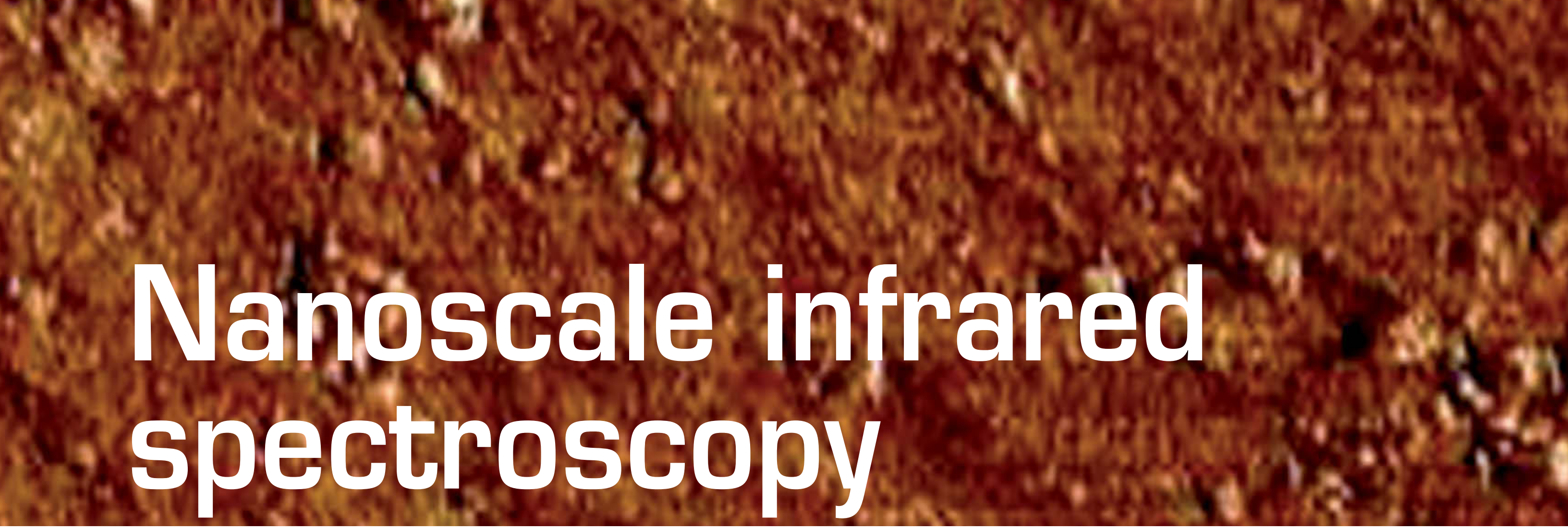

Nanoscale infrared spectroscopy

In the early days of scanning probe microscopy, researchers and instrumentation developers were often postulating about the future and, perhaps one day, the advent of the "lab-on-a-tip." While the technology has seen the development of highly spatially resolved topography imaging coupled to a series of different physical measurements, it is only recently that is has been possible to perform chemical characterization measurements with infrared spectroscopy on the nanoscale. The enabling technique is known as nanoIR™.

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For many years, infrared spectroscopy has provided the ability to characterize and identify chemical species. However, it has always been restricted to resolution in the order of 5 – 10 microns and then only when applying attenuated total reflection spectroscopy, ATR. Now, when combined with the nanoscale spatial resolution of an AFM tip, it is possible to measure and map local chemical composition below the diffraction limit of light. The technology described here as nanoIR will also perform nanoscale topographic, mechanical and thermal analyses.

This exciting and unique technology is provided through a new platform called nanoIR (Anasys Instruments, Santa Barbara, CA). The nanoIR is a probe-based measurement tool that reveals the chemical composition of samples at the nanoscale (Fig. 1). This laboratory solution combines key elements of both infrared spectroscopy and atomic force microscopy (AFM) to enable the acquisition of infrared spectra at spatial resolutions of 50 - 200 nanometers, well beyond the optical diffraction limit. Potential application areas span polymer

Fig. 1 NanoIR system.

ISSN:1369 7021 © Elsevier Ltd 2010

science, materials science, and life science, including detailed studies of structure-property correlations.

The science behind the system applies the patent-pending technology of infrared nanospectroscopy, a technique pioneered by award-winning researcher Dr. Alexandre Dazzi of the Laboratoire de Chimie Physique ,CLIO, Université Paris-Sud, Orsay, France. This is a photothermal method which follows the absorption of the infrared and the subsequent generation of heat.

Instrumentation

The nanoIR system uses a pulsed, tunable IR source to excite molecular absorption in a sample that has been mounted on a ZnSe prism (Fig. 2). Samples are prepared in one of two ways. For many samples, ultramicrotomy is used to cut sections with thicknesses between 100 nm and 1000 nm. These are then transferred to the prism surface. In other sample preparations, it may be possible to cast thin films from solvent directly on the prism surface.

The IR beam illuminates the sample by total internal reflection similar to conventional ATR spectroscopy (Fig. 3). As the sample absorbs radiation, it heats up, leading to rapid thermal expansion that excites resonant oscillations of the cantilever which is detected using the standard AFM photodiode measurement system. These induced oscillations decay in a characteristic ringdown which can be analyzed via Fourier techniques to extract the amplitudes and frequencies of the oscillations. Then, measuring the amplitudes of the cantilever oscillation as a function of the source wavelength, local absorption spectra are created.

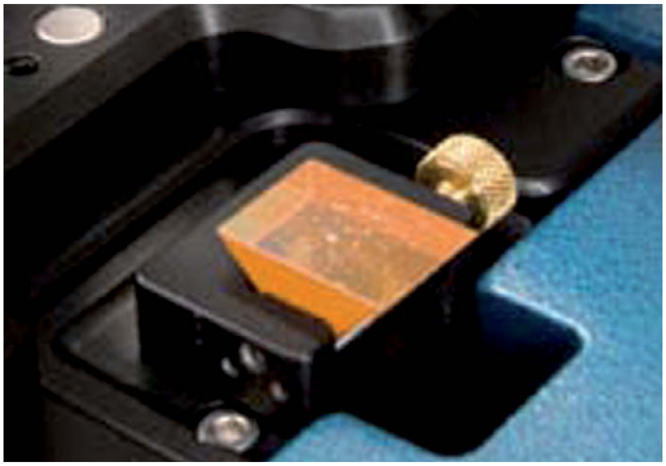

Fig. 2 Samples are mounted on a zinc selenide prism.

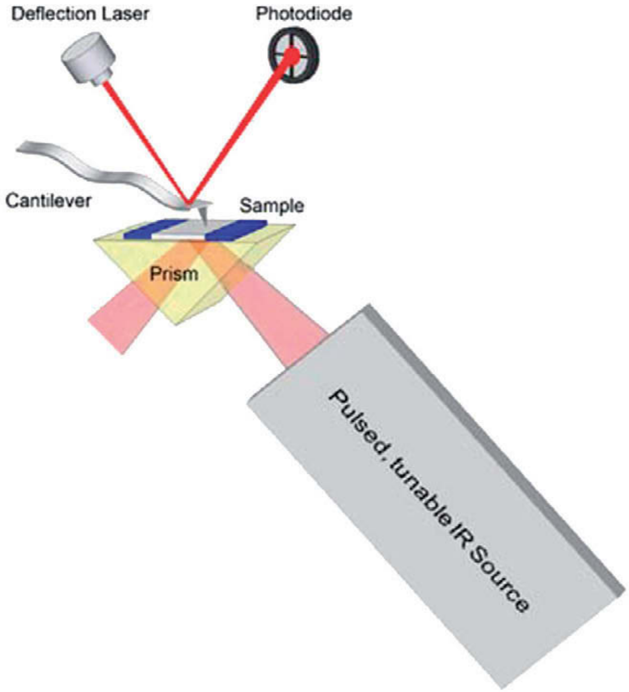

Fig. 3. Schematic shows the illumination of the sample by the IR laser.

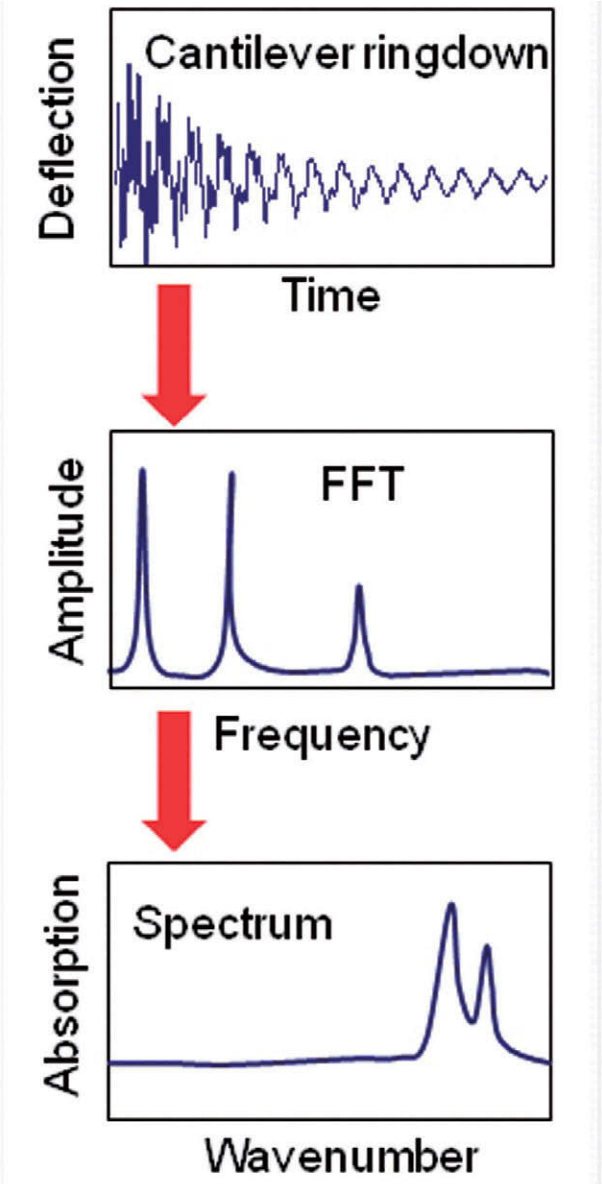

Fig. 4. Schematic to illustrate the process of analyzing the ringdown of a cantilever to generate a familiar IR spectrum.

The oscillation frequencies of the ringdown are also related to the mechanical stiffness of the sample. With maximum flexibility, the IR source can also be tuned to a single wavelength to simultaneously map surface topography, mechanical properties, and IR absorption in selected absorption bands Fig. 4.

The results are spectacular as established analytical techniques are linked together as never before possible. The potential application areas are found in the polymer, materials and life sciences offering notable potential in producing detailed studies of structure-property correlations.

The ability to combine nanoscale spatial resolution with chemical spectroscopy provides users of nanoIR technology with the tools to quickly survey regions of a sample via AFM and then rapidly acquire high-resolution chemical spectra at selected regions on the sample. Making additional mechanical and thermal properties measurements with nanoscale resolution adds significantly to the power of this technique.

Applying mid-IR spectroscopy

The nanoIR system enables researchers to harness the full power of mid-IR spectroscopy. The system's IR source, designed using proprietary technology, is continuously tunable from 3600 to 1200 cm^{-1}. This range covers a major portion of the mid-IR, including important CH, NH, and CO bands, as well as carbonyl and amide I/II bands. Polymer spectra acquired with the nanoIR system have demonstrated good correlation with bulk FTIR spectra. The nanoIR software also allows researchers to export nanoscale IR absorption spectra to standard analysis packages (e.g., Bio-Rad's KnowItAll®) to rapidly analyze samples and identify chemical components.

The nanoIR software also allows integrated thermal and mechanical property mapping in addition to its ability to provide high-resolution infrared spectra. Mechanical properties of a sample can be collected using a contact resonance method to map stiffness variations simultaneously with the topography while the nanoIR platform can also perform nanoscale thermal analysis providing researchers to work beyond bulk thermal analysis measurement to obtain information not available with any other technique.

Applications of nanoIR

Polymer blends and composites

Typical data sets will show deflection, IR absorption and stiffness. The images of two different polymer blend samples were taken by tuning the IR source to a fixed wavenumber and then scanning the sample while measuring the amplitude of the nanoIR signal for the IR absorption and the frequency of the fundamental contact resonance for the stiffness. The first example is a sample which is 100% ABS, acrylonitrile butadiene styrene where the AS intermixes and the butadiene phase separates, Fig. 5.

The butadiene is soft and so can easily be seen in the stiffness image. It also has a stronger absorption at 3025 cm^{-1}. It is interesting to correlate the light areas in the IR absorption with the dark areas in the stiffness. These should be the same material but there are differences which may correlate with differences in thickness or whether the material is at the surface or subsurface.

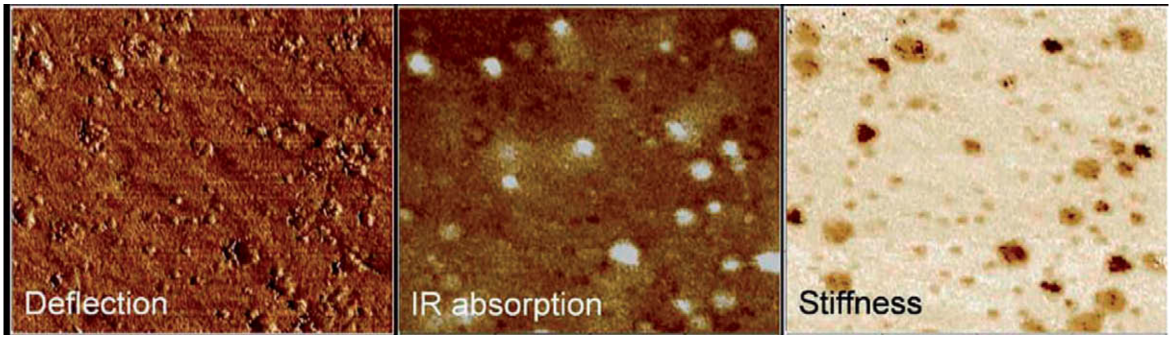

Fig. 5 Comparison of the deflection, infrared and stiffness signals of a sample of ABS.

Fig. 6 A blend of ABS (40%) and polycarbonate (60%) mapping deflection, infrared and stiffness signals.

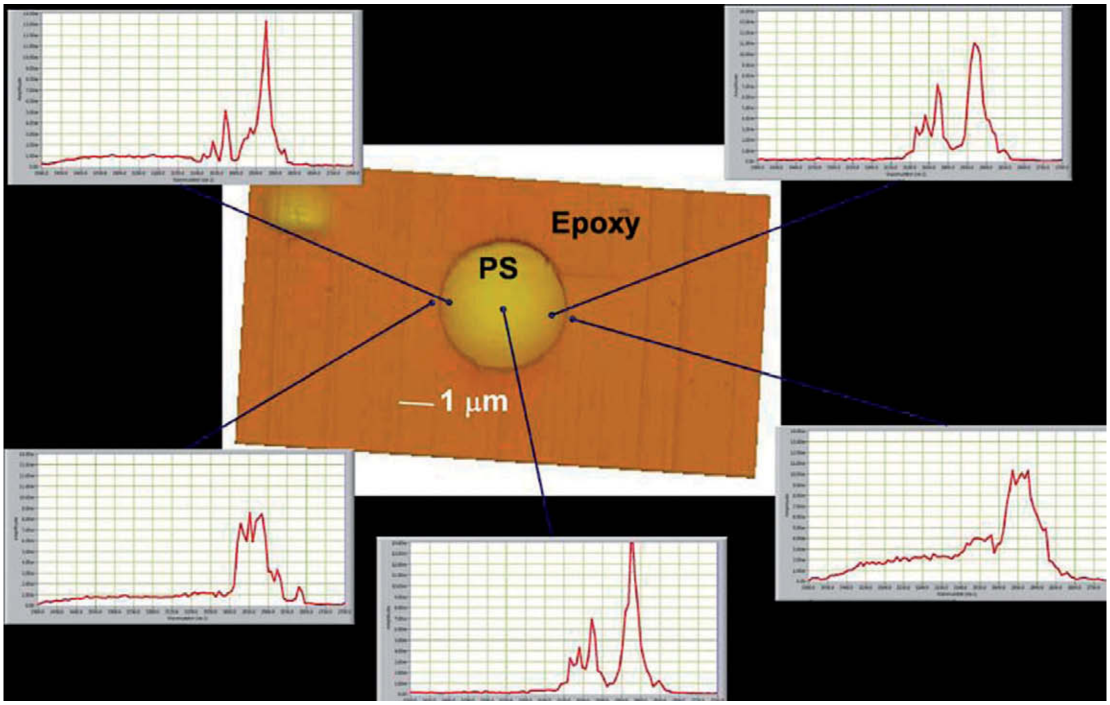

Fig. 7 A polystyrene sphere in an epoxy matrix demonstrating the spatial resolution of the nanoIR system. Note that a characteristic polystyrene spectrum is observed in the center, and edges of the PS bead, but a very different epoxy spectrum is observed just 100 nm across the material boundary.

The second example is a blend of 40% ABS and 60% polycarbonate, Fig. 6. At 1780 cm^{-1} wavenumber, the polycarbonate exhibits a strong signal while the soft butadiene domains are clearly seen in the stiffness map.

The next example is a sample where polystyrene spheres (PS) were embedded in epoxy to form a composite. It was microtomed before study. (Fig. 7). There is an absorption band at 3025 cm^{-1} which corresponds to the aromatic bonds in the polystyrene. This is clearly

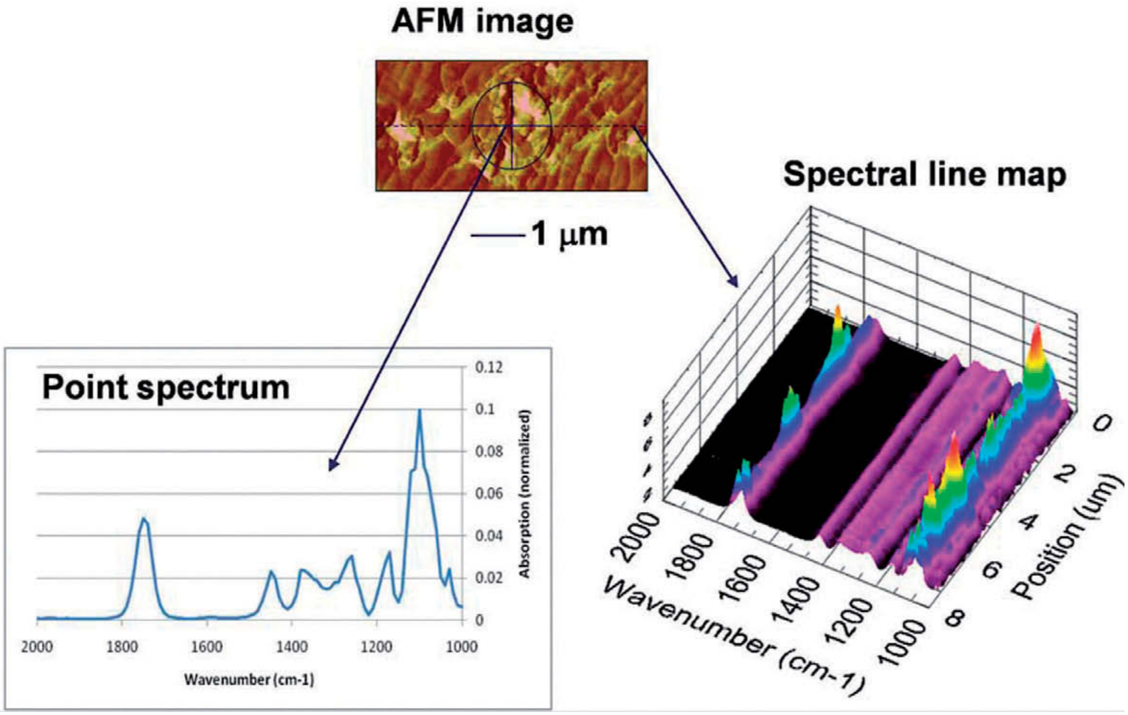

Fig. 8 The spectral mapping of a degradable polymer blend.

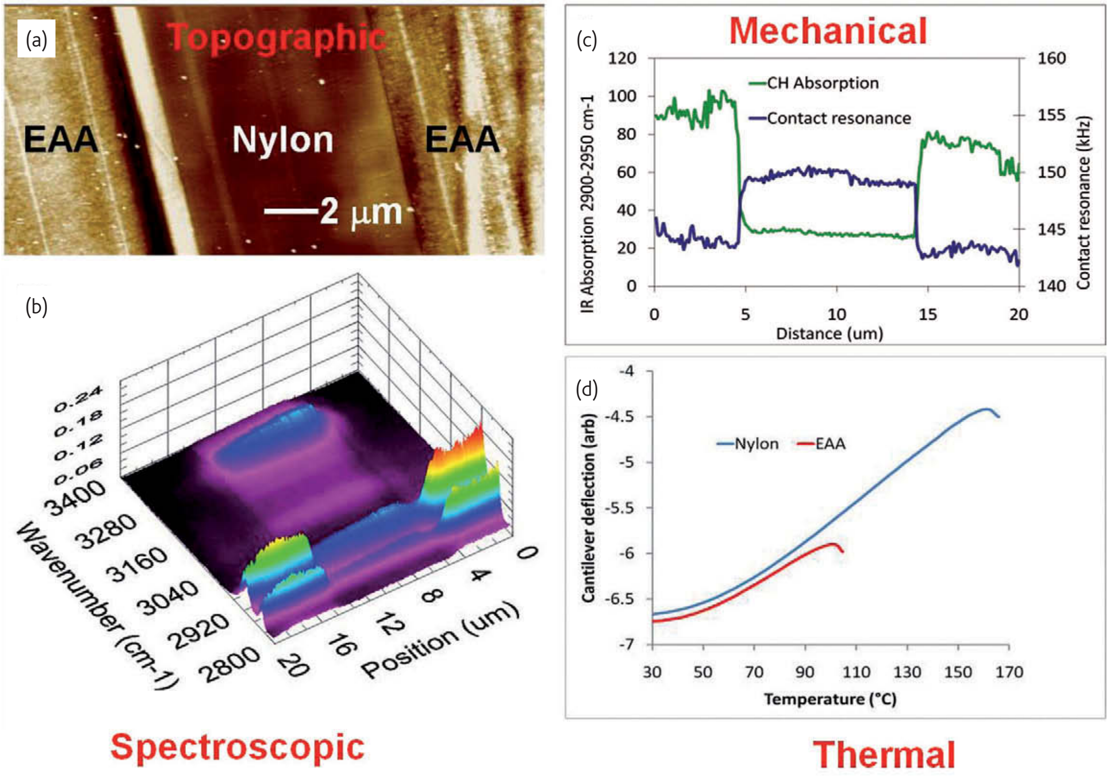

Fig. 9(a) AFM topographic image clearly showing regions of nylon and ethylene co-acrylic acid (EAA). (b) Spectroscopic map showing different regions of the polymer composite; (c) Mechanical map showing the correlation between the CH absorption spectrum and the contact resonance frequency; (d) Point nano-thermomechanical analysis data showing the different softening points of the nylon and EAA regions.

seen in the spectra taken from the center of the PS sphere and is also clearly resolved in spectra that were taken within ~100 nm of the interface and is not seen in the epoxy. This is a good resolution test for the nanoIR technique.

Degradable polymers

In this example, the spectral mapping of a degradable polymer blend is shown. The AFM measurements allow spatial mapping of polymer matrix and additives. The nanoIR can then spatially map the variations in chemical components. These are then interpreted In the line spectral map noting the spatially varying concentration of the C=O carbonyl band (1740 cm^{-1}) and the single bond C-O peak at around 1100 cm^{-1}. This data is summarized in Fig. 8.

Multifunctional measurements on a composite

With the nanoIR system provides the capability of multifunctional measurements. These enable a more complete picture of samples, integrating topographic, spectroscopic, mechanical and thermal property data.

High resolution topographic measurements are performed by AFM, Fig. 9a, while the nanoscale infrared spectroscopy technique enables both local chemical characterization and contact resonance frequency measurements to be made, Figs. 9b and 9c.

Going one stage further, the system accommodates thermal probes to give thermomechanical measurements again with spatial resolution on the nanoscale, Fig. 9d.

Looking forward – applications developments

The nanoIR system combines infrared spectroscopy and atomic force microscopy to provide high resolution topographic, chemical, mechanical and thermal mapping. This combination provides spatial resolution at length scales well below the diffraction limit of conventional IR spectroscopy and adds chemical spectroscopy to the field of atomic force microscopy. The potential for future applications is very broad and includes polymer blends, multilayer films and laminates. In the life sciences, sub cellular spectroscopy and the study of tissue morphology/histology will be eagerly awaited while in materials science, prospects are good for the study of organic photovoltaics and defect analysis. mt

Acknowledgments

The authors would like to acknowledge the input of co-corkers Debra Cook (Anasys), Gregory Myers, Carl Reinhardt (both from the Dow Chemical Company) , Jonathan Felts, William King (both from the University of Illinois), Konstantin Vodopyanov (Stanford University), Alexandre Dazzi (Université Paris-Sud) and Jiping Ye (Nissan Analytical Research Services).

Lecture 26

MNS 102: Techniques for Materials and Nano Sciences

Reference: #1 C. R. Brundle, C. A. Evans, S. Wilson, "Encyclopedia of Materials Characterization", Butterworth-Heinemann, Toronto (1992), Ch. 2, Ch. 3.

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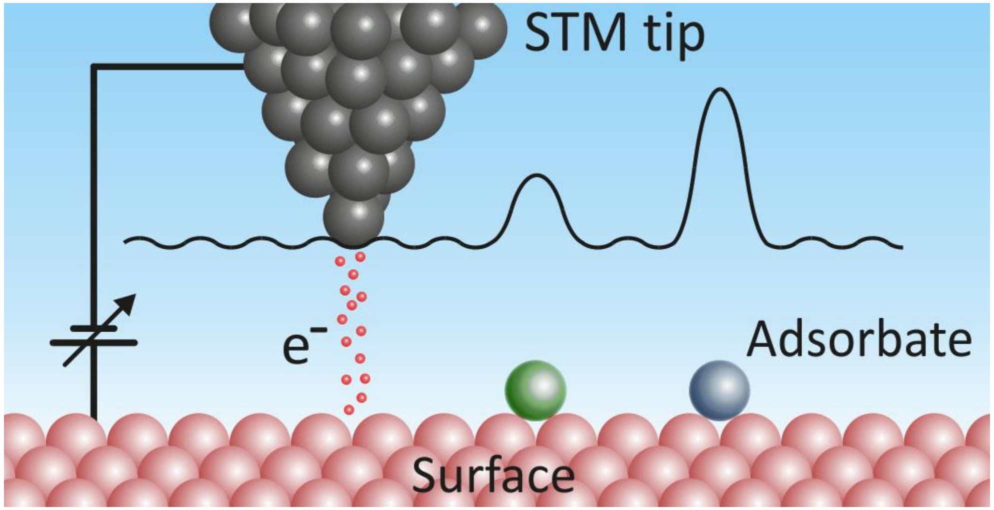
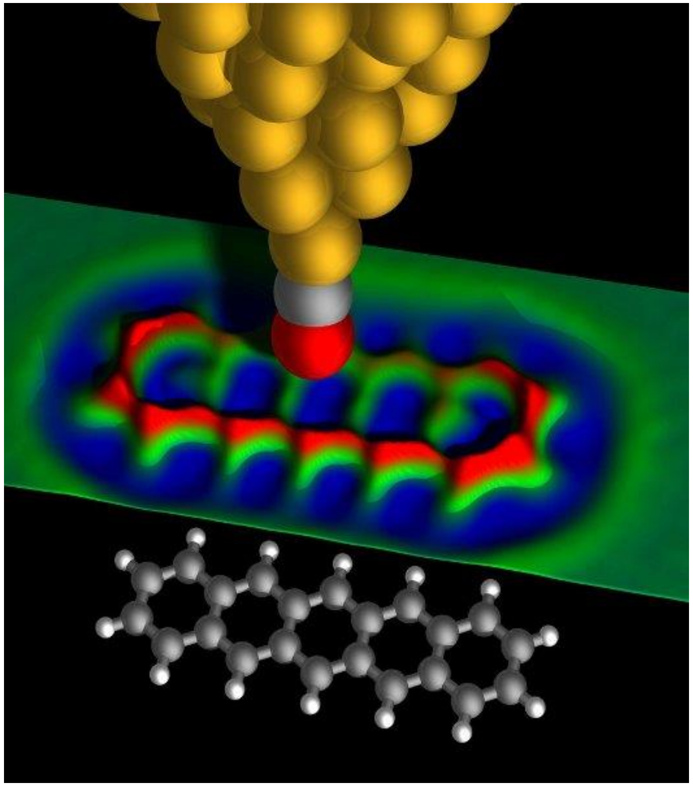
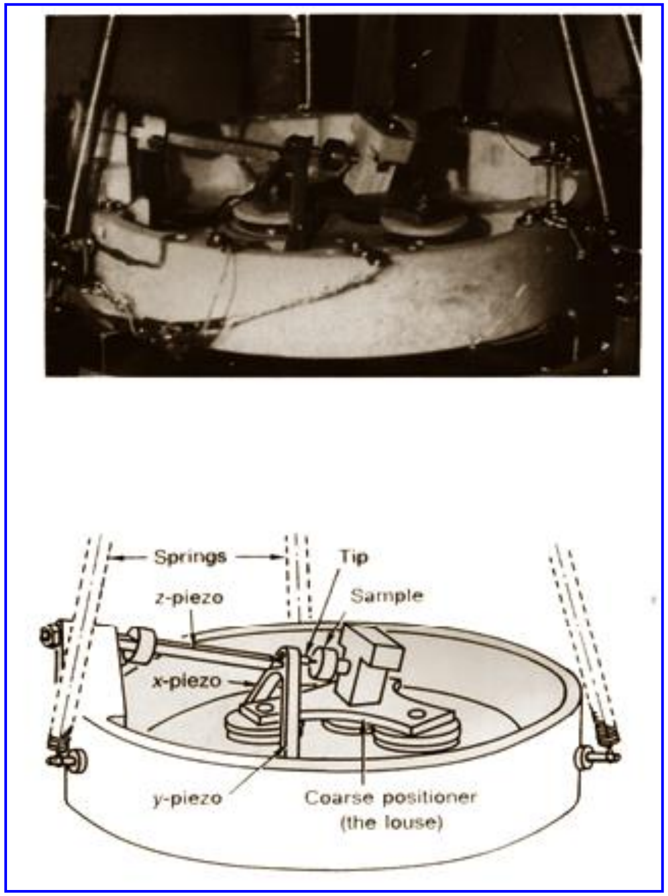
http://www.chembio.uoguelph.ca/educmat/chm729/STMpage/stmtutor.htm
http://www.almaden.ibm.com/vis/stm/blue.html
http://virtual.itg.uiuc.edu/training/AFM_tutorial/

- Tip-based Microscopy – History
- Scanning Tunnelling Microscopy (STM): QM tunnelling; basic principle; instrumentation; modes of operation; pros and cons; applications
- Atomic Force Microscopy (AFM): Atomic forces; principle; modes of operation; static vs dynamic modes; applications
- STM vs AFM





History

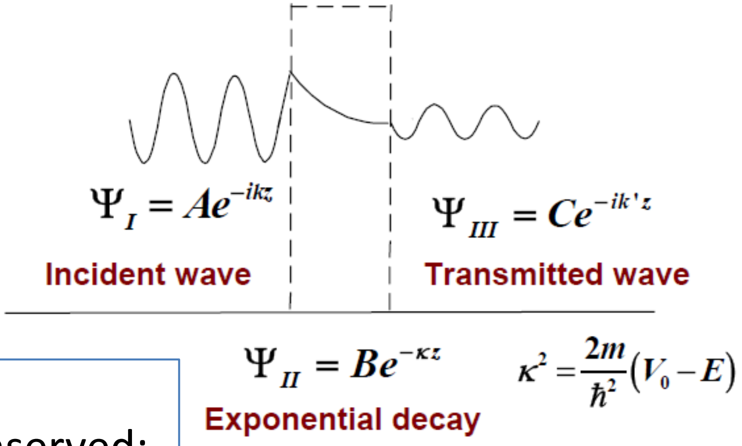


- 1982 Phys. Rev. Lett. 49, 57 - Heinrich Rohrer and Gerd Binnig, IBM Zurich - first discussed the concept of STM.
- 1986 Nobel Prize in Physics.
- 1986 Phys. Rev. Lett. 56, 930 - Binnig, Calvin Quate (Stanford), Christoph Gerber (Basel) invented AFM.
- SPM is often considered a main driver for nanotechnology.


Photo: IBM

Quantum Mechanical Tunnelling

- One-dimensional electron tunnelling through a rectangular barrier – Start with the particle-in-a-double-box case and lower the barrier between the two boxes…



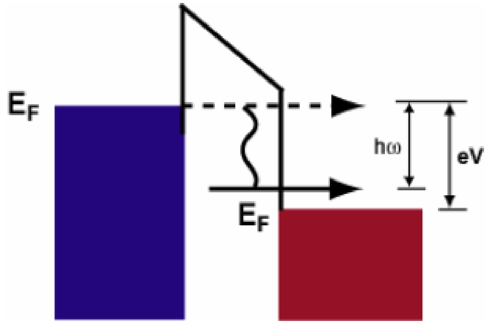
$$\Psi_I = Ae^{-ikz}$$

$$\Psi_{III} = Ce^{-ik'z}$$

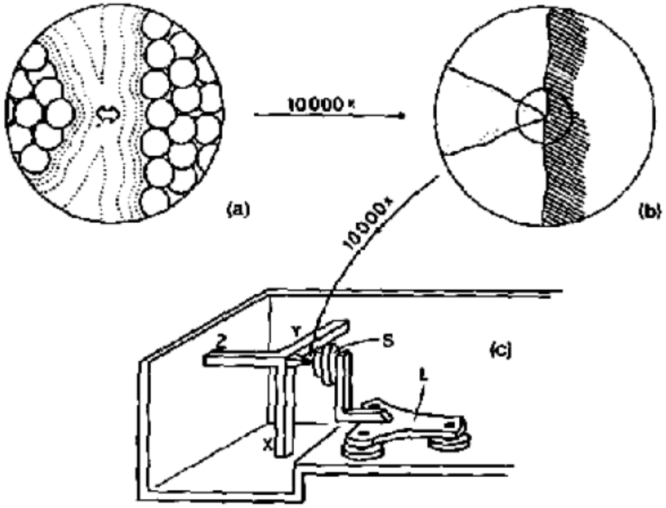
$$\Psi_{II} = Be^{-\kappa z}$$

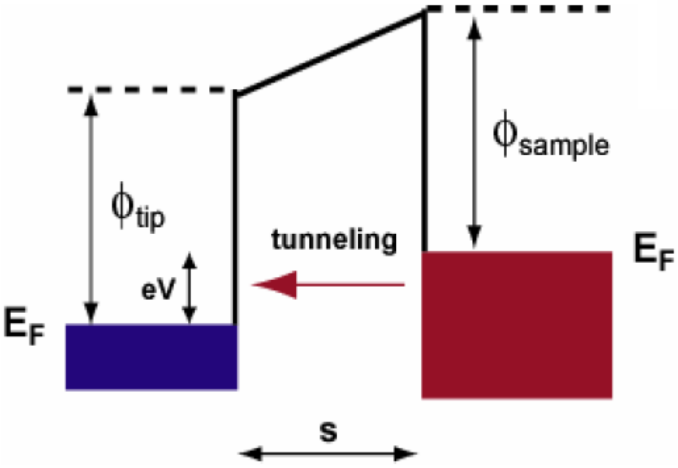
$$\kappa^2 = \frac{2m}{\hbar^2}(V_0 - E)$$

- Elastic vs inelastic tunnelling:
  Elastic tunnelling – energy of tunnelling electron is conserved;
  Inelastic tunnelling – electron loses a quantum of energy inside the tunnelling barrier.



- Electron tunnelling in STM:

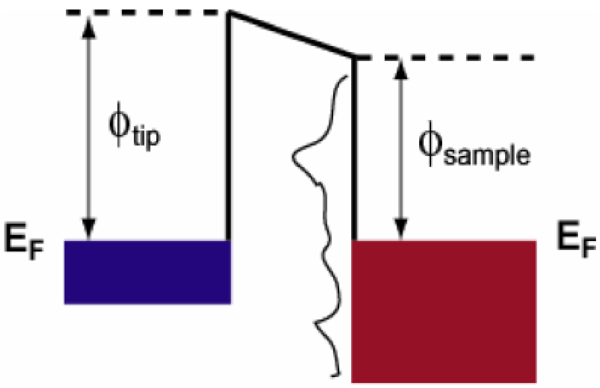




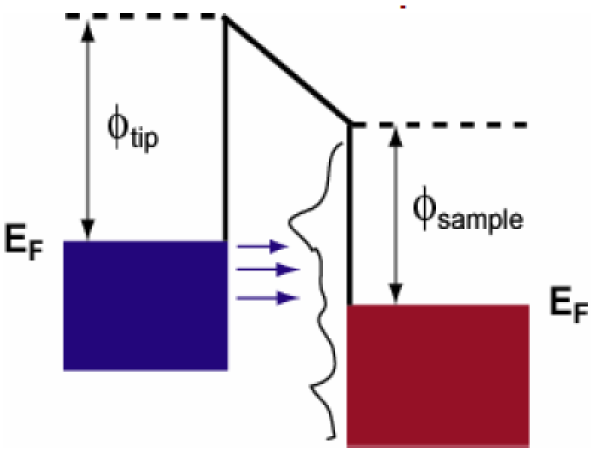
STM: Basic Principle

- “Move” the tip so close to the sample that their wavefunctions begin to overlap and to enable quantum mechanical tunnelling;
- Apply a bias voltage to the tip to “facilitate” electron transport (i.e. tunnelling);
- **Positive sample bias**: Tunnelling from tip (filled state near the Fermi energy) to the empty states of the sample – Empty state imaging;
- **Negative sample bias**: Tunnelling from sample (filled states near the Fermi energy of the sample) to empty states of the tip – Filled-state imaging.

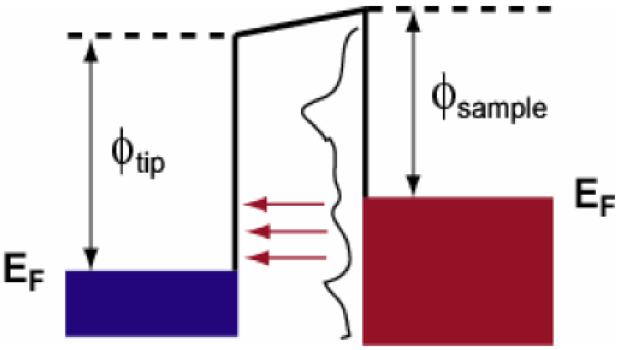
Thermal equilibrium - Zero Bias



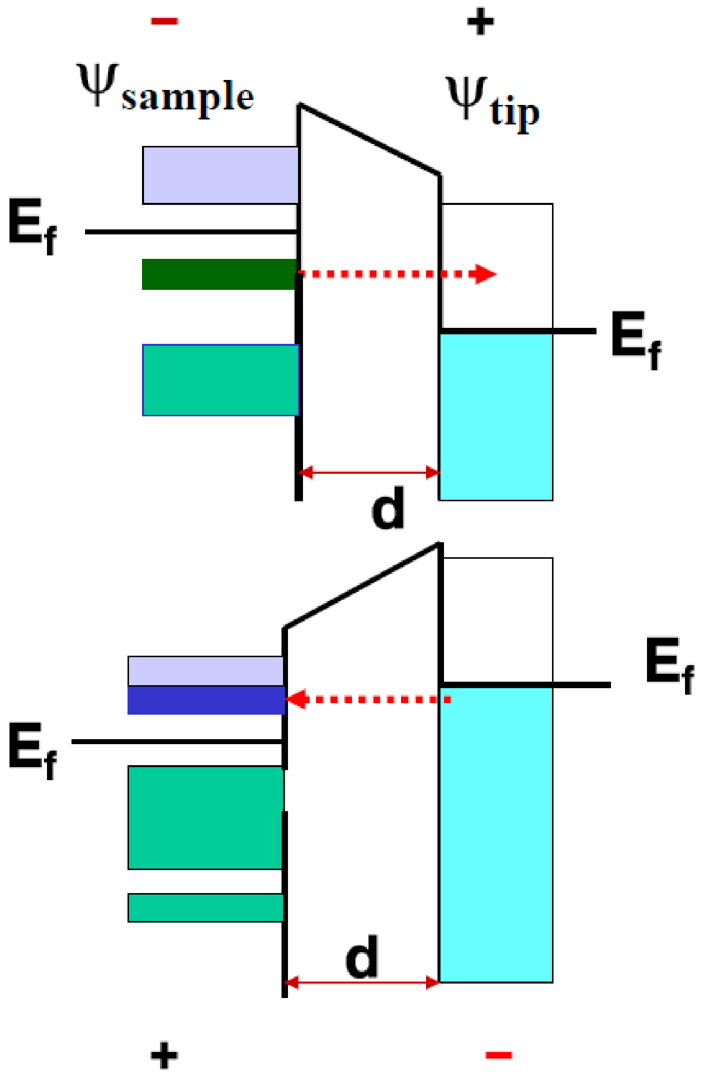
Positive Sample Bias



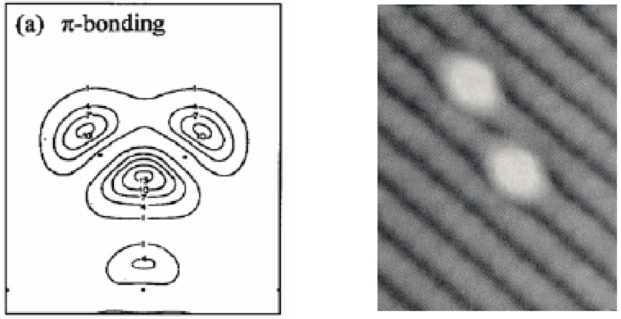
Negative Sample Bias



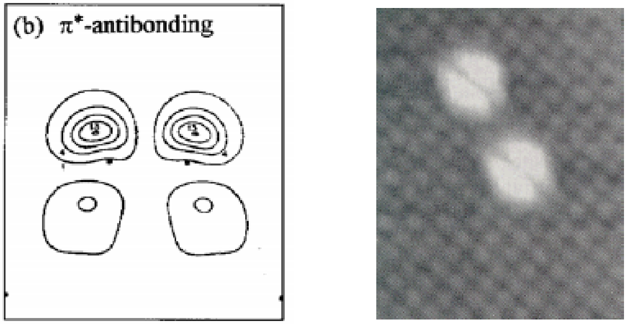
Filled-state vs Empty-state Imaging



Occupied state (HOMO)



Unoccupied state (LUMO)



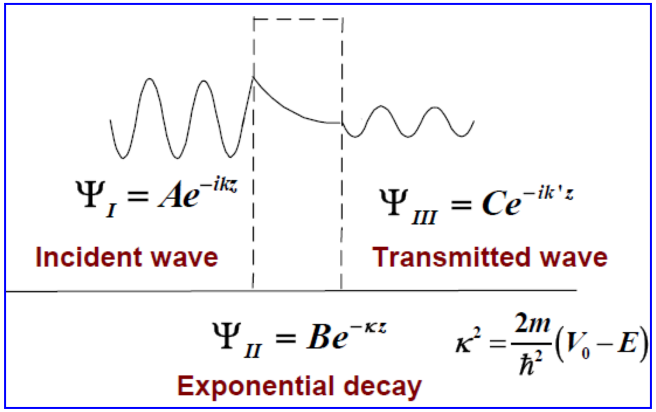
Ref: J. J. Boland, Adv. Phys. 42 (1993) 129.

Tunnelling Current

- Quantum Mechanics predicts that the wavefunction decays exponentially through the barrier:

$$\Psi(d) = \Psi(0)e^{-\kappa d} \quad \text{where} \quad \kappa = \frac{\sqrt{2m(\Phi - E)}}{\hbar}$$

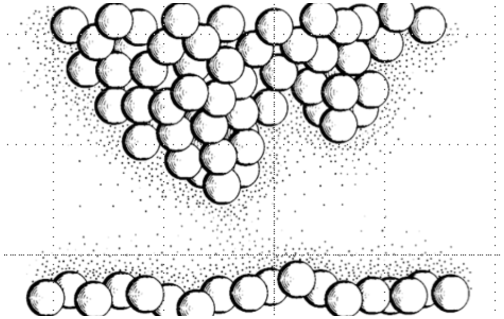
- Probability of finding the electron after the barrier of width d is: $W(d) = |\Psi(d)|^2 = |\Psi(0)|^2 e^{-2\kappa d}$



$$\Psi_I = Ae^{-ikz}$$

$$\Psi_{III} = Ce^{-ik'z}$$

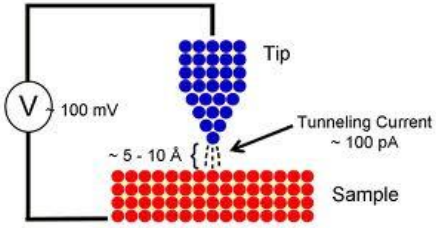
$$\Psi_{II} = Be^{-\kappa z} \qquad \kappa^2 = \frac{2m}{\hbar^2}(V_0 - E)$$

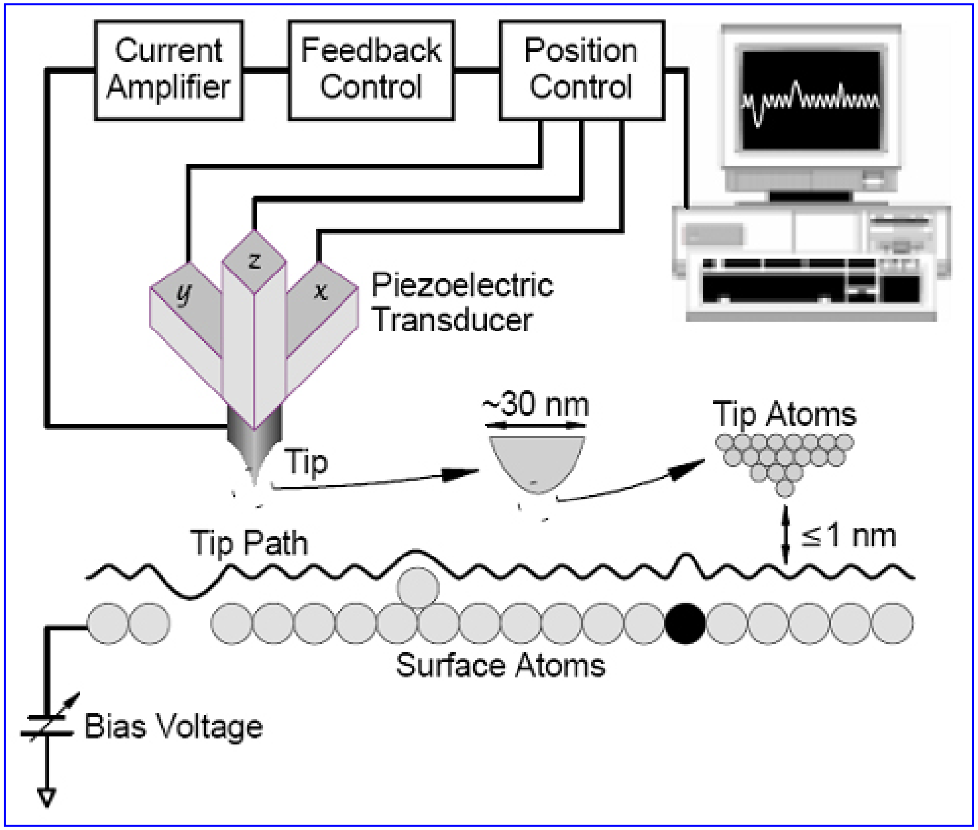


- The current is: $I = f(V)\, e^{-2Kd}$
where f(V) is a function that contains a weighted joint local density of states (LDOS) that reflects the property of the material.
- The tunnelling current is therefore: $I \propto e^{-2Kd}$
where $K \approx \sqrt{(2m\,\Phi)} / (h/2\pi) = 0.51\sqrt{\Phi}$ Å^{-1} and Φ is the work function (in eV).
When $\Phi \approx 4$ eV, $K \approx 1$ Å^{-1} and $e^2 \approx 7.4$. This means tunnelling current goes down by 7.4 times per Å. (In the 2nd tip, two atoms away from the atom in the first tip. This means that the second tip will detect ~10^6 less current than the first tip. Extreme z sensitivity!)

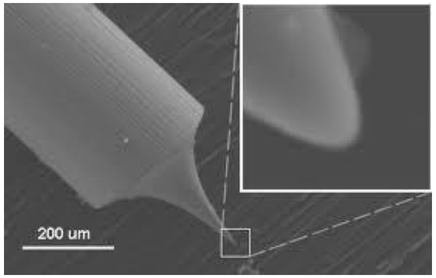
- Note that the tunnelling current does not reflect the nuclear position directly. STM measures the local electron density of states and not nuclear position.

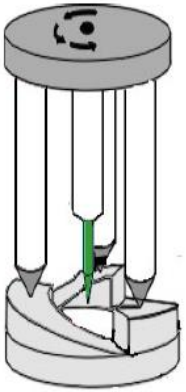
Instrumentation

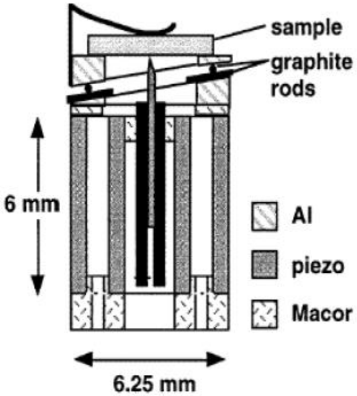




- **Anti-vibration**: 1 Hz – general human movement; 10-100 Hz – electronics, ventilation; Target 1-10 kHz resonant frequency for STMs
- Building vibration 1 μm will generate 1 pm at the STM tip
- Make STM system as rigid as possible so that internal resonance is above 1 kHz and mount it on a low resonant frequent support



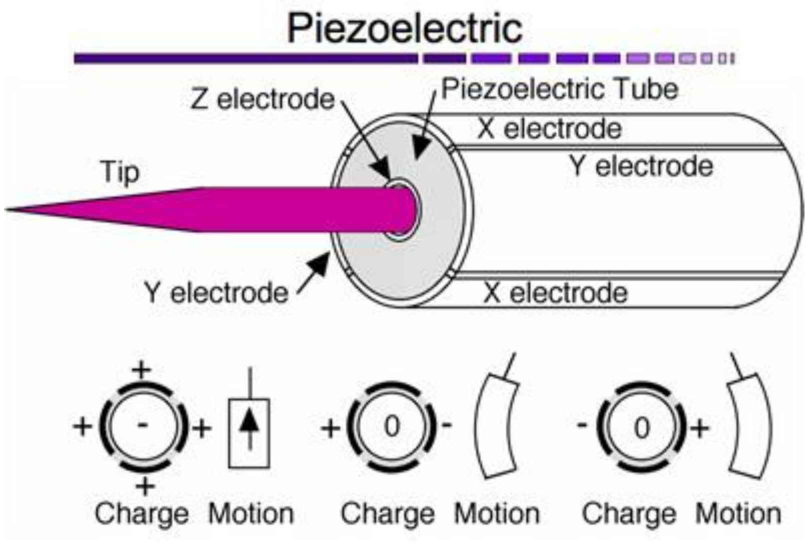




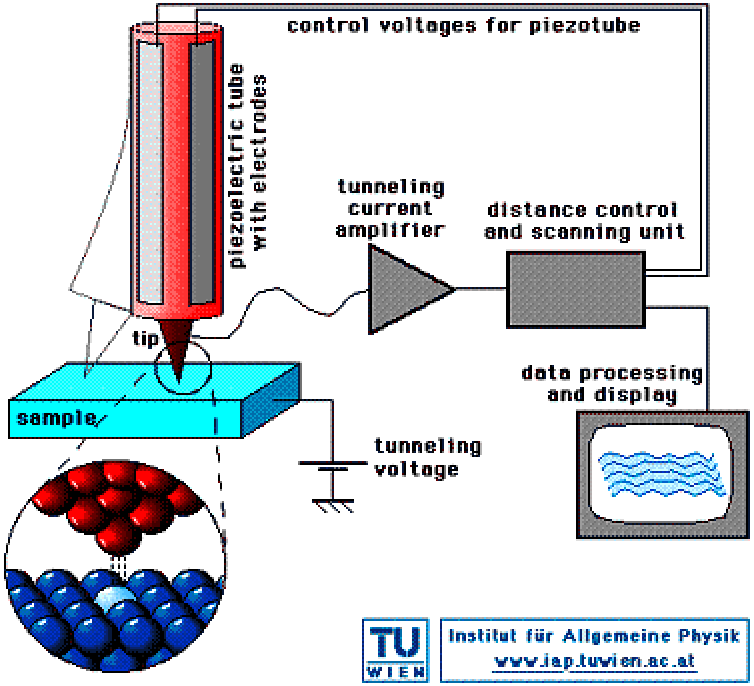
- **Coarse approach**: Move tip up and down from mm to sub-μm; use beetle-type motion and inertial slider; base materials must undergo similar thermal expansion of piezoelectric tube (the scanner), mechanically rigid – macor is used b/c stiff and lightweight

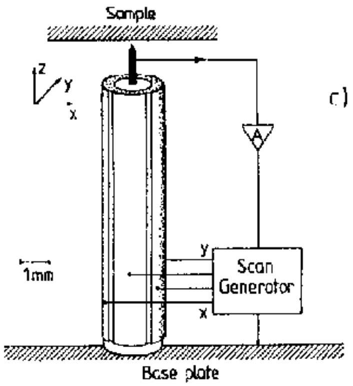
Fine Approach: Piezoelectric Scanner

- Piezoelectric material is a “smart” material that changes in dimension under an applied voltage.
- Piezoelectric scanner must have high resonance frequencies and scan speed, high sensitivity, low crosstalk among x, y, z drivers, and low thermal drift.



Tube scanner: 15 mm long, 5 mm dia, 0.75 mm thick can provide motions up to 1.0 μm vertically and 2.8 μm laterally.

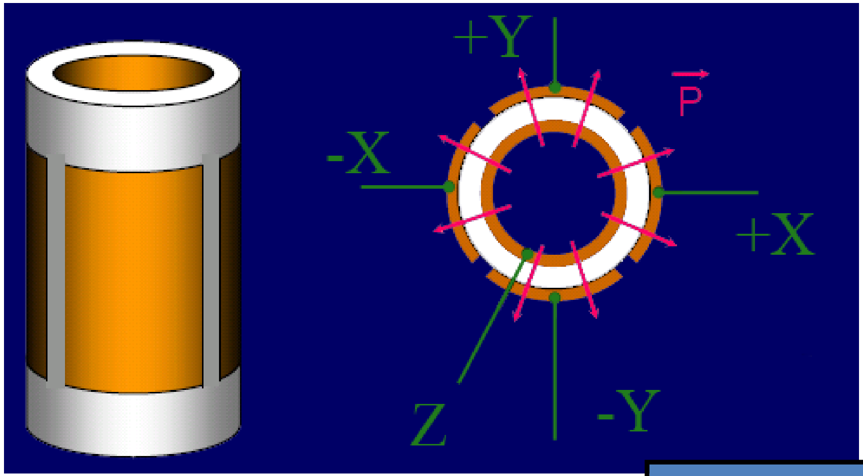




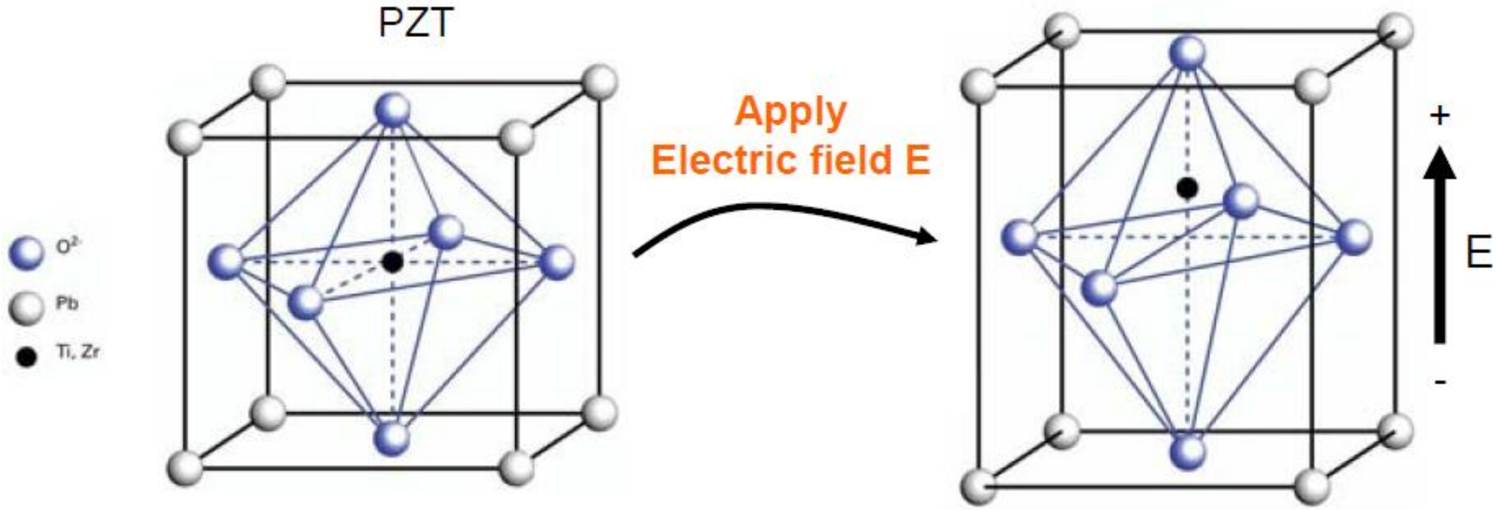
Omicron VT STM tip setup with tip coming from below, and sample facing down.

Piezoelectric Materials

- Piezoelectric materials produce a voltage in response to an applied force, i.e. Displacement $\propto$ electric field
- Piezoelectric materials have an asymmetric unit cell like a dipole. E.g. PZT = lead zirconium titanate (250-365x10^{-12}m/V); barium titanate (100-149x10^{-12}m/V); lead niobate (80-85x10^{-12}m/V); quartz (2.3x10^{-12}m/V).
- Issues: Nonlinearity; creep; hysteresis; aging – Keep the Voltage low when not in use.



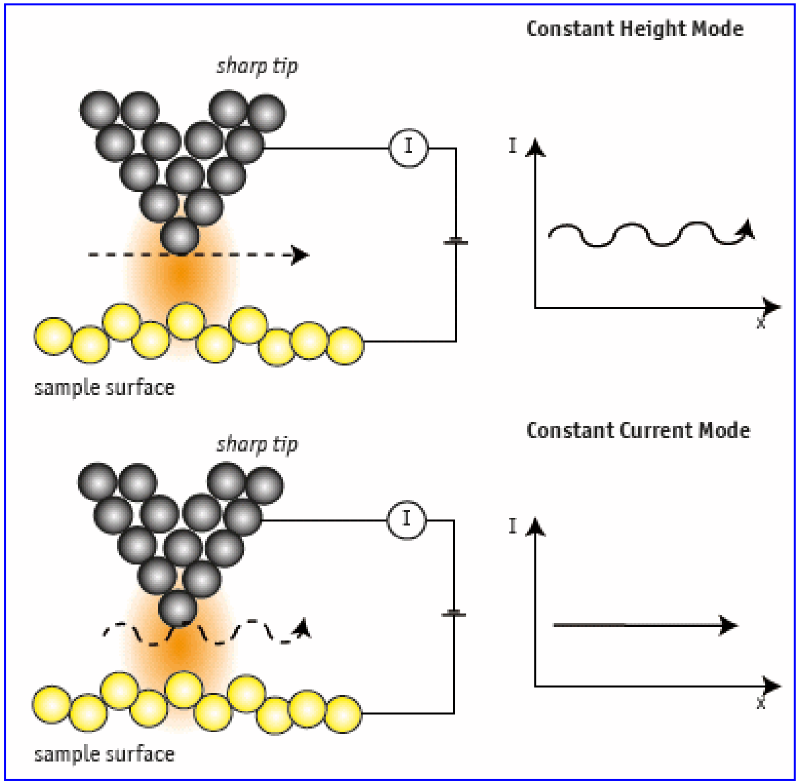
$$\Delta Z = d_{\perp}\frac{l_0}{h}U$$

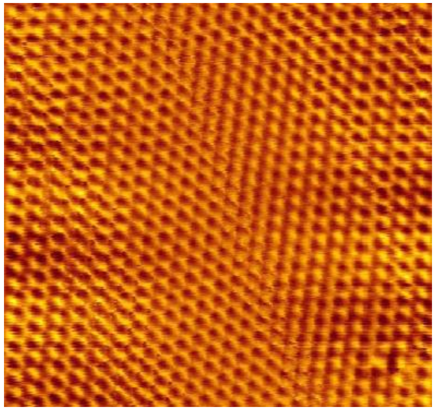


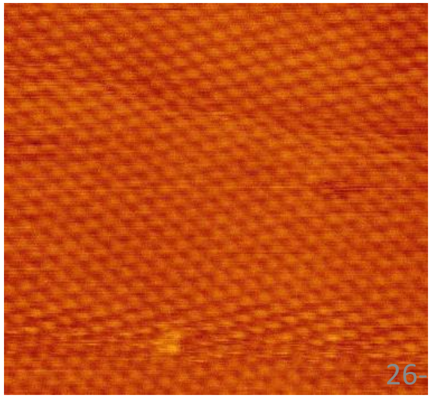
Barium titanate - replace Pb with Ba in the tetragonal perovskite structure.

Modes of Operation for Imaging

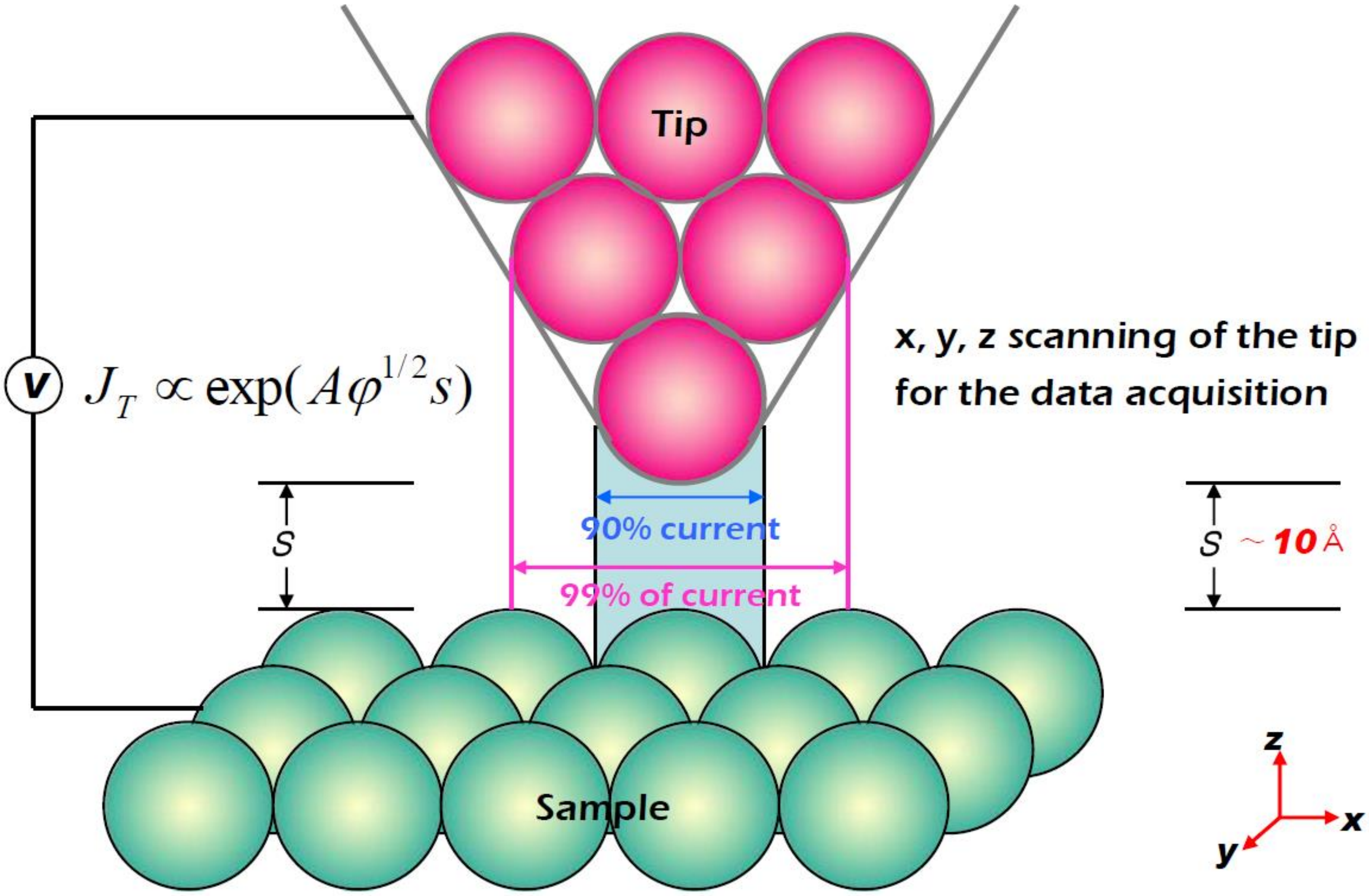
- **Constant height mode**: Measure ΔI(x,y) at a fixed height z (with feedback off) – This corresponds to variation of the Density of States (DOS) at fixed height. Usually high contrast and fast scanning, insensitive to low-frequency mechanical vibrations and electronic noise. Good for relatively smooth surface.
- **Constant current mode**: Measure Δz(x,y) at a constant I (with feedback on) – This corresponds to the contour of atomic corrugation at a constant DOS. This is the more common mode, with the spatial resolution depending on how sharp is the tip, electronic properties of the sample, and the applied bias voltage. Good for irregular/ rougher surface.







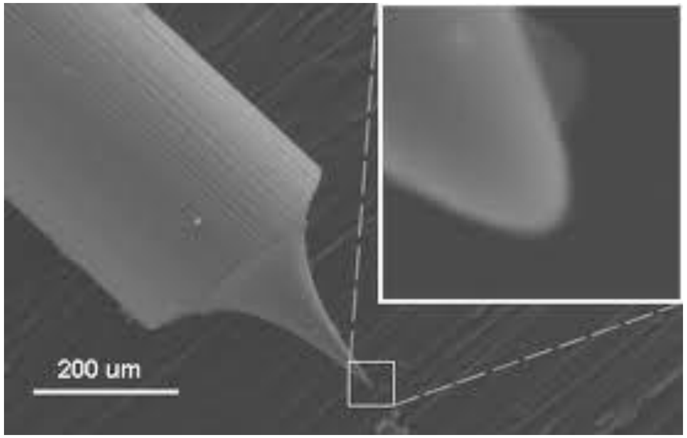
Atomic Resolution



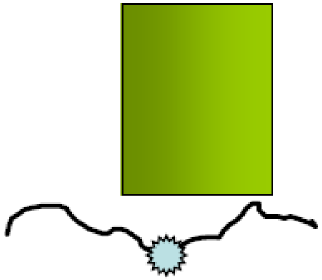
$$J_T \propto \exp(A\varphi^{1/2}s)$$

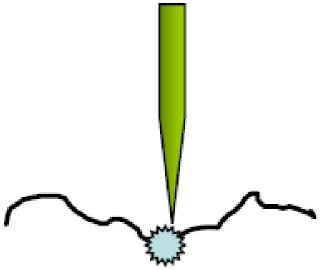
x, y, z scanning of the tip for the data acquisition

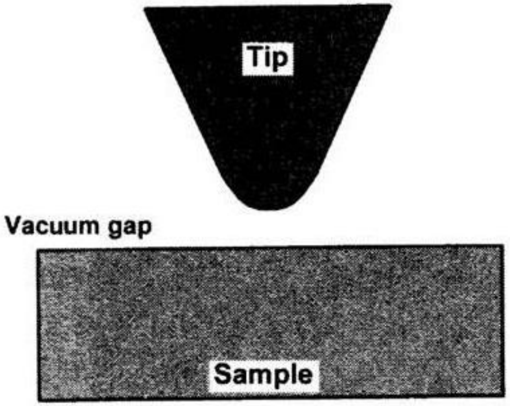
STM Tip



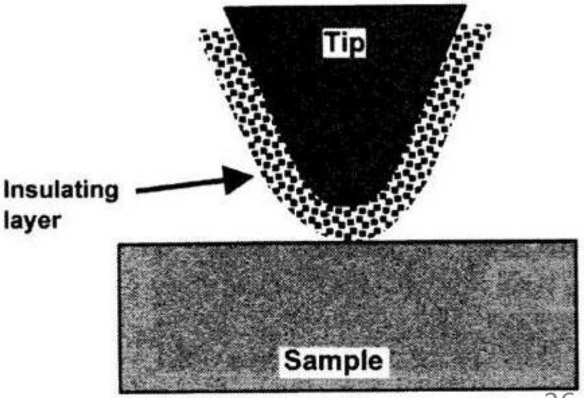
- Resolution of the STM (and AFM) depends on (a) tip size, and (b) tip-to-sample separation – rule of thumb: tunnelling current goes down by 7-10 times per Å or 1000 times per atom .

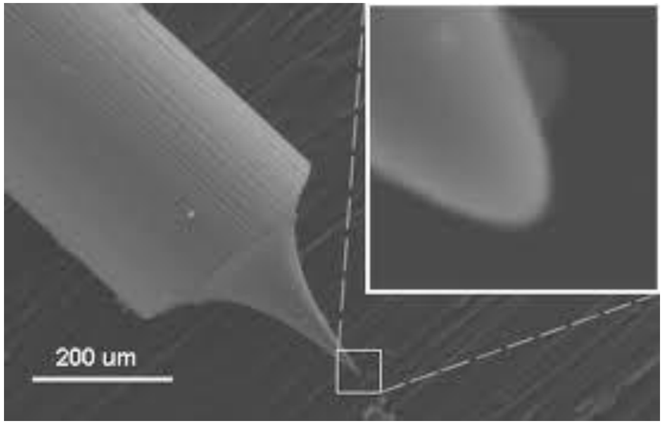




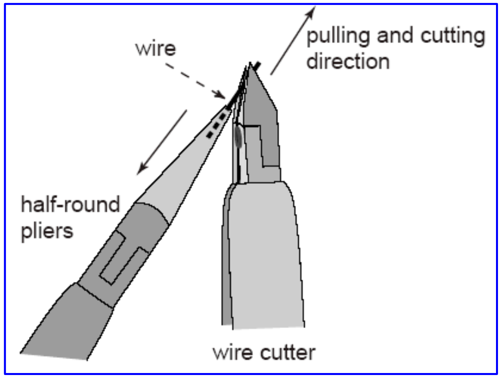


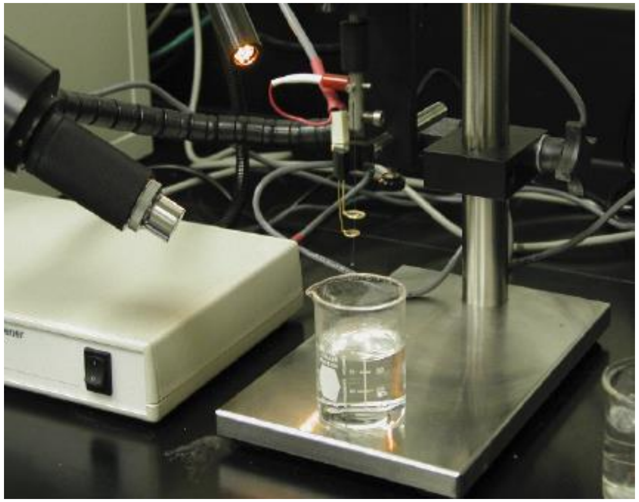
- Nonconducting or insulating layers of a few nm thick (e.g. oxides, contamination layers) can prevent tunnelling in vacuum. This may lead to crashing of the tip into the substrate and damaging the tip. Periodic voltage pulsing of the tip can help to “blow off” contaminants and oxide layers.





STM Tip





- Want: Single-atom termination; narrow cone angle; chemically inert (no oxide);
- Usually made of W, Mo, Ir, Pt, Au, PtIr – 200 μm dia;
- Use **electrochemical etching** – so-called Schrodinger's sharpener – to create tip down to 10 nm radius of curvature; OR use a wire cutter (e.g. PtIr) OR etching by a focussed ion-beam.

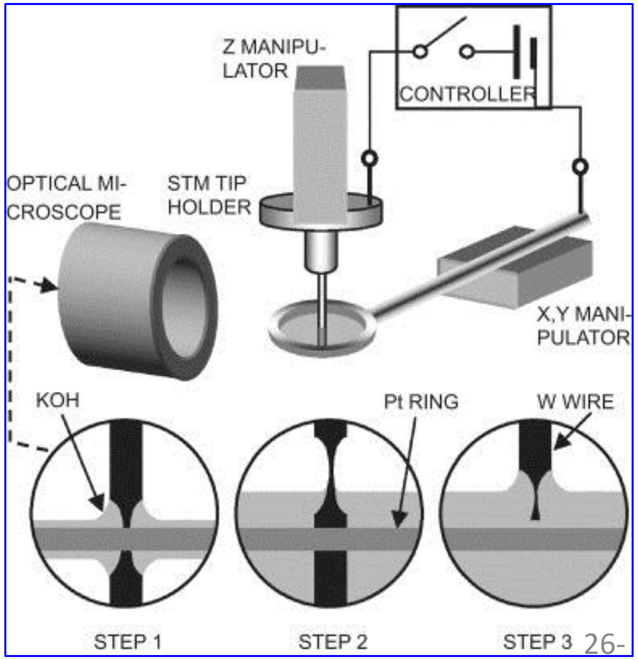
Cathode: $6H_2O + 6e^- \rightarrow 3H_2(g) + 6OH^-$

reduction potential = -2.45V

Anode: $W(s) + 8OH^- \rightarrow WO_4^{2-} + 4H_2O + 6e^-$

oxidation potential = +1.05V

$$W(s) + 2OH^- + 2H_2O \rightarrow WO_4^{2-} + 3H_2(g) \qquad E^0 = -1.43\ V$$



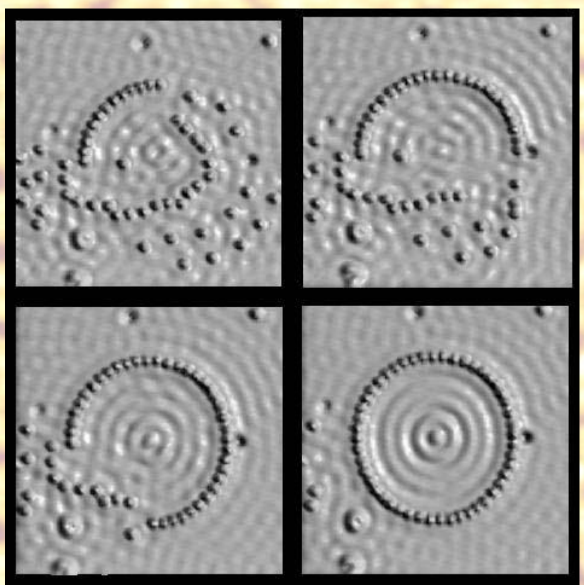
STM: Pros and Cons

- **Pros**:
  - Very high vertical spatial (z) resolution, and atomic spatial (x,y) resolution – can go higher if one can make an even sharper tip (with smaller curvature);
  - "Extreme" surface sensitivity;
  - Can be used (a) to study single-atom processes (e.g. catalysis), dynamic effects, novel single-atom properties; (b) to manipulate (move and relocate) atoms and molecules to build 3D nanoscale architecture one atom at a time, (c) to develop new spectroscopic tools (based on DOS) and physics.

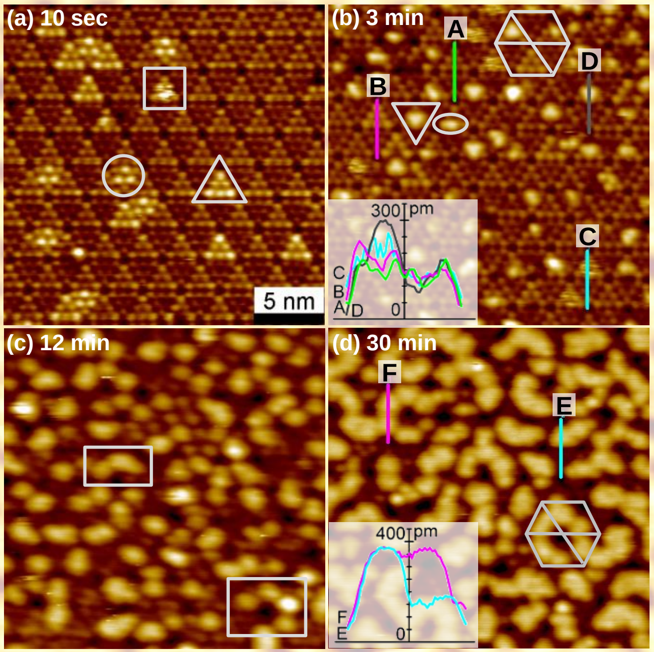
- **Cons**:
  - Sample must be conducting;
  - "Extreme" surface sensitivity – sensitive to dirt pick-up by the tip, which would lead to artefacts;
  - Low coverage – the surface must remain relatively free of adsorbate (i.e. bare or clean) to expose the reference template;
  - Very difficult to do chemical identification – electron density is electron density;
  - DOS info only – Image does not really correspond to the physical locations of the nuclei;
  - Rather slow technique compared to electron microscopy.

STM: Applications

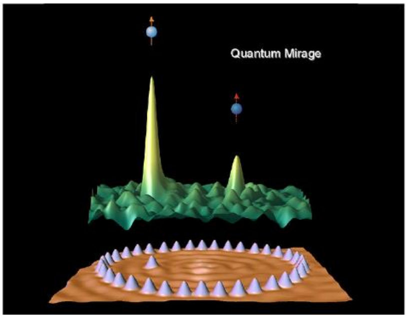
- **Atom-resolved Imaging of surface geometry**
- Molecular structure
- Local electronic structure – Local Density Of States
- Local spin structure – LDOS
- Single molecular vibration
- Electronic transport
- **Nanofabrication**
- **Atom manipulation**
- Nano-chemical reaction – Single atom



Quantum corral – Interference patterns of 48 Fe atoms on Cu(111) surface – radius = 7.13 nm
Ref: M.F. Crommie, C.P. Lutz, D.M. Eigler, Science 262 (1993) 218-220; M.F. Crommie, C.P. Lutz, D.M. Eigler, Nature 363 (1993) 524-7.

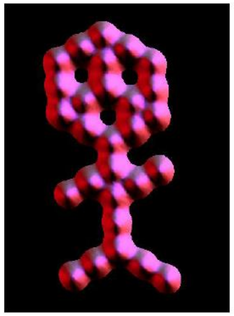


Quantum Corral



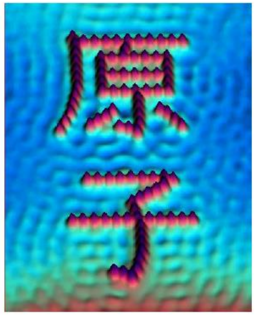
Cobalt on Copper (111)

Carbon Monoxide Man



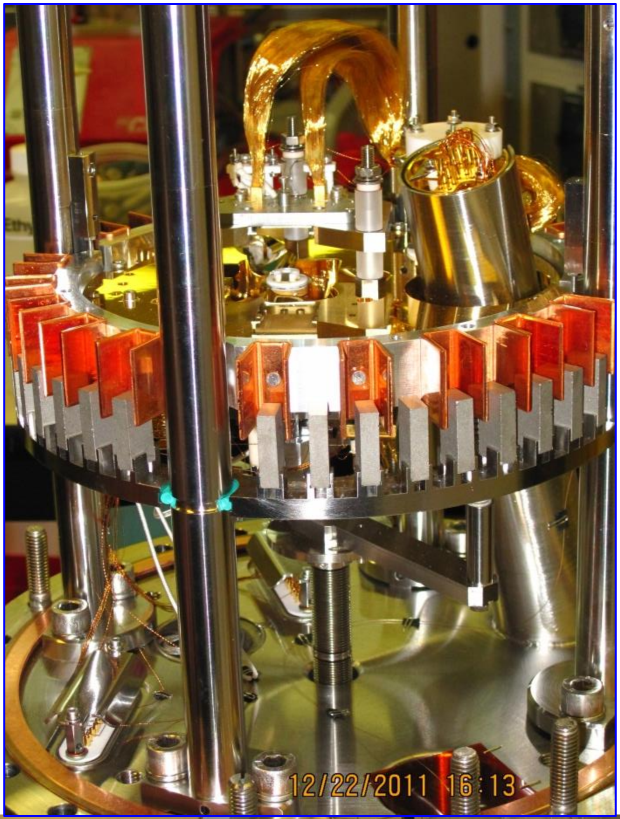
Carbon Monoxide on Platinum (111)

The Kanji for "atom."

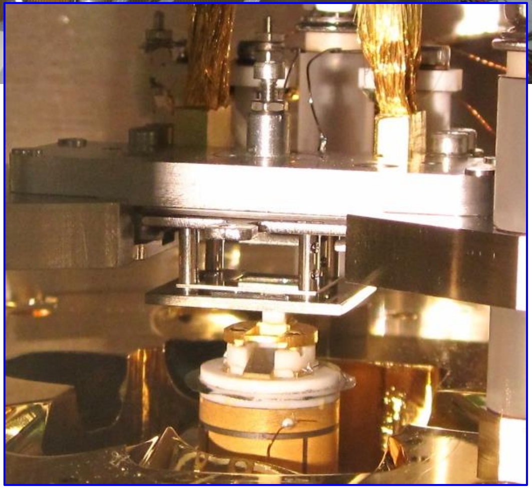


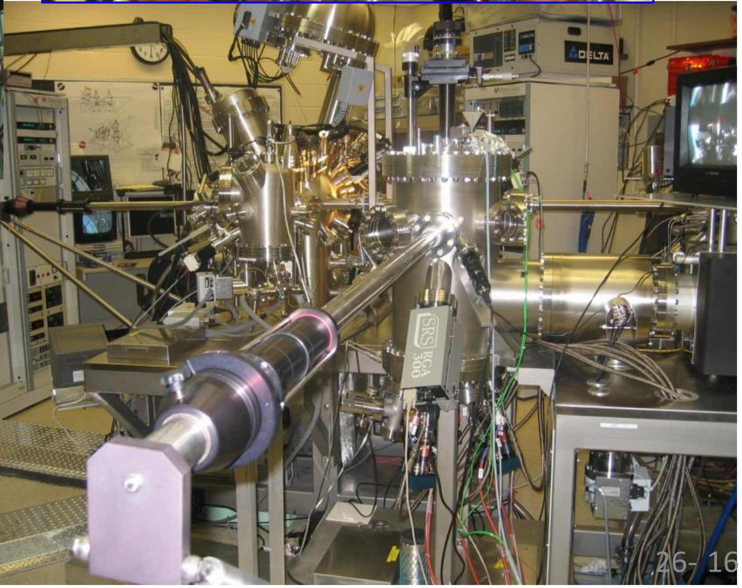
Iron on Copper (111)

WATLab: Omicron VT-SPM

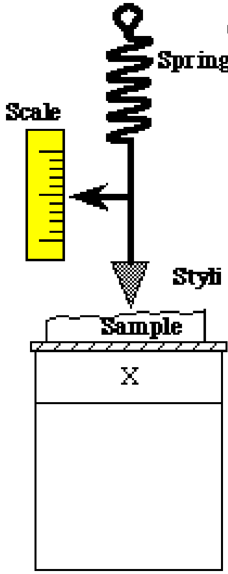


http://www.omicron.de/en/products/variable-temperature-spm/instrument-concept

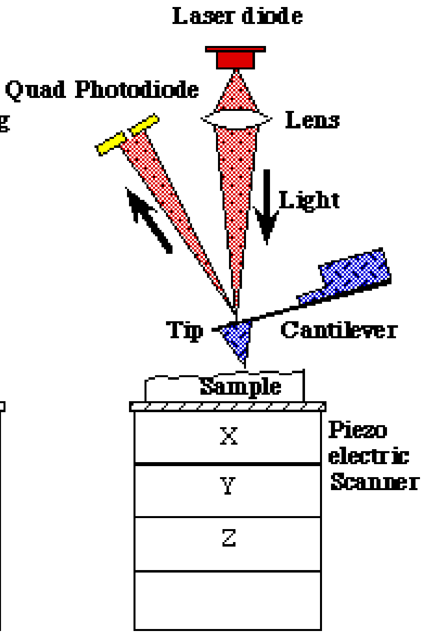




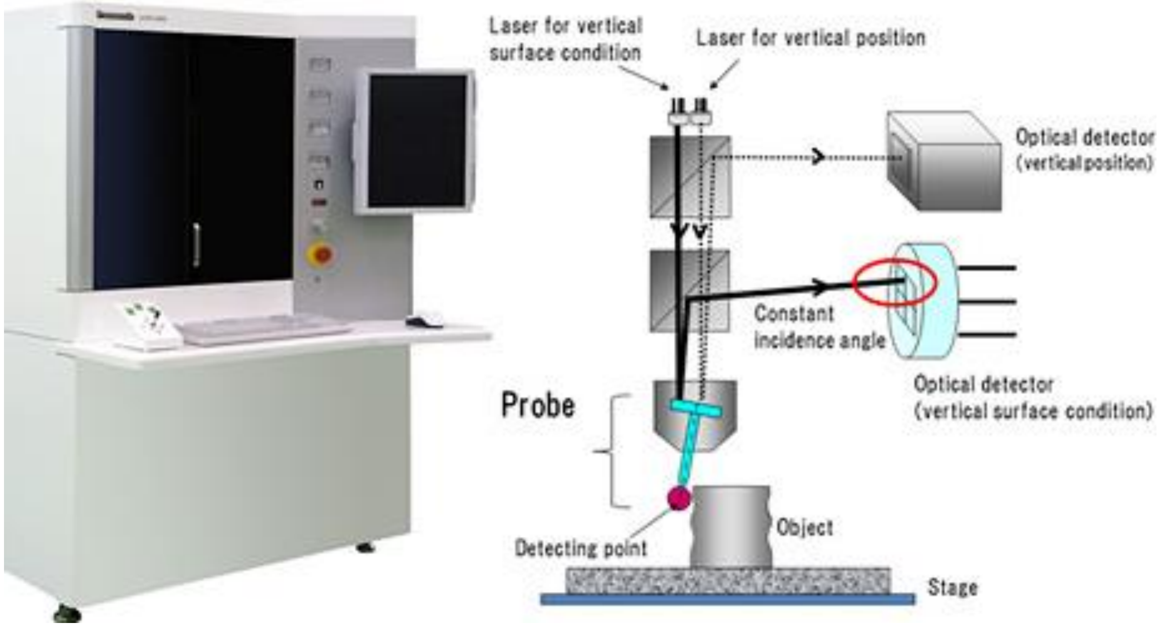
Stylus Profilometer

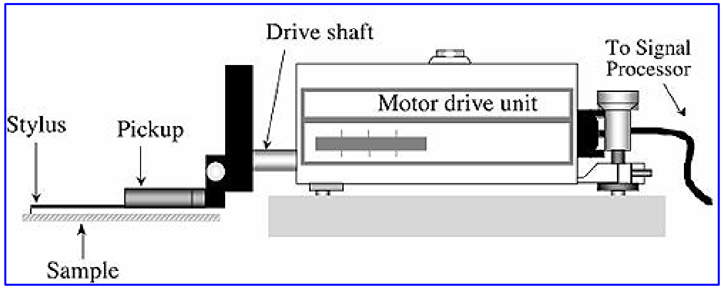


Idea of Styli profilometer

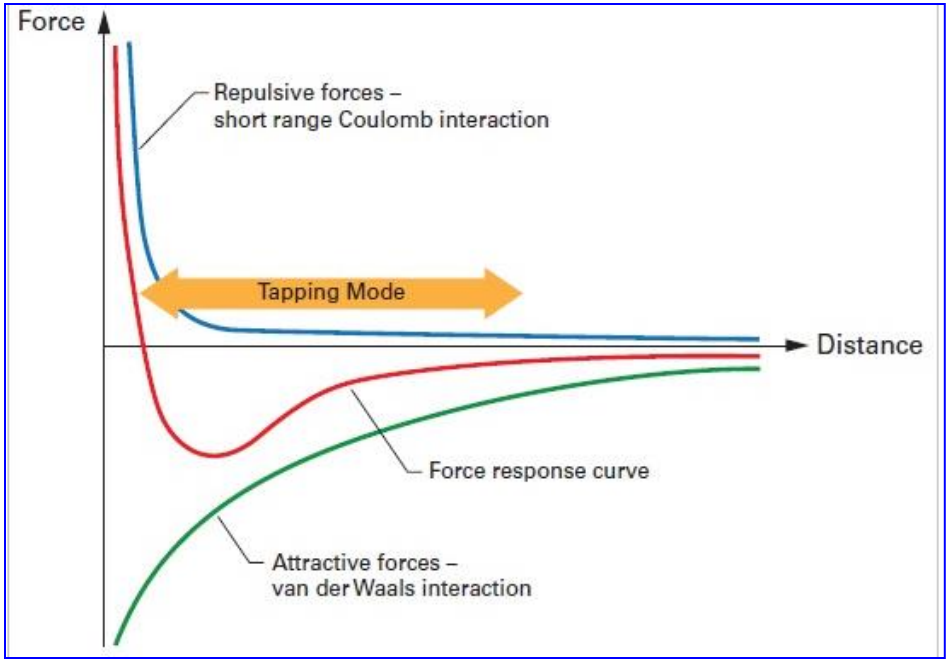


Atomic Force Microscope



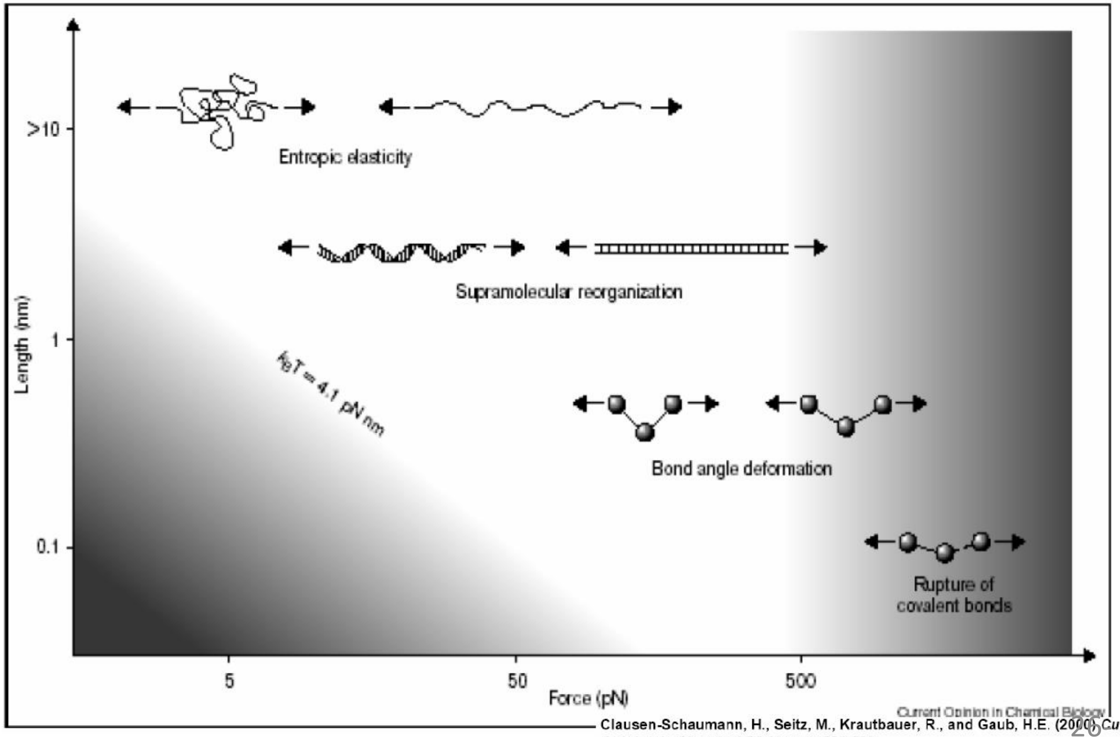


Atomic Forces



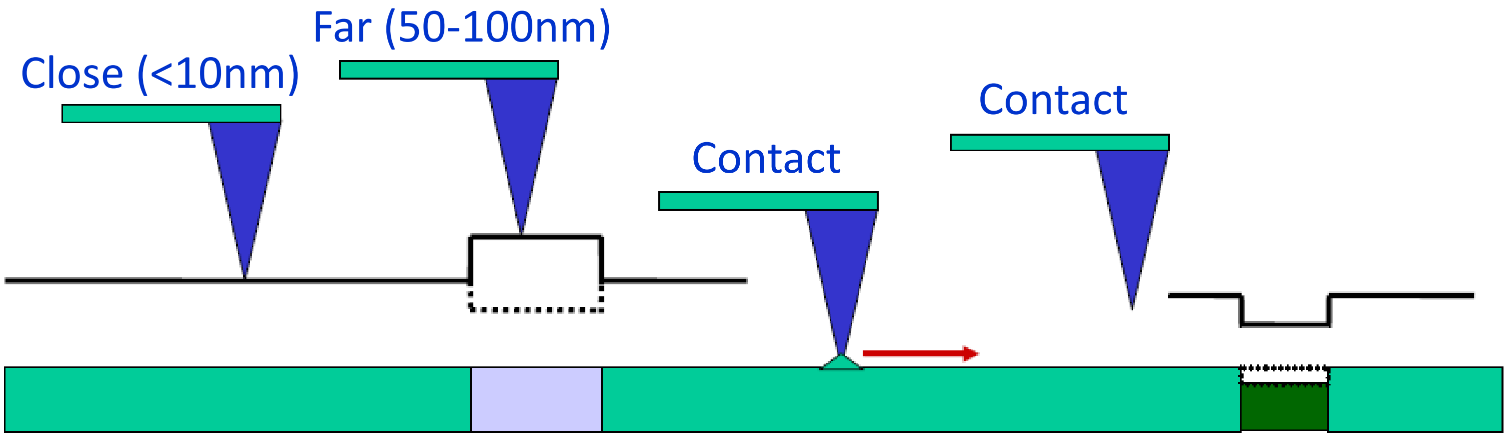
- Surface profilometers: for measuring thickness of “rough” materials; use stylus tip in mechanical contact with the surface (10^{-4} N); stylus tip radius of curvature = 1 μm.

- Long-range forces – 100 nm: Electrostatic force in air; Magneto-electrostatic forces; Electrostatic forces in double layer in fluid.
- Short-range forces: Van der Waals – 10 nm; Surface-induced solvent ordering – 5 nm; Hydrogen-bonding – 0.2 nm; Contact – 0.1 nm.



Clausen-Schaumann, H., Seitz, M., Krautbauer, R., and Gaub, H.E. (2000) *Current Opinion in Chemical Biology*, 4: 524-530.

Tip-Sample Interactions & Force Microscopy

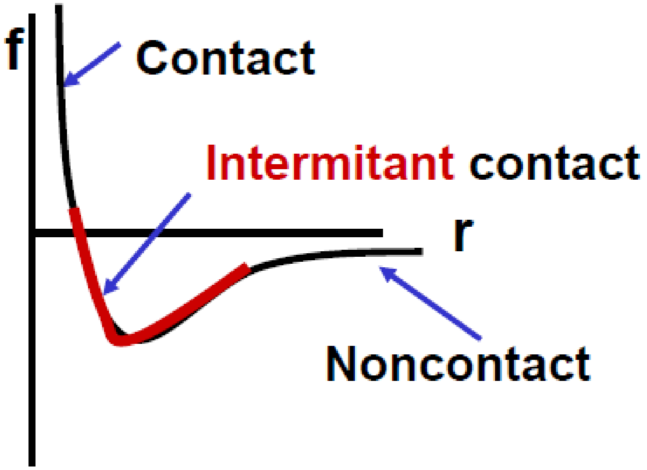


vdW force
attractive
ionic repulsion

magnetic or
electrostatic
forces

adhesion
bonding
friction forces

elastic and
plastic properties

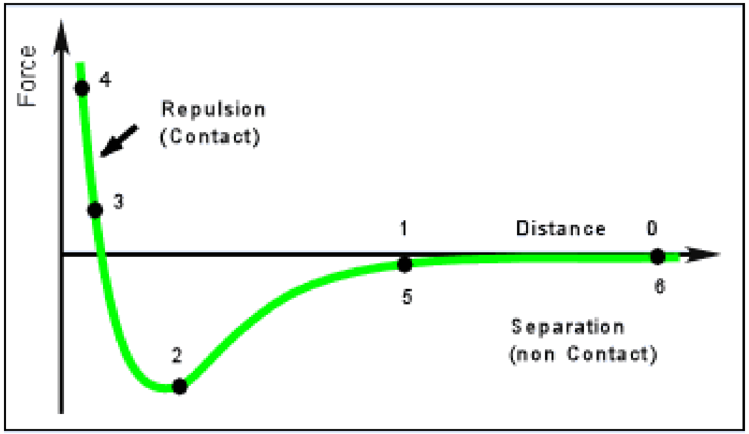


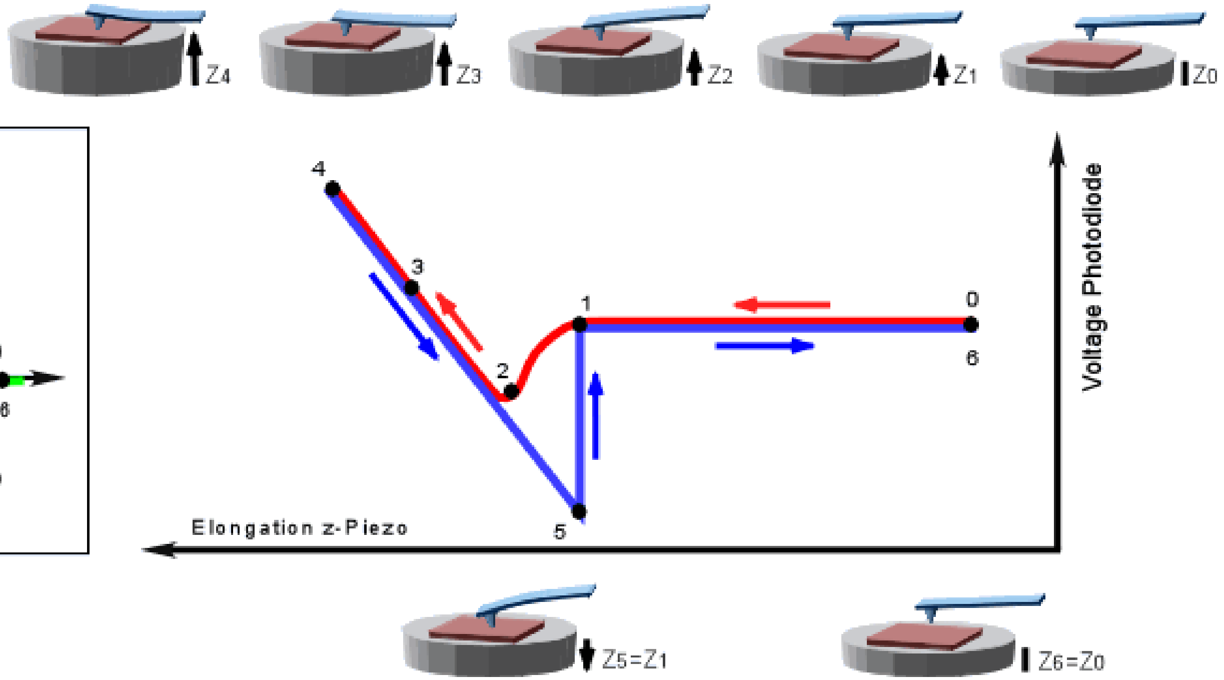
van der Waals force

$$f(r) \sim -1/r^6 + 1/r^{12}$$

total force on sample ~ $10^{-7} \sim 10^{-11}$ N

Tip Approach & Tip-to-Sample Interaction

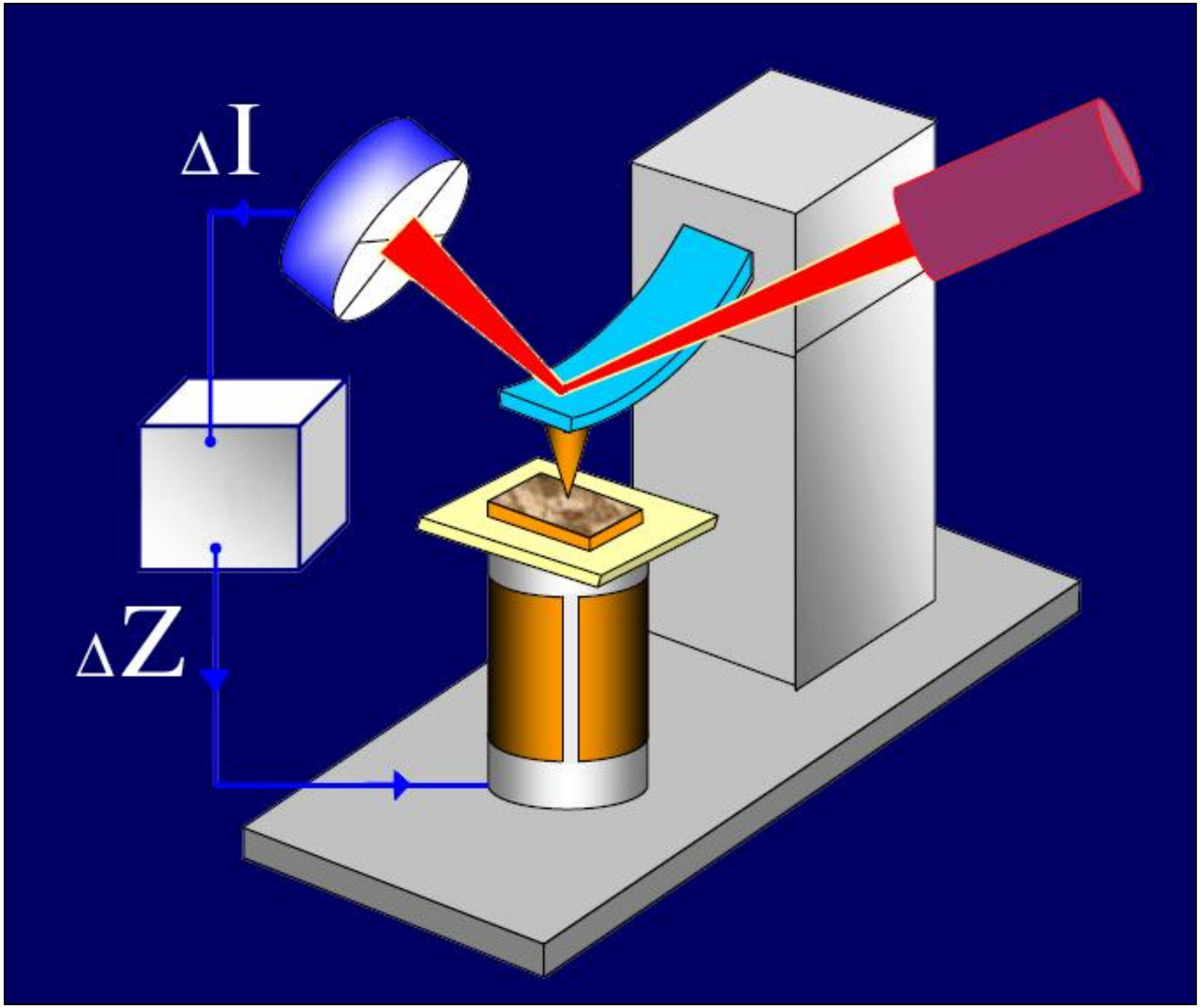




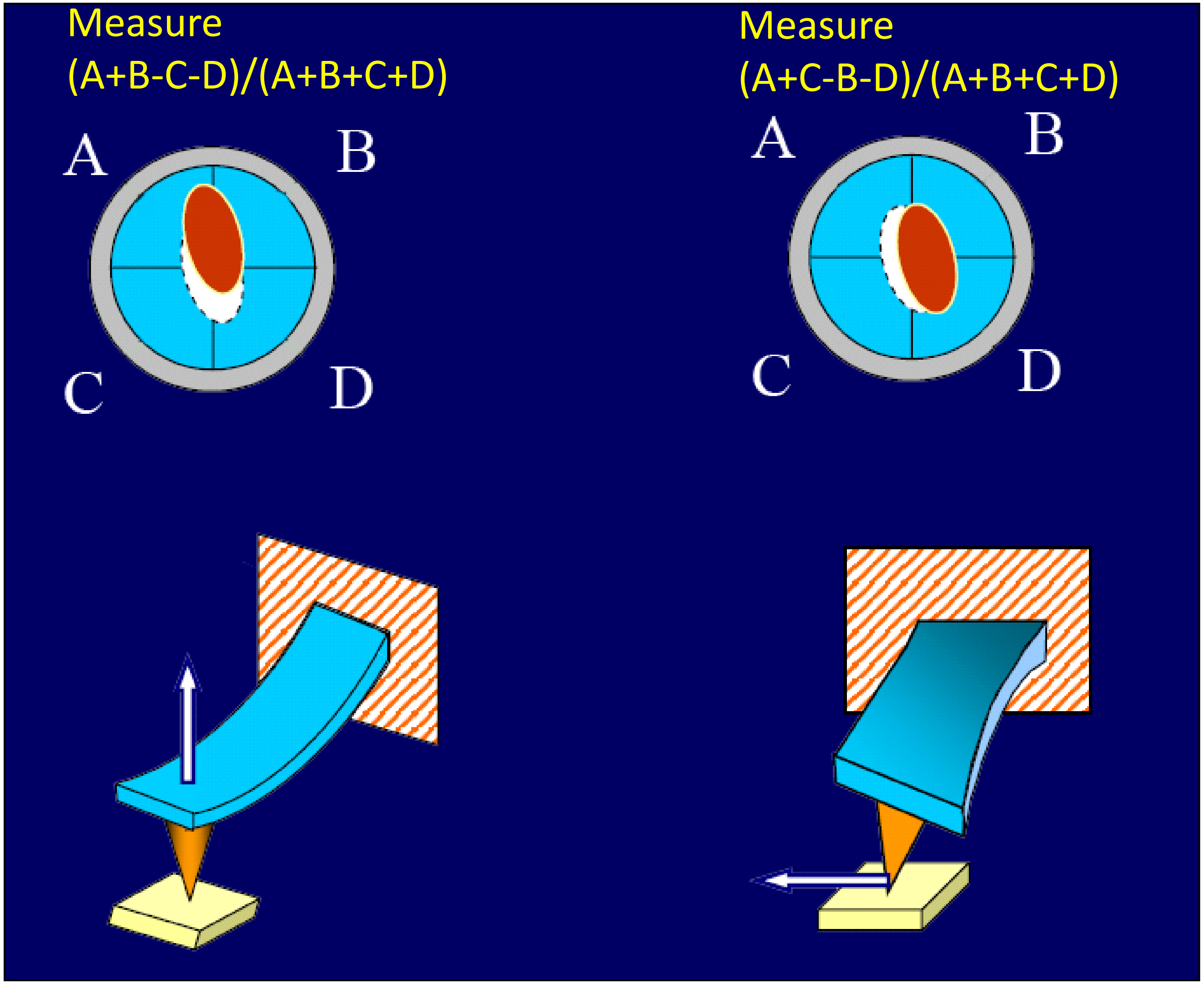
0-1 Large tip-sample separation – no detectable interaction force
1-2 Tip experiences attractive surface forces and the cantilever is deflected downward.
2-4 Tip is in contact with the surface and it exerts a pressure on the surface and the cantilever is deflected upward.
4 Tip retraction starts… But the adhesion forces may still keep the tip attached to the surface until the spring force exerted by the cantilever can overcome the adhesion.
5 Spring force of the cantilever overcomes the adhesion and the tip snaps back to its initial position.
6 Cycle starts again.

AFM: Basic Principle

- Move a sharp tip to approach the sample surface gently.
- Upon contact, deflection of cantilever causes large movement of laser spot on the 4-quadrant photo-diode.
- ΔI is related to ΔZ – the topography of the sample.
- Feedback loop can be used to maintain constant force.
- The tip and/or the sample can be mounted on piezo-mechanisms.

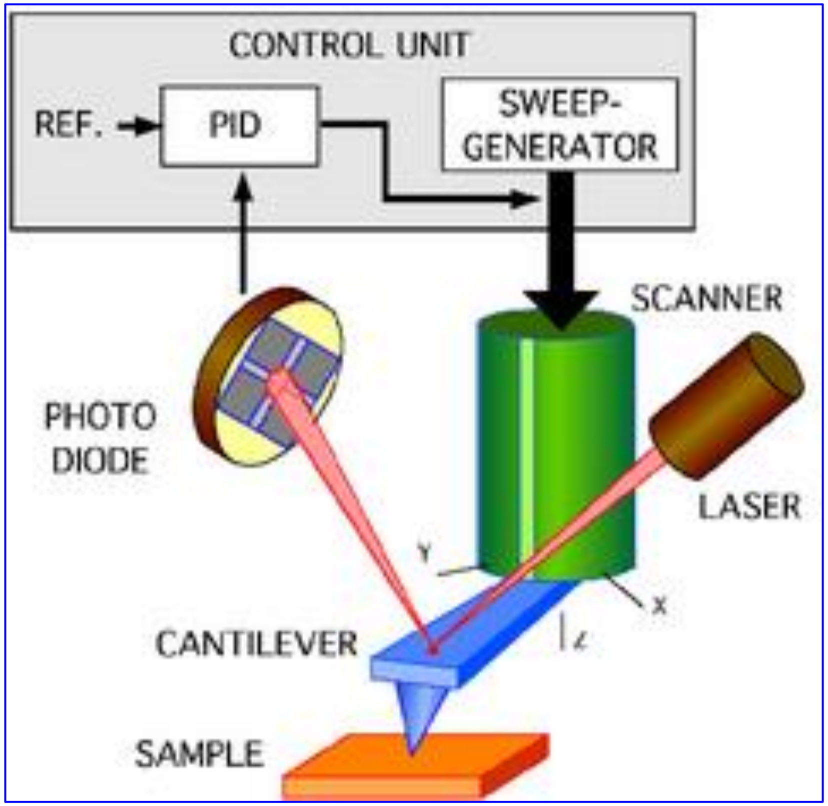


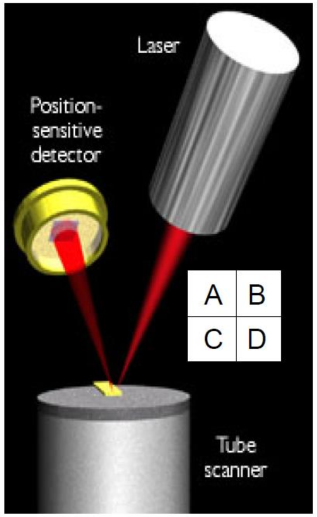
Position-sensitive Quad Photo-detector

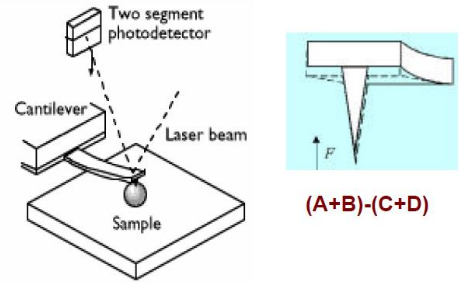


- Deflection in the Z direction can be used to maintain constant force – topography
- Deflection in X Y direction is used for lateral force or friction/tribology measurement.

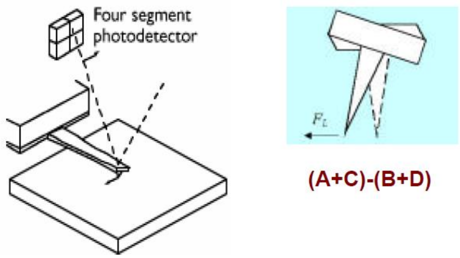
Modes of Operation







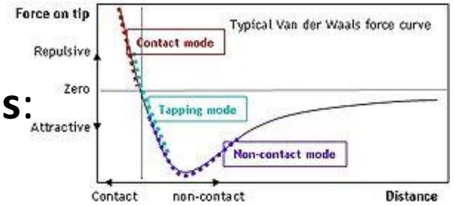
(A+B)-(C+D)



(A+C)-(B+D)

Basic AFM Modes:

- Static or Contact mode (no vibrating tip): strong (replusive) – constant force or constant distance.
- Dynamic modes [non-contact and tapping modes] (vibrating tip): weak (attractive and repulsive).



More Advanced Modes:

- Liquid AFM
- Magnetic Force Microscopy (MFM)
- Lateral Force Microscopy (LFM): frictional forces exerting a torque on the cantilever
- Force Modulation Microscopy (FMM)
- Electrostatic Force Microscopy (EFM)
- Plus...

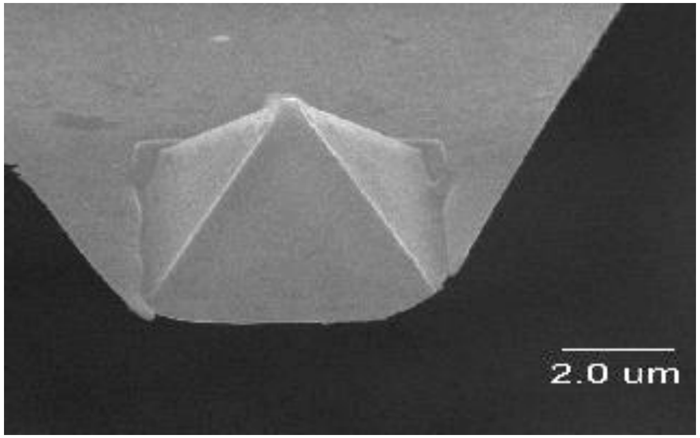
Samples:

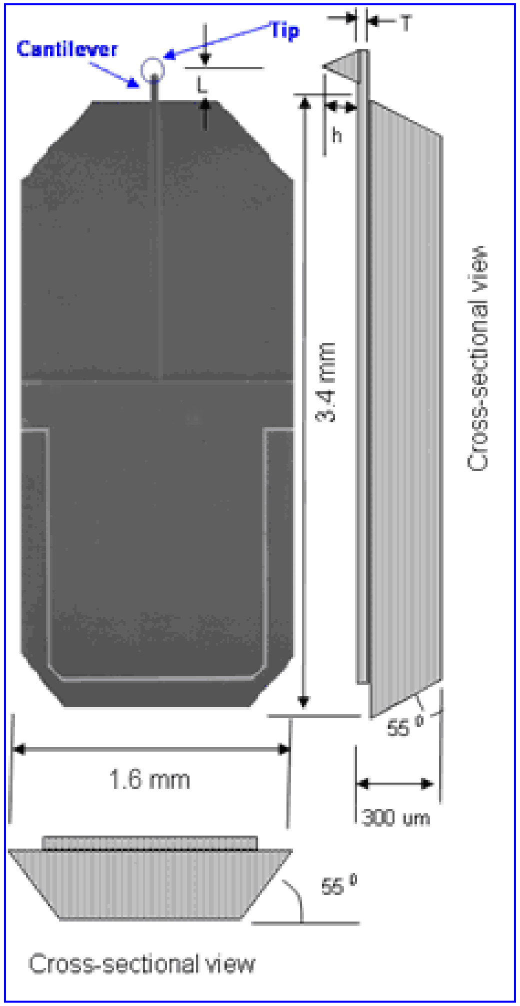
- Conductors – metals, semiconductors...
- Insulating materials – all types: oxides, polymers, biological materials

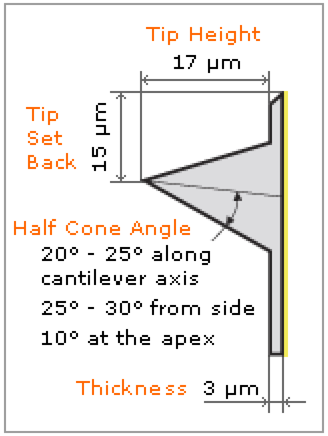
AFM Probe – Tip plus Cantilever

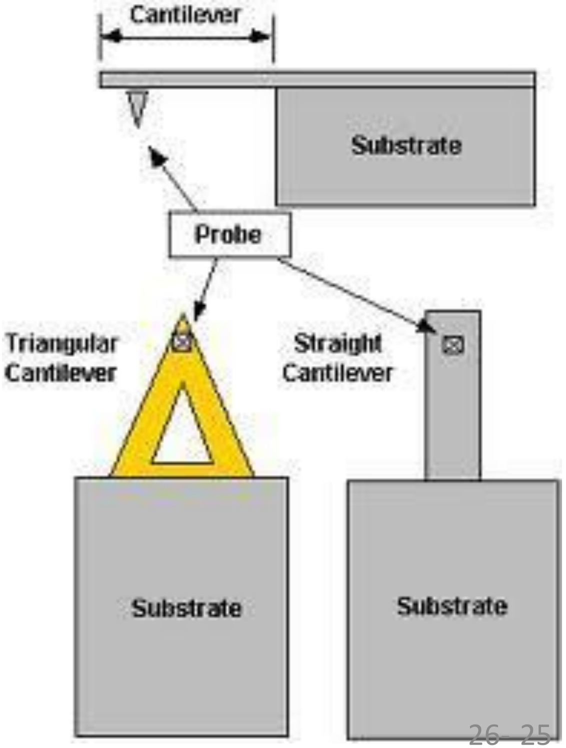
- Materials: Si, Si_3N_4
- Pyramidal, conical shapes
- Cantilever: 100-200 μm long,
  1-4 μm thick
  Tip: 10-20 μm; curvature radius ~ r

- Contact tip: soft $k < 1$ N/m;
  $r < 50$ nm; f ~ 15 kHz
- Non-contact tip: stiff k ~20-100 N/m;
  $r < 10$ nm; f ~ 200-400 kHz
- Non-contact sharper than contact tip

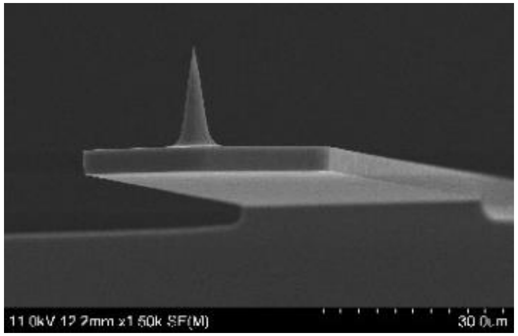


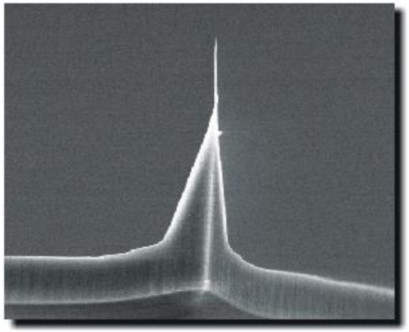


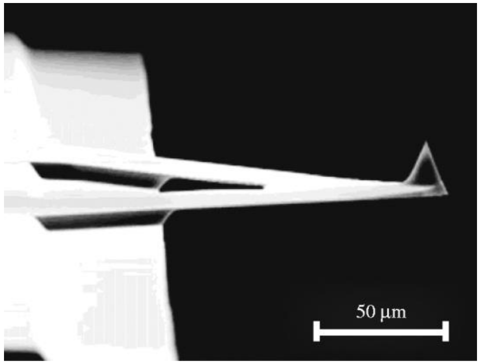


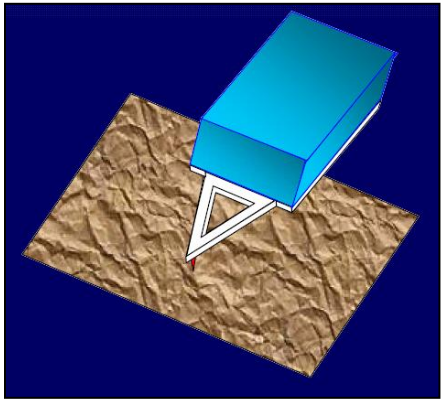


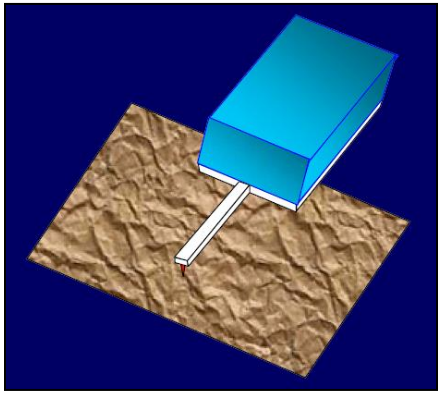
AFM Tips

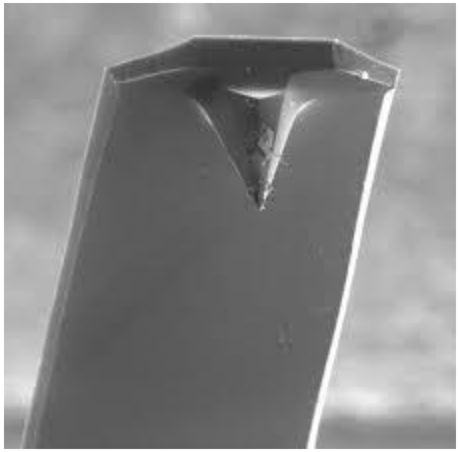


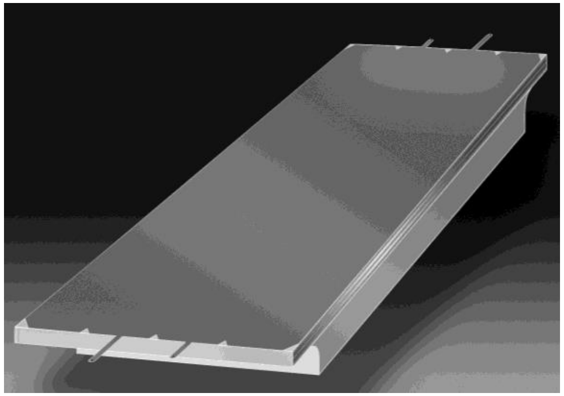


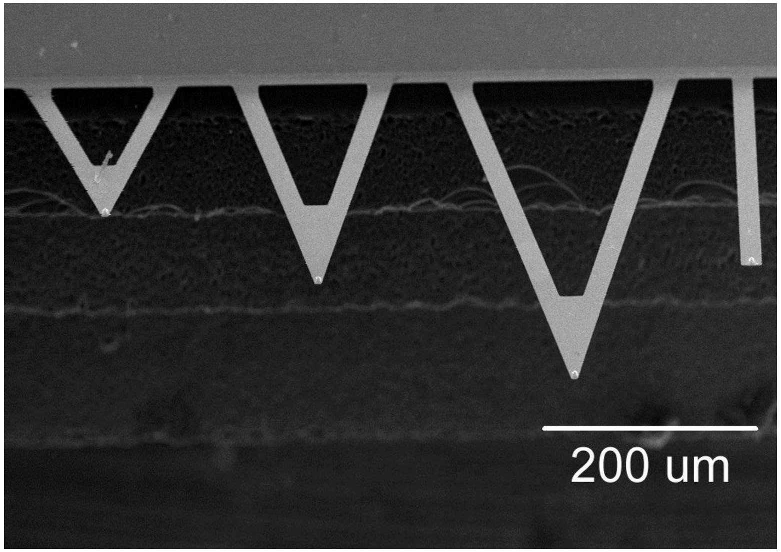


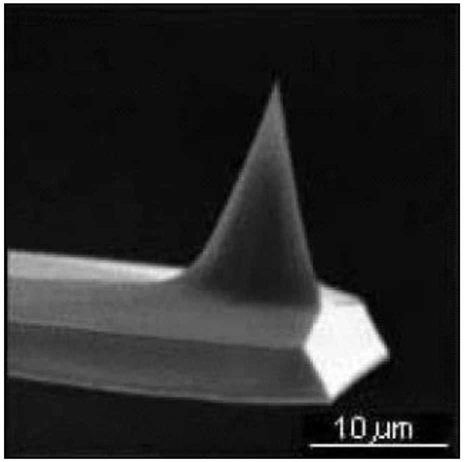




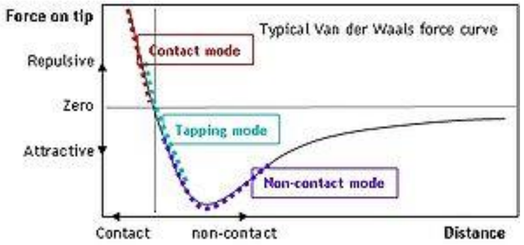








Static vs Dynamic Mode Imaging



Static or Contact Mode

- Constant force deflection;
- Force in strong replusive regime;
- Tip in physical contact with the surface;
- “Soft” cantilever with stiffness less than force constant in atoms (10 nN/nm);
- Van der Waals forces.

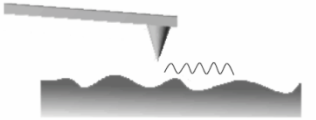
Static Mode

- Good for imaging hard and shallow samples, samples with periodicity, and samples in liquid environments.

Dynamic Modes

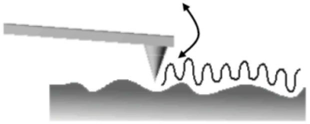
- Good for imaging soft (polymers, biomolecules), or delicate samples (with poor surface adhesion), samples in ultrahigh vacuum.

Dynamic Modes:



Non-contact or Frequency Modulation

- Constant force gradient deflection;
- Resonance frequency feedback;
- Force in weak attractive regime;
- Tip is oscillating 1-10 nm above the surface;
- “Stiff” cantilever with tip to sample forces about pN.

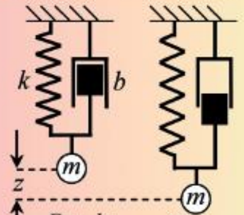


Tapping or Amplitude Modulation

- Constant force gradient deflection;
- Amplitude feedback
- Force in weak repulsive/attractive regime
- “Stiff” cantilever making intermittent contact with the surface.

The Physics of Atomic Force Microscopy

Simple Harmonic Oscillator



$$F = -kz \qquad T = \frac{2\pi}{\omega_0}$$

$$\omega_0 = 2\pi f_0 = \sqrt{\frac{k}{m}} \qquad A \propto \exp(-t/\tau)$$

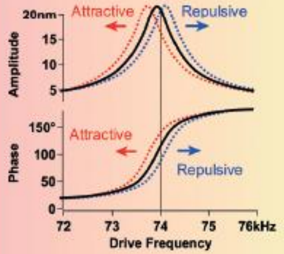
$$Q = \frac{k}{\omega_0 b} = \frac{\pi\tau}{T} = \frac{A_{\max}}{A_{drive}} \cong \frac{\omega_0}{\Delta\omega}$$

$$m\frac{d^2z}{dt^2} = F_{drive} - b\frac{dz}{dt} - kz + F_{ext}$$

$$F_{drive} = kA_{drive}\cos\omega t$$

$$A = \frac{A_{drive}\omega_0^2}{\sqrt{\left(\omega_0^2 - \omega^2\right)^2 + \left(\omega\omega_0/Q\right)^2}}$$

$$\tan\theta = \frac{\omega\omega_0/Q}{\omega_0^2 - \omega^2}$$



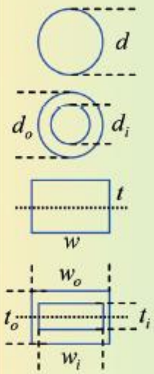
$$\delta A_{(\text{max slope})} = \frac{2QA_0}{3\sqrt{3}(k - F')}F'$$

$$\delta\omega_0 \approx -\frac{\omega_0 F'}{2k} \qquad \delta\theta_{(\text{res})} = \frac{Q}{k}F'$$

$$\overline{P}_{tip} = \frac{1}{2}\frac{kA^2\omega}{Q}\left[\frac{QA_{drive}\sin\theta}{A} - \frac{\omega}{\omega_0}\right]$$

Cantilever Beam Theory

$$k = 3\frac{EI}{l^3} \qquad f_0 = \frac{C}{2\pi}\sqrt{\frac{k}{m_t + 0.24m_c}} \qquad m_c = \rho A l$$

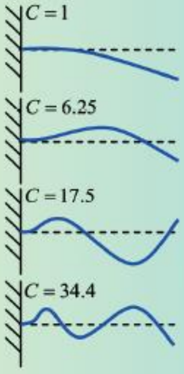


$$I = \frac{\pi d^4}{64}$$

$$I = \frac{\pi}{64}\left(d_o^4 - d_i^4\right)$$

$$I_z = \frac{wt^3}{12}$$

$$I_z = \frac{w_o t_o^3 - w_i t_i^3}{12}$$



Energies

k_BT = 4 pNnm

ATP hydrolysis
12-21 k_BT
Hydrogen Bond
4-18 k_BT
Covalent Bond
100-200 k_BT
Protein Stability
6-20 k_BT

	Young's Modulus E (GPa)	*Density ρ (kg/m³)*	*Speed of Sound (m/s)*	*Thermal Expansion (um/mK)*	*Thermal Conductivity λ (W/mK)*	*Heat Capacity c_p (J/gK)*
Stainless	200	7760	5100	10-13	12-25	.5
Steel	210	7850	5200	11	35	.46
Ti	116	4500	5100	8.9	17	.528
Al	70	2700	5100	24	190	.88
Invar	148	8050	4300	1.3	10.15	.515
SiN	260-320	3100	~9800	3	30	.71
Si	179	2330	8800	2.6	150	.7
Cu	117	8900	3600	17	383-391	.385
W	400	19300	4500	4.4	163	.134
Granite	20-60	2500-2700	~5000	3.7-11	1.4-4.2	.21-.35
Pyrex	61	2250	5500	4.4	163	.134

Cantilever Shapes

$$h_{end}(x) = \frac{3Lx^2 - x^3}{2L^3}$$

$$h_{dist}(x) = G(\cosh\kappa x - \cos\kappa x) + H(\sinh\kappa x - \sin\kappa x)$$

Added Mass Correction

$$m_t = m_m\left(\frac{L - \Delta L}{L}\right)^3$$

Reference Spring

$$k = k_{ref}\left(\frac{\Delta z_{ref}}{\Delta z} - 1\right)$$

Shot Noise

$$\delta V_{rms} = R\sqrt{2e\eta P_0 B}$$

Johnson Noise

$$\delta V_{rms} = \sqrt{4k_BTRB}$$

Thermal Noise

on resonance

$$\delta z_{rms} = \sqrt{\frac{4k_BTBQ}{k\omega_0}}$$

off resonance

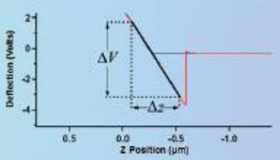
$$\delta z_{rms} = \sqrt{\frac{4k_BTB}{Qk\omega_0}}$$

Forces
Covalent Bonds
2-5 nN
Unzipping DNA
20 pN (GC)/10 pN (AT)
1 mW of light reflecting off of a surface
7 pN

Distances
Covalent Bonds
0.1nm
Hydrogen Bond
0.25 nm
Tip Radius of Curvature
2-50 nm
DNA diameter
2nm

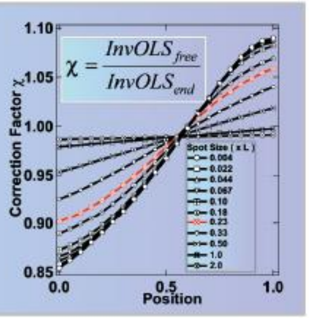
Stiffness
Covalent Bond
10N/m
Cantilevers
0.01 -100N/m

Thermal Method



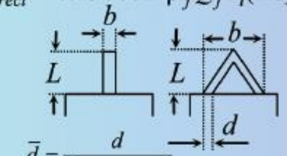
$$InvOLS_{end} = \Delta z/\Delta V\,(nm/volt)$$

$$k = \frac{k_BT}{\langle\delta V^2\rangle\chi^2 InvOLS^2}$$



Sader Method

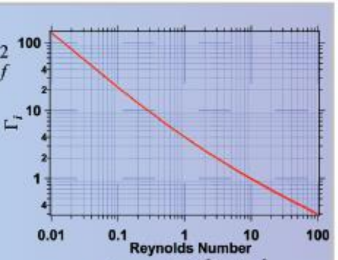
$$k_{rect} = 0.1906bL^2\rho_f Q_f \Gamma_i(\mathrm{Re})\omega_f^2$$



$$\bar{d} = \frac{d}{\sqrt{1 + b^2/4L^2}}$$

$$D_0 = k_{rect}\frac{4L^3}{b} \qquad \mathrm{Re} = \frac{\rho\omega b^2}{4\eta}$$

$$k_{tri} = \frac{D_0\bar{d}}{2L^3}\left(1 + \frac{4\bar{d}^3}{b^3}\right)^{-1}$$



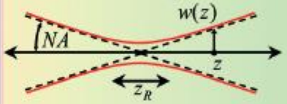
$$\rho_{water} = 1x10^3 kg/m^3$$

$$\eta_{water} = 8.9x10^{-4} kg/m\cdot s$$

$$\rho_{air} = 1.18 kg/m^3$$

$$\eta_{air} = 1.86x10^{-5} kg/m\cdot s$$

Gaussian Optics



$$w(z) = w_0\sqrt{1 + \left(\frac{\lambda z}{\pi w_0^2}\right)^2}$$

$$z_R = \frac{\pi w_0^2}{\lambda} \qquad N.A. = \frac{\lambda}{\pi w_0}$$

Coherence Length

$$\Delta l = c\Delta t \cong \frac{\bar{\lambda}_0^2}{\Delta\lambda_0}$$

Thin Lens

$$\frac{1}{s} + \frac{1}{s'} = \frac{1}{f}$$

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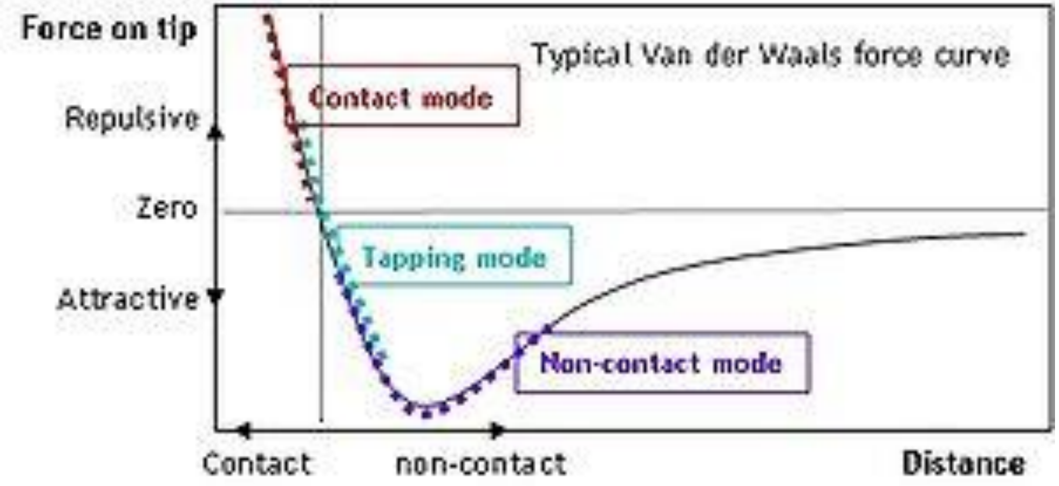
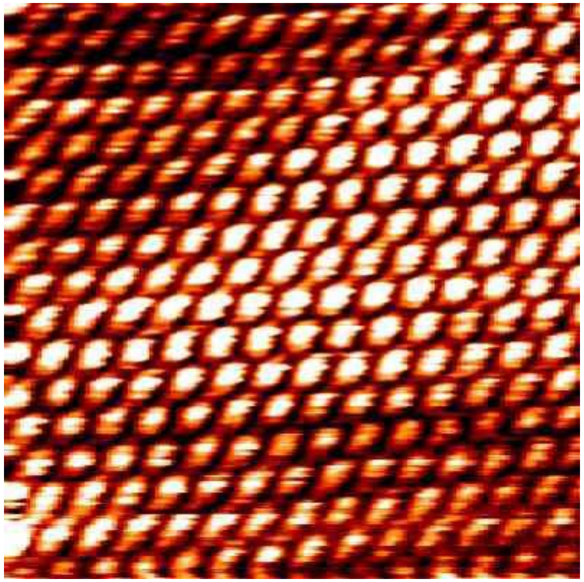
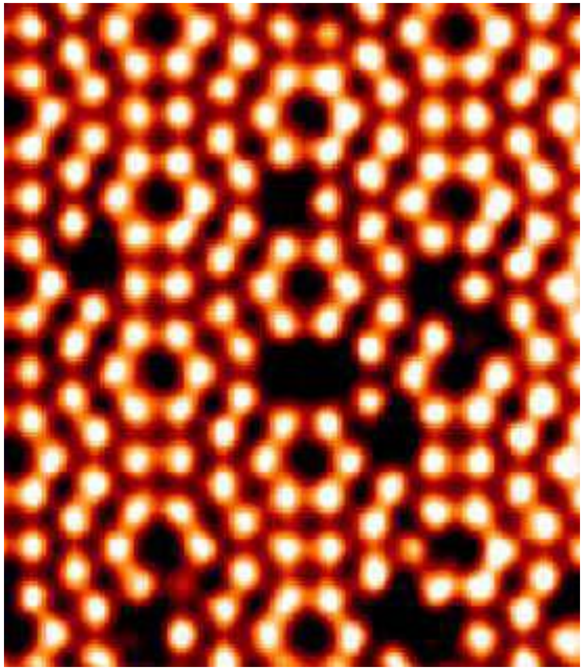




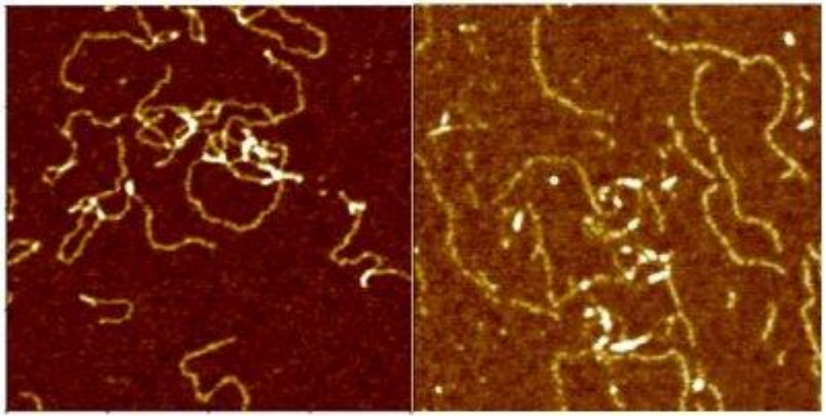
Contact Mode: Au(111) polycrystalline film on a glass substrate

Tapping Mode: Arene on graphite

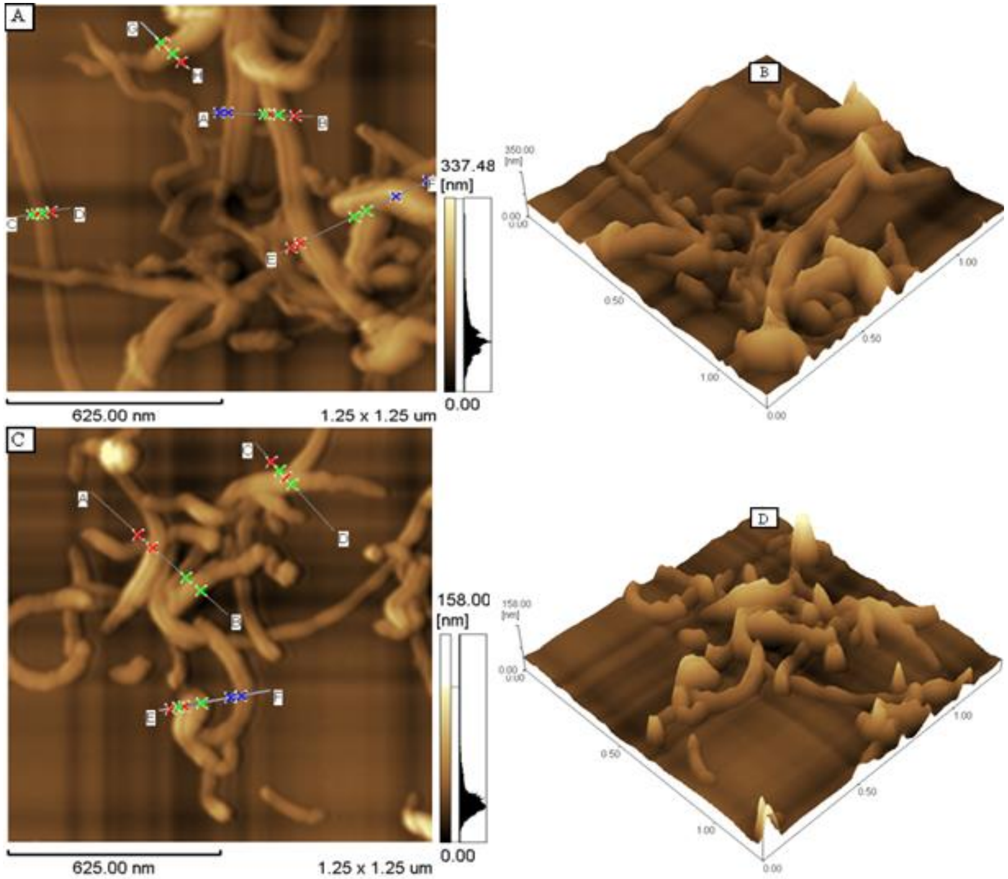


Non-contact Mode: Si(111) 7x7

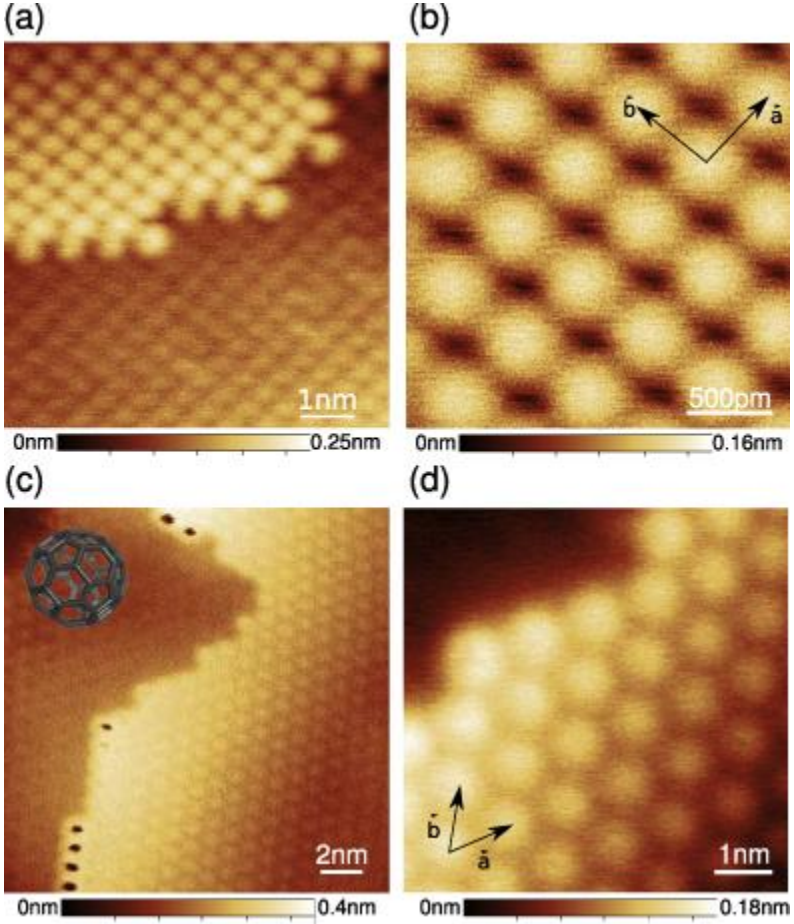
AFM: Applications



Single-strand G4 DNA – 1x1 μm^2



Carbon nanotubes on mica



C_{60} on KBr(001) – lower – Pawlak et al.
J Phys C 24 (2012) 084005.

STM vs AFM: True Nanotools

STM	**AFM plus**
• Real space imaging; • Not true topographic imaging b/c it measures local electron density of states, not nuclear positions;	• Real topographic imaging;
• High lateral and vertical resolution – atomic resolution; • Probe electronic properties (LDOS – including spin states);	• Lower lateral resolution; • Probe various physical properties: magnetic, electrostatic, hydrophobicity, friction, elastic modulus, etc.; • Can manipulate molecules and fabricate nanostructures;
• Sensitive to noise; • Image quality depends on tip conditions (atomically sharp, dirt, etc.); • No direct chemical identification;	• Contact mode can damage the sample; • Image distortion due to the presence of water; • No direct chemical identification;
• Only for conductive materials.	• Apply to both conducting and non-conducting materials, including polymers, biomolecules, ceramics.