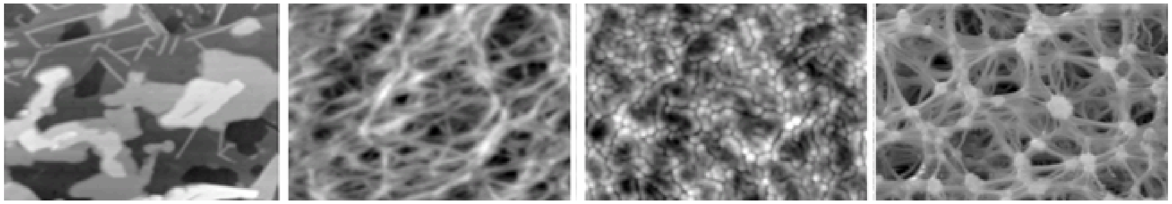


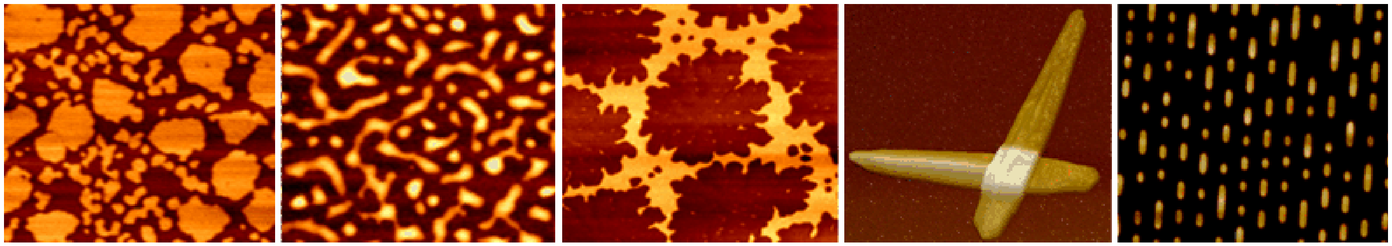
Scanning Probe Microscopy

for Physics 9826 – Surface Science

Heng-Yong Nie (hnie@uwo.ca)

May 8, 2014

P&A 026



What is SPM?

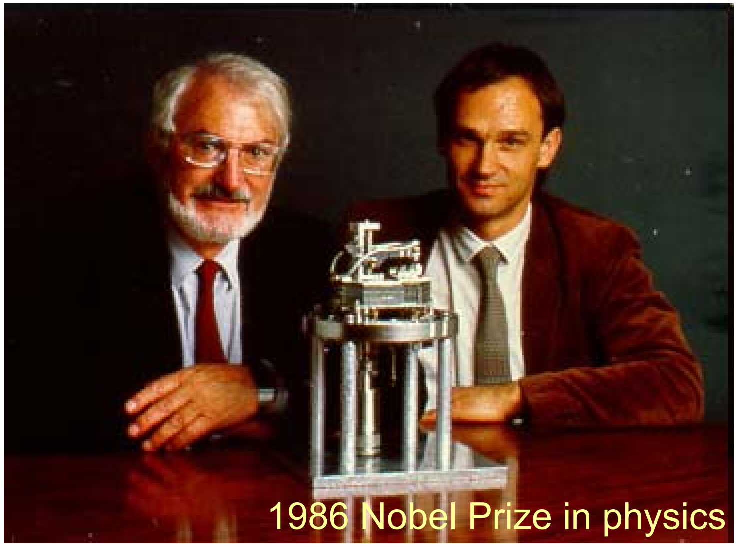
Scanning Probe Microscopy is a family of the following microscopes:

Scanning Tunneling Microscopy
Tunneling current
Surface morphology at atomic resolution in UHV (in principle)
Local electronic structure on surface
Conductive required

Atomic force microscopy / Scanning Force Microscopy
Atomic force or tip-sample interaction
Mechanical probe microscopy
Measuring almost any materials in any environment

STM was invented in 1981

Heinrich Rohrer Gerd Binnig

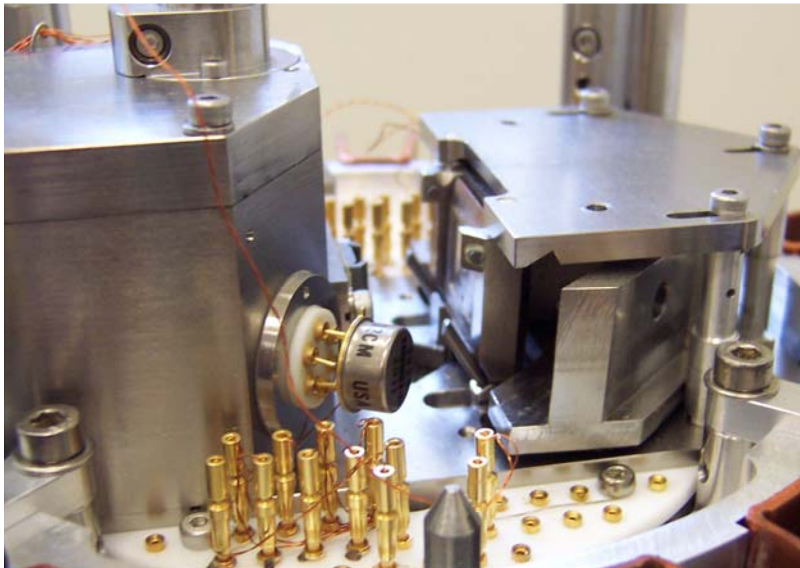


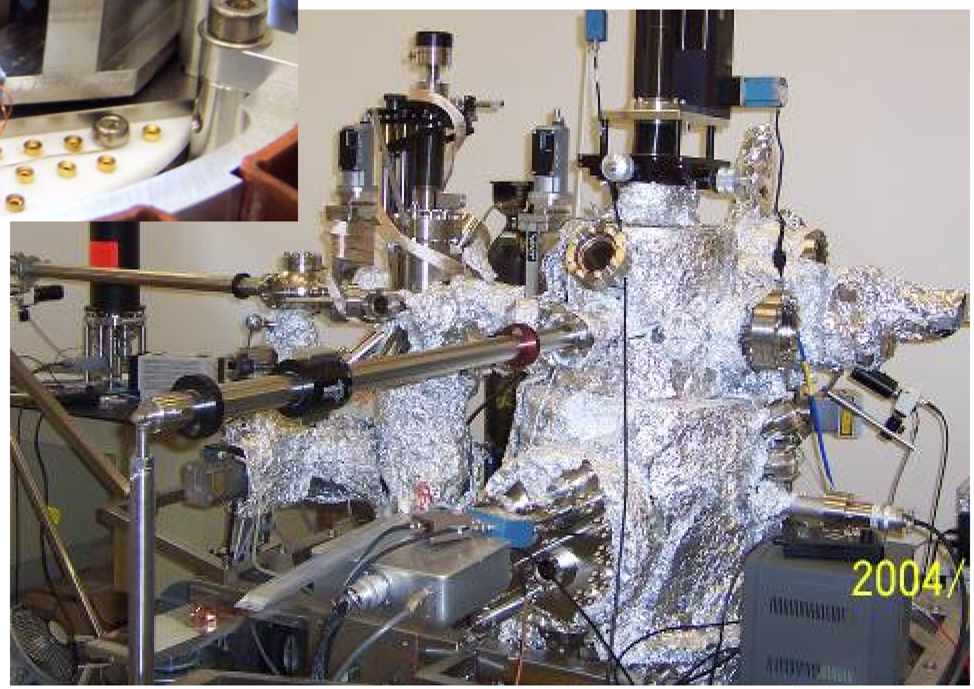
AFM invented in 1986 by

Gerd Binnig
Calvin Quate
Christopher Gerber

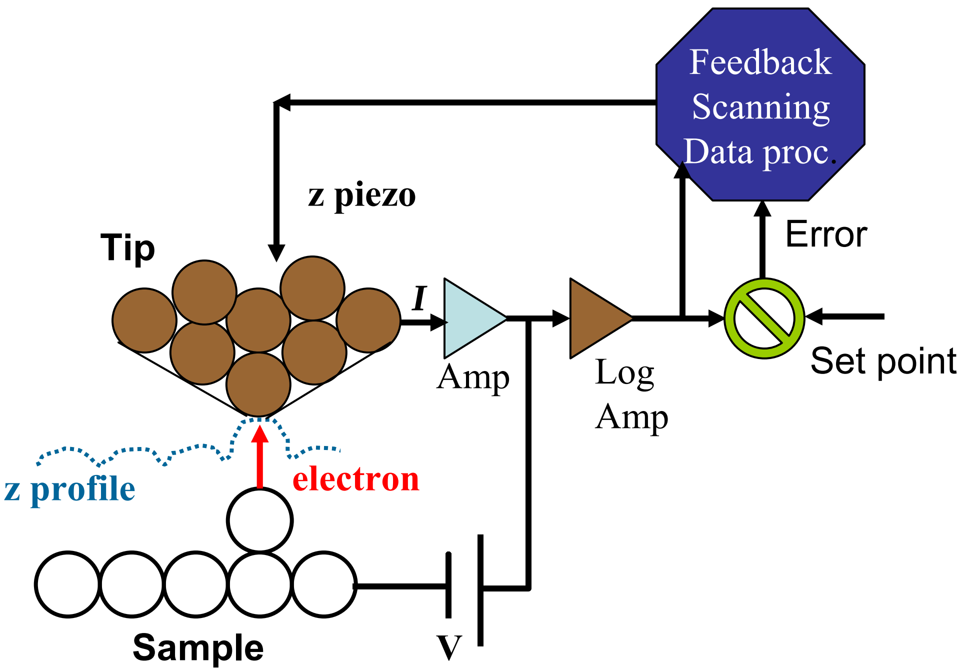
Scanning probe microscopy (SPM) is a mechanical probe microscopy that measures surface morphology in real space with a resolution down to atomic resolution. SPM was originated from the scanning tunneling microscopy (STM) invented in 1981-83, in which electrical current caused by the tunneling of electron through the tip and the biased sample is used to maintain a separation between them. Because STM requires that the sample surface be conductive, atomic force microscopy (AFM) was developed in 1986 to measure surface morphology that are not a good conductor. AFM has since been developed very rapidly and has found much more applications than STM in many fields. The majority of the developments in nanotechnology will have to rely on SPMs in feasible future.

An Omicron STM/AFM system





Scanning tunneling microscopy



By approaching the tip with a specified bias and current, the tip will be held at a certain distance from the sample surface so that the specified current (set point) is realized. By scanning the tip across the sample under this condition, the system compares the measured current I and the set point current I_s (I-I_s) and uses this error signal as the feedback parameter to apply an appropriate voltage to the z-piezo to adjust the tip-sample distance so as to diminish the error signal (i.e., I-$Is \rightarrow 0$), thus providing the height profile of the "*topography*" of the surface. This is the constant current mode. The other operation (constant height) mode is to keep the tip-sample distance while recording the current, which apparently requires the scanned area to be flat.

constant current mode:
current is the feedback parameter

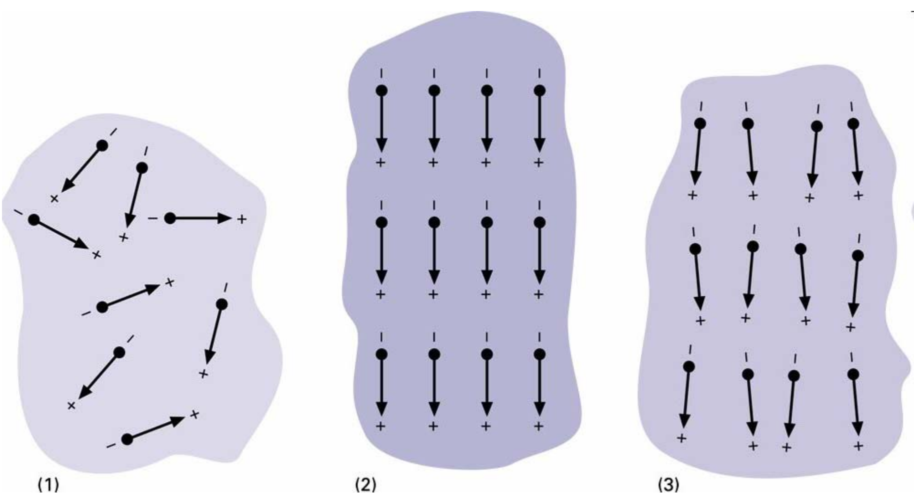
Piezoelectric scanners

Piezoelectric effect: electric field induced displacement of crystalline lattice and vice versa.

Material: lead zirconate titanate: PZT.

Powders are fired (1350º C) to form films. After polarization under an electric field (e.g., 60 kV/cm for an hour), they are used as scanner elements.

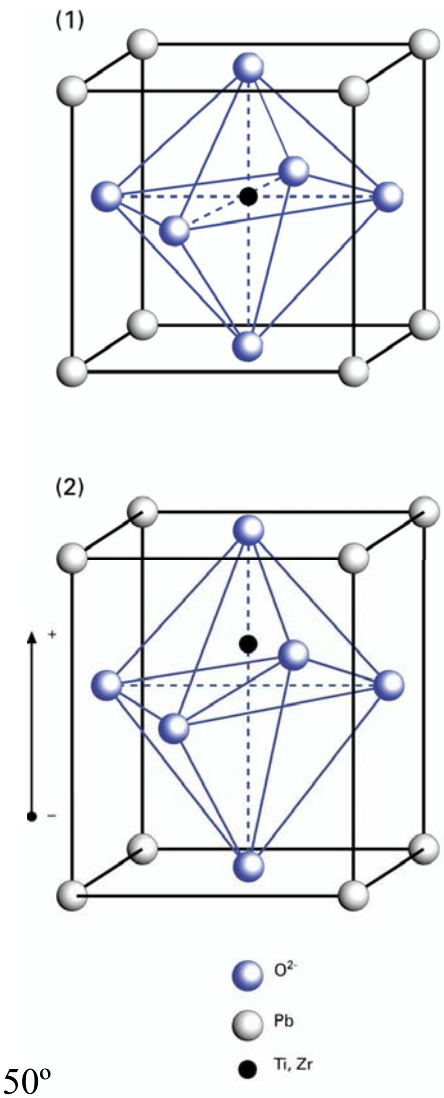
Calibration are necessary.



Unpoled   During poling   After poling

T>CT

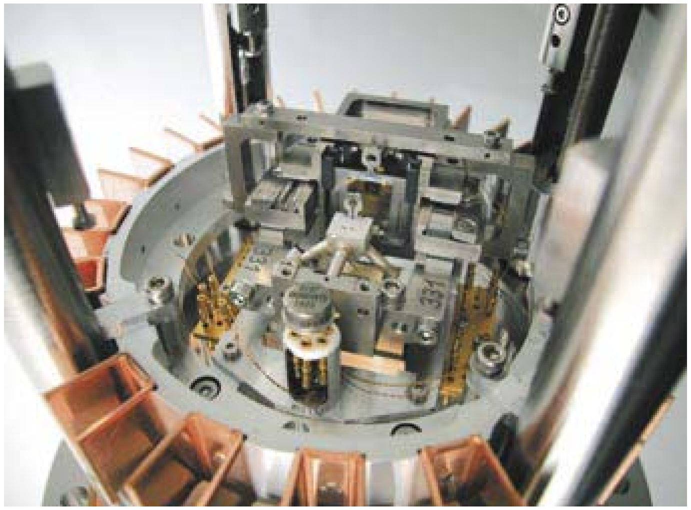
T<CT



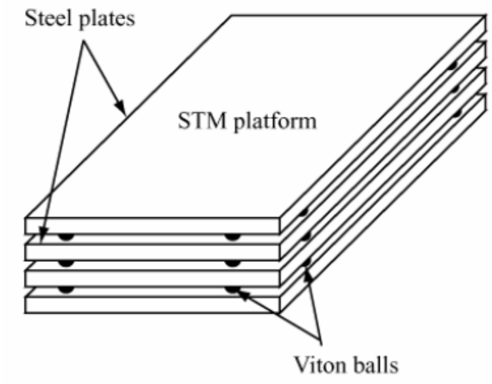
Curie temperature ~ 350º
Operated significantly below CT

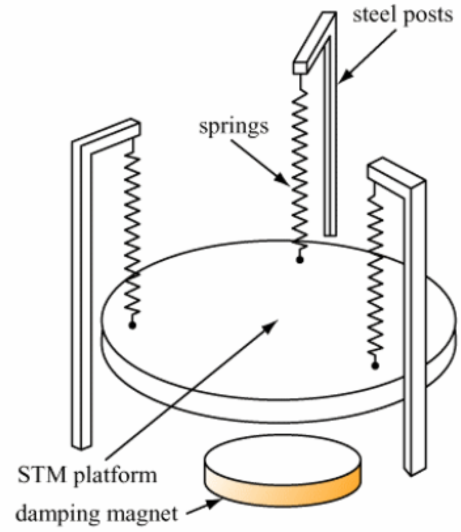
www.physikinstrumente.com/

Vibration isolation is critical to achieve atomic resolution



Combination of spring suspension and eddy current damping brings an optimum damping for STM.

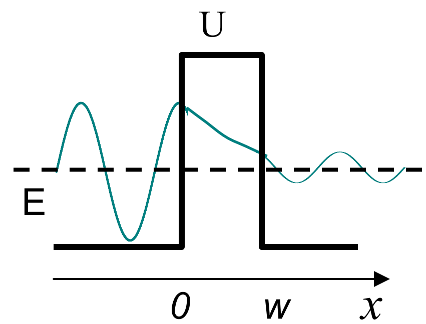




Electron tunneling through a barrier

Wavelike behavior governed by Schrödinger's equation

$$(-\frac{\eta^2}{2m}\frac{\partial^2}{\partial x^2}+U)\psi(x)=E\psi(x)$$



Electrons incident to the barrier

$$\psi_1(x) = Ae^{ikx} + Be^{-ikx} \qquad k=\frac{\sqrt{2mE}}{\eta}$$

Wave number k

Electrons within the barrier

Tunneling constant κ

$$\psi_2(x) = Ce^{kx} + De^{-kx} = \psi_1(0)e^{-kx} \qquad \kappa=\frac{\sqrt{2m(U-E)}}{\eta}$$

Electrons tunneling to the other side of the barrier

$$\psi_3(x) = Fe^{ikx} + Ge^{-ikx} \qquad k=\frac{\sqrt{2mE}}{\eta}$$

Wave number k

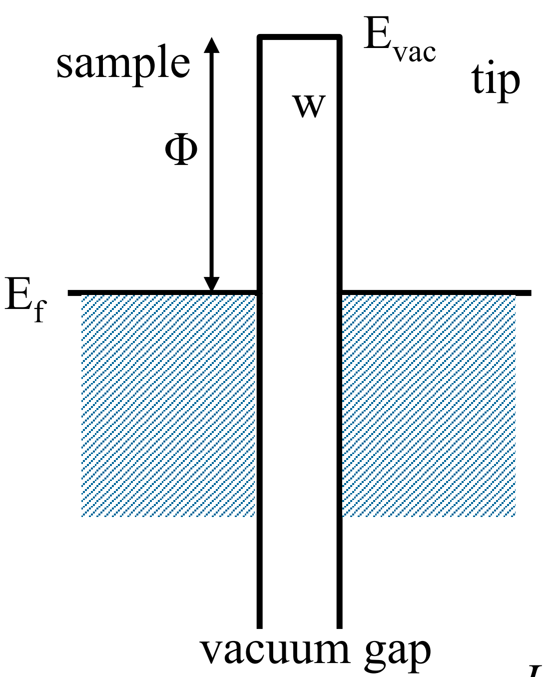
Probability of finding electrons on the other side of the barrier

$$|\psi_1(0)|^2 e^{-2\frac{\sqrt{2m(U-E)}}{\eta^2}w}$$

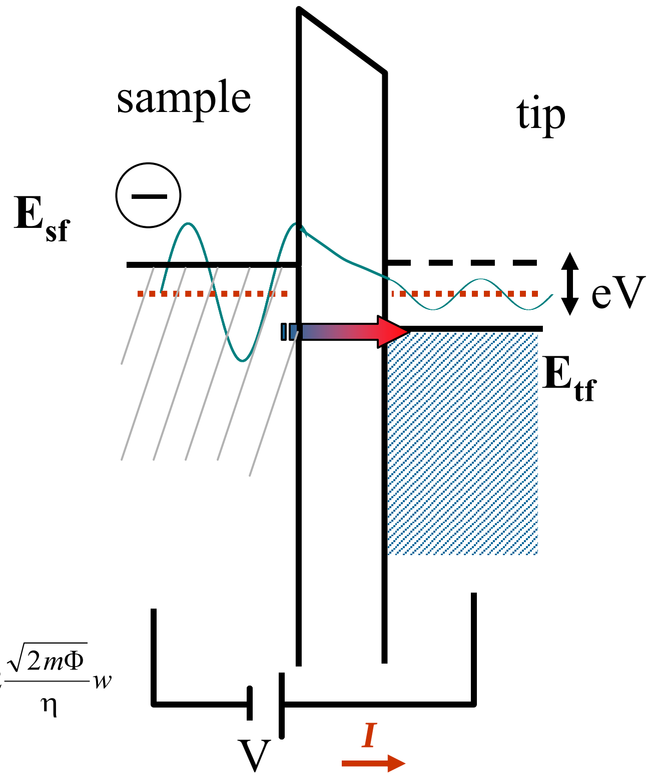
Tunneling current scales exponentially with the barrier width *w*

Tunneling current between biased tip-sample

Zero bias



Negative sample bias
Electrons below E_f tunnel to tip



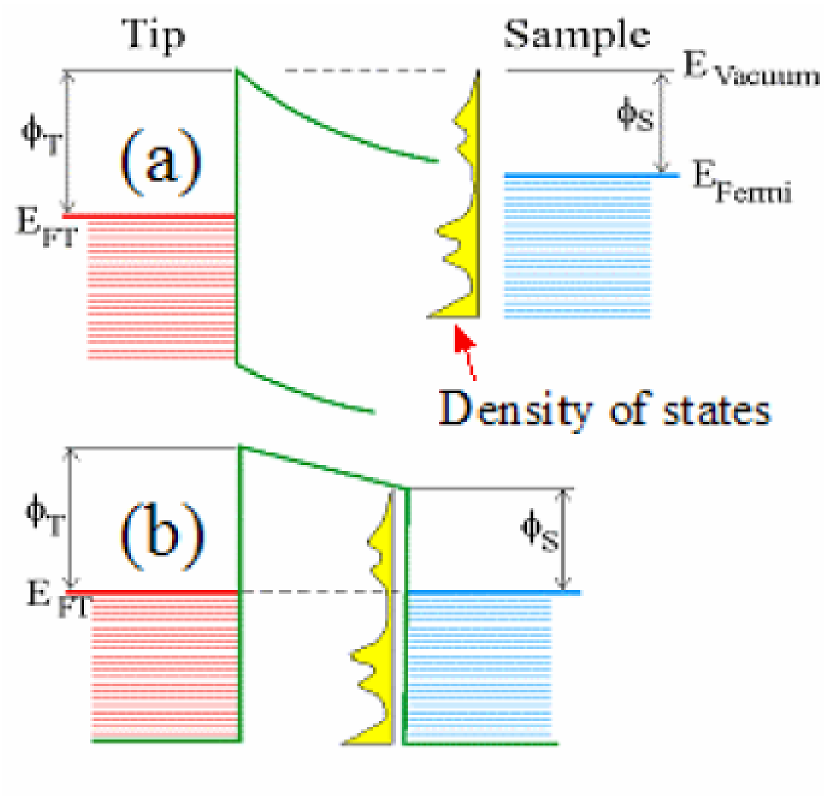
$$I \propto |\psi_1(0)|^2 e^{-2\frac{\sqrt{2m\Phi}}{\hbar}w}$$

Electrons in the sample with energy within E_{sf}-eV to E_{sf} tunnel into the tip above its E_{tf} to E_{tf}+eV. This tunneling of electrons will be measured by the circuit connecting the tip and sample and used as the feedback parameter to maintain a constant current (setpoint).

Local density of states

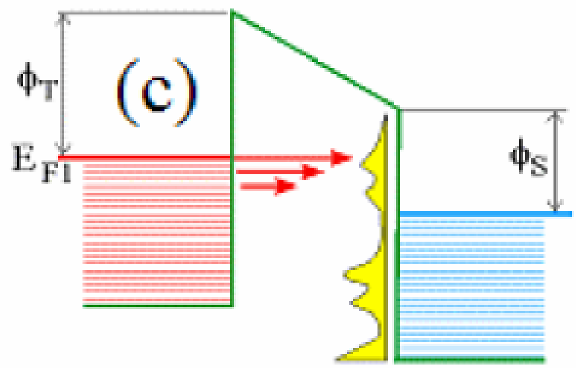
By varying bias, the tunneling current becomes a measure of local density states for electrons

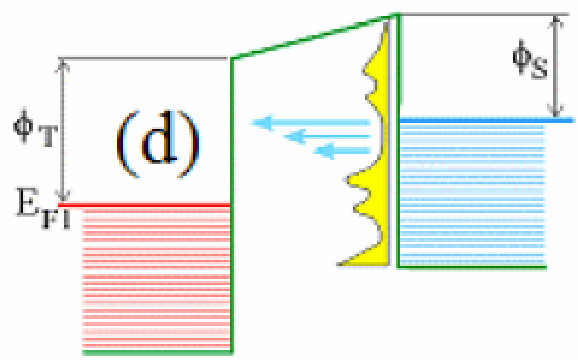
Tip far away



Tip close to sample (within tunneling distance)
but no bias

Sample positively biased:
Electrons from tip tunnel to empty states of sample





Sample negatively biased:
Electrons from occupied states of sample tunnel to tip

Scanning tunneling spectroscopy

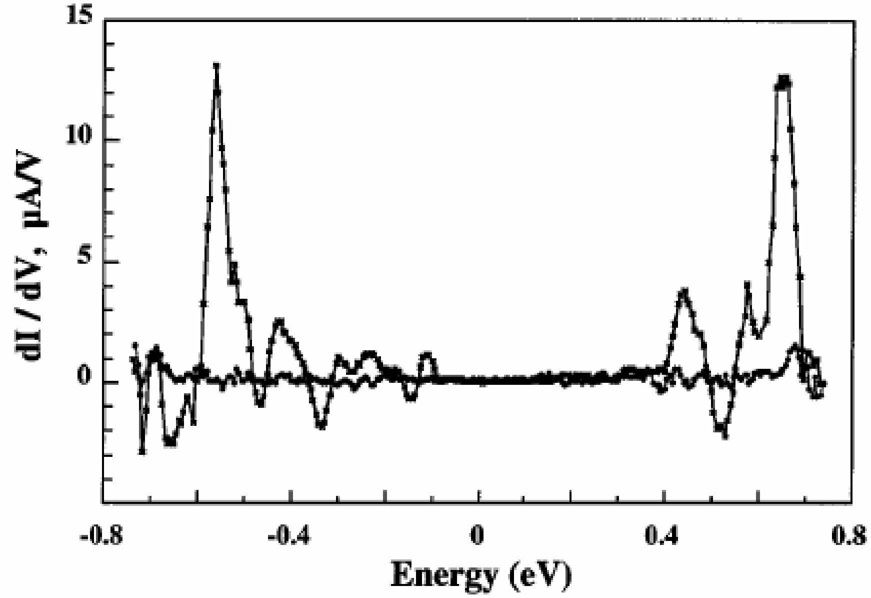
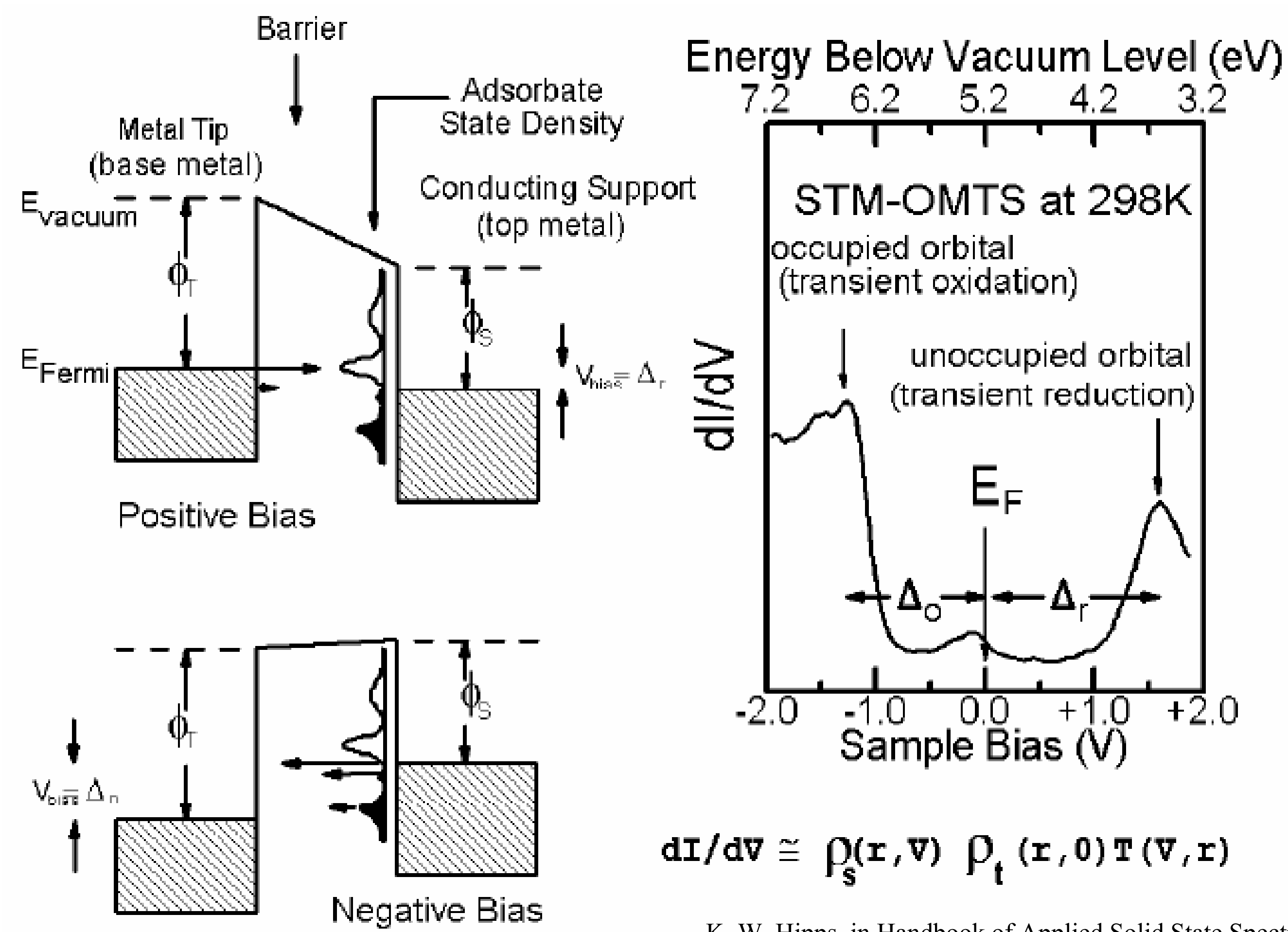


FIG. 1. Differential conductivity of a bare Au surface and a C_{36}-covered Au surface. The difference between the two curves clearly delineates electronic features of the C_{36} molecules, including an 0.8 eV electronic gap. The data were acquired after stabilizing the tip with a 0.75 V sample bias and 0.5 nA tunneling current.

P.G. Collins et.al., Phys. Rev. Lett. 82, 165 (1999)

Scanning tunneling spectroscopy

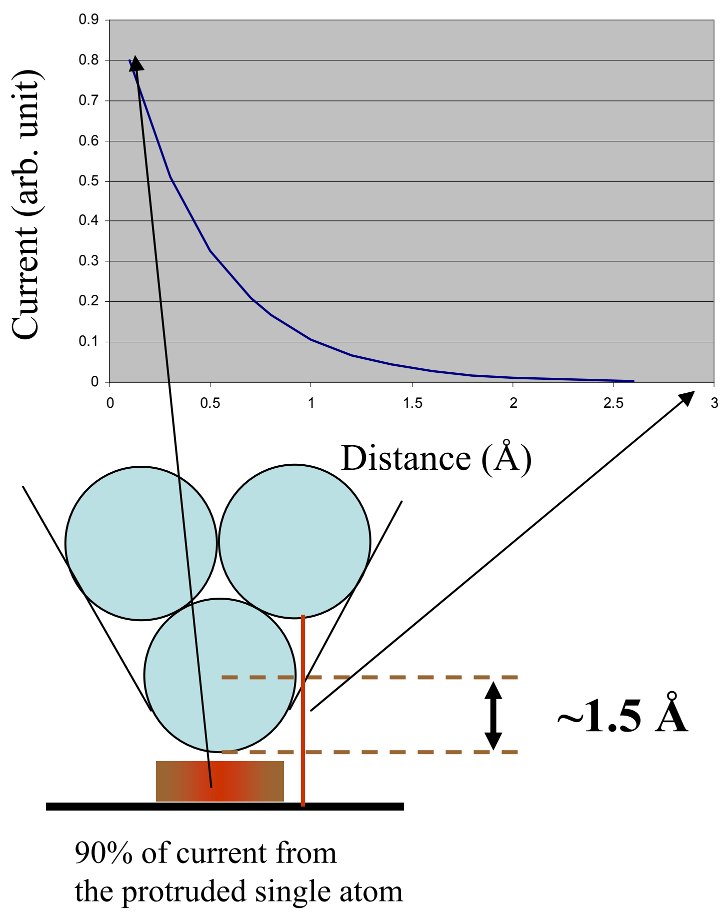


$$dI/dV \cong \rho_s(r,V)\ \rho_t(r,0)\,T(V,r)$$

K. W. Hipps, in Handbook of Applied Solid State Spectroscopy, ed. D. R. Vij, Springer, Berlin, 2006.

Schematic diagram of Orbital Mediated Tunneling Spectroscopy and a representative spectrum obtained from cobalt(II) tetraphenylporphyrin in an STM under UHV conditions at room temperature. The central diagram shows resonant tunneling through unoccupied (upper) and occupied (lower) orbitals in positive and negative bias, respectively. This diagram works equally well for a M-I-M junction (base and top metal labels) and for an STM (tip and substrate labels).

Tunneling current sensitive to tip-sample distance: feedback parameter

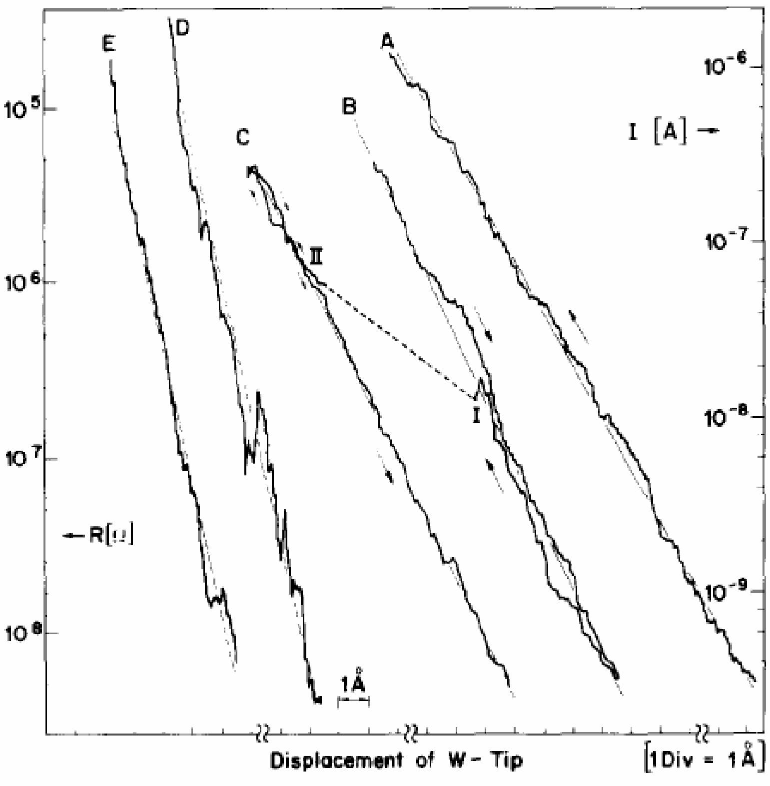


$$I \propto e^{-1.025\sqrt{\Phi}w}$$ Φ in eV and w in Å

With averaged work function ~4 eV, $I \propto e^{-2w}$

When tip-sample distance changes by 1 Å, the tunneling current will change 7.3-10 times. A consequence of this sensitivity is the physics behind STM. Suppose an STM tip is terminated by a single atom (radius ~1.5 Å). The next atom is therefore ~2.6 Å away from the terminus atom, whose contribution is $e^{-5.2}$=0.6% of the current contributed by the terminus atom. This high sensitivity of current over distance makes STM an imaging tool having atomic resolution (of course with good tips and samples).

Tunneling resistance and current measured on Pt



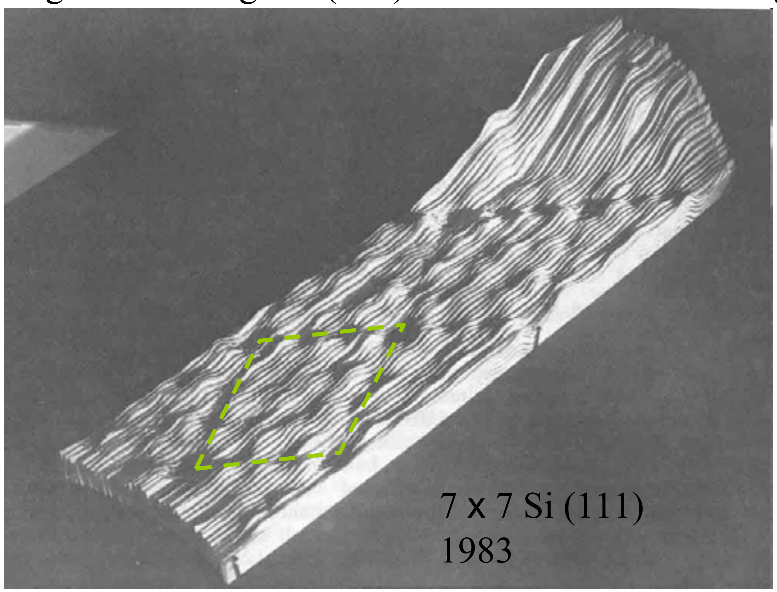
G. Binnig et.al., App. Phys. Lett. 40 , 178-180 (1982)

$$I = \frac{V}{R} e^{-2\frac{\sqrt{2m\Phi}}{\eta} w}$$

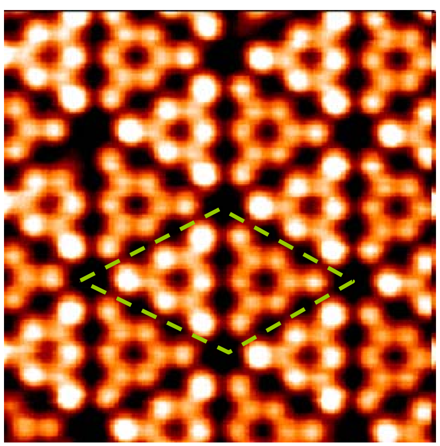
FIG. 2. Tunnel resistance and current vs displacement of Pt plate for different surface conditions as described in the text. The displacement origin is arbitrary for each curve (except for curves B and C with the same origin). The sweep rate was approximately 1 Å/s. Work functions $\phi = 0.6$ eV and 0.7 eV are derived from curves A, B, and C, respectively. The instability which occurred while scanning B and resulted in a jump from point I to II is attributed to the release of thermal stress in the unit. After this, the tunnel unit remained stable within 0.2 Å as shown by curve C. After repeated cleaning and in slightly better vacuum, the steepness of curves D and E resulted in $\phi = 3.2$ eV.

STM accepted as a tool being capable of probing atoms in real space

Being able to image Si (111) 7x7 → STM breakthrough



Phys. Rev. Lett. 50, 120-123 (1983)



Pys. Rev. B **70**, 073312 (2004)

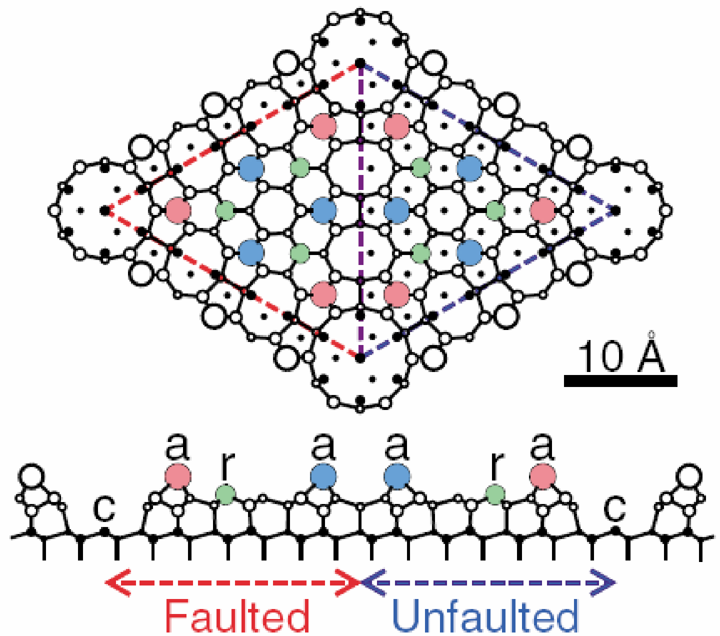
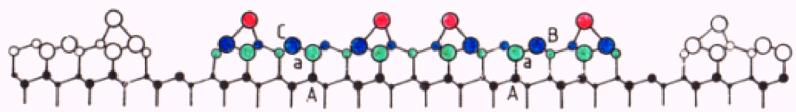


FIG. 1 (color). Si(111)-(7 × 7) structure [11]: Top view (top) and cross section (bottom). Atoms closest to the viewer are drawn largest. Twelve adatoms ("a"), among which are six corner and six center adatoms, constitute the topmost atomic layer. Rest atoms ("r") are located 1 Å below in the second layer. Corner-hole atoms ("c"), 4.4 Å below the adatom layer, mark the corners of the unit cell.

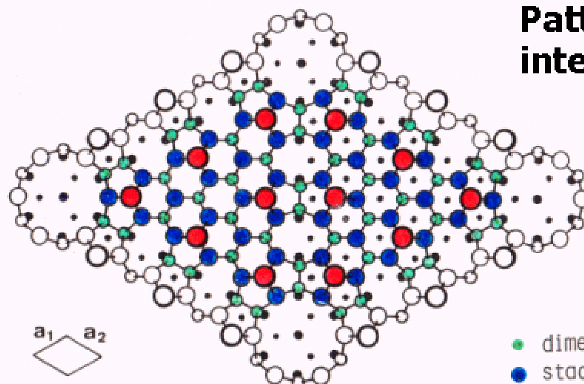
Phys. Rev. Lett. 90, 116101 (2004)

Standard test sample for atomic resolution of STM and AFM

DAS-model of Si(111)7×7



Model was derived by Patterson analysis of TED intensities in 1983



- dimer layer atoms
- stacking-fault layer atoms
- adatoms

two triangular subcells in the 7x7 unit cell

the 7x7 reconstructed layer consists of

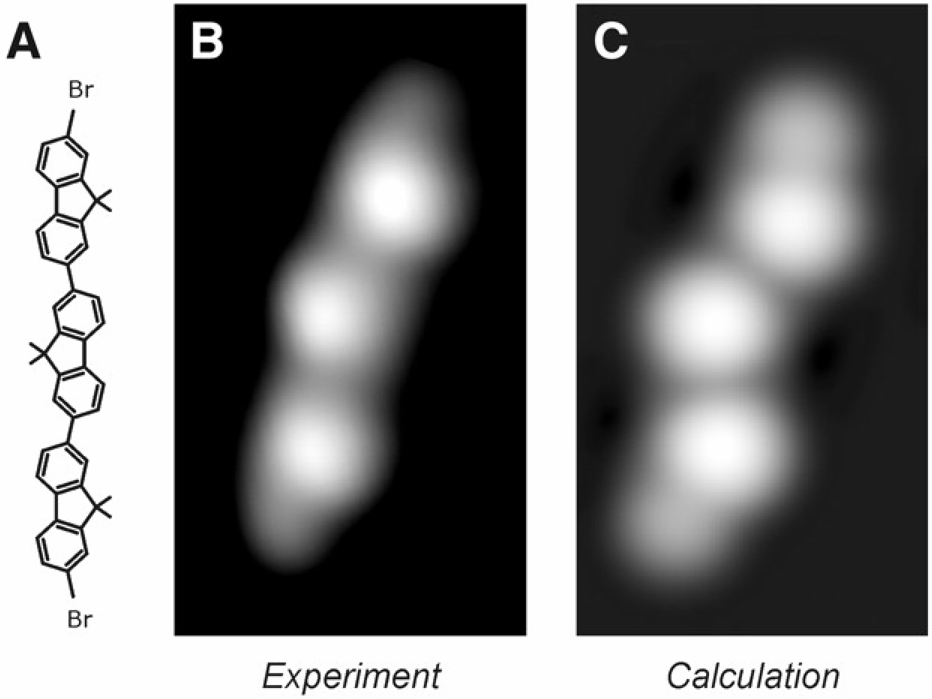
a dimer layer (9 dimers on the sides of the subcells)
a stacking-fault layer (faulted sequence in the left subcell)
twelve adatoms on the stacking-fault layer

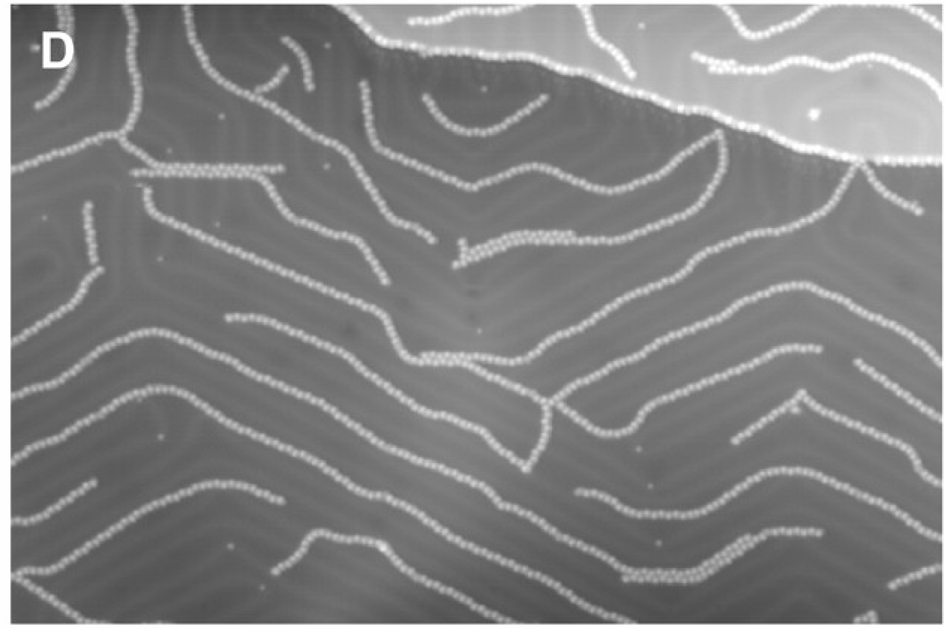
K.Takayanagi,Y.Tanishiro, S.Takahashi, M.Takahashi; Surface Sci. (1985)

STM on polymerization of dibromoterfluorene on Au(111)

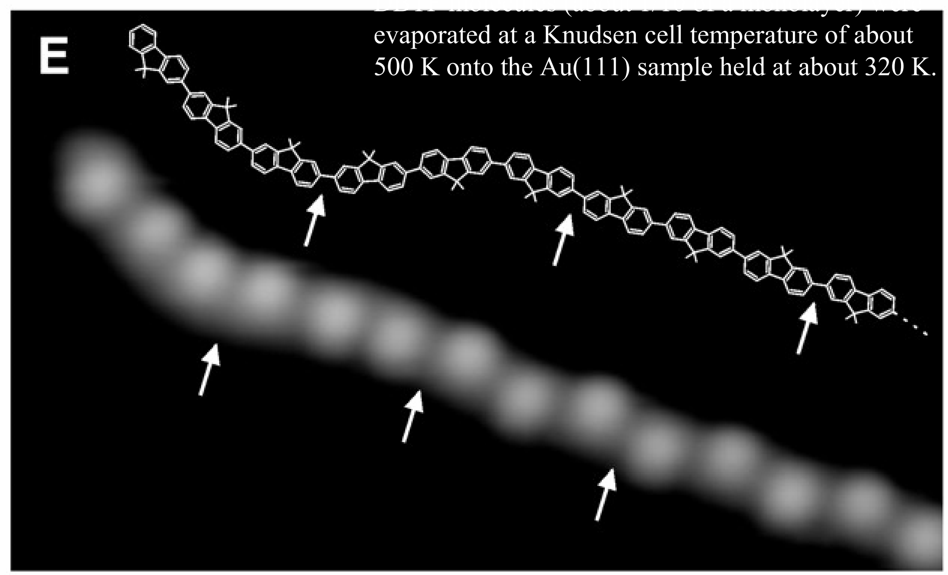
L. Lafferentz et al., *Science* 27 February 2009:

Vol. 323. no. 5918, pp. 1193 -1197





On-surface polymerization of DBTF to conjugated molecular chains. (**A**) Chemical structure of DBTF molecules with experimental (**B**) and calculated (**C**) STM images (2.5 by 4.5 nm) of intact molecules, with bright protrusions associated with the lateral dimethyl groups. (**D**) Overview STM image (80 by 120 nm, 1 V, and 0.1 nA) after on-surface polymerization. The produced long covalently bound molecular chains, i.e., polyfluorene, follow the herringbone reconstruction of the substrate. (**E**) STM image (5.9 by 3.6 nm) of a single polyfluorene chain end with its chemical structure superimposed (using a different scaling). The arrows indicate three identical (in the STM image and the chemical structure), newly formed covalent bonds between individual building blocks.



Metal nanowire

Appl. Phys. Lett. 83, No. 22, 1 Dec. 2003.

When Pt atoms adsorb onto Ge(001) surface, they intermix with the substrate and locally lift the reconstruction, while submerging into the crystal. As a result of high temperature annealing of the Ge substrate at ~1000 K they partly re-appear at the surface, forming extremely well ordered nanowire arrays by self-organization. These wires are stable at room temperature.

Scanning Tunneling Spectroscopy / Microscopy, shows they are metallic, kinkless and defect free. They are only 0.4 nm thin with a spacing of 1.6 nm in-between and have aspect ratios up to 1000. Besides patches of nanowires, individual ones with varying lengths are also common on the surface.

To achieve atomic resolution, an STM probe has to be effectively terminated by a single atom

Tungsten tip: electrochemistry (anodic oxidation) in NaOH

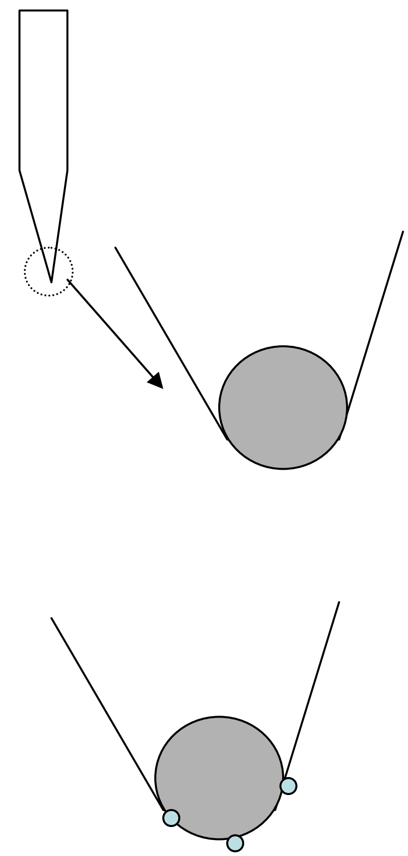
A tungsten wire positively biased (relative to a circle of stainless steel wire) is thinned in NaOH by anodic oxidation and it eventually breaks by the weight of the lower part of the wire.

Annealing treatments are necessary to remove oxide left on the probe.

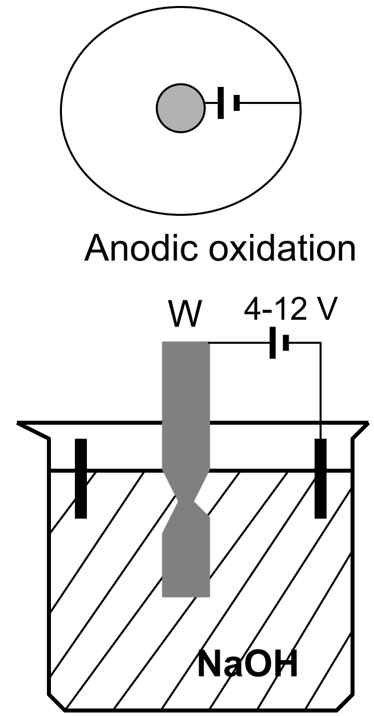
Still the overall probe size is tens of nanometers.

Scanning on surface, applying high voltage to the tip → in the hope that a single atom protrudes over the tip apex.

Keep scanning and perhaps purposely crash the tip to sample surface…



Single atom terminating tip



STM → AFM

It is realized in the early days of STM that the tip impose forces on the sample when they are close to each other. This, plus the need to scan insulating samples, drove the effort in the invention of atomic force microscopy in 1985.

VOLUME 56, NUMBER 9 PHYSICAL REVIEW LETTERS 3 MARCH 1986

Atomic Force Microscope

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Edward L. Ginzton Laboratory, Stanford University, Stanford, California 94305

and

Ch. Gerber[c]
IBM San Jose Research Laboratory, San Jose, California 95193

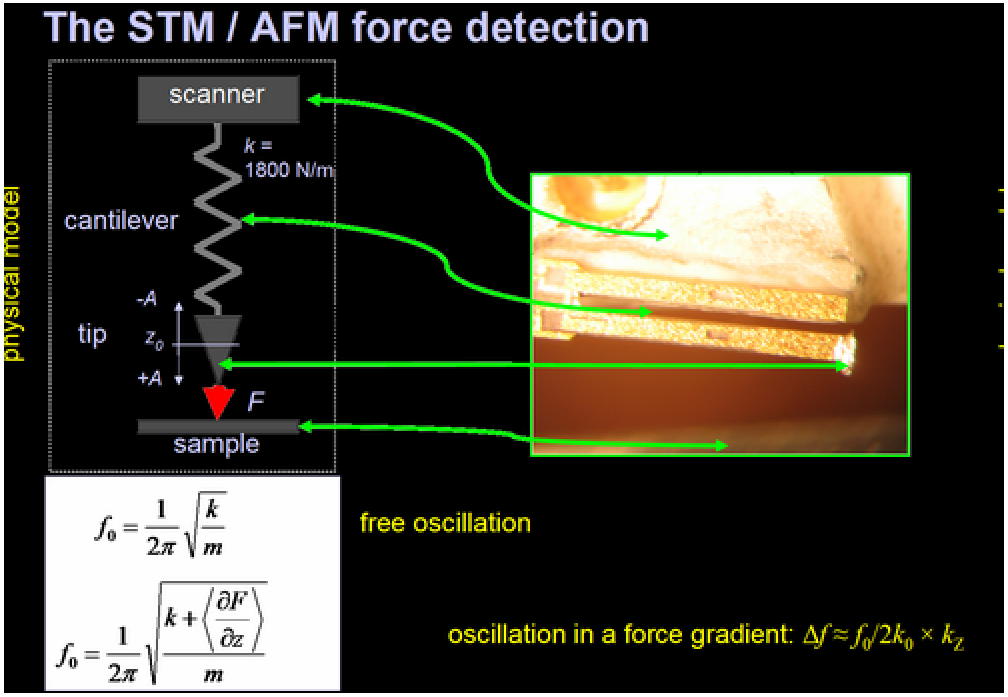
(Received 5 December 1985)

The scanning tunneling microscope is proposed as a method to measure forces as small as 10^{-18} N. As one application for this concept, we introduce a new type of microscope capable of investigating surfaces of insulators on an atomic scale. The atomic force microscope is a combination of the principles of the scanning tunneling microscope and the stylus profilometer. It incorporates a probe that does not damage the surface. Our preliminary results *in air* demonstrate a lateral resolution of 30 Å and a vertical resolution less than 1 Å.

PACS numbers: 68.35.Gy

Tunneling current & forces exerted on the probe: approach

Shown here is the use of a tuning fork to measure both tunneling current and force. The tunneling current is measured as in STM and the force is measured by way of measuring resonance frequency change (details to come…). A very small oscillation amplitude must be used to avoid disturbing the tip-sample interaction (0.25 Å).



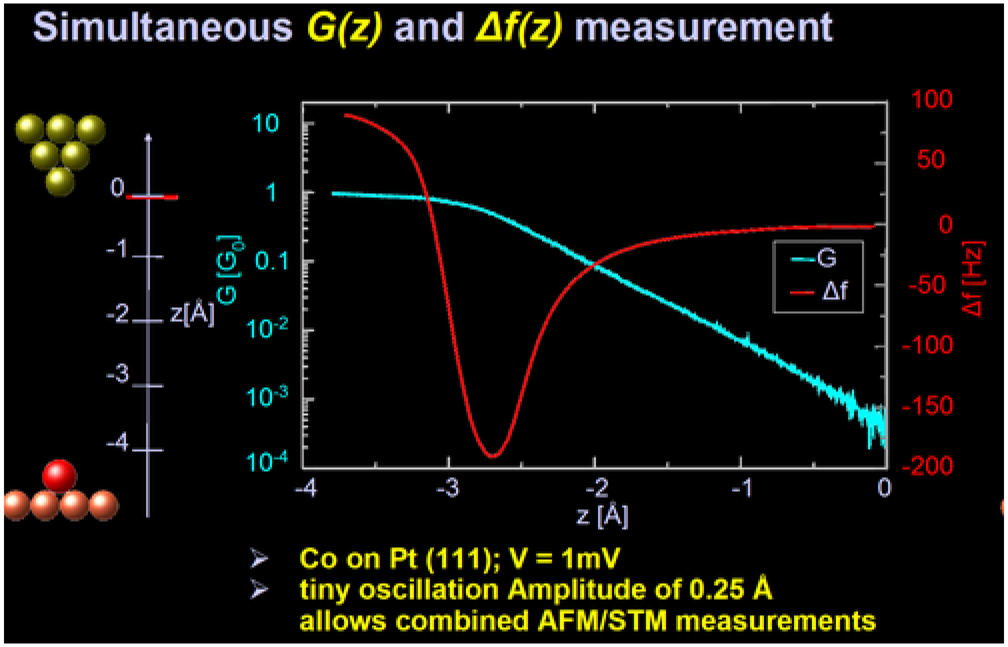
$$f_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

$$f_0 = \frac{1}{2\pi}\sqrt{\frac{k + \left\langle \frac{\partial F}{\partial z} \right\rangle}{m}}$$

http://www.almaden.ibm.com/st/nanoscale_st/nano_science/STMAFM/design/

Tunneling current & forces exerted on the probe: results

STM operates in the attractive force region (tip-sample)

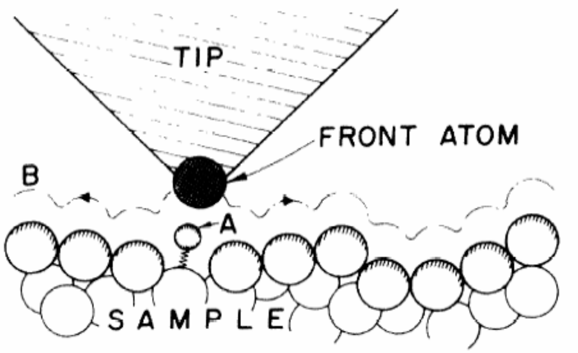


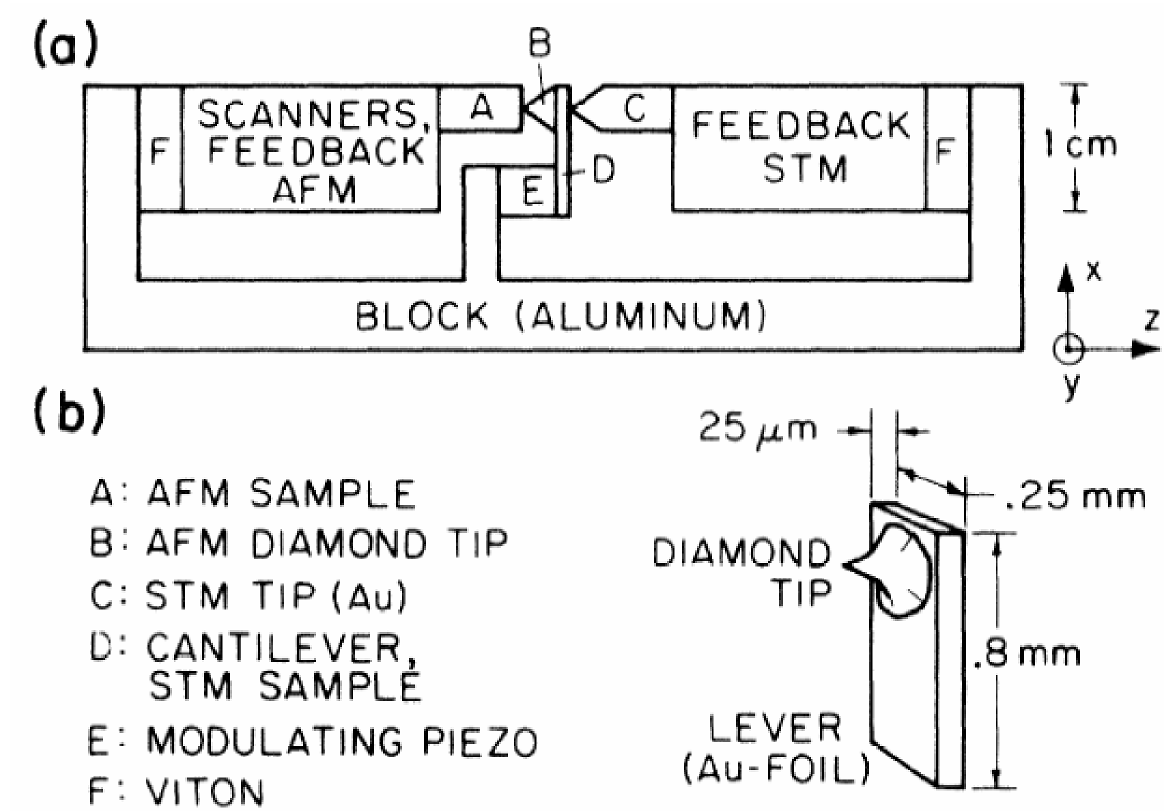
Maximum attractive force ~2 nN

http://www.almaden.ibm.com/st/nanoscale_st/nano_science/STMAFM/design/

The first AFM

The cantilever is a metal foil and the tip is a piece of diamond glued on the foil. Naturally, an STM tip was used to detect the deflection of the cantilever. The deflection detection scheme was soon replaced by optical lever detection.





Atomic force microscopy: force used as the feed back parameter

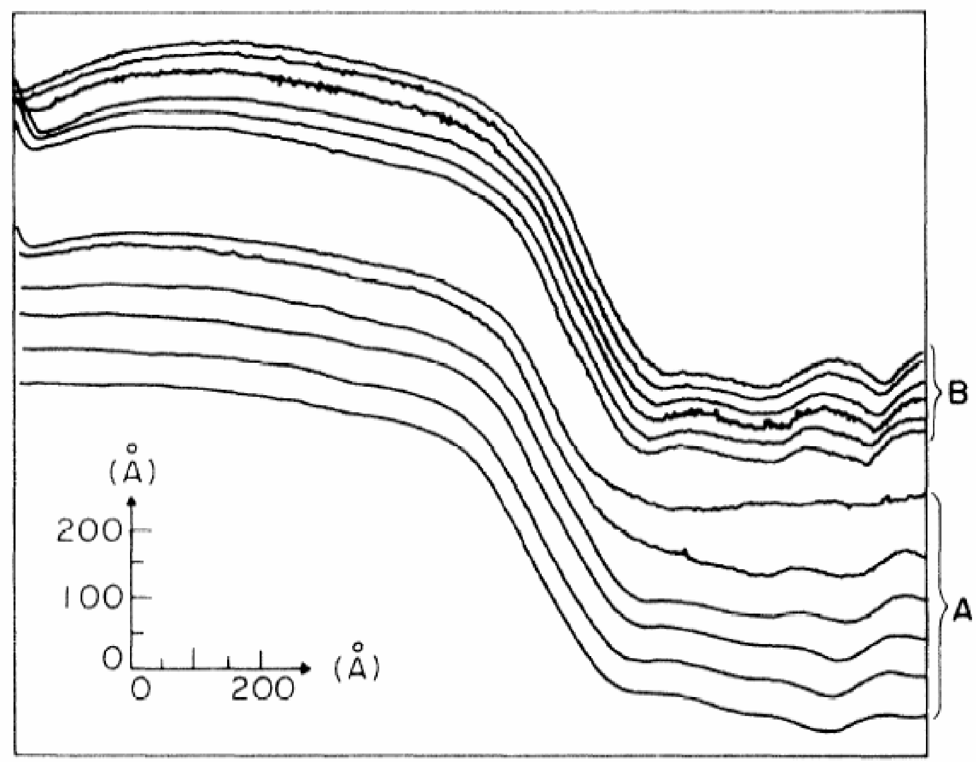


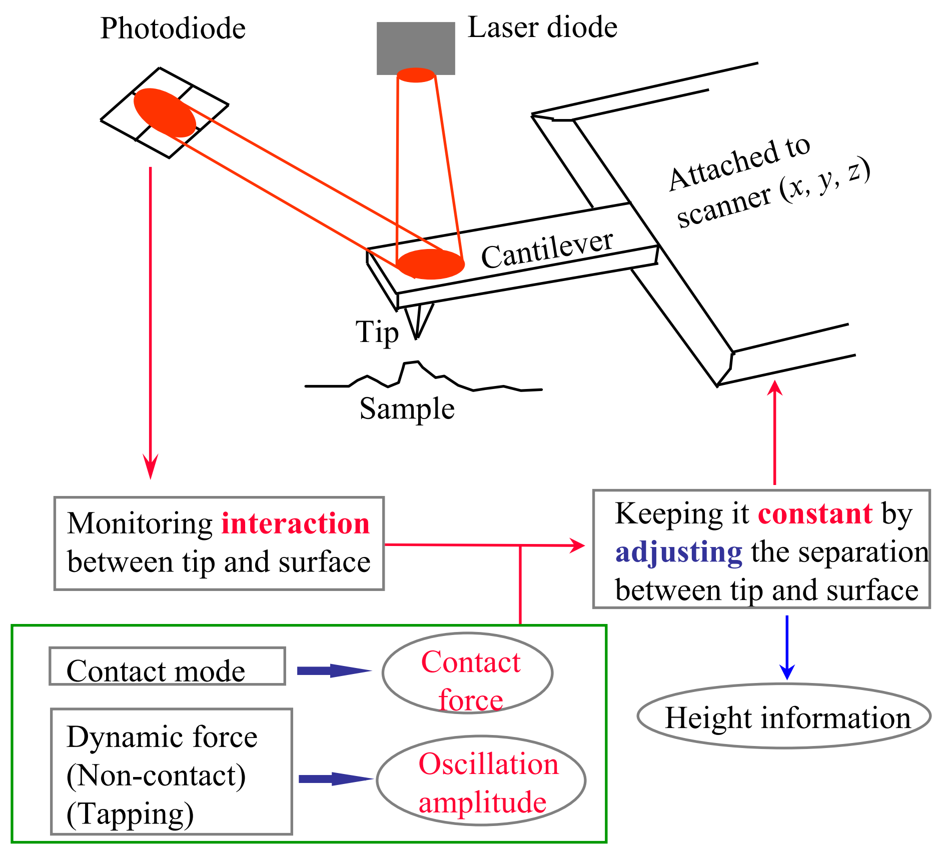
FIG. 4. The AFM traces for another area of the ceramic sample. The curves grouped under *A* were recorded with additional low-pass filtering. For this set the stabilizing force, f_0, was reduced by thermal drifts as we moved from the lowest to the highest traces of set *A*. The force f_0 is near 10^{-8} N for the highest curve. We note that the structure vanishes on the traces when the sample-to-tip force is reduced below this level. The force f_0 was reset to a higher value near 5×10^{-8} N for the traces marked *B*.

How AFM works...

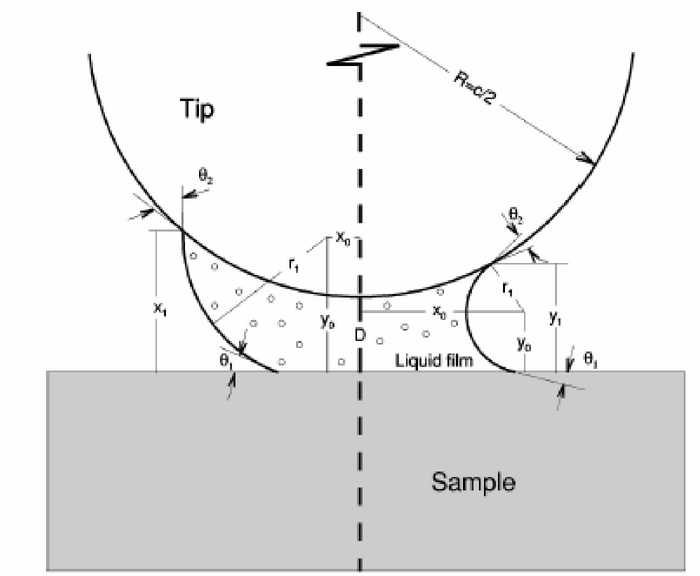
AFM images surface features of a sample by scanning a sharp tip attached to a cantilever. The basic principle for AFM is schematically shown on the right. The key point in AFM is the measurement of the interaction between the tip and surface features, which is sensed through the deflection of the cantilever using a laser beam. There are two operation modes for AFM:

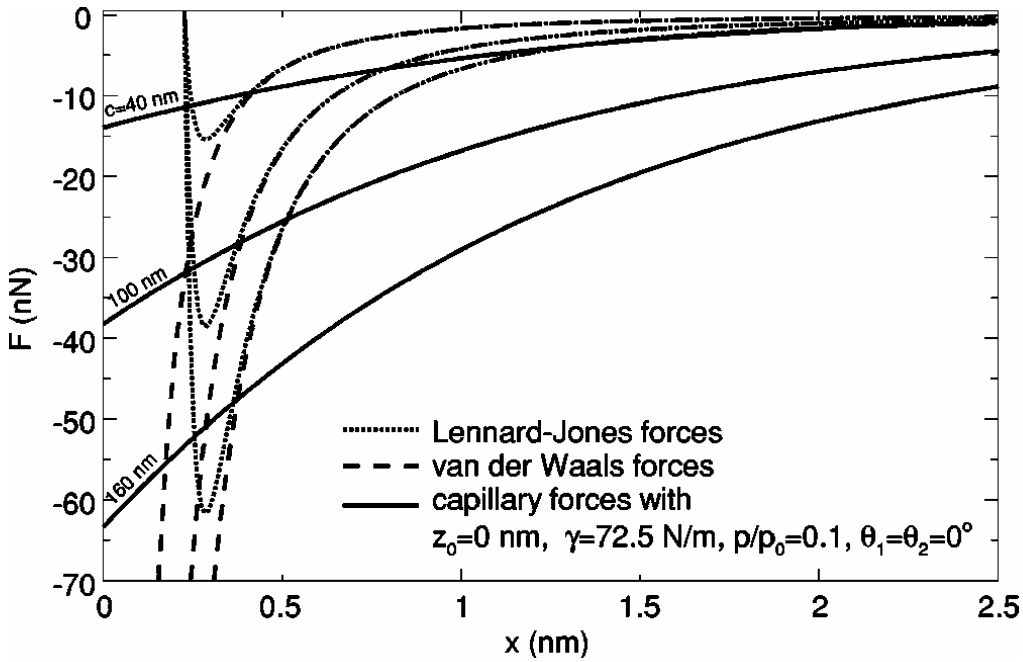
1) Contact mode AFM---the tip is mechanically contacted with sample surface at an applied force. Lateral force detection in this mode can be used to probe local surface properties.

2) Dynamic force (tapping, non-contact) mode AFM---It is the oscillation amplitude (or phase) that is used as the feedback parameter to keep the tip-sample interaction constant. Surface can be imaged without (or with less) surface degradation due to the elimination of lateral force in this mode.



Contact mode AFM: tip contacts with sample





T. Stifter et. al., Phys. Rev. B 62 (2000) 13667.

Attractive forces: Capillary and van der Waals forces

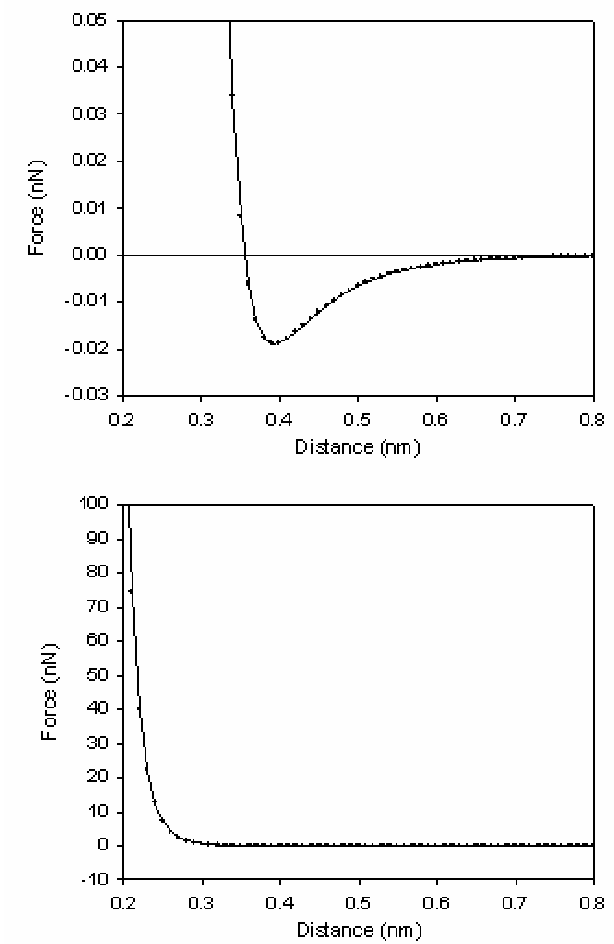
Repulsive forces: Overlapping of electron clouds (Coulomb interaction)

Interaction forces between two atoms

What is behind AFM?

One can understand the interaction forces between the tip and the surface in AFM through the equation for Lennard-Jones potential $w(r) = -A/r^6 + B/r^{12}$, which deals with the interaction between two atoms. The force is thus $\mathbf{F = -dw(r)/dr = -6A/r^7 + 12B/r^{13}}$. According to the text, A and B are known to be $10^{-77}\,Jm^6$ and $10^{-134}\,Jm^{12}$, respectively. We show the calculated results here in two regions: 1) around 0.4 nm a small attractive force is seen and 2) when the separation between the two atoms gets close to 0.2 nm the repulsive force increases steeply. Note the difference in force scale in the two figures.

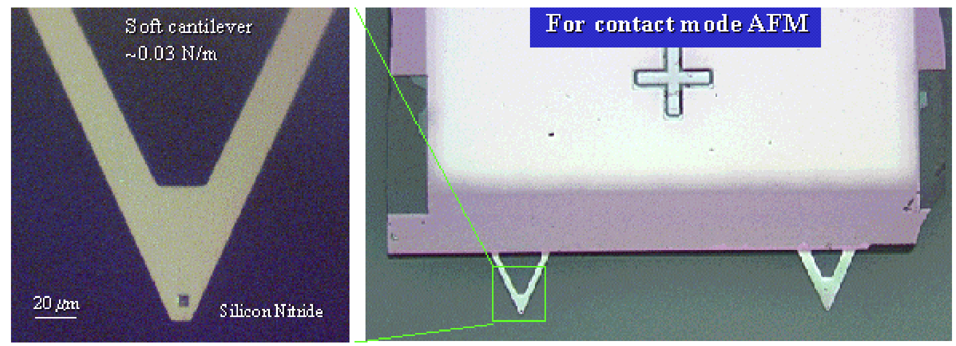
In practice, the AFM probe tip and the sample surface will have attractive force much larger than what is shown here. Also, other longer-range forces could occur. This is because the size of the tip is nominally ~10 nm nowadays and, in air, there are water films covering everything.

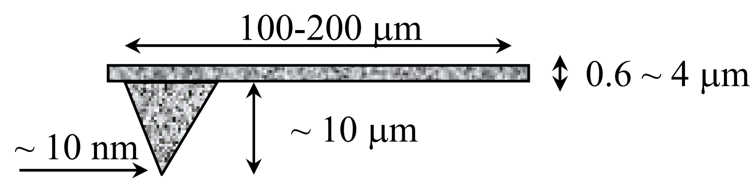


AFM cantilevers

A tip-cantilever sensor system

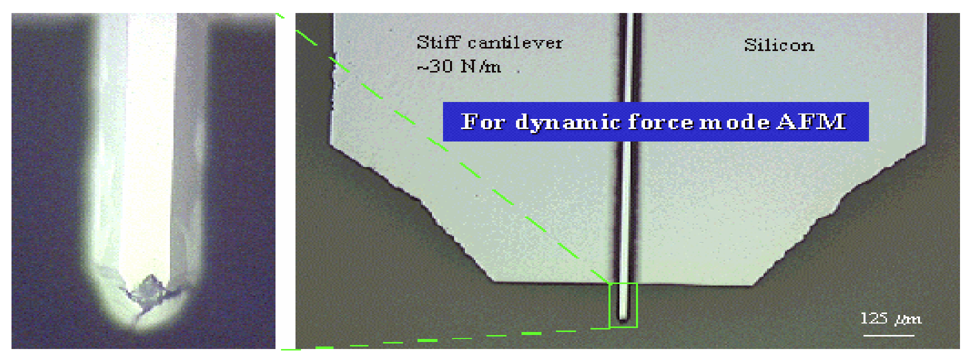
The interaction between the sharp tip and the sample surface is detected by the deflection (contact mode AFM) or the oscillating amplitude (dynamic force mode AFM) of the cantilever. A photodiode is used to detect the movement of the cantilever from a laser beam irradiated on the cantilever.





Two types of cantilever

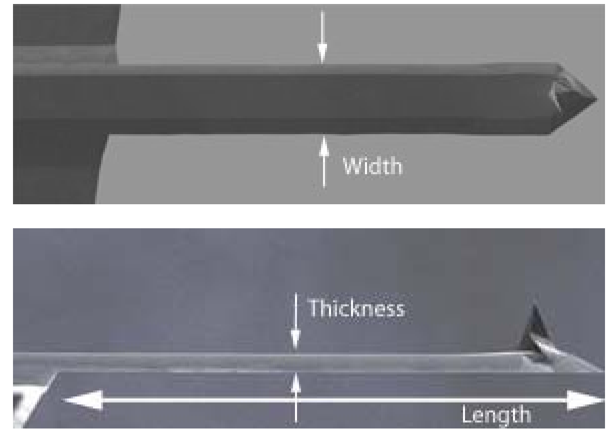
Soft cantilever (spring constant < 1 N/m) and stiff cantilever (spring constant > 5 N/m) are used in contact and dynamic force AFM, respectively. The geometry of cantilever is schematically shown (width for both types is 20-30 μm) between the two optical images for the two types of cantilever.



Cantilever → detection of force exerted on tip

Spring constant

$$k = \frac{Ewt^3}{4\lambda^3}$$



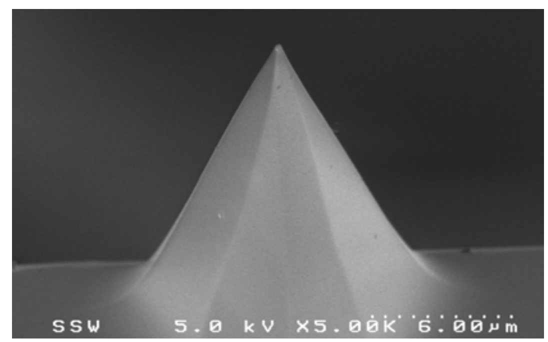
www.nanoscience.com/products/AFM_cantilevers.html

Force exerted

$$F = -kz$$

Optical detection scheme: Laser and position sensitive photodetector

Sensitivity: photodetector output → deflection of cantilever (mV/nm)



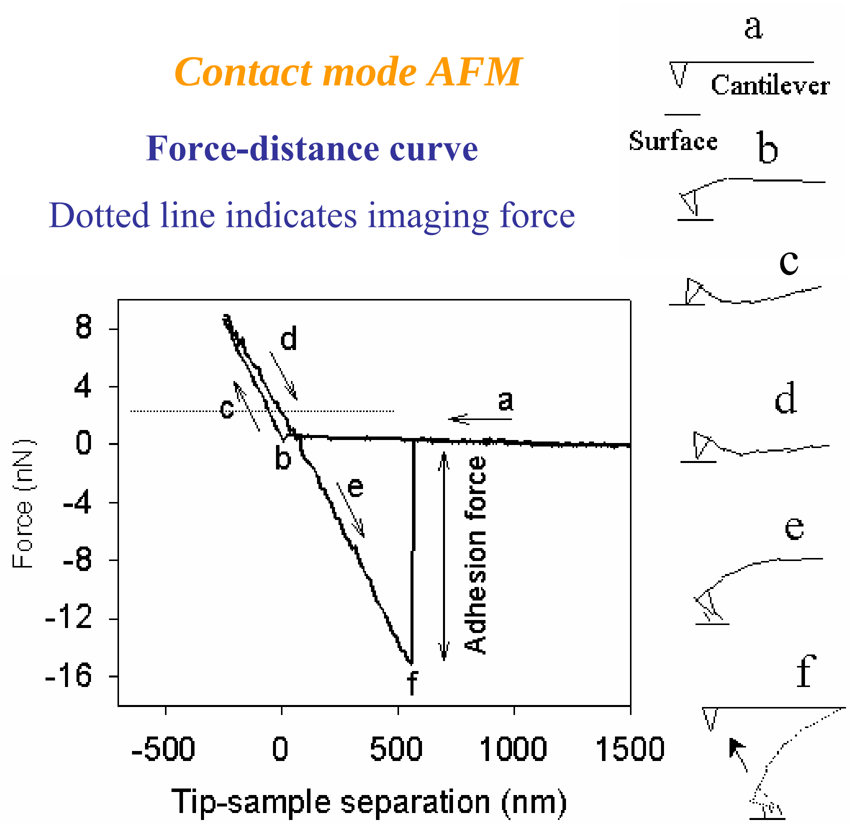
Imaging mechanism of contact AFM

A soft cantilever (<1 N/m) is usually used. The tip is in contact with the sample surface. Imaging force can be selected at the repulsive force region at a couple of nanonewton (nN). Morphology is obtained through scanning the surface at a constant force.

Contact mode AFM

Force-distance curve

Dotted line indicates imaging force

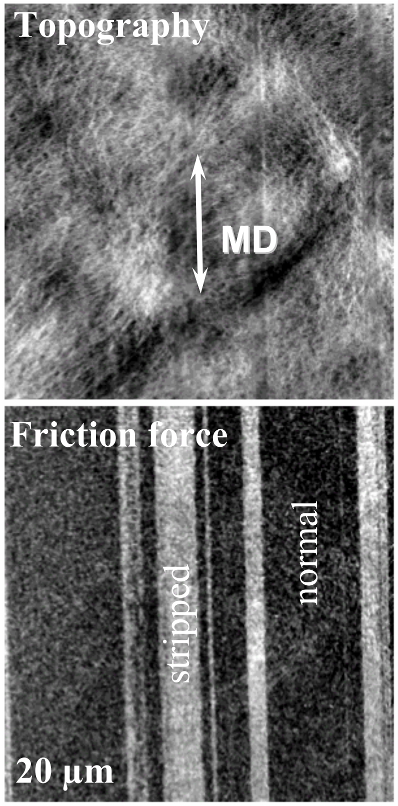


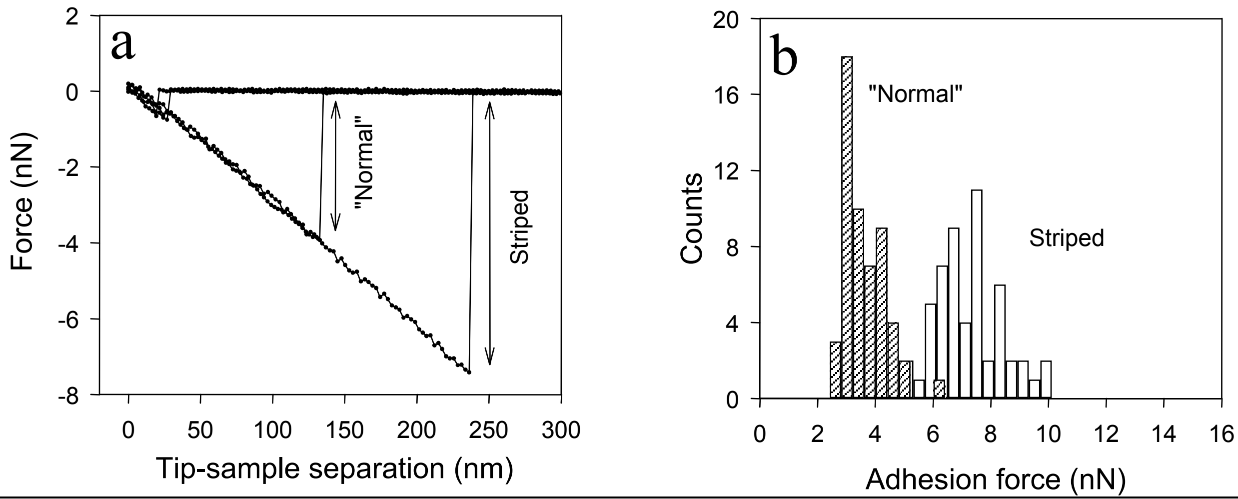
A force-distance curve shown here was obtained on a UV/ozone modified polymer surface with a cantilever having spring constant of 0.03 N/m. Interaction between the tip and the surface at different separation is indicated by a-f. Adhesion force between the tip and sample due to their contact can be measured as shown in the force-distance curve. Because the tip is in contact with the sample surface, damage on soft sample during scanning could happen. This can be largely avoided in the dynamic force mode AFM.

Adhesion force from force-distance curve

Force-distance curves are obtained by extending the tip to the surface to make a contact between the tip and the sample surface followed by retracting the tip from the surface. The original point for the distance may be defined as the mechanical contact between the tip and surface in the extending cycle. Extending the tip beyond that point will result in load forces applied to the surface. The slope of t his load force is a measure of the Young's modulus of the surface, possibly mixed with the spring constant of the cantilever. As a result, a cantilever whose spring constant is comparable with the surface stiffness should be used to measure the elasticity information.

In the retracting cycle, because of the adhesion properties between the tip and surface, the tip will not depart from the surface until the force used to pull the tip from the surface exceeds the adhesion force between them. This pull-off force can be considered as a measure of the adhesion force between the tip and surface. Adhesion force can be related to surface energies of the tip and sample surfaces, as well as their interfacial energy. Shown here is an example of measuring adhesion force at different regions on a polymer film. The striped areas have higher adhesion as well as friction forces than the normal surface.



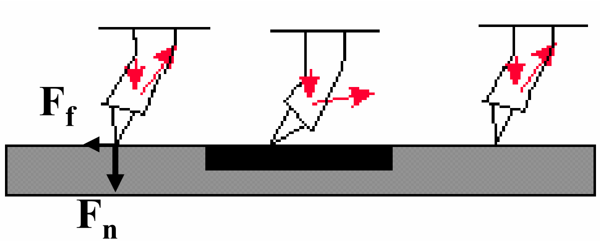


Friction force detection

During the scanning of the tip over an surface, the torsional movement of the cantilever can be recorded, which results in lateral (friction) force imaging. This imaging technique provides information on friction force or chemical force distribution on the surface. With some modifications on AFM, resistance distribution and mechanical properties can be obtained simultaneously with the morphology.

Torsional movement of cantilever: Friction microscopy

$$F_f=\mu F_n$$



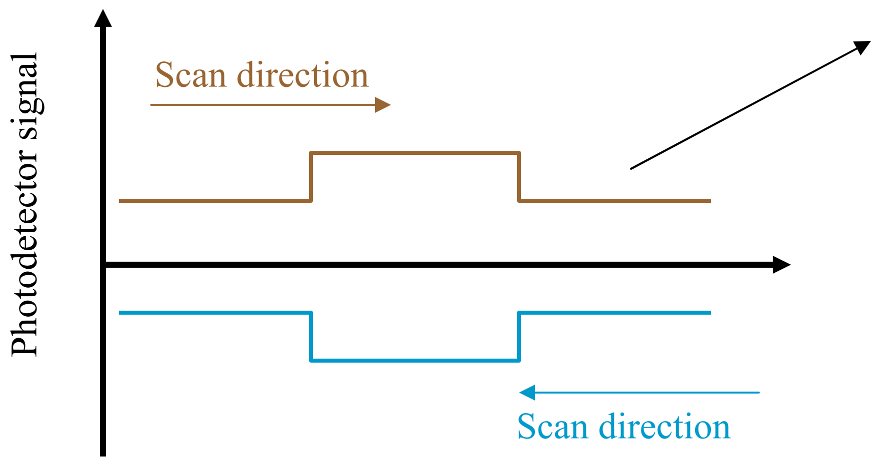
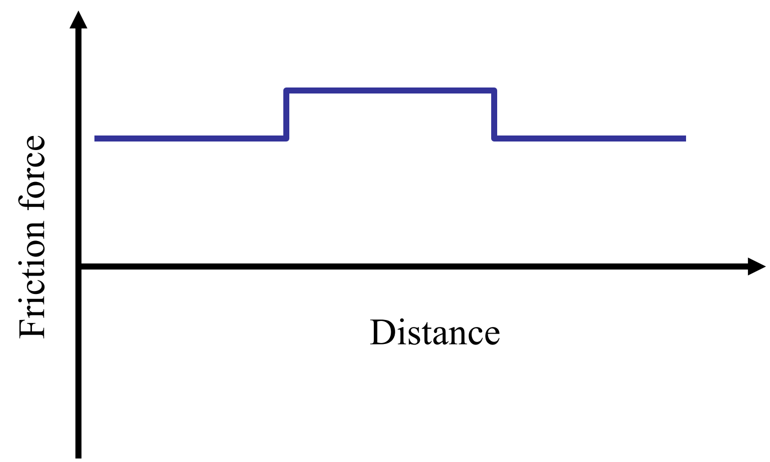


Image with a contrast related to friction force

The difference of the phtodetector signal corresponding to the two direction scans is a measure of friction force



Quantitative measurement of friction force requires converting factors

$$F_f= \Delta V \times S \times k_t$$

ΔV: Torsional signal-difference (V)
S: Cantilever torsional sensitivity (m/V)
kt: Cantilever torsional spring constant (N/m)

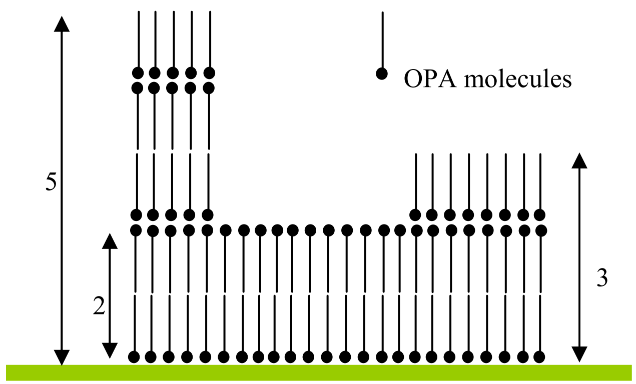
Amphiphilicity of a molecule revealed by friction force imaging

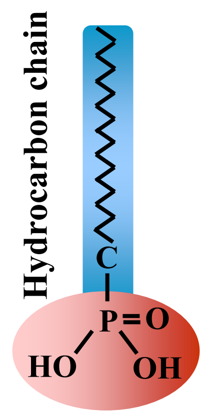
<u>Imaged by a Si tip, which is terminated by OH → friction force on OPA headgroup is greater than on OPA tail.</u>

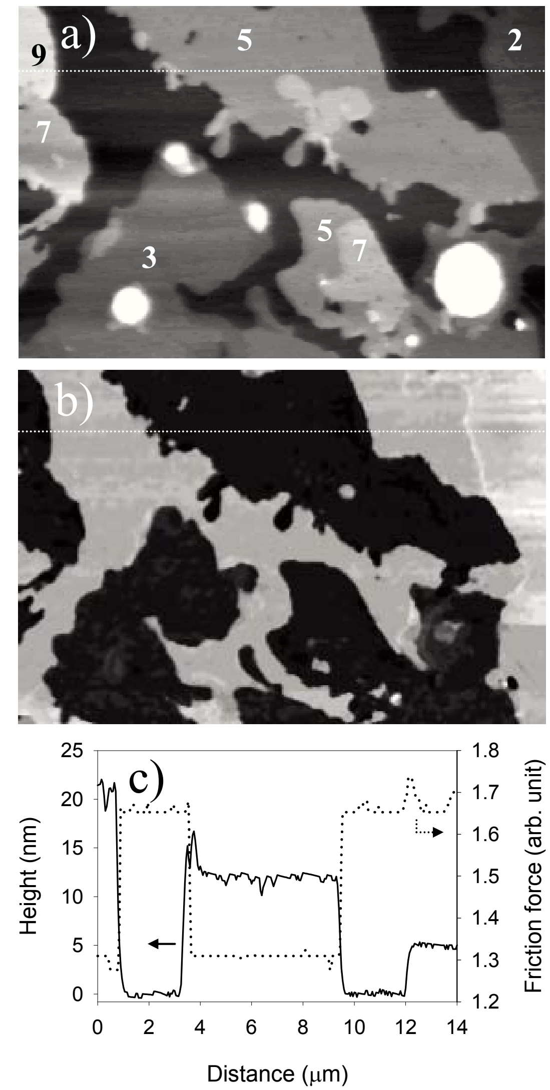
Amphiphilicity of molecular layers

Excessive amount of OPA molecules were observed to form bilayer and odd-numbered multilayers when their solution was placed on a Si substrate followed by a heat treatment at 50-60 ☜C.

n-Octadecylphosphonic acid
$CH_3(CH_2)_{17}P(O)(OH)_2$

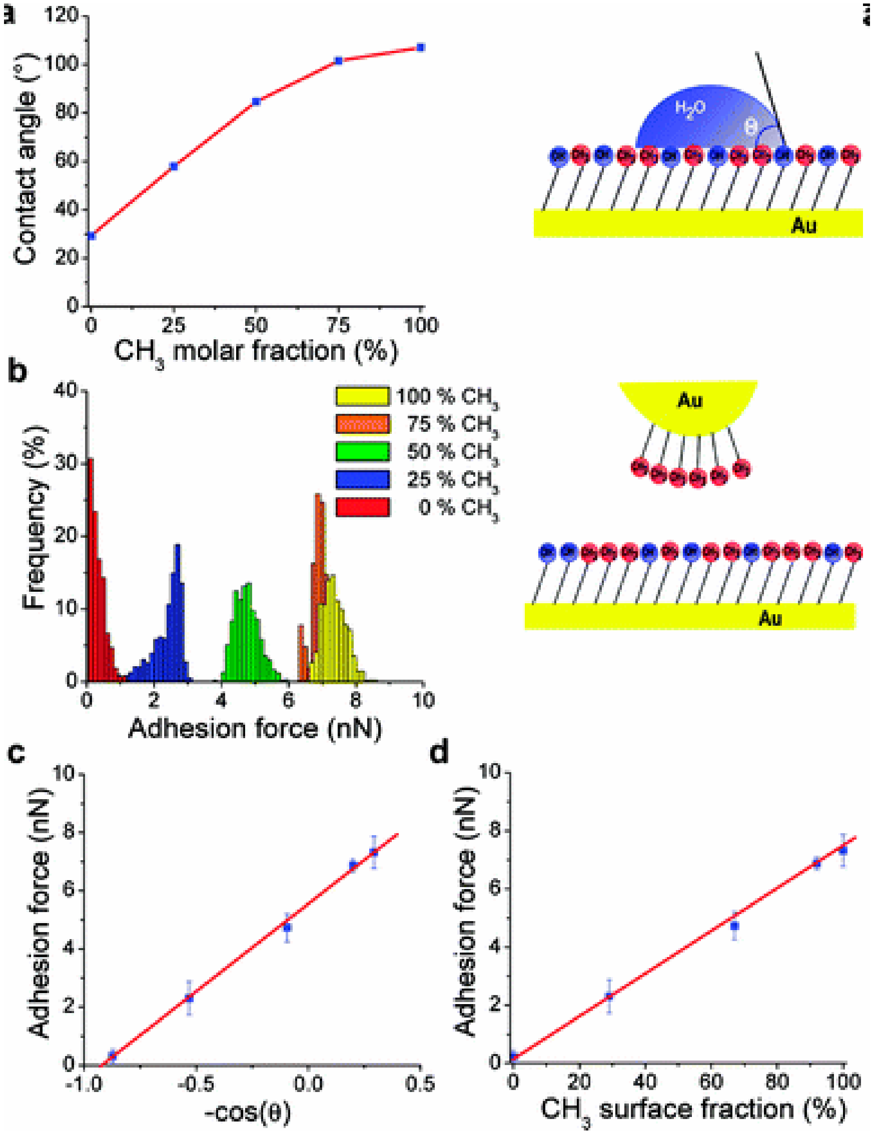






Topographic (a) and friction force (b) images (scan area: 14.0 μm × 8.8 μm) showing bilayer and odd-numbered multilayers. Numbers shown in (a) indicate the number of molecular layer in the multilayers. Shown in (c) are profiles indicated by insert dotted lines in (a) and (b) for the height and friction force. The gray scale is 0 to 40 nm for (a) and 1.3 to 2.0 nA for (b), respectively.

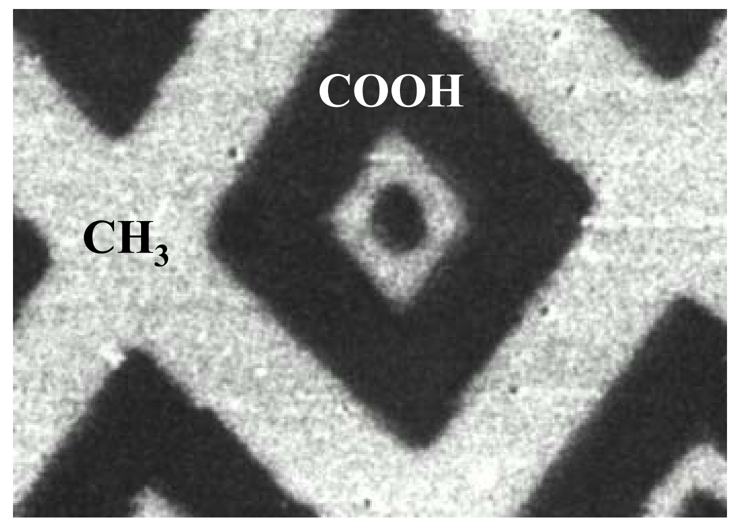
Chemical force microscopy:
friction force microscopy with a functionalized tip



D. Alsteens et al., ***Langmuir*** 23, 11977-11979 (2007).

If surface chemistry of the probe tip is known, then adhesion force mapping serves as chemical force microscopy

CH_3-terminated tip

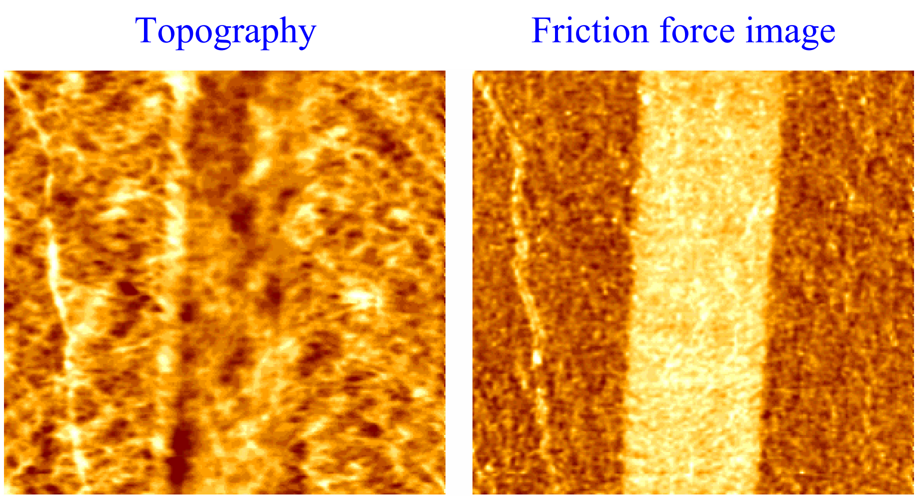


A. Noy et al., ***Ann. Rev. Mater. Sci.*** 27, 381-421 (1997).

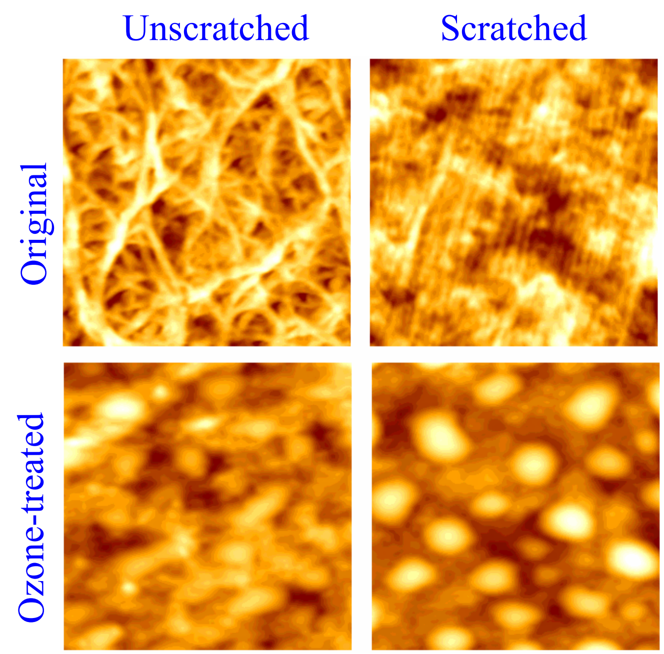
Surface energy increase determined by AFM

Preferential oxidation on scratched areas

Lateral force imaging and adhesion force measurement are used to investigate preferential oxidation on scratched areas. It is clear from the friction force image shown below (scan area is 6 µm square) that the shear-force deformed PP areas have higher friction force (and higher adhesion force) than the unscratched area. The images (scan area is 1 µm square) on the right column show clearly preferential oxidation caused by ozone treatment on the scratched area.



Creating local active areas



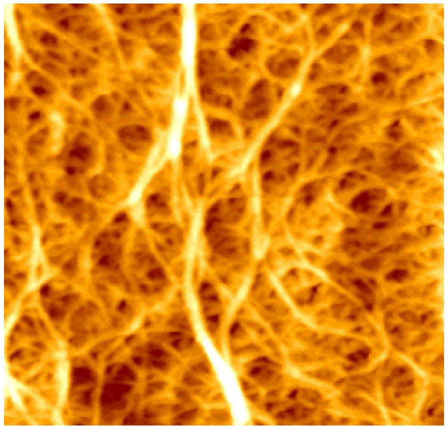
Adhesion force increase by surface oxidation

Modification of Surface morphology and energetics on polymer surfaces

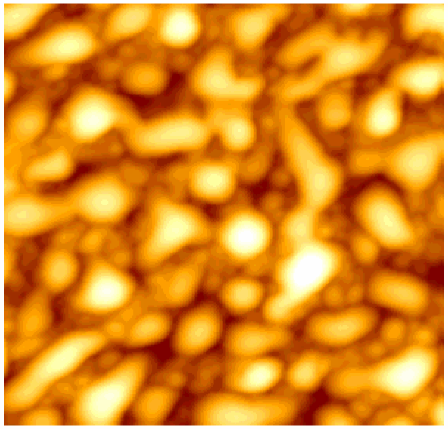
Surface modification of polymer films

AFM measurements clearly show formation of mounds on UV/ozone treated polypropylene (PP) film from the original surface characterized by fiber-like network structure (scan area is 2 μm square and height range is ~ 25 nm) and an increase in adhesion force. This increase in adhesion force indicates an increase in surface energy due to the oxidation of the modified polymer films.

Original PP

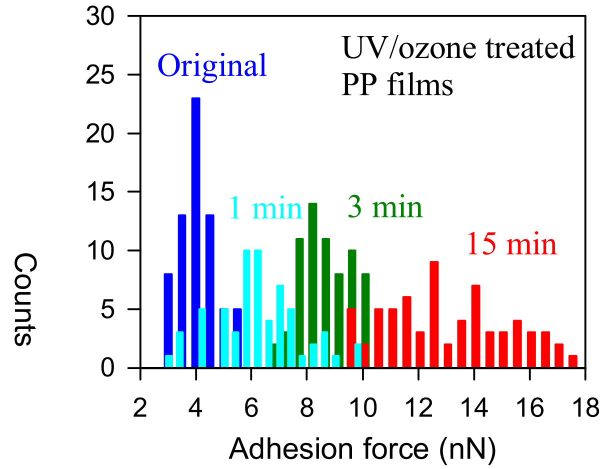


15-min treated PP



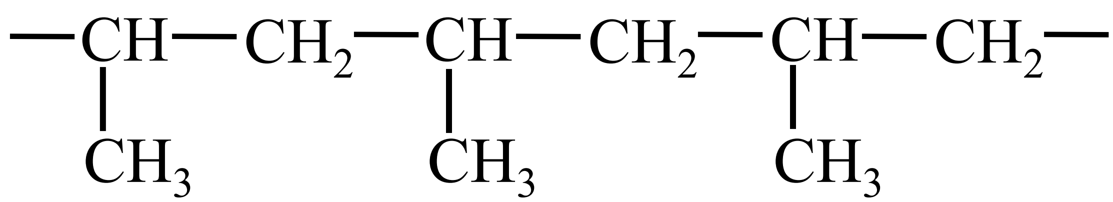
Adhesion force increase

The adhesion force distribution for original and UV/ozone treated PP films shown below was obtained from force-distance measurements. It is clear that the adhesion force was increased with the UV/ozone treatment time.

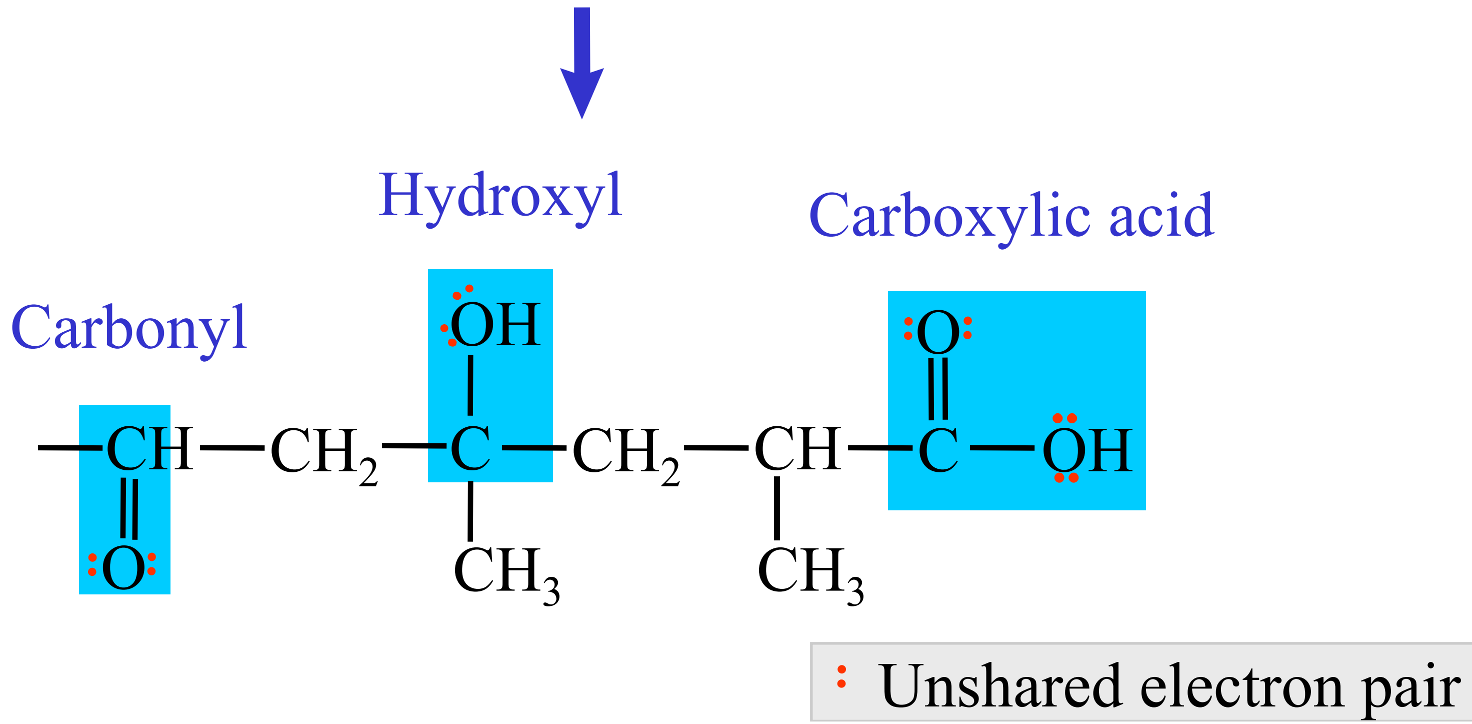


Why adhesion force increases?

Polypropylene (PP)



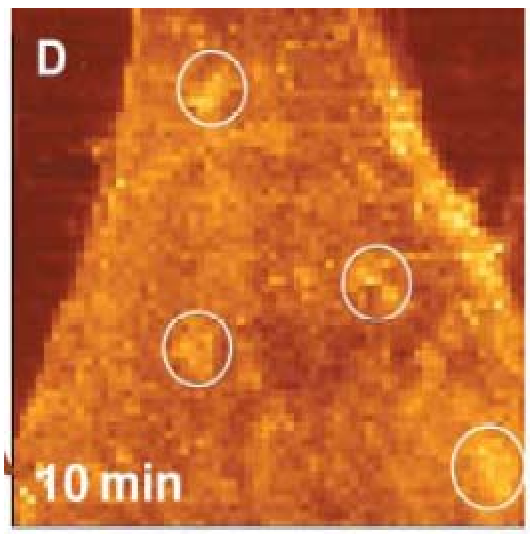
Formation of polar (functional) groups by UV/ozone treatment



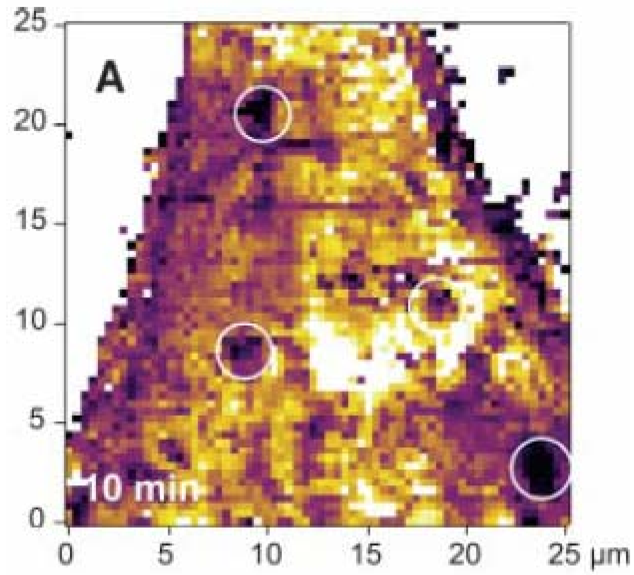
Force volume mapping:
Young’s modulus and adhesion force

Force volume mapping: low pixel density (64 x 64)
because a force-distance curve is taken at each pixel.

Morphology



Young’s modulus



N. Almqvist et al., ***Biophys. J.*** 86, 1753–1762 (2004).

Dynamic force mode AFM

Cantilever is vibrated at a frequency close to its resonance.

The amplitude of the vibration will be reduced when the tip is in the regime where tip-sample interaction exists. A reduced amplitude is used as the feed back parameter to follow the morphology of the samples surface.

Moreover, surface properties such as viscoelasticity and surface chemistry can be visualized simultaneously with the morphology

Point mass – spring model for AFM:
Equation of motion for forced damped oscillation in free space

mass

$$m\frac{d^2z}{dt^2} + c\frac{dz}{dt} + kz = F_0\cos\omega t$$

damping coefficient

spring constant

driving force

$$\omega_0^2 = k/m$$

$$Q = \frac{\sqrt{mk}}{c}$$

quality factor

$$c = m\omega_0/Q$$

$$\frac{d^2z}{dt^2} + \frac{\omega_0}{Q}\frac{dz}{dt} + \omega_0^2 z = \frac{F_0}{m}\cos\omega t$$

Steady state solution

$$z = A\cos(\omega t + \phi)$$

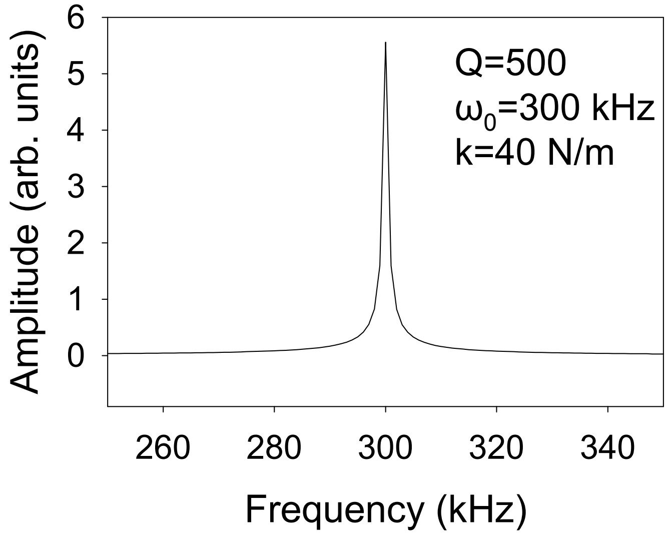
amplitude

phase shift

Resonance frequency and phase lag (frequency sweep)

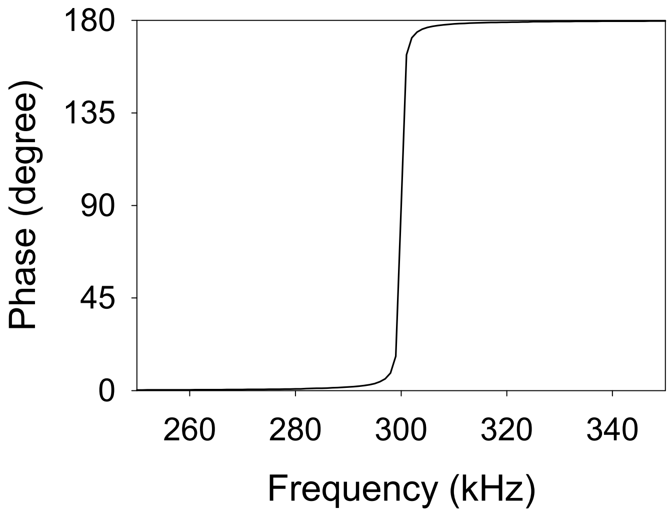
Amplitude

$$A = \frac{F_0 / m}{[(\omega_0^2 - \omega^2)^2 + (\omega\omega_0 / Q)^2]^{1/2}}$$



Phase

$$\tan(\phi) = \frac{\omega\omega_0 / Q}{\omega_0^2 - \omega^2}$$



Oscillating cantilever to detect force gradient between tip and sample

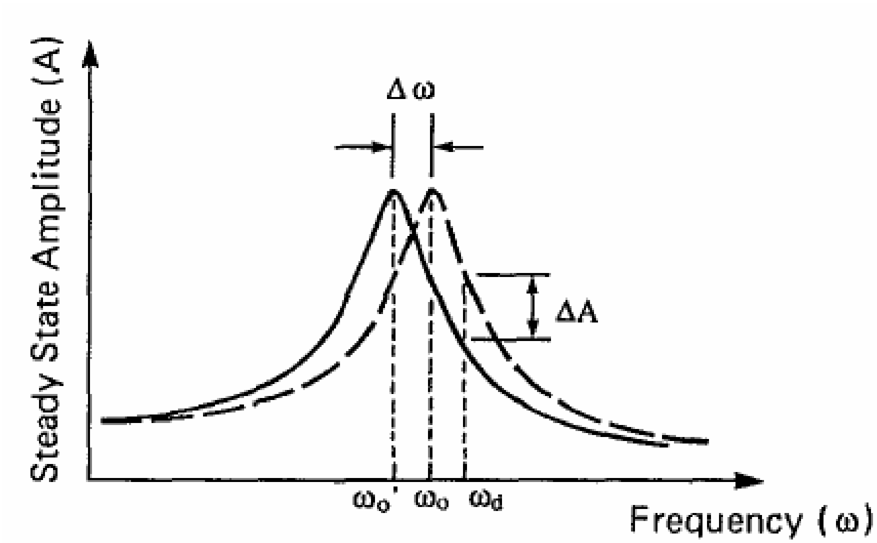
Resonance frequency changes when there is force exerted to the tip:

$$f = 2\pi\sqrt{\frac{k + \frac{\partial F}{\partial z}}{m}}$$

Causing changes in amplitude and phase lag.

Thus, amplitude-modulation AFM and phase imaging.

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



J. Appl. Phys. 69 (2), 15 January 1991

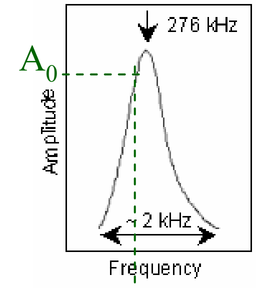
$$\Delta f = 2\pi\sqrt{\frac{k + \frac{\partial F}{\partial z}}{m}} - 2\pi\sqrt{\frac{k}{m}} = f_0\left(\sqrt{1 + \frac{\partial F}{k\partial z}} - 1\right) \approx f_0\left(1 + \frac{\partial F}{2k\partial z} - 1\right) = f_0\frac{\partial F}{2k\partial z}$$

Imaging mechanism of dynamic force AFM

A stiff cantilever (~40 N/m) is oscillated around its resonant frequency (see the insert in the figure shown here). The tip is not in contact with (very small amplitude, say 1 nm; this is non-contact mode) or only taps (large amplitude, usually > 10 nm; this is tapping mode) the sample surface. That way, lateral dragging due to scanning is largely eliminated, effectively preventing soft sample surface from being damaged as could be using contact mode AFM. Information available from this mode: Morphology, phase imaging (due to differences in friction force, chemical force, adhesion force, mechanical properties).

An amplitude-distance curve should look like the one shown on the right. Interactions between the tip and the surface at different separation are indicated. In free space, the tip is far away from the sample. After the tip is in contact with the sample, the cantilever no longer oscillates. In the working area, the amplitude is reduced as a function of tip-sample separation, which is used as the feedback parameter to obtain surface morphology. Usually, surface is scanned by maintaining a reduced amplitude at 50 %.

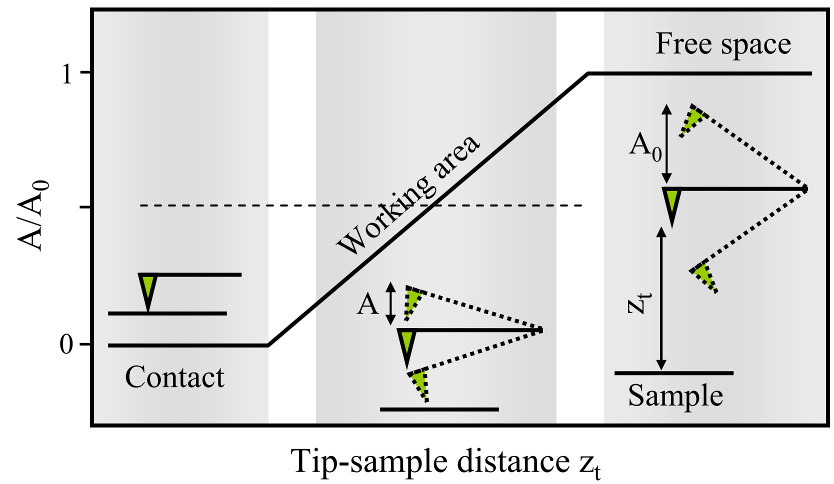
Cantilever is vibrated by applying an AC voltage (sine wave) at a frequency f (close to resonance frequency) to a piezo device on which the cantilever is attached. In free space, the cantilever oscillation amplitude is A_0 (say, 20 nm).



Amplitude-distance curve

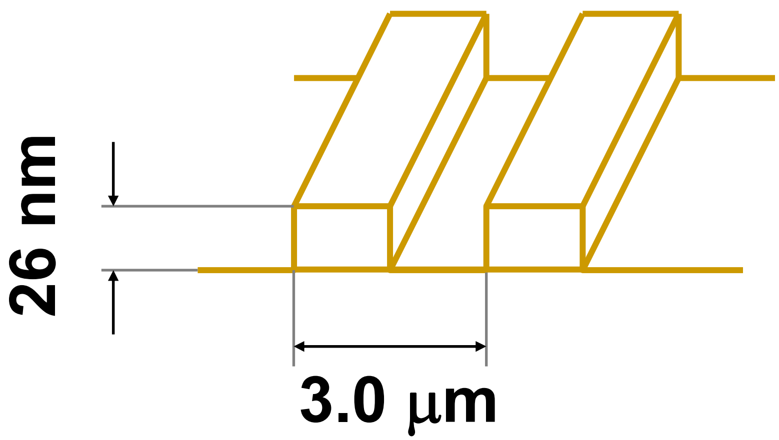
Dotted line indicates imaging condition

(amplitude is damped to ~ 50 %)

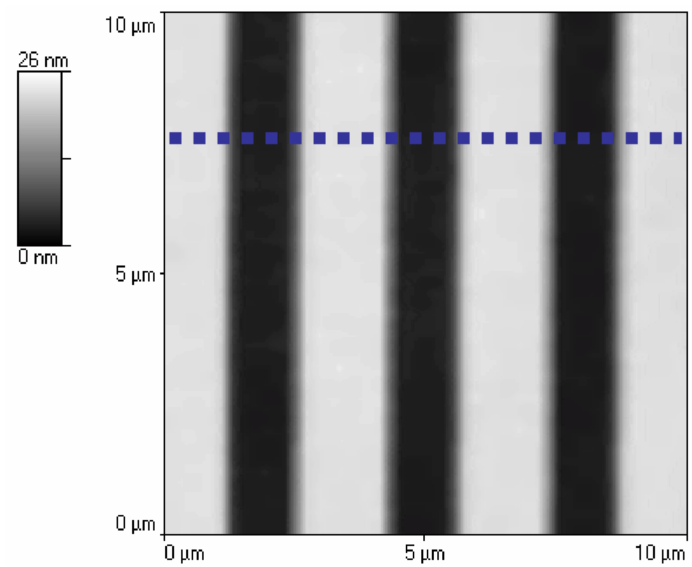


Examples of AFM image

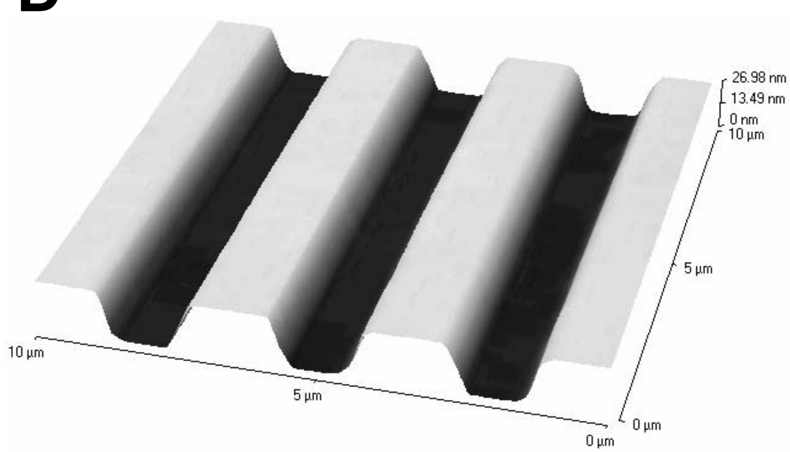
AFM image of a grating (26 nm height standard)



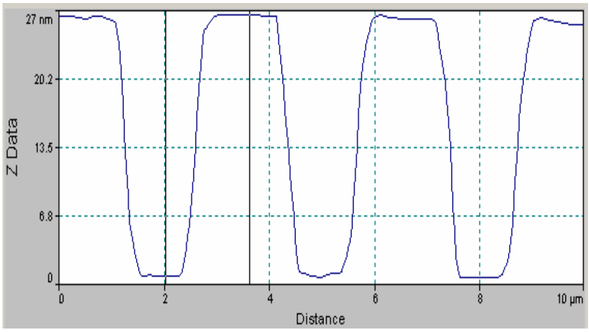
Topview



3-D

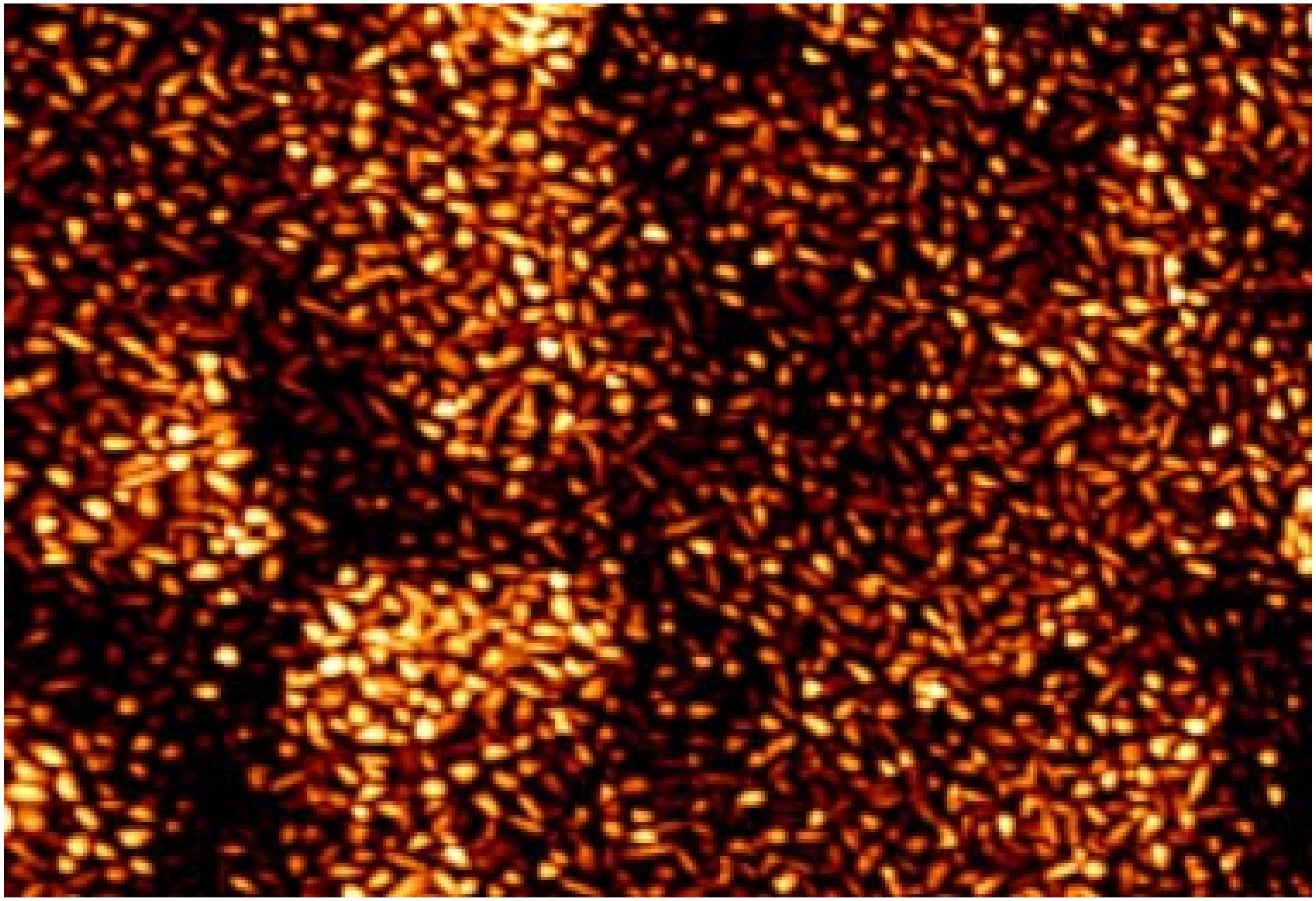


Profile



Example of AFM image: metal oxide

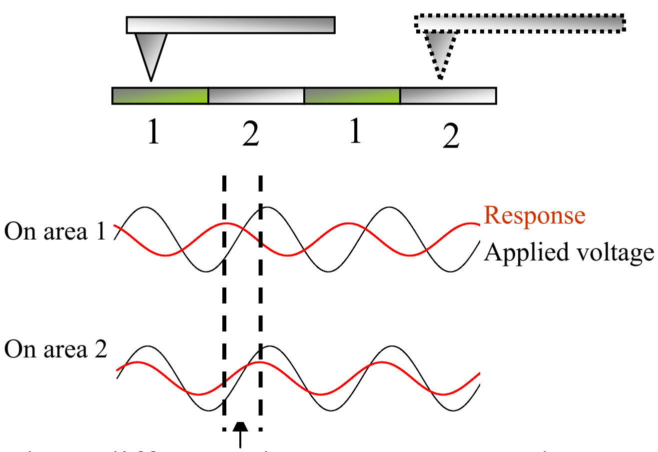
High spatial resolution



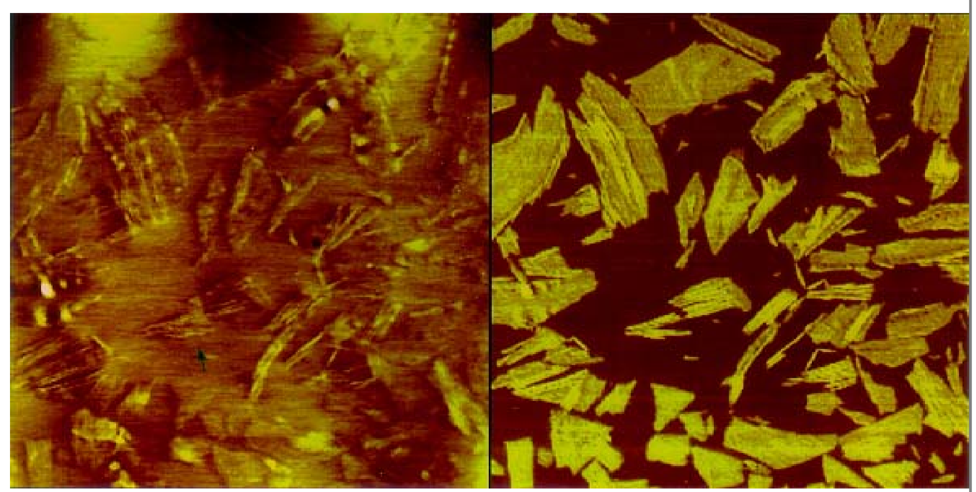
1 µm × 1.5 µm

Phase imaging

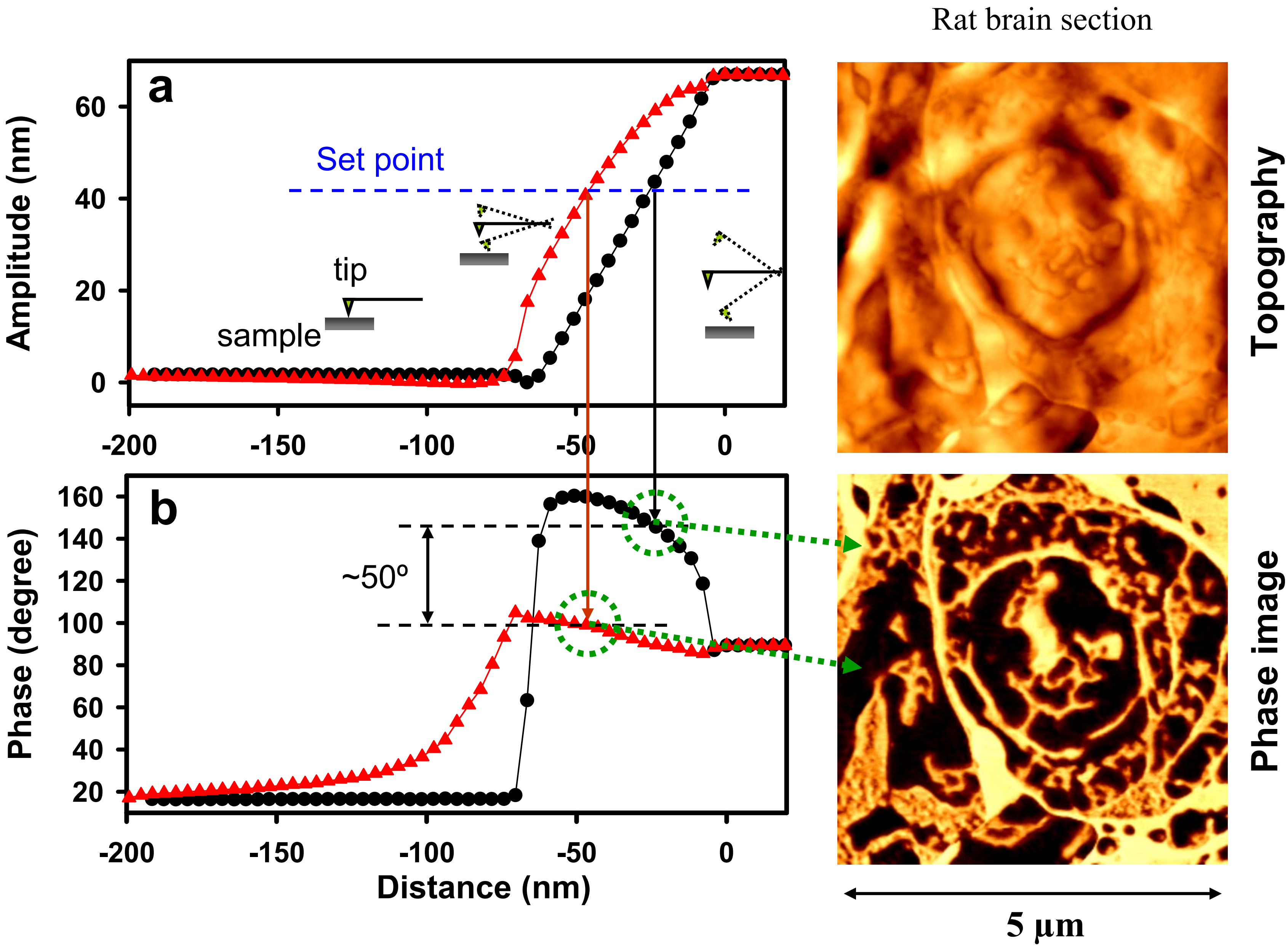
In dynamic force mode AFM, phase shift between the sinusoidal voltage source applied to oscillate the cantilever and the actual oscillation of the cantilever can be effected by the interaction between the tip and the sample. The phase shift in the oscillating cantilever is related to tip-surface interaction which is basically material specific. Therefore, phase shift in tapping AFM can be used to distinguish different surface compositions on a surface (see the schematic below). There are many surface properties that may have an effect on the phase shift contrast. They could be differences in friction, viscoelasticity, adhesion, material, etc. Phase imaging usually gives clear contrast on a surface if there are any differences in surface properties as described above. Applications include visualizing phase separation in polymer blends, distinguishing different compositions on surface. Shown here is topography (left) and phase image (right) for a surface of a toner particle of carbon black matrix with polymer filler (scan area is 3.5 μm square).



Phase difference between area 1 and 2



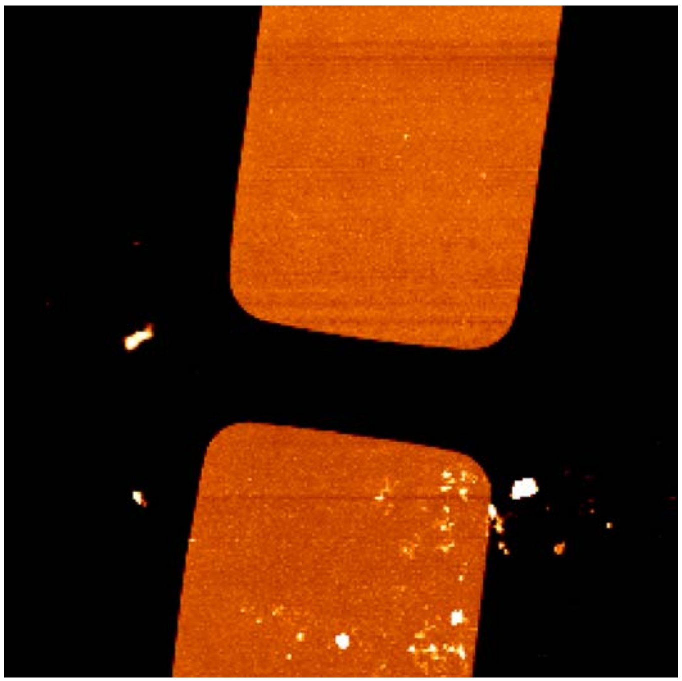
Phase imaging sensitive to mechanical properties



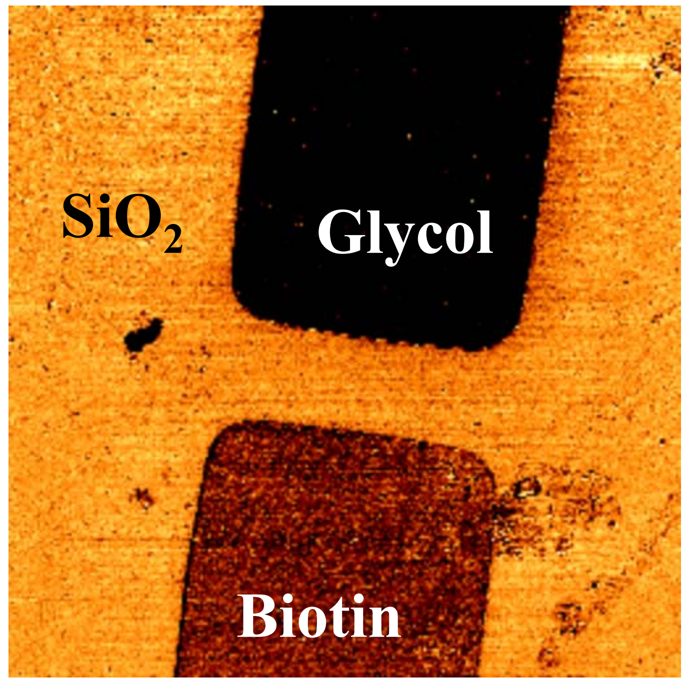
Phase imaging sensitive to surface chemistry

Two thiols terminated by different functional groups are self-assembled on Au films

Topography

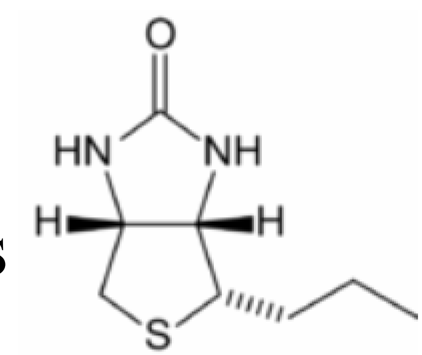


Phase image

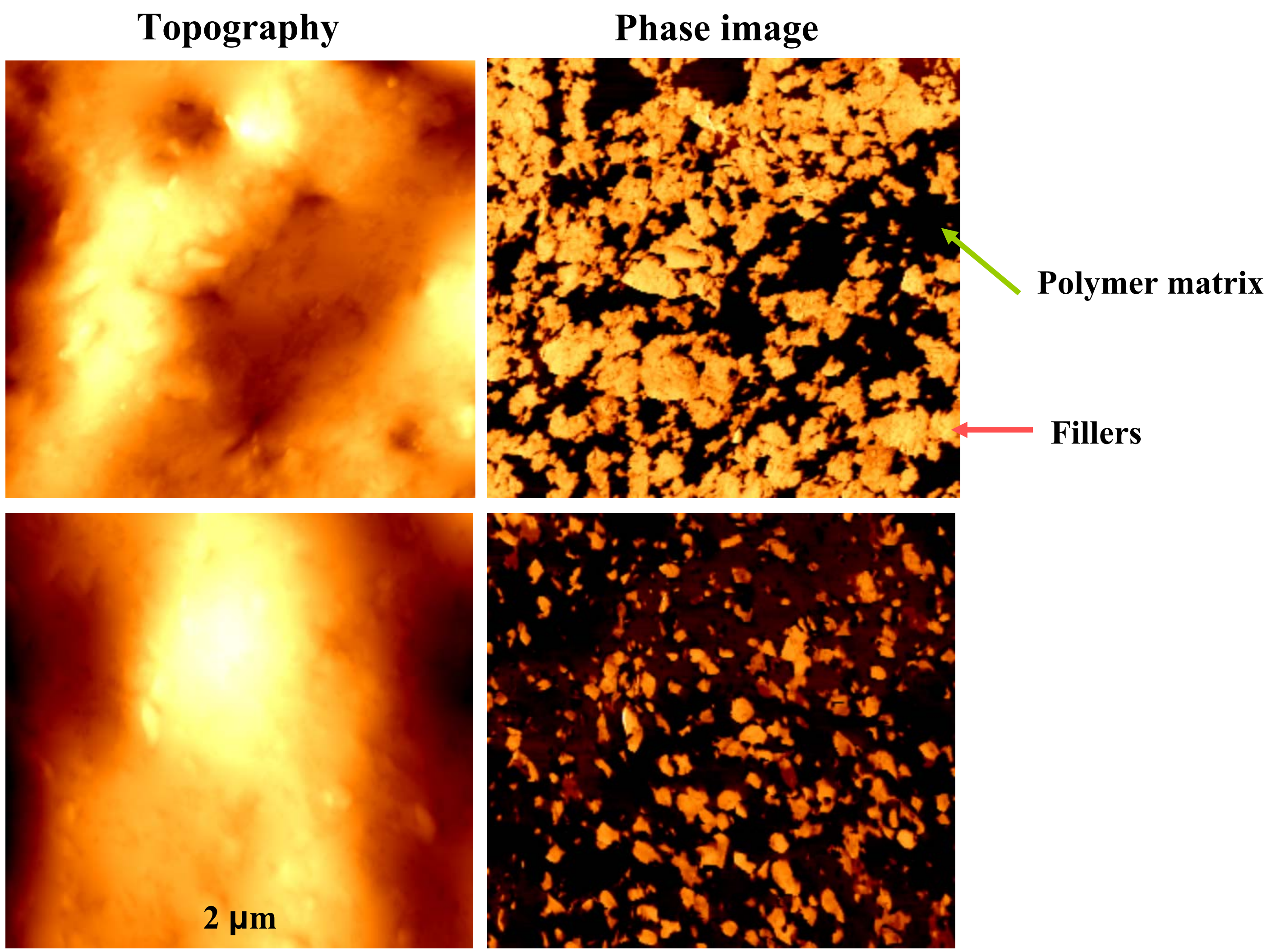


$HS(CH_2)_{11}(C_2H_4O)_3OH$

$HS(CH_2)_{11}NHCOC_9H_{15}N_2OS$

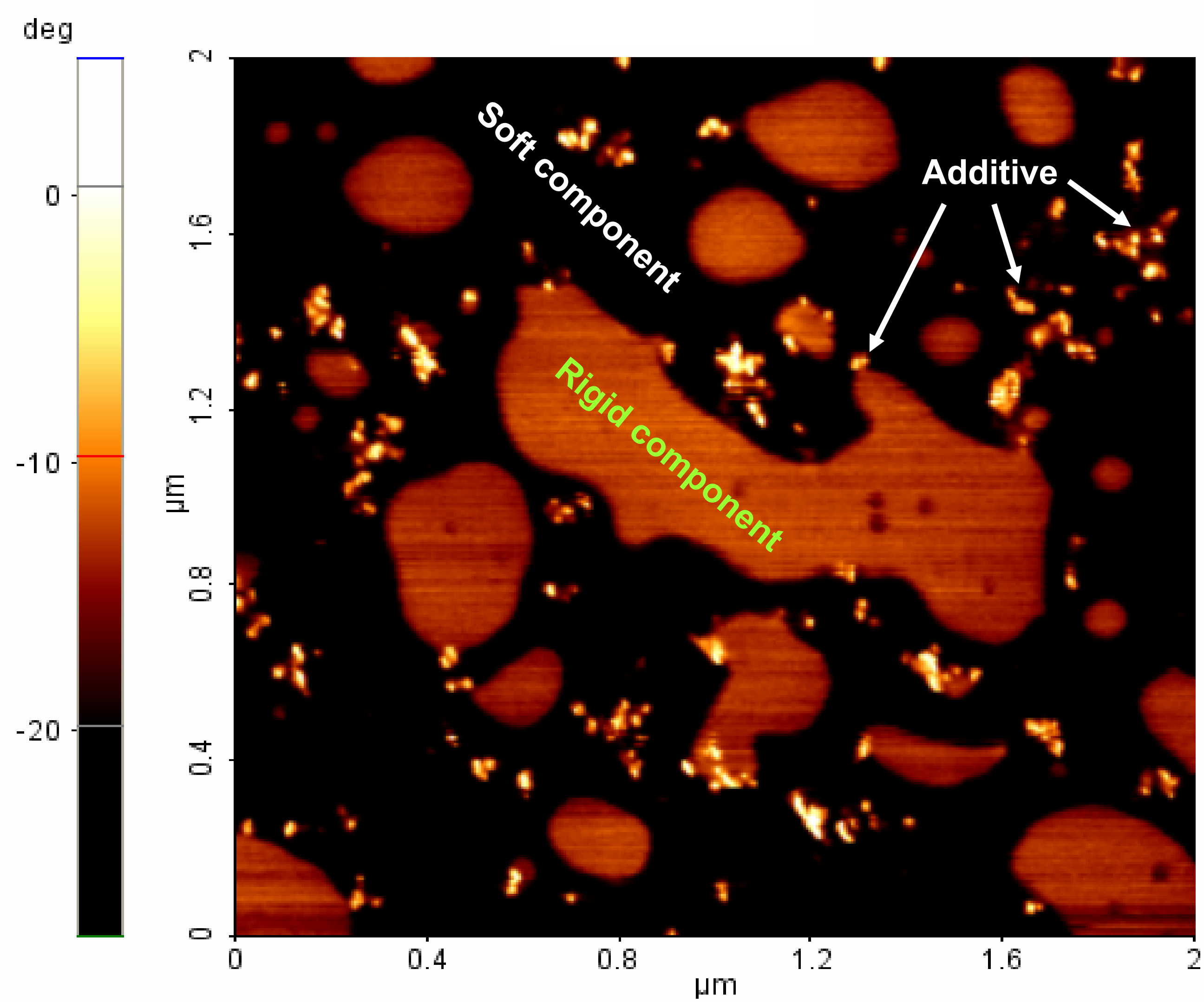


Phase imaging: revealing fillers in polymer matrix



AFM phase imaging is a powerful technique to visualize additives in a polymer matrix due to their significantly different viscoelasticity. Shown here is an example of comparing two samples made under different conditions. Phase images in the right column display striking contrasts between the additive and the matrix. It is immediately clear that the dispersion of the additive is quite different in the two samples.

Atomic force microscopy (AFM) visualizes components having different mechanical and/or chemical properties at nanometer scales.



New technology: Peakforce tapping mode for quantitative nanomechanical mapping

Back to the AFM basics: force-distance curve measured while the cantilever taps the surface during AFM imaging scans

1. Cantilever vibrated at 2 kHz (<< resonant frequency ~300 kHz)
One tap: 0.5 ms

2. AFM scan speed 1 Hz (256 × 256 pixels)
1.95 ms on each pixel → enough time for measuring force-distance curve while imaging the sample surface

3. Peak force as the feedback parameter

↓

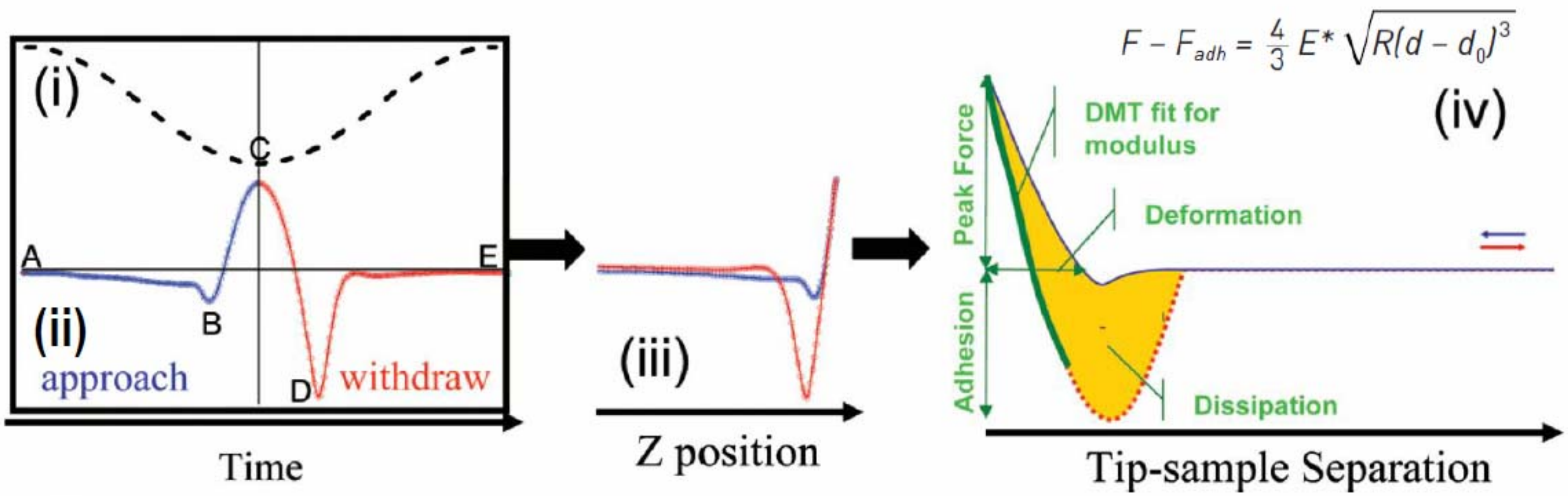
Mapping of Young's modulus and adhesion force

Bede Pittenger

How does PeakForce QNM work?

Every interaction between tip and sample is analyzed, allowing:

- The benefits of Peak Force Tapping
- Modulus, Adhesion, Dissipation, Deformation are mapped simultaneously with topography
- Individual curves can be examined and analyzed offline (PeakForce Capture)



Examples of quantitative nanomechanical property mapping

Bede Pittenger, Natalia Erina, Chanmin Su

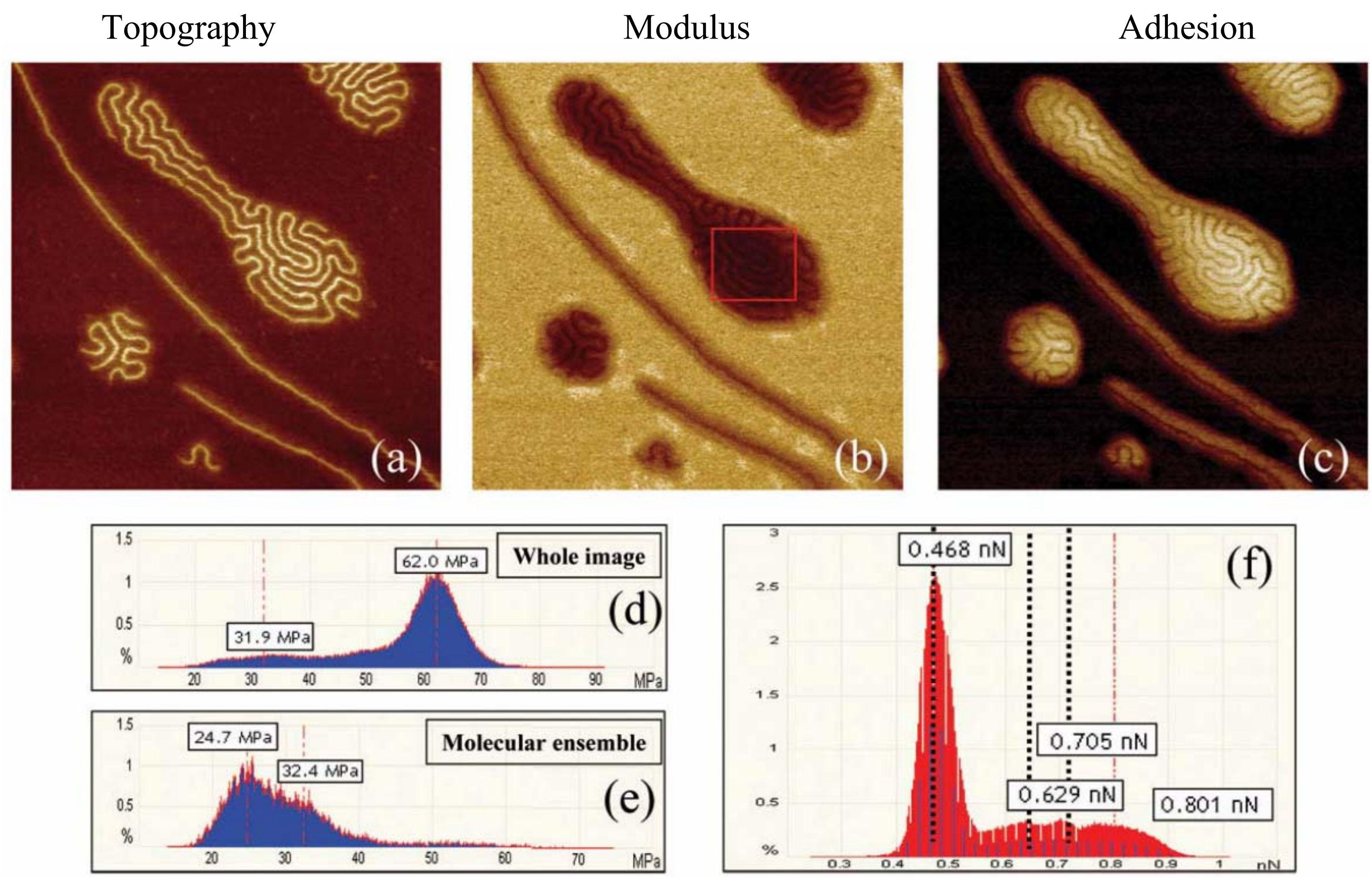
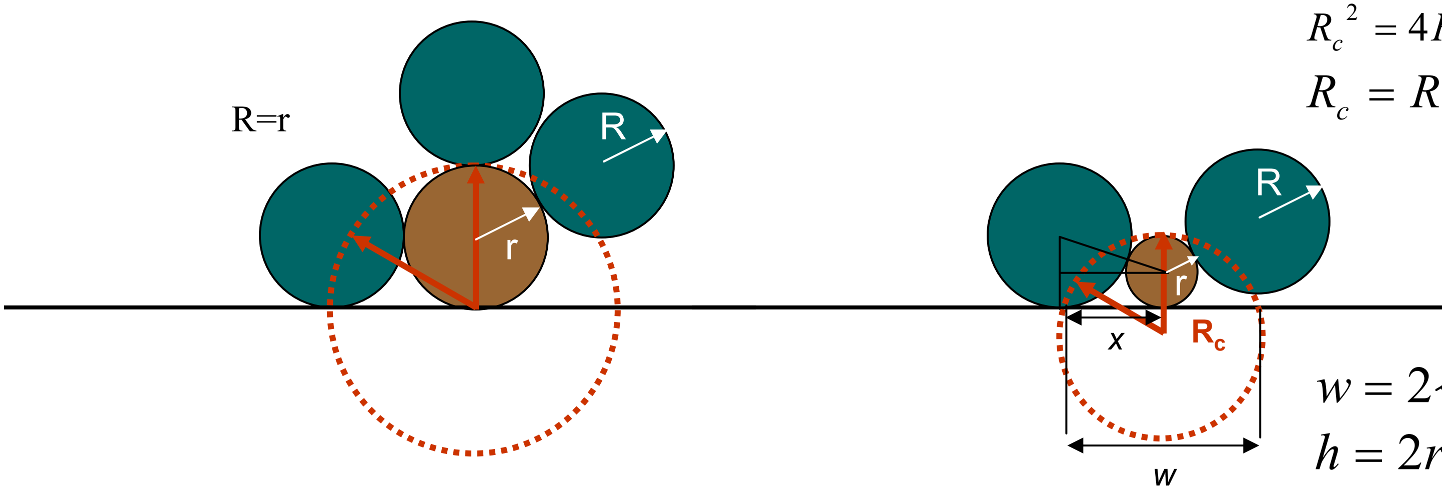


Figure 7. Poly(butyl acrylate) brush-like macromolecules and molecular ensembles on a mica substrate. (a) Height, (b) modulus, (c) adhesion, (d) histogram of area within red box in modulus map, (e) histogram of modulus map (f) histogram of adhesion map. Sample was imaged with a MultiMode® 8 using PeakForce QNM with a scan size of 500nm. Sample courtesy of Sergei Sheiko (University of North Carolina, Chapel Hill, NC) and Krzysztof Matyjaszewski (Carnegie Mellon University, Pittsburgh, PA).

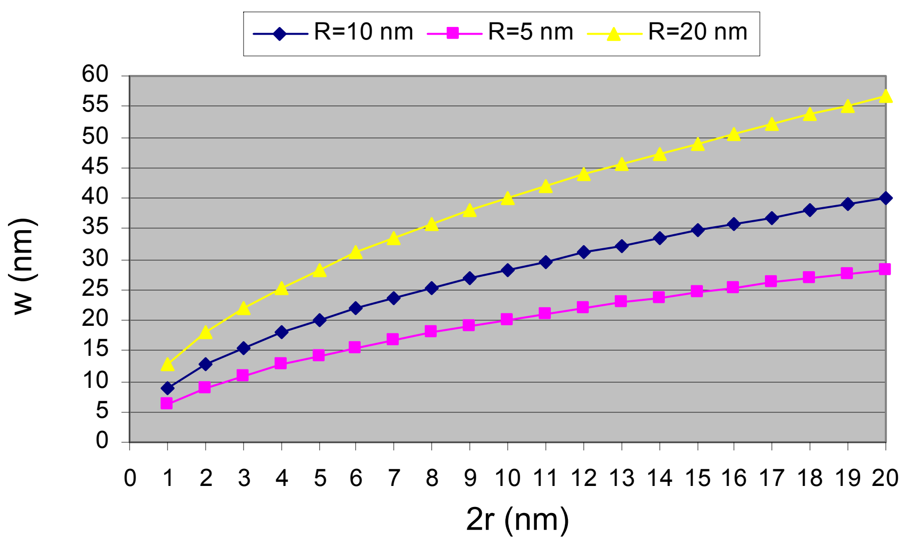
Accuracy of AFM measurement: Convolution

Convolution of tip geometry into measured features when tip apex radius is comparable with dimension of surface features.

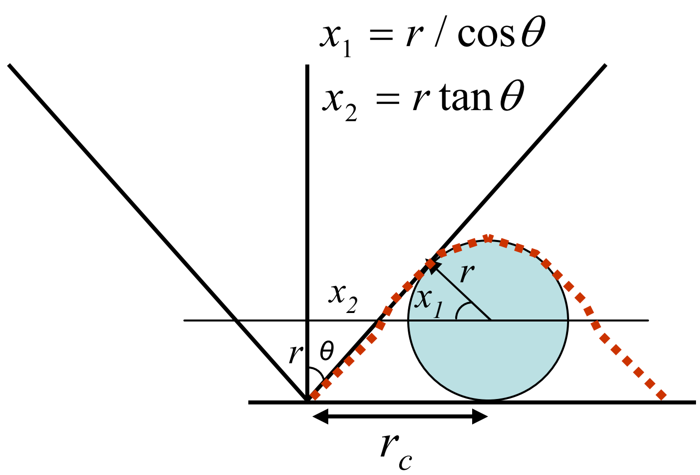
$$x^2 = (R+r)^2 - (R-r)^2 = 4Rr$$
$$R_c^{\ 2} = 4Rr + (R_c - 2r)^2$$
$$R_c = R + r$$



$$w = 2\sqrt{2Rh}$$
$$h = 2r$$

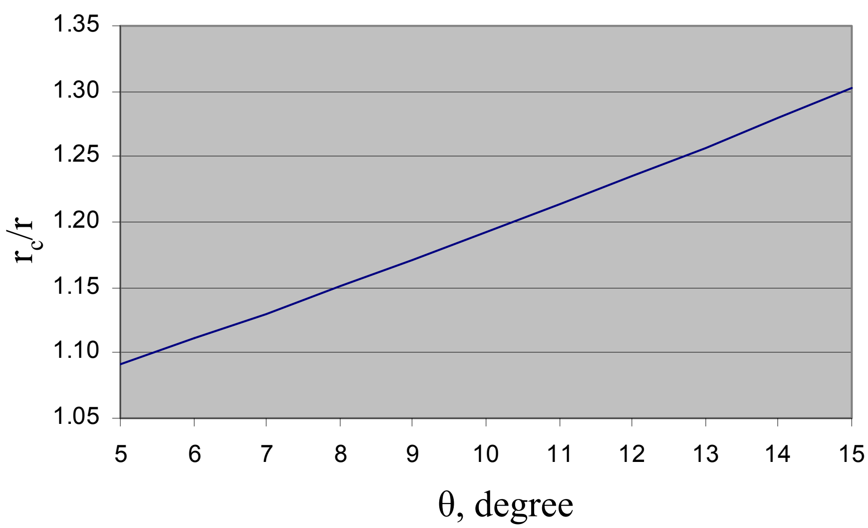


Accuracy of AFM measurement: Convolution



When tip radius « dimension of surface feature, the overall tip shape (cone angle), rather than the tip apex, dominates the convolution.

$$r_c = x_1 + x_2 = r\left(\frac{1}{\cos\theta} + \tan\theta\right)$$

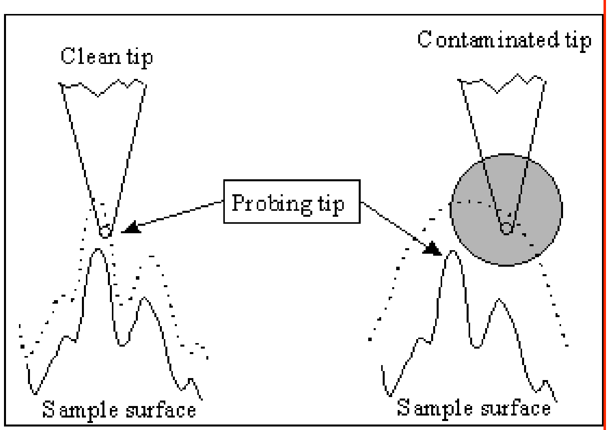


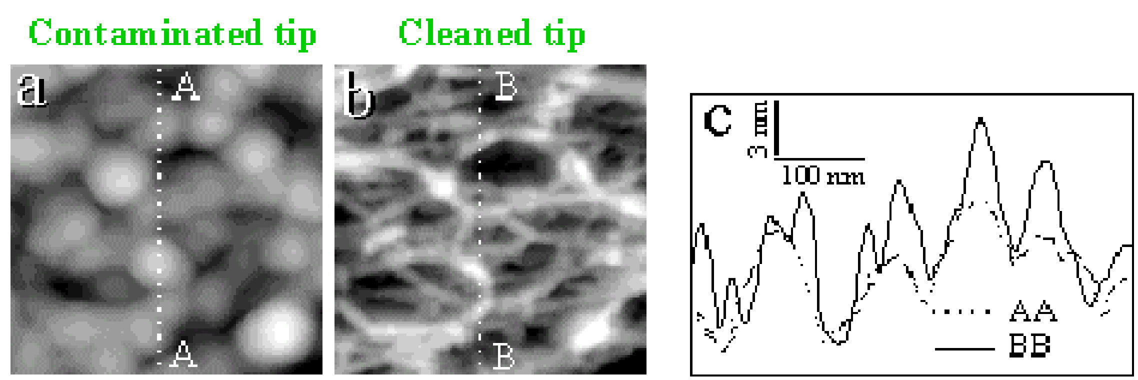
Accuracy of AFM measurement

The morphology of a surface imaged by AFM is obtained through an interaction between the probe tip and surface features. When the tip is contaminated and the size of the contaminant is comparable to or larger than the size of the features on the sample surface, artefacts attributable to the contaminant are observed to dominate the image (see the following figure on the left-hand side: dotted lines represent the measured profiles). Here is a simple and effective method of evaluating tip performance by the imaging of a commercially available biaxially-oriented polypropylene (BOPP) film, which contains nanometer-scale sized fibers. The BOPP film surface is appropriate for use as a reference because a contaminated tip will not detect the fiber-like network structure. The very fine fiber-like structure of the BOPP film surface is a good **criterion** for the tip performance as shown in the following figure (right-hand side).

Because the polymer film is soft compared to the silicon tip (Young's modulus for polypropylene is 1-2 GPa, while for silicon it is 132-190 GPa), the polymer will not damage the tip when the tip is pushed into the polymer. This property can be used to clean a contaminated tip, i.e., by pushing the contaminated tip into the polymer, contaminants are most likely removed from the tip apex, probably to the side of the tip. Another important property of the BOPP is that the polymer film is highly hydrophobic and has a very low surface energy of ~ 30 mJ/m^2 (The surface energy for Si is ~ 1400 mJ/m^2; and the surface tension of water is 72 mJ/m^2). These properties prevent contaminants from accumulating on the surface and hence prevent the contamination of the tip in the evaluation process.

The smaller object images the larger one: thus tip effect possible



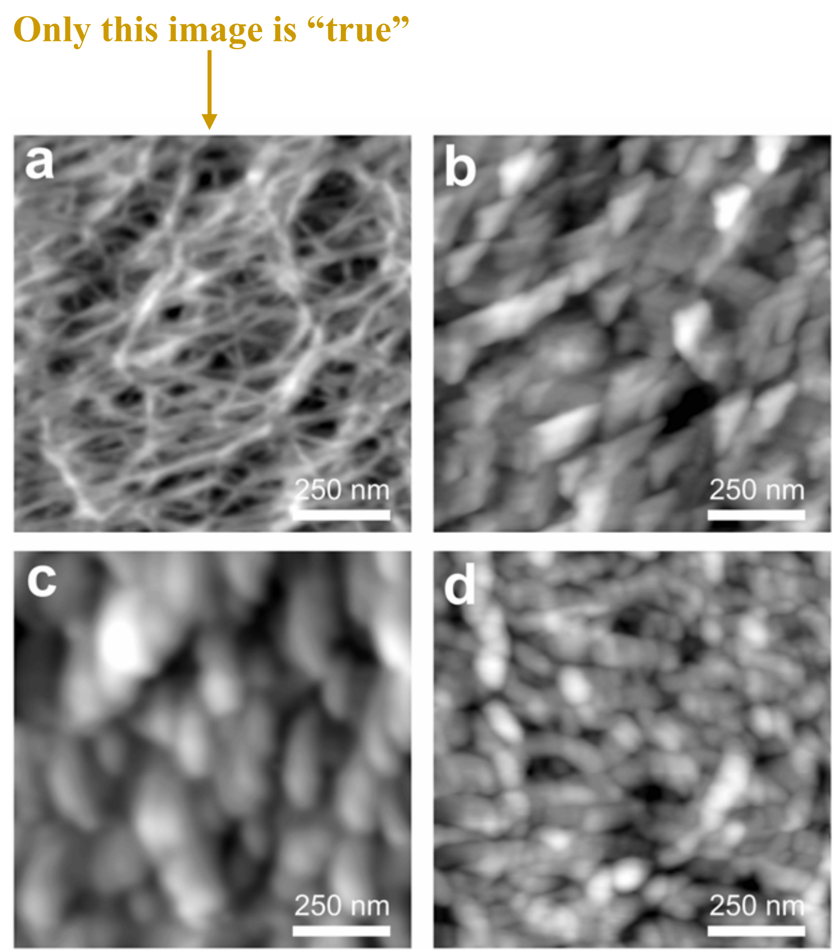


Note: a) and b) are AFM images obtained at same location on a BOPP film.

BOPP as a test sample to check AFM tip performance

An AFM image (a) obtained on a BOPP film using a clean tip, reflecting the true morphology characterized by the fiber-like network structure. When damaged or contaminated AFM tips were used, the fiber-like features are no longer seen in the AFM images [(b)- (d)]. These three images are obviously dominated by three different tip shapes. Comparison of the AFM images strongly suggests that the BOPP film can be used as a reference sample to check the performance of an AFM tip.

The criterion is simple and straight forward: if the fiber-like features are revealed by an AFM tip, then the tip quality is sufficient to collect "true" images. An AFM tip can be easily contaminated or damaged depending on the chemical and mechanical properties of the sample surface it scans. It is therefore desirable to adopt a simple qualifying method such as this one using BOPP film to check the performance of the AFM tips to make sure the collected AFM images be meaningful.



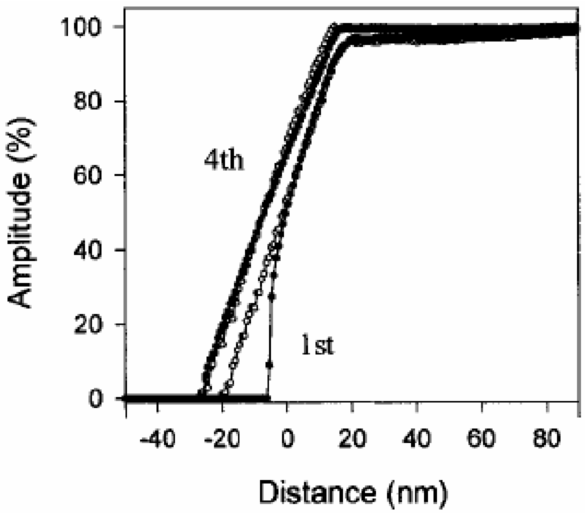
Cleaning contaminated tip on BOPP

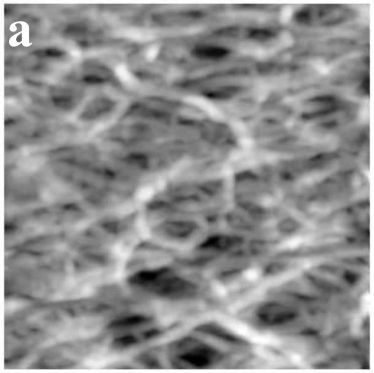
In order to prove that BOPP film is indeed useful for checking AFM tip performance, we managed to image the same area using the same tip when it was clean, after it had been contaminated and then after it was cleaned again. That way, any change in the AFM images obtained would be solely due to the contamination on the tip apex.

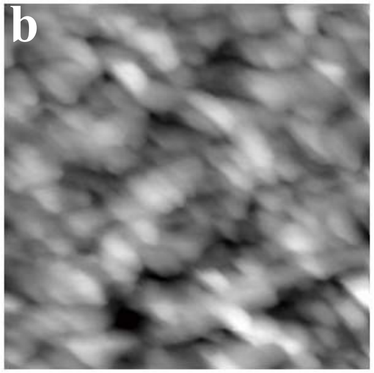
AFM images shown in (a), (b) and (c) were obtained on the same area of a BOPP film using the same tip when it was clean, contaminated and re-cleaned, respectively. The tip was contaminated by being scanned on an organic acid coated Si substrate. It is clear that the image collected by the contaminated tip is dominated by tip effect (b). We cleaned the contaminated tip by pushing it into the polymer film, and its cleanliness is evidenced in AFM image shown in (c). Therefore, the use of the BOPP film to check the AFM tip performance and to clean the contaminated tip was successful.

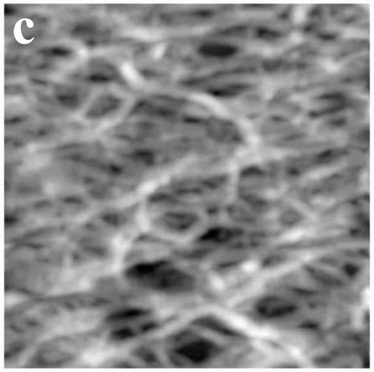
How to clean a contaminated tip

The amplitude versus the tip-sample separation when the tip is brought to and retracted from the sample surface is represented by open and filled circles, respectively. For clarity only the first and fourth curves are shown here. The speed of the tip movement was 100 nm/s.



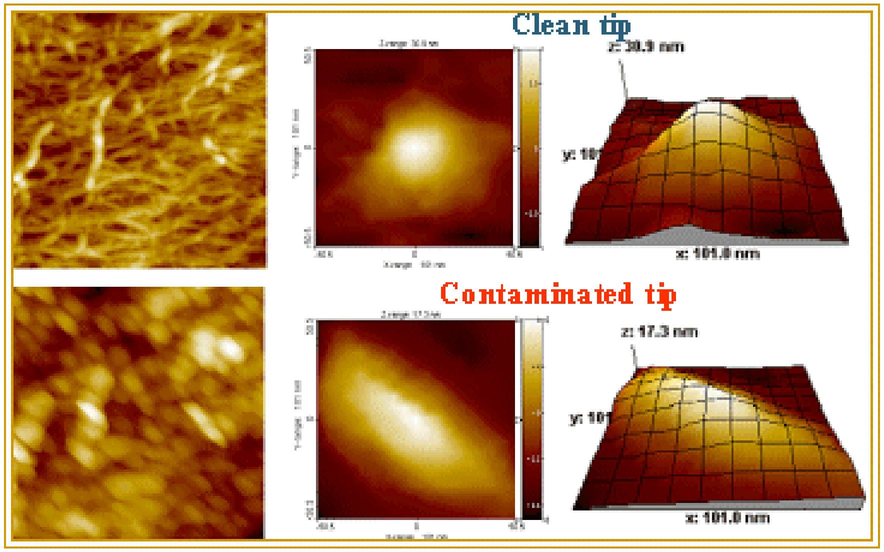




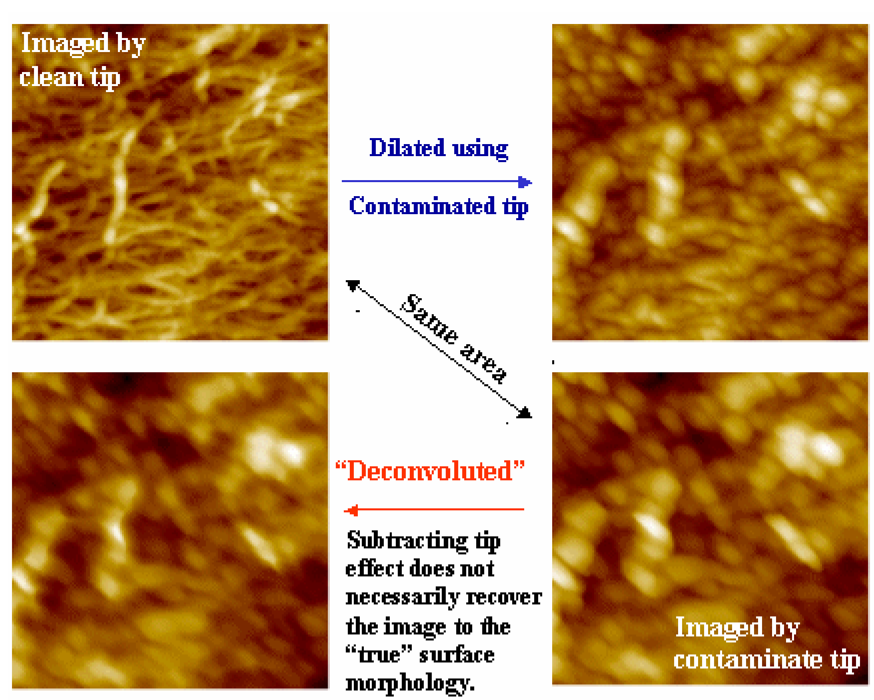


Use of BOPP film: Application to blind tip reconstruction

Use of the morphology of BOPP as a standard to check probe performance (and even to estimate the tip geometry).

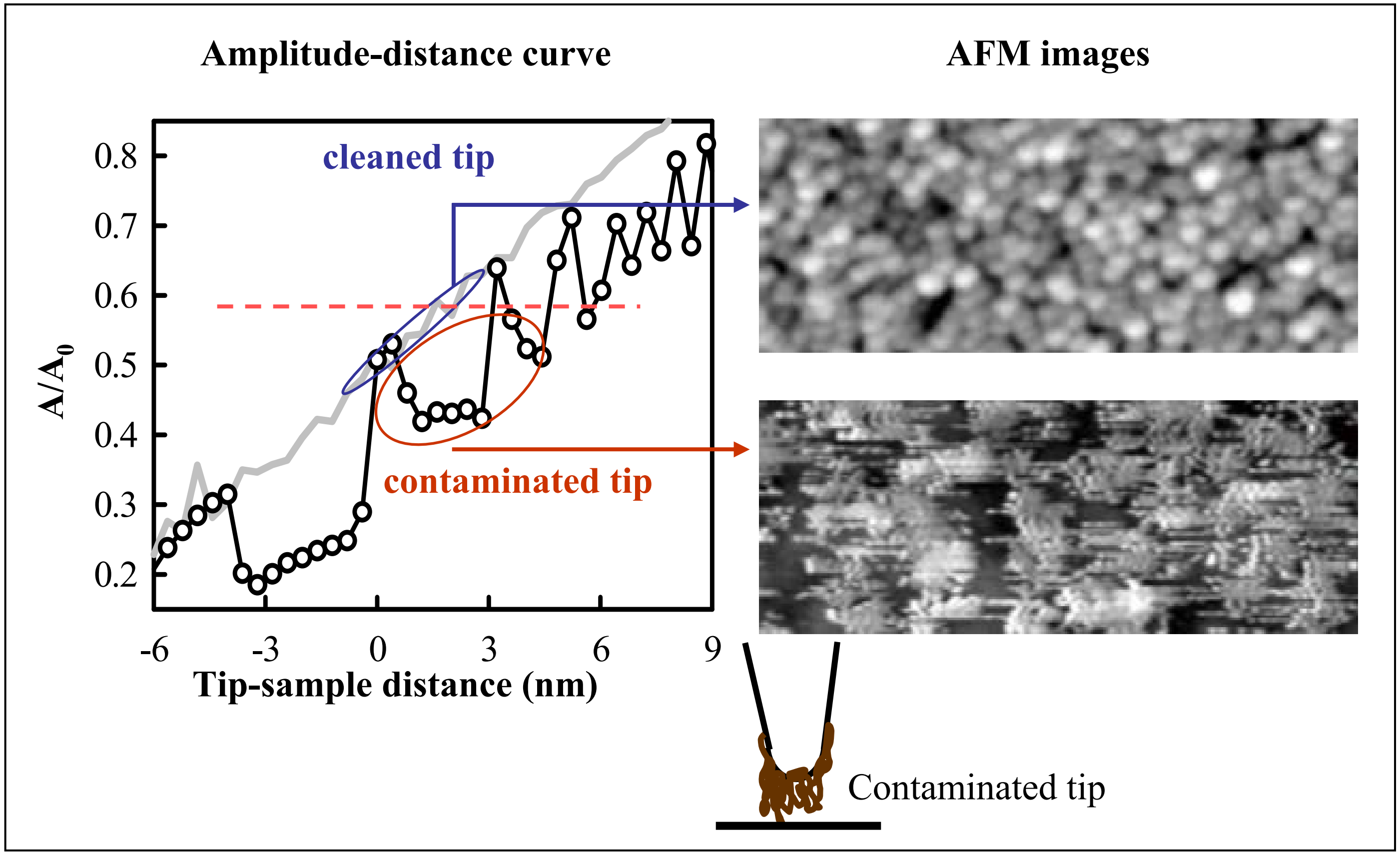


Tip effect is unlikely to be completely removed from the image.



AFM tip contamination

If a material contaminating the tip apex is sticky (active in producing extra forces), the contaminated tip may causes noises in AFM imaging.



SPM

STM

Atomic resolution

Local density of states for electron

Empty or filled electronic state imaging

AFM

Nanometer resolution (atomic resolution ultimately)

Probe various surface properties

Quantitative mechanical mapping