Atomic force microscopy

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1 Overwiev

Scanning probe microscopy (SPM) covers a lateral range of imaging from several 100mto 10 pm. Surfaces of solids can be mapped with atomic resolution, revealing not only the structure of perfect crystalline surfaces but also the distribution of point defects, adsorbates, and structural defects like steps. Scanning probe microscopy has become an essential tool in the emerging field of nanoscience, as local experiments with single atoms or molecules can be performed. Force measurements of single chemical bonds or optical spectra of single molecules may serve as examples. Furthermore, the local probe can be used to manipulate single atoms or molecules and hence to form artificial structures on the atomic scale. The starting point of SPM was the invention in 1982 of the scanning tunneling microscope (STM) by Binnig and Rohrer, who were awarded the Nobel Prize for Physics in 1986. In the STM, a sharp metallic needle is scanned over the surface at a distance of less than 1 nm. This distance is controlled by the tunneling current between the tip and the conducting surface. The tunneling current is a quantum mechanical effect, with two properties important for STM: it flows between two electrodes even through a thin insulator or a vacuum gap, and it decays on the length scale of one atomic radius. In the STM the tunneling current flows from the very last atom of the tip apex to single atoms at the surface, inherently providing atomic resolution. In a standard experiment, the tip is moved in three dimensions by piezoelectric actuators. An electronic controller guides the tip at a tip–sample distance corresponding to a constant preset tunneling current. This distance is recorded by a computer as a function of the lateral position and displayed as a microscope image. The high mechanical stability of the experimental setup turns out to be a prerequisite for successful measurements on the atomic scale. With this example of the STM, all elements of a scanning probe microscope have been introduced. A short-range interaction, yielding the desired resolution, is sensed by a local probe. The probe is scanned over the surface under study, and the measured quantities are recorded and processed in a computer system. The experiment needs a rigid construction and an effective[1].

2 Basic concept of AFM

The basic concept of force microscopy is the measurement of forces between a sharp tip and a sample surface. The tip is commonly mounted on the end of a cantilever , which serves as a force sensor. Either the static deflection of the cantilever or the change in its dynamic properties due to tip–sample forces can be exploited. The limit of force detection is far lower than the force between atoms at lattice distances, explaining the widely used term atomic force microscope.

There are different techniques to detect the small bending of the cantilever due to tip-sample forces (see Fig. 3.1). Most instruments use the beam-deflection method. A light beam is reflected at the rear side of the cantilever and the deflection is monitored by a position-sensitive photodiode. A schematic drawing of the setup is shown in 1. A four-segment photodiode allows one to detect the normal bending and the torsion of the cantilever caused by lateral forces acting on the tip. There are alternative deflection sensors, such as with capacitance or with piezoresistance [1].

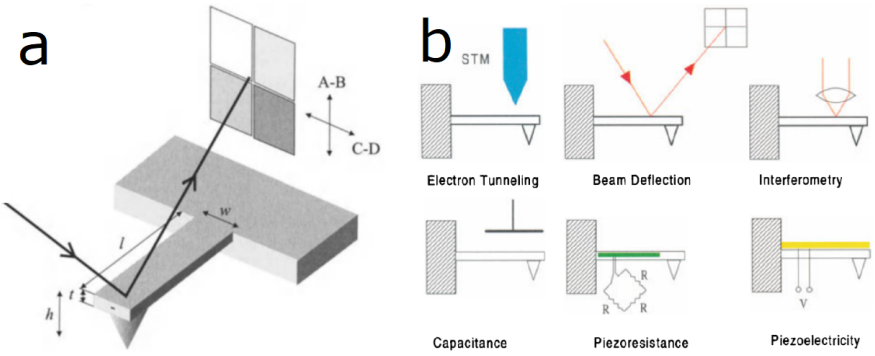

Figure 1: (**a**) Deflection monitoring with with a four-segment photodiode. **b**) Alternative deflection detections. [1].

Force microscopy has introduced several operational modes, each characterized by their unique names and distinctive features. These modes can be classified into two categories: static and dynamic. Static modes focus on measuring the static bending of the cantilever, while dynamic modes involve the measurement of the cantilever's dynamic properties. Additionally, these operational modes are often categorized based on whether the tip is in contact with the surface. It's

important to note that in dynamic modes, the tip may briefly come into contact during each oscillation cycle. The most significant static mode is known as "contact mode," where a feedback loop is employed to maintain a constant cantilever bending by controlling the tip-to-sample distance. In this mode, a topographic surface is recorded while maintaining a constant force. On the other hand, scanning at a constant height above the surface results in force maps. In dynamic modes, the focus is on measuring changes in the vibrational properties of the cantilever due to interactions between the tip and the sample. These measured properties include eigenfrequency, oscillation amplitude, and the phase relationship between excitation and cantilever oscillation. Different dynamic modes can be distinguished by the specific feedback parameters used for distance control. Utilizing the frequency shift of a self-exciting oscillation loop as a feedback parameter offers the potential for a reliable non-contact mode [1].

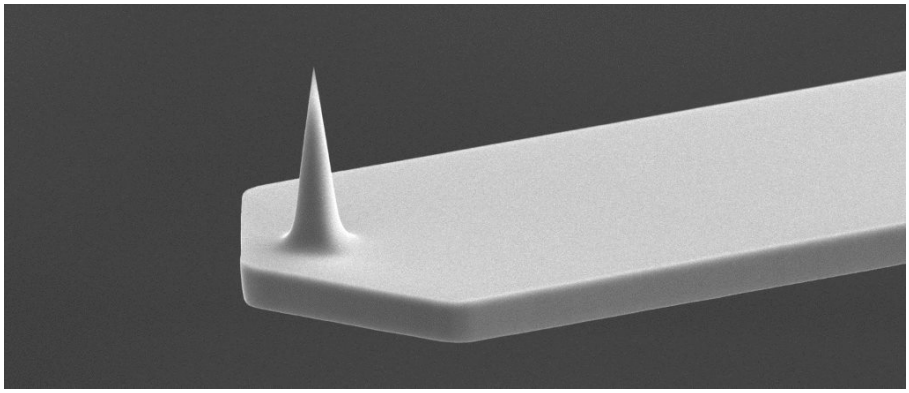

Figure 2: Scanning electron microscope image of the cantilever and the sharp tip. [2]

2.1 Relevant interactions

The interaction range of the different types of force is of great importance for force microscopy, since different parts of the tip and cantilever contribute differently to the total force which is measured.

Short-range forces

Short-range chemical forces arise from the overlap of electron wave functions and from the repulsion of the ion cores. Therefore, the range of these forces is comparable to the extension of the electron wave functions, i.e., less than one nanometer. This force can be modeled by Lennard-Jones potential:

$$U_{LJ} = -4\epsilon \left(\frac{\sigma^6}{r^6} - \frac{\sigma^{12}}{r^{12}} \right), \tag{1}$$

where σ and ϵ are free parameters, r is the distance. This representation of force contains the van der Waals interaction, whis is represented by $\frac{1}{r^6}$.

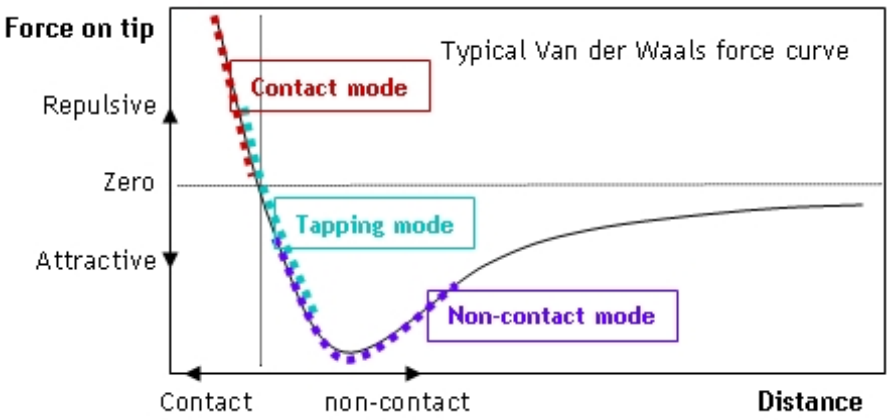

Figure 3: Schematics of force between the tip and the sample as the function of separation distance. The different scanning modes work in different regions on the force-distance curve [3]

Van der Waals forces

Van der Waals forces are dipole–dipole forces. The most important forces are not those between permanent dipoles but the so-called dispersion forces. These act

between dipoles that arise from fluctuations and dipoles induced in their electric field. They are always present and attract even chemically inert noble gas atoms. The range of dispersion forces is limited. When the distance between molecules is larger than the distance light can travel during the characteristic lifetime of the fluctuations, the dispersion forces are weakened. Since the range of van der Waals forces is limited, the tip–sample geometry of the force microscope can be well approximated as a sphere approaching a semi-infinite body. For this configuration, the van der Waals force is: :

$$F_{vdW} = -\frac{HR}{6D^2}, \tag{2}$$

where H is the Hamaker constant, R is the tip radius and D is the distance between the tip and the sample.

Electrostatic force

Electrostatic forces act between localized charges on insulating tips and samples. Their strength and distance dependence obey Coulomb's law. Charges can easily be trapped at sample surfaces in the course of surface preparation, for example by sample cleavage or by UHV techniques like ion sputtering. Furthermore, contact electrification can charge tip and sample after their contact is broken. Even in air, such charge can persist for hours particularly on polymers, and in vacuum for days. Electrostatic forces also act between conductive tips and conductive samples when they are at a different potential. If we apply a bias voltage, and the tip-sample distance is small, and we assume that the tip is spherical, the electrostatic force is [1]:

$$F_C = -\frac{\pi\epsilon_0 R(U_{bias} - \Phi)^2}{r}, \tag{3}$$

where R is the tip radius, Φ is the contact potential and r is the distance, ϵ_0 is the vacuum permittivity.

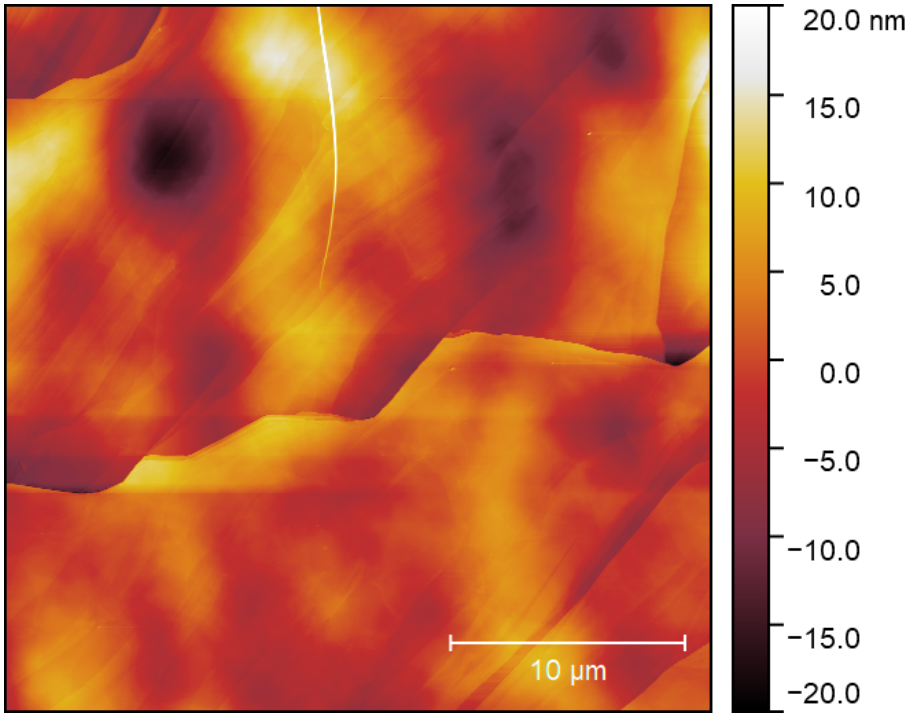

Figure 4: AFM contact mode image of HOPG (highly ordered pyralitic graphite).

3 Scanning tunneling microscope

Scanning tunneling microscopy (STM) was invented by Binnig and Rohrer (see Fig. 2.1) [80,109]. Using the combination of a coarse approach and piezoelectric transducers, a sharp, metallic probing tip is brought into close proximity to the sample. The distance between the tip and sample is only a few angstrom units, which means that the electron wave functions of the tip and sample start to overlap. A bias voltage between the tip and sample causes electrons to tunnel through the barrier. The tunneling current is in the range of pA to nA and is measured with a preamplifier. This signal is the input signal of the feedback loop, which is designed to keep the tunneling current constant during (x, y)-scanning. The output signal is amplified (high voltage amplifier) and connected to the z-piezo. According to the feedback output voltage and the sensitivity of the piezo (typically nm/V), the tunneling tip is moved backward or forward, and the tunneling current is kept constant during acquisition of the image. This operation mode is called constant current mode. There exist other modes, such as the constant height mode, where the tip is moved at a constant height, and variations in the current are measured. The (x, y)-movement of the tip is controlled by a computer. The z-position (output of feedback loop) is measured at discrete (x, y)-positions. The data z(x_i, y_j) can be displayed in several ways: line-scan image, grey-scale image, or color-encoded image.2 The line-scan image is the most natural way to represent the data because each line represents the scan of the tip in the fast direction. However, grey-scale images or colour-encoded images are more frequently used because they are better adapted to human pattern recognition [1].

3.1 Quantum tunneling

According to quantum mechanics, a particle with energy E can penetrate a barrier $\phi > E$. In the classically forbidden region, the wave function ψ decays exponentially:

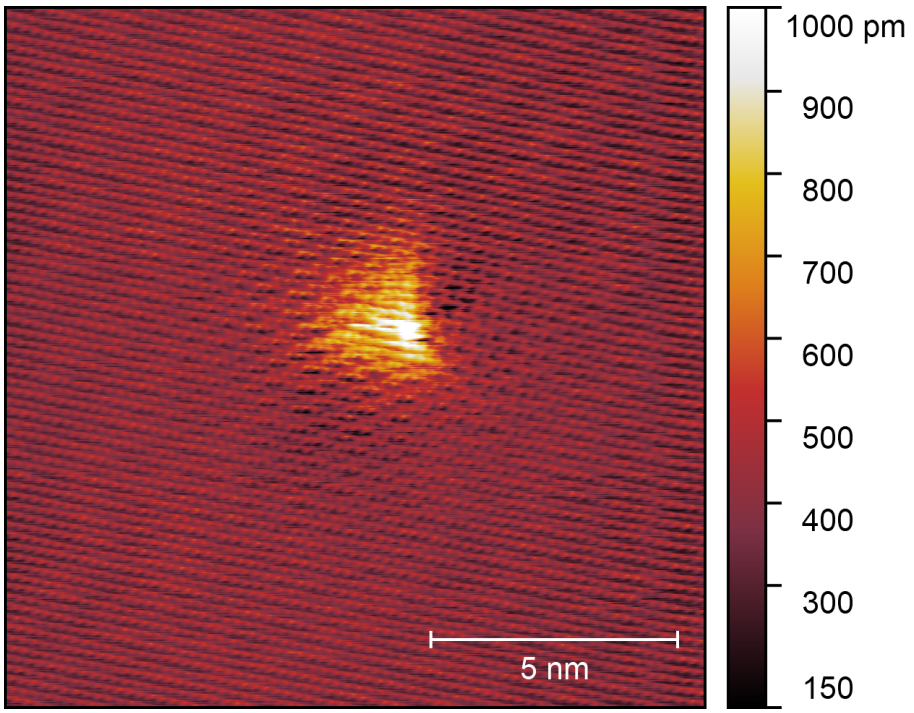

Figure 5: STM image of a hydrogen atom localized on the surface of graphite. The crystal structure and the point defect-induced Friedel oscillations are observable.

$$\psi(z) = \psi(0)\exp\left(-\frac{\sqrt{2m(\phi - E)}z}{\hbar}\right), \tag{4}$$

where m is the mass of the particle and $\hbar = 1.05 \cdot 10^{-34} Js$. In STM the barrier is given by the vacuum gap between the sample and tip. Then the tunneling current I_t can be calculated by taking into account the density of states of the sample $\rho_s(E_F)$ at the Fermi edge:

$$I_t \propto V\rho_s(E_F)\exp\left(-2\frac{\sqrt{2m(\phi - E)}z}{\hbar}\right) \propto V\rho_s(E_F)e^{-1.025\sqrt{\phi}z}. \tag{5}$$

where the barrier height ϕ is in eV and z in angstrom units. With a typical barrier height of $\phi = 5$eV, which corresponds to the work function of gold, the tunneling current decays by an order of magnitude when the vacuum gap is changed by 1 angstrom.

4 Short description of the measurement

During the measurement, students become familiar with the basics of atomic force microscopy and its applications. The measurements are conducted under the supervision of the laboratory instructor. The measurements are performed using a scanning probe microscope manufactured by NT-MDT. During laboratory practice, various samples, including HOPG, DVD discs, etc., need to be subjected to both AFM and STM measurements, with an aim to achieve the highest possible quality of images.

The practice begins with the insertion of the probe holder chip into the probe head, following the activation of the computer and the measurement equipment. After its insertion, the task for students is to position the laser beam correctly onto the cantilever to maximize intensity on the four-quadrant photodiode and ensure that the laser spot is centered on the photodiode. Subsequently, for non-contact AFM measurement, using the measurement software, students calibrate the probe to determine the cantilever's resonance frequency. Once the calibration is completed, an optical approach to the sample is possible, and the approach continues with the assistance of the measurement software. When the tip reaches the surface of the sample, the measurement can begin. Calibration should be carried out for different tips.

Following AFM measurements, STM measurements are conducted. In this case, fewer preparations are needed, as only the measurement head needs to be exchanged, and a freshly cut platinum-iridium tip must be inserted into the probe head. The approach of the tip works similarly to that in the case of AFM. The task in STM is to examine a graphite sample, and students attempt to create atomic-resolution images, if it is possible.

References

1. Meyer, E., Bennewitz, R. & Hug, H. J. *Scanning Probe Microscopy* ISBN: 978-3-030-37088-6 (Springer International Publishing, 2021).

2. `https://www.team-nanotec.de/UserFiles1/Gallery/images/2B681077-C29D-8484-0A97C8C014BDDA3A.jpg`.

3. `https://upload.wikimedia.org/wikipedia/commons/6/67/AFM_contact_ICM_and_NCM.jpg`.