Advanced Lab Course

Atomic Force Microscopy

Experiment instructions

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Experimental Physics

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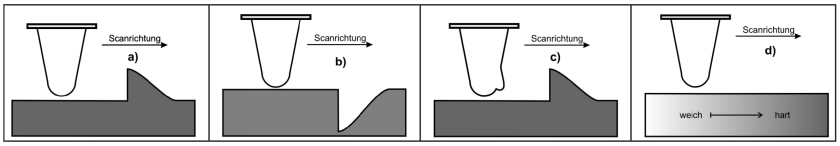
1 Preparation

1.1 Preparatory work

- Familiarize yourself with the theory of atomic force microscopy. Consult further literature (see bibliography).
- Answer the questions to be found in the following section in writing.
- Find an interesting sample of your own that is suitable for observation in the atomic force microscope. Think about questions about this sample. Prepare the sample in a suitable way and bring it with you on the day of the experiment.

1.2 Questions

- What limits the resolution (lateral and vertical) of the atomic force microscope? In what order of magnitude is this limit?
- Draw the expected scan lines for the situations shown in the following figure. Describe typical scanning artifacts. How can you identify and prevent/minimize them?



- What are the classic advantages of atomic force microscopy compared to scanning electron microscopy (SEM)?
- Explain the different measurement modes of the atomic force microscope in keywords and describe their possible advantages and disadvantages.
- What possibilities - apart from the light pointer principle - are there to detect the bending of the cantilever? Name their advantages and disadvantages.
- What external factors can interfere with a measurement using the atomic force microscope? How can their influence be minimized?
- Sketch an expected force-distance curve for a soft and, in comparison, an (infinitely) hard sample. What influence does the spring constant of the spring bar have on the force-distance curve? How do force-distance curves differ in principle in air and in a vacuum?
- Explain how a four-quadrant photodiode works.

2 Fundamentals of theory

2.1 Atomic Force Microscopy

2.1.1 Introduction

When Gerd Binnig and Heinrich Rohrer laid the foundations for modern atomic force microscopy (AFM) in 1986[2], the variety of possible applications could only be guessed at. Nowadays, it is a standard method and is used in many different fields of research, from surface physics to materials science and the life sciences. Although the technology is comparatively young, it has already found its way into industry, e.g. in semiconductor production, the manufacture of plastics or in the pharmaceutical industry for quality control.

2.1.2 Basic principle

If you compare the way optical microscopes work with the human eye, you can use the human hand or sense of touch as a counterpart for the atomic force microscope. The measuring principle is based on scanning the sample surface using a microscopically small tip attached to a cantilever. The typical range that can be characterized with an AFM is between a few nanometers and a few hundred micrometers. The great advantage of the atomic force microscope is its ability to reproduce the topography of a sample and determine material-specific properties at the same time. In addition, images can be taken in air, in a vacuum and in liquid media, i.e. experiments can even be carried out on living cells.

2.1.3 Setup

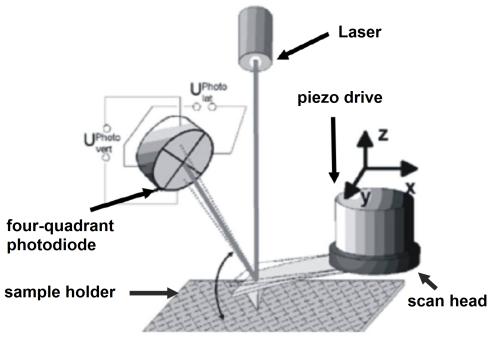


Abbildung 1: Schematic setup of an atomic force microscope.

In addition to the control electronics, an atomic force microscope essentially consists of three parts (see Fig. 1), namely

- the sample holder,
- the scan head

- and a laser with a corresponding detection unit.

The main task of the sample holder is to hold the sample in a stable position. It can also be equipped with functional units, such as a heater or a chamber for liquids. The scan head is used to fix the cantilever and move it over the sample. Typically, piezo drives serve as precise motors that scan the sample in the x and y directions. The movement in the z-direction is usually also performed by piezo motors.[1] The most important part of the scan head is the tip, which is located at the end of the small cantilever. The cantilever is about as long as a hair is wide (0.1 mm) and is usually made of silicon or silicon nitride (Si_3N_4). The tip itself typically has a radius of 4-30 nm (see Fig. 2 a). A four-quadrant photodiode serves as the detection unit for a laser reflected from the back of the cantilever (see Fig. 2 b).

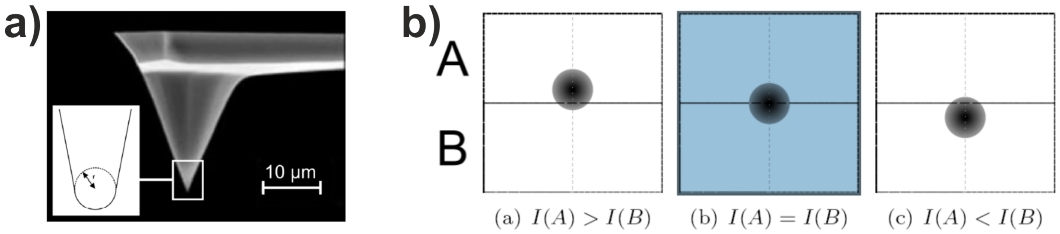


Abbildung 2: a) Typical measuring tip; b) Scheme for detecting the position of the laser on a (here two-part) photodiode by a change in the ratio of the intensities measured in areas A and B.

2.1.4 Operating principle

If the tip is brought into contact with a sample and moved over it, it follows the contours of the surface like a finger scanning an egg carton. To track the movement of the spring bar, the light pointer principle is used: a laser beam is focused on the back of the spring bar and the reflected beam is centered on a position-sensitive photodiode (PSPD). The PSPD consists of four independent photodiodes arranged in quadrants (siehe Abb. 2 b). A movement of the cantilever now leads to a movement of the laser beam that is reflected by it, which hits the photodiode. The advantage of the light pointer principle is that movements of the tip or the cantilever in the nanometer range are converted into movements of the light spot in the millimeter range. The position of the light spot can be determined by the change in the ratio of the intensity detected in the different areas of the photodiode.[2]

2.1.5 Scanmodes

There are basically two operating modes of the atomic force microscope (see Fig. 3), namely

[1] Depending on the design, the probe holder can also be moved instead of the scan head.

[2] Two of the four quadrants are combined to detect vertical movement. The division into four quadrants is necessary as the horizontal movement of the laser spot can also be measured.

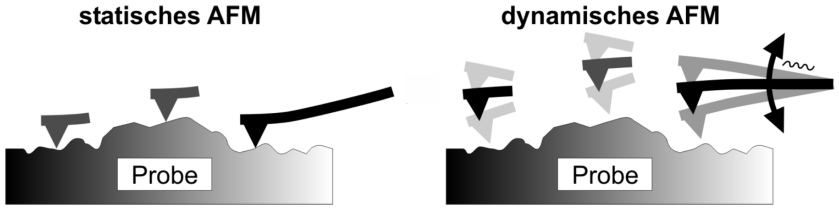


Abbildung 3: Sketch of the function of the static and dynamic mode.

- the static mode
- and the dynamic mode.

Static Mode In this mode, also known as contact mode, the tip is in constant contact with the surface during scanning. A distinction is then made between „constant height“ and „constant force“ control.

In the case of constant height control, the cantilever (not the measuring tip!) is rastered over the sample at a constant height. As already mentioned, the tip then follows the topography, which in this case can be determined directly from the signal of the photodiode. This can lead to strong distortions of the height information, as the force transferred to the surface depends on the height of the respective grid point. This can cause the sample to be deformed, e.g. dented.

In most cases, constant force is therefore used for control. This is achieved by controlling the z-axis piezo via a feedback loop so that the signal at the photodiode maintains a preset value. value is maintained. This value corresponds to a certain deflection of the cantilever. If this is kept constant, the tip scans over the surface with a constant contact force (*force setpoint*). The topography information is obtained via the feedback signal sent to the z-piezo. Both variants of the contact mode have the disadvantage that structures to be imaged can be moved across the surface by the tip. This is particularly problematic with soft surfaces.

Dynamic mode In this mode, the cantilever is excited to vibrate close to its resonance frequency and scanned across the surface without contact. How conclusions about the surface can be drawn from the change in the oscillation state is explained below.

Basically, you can imagine the tip as being clamped between two springs (see Fig. 4). The upper spring here is the cantilever with a spring constant of k_F. The lower spring represents the interaction between the tip and the surface. However, this „spring constant“ k_SP (engl. *surface potential*) is variable and depends on the distance between the tip and the sample surface z_SP. This results in the spring constant of the overall system k_ges:

$$k_\mathrm{ges} = k_\mathrm{F} + k_\mathrm{SP} = k_\mathrm{F} - \frac{\partial F_\mathrm{SP}}{\partial z_\mathrm{SP}} \tag{1}$$

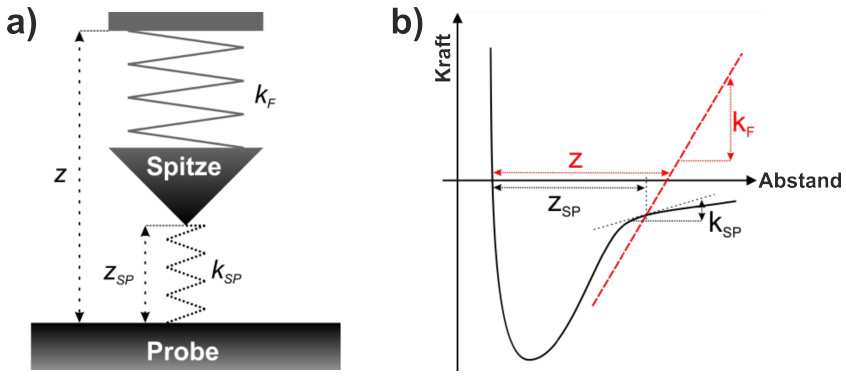


Abbildung 4: a) Model of a measuring tip in an interaction potential: The tip is located on a cantilever with a spring constant k_F and the force of the interaction between tip and sample is assumed to be another spring with a distance-dependent spring constant $k_\mathrm{SP}(z_\mathrm{SP})$. b) Typical force-distance curve (black) superimposed with the force-bending curve of the cantilever (red) at a distance z from the surface. (For details on force-distance curves, see section 2.2).

The system can be described as an externally excited damped harmonic oscillator for which the following applies:

$$m^* \cdot \ddot{z}_{SP} + \frac{m^* \omega}{Q} \dot{z}_\mathrm{SP} + k_\mathrm{ges} \cdot z_\mathrm{SP} = F_0 \cos\left(\omega_\mathrm{A} \cdot t\right) \tag{2}$$

where m^* is the effective mass of the cantilever, ω is the resonant frequency of the system, Q is the quality factor, F_0 is the external excitation force and ω_A is the excitation frequency. Without taking damping into account, the resonant frequency of the overall system is

$$\omega = \sqrt{\frac{k_\mathrm{ges}}{m^*}} = \sqrt{\frac{\left(k_\mathrm{F} - \frac{\partial F_\mathrm{SP}}{\partial z_\mathrm{SP}}\right)}{m^*}} \tag{3}$$

It is shifted with respect to the free resonant frequency ω_0 by

$$\frac{\Delta\omega}{\omega_0} \approx \frac{1}{k_\mathrm{F}} \frac{\partial F_\mathrm{SP}}{\partial z_\mathrm{SP}} \tag{4}$$

From equation 4 follows: If the distance between the tip and the surface changes because the height of the surface varies, the resonant frequency of the system changes, because the interactions between the tip and the sample depend on the distance: they are stronger the smaller the distance between the tip and the sample surface. As the tip normally oscillates mainly in the attractive range, $\frac{\partial F_\mathrm{SP}}{\partial z_\mathrm{SP}} > 0$, i.e. the resonant frequency becomes lower the closer the tip and sample surface are to each other. As can be seen in Figure 5 a, the oscillation amplitude also decreases as a result, as the excitation frequency remains the same. For imaging, the amplitude is typically kept constant by adjusting the distance between the tip and the surface using the feedback mechanism. If the amplitude is too low, the distance is increased. This allows the surface to be characterized without contact.

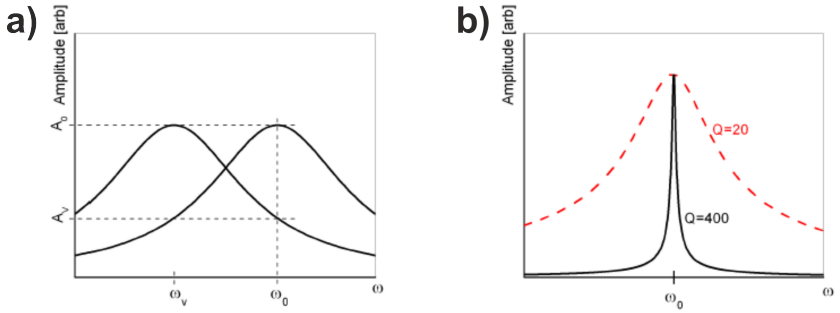


Abbildung 5: Oscillation amplitude as a function of frequency ω: a) Change in oscillation amplitude (from A_0 to A_v) due to a shift in resonance frequency ((from ω_0 to ω_v). b) Effects of different quality factors Q on the width of the resonance peak.

Due to the damping, there is also the following shift in the resonant frequency:

$$\omega_0^* = \omega_0 \sqrt{1 - \frac{1}{2Q^2}} \tag{5}$$

However, this shift is negligible for typical quality factors in air and in a vacuum ($Q > 100$). When working in liquids, however, significant shifts can occur. In addition, the strength of the damping is relevant for the sensitivity of the atomic force microscope. As can be seen in Figure 5 b, the width of the resonance peak depends on the quality factor Q. Qualitatively, this means that high quality factors, i.e. low damping, lead to narrow resonance peaks and thus to a strong change in the oscillation amplitude even with small resonance frequency shifts. Qualitatively, the minimum detectable force gradient can be approximated as follows:

$$\frac{\partial F}{\partial z}\Big|_{\mathrm{Min}} \propto \frac{1}{\sqrt{Q}} \tag{6}$$

Another strength of the dynamic mode is that you not only gain information about the topography, but can also see the energy dissipation during an oscillation in the so-called phase image. The average power dissipated due to interactions between tip and sample $\bar{P_{\mathrm{SP}}}$ can be calculated as:

$$\bar{P}_{\mathrm{SP}} = \bar{P}_{\mathrm{in}} - \bar{P}_0 = \frac{1}{2}\frac{k \cdot \omega_0}{Q}\left(A_0 A \sin\phi - A^2\right) \tag{7}$$

Here P_{in} is the average power of the external excitation mechanism, P_0 the average dissipated power of the cantilever movement, ϕ the phase of the oscillation, A its amplitude and A_0 the amplitude of the free oscillation. As the oscillation amplitude is normally kept constant, changes in the energy dissipation can be qualitatively tracked in the phase image. However, a quantitative analysis is very difficult, as it is not possible to differentiate between dissipation due to the adhesion properties of the sample, its elasticity or other properties.

The advantage of dynamic mode is that the force acting laterally on the sample is minimized and displacements are therefore prevented. Compared to measurements in contact mode, however, it has the disadvantage that the scanning speed is typically an order of magnitude lower, meaning that imaging takes longer. In addition, the height signal is not an absolute signal in this mode either: Assume that a perfectly smooth surface consists of two materials that lie next to each other in strips. As different materials normally interact with the tip to different degrees, scanning such a sample in dynamic imaging mode would result in a difference in height between the two materials. To rule out such height artifacts, it is advisable to scan surfaces with different vibration amplitudes and check whether the registered height differences are constant. If this is not the case, the height signal does not provide information accurate to the nm.

In addition to the dynamic mode without contact between tip and sample (*non-contact mode*) described above, there are other dynamic modes in which the cantilever also oscillates close to its resonance frequency, but briefly touches the sample during an oscillation (*intermittent contact mode*). One of these modes, which you also use in the experiment, is the so-called „tapping mode“, which was developed by the manufacturer of the atomic force microscope used in the experiment.

Further information on atomic force microscopy can be found in the book by B. Bhushan [1].

2.2 Force-distance measurements

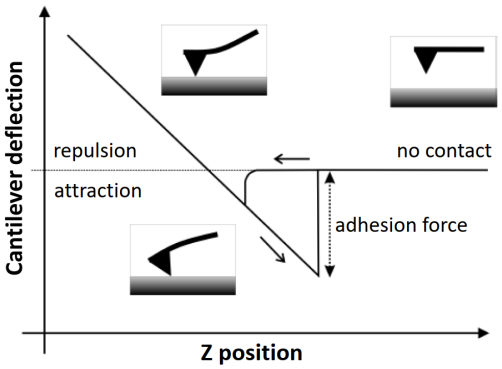


Abbildung 6: „Raw data“ of a force-distance curve: The force can be calculated from the bending of the cantilever (knowing its spring constants) and the distance traveled can be calculated from the vertical z-position of the cantilever.

One of the strengths of the atomic force microscope is that not only topographies can be imaged, but other surface properties can also be determined. In addition to the scanning operating modes, this is also possible with so-called force-distance measurements (*force spectroscopy*) (see Fig. 6). The great advantage of this operation mode is that quantitative results can be achieved. The distance between the tip and the material is first reduced and then increased again at a fixed position on the surface while simulta-

neously measuring the bending of the cantilever. The spring constant k of the cantilever can be used to deduce the acting force F from the measurement of the deflection x of the cantilever using

$$F = k \cdot x \qquad \text{(Hooke's law)} \tag{8}$$

This makes it possible to characterize the interacting forces between the tip and the material as a function of the distance and thus create an image of the vertical force field. This force field is made up of various components, which are explained in more detail in chapter 2.3. In addition to the force field, information is also obtained about the material properties (elasticity, adhesion) of the sample. A frequent area of application for force-distance measurements is the determination of adhesive forces. If a sample has adhesive properties, the respective force-distance curves (Figure 9) have a range in which the approach and retraction curves differ greatly. The so-called „adhesion peak“ can be seen in the retraction curve. The adhesion force can be determined directly from the height of this peak. In order to determine not only the adhesion between the tip material (typically SiO_2 or Si_3N_4) and a sample, it is also possible to functionalize tips. To do this, they are coated with any material and the interactions between this material and the sample are investigated. The possibilities for choosing this material are quite diverse and range from simple coatings to biological macromolecules (proteins, DNA, bacteria). For more details on force-distance measurements, we recommend reading the publication by Y. Seo and W. Jhe [6].

2.3 Relevant interactions

Atomic force microscopy is based on intermolecular forces that act between the tip and the surface. These can be divided into long-range and short-range forces. The long-range forces include

- van der Waals interactions,
- electrostatic force,
- magnetic force.

Van der Waals interactions are always present and fundamentally attractive. The strength or existence of the other two forces depends on the system in question. The short-range forces are made up of

- the steric interaction,
- the chemical or entropic forces,
- the Born repulsion.

When measuring in air, capillary forces usually also occur: As every surface is in principle covered with a thin layer of water under normal conditions, water menisci form between two contacting surfaces. Depending on the angle of water contact between the

two surfaces, these can have an attractive or repulsive effect and may have a strong influence on the measurements.

Important: Since knowledge of the topic „Intermolecular Forces“ is assumed on the day of the experiment, further literature – e. g. „Intermolecular and Surface Forces“ by J. Israelachvili [5] – should be consulted if necessary.

2.4 Samples

2.4.1 CD

A CD (*compact disc*) typically consists of three to four layers. At the bottom is a stable polycarbonate layer around 1.2m̈m thick. Above this is a reflective metal layer, typically aluminum. This is covered by a thin protective layer to protect it from corrosive external influences, to which another layer consisting of printing ink is applied - often for optical reasons. So-called „pits“ are pressed into the polycarbonate layer. The areas between the pits are called „lands“ . Pits and lands are arranged alternately in a spiral on the data area of the CD.

Reading a CD is based on interference. For this purpose, an infrared laser ($\lambda = 780\,\mathrm{nm}$) is focused on the track of the CD. While the laser scans the CD „“, a photodiode detects the intensity of the reflected light. By selecting a suitable pit height, destructive interference occurs between light reflected from the pit or land when the land/pit boundary is crossed. The photodiode then detects a drop in intensity. The coding of a CD is based on the „non-return-to-zero invert“method, in which a transition from land to pit (or vice versa from pit to land) is interpreted as „1“ and no change as „0“ .

2.4.2 Blockcopolymer

Polymers are macromolecules made up of many individual subunits, the monomers. If a polymer consists of only one type of monomer, it is referred to as a homopolymer. If several different monomers are fused together, heteropolymers or copolymers are obtained (see Fig. 7).

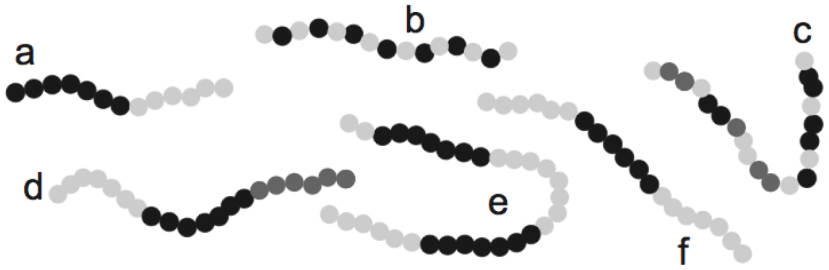


Abbildung 7: Examples of chain architectures in copolymers: a) diblock, b) alternating, c) random, d) (ABC-)triblock, e) multiblock, f) (ABA-)triblock. (taken from reference [4])

In coplymers, the different monomers can either be arranged irregularly, as is common in biopolymers (DNA, proteins), for example, or arranged in blocks. In the latter case,

they are referred to as block copolymers. Depending on the strength of the interaction between the individual blocks, they mix or separate. Most block copolymers are segregated at room temperature. As the different blocks usually have different properties (surface energies, elasticities), surfaces can be structured by coating them with block copolymers. In this experiment, the linear diblock copolymer Kraton G1701 from the company Kraton^{TM} is used. It consists of 37 % polystyrene (PS) and 63 % polyethylene propylene (PEP) and is mainly used in shoe soles in everyday life. The craton sample to be used was obtained by so-called spin coating. To do this, the polymer was dissolved in a suitable solvent and a small amount of the solution was dripped onto a rapidly rotating piece of silicon. Due to the centrifugal force and the rapid evaporation of the solvent, a uniform polymer film is formed.

2.4.3 Hydroxyapatite and real tooth enamel

Tooth enamel essentially consists of hydroxyapatite (HAP), a mineral with the chemical formula $Ca_{10}(PO_4)_6(OH)_2$. The high proportion of HAP of around 95 % in tooth enamel [3] is one of the reasons why it is the hardest material in the human body. In this experiment, you will examine both a sample of real tooth enamel and a sample of pure HAP. The latter was pressed from commercial HAP powder under high pressure ($\approx$ 100 MPa) and then sintered. The sample was then polished to a high gloss using different abrasive papers (maximum grit 4000) and diamond solution (30 nm maximum particle size). In a final step, polishing residues were removed by etching the sample for a short time (a few seconds) at a low pH value. The sample of real tooth enamel is a part of a bovine tooth. This sample was prepared in the same way as the HAP sample.

3 Experimental procedure

3.1 Workstation and evaluation software

The measuring station consists of two areas, namely the FastScan Icon atomic force microscope (Bruker, Santa Barbara, USA), which is mounted on an active vibration damping table and protected by a hood. Next to it is a workstation with the control unit and a PC.

Caution: Handle the appliance with care. It consists of very sensitive and expensive parts. Make sure you ground yourself before touching the microscope and do not touch any mirror or window surfaces on the scan head.

The free software *Gwyddion* is recommended for evaluating the images and for suitable presentation. It is quite intuitive to use and will be explained to you by the supervisor.

3.2 Preparation and procedure

To be able to carry out measurements with the atomic force microscope, the following steps must be carried out. Most of the steps require practice and the supervisor will help you with this.

1. If not already the case: Start the PC and the software *Nanoscope 9*.
2. Install a cantilever with a tip in the holder provided. To do this, carefully grip the so-called „chip“on which the cantilever is located with tweezers and slide it under the clamp on the holder.
3. Attach the holder to the scan head. **Caution:** Avoid touching the windows on the scan head.
4. Attach the scan head to the atomic force microscope.
5. Focus the laser spot on the back of the spring bar and adjust the photodiode so that the reflected beam hits it in the middle and maximum intensity is measured.
6. Check the last step by recording a resonance curve of the spring bar oscillation („Auto Tune“button in „Setup“mode).
7. Select the type of experiment, i.e. mainly the imaging mode („Select Experiment“button).
8. Place the sample to be analyzed on the sample table.
9. Approach the tip to the sample surface using the stepper motors until it can be seen in the camera image („Navigate“mode).
10. Find a „suitable“ spot on the sample. This spot should be free of clearly visible contamination or scratches.
11. Enter the desired parameters (image size, grid speed, sensitivity of the feedback loop, ...) for image acquisition („Scan“mode).

12. Create a folder with your name in the path „D:Capture/FoPra/“. To record your individual measurements, you must name your measurement each time in the menu item „Filename/“ Your measurement and select the storage location (your folder).
13. Start the automatic approach process using the stepper and piezo motors and the automatic subsequent image recording („Engage“button).
14. You can then click on the „Capture“button to capture the next image that has been completed without changing the parameters of the scan.

In this experiment, you can basically measure independently after familiarization. However, it is advisable to consult the supervisor briefly after measuring each sample to clarify whether the recorded data is meaningful.

3.3 Imaging of the CD

- Work in contact mode.
- Take sufficiently large images at different points on the CD. Measure the width and length of the pits and plot them in a suitable way as a histogram.
- Image one and the same spot at different scanning speeds. How does the scanning speed affect the image quality and the measured pit depth?

3.4 Imaging of the Kraton sample

- Install a new tip.
- Work in „Tapping-Mode“.
- Scan different positions of the sample. What are the differences, advantages and disadvantages of the height and phase images?
- Determine the amount of the two polymers in Kraton. How can deviations from the manufacturer's specification be explained?

3.5 Imaging the hydroxyapatite sample and the real tooth sample

- Work in „Tapping-Mode“.
- Image different positions of both samples.
- Determine the average grain size of the hydroxyapatite sample.
- Determine the roughness (*root mean square roughness*) of different grains and plot it as a function of the depth of the respective grains.
- Determine the roughness of the real tooth sample.

3.6 Force-distance measurements

Record several force-distance curves with different maximum contact forces on Sapphir and Parafilm (50:50 mixture of kerosene wax and polyethylene) („Ramp“-button of the experiment „FOPRA_FS.wks“). Describe the differences between the curves on both surfaces qualitatively. Can you determine the spring constant of the cantilever used from the curves?

3.7 Your samples

Consider which mode and parameters are suitable for answering your question and carry out appropriate measurements.

Literatur

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