39) \]

This allows us to find the relative displacement, \( d \), which is

\[ d = \frac{1}{\omega^2 m^2 + \xi^2} \left[ -\omega m^2 v_0 \cos (\omega t) + \xi m v_0 \sin (\omega t) \right]. \quad (3.40) \]

This can be simplified to

\[ d = \frac{m v_0}{\sqrt{\omega^2 m^2 + \xi^2}} \sin (\omega t + \phi), \quad (3.41) \]

where \( \phi \) is the phase given by

\[ \tan \phi = \frac{\xi}{m \omega}. \quad (3.42) \]

Using \( m = 7.7 \times 10^{-22} \) kg, \( v_0 = 35.6 \) cm/s (the highest value we reached), and \( \xi = 8.6 \times 10^{-14} \) kg/s, the maximum value of the displacement amplitude is \( d = 3.1 \) nm. We estimate the range of \( \phi \) to be \( 20^\circ \) using the range of diameter deviations of \( \pm 1 \) nm. The mean center-to-center distance between nanocrystals is \( \approx 10 \) nm, so the displacement amplitude and phase that we found are not large enough to allow the majority of nanocrystals to collide with each other.

### 3.5.4 Inference of surface interaction energy

"Ballistic" nanofriction is expected to occur at very high sliding velocities on the order of 100 m/s.\textsuperscript{25,26} However, we estimate the sliding velocity in our system, using Eq. 3.39 and \( v_0 = 35.6 \) cm/s, to be \( v = 9.6 \) cm/s \( \approx 0.1 \) m/s. Why is it that we are observing behavior that is consistent
with ballistic nanofriction if our sliding speeds are so low? It may be that the values found from simulation were simply not physically accurate. Ideally, we would like to know what a fully-fledged simulation for very low (diffusive) sliding velocities would give for the drag coefficient so that we could better gauge the accuracy of the simulation model. However, those simulations, according to the authors, were unfeasible as they would have taken a prohibitively long time.\textsuperscript{26} We make the assumption that the model simply needs some refinement.

Our collaborators in the Martini group at UC Merced refined the molecular dynamics simulation based on our QCM results.\textsuperscript{27} In their simulations, the interaction between the gold nanocrystals and graphene is modeled by a Lennard-Jones potential (as was done in Guerra, et al.), given by

\[ V_{LJ} = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right], \]  

(3.43)

where \( \epsilon \) is the maximum depth of the potential well, \( \sigma \) is the interatomic distance at which the \( V_{LJ} = 0 \), and \( r \) is the interatomic distance. Previous simulations\textsuperscript{25,26} assumed that \( \sigma = 2.74 \text{ Å} \) and \( \epsilon = 22 \text{ meV} \). These parameters depend on the particular materials that make up the interface, and have not been measured for either gold on graphene or gold on graphite. These values were taken from a paper by Lewis et al., who noted that these values were loosely determined from two-body models for silver-graphite and platinum-graphite interactions and are, likely, only qualitatively correct.\textsuperscript{23} As such, our refinement of the simulation is justified.

Previous calculations of \( \epsilon \) and \( \sigma \) for gold on graphite determined \( \epsilon \) to be in the range of 12.7 to 34.1 meV and \( \sigma \) to range from 2.74 Å to 3.00 Å.\textsuperscript{22,23,87} The Martini group simulated gold nanocrystals, ranging in diameter from 2nm to 4.5 nm, sliding on graphene and looked at the drag coefficient \( \xi \). They found that the wider range for \( \epsilon \) had a stronger effect than \( \sigma \) on \( \xi \), which had a comparatively narrow range.\textsuperscript{27} Their simulations were able to reproduce our experimental data of \( \xi = 8.6 \pm 6.1 \times 10^{-14} \text{ kg/s} \) when \( \epsilon \approx 6 \) to 15 meV.\textsuperscript{27} Therefore, we conclude that the interaction potential between gold and graphene is weaker than previously anticipated.\textsuperscript{27}
CHAPTER 4: SCANNING TUNNELING MICROSCOPY OF ZrSiS

Departing from tribology, I shift now to an experiment-based study of the electronic properties of a novel electronic material. In the last decade, many condensed matter physicists have taken a fervent interest in predicting and realizing materials that exhibit topological ordering.\textsuperscript{88–100} The defining features of these materials is the large disparity between the electronic properties at the material’s boundaries and in the material’s bulk and the robustness of their topologically-protected band structures.\textsuperscript{88, 89, 92} For example, topological insulators are insulators in their bulk, but have conducting states at their edges.\textsuperscript{91, 92} Another group of materials that display topological ordering are the topological semimetals, whose bulk states are semimetallic; that is, there is a small, or vanishingly small, overlap between the bulk quasiparticle energy bands.\textsuperscript{97} These bulk band crossings can be point-like,\textsuperscript{94–96, 98, 99, 101} or line-like,\textsuperscript{93, 102–105} and can exhibit band dispersion in two\textsuperscript{106} or three\textsuperscript{101} dimensions. Here, I describe our experiments to investigate the band structure of a semimetal predicted to exhibit a line-like touching of quasiparticle energy bands, and describe some implications on the material’s electronic properties. In addition, I describe our observation of apparent $E$-dependent non-conservation of the pseudospin degree of freedom, which is expected for line-node materials.\textsuperscript{107}

Our STM results are compared to surface spectral weight calculations from our collaborators, Prof. Hsin Lin’s group at National University of Singapore (currently at Academia Sinica, Taipei, Taiwan), some of which appear in \textit{Lodge 2017}.\textsuperscript{100} The details of these calculations can be found in the reference. All band structure calculations/spectral surface weights in this section were generated by Prof. Lin’s group specifically for this project.
4.1 Zirconium silicon sulfide: A topological semimetal

Realizing a nodal-line semimetal that does not have other bands vicinal in energy or momentum such that the line node’s electronic properties can be easily accessed by experimentation has been a major challenge. One candidate material is zirconium silicon sulfide (ZrSiS), which was predicted to host a closed-loop line node with linearly dispersing, or Dirac, bands in the vicinity of the line node that are protected by glide-mirror symmetry. The atomic structure of ZrSiS is shown in Figure 4.1. All bands constituting the line node in this materials are expected to disperse linearly over 0.5 eV with the line node existing near the Fermi level, and Dirac line nodes are expected to exist in this material in three dimensions. Originating from its Dirac nature, this material’s orbital topology at the Fermi surface results in large, anisotropic magnetoresistance, which has been measured, making it attractive in geomagnetism sensing applications. Additionally, this material may also lead to interesting pseudospin physics, such as vortex rings and Skyrmionic pseudospin patterns, a maximal anomalous Hall effect, and optically-tunable...
phase transitions. The most easily accessible part of line node to experimentation in ZrSiS was predicted to exist $\sim 200$ meV above the Fermi level.

The primary tool for directly observing the band structure of materials is angular-resolved photoemission spectroscopy (ARPES). In this method, the photoelectric effect is leveraged to detect emitted photoelectrons from the valence band of a material as a function of angle of the ejected electrons. One uses the geometry of the system and energy conservation to map the momentum $k$ of the outgoing electron as a function of the electron’s band energy. However, this technique is only sensitive to valence-band electrons, and can, therefore, give no information about electrons whose energy is above the Fermi level. Indeed, ARPES has been used to provide valuable insight to the electronic structure of ZrSiS up to the Fermi level. However, most of the interesting physics in ZrSiS is predicted to occur above the Fermi level, like the existence of a line node. There is another technique that is sensitive to conduction-band electrons, called quasiparticle interference (QPI) mapping, using scanning tunneling microscopy that can locate the line node in this material. It was our goal to directly observe the line node in this material using QPI mapping.

### 4.2 Principles of scanning tunneling microscopy

Scanning tunneling microscopy, or STM, is a scanning probe technique that rasters an atomically sharp, conducting tip within several angstroms of a conducting sample such that the respective electronic wavefunctions of the tip and sample do not significantly overlap with one another. The tip and sample are held at different electric potentials, forcing electrons to tunnel between the tip-sample spatial gap in a preferential direction. The tunneling phenomenon through a spatial gap, in a similar construction to the STM configuration, was first described mathematically by Bardeen in 1961, and corrections were later given by Tersoff and Hamann in 1985. Essentially, the rate at which electrons tunnel is sensitively influenced by the tip-sample separation distance such that the difference in height at the position of atoms is measurably different than be-
tween atomic sites. As such, one may raster the tip over the surface of a conductor to gain detailed spatial information about atomic position based on the local density of states (LDOS) of electrons. This technique was invented in 1982 by Binnig and Rohrer,\textsuperscript{118} and earned them a Nobel Prize in 1986. In this section I discuss the details of the tunneling phenomena and how one may determine LDOS information using STM. In this section, and throughout this dissertation, the voltage convention used is such that the tip is at ground potential and voltages are applied to the sample.

### 4.2.1 Tunneling phenomenon

From first order perturbation theory,\textsuperscript{116,117} the tunneling current $I$ at sample voltage $V$ may be described by the equation

$$I (V) = \frac{2\pi e}{\hbar} \sum_{\mu, \nu} \{ f (E_\mu) [1 - f (E_\nu)] - f (E_\nu) [1 - f (E_\mu)]\} |M_{\mu \nu}|^2 \delta (E_\nu + eV - E_\mu),$$  \hspace{1cm} (4.1)

where $E_\mu$ and $E_\nu$ denote the respective energies of surface eigenstates $\psi_{\mu}$ and tip eigenstates $\psi_{\nu}$, $f_E$ is the Fermi distribution function at energy $E$, and $M_{\mu \nu}$ is the tunneling matrix element between eigenstates of the tip and sample. If we assume that $V$ is small and thermal fluctuations are negligible, one may simplify this expression to

$$I (V) = \frac{2\pi e^2 V}{\hbar} \sum_{\mu, \nu} |M_{\mu \nu}|^2 \delta (E_\mu - E_F) \delta (E_\nu - E_F).$$  \hspace{1cm} (4.2)

Bardeen\textsuperscript{116} derived an expression for the tunneling matrix element $M_{\mu \nu}$ completely in terms of tip and sample wavefunctions as

$$M_{\mu \nu} \equiv \langle \psi_\mu | H' | \psi_\nu \rangle = \frac{\hbar^2}{2m_e} \int_A (\psi_\mu^* \nabla \psi_\nu - \psi_\nu^* \nabla \psi_\mu) \cdot \mathbf{d}A,$$  \hspace{1cm} (4.3)

where one integrates over any surface lying completely within the spatial region separating tip and sample. This expression is called the \textit{Bardeen matrix element}.  

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In order to evaluate this expression, one must have an explicit form for $\psi_\mu$ and $\psi_\nu$. In practice, it is not feasible to obtain an exact expression for the tip states. This is because the structure of the tip is usually unknown and can change frequently. In addition, if the tip-sample separation distance is $\sim 4$ Å, $d$ orbitals from the tip can contribute to the tip wavefunction and their shapes can be complicated. However, Tersoff and Hamann$^{117}$ developed an approximation for the Bardeen matrix element that reduces Eq. 4.2 to

$$I \propto \sum_\nu |\psi_\nu (\vec{r}_0)|^2 \delta(E_\nu - E_F),$$

(4.4)

where $\vec{r}_0$ is the position of the tip. The right hand side of Eq. 4.4 is the definition of $\rho_\mu(\vec{r}_0, E_F)$, the local density of states (LDOS) of the surface at $E_F$ and position $\vec{r}_0$. Therefore, to first order, one measures the spatial variation of the sample’s LDOS in STM.

To obtain the above expression, Tersoff and Hamann$^{117}$ assumed $\psi_\nu$ to have the form of a Bloch wave, which builds in an implicit exponential dependence on tip-sample separation dependence. This allows us to gain some intuition for the sensitivity of the STM to the tip-sample separation. One can approximate the spatial gap of the tunnel junction in one dimension as a rectangular barrier, as illustrated in Figure 4.2. Using the WKB approximation to approximate $\|M_{\mu\nu}\|^2$, the dependence of the tunneling probability $I$ on the tunneling spatial gap $d$ goes as

$$I \sim \exp (-2\kappa d),$$

(4.5)

where $\kappa^2 = 2m_e \Phi / \hbar^2$, $m_e$ is the electron mass, and $\Phi$ is the height of the tunnel barrier. Letting $\Phi \approx 4.5eV$ be the work function, one finds that the tunneling current reduces by an order of magnitude for every increase in $d$ by $\sim 1$ Å.
4.2.2 Scanning tunneling spectroscopy

As one increases or decreases the applied sample voltage $V$, additional states away from the Fermi level contribute to the tunneling current. If we assume the sample LDOS to be a continuum, we can approximate the tunneling current as

$$I(\vec{r}, V) \propto \int_{E_F}^{E_F+eV} \rho_{\nu}(\vec{r}, E) dE,$$

(4.6)
implying that
\[ \frac{dI}{dV} \bigg|_{V_0} = \rho_{\nu}(\vec{r}, eV_0) \] (4.7)

Here, we ignore the LDOS of the tip as well as the energy dependence of the matrix element, which is fine as long as the applied voltage is much smaller than the vacuum barrier. This gives us the ability to measure the LDOS of the sample by measuring \(dI/dV\).

We acquire a \(dI/dV\) spectrum by positioning the tip at a fixed \(\vec{r}_0\) and measuring \(dI/dV\) as we sweep the sample voltage. In practice, we can measure \(dI/dV\) directly using a lock-in amplifier. However, it is also possible to measure the \(I(V)\) and then numerically differentiate. Either method results in a measure of the samples LDOS as a function of energy, typically referred to as *scanning tunneling spectroscopy*, or STS.

### 4.2.3 Topography

A schematic of a typical STM setup is shown in Figure 4.3. In an STM, one applies a constant voltage to the sample and grounds the tip (alternatively, one may ground the sample and bias the tip) in order to establish a tunneling current. Then, the tip, which is mounted to a piezoelectric tube, is rastered laterally over the surface of the sample while measuring the tunneling current with some type of amplifier. As the tip is rastered, the tunneling current is fed into a distance controller unit. The control unit then applies a voltage to the piezo tube to control the tip-sample height and keep the tunneling current constant. Let \(z\) be the height of the STM tip above the sample. One may plot \(z\) as a function of \(I\) and obtain a *constant-current topograph*. If the applied voltage is sufficiently small, \(I(\vec{r}, V_0) \propto \int \text{LDOS}(\vec{r}, E_F + eV_0)\) and the constant-current topograph shows a surface where the LDOS integrated over energy is constant. One may also turn off the feedback control and then acquire an image. This keeps the tip-sample distance constant (except for tip drift), and is referred to as *constant-height* mode.
4.2.4 \( dI/dV \) Mapping

Instead of mapping the integrated LDOS as a function of lateral position \( \vec{r} \), one may instead spatially map the LDOS. This can be accomplished in one of two ways. The most direct way is to acquire an \( n \times m \) grid of \( dI/dV \) spectra, with each spectra acquired at regular, periodic locations. One obtains an \( n \times m \times s \) dimension grid, where \( s \) is the number of sampling points in each spectrum (which is kept constant throughout the experiment). One may then use software to reconstruct an LDOS map for each value of \( s \). This method requires that the tip drift, inherent to all STM systems, to be sufficiently small over the time frame of the experiment. In most commercial low-temperature STM systems, which reach \( \sim 4.5 \) K, the tip drift effect can be prohibitively large, depending on the desired spatial and energy resolutions.

![Schematic of an STM setup](image_url)

Figure 4.3: Schematic of an STM setup. Figure: Michael Schmid, TU Wien
The alternate method, which is more robust against tip drift, is to keep the sample voltage constant and measure $dI/dV$ with a lock-in amplifier as the tip is rastered over the surface. Then, $dI/dV$ can be plotted as a function of lateral coordinates. After acquiring an image, $V$ can be changed to a new value, and another $dI/dV$ map can be acquired. In this way, we can achieve the same kind of measurement as in the previous method.

4.2.5 Thermal broadening

In the Tersoff and Hamann approximation, we assumed that $T = 0$ K. In practice, thermal broadening of the electron energy distribution, which follows a Fermi distribution function, will limit the energy resolution of $dI/dV$. At room temperature $kT \approx 25$ meV, and the combined tip and sample energy broadening is $\Delta E = 4kT \approx 100$ meV.\textsuperscript{119} At 77 K, $\Delta E \approx 26$ meV, and at 4.5 K this value goes down to $\Delta E \approx 1.5$ meV. Therefore, low temperature is necessary for high-resolution STS.

4.3 Quasiparticle interference (QPI)

4.3.1 Scattering phenomenon

One cannot obtain $E(\vec{k})$ dispersion from real-space STM measurements, alone. As mentioned earlier, STM is a measure of the LDOS in the sample. In an ideal metal, the quasiparticle eigenstates are given by Bloch waves. If we try to calculate the LDOS, given by

$$\rho(\vec{r}, E) \propto \sum_k |\psi_k(\vec{r})|^2 \delta(E - E(\vec{k})),$$

using Bloch waves, then we find the LDOS at a given $E$ to be spatially uniform. However, disorder in the surface can elastically scatter quasiparticles. This causes quasiparticle eigenstates of different $\vec{k}$ values of the same energy to mix together. Mixing two eigenstates with wavevectors
\( \vec{k}_1 \) and \( \vec{k}_2 \) generates a standing wave in the quasiparticle wavefunction \( \psi_k \) that has wavevector \( \vec{q}_{\Delta k} = (\vec{k}_2 - \vec{k}_1)/2 \). As a result, the LDOS will be spatially modulated with standing waves having a spatial frequency of \( \vec{q} = 2\vec{q}_{\Delta k} = \vec{k}_2 - \vec{k}_1 \).

Figure 4.4: **Quasiparticle interference.** (a) STM topograph of a single, atomic defect acquired in constant current mode at 4.5 K \( (I = 200 \text{ pA}, V = 150 \text{ mV}) \). (b) \( dI/dV \) map of the same area as (a) with one possible \( k_i \) and \( k_f \) illustrated. (c) Calculated Fermi surface at \( E = 150 \text{ meV} \) with high symmetry directions shown along with the corresponding \( k_i \) and \( k_f \) vectors mapped from (b). The scattering vector is given by \( q = k_f - k_i \). (d) The quasiparticle interference pattern generated by the 2D FFT of (b), showing the mapping of the scattering vector \( q \) from (c). The pixel intensity at each location indicates the probability for that scattering event (a particular \( q \) to occur.

This phenomenon is illustrated graphically in Figure 4.4. Panel (a) shows a point defect
in the constant-current topograph of ZrSiS acquired at $T = 4.5$ K. Panel (b) shows the $dI/dV$ map at $V_{\text{sample}} = 150$ mV for the same area as in panel (a). One can clearly see that the LDOS is modulated and shows standing waves having 4-fold symmetry. The arrows denoting $k_f$ and $k_i$ are two example quasiparticle wavevectors that illustrate how a quasiparticle can be scattered by the point defect. Dropping these vectors onto a constant energy contour, or Fermi surface, of the first Brillouin zone at $E = 150$ meV, as shown in the calculated spectral surface weight in panel (c), we can connect these two wave vectors graphically. The resulting $q$ can be plotted for all connecting wavevectors that satisfy the selection rules for this particular system and be plotted for this energy, as shown in panel (d). For our example wavevector, we see that the pixel intensity at $q$ is low compared to other regions of the panel (d). As such, this particular scattering is not likely to occur often. Note that the $q$ values corresponding to the most intense regions of panel (d) show up in the real-space LDOS modulations of panel (b) as standing waves with wavelength $\lambda = 2\pi/q$. Panel (d) is referred to here as the \textit{quasiparticle interference pattern}, or QPI pattern, and is generated from the symmetrized 2D Fourier transform of panel (b), which will be discussed in-depth later. Clearly, the shape of the QPI map is a direct consequence of the shape of the Fermi surface. With additional assistance from calculations, QPI measurements are capable of yielding high-quality band structure information. In addition, QPI measurements can also give insight into $\Delta k$ selection rules of a system, showing which transitions are favored and which ones are suppressed. Features in the QPI pattern originate from the particular isoenergy contour of the Fermi surface. In addition, scattering can occur both within and between neighboring Brillouin zones. This effect is illustrated in Figure 4.5. Panel (a) shows four neighboring Brillouin zones of ZrSiS calculated at $E = -100$ meV. Shown in panel (b) is the experimentally-derived QPI pattern at the same energy as (a). Both panels have been resized to have matching $q$ scales so that visualizing the scattering vectors is easier. Scattering within the Brillouin zone (red vectors) results in the square outline our the QPI pattern, as well as a thin cross pattern that goes through the center of the QPI pattern. The yellow vectors, when mapped out, generate the series of straight lines that
form the outline of a broad cross pattern. These are the same as the square outline within the Brillouin zone, except they are shifted over by a constant reciprocal lattice vector. Similarly, the black vectors generate shifted thin cross patterns at the corners of the square outline. As a result, many of the features in the QPI pattern are repeated elsewhere, and shifted in $q$ space, due to inter- and intra-Brillouin zone scattering.

Figure 4.5: **Scattering between Brillouin zones.** (a) Calculated constant-energy Fermi surface maps over four neighboring Brillouin zones at $V = -100$ meV. Possible scattering vectors are indicated. (b) Experimental QPI pattern showing how the features generated by the scattering processes in (a) contribute to the interference pattern.

As a final note, the $q$ resolution of the 2D FFT is set by the physical dimensions of the real-space image. In general, if the real-space image has edge-length of 12 nm, then the $q$ resolution, or pixel spacing, of the 2D FFT is $1/12$ nm$^{-1}$. Therefore, if one desires good $q$ resolution, the
one must acquire a large real-space image. However, the raw 2D FFT image contains the same number of pixels as the raw \( dI/dV \) map. If one seeks to identify all the standing wave features in the real-space image, the one needs to have sufficiently high pixel resolution during the real-space image acquisition. Finally, the logic used for automatically acquiring \( dI/dV \) maps is shown in APPENDIX C. For our experiments, this was implemented in LabVIEW.

4.3.2 QPI pattern generation and analysis

QPI patterns are generated by computing magnitude of the 2D discrete Fourier transform of a \( dI/dV \) map. A computer typically calculates the 2D fast Fourier transform (2D FFT) to produce the same result. For our STM system, simply computing the 2D FFT typically results in interference patterns that are difficult to interpret due to (1) low signal-to-noise ratio and (2) artifacts arising from the abrupt termination of periodic features at the edges of the image. Processing the raw data so as not to lose information or to inadvertently fabricate new information is crucial for accurately interpreting the results of quasiparticle interference experiments. Here, I discuss our processing techniques that are designed to safely enhance signal to noise ratio in QPI data. The implementation of these processes in a Python 2.7 script can be found in APPENDIX D.

4.3.2.1 Apodizing Edge Mask

The biggest detriment to the SNR is artifacting from edge effects. This effect can be seen in Figure 4.6a,c,d. Figure 4.6a is an atomically-resolved \( dI/dV \) map, 12x12nm in area, of ZrSiS over a point defect. Taking the raw 2D FFT results in Figure 4.6c; both images are 1024x1024 pixels. To more clearly observe the structural information, we zoom into the center 150x150 pixels, shown in Figure 4.6d. At every wavenumber corresponding to a lattice peak, also known as the Bragg peaks, there is a prominent star-shaped artifact. This artifact arises from the periodic square lattice abruptly terminating at the edges of the real-space image. At each edge, the lattice is periodic in only one direction. As a result, the 2D FFT becomes extended in the aperiodic direction, but is
quite narrow in the periodic direction. The overall feature is, therefore, an extended line in the 2D FFT, and the opposite edge pairs form the extended lines in the horizontal and vertical directions, respectively.

Figure 4.6: **Apodizing edge mask for QPI analysis.** (a) Raw, atomically-resolved $dI/dV$ map of a crystal. The edge length of the image is 12 nm. (b) Image of (a) after processing with an apodizing edge mask. (c) Raw 2D FFT of (a). (d) Zoom-in to the center 150x150 pixels of (c). (e) Center 150x150 pixels of the 2D FFT of (b).

Rotating the image can help to correct the star artifacts from the Bragg peaks, but it intro-
duces additional abrupt edges that the FFT algorithm cannot deal with easily. However, one can correct the edge effects altogether by first multiplying the raw, real space image by an apodizing mask that forces the image edges to smoothly go to zero. The general apodizing matrix $C$ used to generate Figure 4.6b is given by

$$ C = \vec{u}\vec{u}^T, $$

(4.9)

where $\vec{u}$ is the vector

$$ \vec{u} = \begin{bmatrix} \cos \left[ \frac{2\pi}{N} \left( \frac{-N}{2} + 0 \right) \right] & \cos \left[ \frac{2\pi}{N} \left( \frac{-N}{2} + 1 \right) \right] & \cdots & \cos \left[ \frac{2\pi}{N} \left( \frac{-N}{2} + N \right) \right] \end{bmatrix} $$

(4.10)

and $N$ is the number of pixels along one axis of the image to be processed (assuming an $N \times N$ image). The quantity $\vec{u}^T$ is the transpose of $\vec{u}$. Multiplying the image from Figure 4.6a by this edge mask results in Figure 4.6b. The 2D FFT of this image is shown in Figure 4.6e, which shows no signs of the star artifacts.

4.3.2.2 Drift correction

Spatial information from raw STM data can sometimes be skewed slightly due to inherent tip drift. This can cause features like a square atomic lattice to appear more like a parallelogram. Most commercial STM software comes with a way to compensate for tip drift while scanning, but it is also possible to compensate for drift post-acquisition. To accomplish this, one typically must both shear and stretch transform the STM image. First, the image is rotated by an angle $\theta$ such that one of the high-symmetry crystal directions is parallel with one edge of the image frame. We assume that the image is "correct" along this direction and use it as a reference for the the drift-correction processing. Note that we will need to recalibrate the scale bar later so that spatial distances are reported correctly.
Figure 4.7: **Drift correction and symmetrization.** (a) 2D FFT of a square lattice appearing slightly skewed and stretched due to tip drift. The dashed, white box shows a perfect square. (b) Corrected 2D FFT data showing alignment with the dashed, white square. (c) Rotation and reflection averaged image of (b).

Processing begins by operating on the STM image with a rotation matrix $R$, where

$$
R = \begin{pmatrix}
\cos \theta & -\sin \theta \\
\sin \theta & \cos \theta
\end{pmatrix},
$$

(4.11)

and using a bilinear interpolation when remapping the old pixels to their new locations in order to minimize information loss. The result of rotating is shown in Figure 4.7a.

Next, the image is sheared along one direction by operating on the rotated STM image with a shear matrix, $S$, equal to

$$
S = \begin{pmatrix}
1 & \theta_{\text{shear}} \\
0 & 1
\end{pmatrix},
$$

(4.12)

where $\theta_{\text{shear}}$ is the shearing angle (typically $\leq 3^\circ$).

Then, it is necessary to either shorten or elongate the image along one direction. One
multiplies the image by another matrix $Q$ that has the form

$$Q = \begin{pmatrix} x & 0 \\ 0 & y \end{pmatrix}, \quad (4.13)$$

where $x$ and $y$ are the amount by which one wishes to compress or elongate the image in the horizontal or vertical directions, respectively. Setting $x = y = 1$ returns the original image.

4.3.2.3 Rotation and reflection averaging to improve signal-to-noise ratio

To improve the signal to noise ratio of the quasiparticle interference patterns, each drift-corrected 2D FFT image is averaged with rotation and reflection transformations of itself. The FFT images are averaged along high-symmetry directions, with the four-fold symmetry of the ZrSiS crystal taken into account. Let $R(\theta)$ be a drift-corrected 2D FFT image rotated by an angle $\theta$. The rotation averaged image $R_{\text{avg}}$ is simply

$$R_{\text{avg}} = \frac{1}{4} [R(0^\circ) + R(90^\circ) + R(180^\circ) + R(270^\circ)]. \quad (4.14)$$

Then, $R_{\text{avg}}$ is reflected over the y-axis using the reflection transformation matrix

$$T = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (4.15)$$

and averaged with $R_{\text{avg}}$ to produce the final, symmetrized QPI pattern. The results of rotation and reflection averaging can be seen clearly in Figure 4.7, where panel (b) is the image before averaging and panel (c) is after averaging.
4.4 Methods

4.4.1 Sample preparation

We obtained single crystal samples of ZrSiS that had been synthesized via vapor phase transport methods\textsuperscript{113,121} from our collaborator Madhab Neupane.\textsuperscript{100} In order to obtain a fresh ZrSiS surface for study with STM, we first epoxy a small ceramic post onto a ZrSiS crystal mounted on a Si substrate. Then, once the ZrSiS crystal was inside the UHV environment of the STM ($P < 3 \times 10^{-12}$ Torr), the ceramic post was removed, taking some amount of crystal with it to reveal a clean surface. To remove the epoxied ceramic post from the crystal, the sample plate was first loaded into the sample carousel. Then, the user gently pushed on the ceramic post in one direction with the "wobble stick," followed by a push in the opposite direction if the post had not already fallen away from the sample. The sample was loaded into the STM cryostat ($T = 4.5$ K) within $\sim 20$ seconds of cleaving. The same crystal was cleaved multiple times using this method.

We found this crystal to be somewhat temperamental with regards to changes in temperature. Cycling the temperature of the in-vacuo cleaved crystal somehow affected its surface. This was discovered when we removed the sample, on which we were able to achieve atomic resolution, from the cryostat to recalibrate the STS on Au(111). After reinsertion of the sample into the cryostat, atomic resolution was no longer achievable. This behavior was remedied by re-cleaving the sample every time it was removed from the cryostat.

4.4.2 Measurement system

STM measurements were carried out in two different commercial STM systems. Preliminary topography and spectroscopy measurements were acquired in the Omicron LT-STM system in Masa Ishigami’s lab at UCF. In this system, we used a chemically-etched tungsten tip and measured at $T = 4.5$ K. QPI measurements were done in a Createc LT-STM system (Michael Fuhrer’s lab at Monash University) at $T = 4.5$ K using a platinum-iridium tip. Both systems were controlled.
using Nanonis controllers and software. STS measurements were acquired using the respective built-in lock-in amplifiers of the systems.

QPI patterns were generated from 2D FFTs of spatially-mapped $dI/dV$ images at fixed tunneling biases. $dI/dV$ maps were acquired simultaneously with topography. For these measurements, the lock-in frequency used was $f_{LI} = 707$ Hz with an RMS amplitude $V_{RMS} = 20$ mV. These measurements were acquired in constant current mode. This was done for several reasons. With feedback on, QPI does not allow us to collect data at small bias. A small bias would cause the STM to crash into the surface in order to satisfy the requested feedback current. Since crashing the tip into ZrSiS necessitates cleaning and recalibrating (discussed below) the tip, we were very cautious to not acquire data with $|V| \leq 100$ mV. This gives rise to the gap in our QPI data between +/- 100 mV. Having feedback on gave the instrument more stability against low-frequency vibration and drift. We performed these measurements using high frequency lock-in modulation to minimize the feedback from contributing. It is known that artifacts can arise in Fourier transformations of $dI/dV$ maps depending on how the tip is stabilized\textsuperscript{122} during measurement, particularly with acquisitions in constant current mode. I will show later that we do not observe any such artifacts.

In QPI, we focused on the interference pattern generated by only a single atomic defect. This was largely due to the ease with which we could resolve the standing waveform. Including defects at once in each QPI data would have yielded richer data; however, there is a finite amount of time ($\sim 60$ hours) before the cryostat was depleted, or nearly so, of liquid helium and needed to be refilled. Acquiring data with sufficiently high spatial resolution would require prohibitively long acquisition times to complete the experiment before we needed to refill the cryostat. We could not reliably return to the same exact defect to continue the measurement since we needed to retract the STM tip during filling.

Each QPI measurement originates from an $dI/dV$ image that is $1024 \times 1024$ pixels and $12 \times 12$ nm$^2$. As a result, the 2D FFT of our images have a pixel resolution $\delta q = 2\pi/12\text{nm} = 0.52\text{nm}^{-1}$. 

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4.4.3 Calibration of STS and tip conditioning

In order to ensure that STS measurements gave reliable measurements, the STM tips were all calibrated on clean Au(111). A constant current topograph of Au(111) at $T = 4.5$ K is shown in Figure 4.8(a). This image shows the famous herringbone reconstruction of the surface, wherein a stress-induced surface contraction along the $[1\bar{1}0]$ direction causes half the surface atoms in the reconstructed unit cell to occupy fcc cites and the other half to occupy hcp cites.$^{123-125}$

In Figure 4.8(b), I show Au(111) spectra acquired at both fcc and hcp sites. Both spectra are very similar to one another. For proper calibration, it is necessary to see the sharp surface band edge at -0.5 V. Additionally, the hcp region shows an enhancement in the spectra feature at $\sim -0.48$ V due to a weakly attractive potential of the hcp region compared to the fcc region.$^{125}$

Figure 4.8: Calibration of STS on Au(111). (a) Constant current topography of the Au(111) surface showing both fcc and hcp regions of the herringbone reconstruction at 4.5 K ($I = 100$ pA, $V = 1$ V). (b) $dI/dV$ spectra acquired with the PtIr STM tip placed over fcc and hcp regions, respectively. The dashed ellipse highlights the enhancement of the hcp spectrum near the band edge.
For the QPI experiments here, the tip was conditioned until (1) the sharp band edges and the enhancement at -.48 V could both be observed and (2) atomic resolution was readily observed on ZrSiS. The reference parameters for conditioning the tip were $V_{\text{sample}} = 1 \text{ V}$ and $I_{\text{tunnel}} = 300 \text{ pA}$. For tips that were far from giving good spatial resolution or spectroscopic features, the STM tip was modified by applying a $V_{\text{sample}} = 8-10 \text{ V}$ pulse to remove debris from the tip or by diving the tip into the Au$(111)$ by 1-2 nm. Gentler voltage pulses of 1-3 V, or diving the tip by 0.8 - 1 nm into the Au$(111)$, can stabilize a tip that is slightly noisy or blunt. If the tip was giving good spatial resolution and the spectroscopy results were close to being acceptable, then diving the tip 0.6 nm into the Au$(111)$ one or more times consistently resulted in a good tip. When pulsing or diving the tip into the Au$(111)$, it is recommended that the experimenter do so over clean areas of the Au$(111)$ so as not to redeposit any debris from the surface back onto the tip.

4.5 Results

4.5.1 Atomic and electronic structures of ZrSiS

A raw, constant-current STM topograph of pristine ZrSiS is shown in Figure 4.9(a). This layered compound has a tetragonal crystal structure belonging to the P4/nmm space group. The layers consist of planar, square lattices of Si atom is sandwiched between neighboring Zr-S bilayers, each of which adopts square lattice geometry.\textsuperscript{100} The material is expected to cleave between adjacent ZrS layers,\textsuperscript{100,102} which is consistent with our constant current topograph in Figure 4.9(a). The lattice constant measured here is $a = 3.54 \pm 0.16 \text{ Å}$, and was the same everywhere each time we cleaved the material, indicating S termination. The inset in Figure 4.9(a) shows a constant-current topograph of a step edge with height $c = 8.1 \text{ Å}$. This is consistent with the expected interlayer height of 8.07 Å between Zr-S bilayers.\textsuperscript{121}
Figure 4.9: The atomic and electronic structure of as-cleaved ZrSiS. (a) Constant current topography of the ZrSiS surface at 4.5 K ($I = 1.0$ nA, $V = 0.750$ V) Inset: Edge-on topograph showing the height of a step edge. (b) $dI/dV$ spectrum (blue) acquired on pristine ZrSiS and the calculated LDOS (purple). The calculated band structure along three high-symmetry directions is shown for comparison.
Shown in Figure 4.9(b) is the comparison of our STS data with a calculated LDOS from the tip S and Zr atoms. Our experimental data is shifted by -45 meV with respect to the calculated LDOS, but is in good qualitative agreement. This shift is likely caused by local doping from the atomic defect. The most important feature of each spectra is the dip in intensity near 0 meV, which has been attributed to the vanishing DOS at the line node by other authors. We compare the spectral features to the calculated band structure (spectral surface weight) of ZrSiS, shown in the right side of Figure 4.9(b), which is plotted for three high-symmetry directions. The sharp, dark blue features are pure surface states, while the broader, more diffuse features are projected bulk states. Inspecting this calculation shows there are many overlapping bulk and surface bands near the \( X \) point between energies 25 meV and 75 meV, preventing a clear identification of the line node in both \( E \) and \( k \). Therefore, a single STS spectrum is insufficient to identify the position of the line node and we use QPI to get more detailed information about the electronic structure.

We first locate defects in the ZrSiS crystal from which we can observe QPI. Shown in Figure 4.10 is a constant current topograph showing a variety of point defects in ZrSiS. Three prominent defect types are shown in the insets. The identity of these defects, whether they are adatoms, interstitials, or vacancy defects, is unknown (with exception, perhaps, to the top inset which looks like a surface vacancy). However, they all feature some highly symmetry standing waveform within their near vicinity, which is a signature of interfering quasiparticles. We focused on a single defect type, whichever was the most common, for our study in case we needed to remove the sample to re-cleave it. We decided on the middle defect of the three insets as it could reliably be found at almost all areas we approached with the STM tip.
Figure 4.10: **Single atomic defects in ZrSiS.** STM topograph of as-cleaved ZrSiS at 4.5 K acquired in constant-current mode. The image shows a variety of single atomic defects in the crystal. (Insets) Higher magnification images of three different defects. The scale bars are each 1 nm. Figure adapted from Lodge, et al.\textsuperscript{100}

\subsection*{4.5.2 Energy evolution of QPI}

Symmetrized QPI patterns for a variety of energies in both the (a) occupied and (b) unoccupied states are shown in Figure 4.11. The high-symmetry directions are indicated in the first panel of (a). Observed in all QPI patterns is the Bragg peaks, appearing as dark circles in the center of each panel edge, corresponding to the square atomic lattice. In the context of QPI, there are
several trends that we observe for the respective occupied and unoccupied states. QPI patterns of the occupied states all show a faint, square-shaped outline on the perimeter of the pattern, as well as the thin outline of a four-armed cross centered in the middle of the pattern. However, in the unoccupied states, the majority of \( q \) vectors within the central cross pattern exhibit a high-degree of scattering intensity. In addition, the unoccupied states show broad areas of scattering intensity in the directions of the Bragg peaks, between adjacent arms of the central cross pattern. Since the scattering intensity depends of the initial and final quasiparticle \( k \) states on the respective constant energy contours, we should be able to infer information about the band structure. In addition, we can track the position of QPI features as a function of \( E \) in order to determine any dispersion relationships.

Figure 4.11: **Energy evolution of experimental QPI from a single defect.** Quasiparticle interference patterns from a single atomic defect for both (a) occupied and (b) unoccupied energy levels. High symmetry points are indicated in the left panel of (a).
Figure 4.12: **Interpretation of QPI features above and below the line node.** (a) Calculated band structure in the Γ– M direction in the vicinity of the line node showing three possible sets of interband scattering vectors at $E = 200$ meV (black dashed line). (b) Experimentally derived QPI pattern at $E = 200$ meV with the scattering vectors from (a) correlated with features in the QPI pattern. (c) Calculated band structure along the same direction as (a) below $E_F$ (well below the line node). Two scattering vectors are indicated for $E = -200$ meV (black dashed line). (d) Experimentally derived QPI pattern at $E = -200$ meV, with the scattering vectors from (c) correlated with features in the QPI pattern.
4.6 Interpretation

4.6.1 Identifying scattering features in ZrSiS

In order to gain a qualitative understanding of the features observed in our QPI patterns, we appeal to the SSW calculations in the \( \Gamma - M \). Figure 4.12(a) shows \( E(k) \) in the unoccupied states, centered at 200 meV, in the vicinity of the expected line node. From the calculation, we expect there to be a parabolic projected bulk state centered at \( \Gamma \) that exists above 200 meV. Additionally, we expect two sets dispersing projected bulk bands near both \( M \) points. Quasiparticle scattering in the \( \Gamma - M \) direction should occur within, and between any of pair of, projected bulk state dispersions. We see that there are many such projected bulk states available for scattering. Black, yellow, and orange arrows indicate three sets of possible \( q = k_i - k_f \) vectors. In principle, yellow states with \( k_i \) on one side of the \( \Gamma \) point can have \( k_f \) in a black state on the other side of \( \Gamma \); these transitions were not drawn in the figure in order to emphasize the \( k \) gap between the dispersing bulk projections on both sides of \( \Gamma \), but they are expected to occur. No transitions can begin nor end at points in the \( k \) gap, so we expect a \( q \) gap to occur that widens with increasing \( E \).

The set of all actual \( q \) vectors at \( E = 200 \) meV is shown in Figure 4.12(b). Much of the scattering within the cross shape is explained by the projected bulk states. The ring of scattering intensity near the center of the QPI map makes sense in the context of intraband scattering within the projected bulk bands and between neighboring ones. At larger \( q \), we see the effect of interband scattering between the black and yellow arrows in the figure. Indeed, we also see the results of the \( k \) gap opening up between the black and yellow arrows. However, we expect to see a reasonably large \( q \) gap owing to the large \( k \) gap in the SSW in the vicinity of the \( \Gamma \) point. Instead, we observe nearly continuous scattering intensity throughout the cross structure in QPI. Two explanations for this are that the parabolic state at \( \Gamma \) is lower in energy that calculated, or that the dispersing bulk projections have a wider range of \( k \) than anticipated in this region. The QPI features adjacent to the arms of the cross shape seem to originate from both inter- and intra-Brillouin zone scattering.
between bulk projections. The suppression of scattering between the two sets of features, contributing to the outline of the cross shape and the diamond shapes between the arms of the cross, is attributed to the observed $k$ gap in inter-Brillouin zone scattering. Scattering between surface states is obscured, somewhat, by the projected bulk states simply because they consist of much narrower bands. However, we do expect them to contribute to the size of the $q$ gap, which will be explained later.

We also analyze the scattering features in the occupied states. Figure 4.12(c) shows the calculated SSW in the $\Gamma - M$ direction for the occupied states, centered about $E = -200$ meV. In this region, the projected bulk states overlap significantly with one another. As a result, there is a much narrower range of $k$ values that contribute to scattering. This is clearly observed in the QPI shown in Figure 4.12(d), wherein the QPI patterns show sharp, narrow line features with either large $q$ or small $q$.

Since we are measuring scattering phenomena, we may also observe the effect of scattering selection rules on the QPI patterns. In order to accomplish this, we appeal to QPI simulations using two different theoretical models that represent, respectively, the cases for minimal and maximal $k$ mixing. The first is the joint density of states (JDOS) model. JDOS does not make any assumptions about spin, orbital or pseudospin composition of electronic states. In this model, quasiparticles are scattered between any two points on the Fermi surface with a weight given purely by the respective initial and final densities of states, not by pseudospin polarities or other quantum degrees of freedom. In that sense, the JDOS can be regarded as the limit of maximal mixing of different quantum degrees of freedom. The second model is the T-matrix method, which accounts for both orbital and spin composition, in addition to complex matrix elements and impurity structure, which can cause quantum interference effects absent in the JDOS. The T-matrix model considered here sets $T = 1$, which perfectly preserves the quantum degrees of freedom. While we do not expect either model to perfectly describe our data, they are instructional references in understanding it.
Figure 4.13: **Comparison of experimental QPI patterns with theory and observation of line node splitting.** (a–d) Experimentally-derived QPI patterns at selected energies above and below $E_F$. (e–h) T-matrix calculations of the QPI patterns depicted in (a–d). (i–l) JDOS calculations of the QPI patterns depicted in (a–d). The red ellipses in (d,h,l) highlight the line node splitting. Figure adapted from *Lodge, et al.*\(^\text{100}\)

Figure 4.13(a-d) shows the evolution of four experimentally-derived QPI patterns within $\pm200$ meV of the Fermi level. Noted in panel (g) are the $q$ gaps (red ellipses) that we have attributed to the line node opening. We compare these to both T-matrix calculations in (h–k) and JDOS calculations in (l–o), with emphasis on the $q$ gap feature. We expect that only two of the
four possible scattering processes between the two Dirac bands on opposite sides of the Brillouin zone are possible.\textsuperscript{100} That is, only scattering from inner and inner, or outer to outer, bands should be allowed in order to conserve the pseudospin degree of freedom. As such, the $q$ gap depends heavily on the topological nature of the line node, unless the topology is locally destroyed somehow in the vicinity of the impurity site. Since the splitting is evident in the T-matrix simulation, which preserves pseudospin, and is not evident in JDOS, we conclude that our experimental data is consistent with pseudospin conservation at these energies.\textsuperscript{100,128}

### 4.6.2 Identification of the line node

Our strategy to identify the line node begins by looking at the dispersion of the scattering features in the $\Gamma - M$ direction. Plotted in Figure4.14(a) are the line cuts through all the QPI patterns along the $\Gamma - M$ direction as a function of energy from $E = -375$ meV to $E = 650$ meV. Shown in panels (b) and (c) are, respectively the calculated dispersions from T-matrix and JDOS. In the measurement, I note again the lack of data in the $E$ range of $\pm 100$ meV of $E_F$ due to the concern about crashing the STM tip into the sample. In (a), the white ellipse highlights the expected suppression of scattering due to the presence of the $k$ gap. This split seems to persist from 100 meV up to 250 meV, above which it disappears. This is interpreted as the preservation of pseudospin up to $E = 250$ meV. Outside of this energy range, our measurements no longer resemble the T-matrix calculation. Indicated with red arrows in (a) are two dispersing features far above $E_F$, one with relatively weaker intensity, that closely follow each other. In addition, there is a very strong, non-dispersing feature extending through all measured energies below $E_F$. Also plotted are the scaled dispersions before $E_F$ from ARPES\textsuperscript{109} measurements for a visual guide. Neither the secondary dispersing feature above $E_F$ nor the non-dispersing feature are predicted by the T-matrix calculation. However, JDOS does reproduce similar features, suggesting that these features originate from a scattering process that does not conserve pseudospin. Evidently, the particular defect we investigated possesses a nontrivial scattering potential and selectively lifts
the topological protection of certain scattering phenomena at some energies away from the line node. This kind of impurity is expected to cause additional scattering and limit the quasiparticle mean free path in transport.

Figure 4.14: **Dispersion of QPI along the \( \Gamma - M \) direction.** (a) Dispersion derived from experimental data. Red arrows at the top of the panel highlight two dispersing features above \( E_F \). The red arrow at the bottom of the panel indicates the presence of a single nondispersing feature before \( E_F \). The dashed, white ellipse highlights suppression of QPI scattering in the vicinity of the line node. Two dashed, white lines below \( E_F \) show the expected dispersion from previous ARPES measurements. (b) T-matrix calculation of the dispersion from (a) from an isotropic scatterer. (c) Joint density of states calculation of the dispersion in (a). Red arrows highlight two dispersing features above \( E_F \) and a nondispersing feature below \( E_F \), similar to features observed in (a). (d) Position of the intensity maximum from (a) for the bright dispersing feature above 100 meV and the nondispersing feature below -100 meV. The lines are linear fits to the intensity maxima above 300 meV and below -100 meV, respectively. Figure adapted from Lodge, et al.

With the dispersion plotted, we are now poised to locate the \( E \) and \( q \) positions of the line node. Figure 4.14(d) shows a plot of the local maxima of the dispersing and nondispersing features
from (a) as a function of $q$ in units of Å$^{-1}$. Fitting a line of the form $y = mx + b$ to the data above $E = 300$ meV yields a Fermi velocity of $\hbar v_F = 2.65 \pm 0.10$ eV Å in this region. This is much lower than the value of $\hbar v_F = 7.1$ eV Å below $E_F$ determined by ARPES in the $\Gamma - M$ direction. This difference is attributed to the nonlinearity transition of the surface bands at high energies, which is reflected in the SSW calculation from Figure 4.12(a). From the JDOS dispersion in Figure 4.14, the non-dispersing feature should be at the correct $q$ position of the line node. We estimate this position to be $q = 0.98 \pm 0.05$ Å$^{-1}$. Extrapolating the dispersive from 300 meV to the line node’s $q$ position places the energetic position of the line node in the $\Gamma - M$ direction at $E = 140 \pm 40$ meV. Note that this value is higher than the estimate value of 45 meV obtained from the LDOS calculation in Figure 4.9(b). The higher energy results from the anisotropy of the $E$ position of the line node, which can be seen from the SSW calculation in Figure 4.9(b); the line node in the $\Gamma - M$ direction is expected to be higher than the in the $\Gamma - X$ direction. Additionally, the LDOS calculation is insensitive to the particular $k$ values; overlapping the line node in the $\Gamma - M$ direction are many other states, some of which can be seen in the $\Gamma - X$ direction.

As a final note, I would like to comment about the possibility of the nondispersing feature below $E_F$ results from a feedback-related artifacts originating from our constant-current mode data acquisition. In Figure 4.15 we compare data acquired in constant height (left) and in constant current (right) mode, and for a different defect of identical type as the one studied in the rest of the data. Notably, a non-dispersive feature in the valence band is present in both data sets, supporting our conclusion of effective pseudospin-flip scattering.
Figure 4.15: **Closed versus open loop feedback**. (Left) Open loop feedback acquisition and (Right) Closed loop feedback acquisition. Each dispersion was measured on a different defect of an identical type. Both data sets show a single non-dispersing $q$ vector below $E_F$, indicating effective pseudospin scattering.
APPENDIX A: PROCEDURE FOR BAKEOUT OF QCM CHAMBER
1. Load QCMs into the QCM mounts and secure the K-type thermocouple near the QCMs.

2. Bolt the vacuum components together and ensure the chamber is vacuum tight. One may check for leaks by spraying isopropyl alcohol on targeted joints and monitoring the pressure. If necessary, the residual gas analyzer (RGA) may be installed and operated in continuous mode, checking for leaks by spraying joints with gaseous helium. Consult the RGA manual for instruction on proper usage.

3. Thoroughly wrap chamber with heater tape.

4. Insert heater tape into the LN$_2$ reservoir to ensure that QCM mounts and QCMs get baked out properly.

5. Completely cover chamber with aluminum foil.

6. Divide the heater tapes amongst two power strips and plug each power strip into a separate Variac. Ensure the Variacs are plugged into two different electrical circuits to prevent tripping a circuit breaker.

7. If not already done, pump entire chamber to at least rough vacuum.

8. Switch on turbopump and set Variacs to $\sim 30\%$ to begin heating to $\sim 180^\circ C$ as measured by the thermocouple.

9. Bake the chamber for $\geq 60$ hours.

10. Shut off the Variacs.

11. While the chamber is still hot, outgas the e-beam evaporator following the procedure in the OS-VAP manual.
APPENDIX B: LABVIEW 8.2 CODE FOR QCM DATA ACQUISITION
Shown here is the LabVIEW code used to acquire QCM frequency and ring down data, in addition to temperature. Prior to using this code, it is assumed that the user has already switched on the power supply that drives the Clapp oscillator circuits and that both QCMs are oscillating. This power supply is not controlled by the LabVIEW program. The measurement logic shown here begins by initializing the Tektronix TDS2024B oscilloscope, the Agilent 53220A frequency counter, and the UNI PS-3305U power supply (switch PSU) that is used to trigger the reed relay switch to output the QCM signal to the oscilloscope. Data acquisition begins with a single ring down measurement on both QCMs as well as temperature, then the program proceeds to sequentially measure the frequencies and amplitudes of both QCMs 10 times each before the next ring down measurement. During the first frequency/amplitude measurement of the loop, temperature is also measured. The ring-down, frequency and amplitude, and temperature measurements are looped an arbitrary number of times.

Due to the graphical nature of the LabVIEW code, the QCM measurement code is separated into two figures. Figure B.1 shows the instrument initialization and ring down measurement, as well as the accompanying temperature measurement. Figure B.2 shows the sequential frequency measurements and temperature measurement nested inside a for loop. The ring-down and frequency/amplitude measurements are placed inside the first and second panels, respectively, of a flat sequence. This flat sequence is placed inside of a while loop that repeats until some condition is satisfied, or the user manually terminates it.
Figure B.1: **LabVIEW code: Instrument initialization and QCM ring down measurements.**

Figure B.2: **LabVIEW code: QCM frequency measurements.**
APPENDIX C: LOGIC FOR AUTOMATED QPI ACQUISITION
For reasons beyond my control, the LabVIEW code for QPI data acquisition is not shown here. Instead, I provide an overview of the logic employed in LabVIEW to automatically acquire QPI data via $dI/dV$ mapping in constant current mode. Due to the repetitive nature of the data acquisition, the logic is employed as a loop. Prior to utilizing this logic, the user is assumed to have already (1) located an appropriate area for QPI data acquisition, (2) be tunneling, (3) set the size, in nm$^2$, of the scan area and the number of pixels for the scan frame, and (4) have the lock-in signal switched on.

1. Move tip several nm away from the sample (∼5 nm)

2. Position the tip at a location coincident with a corner of the scan frame.

3. Set an appropriate value for $V_{\text{sample}}$

   (a) If this is the first iteration of the loop, set $V_{\text{sample}}$ to the desired starting value

   (b) If this is any other iteration of the loop, increment $V_{\text{sample}}$ by $\Delta V_{\text{sample}} = V_{\text{LI}}$, where $V_{\text{LI}}$ is the RMS value of the lock-in signal amplitude.

4. Engage the feedback loop and approach the surface to establish the tunneling current.

5. Wait 10 seconds.

6. Begin either an up scan or down scan, whichever requires the least tip movement, and acquire simultaneous topographic and $dI/dV$ maps.

7. After data acquisition, save the output file to a folder

8. Repeat from Step 1 until desired final $V_{\text{sample}}$ is reached
APPENDIX D: PYTHON 2.7 SCRIPT FOR QPI ANALYSIS
One of the most helpful bits of the Nanonis software’s Help file is the inclusion of a Python 2.7.X script written by Felix Wahlisch, as well as a comparable MATLAB script, for importing data from .sxm files into Python. The python class below processes the data from Felix’s script, which is not reproduced here, to generate drift-corrected 2D fast Fourier transformations of real-space dI/dV maps. One must pass the script values for nametag, refSym, and rotSym as input. Since we are interested in 2D FFT of the dI/dV maps, we pass nametag = "LI_X_1_omega_fwd" or "LI_X_1_omega_bwd" but we may well pass "Z_fwd" or "Z_bwd", instead, if we wish. Additionally, refSym = 'yes' or 'no' to indicate the inclusion or exclusion of reflection-averaging. Also, rotSym = 0, 2, or 4 to denote averaging over 0, 2, or 4 rotations of the data. For symmetrization, the script shown below is suitable for data that exhibits 2 or 4-fold rotation symmetry and nothing else. Once the 2D FFT is found, it can be used to generate a figure. I direct the reader to Felix Wahlisch’s script, if he or she has access to it, for a simple way to do this. If not, then the reader is encouraged to read more about the *pylab.figure()* routine.

I also show a separate python class that this script calls in order to do the rotation averaging. This class takes the numpy array *Marray*, as well as an angle *Mtheta*, in degrees, as input and returns the rotated array.

**2D FFT Class**

```python
import numpy as N
import pylab as P
from scipy.misc import imrotate
from scipy.ndimage.interpolation import affine_transform

def create_fftD2(self, nametag, rotSym, refSym):
    global F_magZ
    global F_phaZ
    global zoomPix
```
"""generates fft image of signals whose name contains the nametag ."""

x_pix, y_pix = string.split(self.infos["SCAN_PIXELS"])
x_len, y_len = string.split(self.infos["SCAN_RANGE"])
x_len = float(x_len)
y_len = float(y_len)
x_len *= 1e9 #convert to nm
y_len *= 1e9 #convert to nm
x_pix = int(x_pix)
y_pix = int(x_pix)
Fs_x = 1/x_len #[1/nm]
Fs_y = 1/y_len #[1/nm]
zoomPix = 150
zFs_x = zoomPix*Fs_x
zFs_y = zoomPix*Fs_y

# Apodizing edge mask to make real-space image go to zero at
# edges and prevent
# Bragg peak streaking in the 2D FFT

cospace = (N.cos(N.linspace(-N.pi,N.pi, int(x_pix)))+1)/2 #cosine filter
cosarray = N.array([cospace]) #cosine filter
ccfilt = N.transpose(cosarray)*cosarray #cosine filter

for i in self.signals:
    if nametag in i.name:
        print "create_fftD2(): creating", i.name, "2D FFT image..."
# Rotate and skew process the data

```python
i.data = imrotate(i.data, -18, interp='bilinear')
theta = N.deg2rad(3)  # change from degrees to radians
zSkew = N.array([[1, N.tan(theta)], [0, 1]])
i.data = affine_transform(i.data, zSkew, order=2, output=
    float, prefilter=False)
```

# Squeeze along x

```python
zSqueeze = N.array([[0.956, 0], [0, 1]])
i.data = affine_transform(i.data, zSqueeze, order=2, output
    = float, prefilter=False)
```

# Apply apodizing edge mask

```python
i.data = i.data * ccfilt
```

# Take 2D fft, subtract mean value first

```python
F = N.fft.fft2(i.data - N.mean(i.data))
```

# Find the mag and phase, and shift data to put 0 wavenumber at the center

```python
F_mag = N.abs(N.fft.fftshift(F))
# F_phase = N.angle(N.fft.fftshift(F))
# F_real = N.real(N.fft.fftshift(F))
# F_imag = N.imag(N.fft.fftshift(F))
```

# Zoom in to the center zoomPix by zoomPix pixels

```python
#Zoom in to the center zoomPix by zoomPix pixels
```
\[
\begin{align*}
F_{\text{mag}}(x_{\text{pix}}/2)-\text{zoomPix}/2:x_{\text{pix}}/2+\text{zoomPix}/2, \quad & \\
F_{\text{pha}}(x_{\text{pix}}/2)-\text{zoomPix}/2:x_{\text{pix}}/2+\text{zoomPix}/2, \quad & \\
F_{\text{rea}}(x_{\text{pix}}/2)-\text{zoomPix}/2:x_{\text{pix}}/2+\text{zoomPix}/2, \quad & \\
F_{\text{ima}}(x_{\text{pix}}/2)-\text{zoomPix}/2:x_{\text{pix}}/2+\text{zoomPix}/2, \quad & \\
F_{\text{mag}} &= \text{N.abs}(F_{\text{rea}}) \\
F_{\text{mag}} &= F_{\text{mag}} \quad \text{# no zoom}
\end{align*}
\]

# Find mean and std dev of the zoomed-in array

\[
F_{\text{mean}} = \text{N.mean}(\text{P.log}(F_{\text{mag}}))
\]

\[
F_{\text{std}} = \text{N.std}(\text{P.log}(F_{\text{mag}}))
\]

# generate rotation averaged FFT.

#******* Does not work for skewed STM data! *******

if rotSym == 2:
    print "create_fftD2(): creating", i.name, "2-fold rotation avg FFT image..."
    F_{\text{mag}} = (F_{\text{mag}} + a.Mrot(F_{\text{mag}}, Mtheta=180))/2

elif rotSym == 4:
    print "create_fftD2(): creating", i.name, "4-fold rotation avg FFT image..."
    F_{\text{mag}} = (F_{\text{mag}} + a.Mrot(F_{\text{mag}}, Mtheta=90) + a.Mrot(F_{\text{mag}}, Mtheta=180) + a.Mrot(F_{\text{mag}}, Mtheta=270))/4
else:
    True

# generate reflection averaged FFT

if refSym == 'yes':
    zRef = N.array([[1,0],[0,-1]])
    F_magZ2 = affine_transform(F_magZ, zRef, order=0, offset=(0,zoomPix), output=float, prefilter=False)
    F_magZ = (F_magZ + F_magZ2)/2
else:
    True

**Data rotation script for rotation averaging**

```python
def Mrot(self, Marray, Mtheta):
    Mtheta = N.deg2rad(Mtheta)
    zRot = N.array([[N.cos(Mtheta),-N.sin(Mtheta)],[N.sin(Mtheta),N.cos(Mtheta)]])
    marray = affine_transform(Marray, zRot, order=0, offset=(zoomPix,0), output=float, prefilter=False)
    return marray```
LIST OF REFERENCES


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