

Scanning Tunneling Microscopy

Nanoscience and Nanotechnology
Laboratory course "Nanosynthesis, Nanosafety and Nanoanalytics"
LAB2

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Experiment in room ENC B-0132
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1 Introduction

In this lab course, you will learn about scanning tunneling microscopy (STM).

For the invention of the STM, Heinrich Rohrer and Gerd Binnig received the Nobel prize for physics 1986 [1]. The STM operates by scanning a conductive tip across a conductive surface in a small distance and can resolve the topography with atomic resolution. It can also measure the electronic properties, for example the local density of states, and manipulate individual atoms or molecules, which are adsorbed on the sample surface. Some examples are shown in Figure 1.

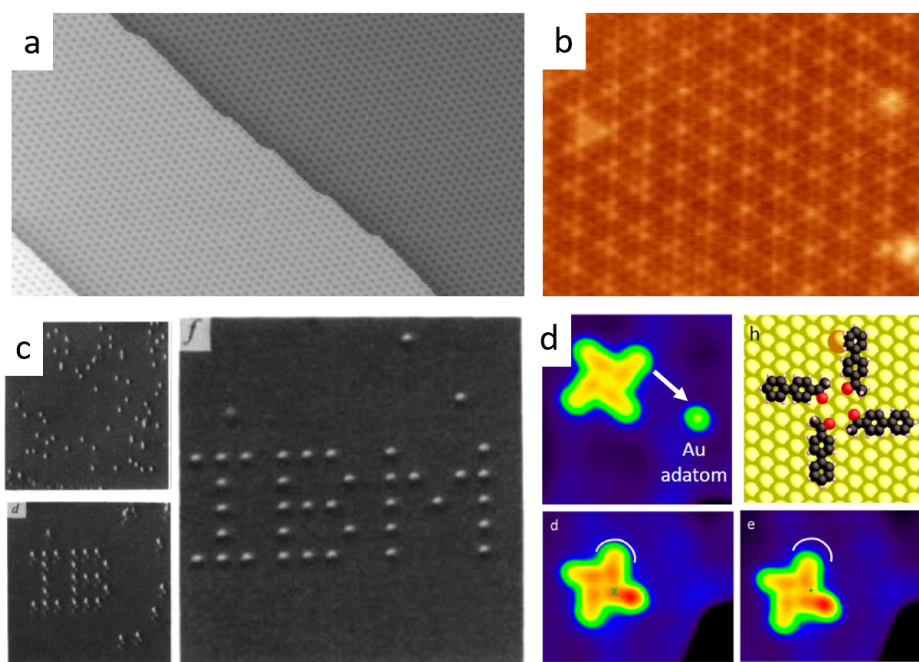


Figure 1: a) Graphene on Ir(111), Voltage $U=0.1\text{V}$; Current $I=30\text{nA}$ [2], b) NbSe₂ (showing atoms and a charge density wave (CDW)) [3], c) manipulation of Xe atoms on Ni(110). $U = 0.01\text{V}$; $I = 1\text{nA}$ [4], d) loading and transport of a single atom with a supra-molecular transporter. $U = 0.1\text{V}$; $I = 0.1\text{nA}$ [5].

Besides the usage of the STM, you will get fundamental insights into quantum mechanics, surface physics, image processing, and data analysis.

To fully understand and successfully conduct this experiment, you should have a good understanding of the basic knowledge of solid state physics, surface physics, STM theory, and organic chemistry beforehand. In this manual, the surface physics (Section 2) and STM concepts (Section 3) are briefly introduced. For basic solid state physics, please refer to any standard textbooks (e.g. Kittel or Ashcroft). It is recommended to read more on the

mentioned topics. The tutor finds the following literature very helpful:

Introduction to solid state physics, C. Kittel
Solid state physics, N. W. Ashcroft, N. D. Mermin
Surface science: an introduction, K. Oura, V. G. Lifshits, etc.
Introduction to scanning tunneling microscopy, C. J. Chen
Theory of scanning tunneling microscopy, lecture note of S. Lounis

2 Surface Science

Any ensemble of matter in nature is finite and its boundary is the surface. Surfaces provide a hint towards the geometric and electronic properties of the bulk and offer interesting physics and chemistry. These include for example heterogeneous catalysis, self-assembly, surface reconstruction, surface states, charge density waves, and adsorption. Investigations occur at the interface of two different phases, which can be solid-liquid, solid-gas, solid-vacuum, or liquid-gas. STM is capable of measuring solid-liquid, solid-gas and solid-vacuum interfaces. In this lab course, you will have the opportunity to study the solid-gas and solid-liquid interface. As a solid, graphite be used, which is described in Section 2.2. But first, let us talk about crystallography in two-dimension (2D).

2.1 2D crystallography

First, recall some concepts of three-dimensional crystallography. An ideal crystal is formed by an infinite repetition of identical groups of atoms. The group of atoms is called the **basis**. The set of points to which the basis is attached to is called the **lattice**. (**crystal** = **lattice** + **basis**.) Equivalently, as a geometric abstraction, the lattice can be defined by three fundamental **translation vectors** $\vec{a}_i (i = 1, 2, 3)$ such that the atomic arrangement of a crystal looks exactly the same when viewed from the points \vec{r} and \vec{r}'

$$\vec{r}' = \vec{r} + n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3,$$

where $n_i (i = 1, 2, 3)$ are any integers. Based on symmetry, Auguste Bravais concluded that only 14 types of lattices exist in 3D (**Bravais lattice**). This number reduces to 5 in 2D.

Any geometrical area (containing one or several lattice points) that can tile the plane (without gaps or overlap) is a **unit cell**. A unit cell with only one lattice point (i.e. minimum area) is a **primitive unit cell**. A special primitive unit cells are the one spanned by the three vectors \vec{a}_1 , \vec{a}_2 , and \vec{a}_3 . The **Wigner-Seitz cell** is the one formed by drawing lines from a given point to all others, and then constructing the perpendicular bisectors of these lines. The smallest enclosed area around the starting point is then the Wigner-Seitz cell (Figure 2a).

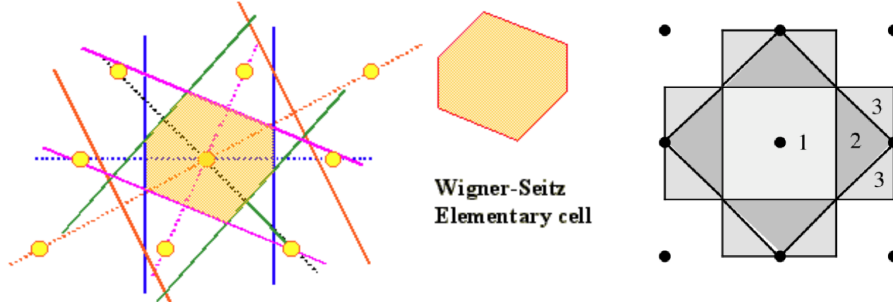


Figure 2: (a) Schematic diagram illustrating the construction of the Wigner-Seitz cell. (b) The first three Brillouin zones of a 2D square reciprocal lattice.

We have seen that a crystal is invariant under any translation of the form $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$. Any local physical property of the crystal, such as the charge concentration $n(\vec{r})$, is invariant under \vec{R} , i.e. $n(\vec{r} + \vec{R}) = n(\vec{r})$. (Please note that the wave function has no such invariance. Think about why, and answer it in the report). Now recall your mathematical analysis course (Fourier analysis), the charge concentration can be also expressed as

$$n(\vec{r}) = \sum_{\vec{G}} n_{\vec{G}} \exp(i\vec{G} \cdot \vec{r}),$$

where $\vec{G} = v_1\vec{b}_1 + v_2\vec{b}_2 + v_3\vec{b}_3$, is a vector of the **reciprocal lattice**. The primitive vectors $\vec{b}_i (i = 1, 2, 3)$, are related to the primitive vectors of the Bravais lattice as follows:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}, \quad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_2 \cdot \vec{a}_3 \times \vec{a}_1}, \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_3 \cdot \vec{a}_1 \times \vec{a}_2}.$$

Unlike the pure math convention you might remember, we normally include, in solid state physics, the 2π in the reciprocal lattice vectors for convenience.

Similar to the Wigner-Seitz cell in the real space, we can now construct the Brillouin zones in the reciprocal space (Figure 2b). The **1st Brillouin zone (1BZ)** is then the Wigner-Seitz cell of reciprocal lattice. The introduction of reciprocal lattice and Brillouin zones comes very handy when we deal with momentum in crystals (diffraction, electronic, and thermal properties).

In 2D, we just need to set the third primitive translation vector \vec{a}_3 to be the normal vector \hat{n} perpendicular to the 2D plane (the plane \vec{a}_1 and \vec{a}_2 are in). The reciprocal lattice vectors are

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \hat{n}}{|\vec{a}_1 \cdot \vec{a}_2|}, \quad \vec{b}_2 = 2\pi \frac{\hat{n} \times \vec{a}_1}{|\vec{a}_1 \cdot \vec{a}_2|}.$$

2.2 Graphite

Graphite consists of carbon atoms, which form layers that are stacked on top of each other. The carbon atoms within a layer are bound by strong

covalent bonds, while the bonding between the layers occurs via the weaker **van der Waals bond**. The carbon atoms in one layer are organized in a **honeycomb lattice** as shown in Figure 3a and b. Pay attention to the values in the figures. They will be used in data analysis.

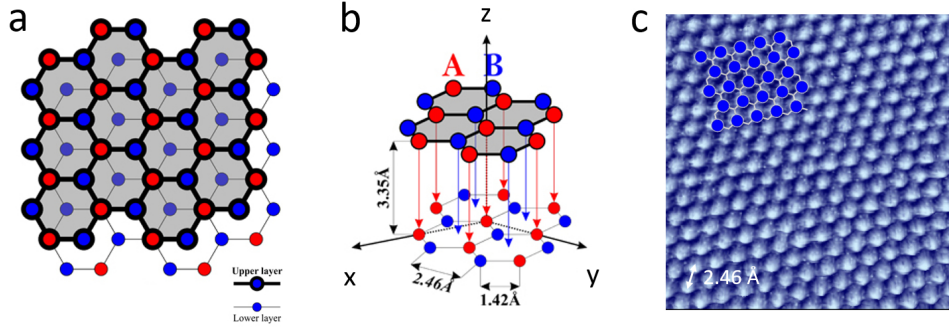


Figure 3: Atomic structure of graphite. a) Top view , b) 3D [17], c) STM image of graphite with atomic resolution[13].

One layer alone is called graphene, which is the prototypical 2D material, that has peculiar electronic properties differing from graphite and for which the Nobel prize in physics was awarded in 2010.

Graphite is commonly used to calibrate the STM as the atoms can easily be imaged and the surface is inert. In comparison to the naturally occurring graphite, synthetic highly oriented pyrolytic graphite (HOPG) is used as individual graphite crystallites are well aligned with each other. In Figure 3c a topographic image of graphite is shown. Notably, a hexagonal pattern is visible, which differs from the honeycomb pattern. This is due to an electronic effect that allows only every second atom to be imaged. Carbon atoms of the surface layer, which sit on top of another atom of the second carbon layer are not imaged as the electron density is localized closer to the bulk [19].

Now it is a good chance to apply the concepts mentioned in 2.1 on this real life material with simple structure. This is left as an exercise (Section 6.1).

3 STM Basics

In STM, piezo-elements move a metal tip across the surface of a sample (see Figure 4a). Piezo-elements change their length under an applied voltage. By changing the voltage one can move the tip with pico-meter precision.

The applied **bias voltage** drives a **tunneling current** through the small distance between the tip and the sample. The scanning of the sample surface can either be done in constant-height or constant-current mode. In the constant-height mode the tunneling current is a function of lateral position of

the tip. In the more commonly used constant-current mode, a feedback loop regulates the height of the tip to keep the tunneling current constant. Thus one obtains a profile of the height out of the z -signal. The good resolution down to the atomic level is enabled by the exponential dependence of the tunneling current on the distance (by changing the distance by one Angström the tunneling current changes by one order of magnitude) and the precise movement with the piezo-elements.

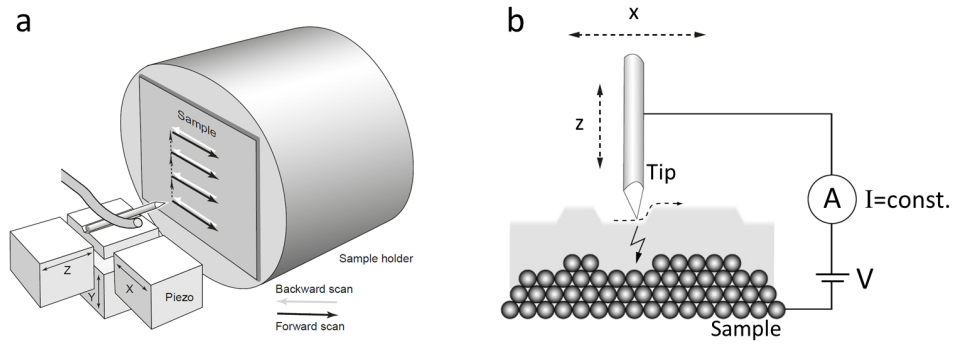


Figure 4: a) Scanning tunneling microscope (schematic) b) constant-current mode shown with circuit [6].

3.1 Quantum mechanical tunneling

This section requires the students to have basic knowledge of quantum mechanics. If forgotten, please refer to any standard textbook (e.g. Sakurai).

In quantum mechanics, a particle with an energy lower than a potential barrier can tunnel through the barrier because of the tunneling effect. In classical mechanics this is not possible.

In general, energy is conserved:

$$E_{\text{kin}} + E_{\text{pot}} = E = \text{const}$$

In classical mechanics the equation of motion in a one-dimensional potential $V(z)$ reads:

$$\frac{1}{2}mv^2 + V(z) = \frac{p^2}{2m} + V(z) = E$$

The momentum p is then given by:

$$p = \sqrt{2m(E - V(z))}$$

which shows that there is no real solution if the particle energy is smaller than the barrier $E < V(z)$.

In quantum mechanics a particle can be described as a wave. This is called the **wave-particle duality**. Instead of the Newtonian equation of motion, one needs to solve the Schrödinger equation. In the 1D case, the time independent Schrödinger equation simplifies to:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(z)}{dz^2} + V(z)\psi(z) = E\psi(z)$$

By rearranging one gets:

$$\frac{d^2\psi(z)}{dz^2} + \frac{2m(E - V(z))}{\hbar^2}\psi(z) = 0$$

Now we use an exponential approach $\psi(z) = Ce^{\lambda z}$ to solve this equation. This gives us two solutions for the coefficient λ :

$$\lambda_{1,2}(V) = \pm \sqrt{-\frac{2m}{\hbar^2}(E - V)}$$

This coefficient can either be real or imaginary, depending on the energy of the particle and the height of the potential barrier. This means that in contrast to classical mechanics the energy of the particle can also be lower than the barrier. The general solution is a linear combination:

$$\psi(z) = A \cdot e^{\lambda_1 z} + B \cdot e^{\lambda_2 z}$$

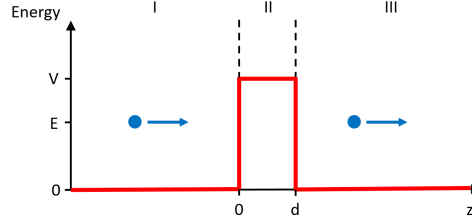


Figure 5: Schematic of a particle tunneling through a constant potential barrier.

Now we use a constant potential $V(z) = V_0$ like in Figure 5 for the energy barrier between the STM tip and the sample surface, and distinguish the three areas. Area (I) and (III) represent the tip and the sample, respectively. Area (II) represents the (vacuum) gap. We consider the situation where the energy of particle is lower than the potential ($E < V_0$). The solutions of the Schrödinger equation, are obtained separately for each area with the

exponential approach:

$$\begin{aligned}
\text{I. } V = 0, \quad \psi_{\text{I}}(z) &= \underbrace{A \cdot e^{ik_I z}}_{\text{incoming wave}} + \underbrace{B \cdot e^{-ik_I z}}_{\text{reflected wave}} & \text{with } k_{\text{I}} &= \frac{\sqrt{2mE}}{\hbar} \\
\text{II. } V = V_0, \quad \psi_{\text{II}}(z) &= \underbrace{C \cdot e^{k_{\text{II}} z} + D \cdot e^{-k_{\text{II}} z}}_{\text{decaying wave function in barrier}} & \text{with } k_{\text{II}} &= \frac{\sqrt{-2m(E - V_0)}}{\hbar} \\
\text{III. } V = 0, \quad \psi_{\text{III}}(z) &= \underbrace{F \cdot e^{ik_{\text{III}} z}}_{\text{transmitted wave}} & \text{with } k_{\text{III}} &= k_{\text{I}} = \frac{\sqrt{2mE}}{\hbar}
\end{aligned}$$

Note that there is only the transmitted term in area (II). (In physics, do not let the mathematical completeness formality constrain you. But at the same time, be careful: make assumptions boldly, and then carefully justify them.) The relation between the coefficients A, B, C, D , and F can be calculated from the continuity condition:

$$\psi_{\text{I}}(0) = \psi_{\text{II}}(0); \quad \psi_{\text{II}}(d) = \psi_{\text{III}}(d);$$

$$\frac{d\psi_{\text{I}}(0)}{dz} = \frac{d\psi_{\text{II}}(0)}{dz}; \quad \frac{d\psi_{\text{II}}(d)}{dz} = \frac{d\psi_{\text{III}}(d)}{dz}$$

The probability of transmission is given as the transmitted particle flow S_{trans} divided by the incoming particle flow S_{in} . In general, the particle flow is the product of probability density $|\psi(z)|^2$ and velocity v . The transmission is then given as:

$$T = \frac{S_{\text{trans}}}{S_{\text{in}}} = \frac{|\psi_{\text{III}}(z)|^2 v_{\text{III}}}{|\psi_{\text{I, in}}(z)|^2 v_{\text{I}}} = \frac{FF^*}{AA^*}$$

Since the velocities v_{I} and v_{III} are equal because of the constant kinetic energy in case of elastic tunneling, one can reduce them in the fraction. For low particle energy ($E \ll V_0$) and wide barriers ($\kappa_{\text{II}} d \gg 1$) the probability of transmission simplifies to:

$$T \approx \frac{16}{3 + \frac{V_0}{E}} e^{\frac{-2\sqrt{2m(V_0 - E)}d}{\hbar}}$$

This derivation is not specified to the type of particle. This is why also protons or neutrons or even bigger particles can tunnel through a potential barrier.

3.2 Tunneling current

In STM, a voltage is applied between the tip and the sample. Typically, this voltage is in the range of -10V to +10V. Thus electrons can tunnel

through the potential barrier, which is given by the **work function** of the tip and the sample. The work function describes the minimum energy which is needed to remove an electron from the solid and typically, it is around a few electron-volt (eV). This current, flowing because of the tunnel effect, is called tunneling current. It can be calculated as follows.

If we consider two flat planes and an insulating material in between, Fermi's Golden Rule (justified by the small bias voltage applied) gives the probability of one electron flowing from one side to the other. For the current this means:

$$I(V, T) = 2e \sum_{\mu, \nu} |M_{\mu\nu}|^2 \delta(E_\mu - eV - E_\nu) \cdot (f(E_\nu - eV, T)(1 - f(E_\nu, T)) - f(E_\nu, T)(1 - f(E_\mu - eV, T)))$$

where the sum goes over all states μ and ν of each electrode, and the temperature dependent Fermi-Dirac distribution $f(E, T)$ of tip and sample get multiplied with the transition matrix-elements

$$M_{\mu\nu} = -\frac{\hbar^2}{2m_e} \int dS \cdot (\psi_\nu^* \nabla \psi_\mu - \psi_\mu \nabla \psi_\nu^*).$$

Tersoff and Hamann have applied this model to describe the particular geometries of the STM [7]. They approximated the tip as spherical s-wavefunction and obtained for the tunneling current:

$$I(V, T, x, y, z) \propto \int_{-\infty}^{\infty} dE \cdot \rho_t(E - eV) \cdot \rho_s(E, x, y) \cdot \tau(E, V, z) \cdot (f(E - eV, T) - f(E, T))$$

where ρ_t is the density of states (DOS) of the tip and ρ_s the local density of states of the sample and z the distance between. If we neglect parallel components of the electron-momentum, the tunneling transmission factor τ is given as:

$$\tau(E, V, z) = \exp \left(-\frac{2\sqrt{m_e(\phi_t + \phi_s - 2E + eV)}z}{\hbar} \right)$$

with ϕ_t and ϕ_s as the work function of tip and sample. For low temperatures, the Fermi-Dirac-distribution becomes a step function. This cut the integral to only $0 - eV$. Furthermore, for low voltages, the dependence of the τ factor from the voltage and energy can be neglected. These two conditions simplify the tunneling current to:

$$I(V, x, y, z) \propto \exp \left(-\frac{2\sqrt{m_e(\phi_t + \phi_s)}z}{\hbar} \right) \cdot \int_0^{eV} dE \rho_t(E - eV) \rho_s(E, x, y)$$

The first term describes the exponential dependence of the current from the distance between tip and sample. The second term is the convolution of the density of states of the tip with that of the sample. If one applies a positive bias voltage between sample and tip, electrons from occupied states of the tip tunnel to unoccupied states of the sample and vice versa (see Figure 6). Based on $I(V)$ curves one can distinguish between conductors and semi-conductors. A semi-conductor has no tunneling current within the band gap ($\rho_s = 0$), because there are no states from where electrons can tunnel from or to.

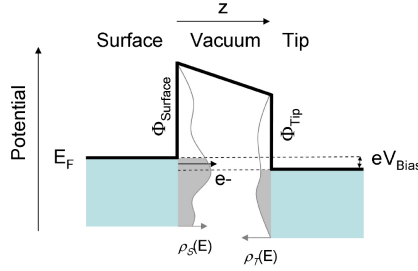


Figure 6: Energy diagram of tip and sample in case of negative bias voltages.

Now let us take another look at this equation. When we keep the tip still, z is a constant. And we assume the DOS of the tip is constant. We reach

$$\frac{dI}{dV}(V, x, y) \propto \rho_s(eV, x, y)$$

Thus by measuring the derivation of the current with respect to the voltage, which mostly is measured by a lock-in-amplifier, we have a way to detect the DOS of the sample. This is called the scanning tunneling spectroscopy (STS). One should notice the tip can only interact with the electrons in a very small area of the sample surface (exponential decay by distance). Thus STS actually measures the local density of states (LDOS).

The energy resolution is given by the temperature and the modulation amplitude of the voltage as $\Delta E \approx \sqrt{(3k_B T)^2 + (2.5eV_{\text{mod}})^2}$. The thermal broadening increases with the temperature and hence the energy resolution decreases, e.g. at room temperature ($T \approx 300\text{K}$) the energy resolution is around 80 meV but at low temperatures ($T \approx 4.2\text{ K}$) around 1 meV.

The exponential decay of the tunneling current with increasing distance between tip and sample depends on the material. By measuring the tunneling current while changing the distance, i.e. $I(z)$, one obtains information about the height of the potential barrier. When keeping the bias voltage constant, and the tip still in x and y directions, one obtains:

$$I(z) = C \cdot \exp\left(-\frac{2\sqrt{m_e(\phi_t + \phi_s)}z}{\hbar}\right)$$

and with the natural logarithm this becomes:

$$\ln(I(z)) = \ln(C) - \frac{2\sqrt{m_e(\phi_t + \phi_s)}z}{\hbar} = \ln(C) - \kappa \cdot z$$

The value of κ , which describes the exponential decay of $I(z)$, is given as:

$$\kappa = \frac{2\sqrt{m_e(\phi_t + \phi_s)}}{\hbar}$$

This means that the mean value of the potential barrier height ϕ_b can be obtained by measuring κ , the slope of the $\ln(I(z))$ curve:

$$\phi_b = \frac{\phi_t + \phi_s}{2} = \frac{\kappa^2 \hbar^2}{8m_e}$$

4 Experimental Setup

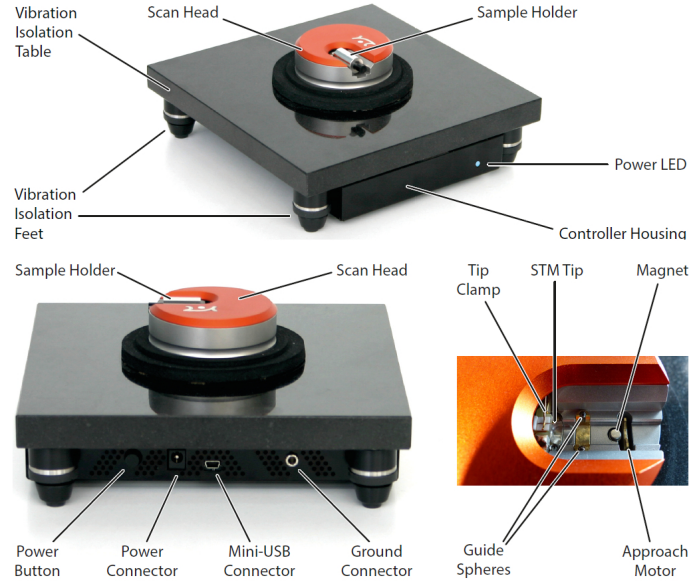


Figure 7: Setup of the NaioSTM [11].

The STM used in this lab course is the NaioSTM from Nanosurf (see Figure 7). It mainly consists of the scanning part colored in orange and a table for vibration isolation. There is also a cover for protection with a magnifier to check tip and sample. The product video [10] provides a good introduction to the setup and the functionalities. Further information about the instrument can be taken from the user manual of the company [6, 11]. The measurements are done by giving commands in the controlling software.

This STM is located in ENC B-0132. The machine is mainly for lecturing purpose. Thus it is at ambient environment. In the same room, there is another STM machine for research usage. It is mounted in an ultra high vacuum chamber (UHV, crucial to surface science study). Please do not temper with this machine during the lab course.

5 Experimental Instructions

In the lab, the most important thing is to protect the safety of yourself, especially since we're dealing with some harmful chemicals. Also, STM is a quite delicate setup, so be gentle with it.

Bearing these two points in mind, you need to finish the following tasks during the lab course, which are explained with more detailed instructions in the latter sections:

1. Prepare your own tip, and mount it into the setup.
2. Scan on HOPG surface in air, and get both large size image (~ 100 nm) presenting the step edges, and small size image (~ 5 nm) with atomic resolution.
3. Calibrate the distortion on the atomically resolved HOPG image, and get the distortion parameters for later usage.
4. Prepare the solution of organic molecules and apply it to the HOPG surface.
5. Scan on the HOPG again, now this time at a liquid/solid interface, and try to get atomic resolution on the organic molecules.
6. Calibrate the molecule images with the distortion parameters obtained from the HOPG images.

The STM can do much more than the things the tutor listed here. If we have time and you're interested, we can try some other things. It might also be possible to take a look at what is going on at the other research STM in the same room.

5.1 Preparing and installing the STM tip

The STM tip can be prepared out of Pt/It wire and installed by yourself. This is the most difficult part of the preparation which has to be carried out very thoroughly. It usually needs patience and practice to get the first good tip. A good tip is very sharp but not too long or bent. Only an accurately cut tip enables optimal measurements. Preparing and installing should be carried out with great care.

Before preparing the tip

1. Wear gloves to avoid any contamination oil from the skins.
2. Clean the cutting part of the wire cutters, the flat nose pliers and the pointed tweezers with isopropanol. Only touch the Pt/Ir wire with these tools.
3. Remove any remaining tip from the instrument using the pointed tweezers just by pulling it out of the tip holder in the STM.

Prepare the tip

1. Hold the end of the wire tightly with the pliers.
2. Holding the wire with the pliers, move the cutters at a wire length of approximately 4 mm, as obliquely as possible (in a very sharp angle, see Figure 8a).
3. Close the cutters until you can feel the wire, but do not cut the wire.
4. In order to obtain the required sharpness, the tip needs to be torn off by pulling the wire cutter quickly away from you, rather than cutting cleanly through the wire.
5. Use the pointed tweezers to hold the tip wire right behind the tip and release the flat pliers.

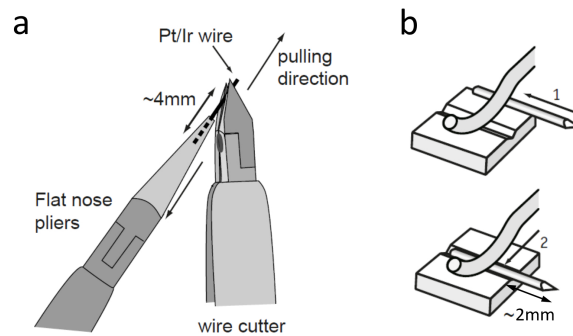


Figure 8: Preparation and installation of the STM tip: a) cutting, b) mounting [11].

Now that you have prepared a fresh tip it is necessary to handle it with care. It is important that you never touch the end of the tip with anything.

Mount the STM tip

Figure 8b shows the tip holder with its groove and the clamp which fixes the tip wire.

1. Put the tip wire underneath the clamp of the tip holder, parallel to the groove and push the blunt end of the tip all the way to the end.
2. Move the tip wire sideways until it is in the groove and held securely under the clamp. It should stick out about 1-2 mm beyond the tip holder.

The tip is now installed and you can go on preparing the sample.

5.2 Prepare and mount the sample

Cleave the HOPG

At first you will test your tip on HOPG. Therefore you need to cleave the HOPG sample once with a piece of adhesive tape (Tesa film) as shown in Figure 9 and explained in the following:

1. Leave the sample fixed on the magnetic stripe in its storing box.
2. Stick a piece of adhesive tape to the graphite surface and apply little pressure with your thumb or the end of the tweezers.
3. Pull off the adhesive tape gently. The topmost layers of the sample should stick to the tape.
4. The surface should be very flat and mirror-like. Any loose flakes in the outer regions of the sample can be removed with the tweezers.

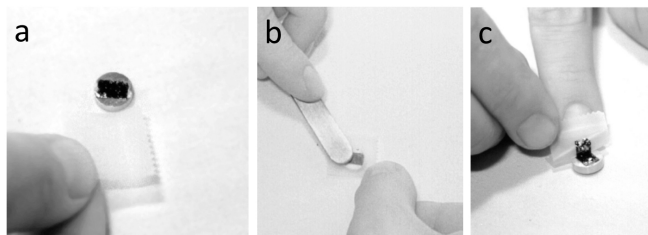


Figure 9: Cleaving graphite with a adhesive tape [11].

Mounting the sample Now you need to put the sample into the setup. The procedure is shown in Figure 10.

1. Unpack the shuttle touching only its black plastic handle. This is very important, because otherwise a grease film on the shuttle will prevent the motor device to move the sample.

2. Use the tweezers to push the sample to the edge of the supporting magnet in the sample storing box. Grab the sample with the tweezers and place it on the magnet of the shuttle.
3. Put the shuttle down to the shuttle guide bars first and release it gently on to the magnet of the approach motor.
4. Push the shuttle carefully in the direction of the tip (until the distance is around 3 mm), but do not let it touch the tip.
5. Put back the cover of the setup, and adjusting the position of the magnifier

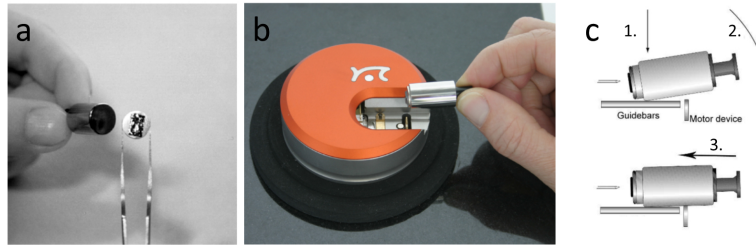


Figure 10: Mounting the sample [11].

5.3 Approach

To approach the sample to the tip you need to use the Nanosurf Naio software. Therefore you need to switch on the NaioSTM by pushing the power button, and start the software on the computer. With the button **Advance** (see the red box in Figure 11) you move the shuttle towards the tip. To check the distance, you may look through the magnifier as shown in Figure 12. At a certain distance one can see the mirror image of the tip in the sample. Now you can approach a little bit more till the gap between the tip and the sample is very small (1 mm or even closer). The smaller it is, the less time the automatic final approach needs. To start the automatic final approach you can click on the button **Approach**. Now the computer approaches the sample step by step, checking the tunneling current each time and stopping the approach when the set-point is reached. In this case, the **Probe Status** shown in the green box in Figure 11, turns to green.

In case that the automatic approach crashed the sample into the tip, it turns to red and you probably need to prepare a new tip. Therefore you click **Withdraw** once and afterwards **Retract** several times. Now the gap should be wide enough to unmount the tip. If the automatic approach is not working at all, you should click **Withdraw** and **Retract**, rotate the shuttle a bit and start a new approach as explained above. If this still does not work, you will need to clean the metallic part of the shuttle with ethanol.

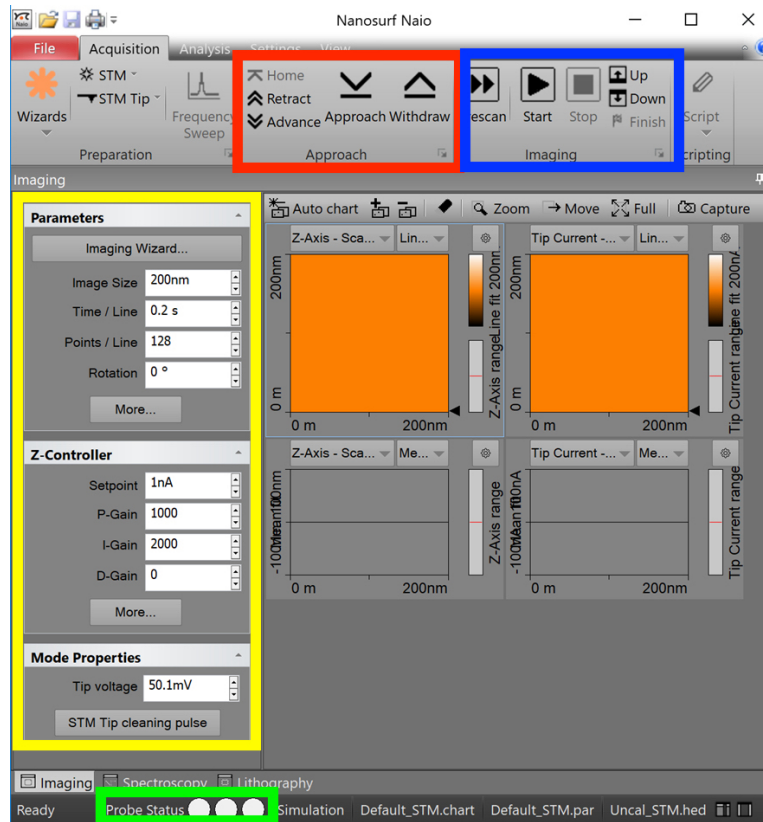


Figure 11: User interface of the Naio software in version 3.8

5.4 Constant-current mode scan

The scanning starts automatically after the approach. It can be stopped or paused any time by clicking the respective buttons in the blue box of Figure 11. In the panels **Parameters**, **Z-Controller** and **Mode Properties** the most important scan parameters can be changed. You will find them in the yellow box of Figure 11.

- **Image Size** Defines the image size in the x and y direction. You should first scan a large area (100 – 200 nm), and then zoom in the interested small areas step by step.
- **Time/line** The time needed to acquire a single data line. The time needed for the entire image is displayed in the status bar. Normally, you choose a time as short as possible to save time, but especially for steps at the end of a terrace this could trigger problems, because the feedback loop, which controls the tip position in z -direction, may not be able to retract fast enough and the step becomes blurred or the tip crashes the sample.

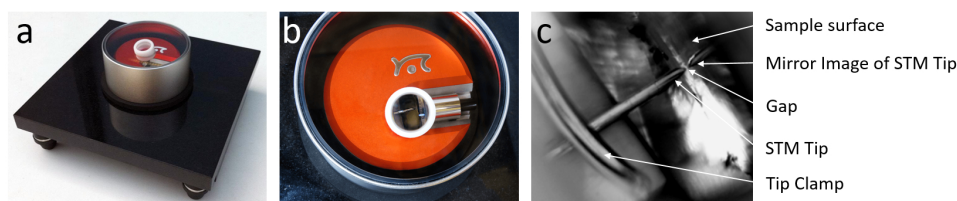


Figure 12: a) glass cover with magnifier, b) top view, c) gap between tip and sample [11].

- **Set-point** The working point for the z feedback loop, which defines at which tunneling current the tip is held. This essentially determines the distance between tip and sample. The higher the set-point, the closer the tip is held above the sample's surface. For example, for atomic resolution on graphite you normally use 5 nA. A good value to start with is typically 1 nA.
- **P-, I-, D-Gain** P-proportional, I-integral and D-derivative controller are the values of the feedback loop. They define the strength of the reaction if the measured current diverges from the Set-point. Values too small could cause the tip to no longer react accurately to changes in altitude. Values too big could cause oscillations of the tip position. Typically, you can set D to zero. P and I need to be chosen in accordance to the current and time/line. The default value 1000 is a good starting point.
- **Tip voltage** This parameter defines the bias voltage applied to the tip. The lower the voltage is, the shorter the distance between tip and surface becomes. A good bias voltage value largely depends on the electronic structure of the sample, i.e. DOS(E). For semiconductors it is important to note that the applied bias voltage is not recommended to be in the band gap. Think about why, and answer it in the report (see Section 6.1).

5.5 Arachidic acid on graphite

Organic molecules are the conceptual, structural, and functional basis of numerous existing and envisaged nanotechnology applications, such as molecular light-emitting and harvesting devices, molecular electronics, biological identification, and molecular sensor technologies. Because devices based on single molecules are still challenging for applications, systems involving molecular thin films appear to be the most promising for the near future. **Self-assembly** is one of the major routes toward novel molecular architectures and is used, for instance, for the realization of electronic and optoelectronic devices.

You need to wear gloves again (and eye-shield), but this time it is for your own safety from the harmful organic compounds. Do not deliberately inhale any organic compound. And if you touch the solution with bare skin, remain calm, and wash thoroughly with soap.

Prepare the solution In this experiment we will investigate the adsorption of arachidic acid on HOPG. For this one needs to set up a saturated solution of arachidic acid in phenyloctane. This is done by the tutor already.

Apply the solution To apply the molecules to the surface first stop the measurement on HOPG when seeing single atoms.

1. Withdraw the sample via the **Withdraw** button, and retract the sample once with the **Retract** button. Remove the cover from the STM carefully.
2. Use the syringe with the smallest (brown plastic top) needle, or a pipette, to aspirate a small volume of the thinned down arachidic acid solution.
3. Push its piston a bit, such that a drop of the solution adheres to the top of the needle.
4. Now touch the HOPG surface near the tip with the drop carefully. The drop will come undone the needle and disperse across the sample resulting in a liquid meniscus between the scanning tip and the sample as shown in Figure 13a. Now we have a liquid-solid interface.

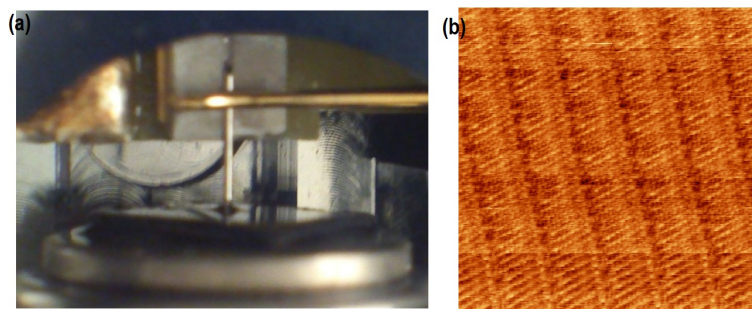


Figure 13: (a) A meniscus forms between the tip and the HOPG [11]. (b) Uncalibrated STM image of arachidic acid molecules on HOPG (0.6 nA, 1.3 V, image size $15.8 \times 15.8 \text{ nm}^2$).

Please be very careful with the solution, and do not drop any superfluous liquid into the setup.

Scan again Now place the cover carefully on the STM again. The status light should be orange all the time. Approach the sample like on the HOPG again, and you should be able to see the atomic resolution of HOPG as before. If not, try scanning a different area of the surface (lower resolution → move → increase resolution on flat terrace).

If you are not able to achieve atomic resolution, you probably have crashed the tip into the sample when applying the solution. Hence you will have to prepare a new tip and start over again.

If successful, you should see some very obvious features from the Arachidic acid (Figure 13b). And on a good day, you could even distinguish individual carbon atoms.

5.6 Data analysis

The raw data for the surface topography image captured with the STM is in .nib format, and consists of a matrix with a size matching the points per line and lines per frame. The measured values get stored and encoded as 16-bit signed integers in a value range from -32768 to 32767. With a calibration on a well known surface the software converts these values in physical units of a length. To display the matrix in a meaningful way, a color scale is assigned to the measured values, where each color value represents a different z -expansion of the piezo. Choose a color scale you like.

In the following some image processing steps are explained using the free software Gwyddion [8]:

- Fast-Fourier-Transformation (FFT): This option is given in the drop down menu **Data Process/Integral Transforms/2D FFT**. The software will do a Fourier transformation of the whole picture. In the resulting reciprocal space one can see periodic signals, which for example come from the periodic structure of the atoms in a crystal or noise. With the option **Process/Correct Data/2D FFT Filtering** it is possible to cut out the noise and transform the picture back in real space, where its now filtered from the noise. In reciprocal space it is also possible to determine the atomic distance.
- Distortion calibration: In principle, what the machine can read from the measurement is only electric signals (voltage, current ...). The STM electronics translates them to dimensions (length in x , y , and z directions). These values might not be accurate. We need to calibrate them with the known dimensions. In drop down menu **Data Process/Distortion/Affine**, we calibrate our measured HOPG image against the HOPG crystal structure in stored already in the software. You just need to make sure the fit lattice mapped on the image is correct. Then you press **OK**, and the software will generate a calibrated image.

- **Line profile:** This option is given in the **Data Process** box, the **Extract Profile** button. Draw a line on the image, and the software will plot the profile of height along this line. This is very practical to get the height of a step or to count the atoms along a line with a known length to determine the atomic distance.
- **Smooth:** Gwyddion gives an option to smooth the picture. It is given in the **Tool** box, the basic filter button. There are several filters available, and you can enter the size of area you want to smooth. You can use Gaussian filter and a size of 2-5 pixels, and press apply button. But note that an average over a big number of pixels will lead to information loss. You should distinguish the real physics information, and the background noise, and use this function.

The program has many more options which are not discussed here. You are free to test this on your own. There is another free software you can give a try. WSxM [12] gives very similar functions as Gwyddion. But some find it more user-friendly.

6 Report

6.1 Exercise

Answers to the following questions should be included in the report. If they are already explained in other part in your report (especially the fifth question), there is no need to repeat.

1. What is the Bravais lattice of graphite and graphene? Draw the unit cells, and label the primitive translation vectors.
2. Calculate the reciprocal lattice vectors of graphene, and draw the 1BZ of graphene. Label all the high symmetry points in 1BZ.
3. Why is wave function not invariant under lattice translation?
4. Why is the bias voltage not recommended to be set within the band gap if the sample is a semiconductor?
5. What is the reason for the arachidic acid molecules to self-assemble? Elaborate on the inter-molecular interactions.

6.2 Requirements

The report should cover things you have done before, during, after the experiment, and what you have learned through the process. In principle, there is no compulsory format. But please make it organized. If you have have no idea, here are some suggested sections:

- **Introduction** for what the lab course is about, what you have learned, how your report is constructed.
- **Theory** for the background information behind this experiment. The theory part about the spectroscopy (and organic molecules) is rather brief in this manual, please elaborate in your report.
- **Experimental** for briefly description of the setup and procedure.
- **Result** to exhibit the experimental results and your analysis. Specify the data analysis process for the presented STM images. Make sure every STM image is accompanied by the length scale indication, and the tunneling parameters (check the STM image in this manual, or STM images in any academic articles for example). The systems we measured have already been studied before, please take the existing articles for references, and compare the results you measured with the ones in literature.
- **Summary**.
- **Exercise** to answer the questions in Section 6.1 of this manual.

The theory and experimental part should not be a simple repetition of the same section of this manual. Please use your own words.

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