SPM Fundamentals, Techniques and Instrumentation

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Contents

Background to SPM - STM

○ In 1981 Binnig and Rohrer invented the Scanning Tunnelling microscope(STM)

○ STM measures the tunnelling current between a fine metal wire and a conducting sample.

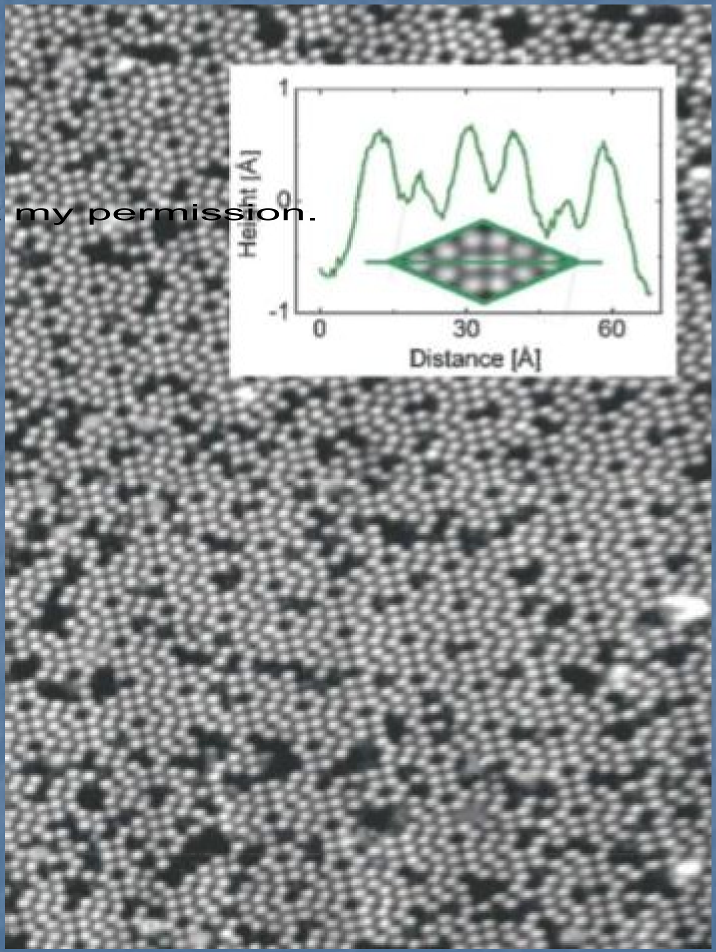
○ The wire is scanned over the surface, and the tip-sample distance maintained by feedback on the tunnelling current.

○ Electron tunnelling probability decays on the length scale of one atom.

○ This means that only the last atom on the wire scans the surface.

Background to AFM - STM

- This means that STM is capable of extremely high resolution.
- For example the image here shows true atomic resolution on the Si(111) 7x7 reconstruction.
- BUT it is limited to conducting samples, or very thin layers of insulators on conducting substrates.
- This problem was overcome with the invention of AFM in 1986.



Jaschinsky et al,
Rev. Sci. Instr. **77, 2006**

Background to SPM - AFM

○ AFM is more suitable for most samples, so today AFM is much more widely used than STM.

○ AFM and STM together are part of a group of families called Scanning Probe Microscopy or SPM.

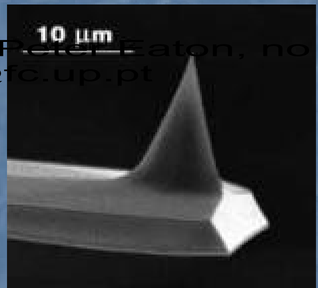
○ This talk will focus on AFM.

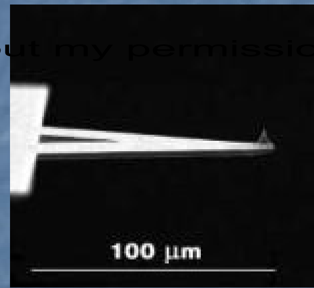
○ To a greater extent than STM, AFM has been extended to measure a wide variety of sample properties, giving rise to
  - ○Magnetic Force Microscopy, MFM
  - ○Lateral Force Microscopy, LFM
  - ○Scanning Thermal Microscopy, SThM

○…and many more!

Background to SPM - AFM

○AFM works by scanning a sharp tip over the sample, and monitoring the deflection of the cantilever attached to the tip.





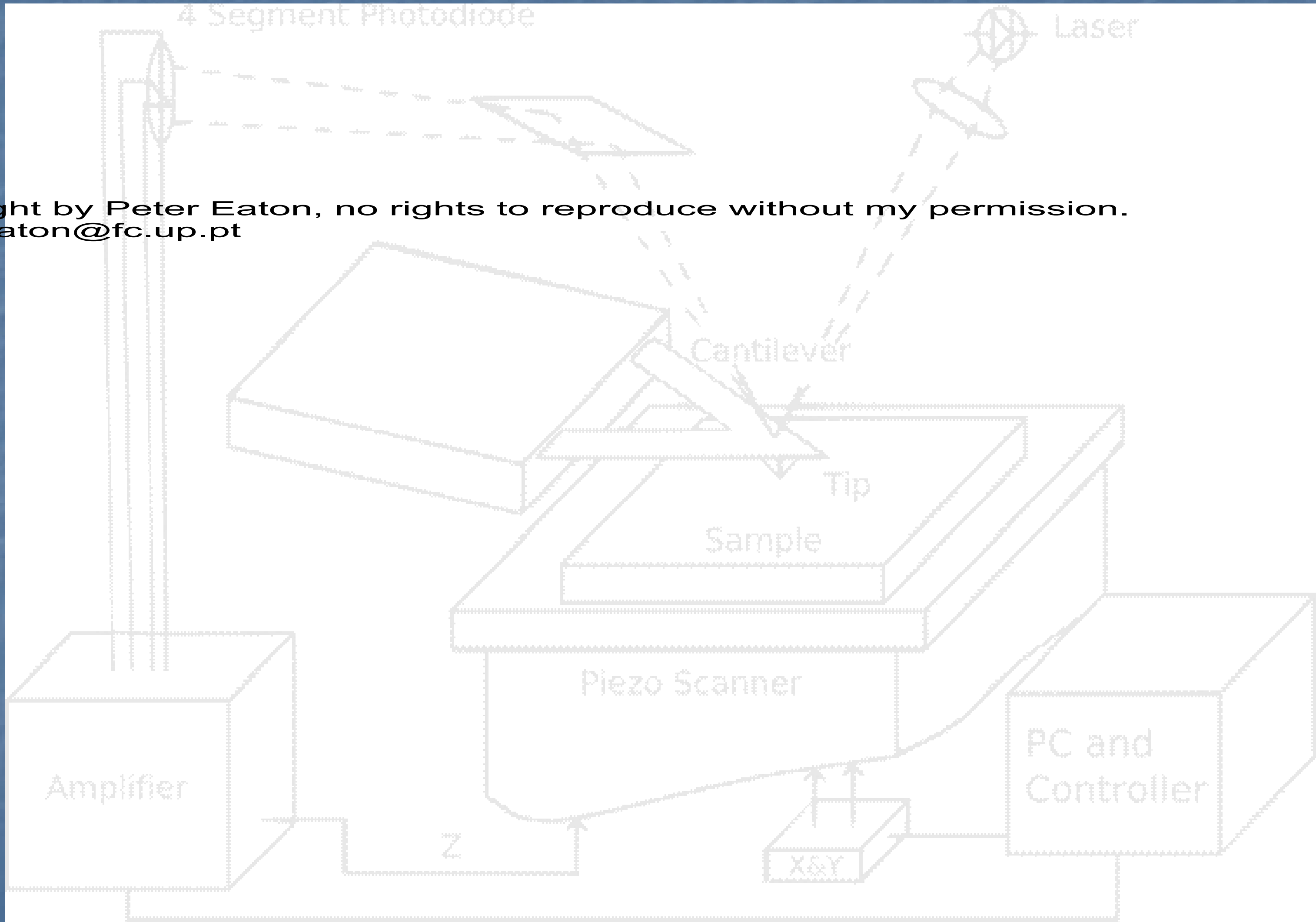
○The force applied by the tip to the sample is kept constant by moving the sample / tip up and down as they scan.

○The force may be less than 10^{-9} Newtons.

○The deflection of the cantilever is generally monitored by an optical lever.

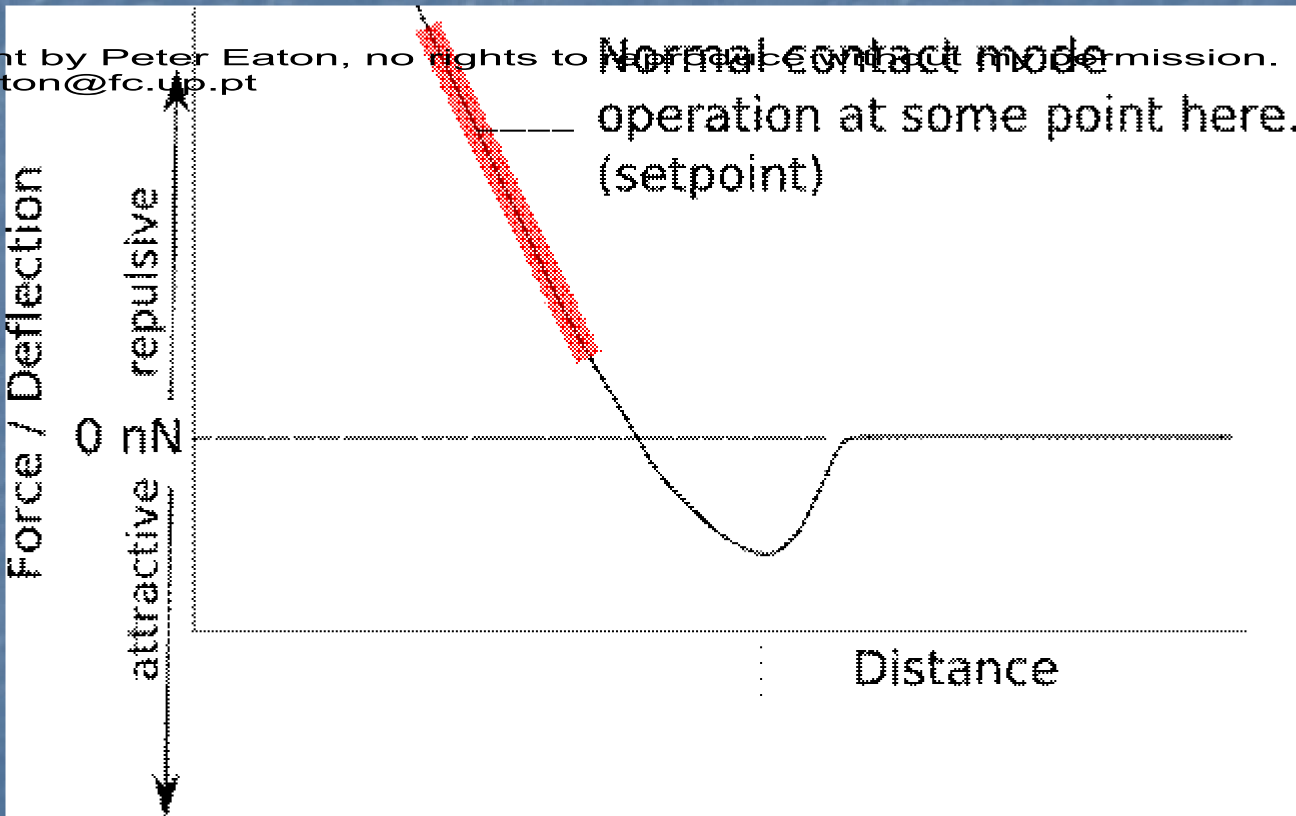
○The sample is moved laterally and vertically by a piezo electric element – can accurately move tip a few nm or a few µm.

Contact Mode



Contact Mode

In contact mode the contact is maintained at a fixed value in the repulsive regime.

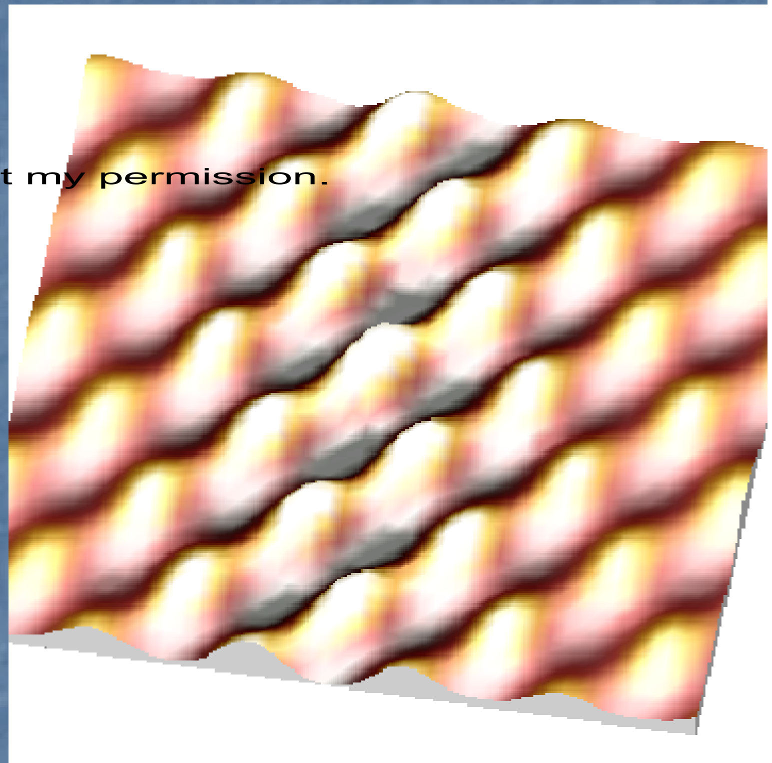


Operating regime – contact mode

Contact Mode

○ Contact mode can give extremely high resolution.

○ The image here shows the atomic lattice of Au(111) in air.



○ However, it leads to high lateral forces applied to the sample.

○ This can be a problem when imaging very soft samples, or poor adhering particles on a surface.

○ Being in contact with the surface allows some additional properties to be measured.

Contact Mode – Other signals

○ The height data is generated by the distance the piezo has to move to maintain the deflection setpoint.

○ However, other signals may be recorded simultaneously.

○ For contact mode, deflection, and friction signals are available.

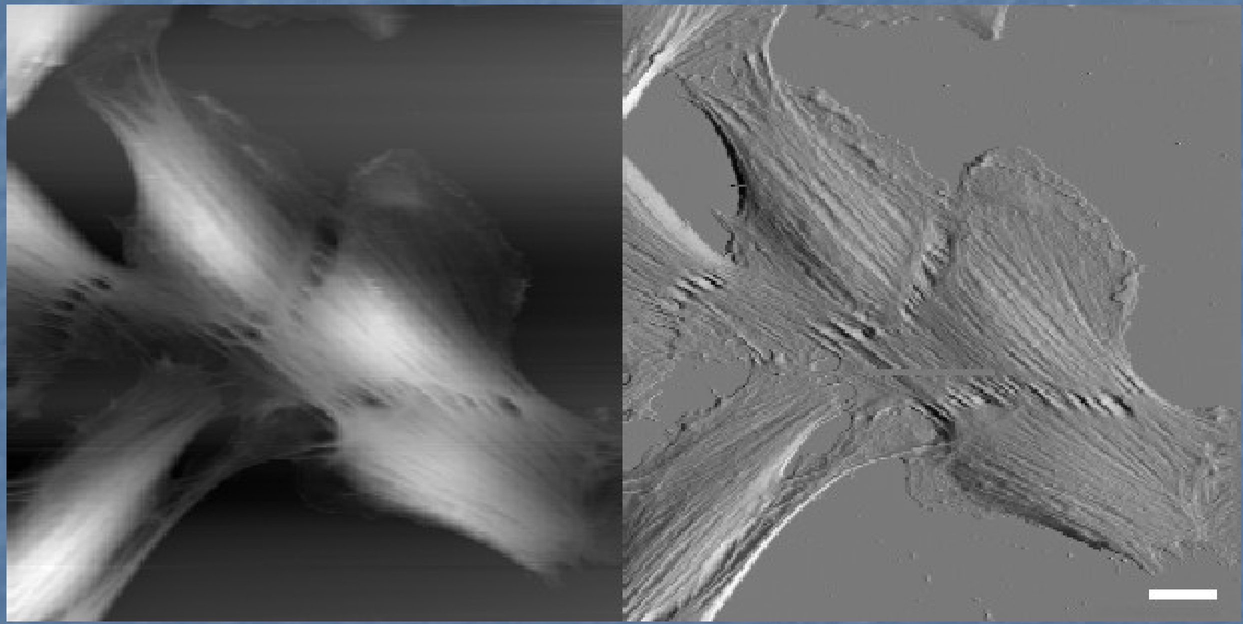
○ The deflection signal is the error signal for contact mode AFM. To optimize the topographic images, the contrast in the deflection image is minimized.

○ However, sometimes deflection images are published as they show clearly the shape of the sample, and can reveal hard to spot topographic features.

Contact Mode

- Contact mode has a relatively quick response to large height changes

- This can make it quite suitable for cell imaging, despite the large forces involved

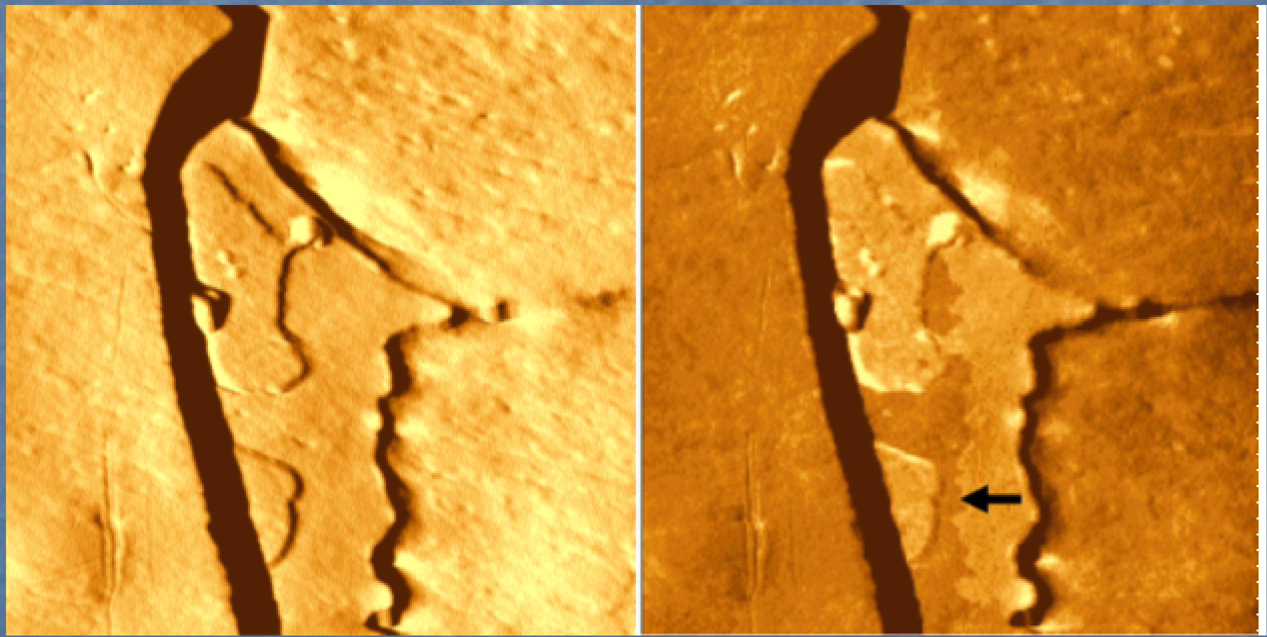


Rat Kidney Fibroblasts by contact mode, topography (left) and deflection (right).

Parak et al., Biophys. J., 76, (1999)

Contact Mode – Other signals

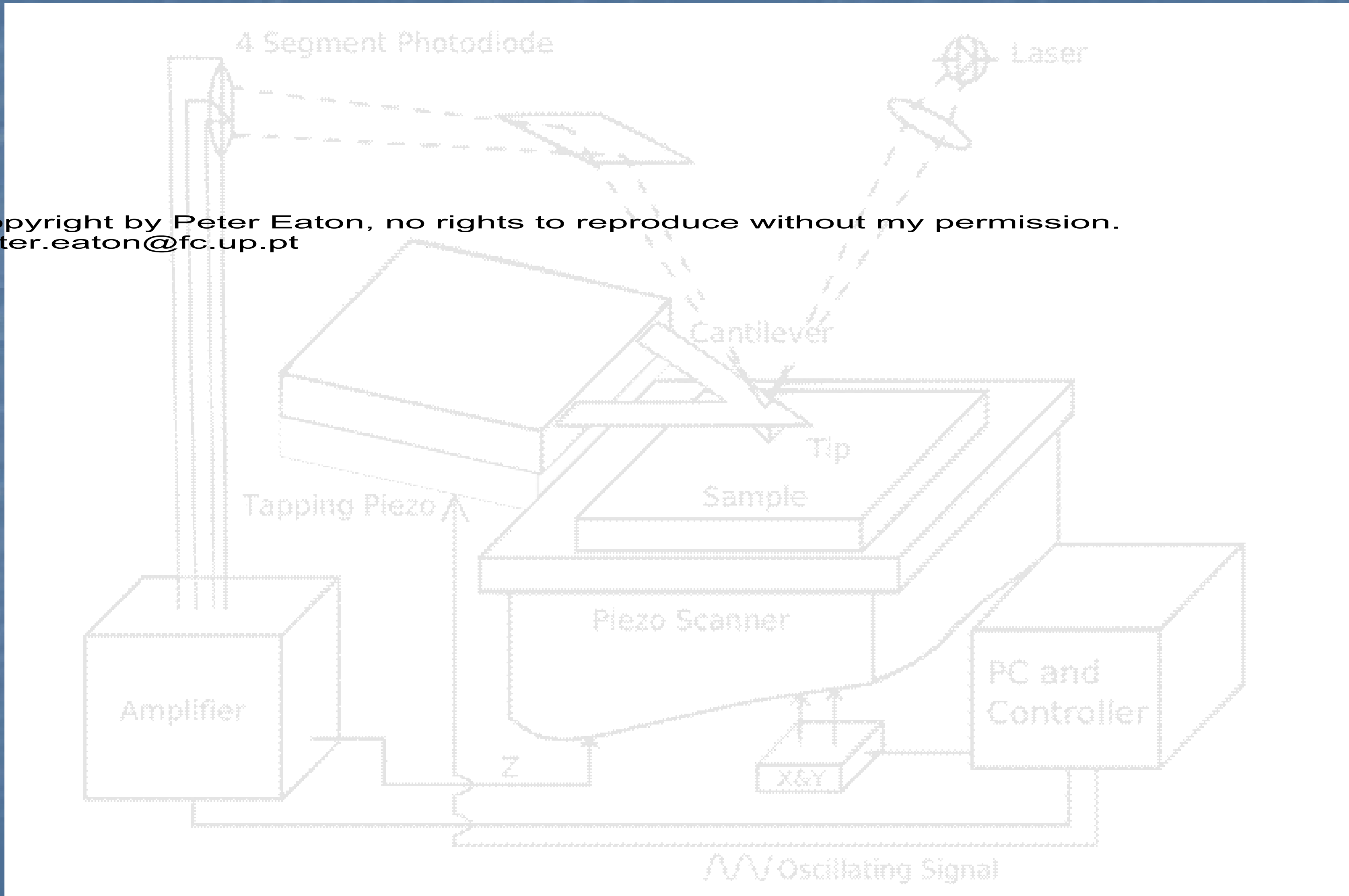
○Friction, or Lateral Force Microscopy (FFM or LFM) measures the lateral twisting of the cantilever as it is scanned along the sample.
○LFM can show material contrast, although it also contains topographical information.



Human hair in contact mode, topography (left, shaded) and friction (right).

J. R. Smith, University of Portsmouth

Noncontact / Tapping Mode



Noncontact mode

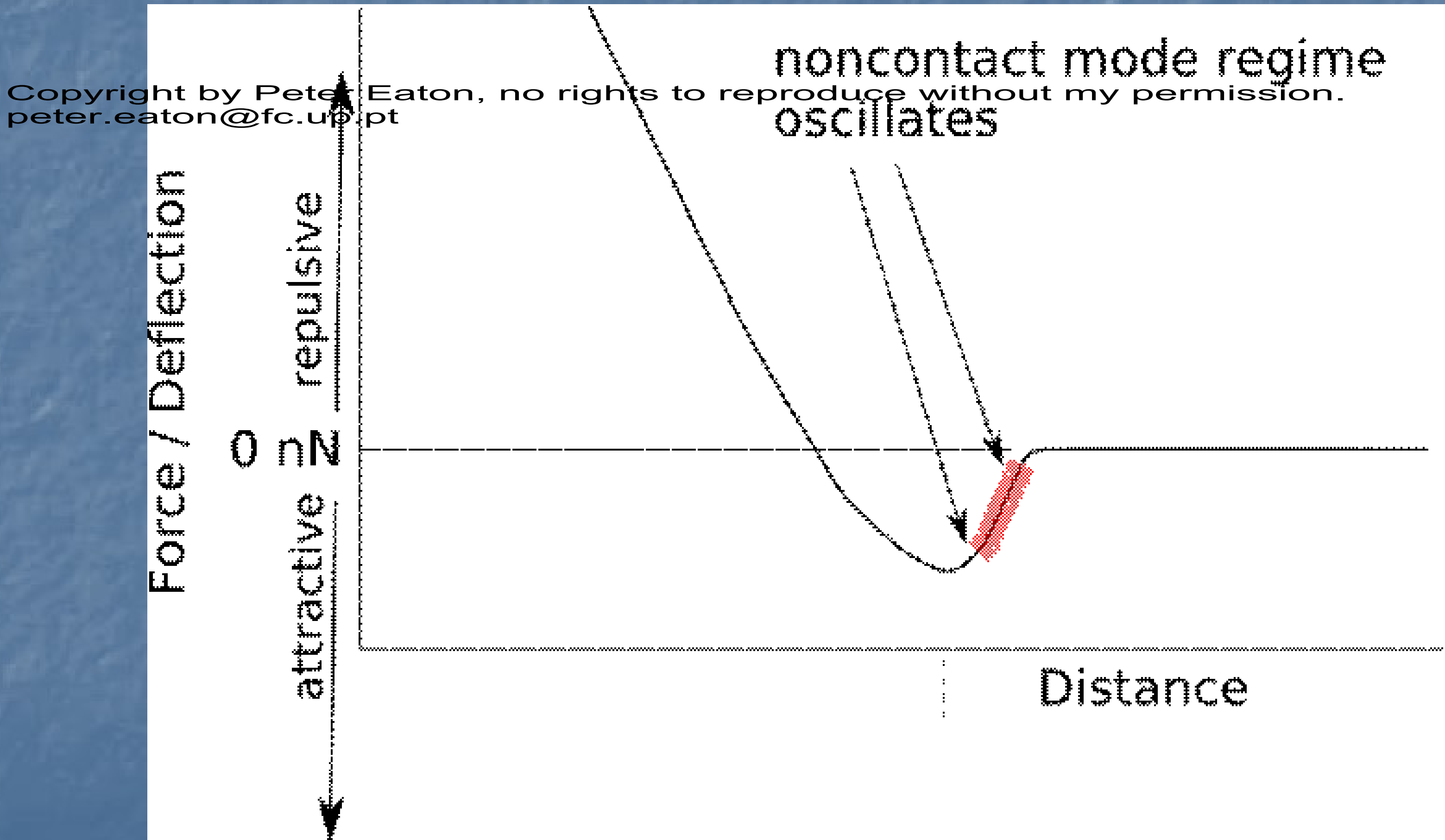
○ In noncontact mode, a smaller piezo attached to the tip oscillates it vertically.

○ The oscillation is highly sensitive to short range force between the tip and the sample.

○ The frequency of oscillation is used for feedback to keep the tip very close to the sample.

Noncontact Mode

In noncontact mode the tip oscillates within the attractive regime.



Operating regime – noncontact mode

Noncontact

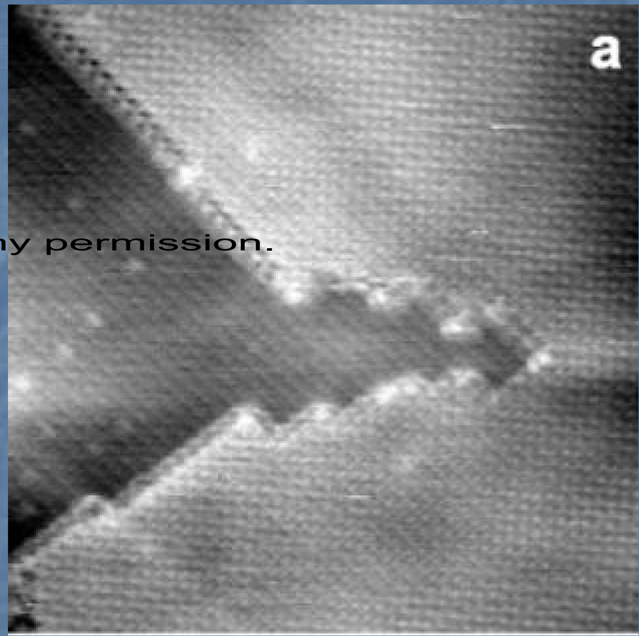
- Noncontact mode can give extremely high resolution, like contact mode.

- The image here shows atomic resolution is possible in vacuum.

- However, operating in the attractive regime is fundamentally unstable.

- This is particularly the case when working in air.

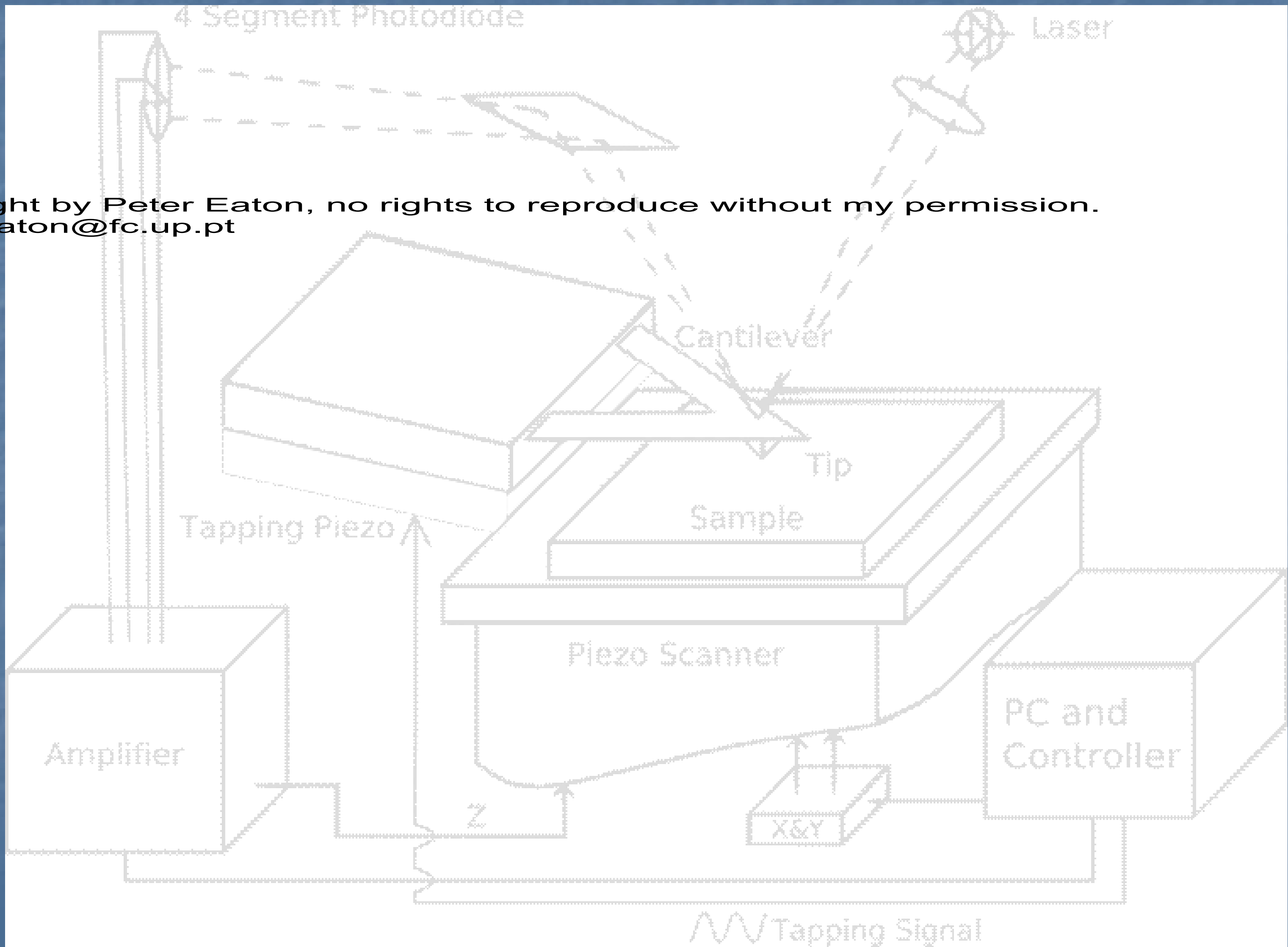
- So, noncontact mode is difficult to use, and less popular than tapping mode.



NaCl island on Cu(111)
Noncontact 18 x 18nm^2*

* Bennwitz et al Phys Rev B 62, 2074 (2000)

Noncontact / Tapping Mode



Tapping Mode

○ Like noncontact mode, in tapping mode a small piezo attached to the tip oscillates it vertically.

○ The oscillation is larger than used in noncontact mode, and the tip actually contacts the sample during each oscillation cycle.

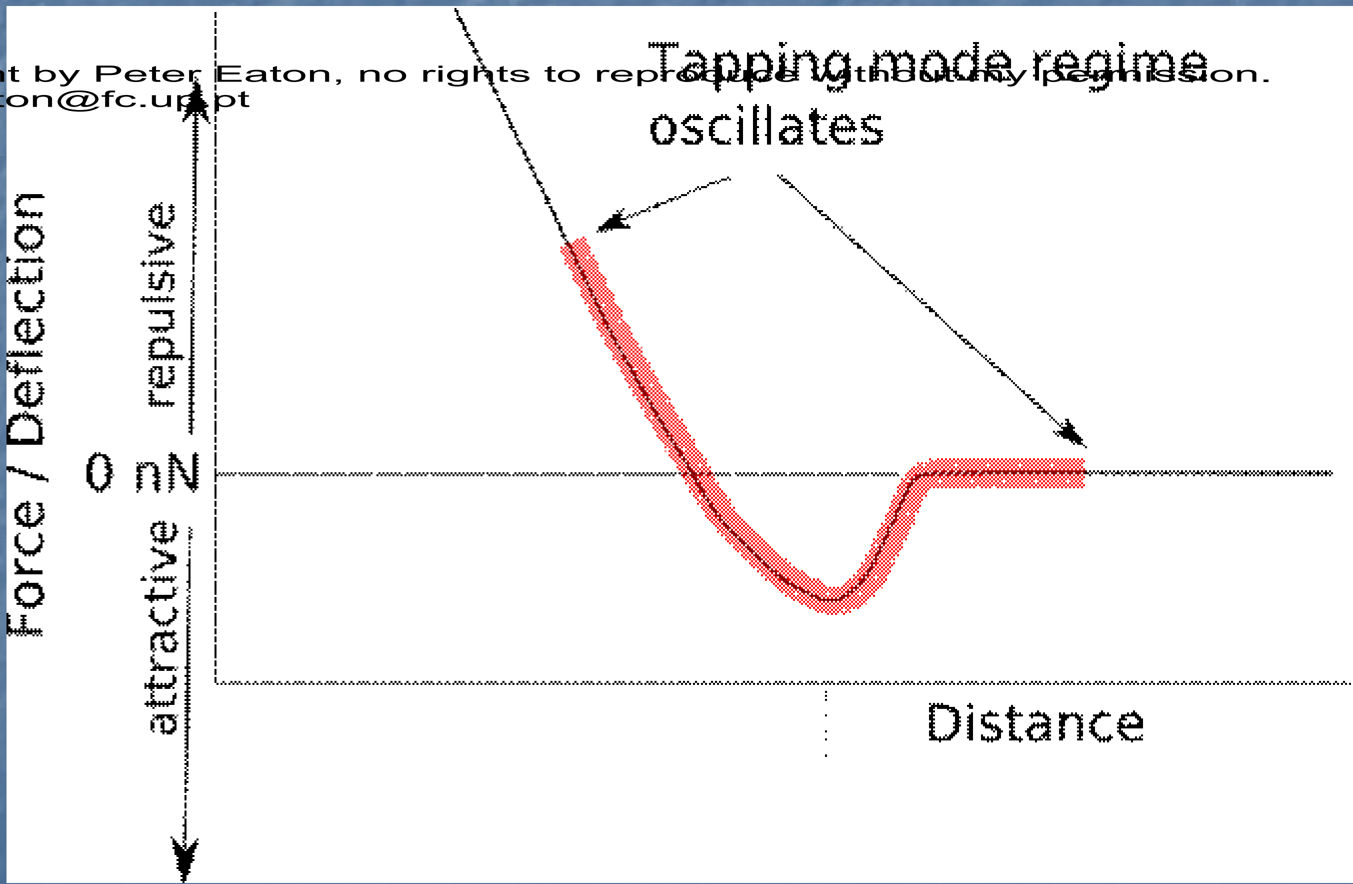
○ The amplitude of oscillation is normally used for feedback.

○ As Tapping Mode is trademarked, AFM manufacturers other than Veeco refer to this technique as:

- Intermittent Contact
- AC mode
- Dynamic Scanning Force Microscopy
- etc…

Tapping Mode

In tapping mode the contact oscillates from non-touching, through attractive to repulsive and back again.



Operating regime – tapping mode

Tapping Mode

○ The lateral forces present in contact mode are avoided in tapping mode.

○ But it is more stable than noncontact in air, as the tip actually touches the sample.

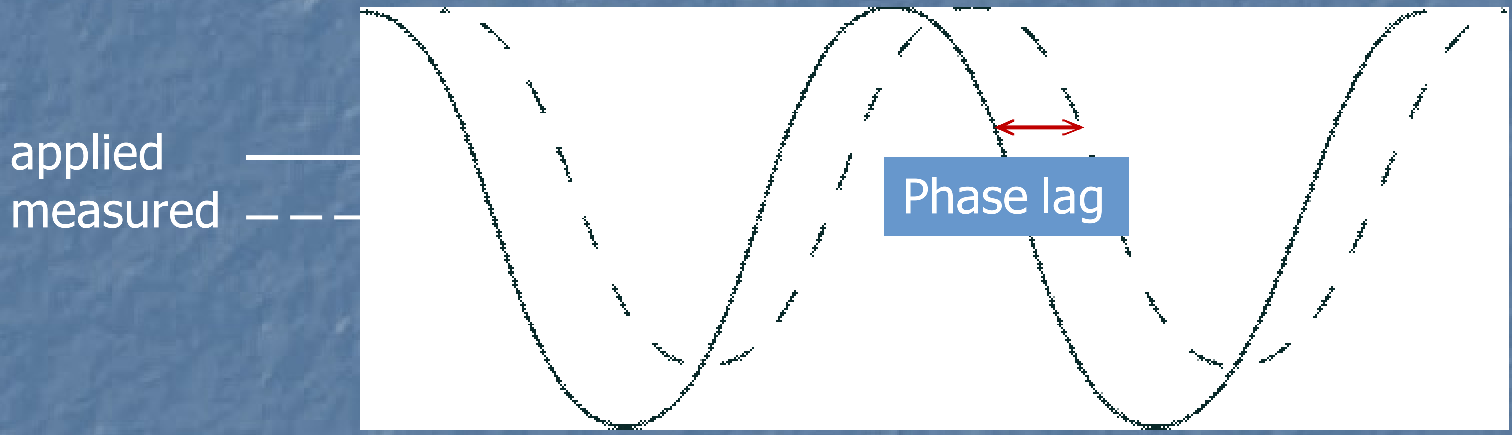
○ For most samples in air, tapping mode is the easiest technique to get good quality images, and is presently the most commonly used imaging mode in AFM.

○ Reports of *very* high resolution with tapping mode are limited, however.

Tapping Mode – Other Signals

- The error signal for Tapping Mode is the amplitude image – it shows essentially the same information as the deflection signal from contact mode.

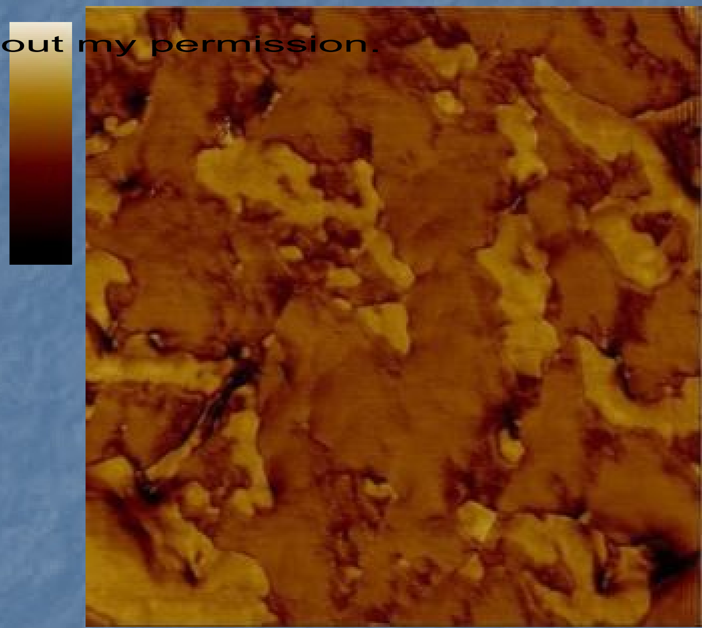
- The phase signal is also often displayed as an image.



- The phase signal is the phase lag of the tip oscillation *vs.* the applied oscillation.

Tapping Mode – Other Signals

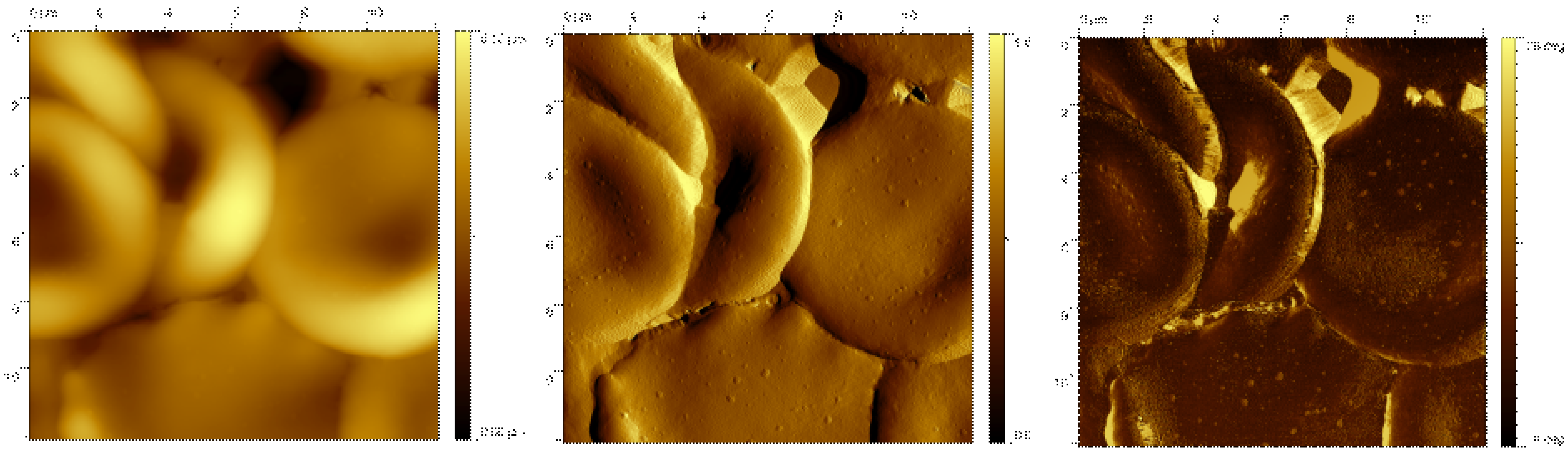
Phase images often show material contrast, although interpretation of the size of the phase signal is complicated.



Two component polymer blend, topography (left) and phase (right)

Tapping Mode – Other Signals

In the case that there is no material contrast, phase images generally look similar to amplitude images – both are affected by the topography in the same way.



Red Blood Cells, topography (left), amplitude (middle) and phase (right)

Advantages and Disadvantages of AFM as a Microscopy Technique

<u>Advantages</u>

- Nanometre / atomic resolution
- Accurate height measurements to within 1 Å
- No requirement for metallic sputter coatings
- Does not require UHV conditions
- Does not use an electron beam
- Ability to perform *in situ* studies in aqueous environments
- Measurement of local surface properties
- Manipulation of surfaces on sub-nanometre scale
- Data may be represented in a variety of ways

Advantages and Disadvantages of AFM as a Microscopy Technique

<u>Disadvantages</u>

- AFM is relatively slow (usually)
- Potentially a destructive technique
- The tip can affect the results, a lot!
- Can have high consumable cost (cantilevers)
- Sample must be quite flat (features < 10µm) and small areas are imaged

Data Representation

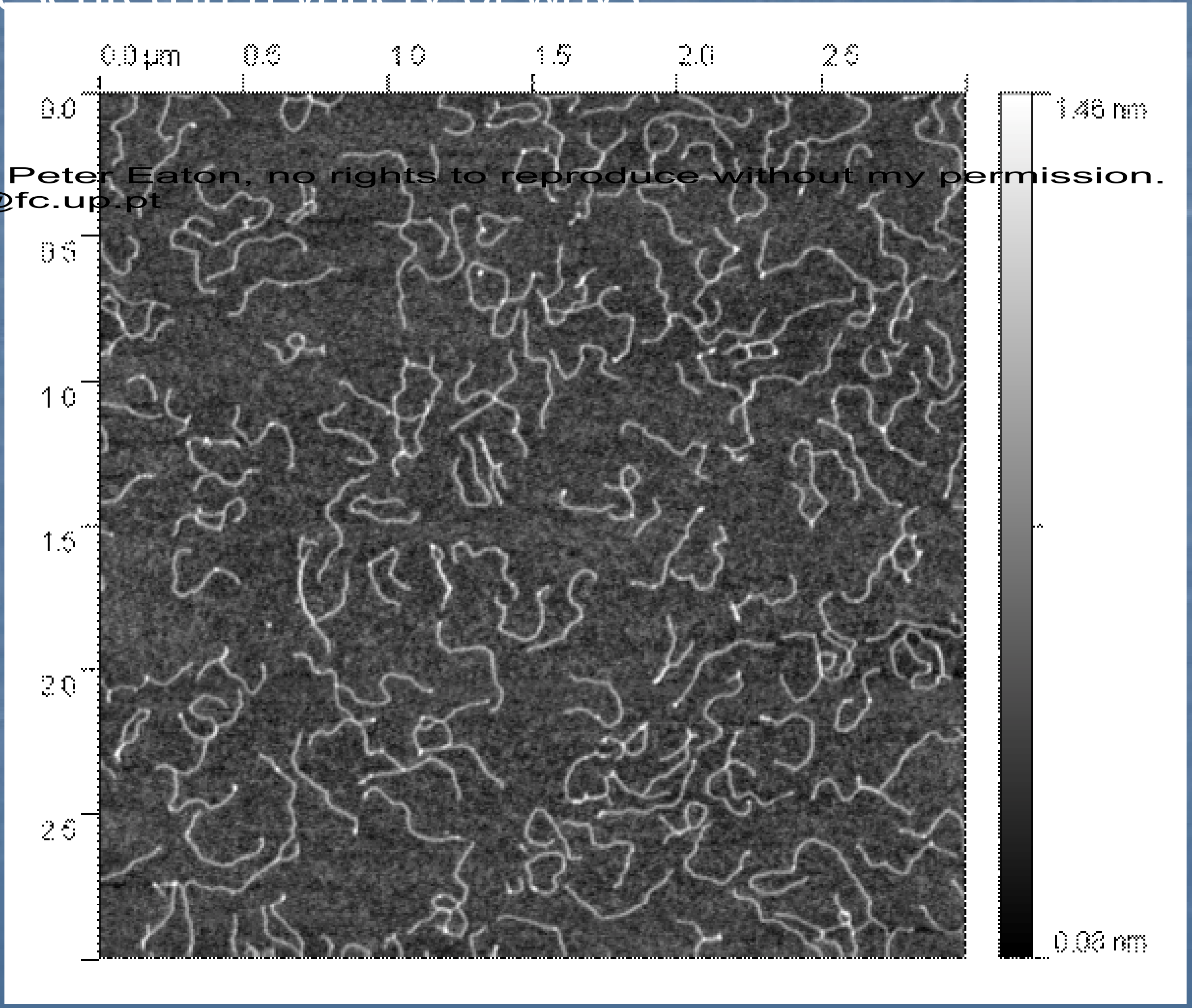
Because the data collected by the AFM is digital, it is particularly easy to make measurements, and collect statistics on the images.

Some of the common measurements are:

- Line profiles – height/width measurements
- Slope and angle measurements
- Roughness
- Fractal dimension
- Particle counting – including VOLUME
- Surface area *vs.* projected area
- Autocorrelation
- Fourier transform analysis

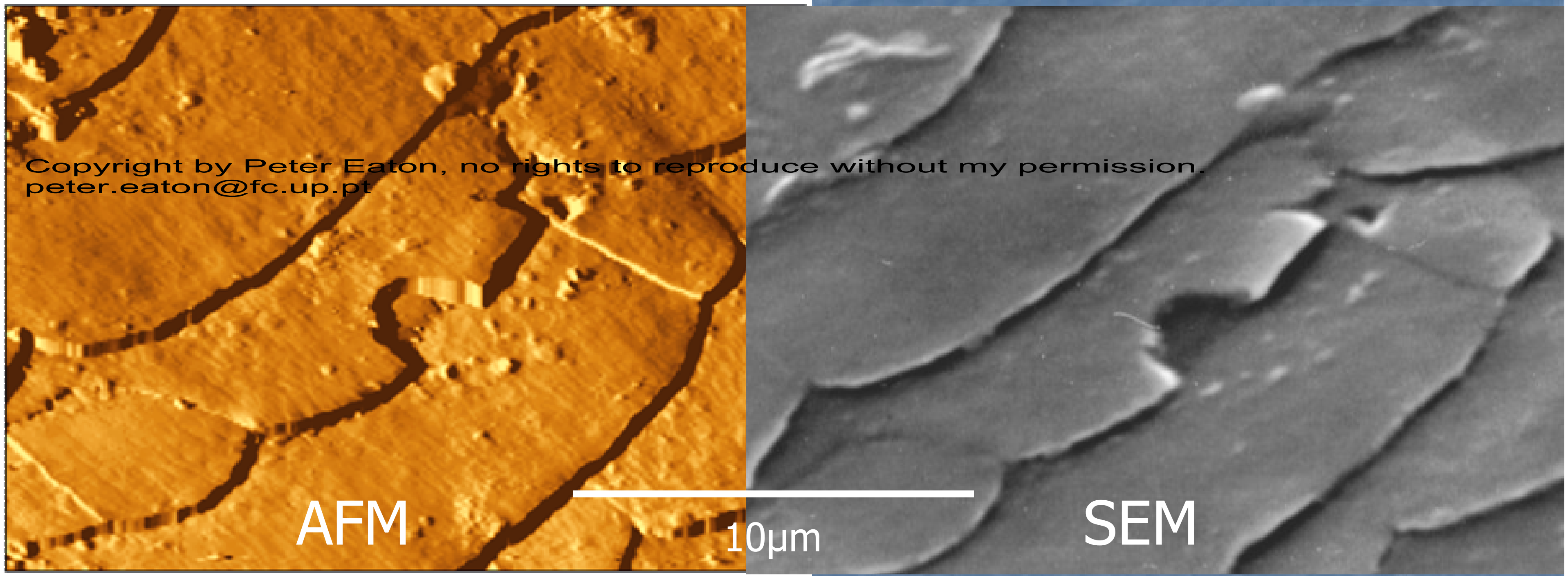
Data Representation

In addition the digital nature of the data means it may be represented in a variety of ways



Standard height colour scale representation

Data Representation

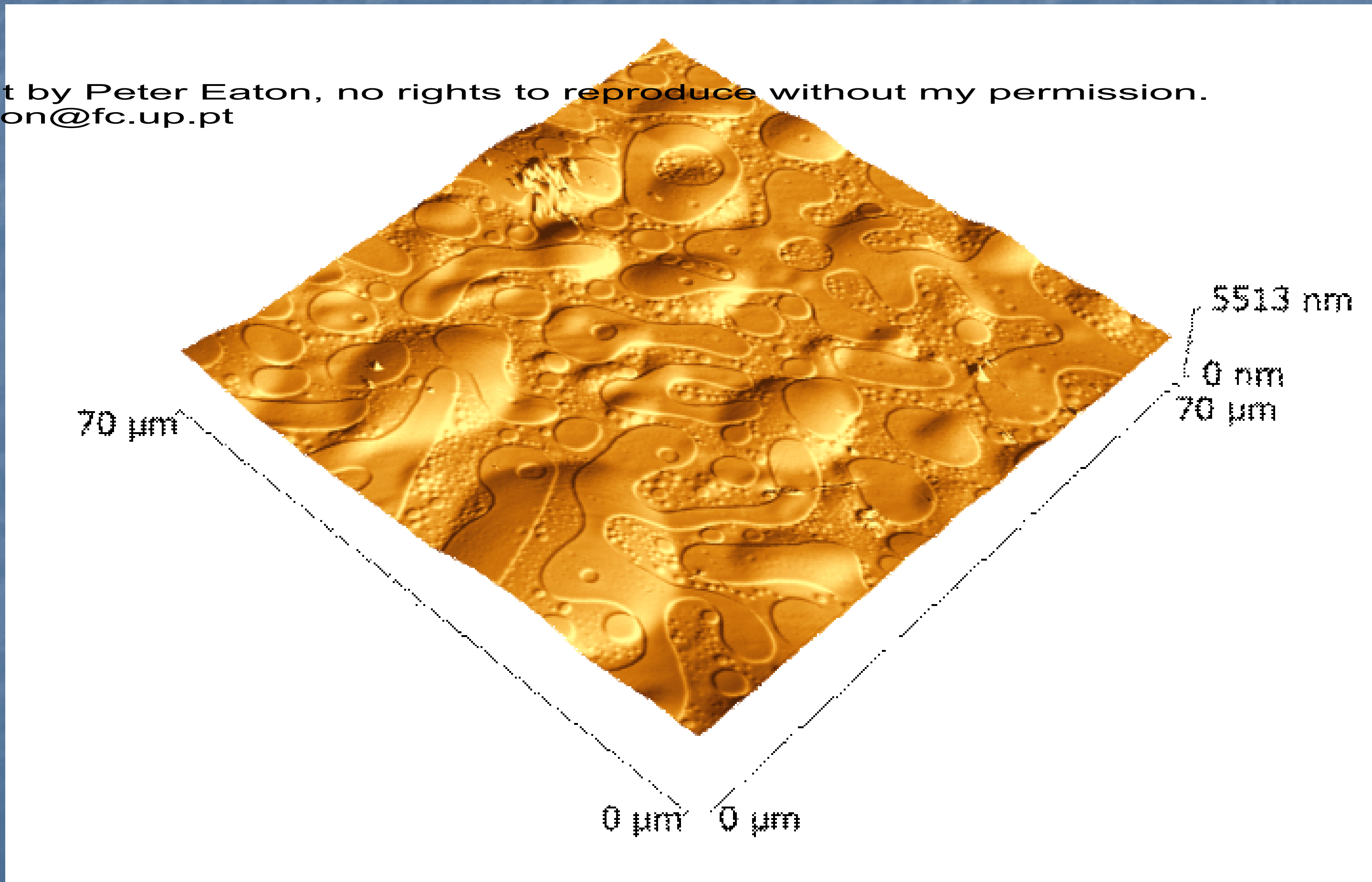


Comparison between AFM and SEM of human hair
- use of shading to enhance contrast

J. R. Smith, University of Portsmouth

Data Representation

In addition the digital nature of the data means it may be represented in a variety of ways…



Polymer blend rendered in 3D and shaded

Spectroscopic Modes

- AFM can measure molecular interaction forces directly – this is often termed Chemical Force Microscopy (CFM). Such techniques are also sometimes referred to as “force spectroscopy”.

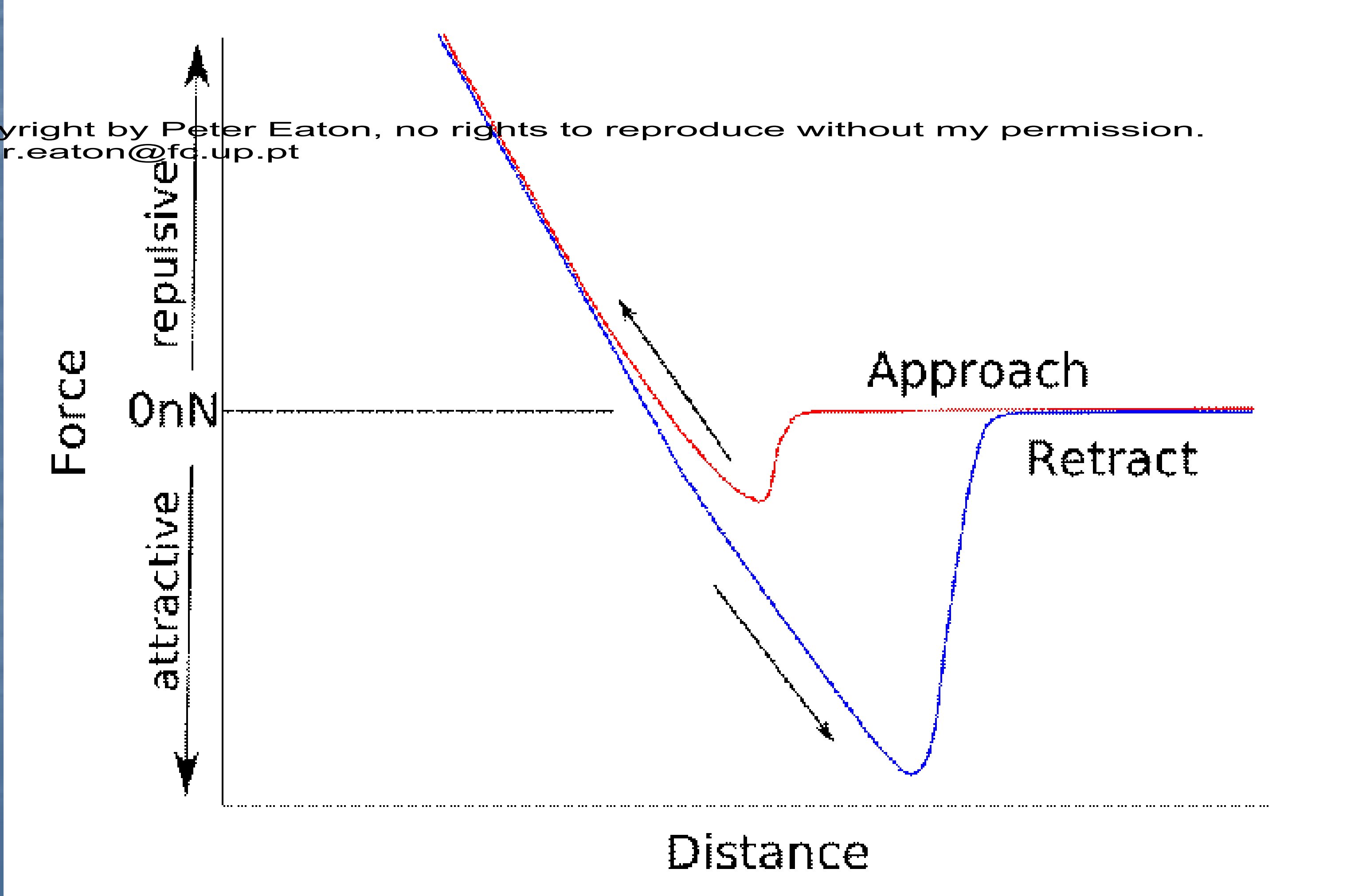
- One molecule of interest is chemically grafted to the AFM tip (e.g. by thiol-gold linkage), and the other to a flat surface.

- The AFM in then used to bring the molecules into contact, and can measure the force required to pull them apart.

- The deflection of the tip as it approaches, contacts and pulls off the surface is represented as a force curve.

Spectroscopic Modes

Approach and retract force curve

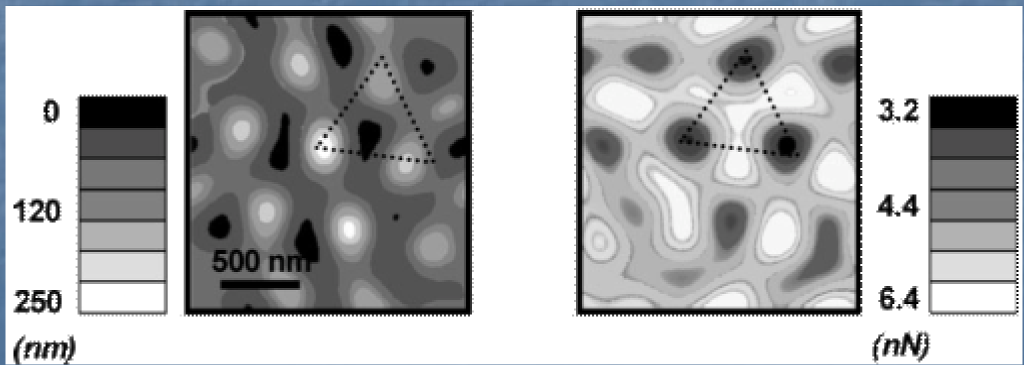


Spectroscopic Modes

CFM can give forces directly in nanonewtons – but care must be taken to ensure only one pair of molecules is probed, and usually several hundred measurements must be made to get adequate data.

Conditions, such as ionic strength, presence of cations, temperature etc may be changed during the experiment.

Data may be measured only in one place in the samples, or measurements mapped over the sample surface.



Topography(left), and Adhesion(right) maps of nanolithography pattern

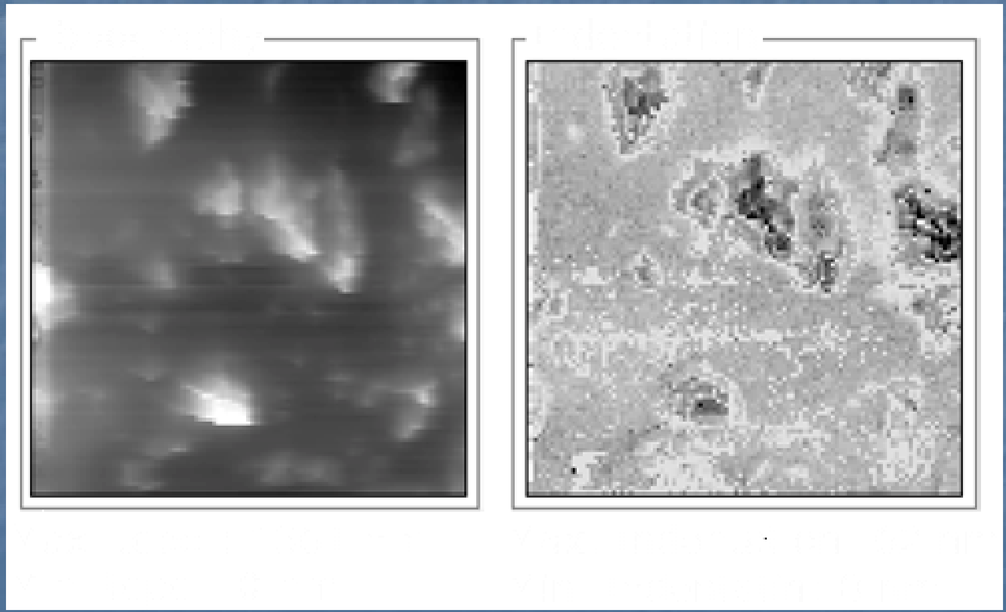
Valsesia et al, Adv. Funct. Mater. 16, (2006).

Spectroscopic Modes

Nanoindentation

The slope of the force distance curve in contact gives, in principal, the stiffness of the sample.

Again, this might be measured in one place, or could be mapped.



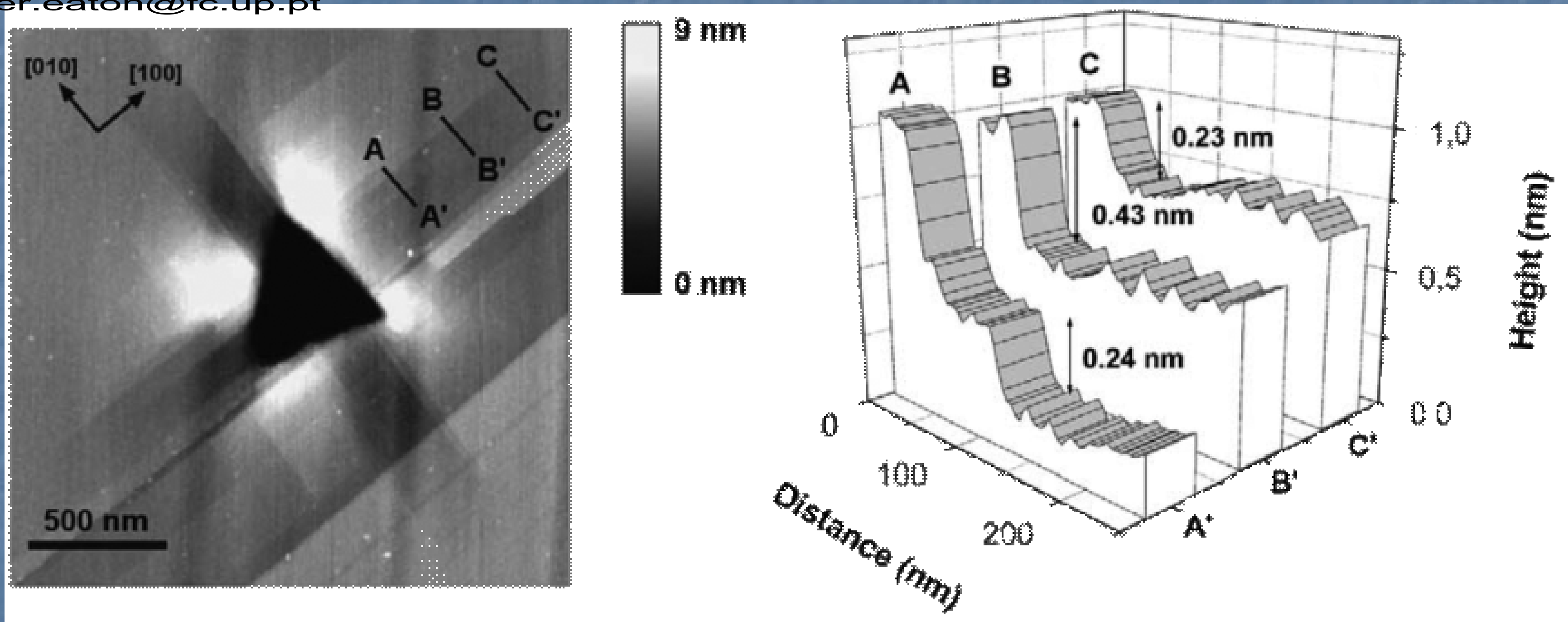
Height and Indentation images on filled siloxane polymer

Eaton, P., *et al.*, Langmuir 18, 10011-10015 (2002).

Spectroscopic Modes

Nanoindentation

Another method is to perform nanoindentation, and then use AFM to image the result.



Nanoindentation and dislocation analysis on MgO

Gaillard et al, Acta Materialia 51 (2003) 1059–1065

Spectroscopic Modes

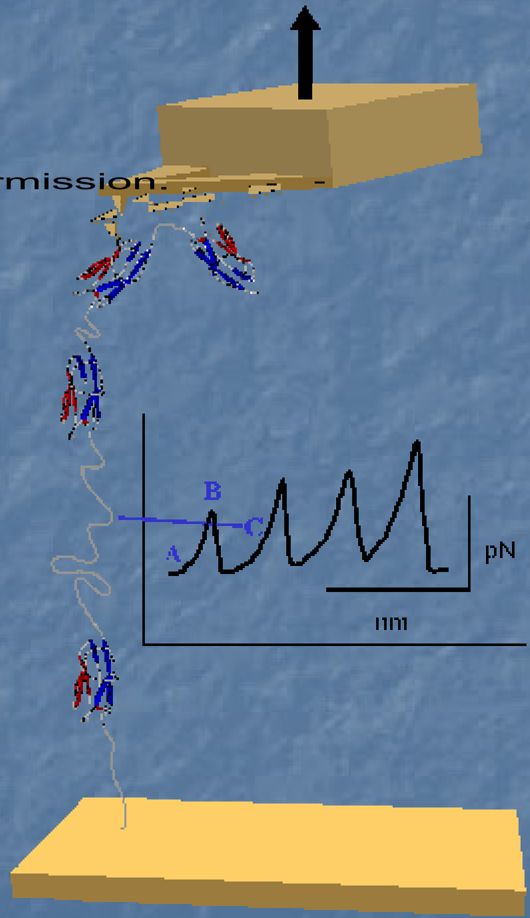
Protein unfolding

Similarly to interaction studies, protein unfolding may by studied by AFM.

By anchoring one end of a large folded molecule (e.g. a protein) to a surface, and picking up the other end with the AFM tip one may mechanically unfold the molecule.

Forces (for a muscle protein) were in the 100's of picoNewtons range.

Results seem to be somewhat different to traditional (thermal or chemical) unfolding. However, may be *more* relevant for some molecules (e.g. muscle protein).



Brockwell, D., *et al.*, Biophys. J. 83, 458-472 (2002).

Surface Modification

The ability of AFM to precisely control the movement of the probe over the surface, has been widely used to perform surface modification on the nanoscale.

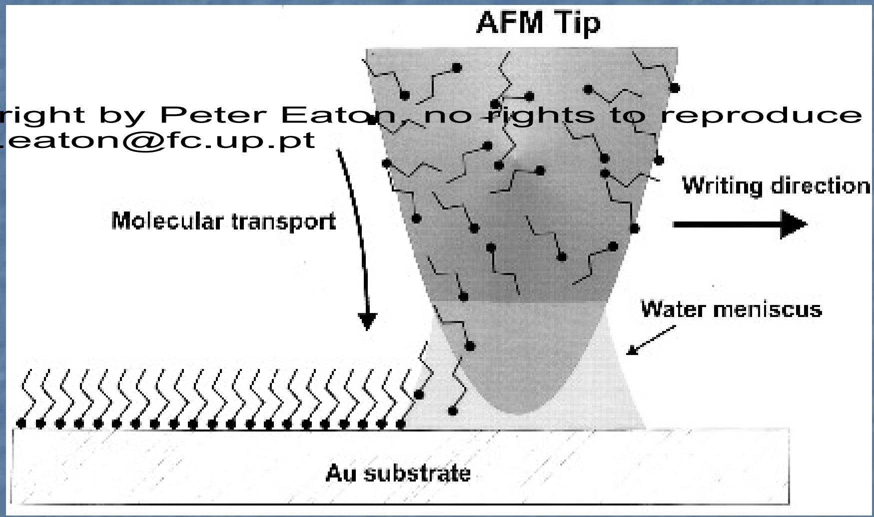
Some techniques used include:

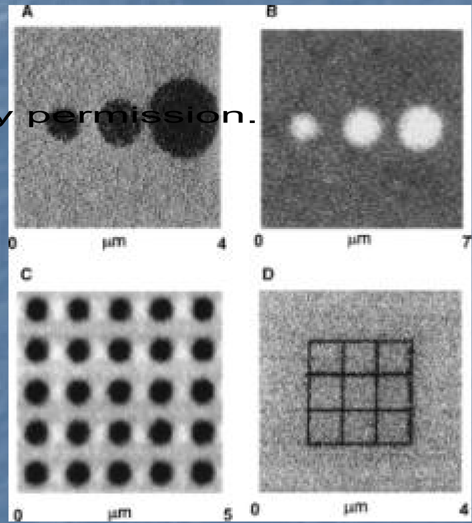
- o Scanning probe microscopy oxidation (e.g. tip induced oxidation of metals and semiconductors)*
- o Nanoscratching†
- o Dip-pen Nanolithography

*Stievenard et al, Progr. Surf. Sci. 81 (2006). †Chen et al, Nanotechnology 16 (2005).

Surface Modification

Dip-pen Nanolithography (DPN)



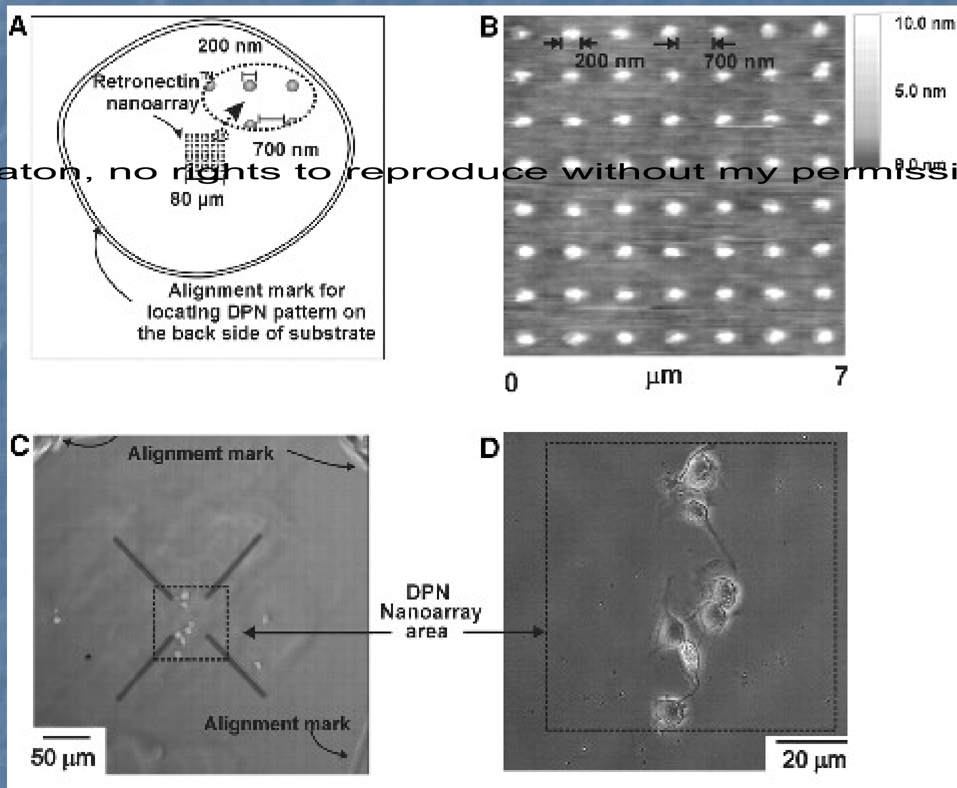


- By dipping the AFM tip in a solution and then scanning it over the surface, controlled patterns of (bio)molecules may be formed.
- Features may be a small as 30 nm diameter.
- Examples include DNA; proteins etc.

Piner RD *et al.*, Science 283 (1999)

Surface Modification

Dip-pen Nanolithography (DPN)



DPN Pattern made from glycoprotein, then immersed in medium containing fibroblast cells; cells adhere to 200 nm features written onto the surface.

Lee, K.B *et al.* Science 295, 1702-1705 (2002)

AFM Instrumental Aspects

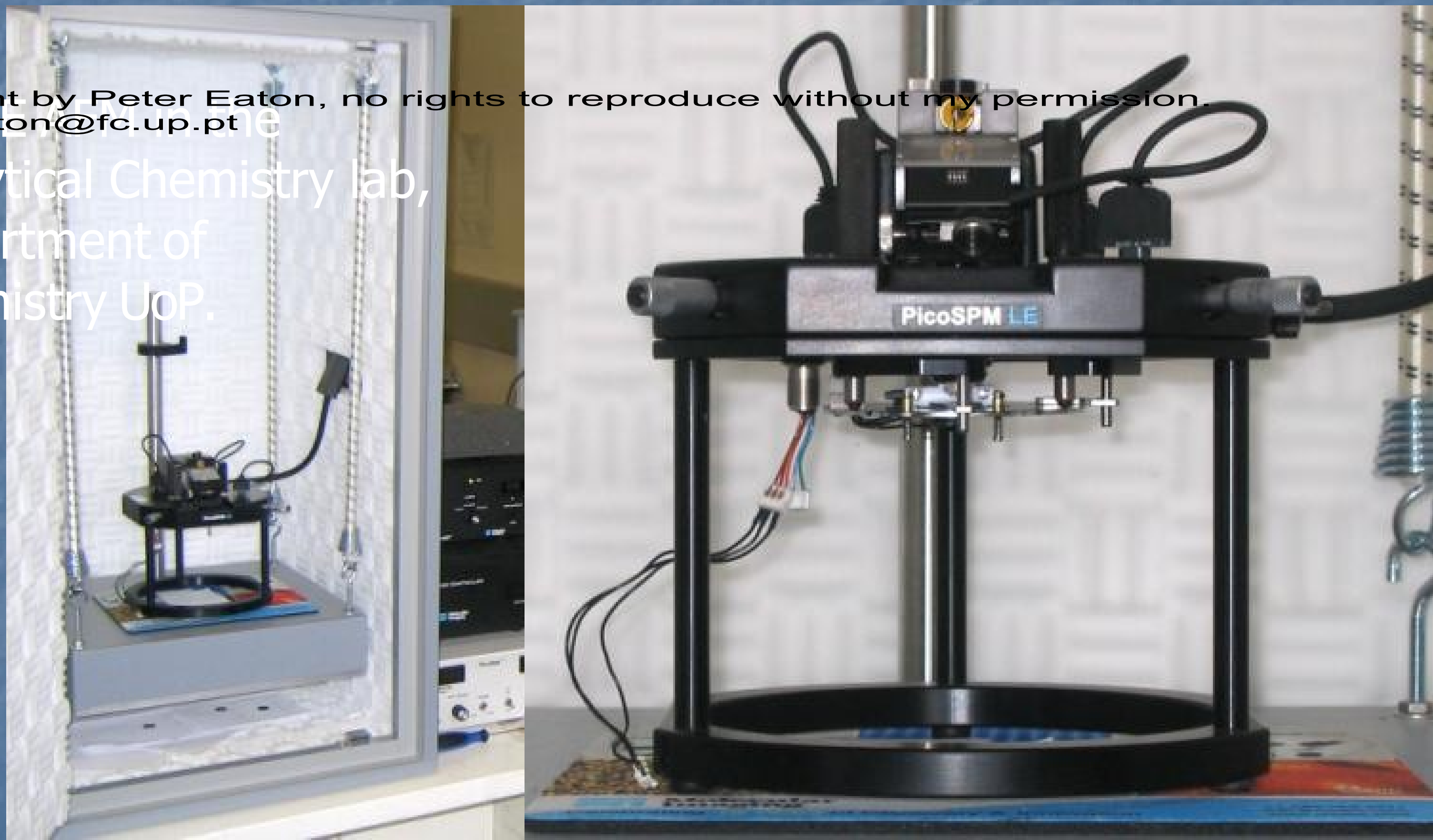
AFM instruments come in two configurations: tip-scanning or sample-scanning AFMs.

Example of a sample-scanning AFM:

Veeco Multimode with Nanoscope IVa controller in the CEMUP.

AFM Instrumental Aspects

Example of a tip scanning AFM:



PicoLE AFM in the Analytical Chemistry lab, Department of Chemistry UoP.

Tip scanning AFMs have the advantage of easy access to the sample area, and the possibility to scan large samples.

AFM Instrumental Aspects

Tip scanning AFMs are also relatively simple to integrate with optical microscopy.

Image shows a JPK Nanowizard 2 mounted on standard inverted optical microscope

This can allows simultaneous measurement of optical, florescence and AFM images

AFM Instrumental Aspects

A recent innovation are AFMs designed specifically to have improved resolution in the z-axis.

These are specifically aimed towards use in spectroscopic modes.

An instrument was recently developed with only 1D movement.

Calculations and noise measurements suggest that the limitation on measurements of forces is about 6 pN*.

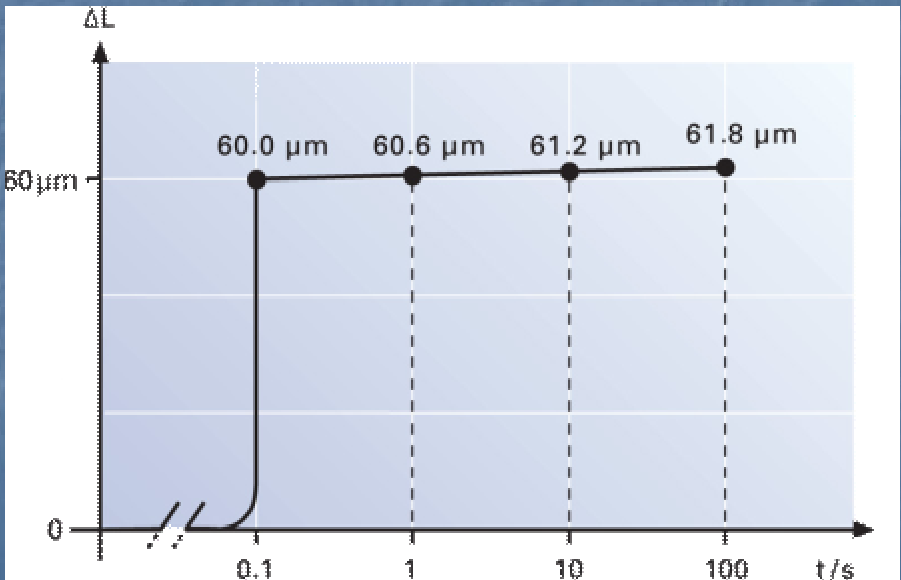
*T. Schäffer et al, Nanotechnology 16 (2005)

AFM Instrumental Aspects

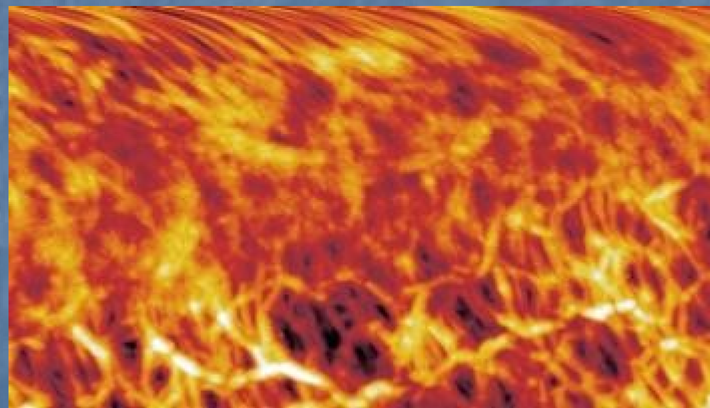
Scan linearisation

Normally the response of piezo scanners is nonlinear. This is taken into account by the complex calibration factors in the AFM controlling software, however it is not perfect.

This leads to a number of artifacts such as scanner creep.



The response of a piezo to an instantaneously applied voltage



An example of the effect of scanner creep

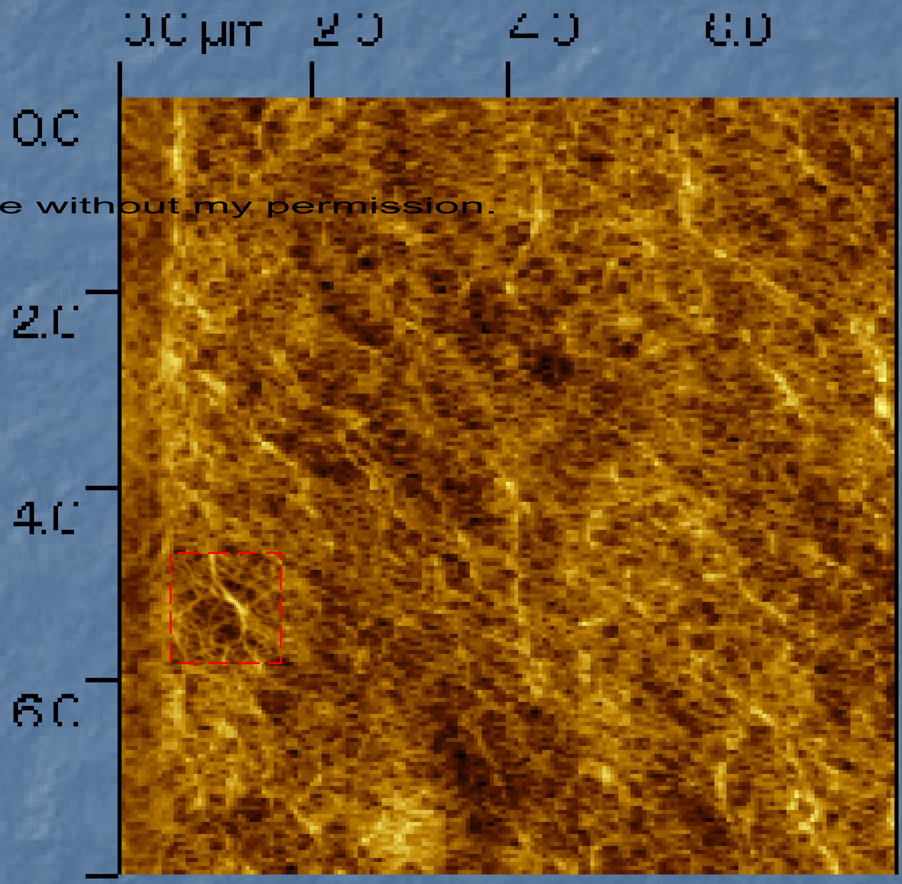
AFM Instrumental Aspects

Scan linearisation

Linearisation is also vital for lithographic applications.

Hardware linearisation senses the movement of the piezo scanner by external sensors (*e.g.* a strain gauge, interferometer or capacitive sensor)

This removes scanner creep, and allows reproducible positioning as seen right.

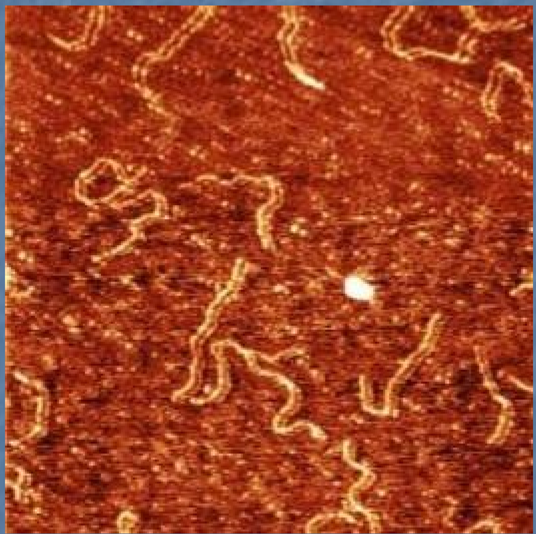


Biaxially Oriented Polypropylene

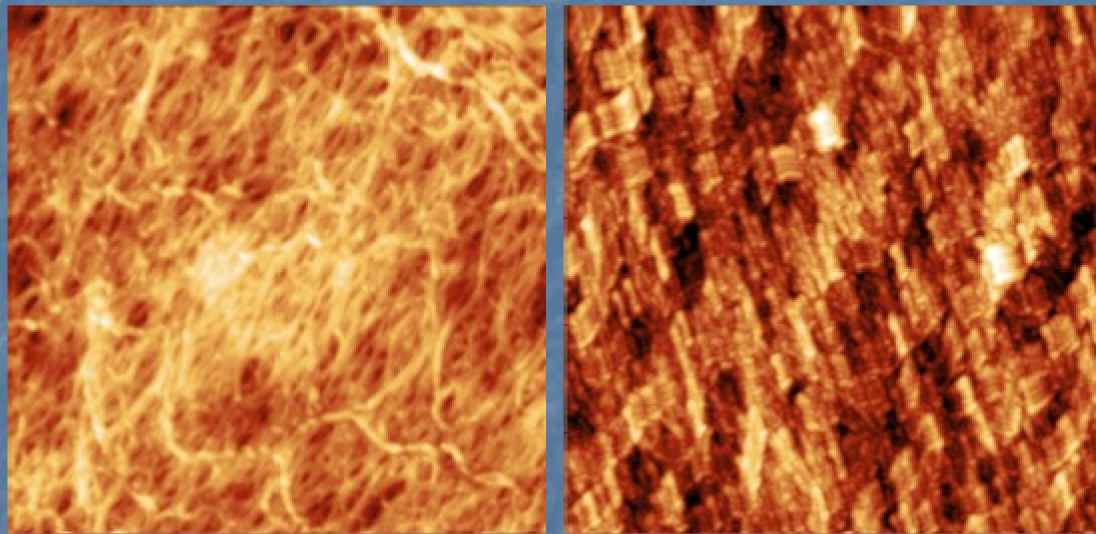
AFM Instrumental Aspects

Tip Effects

The quality, condition and suitability of the tip and cantilever is one of the most important instrumental aspects.



DNA molecules with "double tip"



The same sample imaged with clean and heavily contaminated tips

Other Techniques

MFM / EFM

Magnetic Force Microscopy (MFM)* allows us to measure magnetic fields with the AFM with moderate resolution.

Electrostatic Force Microscopy (EFM)† / Kelvin Probe Microscopy allows us to do the same for electrostatic fields.

Both techniques use "lift mode" – wherein an initial scan measures topography, then a second scan measures the fields with the tip out of contact with the surface.

Resolution by these techniques is limited due to the coated tips used, and the requirement to move the tip out of contact with the sample.

*MFM: Hartmann, Annu. Rev. Mater. Sci. 29, p. 53 (1999).
†EFM: Fujihira, Annu. Rev. Mater. Sci. 29, p. 353 (1999).

Other Techniques

SNOM

Scanning Nearfield Optical Microscopy is a way of obtaining high resolution in optical microscopy – beyond the so-called diffraction limit.

It relies on the light being emitted from an small aperture close (less than a wavelength distance) to the sample surface. A modified AFM is used to keep the probe close to the surface.

The most common design uses an optical fibre, which is metal coated, with a small aperture at the end.

Resolution is practically limited by the size of the aperture (normally 50 - 100nm)

Using light allows access to a variety of techniques eg. Raman or fluorescence techniques.

Conclusions

o AFM is a highly versatile microscopy technique, able to image a wide variety of samples.

o AFM has extremely high resolution, and allows rapid dimensional measurements with sub-Ångström accuracy.

o Measurements in vacuum, air, other gases, aqueous or organic solvents are possible.

o Different modes, signals, and related techniques allow the measurement of surface properties other than topography.

o Recent instrumental developments are allowing new levels of sensitivity and accuracy.