Scanning probe microscopy

Scanning tunneling microscope (STM)

First tool to manipulate single atom ease of operation and construction of STMs → popularized Nanoscience

Later on followed by AFM (not just for conducting and clean surfaces)

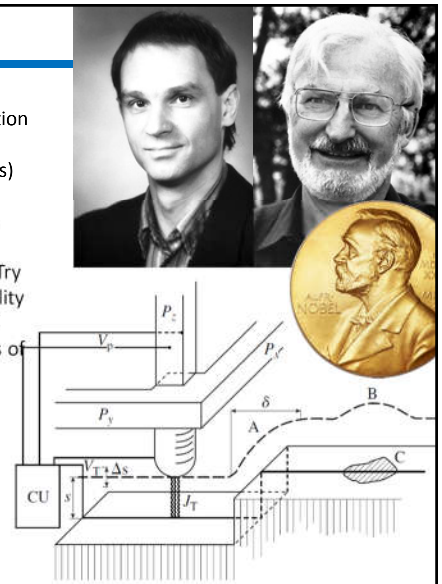
- **1979 Invention of STM** Gerd Binnig and Heine Rohrer at IBM labs. 1986. Nobel prize.

Idea of Binning as grad student: using tunneling to profile surfaces. Try to use very sharp metal whisker. He realized that vibration and stability issues are important. → Make a robust constriction. His expectation that with a tip with 1000A radius due to exponential characteristics of tunneling 45A resolution can be achieved.

1982 First paper about the operation

Basic structure & working principle: metal probe on a tripod consisting of three piezoelectric elements: Px, Py, Pz

- The probe is advanced toward the surface until a preset level of tunnel current is detected.
- *x–y* scan of the surface with feedback to control the tunnel current constant.
- Height change → change of the height of the surface (A) or a change of the local work function (B).
- Height vs. x-y is recorded by computer



(Up) G. Binning and H. Rohrer inventors of STM (Down) Basic structure of STM. Tunnel current J_T flows between a metal tio and surface, which exponentially sensitive to the distance. Piezo christals are used to move the tip up and down (P_z) and above the surface in x-y directions (P_x, P_y).

Wikipedia *Lindsay Section 4.1*

Scanning probe microscopy

Scanning tunneling microscope (STM)

First test of Au surface was a surprise, atomic terraces were measured (height 3A) → Probe is not a sphere but a single atom dangling from the very tip! → Atomic resolution

- The first image of the silicon 7 × 7 surface reported in the 1983 paper. At this early stage even IBM Corp. had not successfully attached a computer to a scanning probe microscope, so this three-dimensional rendition was made by cutting up copies of traces made on an *x–y* chart recorder, stacking them together, and gluing them!

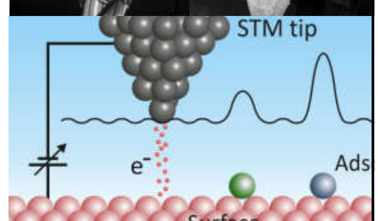
First setup is complicated : magnetic levitation of a superconductor to provide vibration isolation

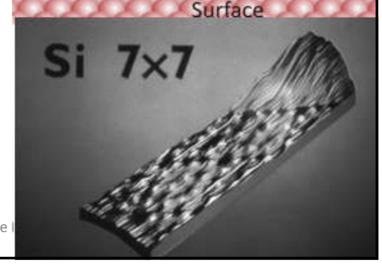
Few generations later STM mechanism became so small, compact, and rigid that it was easily capable of atomic resolution when operated on a tabletop.

Advantages:

- STM can work without vacuum (not like SEM) and also in water
- Cheap few kEUR

→ widely used, big momentum to Nanotechnology





(Middle) Fie sturcutre of the STM tip contains a single atom at the vry and of the tip. Since tunnel current is dominantlycoming from this atom ensures the atomic resolution. (Down) First image of the surface reconstrction of silicon (111) surface. First direct observation of this structure at the atomic level. IBM.

Wikipedia *Lindsay Section 4.1*

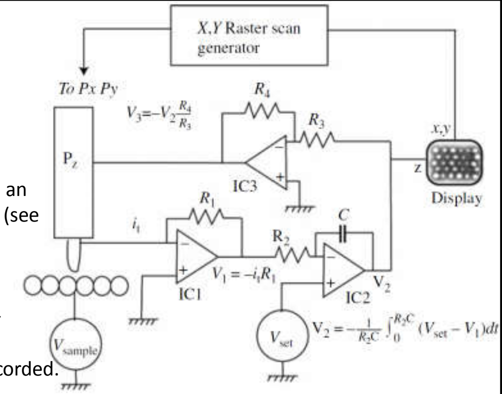
Scanning probe microscopy

Scanning tunneling microscope (STM)

STM setup - height control circuit

- Tip sample tunnel current (i_T) is converted to voltage (V_1). $V_1 = -i_1 R_1$ by IC_1&R_1.
- V_{set} sets the targeted tunnel current. IC_2&R_2&C generates an error signal (V_2) between targeted and measured current (see form of V_2).
- Error signal is sent to the piezo actuator Pz after voltage amplification with IC_3&R_3&R_4.
- Overall phase of the feedback is negative: increased i_T → probe is pulled away as long as $V_{set}=V_1$.
- V_2 represents the height of the sample as well. → It is recorded.
- X and y positions are scanned by a scan generator, it is applied to P_x, P_y.

Today entire feedback arrangement is carried out digitally.

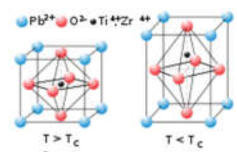


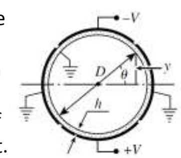
Piezoelectric scanning transducer

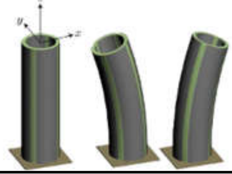
Piezoelectric cheramics e.g. lead zirconium titanate (PZT). V → δz

Scanner tube: metal electrodes both in and outside. Applied voltage across the wall -> changes thickness, increase/decrease depending on direction of P and E. Volume of cheraic ≈ constant → tube length changes. Typical 20A/V.

Driving opposite quardants with different voltage sign → bending of the tube →x, y displacement. Same V on all sides → z displacement.







Wikipedia Lindsay Section 4.1

Scanning probe microscopy

Scanning tunneling microscope (STM)

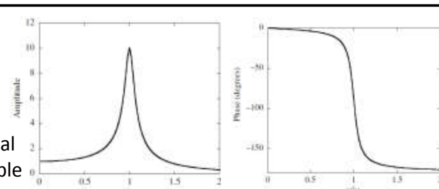
Speed limit of STM response – constant current mode

Typical piezoelectric scanning elements have an intrinsic mechanical resonant frequencies 1 - 50 kHz. → Limitation on the fastest possible response of the microscope. If drive freq > resonance freq. → 180 phase shift in response → feedback loop gets unstable.

Integrator part has to be sufficiently slow, tuned by R_2 and C values. → Shortest time to measure one pixel ~20usec.

This operation mode is the **constant current mode**. It provides safe operation with low risk to crash the tip. (typical tip distance 4-7A)

Other mode: **constant height mode**. Scanning in X-Y direction at fixed height, measuring i_T. → Faster, no need for feedbacking. But thermal drifts, crashing risk.



(Up) Amplitude (see also equation bellow) and phase response of a damped harmonic oscillator when harmonic excitation with frequency, ω is applied. For Q=ω_0 τ=10. ω_0 is the resonance frequency, τ is the friction coefficient.

$$x(\omega) = \frac{A_0}{\sqrt{(\omega_0^2 - \omega^2)^2 + \left(\frac{\omega}{\tau}\right)^2}}$$

(Down) Mechanical transfer function of an STM system. T3 is the transfer function of STM with resonance frequency of 1kHz, T1 and T2 two damping system e.g. springs, several heavy metal plates with viton rings between, etc., which protect the system from external mechanical noises. Goal is to filter out noises above a few Hz. The total transfer function (T) fulfils this requirement.

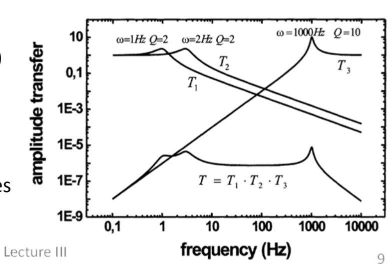
Mechanical isolation

STM is very sensitive to acoustic noises.

Mechanical noise transfer chracteristics of STMs (see T3 on the figure) gets suppressed as f → 0Hz. Mid freq. range has to be filtered out.

Solution: Isolation systems with low resonance frequency. As Eq. 1 shows when $\omega >> \omega_0$, the response of the system gets suppressed ~ ω^{-2}.

Various acustic isolation systems: box, mechanical springs, heavy plates with viton rings between, eddy currents, rubber feet, pendulum etc.



Wikipedia Lindsay Section 4.1, and Appendix D. also E. Meyer: Scanning Probe Microscopy Springer (2004) Sec. 1.2.3

Scanning probe microscopy

Scanning tunneling microscope (STM)

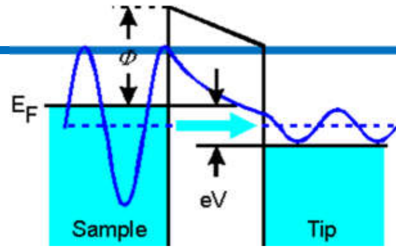
Basics of tunnel current

The tunnel current can be calculated by Fermi's golden rule:

$$I = \frac{4\pi e}{\hbar}\int_0^{eV} \rho_s(r,E)\rho_t(r,(E-eV))T(E,eV,r)\,dE$$

where ρ_S, ρ_t are sample (S) and tip (t) DOS, and T is the tunneling transition probability:

$$T(E,eV,r) \propto \exp\left(-\frac{2S\sqrt{2m}}{\hbar}\sqrt{\frac{\phi_s+\phi_t}{2}+\frac{eV}{2}-E}\right)$$



$$\psi(z) = \psi(0)\exp -\frac{\sqrt{2m(\phi-E)}z}{\hbar}$$

(Up) Energy diagram for tunneling . V voltage is applied between sample and tip, which are separated by a vacuum barrier with height of ϕ. The wave function of e penetrates into the barrier according to the formula.

where m is electron mass, S is the width of tunnel barrier, and $(\phi_S + \phi_T)/2 = \phi$ is an average workfunction of S and t, V is the bias between S and t. T is calculated from according to quantum mechanics, how a particle with energy *E* can penetrate a barrier ϕ > *E*. (See Fig.) If we assume that V<< ϕ, and the DOS of the tip is flat:

$$I = \frac{4\pi e}{\hbar}\rho_t(0)\exp\left(-\frac{2S\sqrt{2m\phi}}{\hbar}\right)\int_0^{eV}\rho_s(r,E)\,dE \qquad (1)$$

Tunnel current depends exponentially on the tip sample distance S, and also influenced by energy dependent DOS of the sample. If ρ_S is constant in the eV window:

$$I_t \propto V\rho_s(E_F)e^{-1.025\sqrt{\Phi}z}$$

where ϕ is the workfunction in eV, z is the barrier width in Å. For a typical barrier height e.g. for Au ϕ=5eV tunnel current decays by factor of 10 when spacing is changed by 1Å. See Tersoff-Hamann Model for more detail.

Lindsay Section 4.1, and E. Meyer: Scanning Probe Microscopy Springer (2004) Sec. 2.1.

Scanning probe microscopy

(Up) Formula for thermal noise of a resistor (R) at finite temerature. T in a bandwidth of Δf. It generates a current noise, <i> which place a limitation on small current signals.

Scanning tunneling microscope (STM)

Sensitivity

Smallest detectable current is limited by thermal noise (Johnson-noise), i.e. by the noise of the resistor in the current to voltage converter (R1). E.g. for R1=100MΩ and bandwidth of Δf=5kHz → the Johnson noise ~ 6pA.

(It can be decreased by R1↗, but bandwidth also ↘.)

As 12kΩ corresponds single atomic contact, and R increases by 10 for 1A displacement → **maximal tip surface distance: ~7Å.**

Typical bias voltage limit is ~1V (avoid field emission). R ~ 100GΩ.

$$P = 4k_B T\Delta f \qquad P = i^2R$$

$$\langle i\rangle_{RMS} = \sqrt{\frac{4k_B T\Delta f}{R}}$$

Scanning tunneling spectroscopy (STS)

Based on Eq. 1 tunnel current is sensitive to the local DOS (E) of the sample. I.e.:

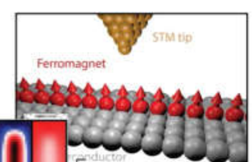
$$\frac{dI}{dV} \propto \rho_s(r,E) \equiv \mathrm{DOS}(eV)$$

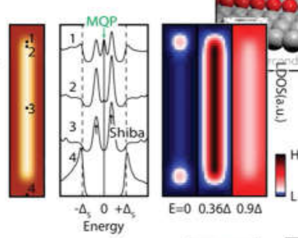
By changing the sign: the occupied and non-occupied states of the sample can be measured.

For STS measurement x, y and z are fixed and I vs. V is measured.

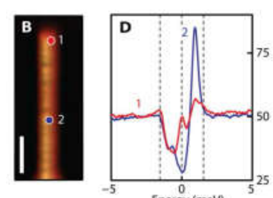
Examples:

- Measuring the gap structure of a superconductor.





Nadj-Perge et al., Science 346, 602 (14)



(Right) STM investigation of chain of ferromagnetic atoms on a superconductor (SC) surface. At the SC surface the STS curve (4) shows the gap structure of the superconductor. While at the end of the ferro chain STS (1) has a peak at zero bias, which is a signature of a new Majorana Frmion state (MF). MF is its own antiparticle. (Mid figs are simulations lower ones are measurements.)

Lindsay Section 4.1, and E. Meyer: Scanning Probe Microscopy Springer (2004) Sec. 2.1.

Scanning probe microscopy

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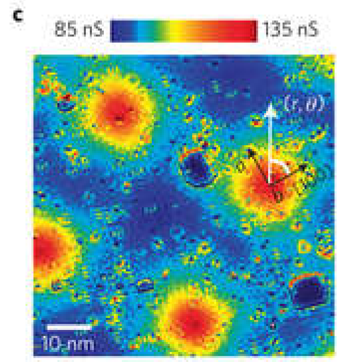
$$P = 4k_B T \Delta f \qquad P = i^2 R$$

$$\langle i \rangle_{RMS} = \sqrt{\frac{4k_B T \Delta f}{R}}$$

Vortex cores in heavy Fermion system CeCoIn5
Nature Physics **9**, 474–479 (2013)
Performing STS at different points and plot dI/dV at V=0



Scanning tunneling spectroscopy (STS)

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By changing the sign: the occupied and non-occupied states of the sample can be measured.
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Lindsay Section 4.1, and E. Meyer: Scanning Probe Microscopy Springer (2004) Sec. 2.1.

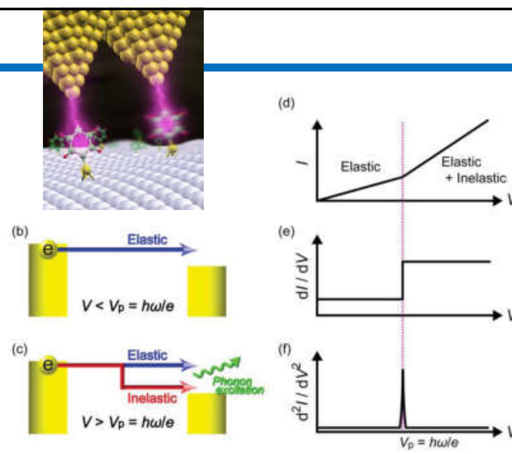
Scanning probe microscopy

Scanning tunneling microscope (STM)

Scanning tunneling spectroscopy (STS)

Example 2: Inelastic tunneling spectroscopy (ITS)

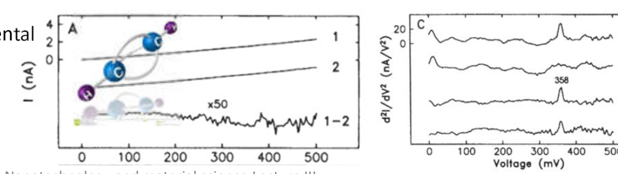
In case of elastic tunneling current increases linearly. Above a trashold the current has additional enhancement.
The origin: when electron has enough energy to excite a vibration mode i.e. eV > ħω, an inelastic channel opens where during tunneling a phonon is created. Panel d shows the typical I – V curves with a characteristic kink. ITS signal is usually very small → Better to use d^2I/dV^2. It results a peak at the vibrational energy.



(Up) (a) Artistic view of ITS (b) Elastic tunneling, (c) Inelastic tunneling (d-f) The resulted I –V characteristics. Figure from Sensors **2012**, *12*(6), 7259-7298 and http://art4science.deviantart.com/art/Inelastic-electron-tunneling-spectroscopy-289208869

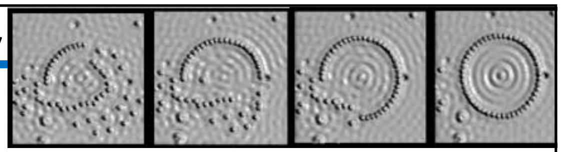
ITC can be used to chracterize a molecule on the surface. See example bellow. Isotope effect is often used as a further experimental check.

(Right) First observation of ITS of acetylene molecule on Cu (100) surface. (a) I-V on the molecule (1) and on Cu surface (2) and their difference.(1-2) (b) Peak at 358 eV corresponds to the C-H stratching mode of the molecule. B.C. Stripe Science 280, 1732 (1998)



E. Meyer: Scanning Probe Microscopy Springer (2004) Sec. 2.2.

Scanning probe microscopy



Scanning tunneling microscope (STM)

Manipulation mode

Vertical and lateral manipulations

(Up) Arranged 48 iron atoms on the surface of a copper substrate. These images show the various stages of the process. Once complete the circular arrangement of the iron atoms forced the electrons in the surface of the copper to specific quantum states as shown by the rippled appearance of the surface. By Don Eigler IBM.

(Down) Tip height curves during lateral manipulation of various atoms on the Cu(211) surface. The tip movement is from left to right, the fixed tunneling resistances are indicated. Vertical dotted lines correspond to fcc sites next to the step edge.

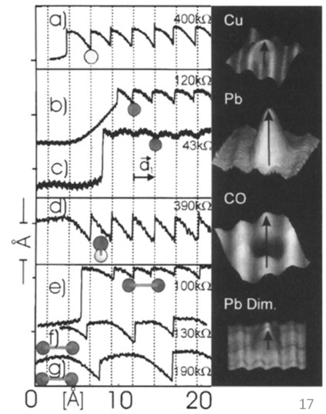
Vertical manipulation

a) transfer of the surface atom to the tip.
b) Tip is moved to the desired position. c) Deposition
Transfer of the adsorbate atom from the surface to the tip, or vice versa, is achieved by bringing the tip close and applying voltage pulse.
E.g. Xe atoms moves same direction as tunneling electrons due to heat assisted electromigration.

Lateral manipulation

a) Tip is moved down a few Å, set point is increased b) Tip forms a weak bond with the adsorbate atom or molecule. c) Tip is then moved along the line of manipulation. Typical threshold resistances to slide an adsorbate are 5k-20kΩ.
Tip height during manipulation can be recorded, which gives some insight about the manipulation process.
See example: e.g. Cu adatoms are shifted sites by sites (a), Pb dimmer (e-g) can jump several sites, since it is larger object.

Other mechanisms: field assisted direction diffsuion, inelastic tunneling induced movement for H adatoms



E. Meyer: Scanning Probe Microscopy Springer (2004) Sec. 2.2.

Scanning probe microscopy

Atomic Force microscope (AFM)

Invented by Binnig, Quate, and Gerber in 1986.

Flexible cantilever (equipped with a sharp diamond point) was scanned over a surface while the height of the cantilever above the surface was kept constant (similar to STM) → detection of attracting force of the surface. First systems with soft cantilevers.

Resonance frequency:

$$f_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

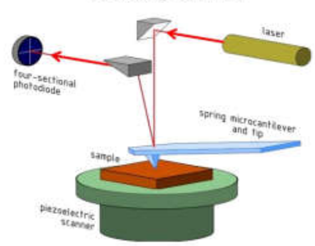
Requirements:

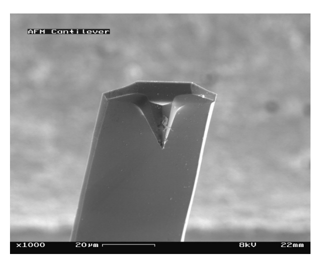
- f_0 large: be independent from vibrations of environment (building etc.)
- k small: be sensitive to tiny forces. Use a spring constant which generates detectable bending for atomic force.
- → m should be small.

AFM „feels” the surface. It has become an ultimate tool to analyze at the nanoscale. It has different operation modes, even conducting AFM. It replaced STM in several fields.

Due to the tip-surface forces small bending of the cantilever has to be detected. There are several detection schemes which requires different stiffness of the cantilever.

Working of AFM





(Up) Usual AFM setup (Down) SEM image of a cantilever showing the small probe fabricated onto the tip of the cantilever. The scalebar is 20 μm. The cantilever is 40 μm wide, 125 μm long, and 4 μm in thickness and has a spring constant of approximately 40 N/m. It is a stiffer type of cantilever, designed to pull away from a sticky surface The radius of curvature of the force sensing probe can be as small as a few nm.

Wikipedia Lindsay Section 4.2

Scanning probe microscopy

Atomic Force microscope (AFM)

Detection scheme

Most widely used to monitor the bending of the force sensing cantilever is **optical deflection**. Light from a small laser diode focused on the back of the cantilever. The reflected light is monitored by a two- (or four-) segment photodiode via the relative photocurrent produced in the two segments, i_A and i_B.

Working point: $i_A = i_B$.

Here the deflection signal is: $$\delta z \propto \frac{i_A - i_B}{i_A + i_B}$$

The signal is calibrated to distance by force distance curves.

Detection limit:

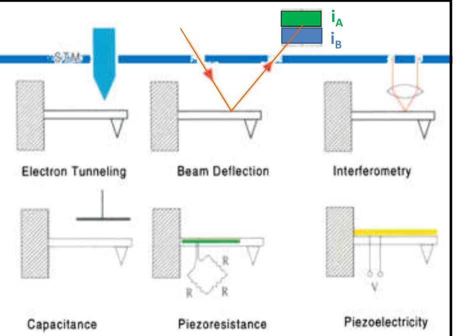
a) It is limited by the **shot noise of the laser signal**. 1mW red laser emits 10^{15} photons/s. Data acquisition is limited by f_0. Typical dwell time is ~1ms. → ~ 10^{12} photons are collected in 1 pixel. Since shot noise is ~√N ~ 10^6 photons/pixel. Signal-to-noise ratio: ~ 10^6.

Thus a deflection of $1/10^6$ is detectable. Thus for a cantilever of 50μm in length ~ 50pm is the detection limit.

b) **Thermal excitation** of the cantilever → noise in the measured signal. Estimation based on equipartition theorem: Elastic term ½ k z^2 gets a thermal energy of ½k_BT, *thus*

$$\sqrt{\langle z^2 \rangle} = \sqrt{\frac{k_B T}{\kappa}}$$

k_BT at 300 K is ~4.2 pN·nm, and k=1N/m the noise is <100pm.



(Up) Various detection schemes of cantilever deflection. (TopLeft) First detection technique based on an STM tip, (TMiddle) Optical deflection method: Focused laser light reflected and detected with 2 or 4 segment photodiode. With 4 segment torsion can be detected as well. (TopRight) Cantilever is one mirror of an optical laser interferometer. (BRight) Based on capacitance between cantilever and an electrode. Fast detection scheme, but internal force has an effect. (BM) Self sensing type, which is based on piezoresistive effect. (BL) Piezoelectric cantilever It is a sensor and actuator at the same time. It has a very compact design and very useful for dynamic operation mode. E.g. quartz tunning fork are cheap version with high frequency and spring constant.

A more accurate estimation of thermal excitation by fluctuation dissipation theorem for damped harmonic oscillator:

$$\delta z_{RMS} = \sqrt{\frac{4 k_B T B}{Q \kappa \omega_0}}$$

Where B measurement bandwidth (~1KHz), ω_0 resonance freq., Q is the Q-factor (typical values 2-50). Typical δz_{RMS} ~10pm. (Formula for off resonance (See Lindsay 4.2.2 for more details)

Lindsay Section 4.2 E. Meyer: Scanning Probe Microscopy Springer (2004) Sec. 3.1.

Scanning probe microscopy

Atomic Force microscope (AFM)

Surface forces in AFM

Interaction between atoms is described by Lennard Jones potential

$$\phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

To get tip-surface force it has to be summed up for all tip and surface atoms. Assuming a sphere with radius R at a distance D from the surface the interaction energy:

$$W(D) = -\frac{\pi^2 C \rho_s \rho_p R}{D}$$

It is a weakly decaying, long range interaction (~D^{-1}). → To achieve high resolution probe must be in hard contact (to sense short range repulsive term). Attractive interaction force: $F_S(D)$ ~ D^{-2}.

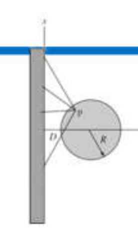
Instabilities for weak cantilevers

In equilibrium surface attraction force is equal to the force of the cantilever $F_C(D)$=k(h-D). Since F_S increases nonlinearly with decreasing D → instability for weak canlilevers (i.e. k<K2). The tip is pulled to the surface.

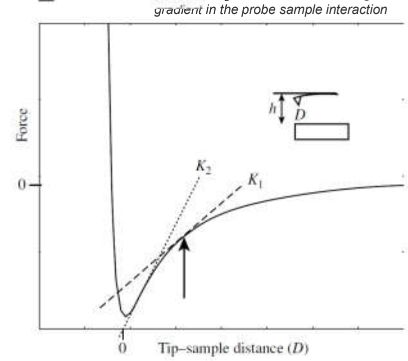
Adhesive force in contact

When tip touches surface energy and surface area defines the adhesive force. For a sphere with radius R: $F_A = 4\pi R\gamma$

where γ ~ 0.5J/m2. Thus for R=1nm → ~6nN. It can be reduced by working in solvents.



(Up) Long-range interactions between a sphere and a plane. The van der Waals interaction is summed for each atom in the sphere with every atom in the surface. (Down) The relationship between force and distance for a spherical probe at height D above a plane. Contact occurs at D = 0 where strong repulsive forces dominate. For a soft cantilever (spring constant K_1) the surface force increases more rapidly than the spring force at the D value marked by the arrow, pulling the tip into the surface. It is necessary to work with a cantilever of spring constant ≥K_2, i.e., stiffer than the largest force gradient in the probe sample interaction



Additional forces:
- Electrostatic force: Charged surface + conducting tip
- Capillary forces: condensed water on the tip water vapor and
- Magnetic forces, - Forces in liquids (See Section 3.2 of Meyer)

Lindsay Section 4.2

Scanning probe microscopy

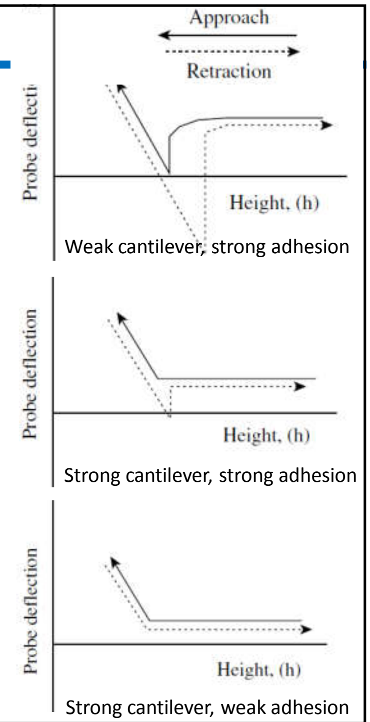
Atomic Force microscope (AFM)

Depending on the stiffness of the cantilever and the adhesion force the deflection signal shows different characteristics during approaching and retraction. See figures. (Up) Effect of jump-to-contact and strong adhesion during retraction is seen. (Middle) With a stiffer cantilever ($k>K_2$) no jump anymore (Down) With a strong cantilever. This condition is used for high quality images.

Force - displacement plots

The measured raw data is deflection signal as a function of cantiler height (h).

The deflaction can be translated to force using the slope when the cantilever is in hard contact with the surface. In this case spring constant of the cantilever (k) and height difference from touching point define the pressing force. The tip - sample distance can be determined by substracting the height of touching point from h.



Wikipedia *Lindsay Section 4.2*

Scanning probe microscopy

Atomic Force microscope (AFM)

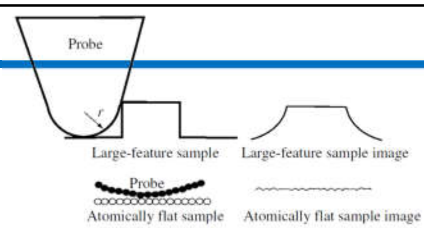
Resolution

Shape of the probe limits the resolution.

It depends on the radius of the tip (r) and also height of surface roughness (dh). (See figure). When r is comaprable to dh spatial resolution is limited by r.

However for close to atomicly flat surfaces atomic scale resolution can be achieved, probing by the last atoms of the tip.

Reconstruction methods: For a probe with characterized shape and for a sharp object on teh surface the otiginal contour can be reconstructed.



(Up) Surface with large scale topography and large probe radius and teh resulted image on teh left. (Down) For atomic flat topography the last atom of the tip probes the surface, which could lead to images with atomic resolution.

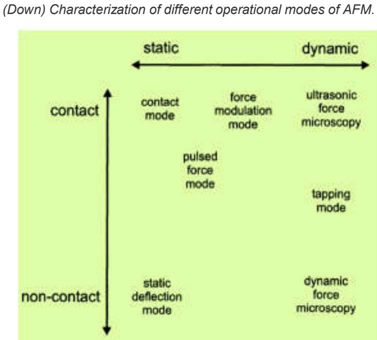
Operational modes of AFM

There are various modes. They can be characterized by **static** and **dynamic** operation or whether the tip is in **contact** or **not in contact** with the surface.

Static: static bending of the cantilever is measured

Dynamic: changes in the dynamical properties of the cantilever is measured due to tip-surface interaction.

(Down) Characterization of different operational modes of AFM.



Lindsay Section 4.2 *E. Meyer: Scanning Probe Microscopy Springer (2004) Sec. 3.3.*

Scanning probe microscopy

Atomic Force microscope (AFM)

Static modes

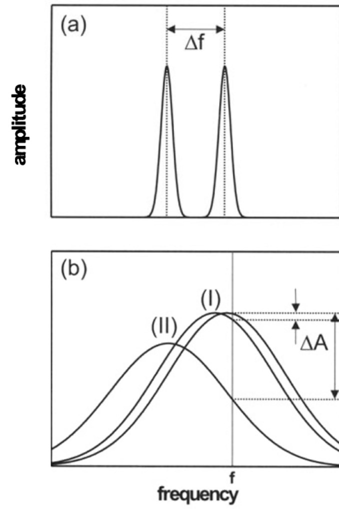
- Contact mode of AFM: The tip-sample distance is controlled to maintain a constant cantilever bending. → Topography of constant force is measured. (Typically soft cantilevers)

- Other static operation is scanning in constant height above the surface. → map of force. Problems with jump-to contact, drifts. It is mainly used for long range magnetic forces.

→ Solution is dynamic mode and applying a feedback.

Dynamic modes

- Using the frequency shift of a self-exciting oscillation loop as feedback parameter → leads to a reliable non-contact mode operation. It is non-contact AFM or dynamic force microscopy. (good in vacuum with high Q-factor cantilevers.)
- Change in amplitde of the oscillation as feedback parameter can also be used for low Q-factor cantilevers e.g. gas or liquid surrounding. Used e.g. in tapping mode.
- Measurements of cantilever oscillations with the tip in permanent contact with the sample allow studies of the mechanical response of the sample. → ultrasonic force microscopy



Two dynamic modes for the detection of tip- sample interactions. (Up) In dynamic force microscopy, the shift in frequency caused by the tip- sample interaction is detected. The oscillation is driven at the actual eigenfrequency of the cantilever. In the tappnig mode (other name intermittent contact mode) (down) , the change in amplitude is detected at a fixed frequency f0 . This mode is suitable for systems with low Q-factors, where the amplitude changes fast enough upon tip- sample interactions. The decrease in amplitude at fo may be due either to a frequency shift (I) or to an additional decrease in the total amplitude due to damping (II)

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Scanning probe microscopy

Atomic Force microscope (AFM)

Contact mode AFM

Topographic images are recorded by scanning the tip over the sample surface at constant cantilever deflection i.e. at constant force in repulsive regime.

Due to strong increase of repulsive force with dispalcement, it is essentialy a **topographic image**.

Artifacts:

- Local varioation of elesticity has influence (can be calibrated).
- Strong torsion of cantilever (exclude by forward and backward scans. Analyze lateral forces with 4 quadrant detectors.)

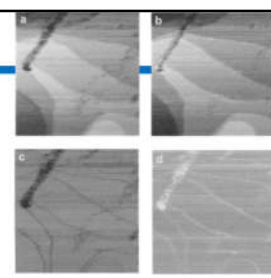
Force can be calibrated by force-displacement plots.

When tip is in contact, the force is tried to be minimized → move up to the close to jump-out-of-contact situation.

Resolution:

Atomic resolution is very challanging (mostly only lattice periodicity is observed) due to the large area of tip-sample contacts. Single atom contact is not favorable, attracting force of neighbouring atoms so high → deformation. Typical contact diameter 1-10nm. →

The resolution in abmient conditions: 5-10nm. In liquids true atomic resolution is possible. In vacuum, best one is ~1nm



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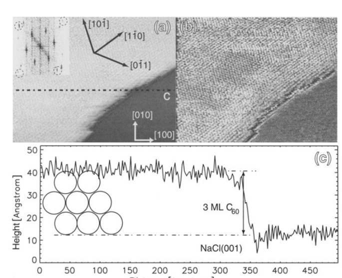

Fig. 3.12. (**a**) High-resolution constant force image of C_{60} on NaCl(001). The *inset* is the FFT image, showing the spots from both the C_{60} periodicity and the NaCl(001) lattice. (**b**) Corresponding friction force map. The molecular structure is visible on both the C_{60} terrace and the NaCl lattice. The observation of molecular structure at the step edge confirms that the resolution is about 1 nm, which corresponds to the distance between C_{60} molecules. (**c**) Profile as indicated in (**a**)

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Scanning probe microscopy

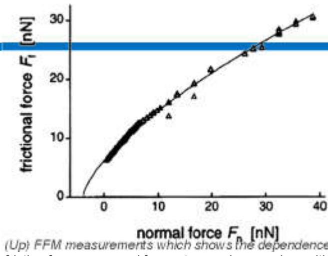
Atomic Force microscope (AFM)

Friction Force Microscopy (FFM)

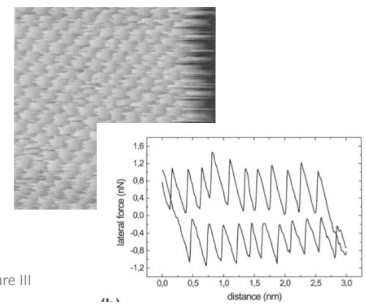
Other contact mode operation.
When tip is moved over the surface, friction in the tip- sample contact will produce a lateral force on the tip apex. → torsional bending of the cantilever, which can be recorded in beam-deflection at constant repulsive force.
E.g. FFM tells, whether wear has taken place during subsequent imaging of an area.
FFM measurements require forward and backward scans and avariging to avoid artifacts from assymetries (e.g. imperfect alignment of the light beam).
It is widely used in nano tribology.

Friction at atomic scale

FFM on well-defined surfaces can exhibit atomic-scale features.
E.g. NaCl(lOO) surface cleaved and studied in ultrahigh vacuum. A sawtooth-like behavior is observed with the periodicity of the surface lattice. This phenomenon is **atomic-scale stick- slip:**
Contact is locked to one atomic position, when force is enough strong, it initiates a slip.



(Up) FFM measurements which shows the dependence of friction force on normal force at amorphous carbon with a tip with a radius of 58nm. The friction force increases with ~ $F_n^{2/3}$ i.e. with the contact area. It deviates from macroscopic laws.
(Down) Friction force map of a Cu(lll) surface showing atomic-scale stickslip. The frame size is 3 nm.
(Downdown) Lateral force vs. scanned distance for one crosssection. Back and forward scan show hysteresis, from teh area one can calculate dissipation.



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Scanning probe microscopy

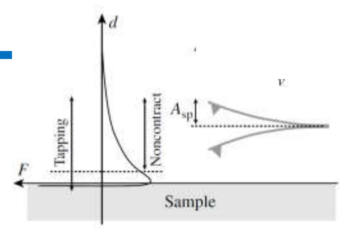
Atomic Force microscope (AFM)

Dynamic Force Microscopy (DFM)

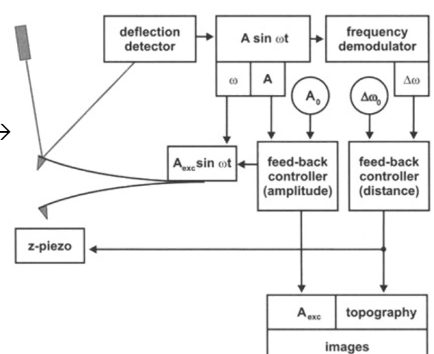
Other name is non-contact AFM.
Only operation mode allows atomic resolution, comparable to STM. Since tip is not in contact the last atoms could play the main role in imaging.

Operation principle:

- Cantilever is excited by piezos at its eigenfrequency using a phase locked loop.
- Due to tip-surface interaction → δf. Fast frequency demodulation unit detects.
- Feedback on the distance with z piezo.
- To maintain oscillations the restoring force has to be larger at the lower turning point than tip attraction (avoid instability) → large excitation amplitude (A_{exc})
- Controll oscillation amplitude:
    - Constant excitation amplitude. Disadv: close to surface significant damping → Crosstalk between topology and damping.
    - Control circuit to maintain constant amplitude, A Disadv: difficult to avoid tip crash



(Up) It shows the ideal setting of tip-sample distance and oscillation amplitude to operate in noncontacting and contacting mode.
(Down) Scheme of the feedbacking system of dynamic force microscope



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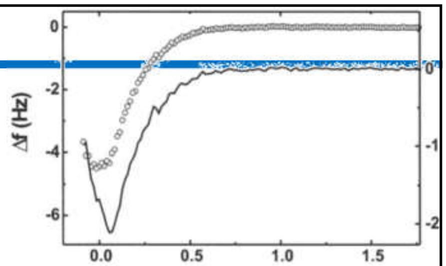
Scanning probe microscopy



(Up) One can show th[...]he form of F(z) can be reconstructed, without assumptions with iterating method. Figure shows an example for silicon tip approaching a Si(111)7x7 surface. The long range attracting contribution is nicely visible. Such force distance curves can be used to understand the different types of acting forces on a system and their characteristics. (E.g. repulsion forces for different orbitals, electrostatic forces etc.)

Atomic Force microscope (AFM)

Dynamic Force Microscopy (DFM)

Let us calculate the frequency shift due to the force of tip surface interaction, F(z).

Equation of motion of the driven cantilever:

$$m\ddot{z} = -k\big[z - A_{\mathrm{exc}}\cos(\omega t + \varphi)\big] - \gamma\dot{z} + F(z)$$

considering a drive with amplitude A_{exc} and phase shift ($\varphi = 90°$

In this case one can assume that the friction term and drive equal and it simplifies to:

$$m\ddot{z} = -kz + F(z)$$

Let us assume that the trajectory of the tip is harmonic, i.e.

$$z = z_0 + A\sin\omega t$$

It yields to

$$-mA\omega^2\sin\omega t = -kA\sin\omega t - kz_0 + F(z_0 + A\sin\omega t)$$

Multiplying with sinωt and integrating over one period:

$$kA\left(1 - \frac{\omega}{\omega_0}\right) = \frac{1}{\pi}\int_0^{2\pi/\omega}\sin\omega t F(z_0 + A\sin\omega t)\mathrm{d}t$$

The frequency shift relates to force averaged over the oscillation cycle:

$$\frac{\Delta f}{f}kA = \frac{1}{\pi}\int_0^{2\pi/\omega}\sin\omega t F(z_0 + A\sin\omega t)\mathrm{d}t \quad (**)$$

Let us consider the van der Waals attraction term from the L-Jones potential, which results a frequency shift, Δf_{VdW} of:

$$\frac{\Delta f_{\mathrm{VdW}}}{f_0}kA = -\frac{HR}{6\bar{s}(2\bar{s}A)^{0.5}}$$

where s is the tip surface distance, R is the radius of the tip, k spring constant, A amplitude and H is a constant (Hamaker).

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Scanning probe microscopy

Atomic Force microscope (AFM)

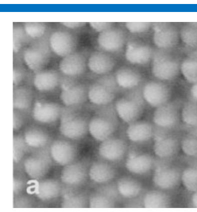
Dynamic Force Microscopy (DFM)

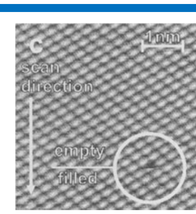
High resolution images

Advantage of DFM: true atomic resolution is achievable.

E.g. point defects, steps, kinks, single molecules can be studied.

Great advantage compare to STM that insulator surfaces can be studied as well.





(Left) DFM images in the constant amplitude mode of Si(111)7 x 7 surface imaged at low temperature. Even the rest atoms of the 7x7 reconstruction have been imaged.
(Up) DFM images in the constant amplitude mode of a single vacancy on a InAs surface. The vacancy is filled in the course of imaging

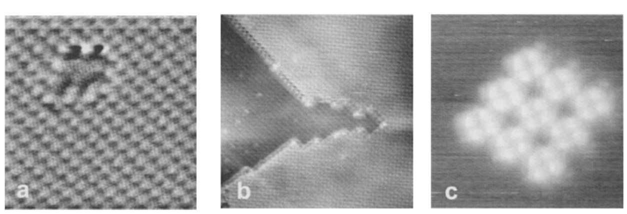


Fig. 3.23. High-resolution DFM images in the constant amplitude mode. (**a**) Initial stages of desorption on a KBr(001) surface after irradiation with low-energy electrons [223]. (**b**) One monolayer of NaCl on a Cu(111) substrate. The step and kink sites appear elevated due to increased forces at these sites of lower coordination and due to a displacement of the ions [227]. (**c**) A group of nine porphyrin molecules on a Cu(100) substrate [230]

- It allows to image atoms which are not visible in STM (up a)
- AFM scans could easily rearrange atoms (up c)

- Interpretation of the images requires modeling of the attracting force.
E.g. different coordination of atoms could result different force (see left b).

- It allows to image molecules (see left c) and even differentiation of their end groups.

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Scanning probe microscopy

Atomic Force microscope (AFM)

Tapping Mode Force Microscopy

It is a dynamic force microscopy mode when the tip gets into contact with the surface.

- Principle:

Instead of detecting Δf, the amplitude change of the oscillation (ΔA) is the control parameter. Amplitude is reduced due to intermittent contact during each cycle of the oscillation.

- Advantage:

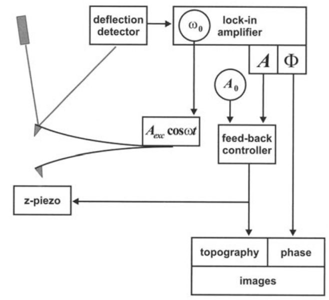
Lower lateral forces than for contact mode while the resolution is similarly limited only by the tip shape.

- Large A is required to overcome attractive capillyar forces by cantilever spring force.
- It is very good for biological samples. Variuos studies in liquids.

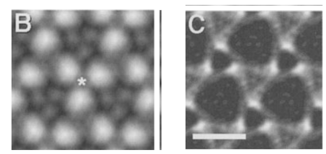
- Setup

Lock-in detector is used to measure A. (see Fig.)

- The phase shift also contains information. E.g. stiffness imaging of soft surface.
- Non-linearities: E.g. for hard surfaces, Amplitude vs. Frequency resonance is truncated. Due to getting into contact hysteresis effects are also presented → non-linear effects: More than one state of oscillation is stable. → Abrupt jumps for certain set of parameters. Way out e.g. working only in repulsive or in attractive force regime.



(Top) Scheme for tapping mode AFM. Amplitude and phase of the cantilever vibration is measured compared to the excitaion signal by lock-in detector. Feedbacking on A regulates the distance, while the phase also contains physical information e.g. stiffness of the soft surface.



Example: Membrane surface imaged by tapping mode force Microscopy (B) and contact mode AFM (C). Tapping mode is demonstrated to be of comparable resolution to contact mode. Scale bars 5nm.

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Scanning probe microscopy

Atomic Force microscope (AFM)

Scanning Kalvin Probe Microscopy (SKPM)

Goal: To measure the contact potential difference between tip and sample.

Principle: Electrostatic potential between tip and sample generates also force. Based on Equation (**) it leads to

$$\frac{\Delta f_V}{f_0} kA = -\frac{\pi \epsilon_0 R (V_{bias} - V_{cpd})^2}{(2\bar{s}A)^{0.5}}$$

where V_{bias} is the applied bias and V_{cpd} is the contact potential difference. To measure V_{cpd} an ac voltage is applied:

$$V_{bias} = V_{DC} + V_{AC} \sin \omega t$$

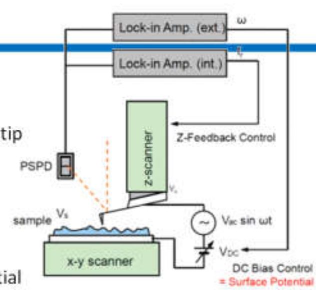
If ω is lower than bandwidth of the frequency demodulator. The component of frequency shift at ω frequency:

$$\Delta f_\omega \propto (V_{DC} - V_{cpd}) V_{AC} \sin \omega t$$

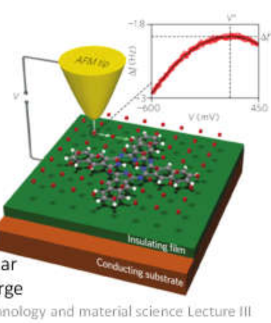
Δf_ω is measured by lock-in technique. Using a feedback circuit V_{DC} can be regulated to keep $\Delta f_\omega = 0$. Thus map of V_{DC} represents the local contact potential difference.

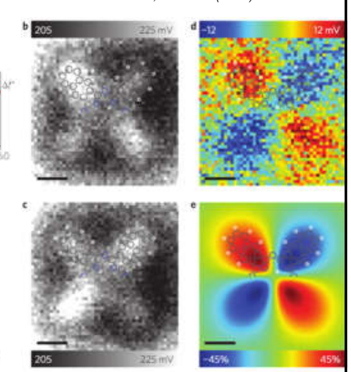
- Tips, e.g. silicon cleaned by argon sputtering has a reproducible work functionof ϕ=4.7eV
- Contact potential can be measured on the atomic scale with energy resolution of 5meV.

See example: charge redistribution after a molecular switching process. SKPF sensitive to the total charge distribution.



(Top) SKPM setup. VDC is controlled to make the amplitude of ω component to be 0, which sets VDC equal to the surface potencial. ω is usually chosen small compared to the bandwidth of the FM demodulator but large compared to the bandwidth of the height feedback
http://www.parkafm.com
(Down) Ccontact potential difference mesured with submolecular resolution on naphthalocyanine molecules before (b) and after switching (c). Recorded with CO functionalized tip. .d is difference between b & c. e is calculation.
F. Mohn Nature Nanotechnology 7, 227–231 (2012)





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Scanning probe microscopy

Magnetic Force Microscopy (MFM)

Goal: sense magnetic field generated by the sample surface
Idea: Scanning force microscope + tip with magnetic moment

Other magnetic scanning sensors: microfabricated Hall probe, Scanning SQUID, Magnetic Resonance Force Microscopy, Scanning diamond vacancy Center, …
MFM is one of the most widely used technique for magnetic signals.

Measuring magnetic force is challenging compare e.g. to map topography.

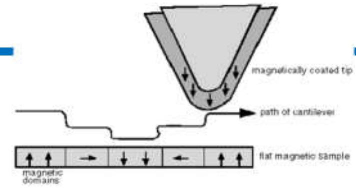
- Small signal (AFM forces ~nN, magnetic forces are 10-1000 smaller.)
- Other forces are also presented (van der Waals-force)

$$\delta z_{\mathrm{mag}} = \frac{F_{\mathrm{mag}}}{k_{\mathrm{eff}}} \quad \text{with} \quad k_{\mathrm{eff}} = k_{\mathrm{L}} + \frac{\partial F_{\mathrm{nonmag}} + \partial F_{\mathrm{mag}}}{\partial z}$$

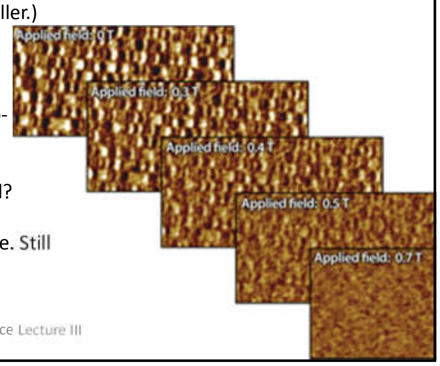
→ measurement at high distance to avoid strong non-magnetic tip-sample interaction

- **Problem with feedback stability**: derivative of the magnetic interaction could change its sign. How to do tip-distance control?

Solution1: Applying strong electric field between the tip and sample. Still image is a mixture of topography and magnetic properties.



(Top) Principle of MFM. An AFM tip with magnetic coating is brought close to the magnetic surface. The stray field of the surface generates force on the tip and thereby the distance from the surface changes, which is detected.
(Down) MFM image of a hard disk in different external B field. As applied field saturates the magnetization of the surface the contrast disappears. (Oxford Instruments)



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Scanning probe microscopy

Magnetic Force Microscopy (MFM)

Solution2: Separate the way to control the feedbacking of the tip-surface distance.
E.g. tip-sample capacitance (monotone with distance)
E.g.2. topography measurement first, (easiest to do by contact) AFM mode.
Then keeping a fixed „far" distance from the surface magnetic interaction is measured. Topography then magnetic force measurement in line-by-line mode. (Typical height for magnetic signal measurement is 20-100nm)

Magnetic force can be measured similar to tapping mode, if frequency shift is small:

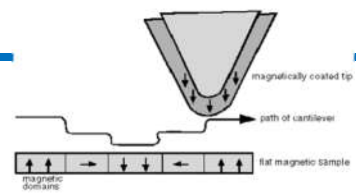
$$\frac{\Delta f}{f_0} = -\frac{1}{2k_{\mathrm{L}}}\frac{\partial F}{\partial z}$$

Which is detected by amplitude or phase modulation.

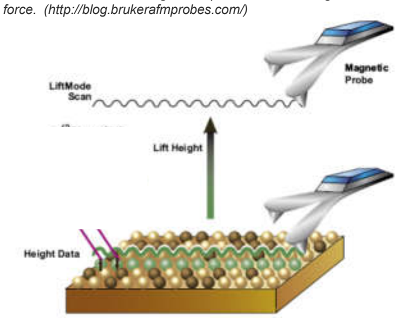
Signal is resulted by interaction of magnetic tip with the **stray field of the sample**.

$$\boldsymbol{H}(\boldsymbol{r}) = -\int_{V_s} \operatorname{grad} \boldsymbol{M}_s(\boldsymbol{r}')\cdot\frac{\boldsymbol{r}-\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|^3}\mathrm{d}V' + \int_{A_s} \hat{\boldsymbol{n}}\cdot\boldsymbol{M}_s(\boldsymbol{r}')\frac{\boldsymbol{r}-\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|^3}\mathrm{d}A'$$

In most case it is complicated to evaluated H(r) field. It is enough to measure z component of H, H_x and H_y can be calculated.
Ferro tip: CoCr or NiFe



(Top) Principle of MFM. An AFM tip with magnetic coating is brought close to the magnetic surface. The stray field of the surface generates force on the tip and thereby deflection, which is detected.
(Down) Lift mode scan: solution to achieve tip-surface distance. control. First in tapping mode the topography is measured in a line scan, then the tip is lifted to far apart, where vdW forces are weak and at a constant height the tip measures the magnetic force. (http://blog.brukerafmprobes.com/)



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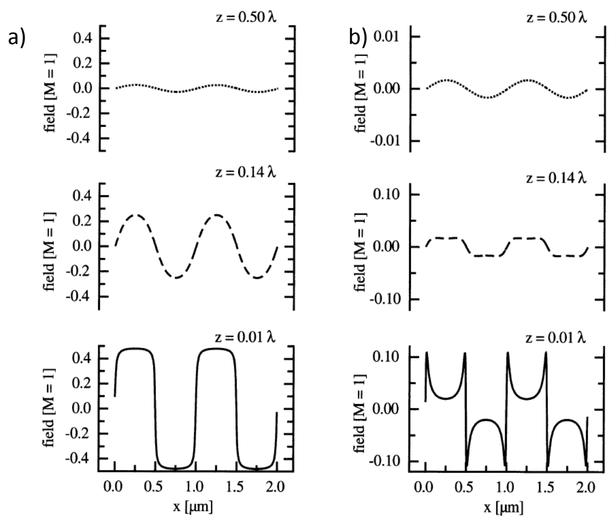
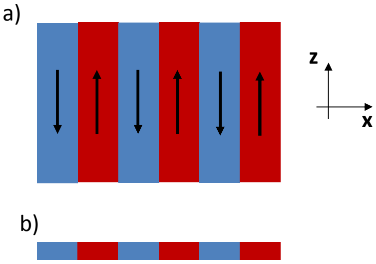


Fig. 4.2. Stray field of a sample with perpendicular magnetization and a periodic stripe domain pattern with infinite thickness (**a**) and a thickness of 10 nm (**b**), i.e., 100 times smaller than the domain period (1 µm). For the thin film sample, the field in the center of the domains becomes small at the surface of the sample, because fields generated by magnetic charges at the top and bottom surface almost compensate. For both samples the stray field decays rapidly with increasing distance from the surface

(Left) Stray field simulations for slab like sample with thickness t but infinite planar dimensions, a perpendicular magnetization and a periodic stripe domain pattern with wavelength λ in the x direction. Left column: t infinite. Right column: t =10nm.
(Bottom) The domain pattern of the two structures



Example for **stray field**:
- Magnitude decays rapidly with distance, z
- For thin samples larges field at the domain walls.
- For thin film the decay in z direction is even faster.

→ Limited distance range, where F can be measured

Remark: Various magnetization pattern can give the same stray field pattern.
It is difficult to track back.

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Scanning probe microscopy

Magnetic Force Microscopy (MFM)

Back action:
Tip may effect the magnetic structure of the surface and vice versa. E.g. for soft ferromagnets (permalloy) with small coercive field it can happen. (Reversible/irreversible effect)

Magnetic force on the tip is a convolution of tip magnetization distribution with sample stray field:

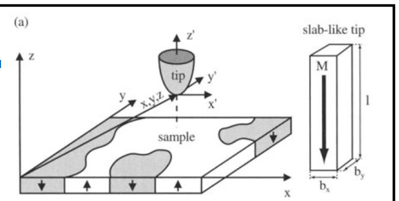
$$F_z(x,y,z) = -\mu_0 \int_{-\infty}^{\infty} \boldsymbol{M}_{\text{tip}}(x',y',z') \cdot \frac{\partial}{\partial z} \boldsymbol{H}_{\text{sample}}(x+x', y+y', z+z')\, \mathrm{d}V'$$

Let us assume a long, thin slab like tip with constant magnetization, and assuming that stray field is much larger on the lower side of the tip results

$$F_z(x,y,z) = q_{\text{tip}} H_{z,\text{sample}}(x,y,z) \qquad q_{\text{tip}} = \mu_0 M_{\text{tip}} b_x b_y$$

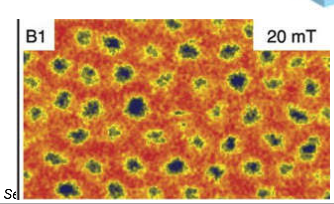
Thus the force in the z direction is a direct measure of the z component of the stray field.

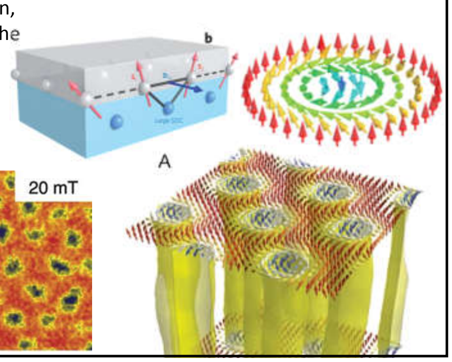
Examples: MFM of Skyrmions
Nanoscale spin configurations.



(Top) The sample coordinate system is attached to the sample surface (z = 0). The primed coordinate system is attached at the tip located at the position (x, y, z). (Top Right) Geometry of the long , thin, slab-like tip. The top and bottom surface area is given by (b x, by) while the magnetization M is homogeneous and directed along the long axis l of the tip

(Down) Physics of skyrmions. Basic interactions generating helical order of spins. In perpendicular B field special spin structure forms (like whirlpool). (Left) MFM image of Skyrmions A. Fert Nature Nanotechnology 8, 152 (2013)





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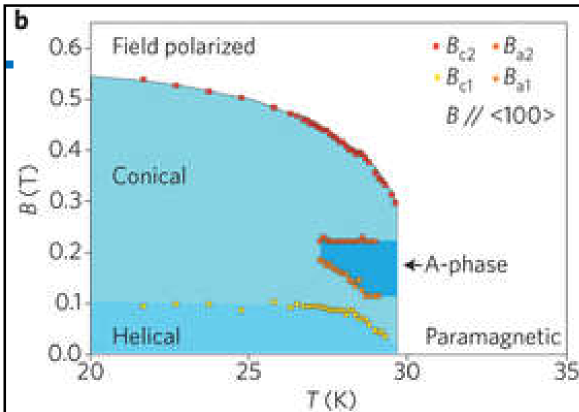

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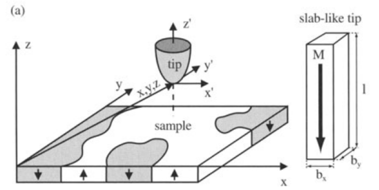

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$+ z') \mathrm{d}V'$

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on,

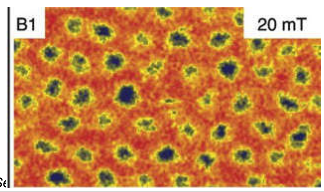
the

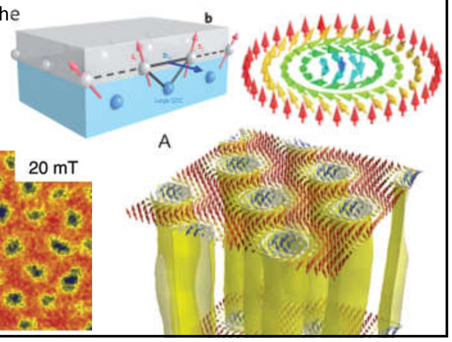
tip results

$$F_z(x,y,z) = q_{\mathrm{tip}} H_{z,\mathrm{sample}}(x,y,z) \qquad q_{\mathrm{tip}} = \mu_0 M_{\mathrm{tip}} b_x b_y$$

Thus the force in the z direction is a direct measure of the z component of the stray field.

Examples: MFM of Skyrmions
Nanoscale spin configurations.





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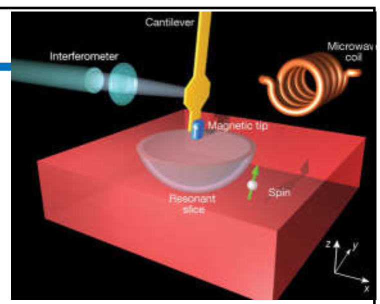
Scanning probe microscopy



(Up) MRFM setup. Small magnet placed at cantilever close to the sample. It generates strongly varying B field in the sample. Microwave excites spins in sperical slice, where resonant condition fulfilled. It changes magnetization in this area, which results a time dependent force in the inhomogeneous B field. Very small forces are detected. (Down) The energy splitting of electron spint states in B_0 external field. Similar splitting takes place for nuclear spin as well. $\Delta E = \gamma B_0$

Magnetic Resonance Force Microscopy (MRFM)

It measures the magnetic forces acting between a magnetic tip and resonantly excited spins in the sample.

Principle

- Magnetic moment at the end of the tip generates an inhomogenous magnetic field.
- The sample is placed in microwave radiation with frequency: ω
- Thin spharic shaped slice of the sample fulfills the magnetic resonance condition: $\hbar\omega = g_e \mu_B B_0(x,y,z)$ (for electrons)
  where the electron spins are excited in the sample with a gradient of ~10^6T/m in a resonant slice thickness ~nm (25nm from the magnet).
- The force sensed by the cantilever:

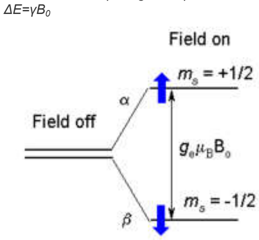
$$F(t) = m_z(t) \frac{\partial B(z)}{\partial z}$$

- Sample magnetization is varied by modulation schemes of the rf frequency. → Periodic inversions of (e.g. ^{1}H) spins in the sample at resonance frequency of cantilever (~kHz) → periodic force that drives the cantilever.
- Forces in the order of 10^{-16}N are sensed! It results a subA vibration in a soft cantilever → detected by interferometer and lock-in technique

Possible to scan subsurface spins as well.

Achievements

2004. Force flipping a single electron spin detected (IBM)
2009. 3D MRI of protons of tobacco mosaic virus. Moving the tip in 3D provides data that allows the reconstruction of ^{1}H density with spatial resolution of 5nm. 10^8 better volume sensitivity than MRI!



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C. L. Degen et al., Proc. Nat. Acad. Sci. U.S.A. (2009).

E. Meyer: Scanning Probe Microscopy Springer (2004) Sec. 4.3.

also https://poggiolab.unibas.ch/research/magnetic-resonance-force-microscopy/