Investigating the time scales of electromechanical motion in graphene drumheads using pump-probe spectroscopy with STM

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Investigating the time scales of electromechanical motion in graphene drumheads using pump-probe spectroscopy with STM

Alana Gudinas

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Abstract

Scanning tunneling microscopy (STM) has transformed the field of condensed matter physics over the past few decades, allowing scientists to image materials at the atomic scale, manipulate individual atoms, and probe electronic states on the surface of materials. In recent years, there have been numerous developments to introduce time-resolved measurements to STM in order to probe atomic-scale dynamic processes and combine spatial and temporal resolution. Advances like THz-STM setups achieve femtosecond resolution, but require complex external setups. All-electronic pump-probe spectroscopy for STM (directly analogous to optical pump-probe spectroscopy) has been pioneered by Loth et al. [1], and newer applications [2] require only an arbitrary waveform generator to apply pump and probe pulses. In this thesis I describe a method of electronic pump-probe spectroscopy with STM to measure the time scale of mechanical deflections in graphene nanomembranes, and the results of a benchtop model experiment measuring the relaxation time of a red LED diode. I measured the upper bound of the relaxation time of the diode to be \( \sim 4 \) ns, and discuss the effect of electronic noise on the measurement. The method of pump-probe spectroscopy described in this thesis has the potential to revolutionize STM, as it provides a relatively low-cost method of introducing time-resolved measurements without requiring complex electronics or optical setups.
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1 Introduction

Scanning tunneling microscopy (STM) is a powerful tool for investigating the surface of materials, as it produces atomic-resolution images and probes local electronic states by measuring the tunneling current of electrons into the states at the surface of a material. However, most STM scans take minutes to produce, meaning that by nature STM only probes static electronic states. STM is too slow to capture dynamic processes on the surface of materials, such as atom and vacancy diffusion and magnetic spin relaxations, which can occur on extremely fast time scales ranging from milliseconds ($10^{-3}$ s) down to femtoseconds ($10^{-15}$ s). Measuring time-dependent atomic processes like spin relaxation is crucial for applications in quantum information [3, 4, 5], for example, and for understanding physics at the nanoscale [6].

For measurements of ultrafast dynamics, a now standard method called optical pump-probe spectroscopy has been successful in achieving femtosecond resolution. This measurement technique uses ultra short laser pulses separated by a time delay to excite a system and record its relaxation. The system is excited by a pump pulse, and the average time response of the system is mapped out by recording the response with a probe pulse over a range of time delays. Optical pump-probe spectroscopy has been used to successfully measure a range of ultrafast processes like the dynamics of photoexcited carriers [7], charge carrier lifetimes [8], and phonon processes [9], but is a method limited to the time domain, as it measures an average response over the $\mu$m diameter of a laser spot versus the sub-nanometer spatial resolution of STM.

What if we could achieve both temporal and spatial resolution? What physics can we uncover by probing the atomic dynamics on the surface of a material we can image with atomic resolution? Since the STM was invented in 1981 [10], various techniques and modifications have been employed to introduce time-resolved measurements to STM. Some include coupling THz pulses to the STM tip [11, 12], combining ultrafast lasers [13, 14], and atom-tracking techniques [15]. However, these methods either require complex external setups or do not allow for 2D imaging. In 2010 Loth et al. reported achieving nanosecond time resolution with a completely electronic pump-probe spectroscopy method that does not require an advanced external setup and can be realized with an arbitrary waveform generator (AWG) [1]. Recent applications of pump-probe spectroscopy require only a tunneling junction, an arbitrary waveform generator, and a lock-in amplifier, all of which do not interfere with the STM setup and can be easily added to existing systems [2].

All-electronic STM pump-probe spectroscopy has been used to measure spin relaxation times (the time it takes for an atom’s spin to drop from an excited state to the ground state) [1, 3], as well as the dynamics of individual atoms [16]. The method
described in this thesis is widely applicable to systems with an accessible time scale (in this case, nanoseconds), which is limited by the electronics used [2]. An ideal understudied target system is the mechanical motion of suspended nanomembranes, or single-layer (2D) materials on the nanoscale. Nanomembranes exhibit numerous interesting mechanical behaviors, such as nonlinear damping in mechanically-actuated oscillations [17], and, in the case of graphene, a breaking strength greater than steel [18], and can be strain-engineered to have specific electronic properties [19, 20]. Understanding the electromechanical properties of 2D materials is critical for applications in nanotechnology, photonics, and optoelectronics, as well as for the design of nanoelectromechanical systems (NEMS) for ultra-low mass sensing [21-23].

In this thesis, I report a design for an experiment to use pump-probe spectroscopy with STM to measure the relaxation time of electromechanical deflections in graphene nanomembranes. I describe the necessary sample preparation, a model benchtop experiment, and the results of pump-probe spectroscopy measurements on a LED diode.

2 Background

2.1 Time-resolved STM

Since the inception of the STM, researchers have sought to extend the microscope to the time domain in order to combine spatial and temporal measurements in a system. Doing so presents physical challenges, however, as conventional STMs take minutes to produce images, far slower than the atomic dynamic processes happening on the surface.

STM operates by using an extremely sharp metal tip to scan a surface of a material (Fig. 1). A bias voltage is applied between the tip and sample, which allows electrons to tunnel from the tip to the surface of the material through the vacuum potential barrier, generating a current. The tunneling current depends exponentially on the distance between the tip and the sample and is measured as the tip scans the surface, generating a topographic image with atomic resolution. By nature, STM only captures the stationary state of the surface it scans, as it averages out the dynamic response.

By design, the STM operates at low frequencies (~kHz). The tunneling current signal produced in STM is weak, in the range of a few dozen picoamperes to a few nanoamperes, so a preamplifier with a gain of about $10^9$ and a low pass filter is employed to measure the signal. The intrinsic time resolution of STM is then set by bandwidth of the preamplifier, since higher-frequency signals will be attenuated.
Figure 1: Diagram of the STM tunneling junction. The space between the tip and the sample is a potential barrier for electrons. When a bias voltage is applied, electrons have enough energy to travel through the barrier, generating a tunneling current. The current produced depends exponentially on the distance between the tip and sample (z). From afm.oxinst.com.

Thus, the fastest resolvable change on the surface of a sample is in the milliseconds range (1/1 kHz = 1 ms), much slower than the scale of atomic dynamics \[22\]. STMs with higher scanning speeds (200 frames/s) require specialized electronic and mechanical components and are only capable of achieving millisecond time resolution \[23\].

One modification of STM to extend measurements to the time domain is with THz pulses. In THz-STM, an ultrafast laser source generates THz pulses that travel in free space and are focused onto the STM probe tip \[11\]. The applied voltage is then a sum of the bias voltage and the time-dependent voltage of the THz pulses. The tunneling current is measured as a function of the THz pulses, resulting in a time-dependent signal capable of achieving femtosecond resolution. While THz-STM offers unprecedented access to both spatial and temporal scales, it requires a laser setup that is complex and not accessible to STM groups without optical expertise.

All-electronic pump-probe spectroscopy offers a non-invasive and relatively cost-effective way to integrate time-resolved measurements with STM. The method of pump-probe spectroscopy described in this thesis can probe atomic dynamics in the nanosecond range, and while not as fast as THz-STM and other setups, requires no modification of the STM and can be easily tested in a benchtop setting before being integrated with a STM.
Figure 2: Schematic of an optical pump-probe spectroscopy setup. The pump and probe pulses are separated by a time delay induced by their differing path lengths. After the pump pulse excites the sample, the probe pulse arrives and its transmission/reflection is measured by a detector after interacting with the sample. From: info.phys.tsinghua.edu.cn/zhou.

2.2 Pump-probe spectroscopy

Pump-probe spectroscopy generally refers to a method of making time-resolved measurements using a pump pulse to excite a system, then a probe pulse to measure the system response after a fixed time delay. By repeatedly cycling the pump and probe pulses over a range of time delays, the average response of the target system is measured as a function of time.

Optical pump-probe spectroscopy (schematic in Fig. 2) was the first method to use the scheme described above to measure ultrafast time-dependent processes with short laser pulses. In a typical optical pump-probe setup, a laser is split into two pulses: a pump and a probe pulse, which travel on different paths to the sample using mirrors. The pump pulse reaches the sample first and excites the sample, followed by the probe pulse after a time delay. The time delay separating the pulses is determined by their path lengths: by making the distance for one pulse to travel longer or shorter, the time it takes for the pulse to reach the sample is altered.

After the probe pulse hits the sample, its transmission or absorption is measured
by a detector, which indicates the state of the sample. If a system is excited by
the pump pulse and relaxes completely before the probe pulse arrives, the probe
pulse will be absorbed. If the system is still excited, some of the probe pulse will
be transmitted. By repeating this process over a range of time delays, the average
response of the system as a function of time is measured, because for each time
increment after the system is excited, its state is recorded [24].

To improve detection of weak signals, mechanical choppers were introduced to
modulate the pump and probe pulses [24, 25]. A mechanical chopper literally "chops"
a signal by allowing light to pass through it at a specified frequency. Imagine a
rotating disk with mechanical shutters: when the shutter is open, light can pass
through, and when it is closed, no signal is transmitted. Using a lock-in amplifier
measuring at the chopping frequency improves the signal-to-noise ratio because the
response from the pump and probe pulses alone will be "subtracted" out [24]. For
example, if the probe pulses are modulated at a certain frequency and the pump
pulses are constant, then a lock-in amplifier will measure the average response due
to the probe pulses, while the effects of the pump pulses alone are subtracted out
since they remain constant over the frequency cycle.

![Figure 3: a) Pump pulses (blue) and probe pulses (red) with time delay between them. b) Pulses with increased time delay. c) Pulse train (blue) with amplitude-modulating square wave (red). d) Changing the phase shift between pulses to change the time delay between them. Starting from left, the phase shift decreases and is zero in the middle when the pulses are simultaneous. Phase shift increases to right and the pulses are separated in time again.](image)

Electronic pump-probe measurements use the same scheme described above, ex-
cept with electronically-generated voltage pulses rather than laser-generated. In the
case of pump probe spectroscopy with STM, the bias voltage line is replaced with
the pump and probe pulses, and the tunneling current response is measured with lock-in detection. In the scheme proposed by Natterer et al. [2], an AWG is used to generate the pulses as well as modulate their amplitude for lock-in detection. Here, the pump pulse still excites the sample, and the probe pulse is used to "clock" the system after a known time delay. The probe pulses are amplitude-modulated, so that their effects are subtracted from the excitation signal via the lock-in (Fig. 3c). Since the pulses are generated in the AWG, the phase shift between the pump and probe pulses is adjusted to alter the time delay (Fig. 3d). The average current is measured for a range of time delays, and the response of the system is mapped out with a resolution approximately equal to the width of the pulses [22].

2.3 Mechanical behavior of graphene

Since graphene was isolated in 2004, the field of 2D materials has exploded, promising widespread applications in electronic devices and providing systems to explore novel physics [26, 27]. Much of the research surrounding 2D materials has been focused on their electronic properties, however, interest in characterizing the mechanical behavior of 2D materials has grown due to their potential applications in nanoelectromechanical systems (NEMS), devices that utilize both mechanical and electronic functionality in nanomaterials. A 2D material is a single atomic layer of a crystal. Though occupying 3D space, 2D materials are called so because their properties can be described by physics in two dimensions. There is no universal definition of nanomembranes, though they are often described as single-layer materials whose lateral dimensions are orders of magnitude larger than their thickness [27].

Electromechanical properties of 2D materials/nanomembranes are particularly interesting because electron mobility is confined to a surface rather than in three dimensions. This makes electronic properties in 2D materials especially sensitive to mechanical perturbations, as stress or strain in a 2D material can change the spacing between atoms, which in turn impacts how easily an electron can propagate through the material. Because of the relationship between mechanical and electronic properties, the mechanical characteristics of nanomembranes can be tuned to generate specific electronic behavior, for example, through strain-engineering.

Graphene has long garnered interest for both its unique mechanical and electronic properties. While graphene’s electronic properties have been well-characterized, its mechanical behavior still contains mysteries. Suspended graphene has exhibited interesting behavior such as: the appearance of nonlinear damping in oscillating membranes [17], strain-induced pseudo-magnetic fields [20], and vibrational modes arising from nonuniform stress [28]. Such phenomena make graphene an excellent
candidate for electromechanical applications, but it is crucial to further explore how changing the physical parameters of graphene affects its electronic structure.

Suspended graphene devices differ from typical graphene devices in that they contain regions where the graphene flake is not touching the substrate (see Fig. 4 for an image of a suspended graphene sample). These suspended regions are often called drumheads, since they can be mechanically actuated and exhibit vibrational modes. In STM experiments, the dominant force on suspended graphene no longer arises from the substrate, but from the STM tip: mechanical deflections in suspended graphene can then occur when the charged STM tip induces a combined electrostatic and van der Waals (vdW) force that overcomes the elastic force of the membrane and the vdW force between graphene and the substrate. The deflection depends on the material's stress and spring constant, and so can be probed in this way.

![Figure 4: Right: image of graphene flake suspended over a silicon dioxide substrate with etched circular holes. From [29]. Left: a) 3D representation of a free-standing graphene nanomembrane. An area of the membrane is lifted by the electrostatic static force caused by the lowering of the STM tip. c) Model of the mechanical motion of the membrane. From [34].](image)

Graphene drumheads can be tuned to be in either a concave or convex state, analogous to what a trampoline looks like when it is depressed versus lifting upward. As shown in Fig. 4, graphene "valleys" induced by the tip will change curvature as the tip distance decreases, creating a lifted region within the valley. Clearly a dynamic process, graphene’s mechanical behavior during the reversible lifting pro-
cess can be explored with pump-probe spectroscopy. Additionally, the hysteretic behavior shown in Fig. 11 (from [34]) could also be studied with time-resolved measurements to probe the evolution of the observed instability. The mechanical motion of graphene nanomembranes provides an excellent test system for time-resolved measurements, since we expect the deflections to occur on a larger time scale than other atomic processes, making it accessible for the equipment described in this thesis.

3 Methods

3.1 STM measurements

2D materials like graphene have been well-characterized using STM. In this section I will describe a standard STM measurement and how atomically-resolved images are obtained.

STM uses a bias voltage applied to a sample and a metal tip situated a distance above to measure the tunneling current of electrons between the probe and the surface. The vacuum separating the metal tip from the conducting sample acts as a potential barrier for electrons. When a bias voltage is applied, the electrons have enough energy to cross the potential barrier and tunnel into electronic states available at the sample surface. The electronic tunneling current depends exponentially on the tip-sample distance, making STM extremely sensitive to changes in the z-direction [10].

The metal probe tip is attached to three perpendicular piezoelectric transducers (for each spatial direction), which contract or expand proportionally to a voltage applied, changing the location of the tip. A STM image can be recorded in either constant current or constant height mode using a feedback loop with the piezoelectric voltages. In constant current mode, the tunneling current between the tip and the sample remains the same, and the piezodrive measures the voltage required to maintain a tip distance (z-direction) to keep the current constant. In constant height mode, the probe tip is held at a fixed distance from the sample and the tunneling current is recorded. In both modes, a topographic image is generated from the tunneling current data [10].

STM is also capable of making scanning tunneling spectroscopy measurements (STS) to probe the density of electrons on a sample surface as a function of their energy. In STS measurements, the STM tip is placed above a location on the surface. With the tip height constant, the tunneling current at that particular location is measured as a function of changing the bias voltage, since the energy of electrons in the sample depends on the voltage applied. STS measures the IV curve at a location
in the sample, and the local density of electron states (LDOS) is computed by taking the derivative (dI/dV) of the curve, which can be measured directly with a lock-in amplifier. The LDOS describes the density of electronic states available in a system [35].

Figure 5: a) Diagram of the model experiment circuit. The arbitrary waveform channels 1 and 2 are combined internally onto Ch. 1., which is the signal input for the diode. The output of the diode circuit is connected to the signal input of the lock-in amplifier. The sync output on the AWG is connected to the reference input of the lock-in to transmit the demodulation frequency. b) The diode rectifier circuit.

3.2 Benchtop model experiment

While it is simple in principle to integrate pump-probe spectroscopy with a standard STM measurement, an advantage of the pump-probe scheme described in this report is that the technique can be specifically tailored for STM experiments in a benchtop setting prior to the STM measurement. In this section I describe a benchtop model experiment with a test system to understand the mechanics and expected results of pump-probe spectroscopy.

One of the simplest test systems for pump probe spectroscopy is a diode, which has a nonlinear IV curve like the STM tunneling junction. The benchtop pump-probe scheme is almost identical to the STM set up, except the STM junction is replaced
by the diode circuit. This way, the experiment can be tested before being integrated into the STM.

The pump-probe spectroscopy experimental setup requires an AWG, a lock-in amplifier, and a test component with a nonlinear IV curve, in this case, a red LED diode (Fig. 5). In this experiment, I used a Keysight 33600A AWG and Signal Recovery 7270 lock-in amplifier. The Keysight AWG has a maximum frequency of 120 MHz and sampling rate of 1 GSa/s, with a minimum pulse width and rise time of 5 ns and 4 ns, respectively. The temporal resolution in the pump-probe setup is limited by the pulse rise time, so we do not expect to detect relaxation times below 4 ns.

3.2.1 Diode circuit

The purpose of the diode circuit in the benchop model experiment was to simulate the STM tunneling junction. The diode was chosen because it has a nonlinear IV curve like the tunneling junction, which is required for pump-probe spectroscopy measurements. Additionally, diodes are inexpensive and easily obtained, making them an ideal test system that can be transported and tested without fear of damaging it.

A nonlinear IV curve is required for pump-probe spectroscopy to ensure that the current response of the voltage pulses arriving simultaneously is greater than the sum of the currents from the pulses alone. This way, as the time delay between the pulses is decreased, an "excess current" is produced when the pulses overlap versus when they are separated [22]. The "excess current" contains the time-dependent signal, since it will be larger when a relaxation time is detected than when not. Nonlinear IV curves are shown in Fig. 6.

The benchtop experimental setup is shown in Fig. 5 along with the diode rectifier circuit. The diode circuit comprises a red LED diode, a 1nF capacitor, and a 47 Ω resistor. This rectifier circuit converts an AC voltage signal to a DC voltage output, which in this case are the AWG output and circuit response measured by the lock-in, respectively.

3.2.2 Diode dynamics

In the benchtop model experiment, I aimed to measure the relaxation time of the excited LED diode. In this section I review the underlying physics of a LED diode and the mechanics of its relaxation.

A LED diode operates using a semiconductor p-n junction (see Fig. 7). A p-n junction is created at the boundary where two semiconductor materials meet together. One side is positively doped with electron holes (p-doping), and the other
is negatively doped with electrons (n-doping). The positively charged holes and negatively charged electrons are attracted by the Coulomb force, and diffuse across the boundary to combine with each other. When the electrons and holes recombine, they leave behind their corresponding positive (donor atom) and negative (acceptor atom) impurities in the crystal. As a result, after the migrating holes and electrons have canceled out the free charges in the n and p-doped regions respectively, there are positive charges near the junction in the n-type material and negative charges near the junction in the p-type material. These ions are not mobile charge carriers and cannot move, while the remainder of the semiconductor is neutrally charged. The buildup of opposite charge impurities around the junction creates an electric field that opposes further mobile carrier diffusion from either side. The region around the junction where only donor and acceptor impurities remain is called the depletion layer; where the mobile charges are forced away by the electric field. This is the equilibrium state of the p-n junction [37].

In order for current to flow across a p-n junction, an external voltage must be applied across the junction to give mobile charge carriers enough energy to cross the potential barrier in the depletion region. In a diode, this is called the forward bias.
(see Fig. 7 for a diagram of the p-n junction in the presence of a forward bias). When a forward bias is applied, free electrons have enough energy to cross the depletion region, producing a current \[37\]. In the context of pump-probe spectroscopy with a diode, the pump pulse excites the system by giving mobile charge carriers enough energy to recombine and produce a current. After the pump pulse is applied, charger carriers can no longer move freely and the energy barrier increases again back to its state of equilibrium. When the probe pulse arrives after a time delay, the junction will have either reached equilibrium or still be in the process. Thus, by measuring the response of the diode with the probe pulse over multiple cycles with varied time delays, we can measure the relaxation time of the diode.

### 3.2.3 Arbitrary waveforms

Generating electronic pulses like the ones needed for pump-probe spectroscopy is simple; pulse generators are widely used in equipment testing to create rectangular
pulses. However, introducing time delays and modulation to a string of pump and probe pulses without adding more external equipment is challenging. An arbitrary waveform generator offers a simple way to create customized waveforms in a computer and save them in the AWG to be used in an analog system. A potential drawback of this method is the use of memory: generating a continuous string of pump and probe pulses with a full range time delays between them requires more storage than afforded in more basic AWGs. An elegant solution that offers both full control over pulse parameters and uses little computer memory is waveform sequencing.

Waveform sequencing is the consecutive execution of a series of predefined arbitrary waveforms to generate a continuous AC signal [2]. With waveform sequencing, individual pulses (which alone take up little memory) can be generated in a computer and sent as arbitrary waveform vectors to the AWG. The AWG then stitches together the arbitrary vectors to create a continuous waveform, producing an AC signal made up of the individual pulses being played over and over again. The advantage of using the AWG for waveform sequencing is that the arbitrary waveform parameters like amplitude and phase can be altered using the AWG controls, without having to recreate the vectors in a computer each time. A visualization of individual pre-defined waveforms being combined to form a larger signal is shown in Fig. 8.

The pump and probe pulses were generated using a MATLAB script written by collaborator Fabian Natterer. The program generates an array containing the pulse, which includes a rising edge, the width of the pulse, and a falling edge. The resulting array has zeros wherever the pulse is not applied, and ones where the pulse is at maximum amplitude. The pulse width is decided by the user, and a longer pulse corresponds to a longer array, since more entries are needed to define the pulse. Each pulse waveform is sent via USB connection to one of the two waveform channels on the AWG (Ch. 1 and Ch 2 outputs shown in Fig. 5). In the model diode experiment, the pump pulses were sent to Ch. 1 and the probe pulses to Ch. 2. Using the modulation function of the AWG, a square wave was applied to Ch. 2 modulating the pulse string amplitudes at a specified frequency. The square wave amplitude modulation (Fig. 3c) here is analogous to the mechanical chopper used in optical pump-probe measurements described in Sec. 2.2. The two waveforms (a continuous string of pump pulses and the amplitude-modulated probe pulses) were combined on Ch. 1 and used as the input to the diode circuit. The AWG has a convenient arbitrary waveform phase shift parameter, so to change the time delay between the pulses, I swept the phase shift of the pump pulses from -180° to 180° (Fig. 3d).

Modulating the probe pulses creates two cycles in the signal, an "on" and "off" cycle, where the probe pulses are nonzero and zero respectively (Fig. 3c). The lock-
in amplifier demodulates the signal at frequency of the cycles (Fig. 8a) by taking the difference in signal between the on cycle and the off cycle. A similar scheme was used in [2] and can be seen in Fig. 8b, where in cycle A the probe pulses are positive, and in cycle B they are negative. The purpose of the on and off cycles is to obtain a clean measurement with the lock-in where the effects of the pump pulse are subtracted out, leaving only the time-dependent signal contained in the probe pulse. This is achieved because the pump pulses are the same in both cycles, so when the lock-in takes the difference between the two cycles, the effects of the pump pulses are subtracted out.
3.2.4 Data acquisition and instrument communication

All instrument communication and data acquisition process are programmed in MATLAB. The Keysight AWG was connected to a computer via USB and communication was performed with a VISA-USB connection using the MATLAB "visa" function. The lock-in amplifier communications were performed with a TCP/IP connection using the MATLAB "tcipip" function, which required the lock-in to be connected to the internet with an ethernet port.

I sent commands to the AWG using SCPI commands described in the Keysight 33600a manual. Data acquisition for pump-probe measurements was performed by querying the X demodulator value from the lock-in amplifier at each time delay between the pulses.

4 Pump-probe spectroscopy experiment

In the proposed STM experiment (Sec. 5), we aim to measure the mechanical deflection relaxation time in graphene nanomembranes. In the model diode experiment (setup in Fig. 5), I measured the electronic relaxation time of a red LED diode. To first determine the excitation energy necessary for the diode, I measured the IV curve of the diode by sweeping a 50 mV, 200 Hz sine wave over a range of DC offsets, and recorded the diode response as a voltage using the lock-in amplifier demodulating at 200 Hz. The IV curve is shown in Fig. 6.

To measure the relaxation time of the diode, I used a 0.95 V pump pulse and a 0.6 V probe pulse to excite and probe the system. The probe pulse was chosen at a voltage where the diode response is zero, in order to not excite the system, and the pump pulse was chosen at a voltage where the diode exhibits a nonlinear response (see Fig. 6). The pump pulse was chosen at a low enough voltage such that when the pump and probe pulses arrive simultaneously (zero time delay), there is no risk of the combined voltage burning out the LED diode. I used pulses with the minimum 4 ns rise and fall times set by the AWG, and a pulse width of 10 ns. The probe pulses were amplitude-modulated with a square wave of 1007 Hz, and the frequency of the modulation was sent to the lock-in reference frequency input ("ref. in") via the "sync" output of the AWG (Fig. 5). The time delay between the pulses (set by the phase shift parameter in the AWG) ranged from -50 to 50 ns, corresponding to a decreasing and increasing time delay to and from zero ns, respectively. As seen Fig. 3d, the negative time delay results in the probe pulse arriving before the pump pulse, and after reaching zero, the positive time delay results in the pump pulse arriving first. The order of the pulses do not matter since they are being applied
continuously: the average diode response is recorded over many cycles of the pump and probe pulses, rather than its response to a single pair of pump and probe pulses.

The pump-probe response of the diode is shaped as a peak: the average response of the diode is zero when the time delay between pulses is greater than its relaxation time. As the pulses become closer the system is still excited when the probe pulse records the response, with the maximum signal occurring when the pulses arrive simultaneously. The results of pump-probe spectroscopy with the diode are shown in Fig. 9.

Figure 9: a) Pump-probe spectroscopy data for red LED diode. The blue curve is the measured signal, and the red curve is the left half the peak reflected over the y-axis to form a background signal. The maximum of the peak occurs when the pump and probe pulses arrive simultaneously. Inset is the full range of the pump-probe data, where ringing can be seen on the left side. b) Subtracted time-dependent signal with exponential fit.

The relaxation time of the diode was computed with the assumption that the time-independent signal of the diode is symmetric, meaning that the left side of the peak in Fig. 9 is the same as the right in the absence of a relaxation or when the relaxation is too fast to record. I then reflected the left (time-independent) half of the peak over the y-axis to form a symmetric peak. A background peak is necessary to extract the time-dependent signal from the pump-probe data because we have to
isolate the effects due to the voltage pulses alone. The "reflected" background peak is shown in red in Fig. 9a, along with the background-subtracted time-dependent signal in b. To compute the relaxation time, I fit an exponential curve to the time-dependent signal and extracted the time constant, $\tau$. I calculated $a = 0.0016 \pm 0.0002$, and $\tau = 4.421$ ns. Because of the uncertainty in the measurement due to electronic noise (described in Sec. 6), and the temporal resolution set by the rise time of the pulses (4 ns), this result sets the upper bound on the relaxation time of the diode to be $\sim 4$ ns.

An alternative method of acquiring a background signal is to use lower pump and probe voltages as to not excite the diode (even when the pulses overlap), so that the resulting peak contains no relaxation signal. However, in this experiment using lower voltages resulted in a much narrower peak that could not be used as a background. This is because at voltages where the diode is excited, as the time delay between the pulses decrease, the response recorded with the probe pulse begins to increase. This signal increase begins where the time delay is short enough that when the probe pulse reaches the diode, it is still excited. Conversely, at voltages that do not excite the diode, the increase in signal only occurs when the pulses start to actually overlap. Thus, at low voltages, the signal peak is narrower, since the peak only occurs once the pulses start touching and there is a combined signal larger than the individual pulses alone.

5 Proposed STM experiment

The methodology and model experiment outlined in Sec. 4 were developed with the intention of applying pump-probe spectroscopy to STM with a suspended graphene sample. The work done on this project has prepared the Hollen Lab at UNH for conducting the target experiment, and in this section I discuss some of the mechanics for the proposed experiment.

5.1 Methodology

With the STM, we hope to uncover the time-dependent processes governing the mechanical motion of suspended graphene. As shown in Fig. 11, interesting unstable and hysteretic behavior emerges in graphene’s mechanical deflections. With static measurements, we can only observe the deflection at fixed voltage points. Using pump-probe spectroscopy, we can measure the behavior in between these points, tracking the motion of the membrane as a function of time.
The Hollen Lab has an ultra-high vacuum RHK Technologies PanScan Freedom system, which includes a STM and four-point probe. With the graphene sample prepared, the next step in this experiment is using the STM to measure the IV characteristics of the suspended regions, as described in section 3.1. To start, a STS measurement will be made on suspended regions of the sample (site A in Fig. 10) to measure the IV curve and LDOS. The LDOS will also be measured in nonsuspended regions on the sample (site B in Fig. 10) for comparison. The applied voltage will increase the electrostatic force between the tip and the suspended membrane, causing the membrane to deflect upward towards the tip. The height between the tip and the sample is captured in tunneling current, so the IV curve will reveal the voltage amplitude required to excite mechanical motion in the membrane.

Changing the bias voltage will excite mechanical motion in the membrane, but it will also excite electrons on the surface, so that the tunneling current signal contains both the mechanical and electronic information in the sample. To isolate the mechanical motion, the electronic excitation of the membrane at the pump and probe voltages will be determined using the LDOS measurement described above by setting
the bias voltage to each of the pulse amplitude voltages. The difference in tunneling current as a result of both voltages will be known and after the pump-probe data is collected, the electronic response can be isolated from the mechanical response.

Figure 11: a) Images of a graphene nanomembrane with STM tip at different heights. There is unstable behavior between the valley and hill states. b) Tunneling current as a function of tip-sample height, showing hysteresis. d) Hysteretic switching. From [34].

The RHK system includes a R9 electronics box with BNC ports for each input/output related to the STM setup. To integrate pump-probe spectroscopy, the bias line should be replaced by the AWG signal, and the tunneling current should be measured with an external lock-in amplifier by connecting the signal output port on the electronics box to the signal input of the lock in. In order to switch between the DC bias line and the AWG output, a relay switch may be used. A schematic of the experimental setup is shown in Fig. 10.

Once the required pump and probe pulse amplitudes are determined from the IV curve on the suspended regions, the pulses can be created and sent to the sample with the AWG. When the pump pulse reaches the sample, the membrane will deflect towards the tip. When the probe pulse arrives, the tunneling current will be larger or smaller depending on the height of the membrane with respect to the tip. By
repeatedly exciting the membrane over multiple cycles (with different time delays) the time scale of the membrane relaxing back down towards the substrate will be mapped out. With this method we hope to investigate mechanical behavior like the reversible deflections shown in Fig. [4] and the hysteresis shown in Fig. [11].

5.2 Graphene sample preparation

To measure mechanical deflections in graphene nanomembranes, we must fabricate a sample with regions where graphene is completely suspended, meaning it has no contact with the substrate. This is typically achieved by placing a sheet a graphene flake on a substrate with etched holes or trenches, so that in the places where the substrate is partially etched away, the graphene remains suspended with its edges still adhered to the substrate (see Fig. [4]a for an example of graphene suspended on silicon dioxide with etched circular holes). Fabricating a suspended graphene sample presents challenges, as an etched substrate is structurally weaker than its whole counterpart. In this section I describe the successful fabrication process of a sample with graphene suspended on a nanoporous silicon nitride (SiN) substrate, our target system for pump-probe spectroscopy with STM. The fabrication was performed by Caitlyn Meditz, a Master’s student in the Hollen Lab, who developed a process to ensure that the graphene flake transfer process does not damage the holey SiN membrane.

The graphene was sourced from Graphenea, who manufactures high-quality monolayer graphene samples that offer an "easy transfer" onto substrates [39]. The SiN substrate was produced by SimPore, a silicon membrane technologies company that manufactures porous silicon substrate [40]. The SiN substrate (Fig. [10]) has an average pore size of 60 nm in diameter with a roughly 20% porosity (fraction of material with holes). The size and number of the holes in the SiN substrate ensure that even if parts of the graphene flake is damaged in the flake transfer process, there is a high chance some regions will be successfully suspended over the substrate holes. The graphene transfer instructions are provided by Graphenea and were modified by Meditz [39].

The Graphenea graphene flake came adhered to paper with a water-release polymer, and has another polymer layer on top. The graphene sample was placed in a shallow bowl of water to release the paper layer. The separated graphene sample remained in the water with a polymer layer facing upward. To ensure the silicon nitride membrane would not be damaged by the pressure of being submerged in water, the substrate was lowered perpendicularly (edge first) into the water using a clamp sitting on a mechanical lift. The stage was slowly lowered until only the top edge of
the substrate remained above the water, and then held very still as to not risk tearing the membrane. Using tweezers, the floating graphene flake was carefully navigated to the substrate. With the graphene just touching the edge of the silicon nitride, the mechanical stage was slowly lifted, so that as the substrate was pulled out of the water the flexible graphene membrane adhered to the SiN. This process resulted in a successful transfer of graphene onto the SiN substrate. The sample was then air dried and stored in vacuum for 24 hours before the top polymer layer was removed by soaking the sample in first acetone at 50°C for an hour, then in isopropyl alcohol at 60°C for an hour. While soaking, the sample was suspended perpendicularly in the liquid. In the last step, the sample was briefly soaked in water [39]. Optical microscope images showed that the graphene flake remained whole with only a few small tears (Fig. 10).

6 Discussion

From the results of the benchtop diode experiment, we can hone the pump-probe scheme to achieve cleaner, more accurate data in the proposed STM experiment. While promising initial results, the measured \( \sim 4 \text{ ns} \) upper bound on the relaxation time of the diode assumed the applied pump and probe pulses are symmetric, so that the left and right sides of the cross-correlation peak are also symmetric in the absence of a relaxation. In this section I discuss the validity of these assumptions, and potential ways to correct for the distortion of pulses traveling through an electronic transfer line.

6.1 Diode relaxation time

The shape of the pulses in pump-probe spectroscopy are extremely important, as the temporal resolution is determined by the rise and fall times of the pulses. This method relies on discretized pulses: we must know exactly when voltage is applied to the system, as well as the exact time delay in between pulses in order to measure an accurate time-dependent signal. In an ideal case, the pulses are exactly symmetric and there is no rise time, i.e. the pulse only has an "on" or "off" state. In reality, we are limited by the electronics and voltage pulses cannot be instantaneously applied; there must be some rise and fall time on either side of the pulse. Therefore, the smallest resolvable signal in time is equivalent to the minimum rise/fall times of the pulses.

Knowing exactly when the pulses excite the system relies on having symmetric pulses that are exactly zero-valued outside of the pulse range (the range includes the
rise time, pulse width, and fall time). Asymmetric pulses leads to an asymmetric cross-correlation peak: if the pulses contain noise on the left side and not the right, for example, the left side of the peak will contain more noise. This presents problems because it could lead to different excitations on either side of the peak. In the pump-probe scheme, we assume the excitation is the same on either side and only the falling side (the right side) contains the time-dependent signal as the pulses separate in time. I used this assumption in calculating the relaxation time in Sec. 4. However, as seen in Fig. 9, the pump-probe data contains more noise on the left side than on the right, indicating an asymmetry in the pulses.

A way to correct for the standing waves appearing in the cross-correlation peak is to perform a fast Fourier transform (FFT) on the data to see the dominant frequencies. By excluding the standing wave modes in the FFT data and performing an inverse transform, the noise in the signal will be improved, yielding a cleaner spectrum. However, in this case, at locations near the base of the peak it is unclear which components of the signal are from electronic noise, and which are part of the excitation and relaxation of the sample. For this reason, I chose not to perform FFT filtering of the data. The difficulty in distinguishing the time-dependent signal from the noise is due to the observed relaxation time having a value so close to the minimum rise time of the pulses. In systems with a longer relaxation time, like in the data presented in [1], separating the time-dependent signal from noise in the electronics is simpler. Because the diode relaxation time is so close to the electronic limitation, the measured relaxation time sets an upper bound on the real value, since a smaller relaxation time is not detectable by this setup.

6.2 Pulse shape distortion

Sinusoidal noise, or ringing, like that in Fig. 9 arises from the experimental setup, including the electronics and the length of cables used. Each junction in the setup, such as cable connections, present a risk of impedance mismatches, which can cause ringing in the signal due to reflections of the pulses. The noise introduced by the setup distorts the pulses, resulting in a change in amplitude and phase when the pulse arrives at the system versus when it is generated in the AWG. An example of pulse distortions is shown in Fig. 12, which were generated by connecting an oscilloscope with a BNC tee to the AWG output. The first column are pulses as they arrive from the AWG, the second is when the AWG output is connected to an open cable, and the third is when connected to the diode circuit. It is clear from the figure that the pulses are distorted by the electronics setup, resulting in a large asymmetry between the left and right sides. This is most obviously seen in the third row, where
Figure 12: Example of pulse distortion under different conditions. First column is the AWG output, second column is pulse distortion when output is connected to an open cable, and the third is when connected to the diode circuit. a) Pulses with 100 ns width. b) Pulses with 10 ns width. c) Pulses with 10 ns width, re-scaled time axis.

The transformation of an electronic signal through a connecting line is described by its transfer function. The transfer function is system-specific, since it depends on cable lengths, resistance, and other variables in an experimental setup. Knowing the transfer function for a given setup allows one to preemptively correct for the noise introduced by the electronics and cabling by performing "pulse-shaping". The AWG offers additional functionality in this regard, since we can generate an arbitrary waveform that, when combined with the pulse signal, offsets the fluctuations and results in the intended signal reaching the target system without distortion. This can be accomplished by measuring the transfer function of the system, i.e. how the signal is distorted, and then using waveform sequencing to create an "offset" waveform. Then, in the AWG, the original signal and the offset waveform can be
combined to correct for the distortions. Using a pulse-shaping technique is best practice for pump-probe spectroscopy measurements, as it ensures that the location and amplitude of the pulses is accurate [41].

7 Conclusion

This thesis describes the method of pump-probe spectroscopy, its integration with STM, and the results of a benchtop model experiment with a LED diode. I measured an upper bound on the relaxation time of the diode to be $\sim 4$ ns, obtained by using an arbitrary waveform generator and waveform sequencing to generate pump and probe pulses. I propose a future STM experiment in the Hollen Lab to measure the relaxation time of mechanical deflections in suspended graphene nanomembranes, using the methodology described in the benchtop diode experiment. The method of pump-probe spectroscopy described in this paper is easily integrated with STM, can be tested in a benchtop setting, and uses equipment that is far more accessible than that required for an optical pump-probe scheme. This method allows any STM lab with an AWG to perform time-resolved measurements, a powerful addition to the STM’s spatial capabilities. Temporal measurements are no longer limited to those with optical expertise and specialized circuitry, promising to revolutionize the study of atomic dynamics. I hope to see this tool become widespread amongst STM groups to increase their measurement capabilities and make progress towards understanding fundamental physical processes.

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