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Atomic Force Microscopy: touching invisibles

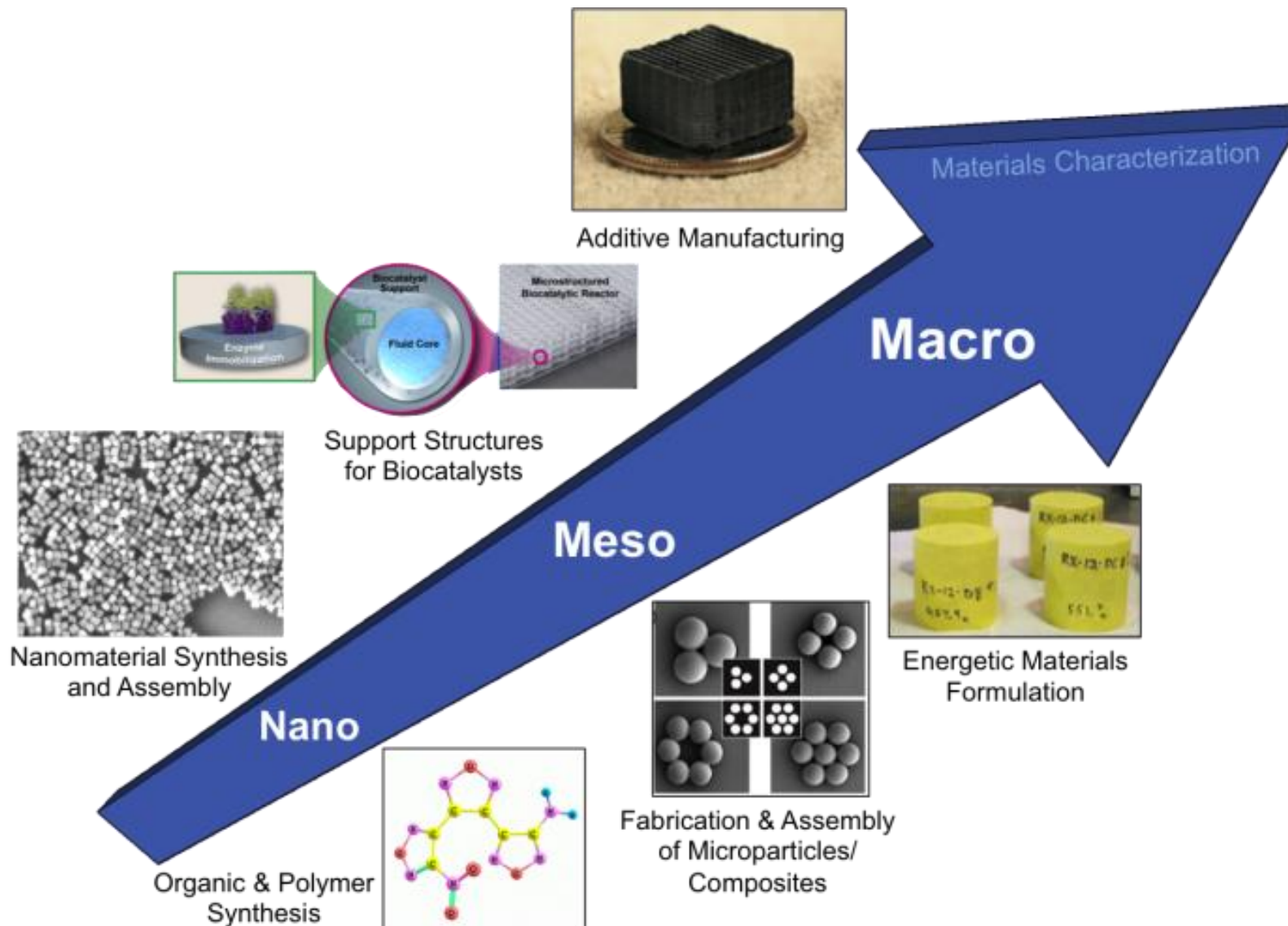
There's plenty of room at the bottom

Richard Feynman,

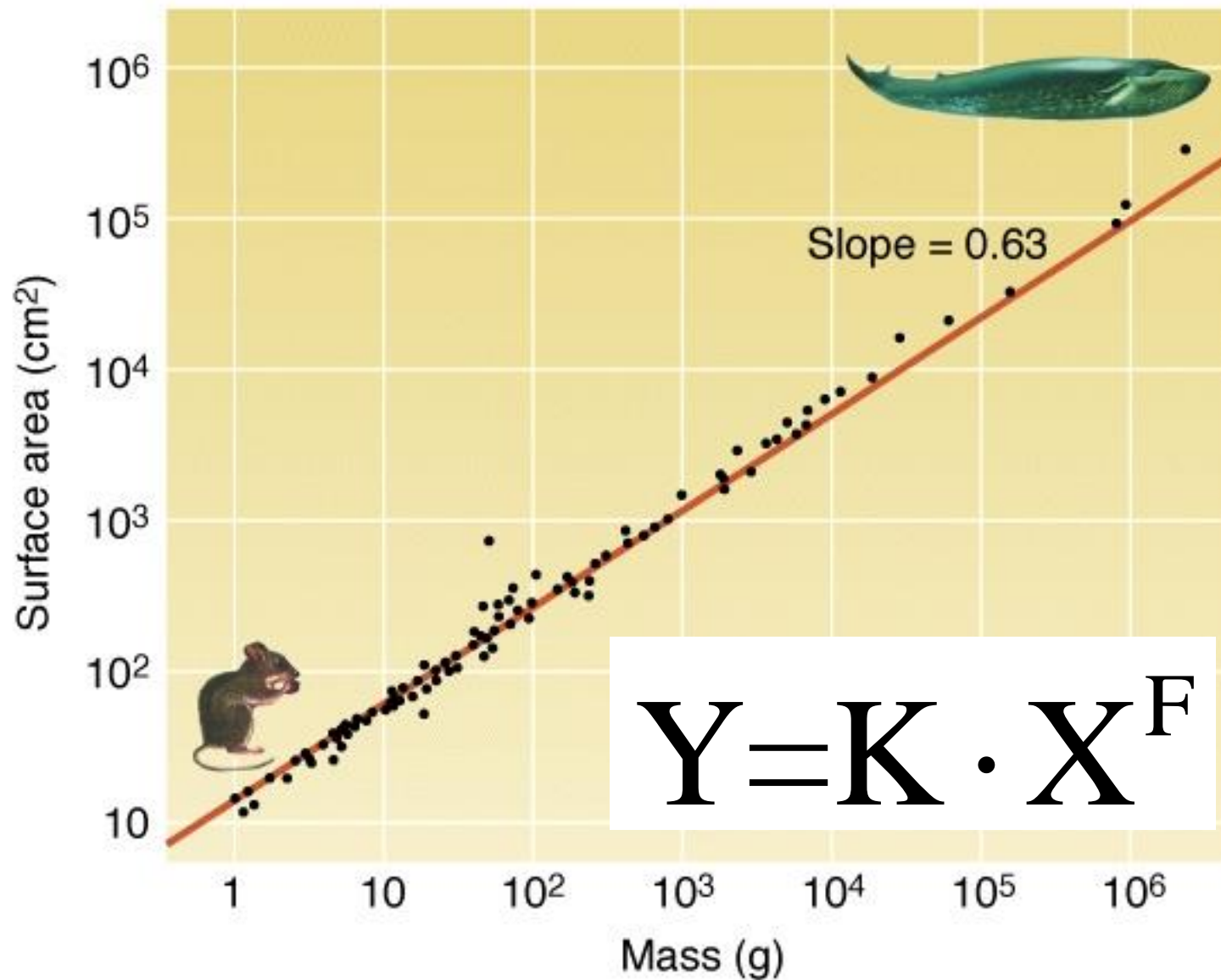
Meeting of the American Physics Society at Cal-Tech, 29/12/1959



What is the length scale?

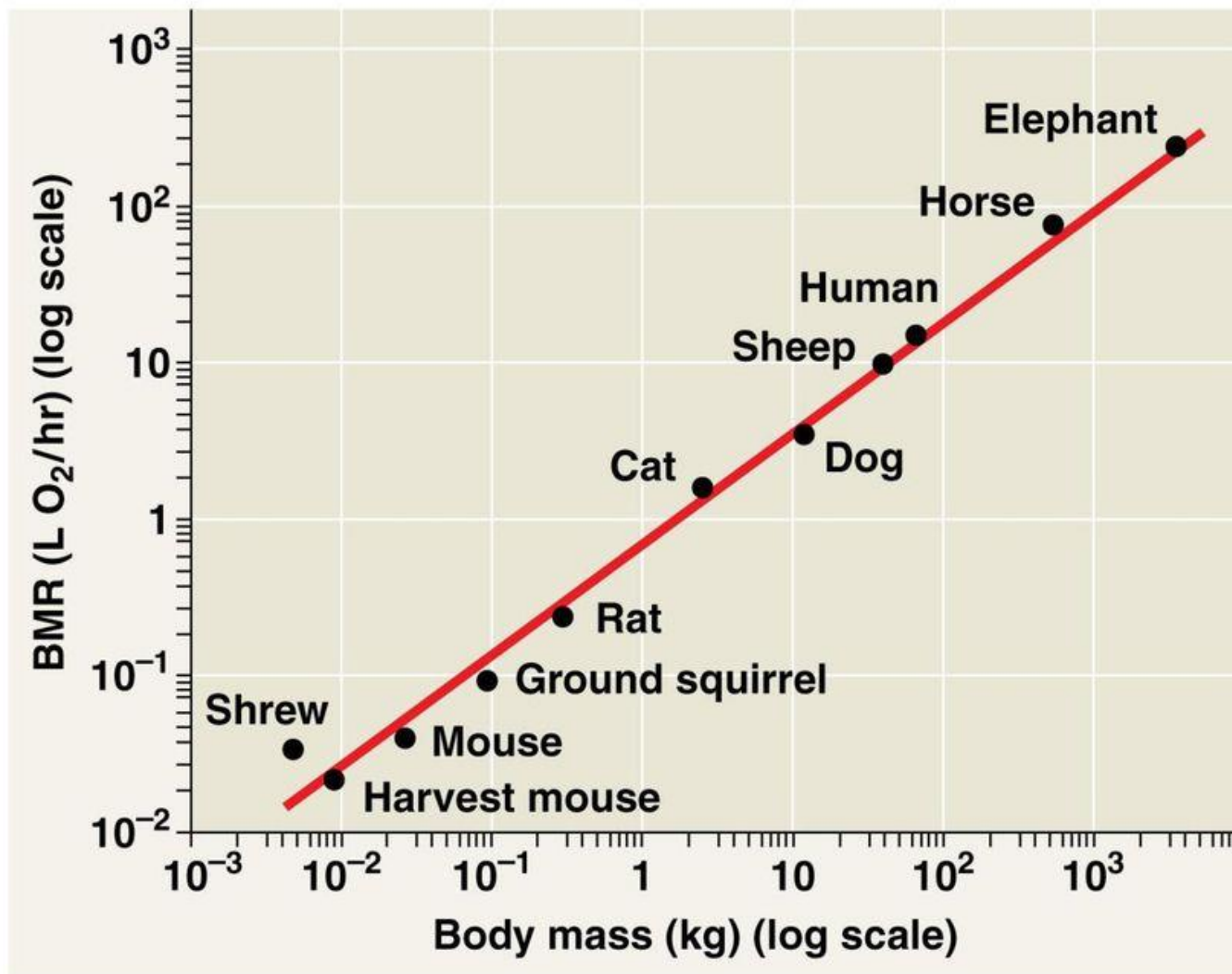


Problem – non-linear scaling



Allometric scaling

Figure 40.19a

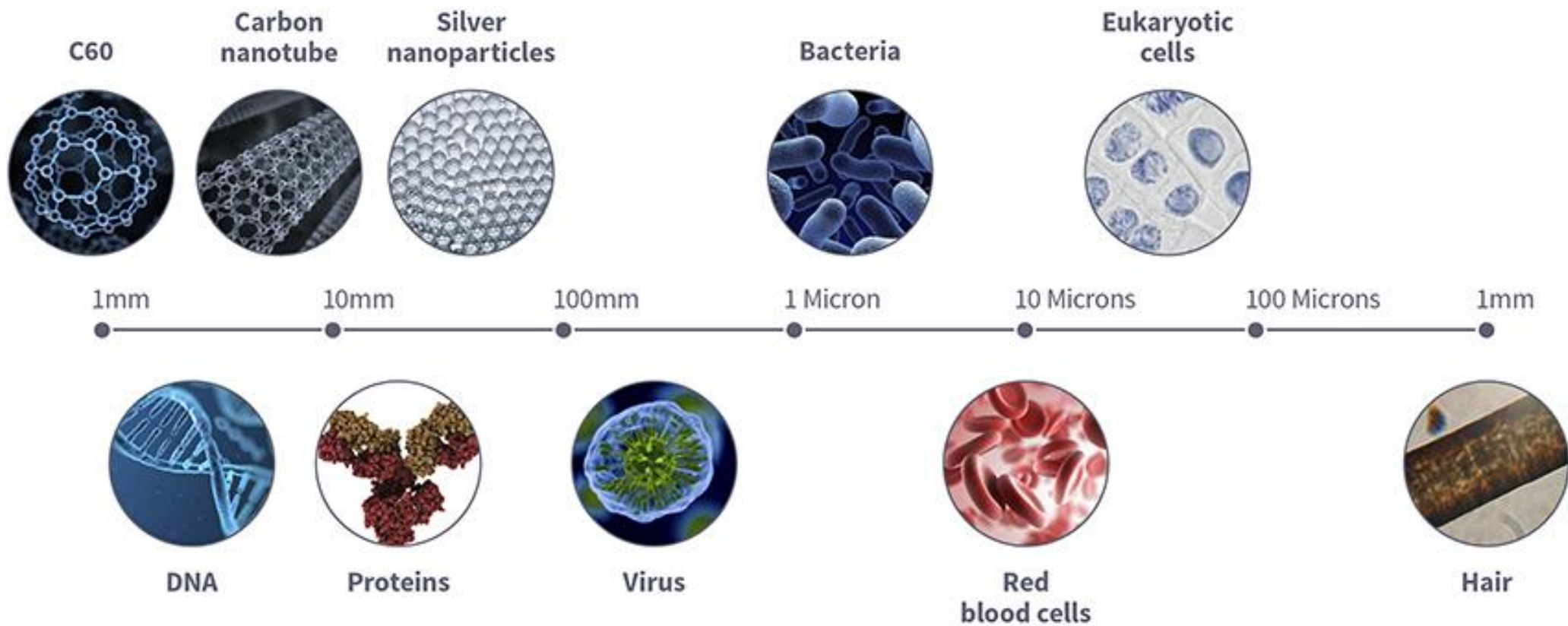


(a) Relationship of basal metabolic rate (BMR) to body size for various mammals

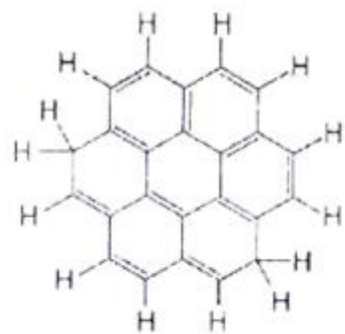
Things change with the scale!



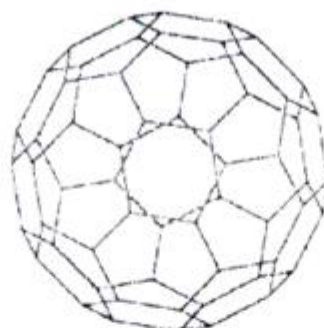
How small is 1 nanometer?



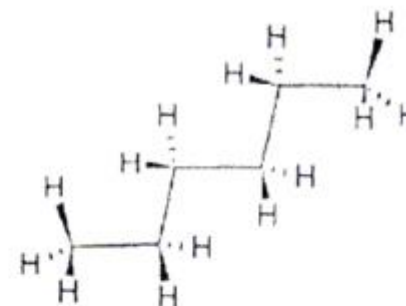
Particle configuration matters



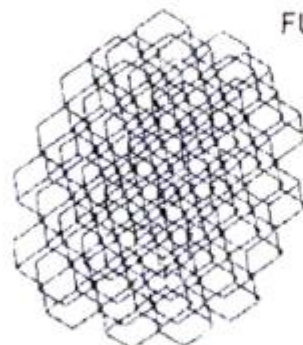
PAHs



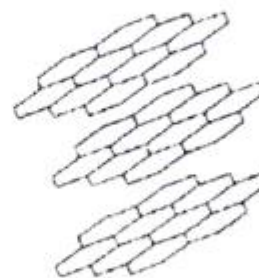
FULLERENES



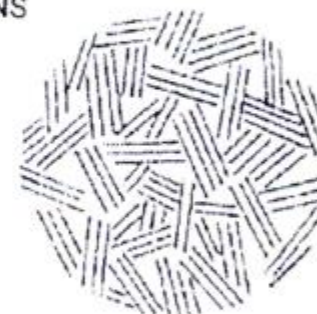
SHORT CHAINS



DIAMONDS



GRAPHITE



SOOT



BUCKY TUBES

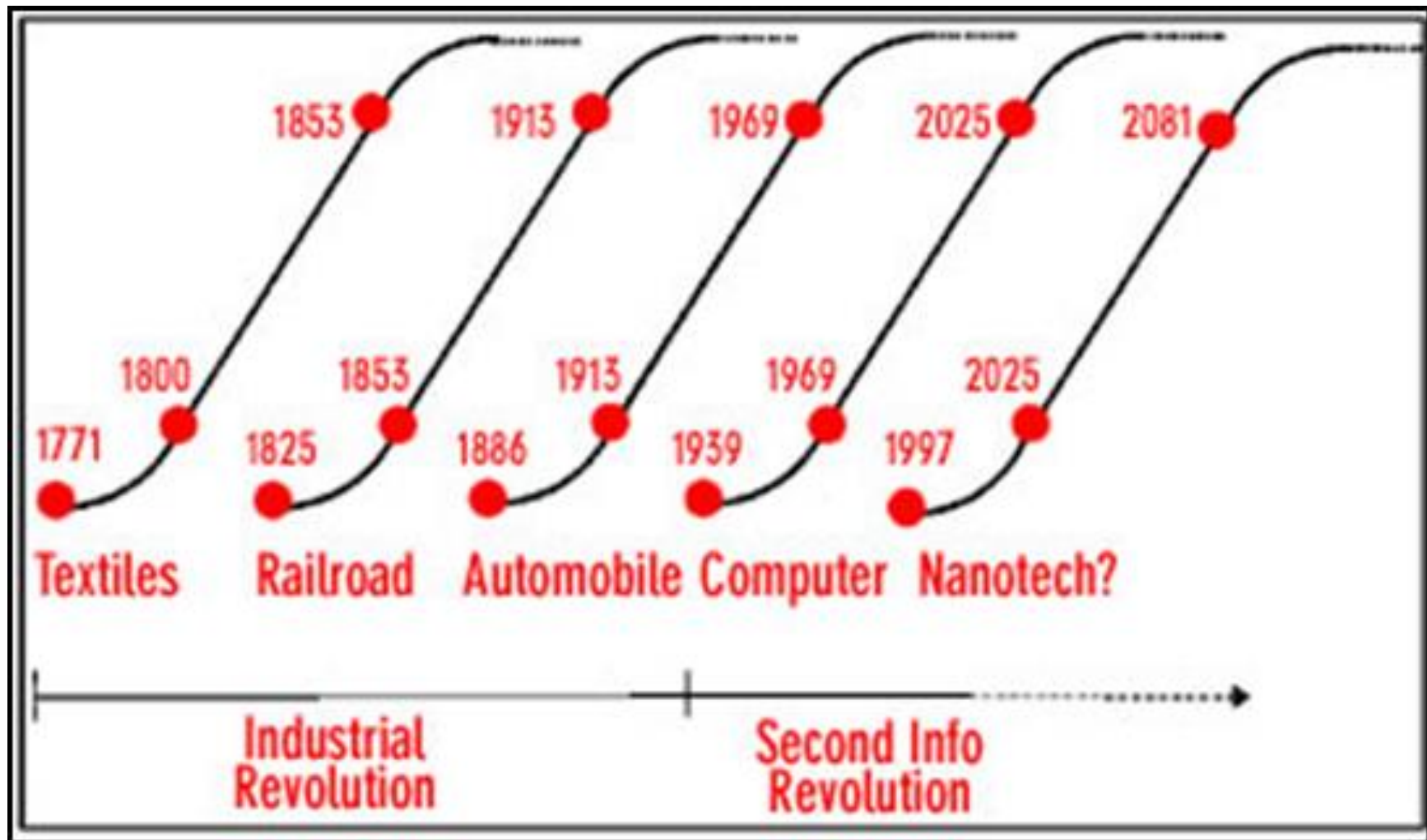


COMPLEX BUCKY TUBES

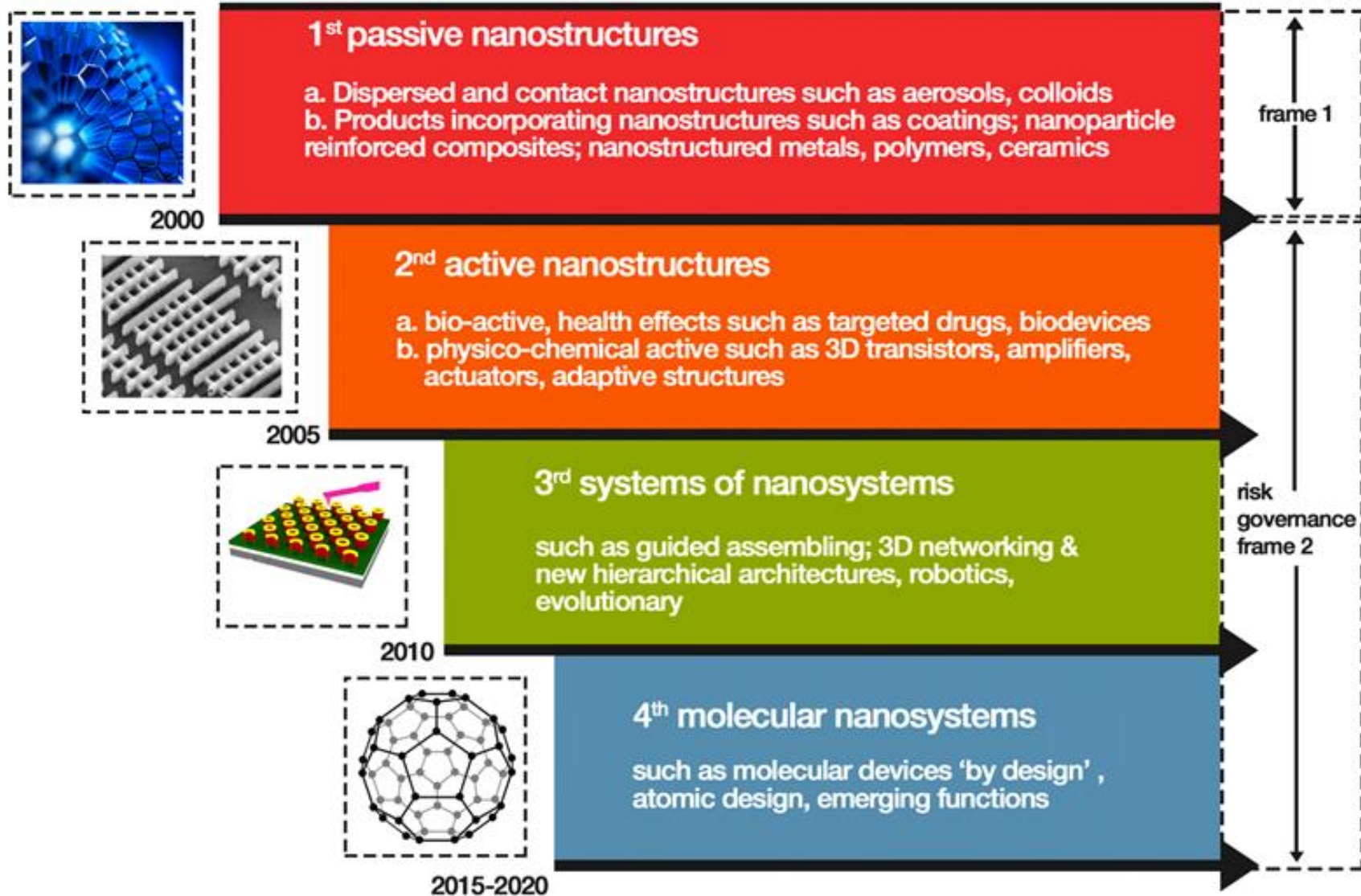


ONION TYPE C PARTICLES

Nanotechnology – revolution of modern era



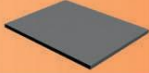



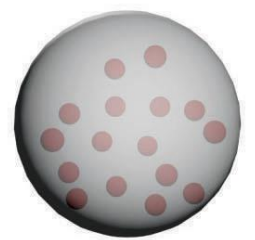

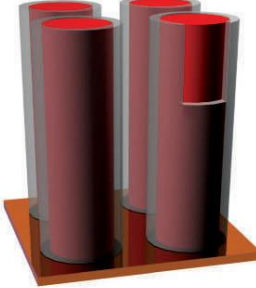
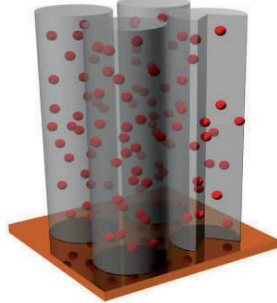
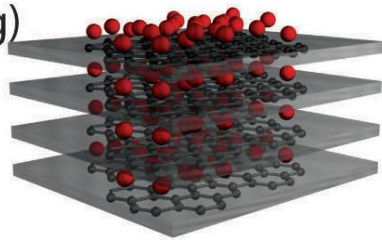
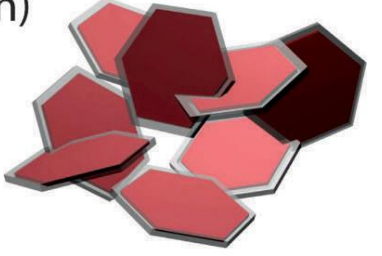

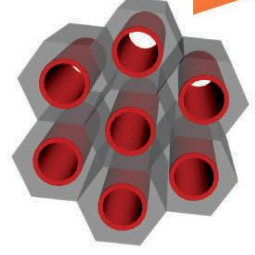
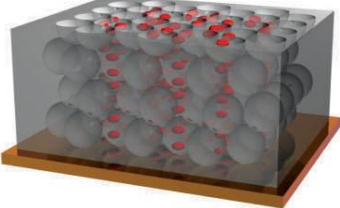
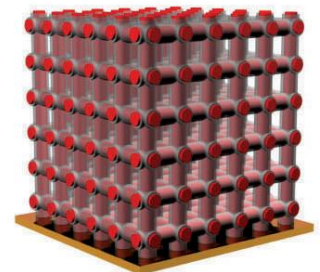


4 generations of nanostructures



Abundance of nanostructures

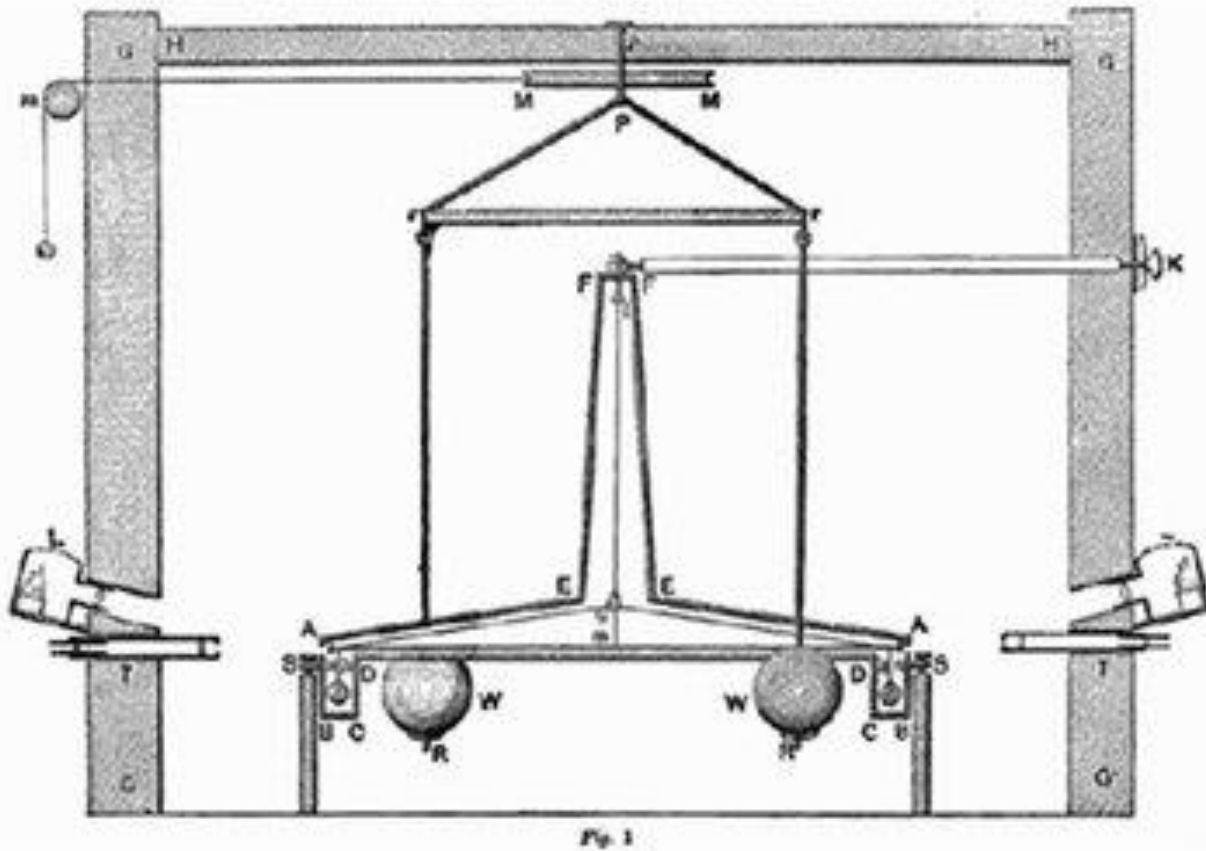
Heterogeneous Nanostructured Materials with Different Morphologies

| 0-D  | 1-D  | 2-D  | 3-D  |
|--|---|--|---|
| <p>a) </p> <p>Core-Shell Nanoparticle</p> <p>b) </p> <p>Nanoparticles Encapsulated in Hollow Nanosphere</p> <p>c) </p> <p>Composite Nanoparticle</p> | <p>d) </p> <p>Carbon Nanotube Based Composite Electrode</p> <p>e) </p> <p>Coaxial Nanowire Array</p> <p>f) </p> <p>Composite Nanowire Array</p> | <p>g) </p> <p>Graphene Based Composite</p> <p>h) </p> <p>Carbon Coated Nanoplates</p> <p>i) </p> <p>Carbon Coated Nanobelts</p> | <p>j) </p> <p>Mesoporous Composite Electrode</p> <p>k) </p> <p>Microporous Composite Electrode</p> <p>l) </p> <p>Future 3-D Electrode</p> |

How to study the structure of solids?

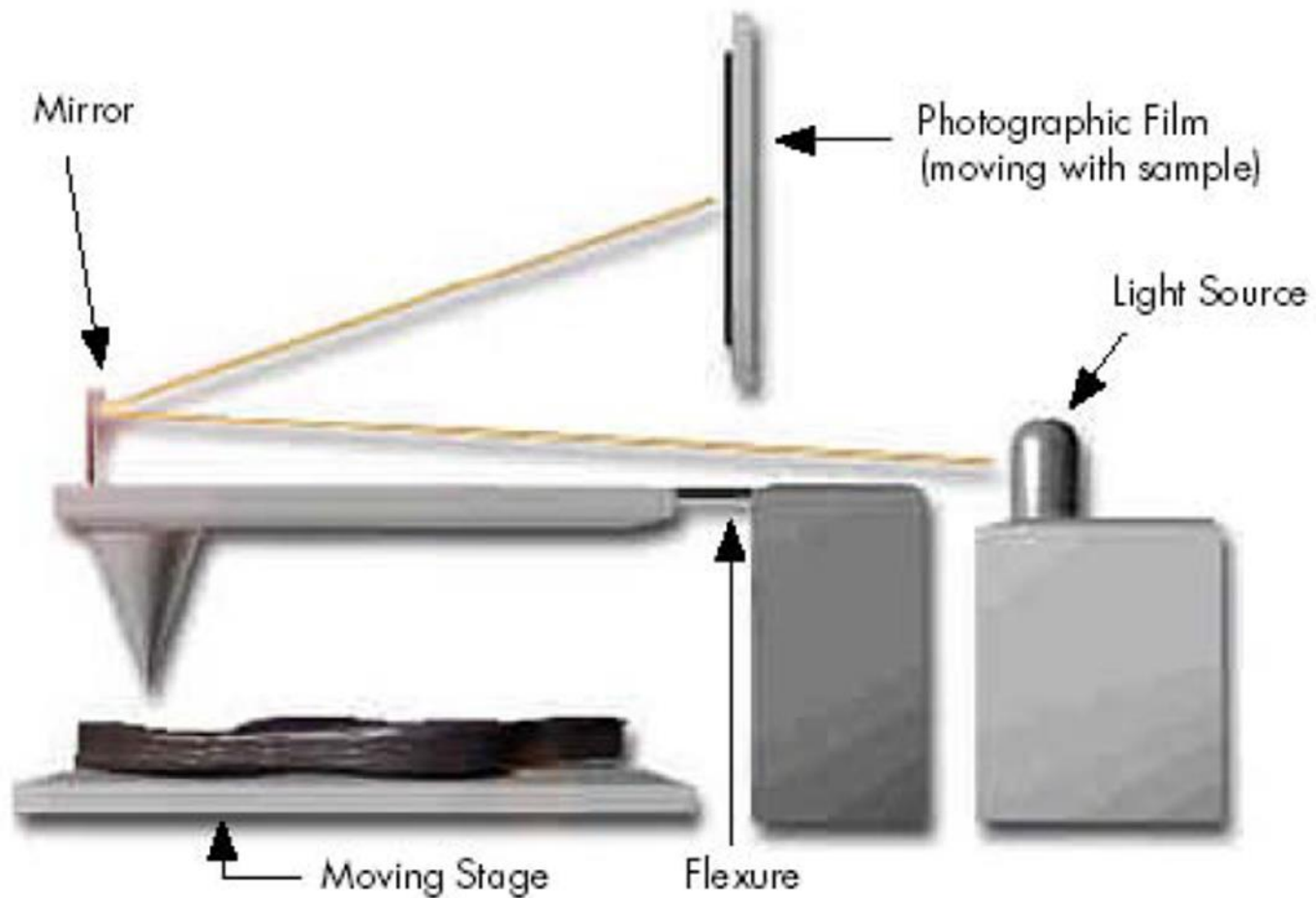
- By sight – microscopes: optical, (SNOM), TEM, SEM
- Wave phenomena: transmission, reflection, secondary emission
- By touch – scanning probes: STM, AFM, MFM, EFM, LFM etc.
- Particle interactions: attractive, repulsive

Torsion balance – Cavendish (1798)

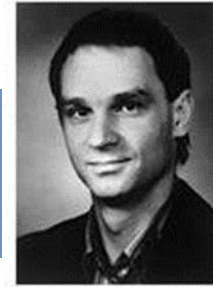


H. Cavendish

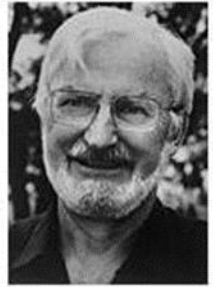
Profilometer – Schmalz (1929)



STM – Rohrer, Binnig (1981)

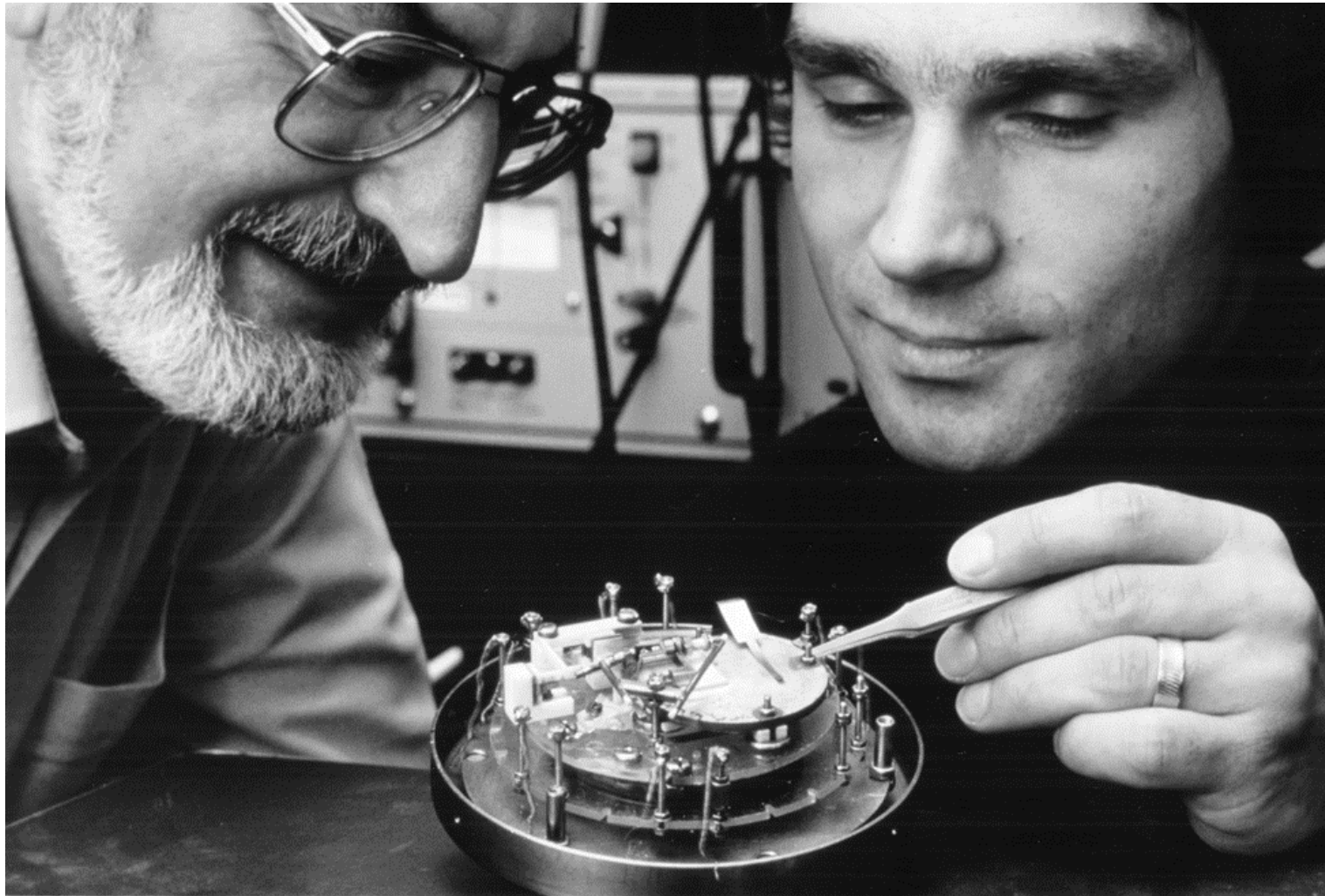


Gerd Binnig



Heinrich
Rohrer

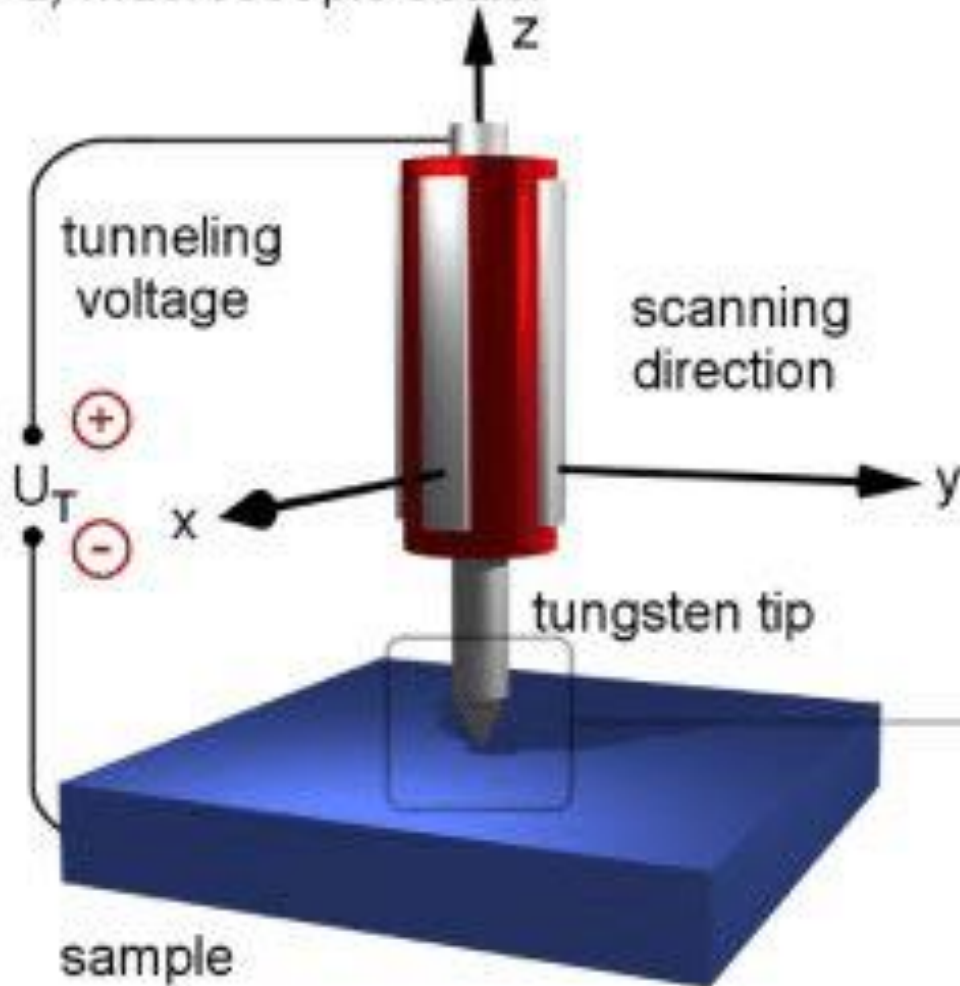
(IBM Zürich)



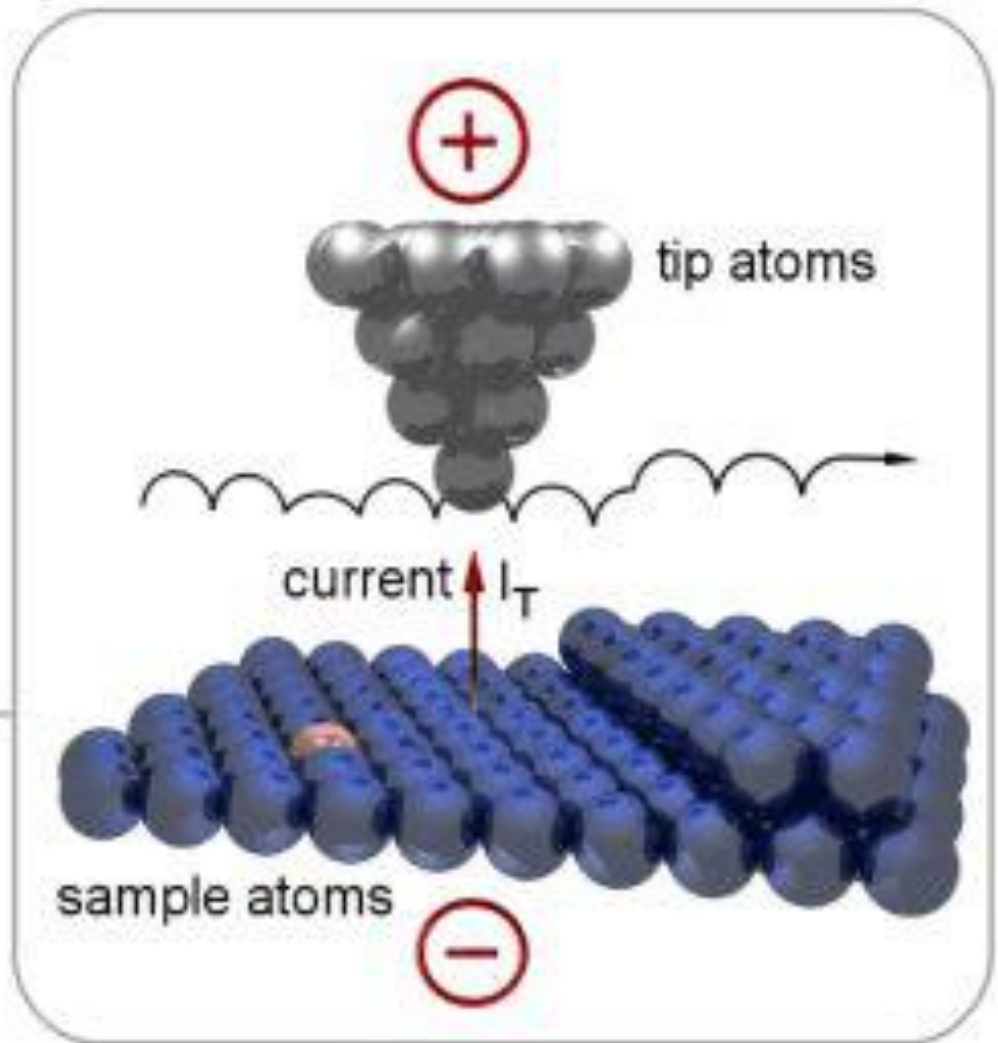
Nobel Prize in physics in 1986 – (semi-) conducting materials.

Scanning Tunneling Microscope

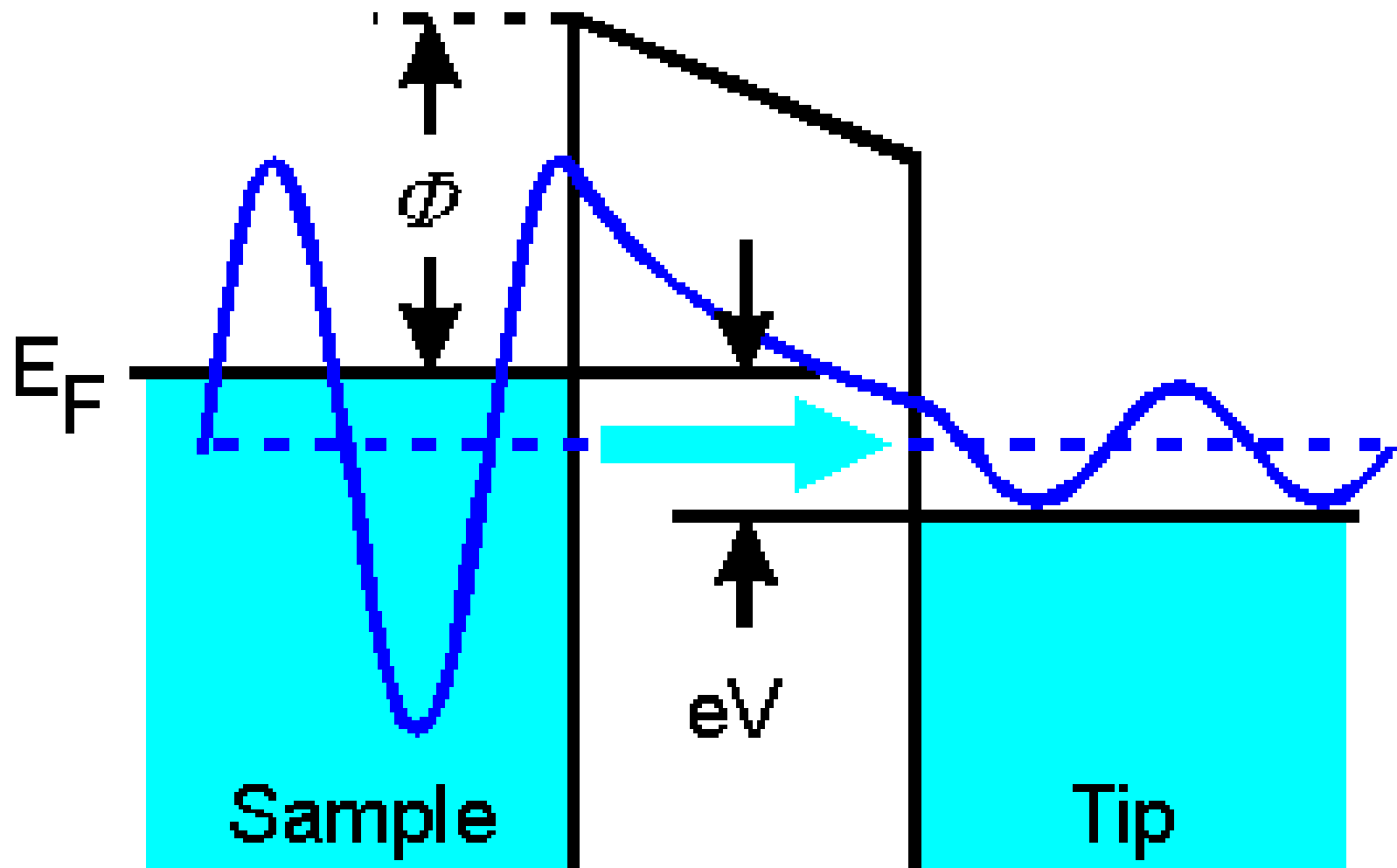
a) macroscopic scale:



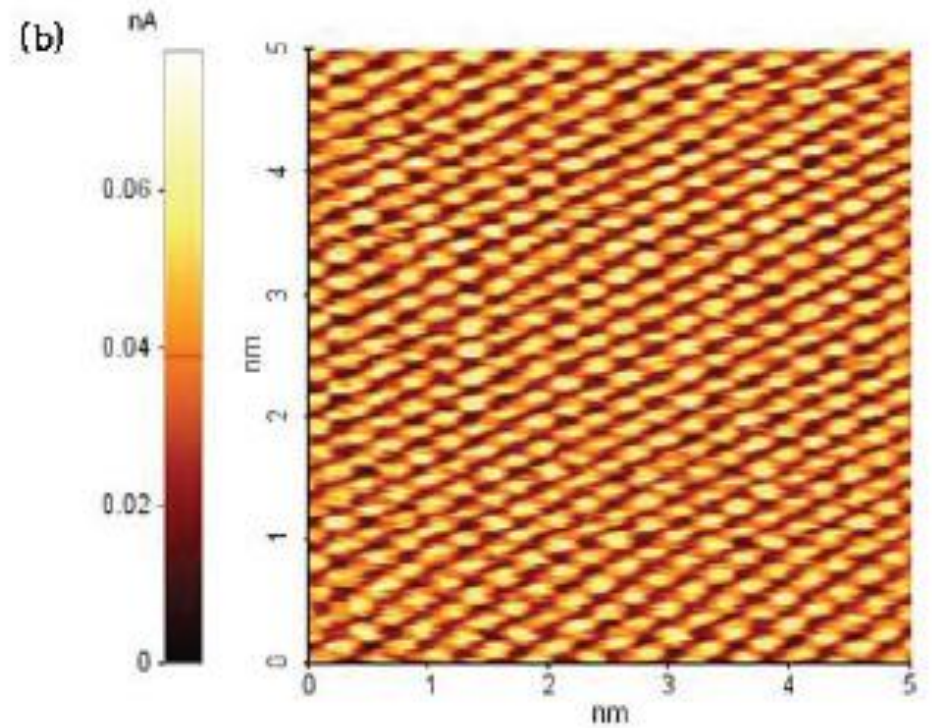
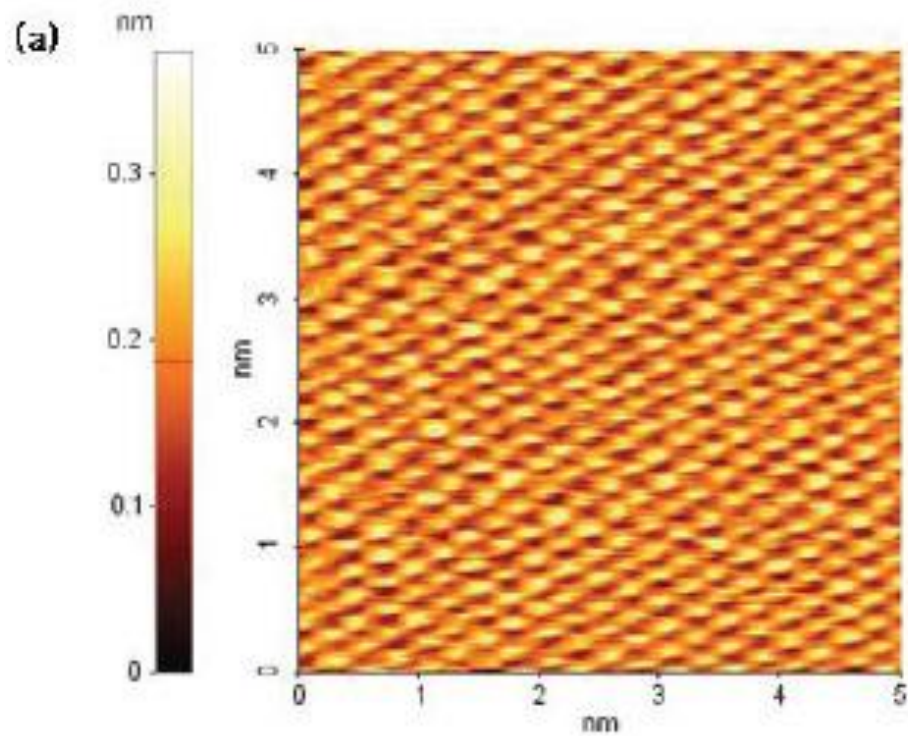
b) atomic scale:



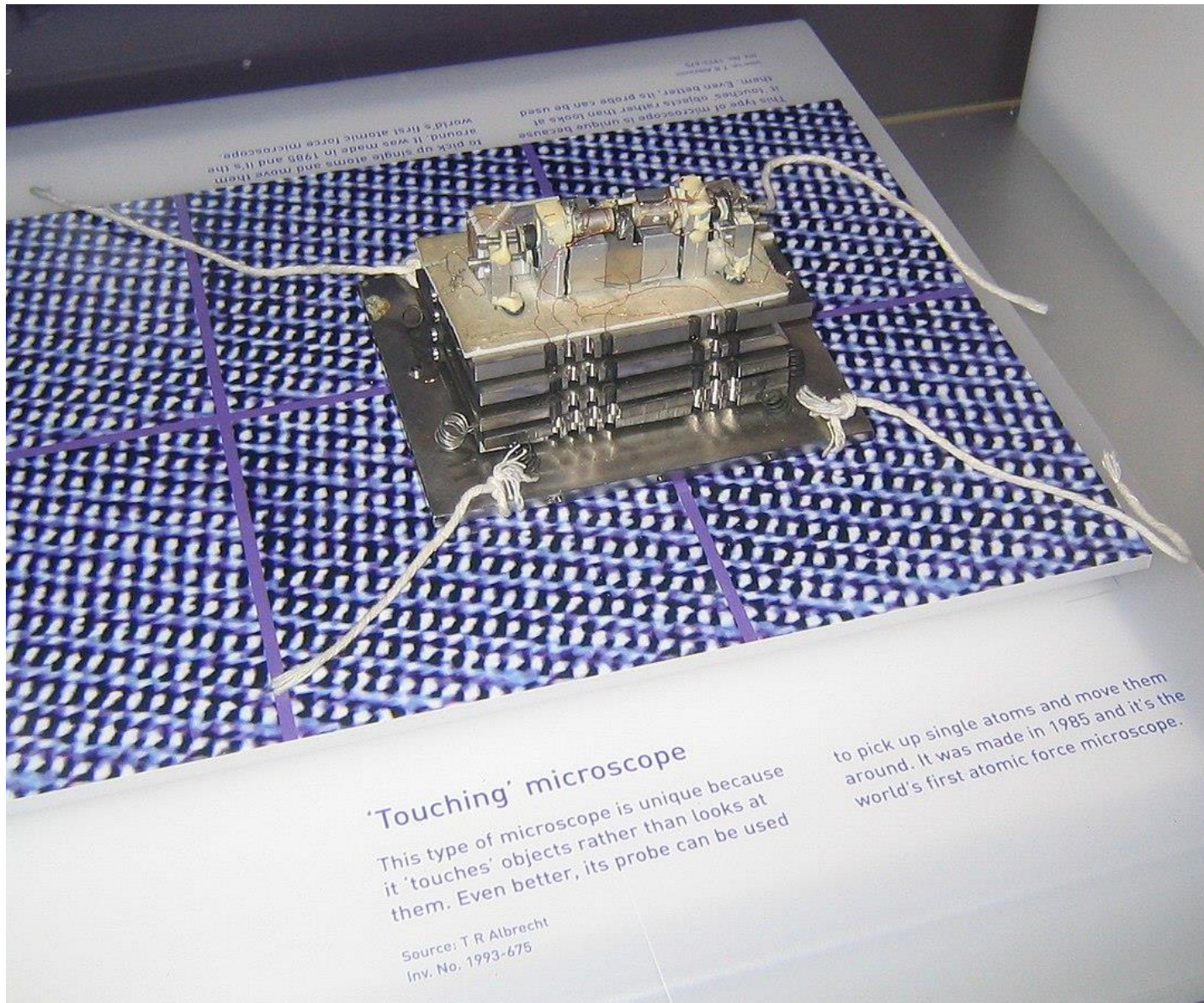
Electron tunneling



Atomic resolution in STM



AFM – improved STM



'Touching' microscope

This type of microscope is unique because it 'touches' objects rather than looks at them. Even better, its probe can be used

Source: T. R. Albrecht
Inv. No. 1993-675

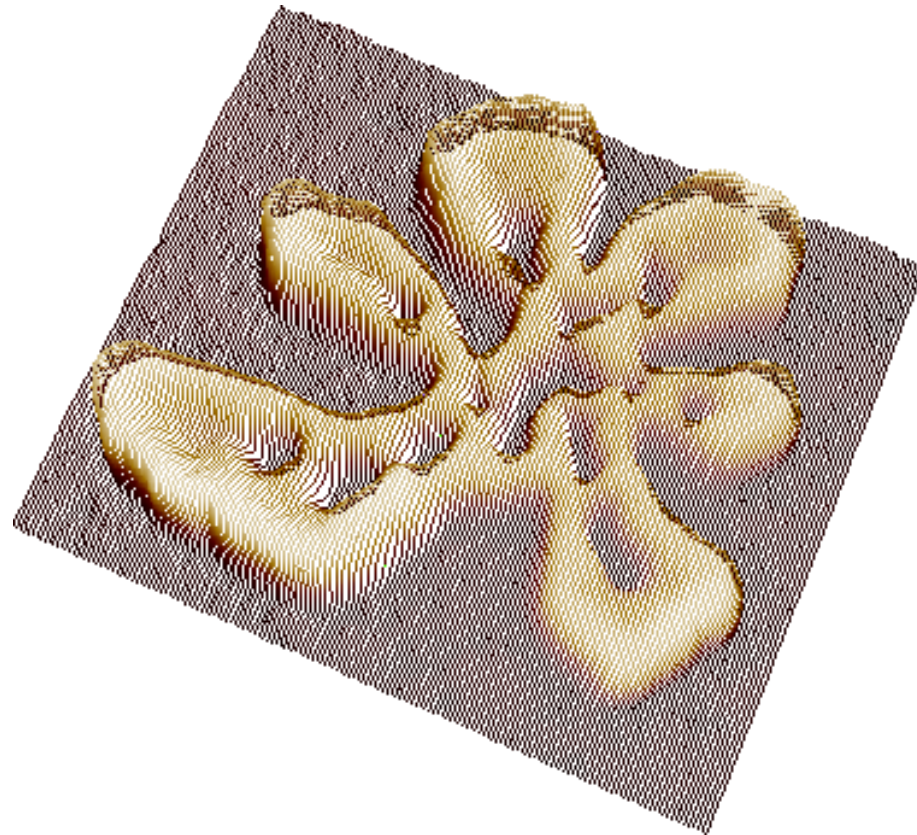
to pick up single atoms and move them around. It was made in 1985 and it's the world's first atomic force microscope.

Comparison

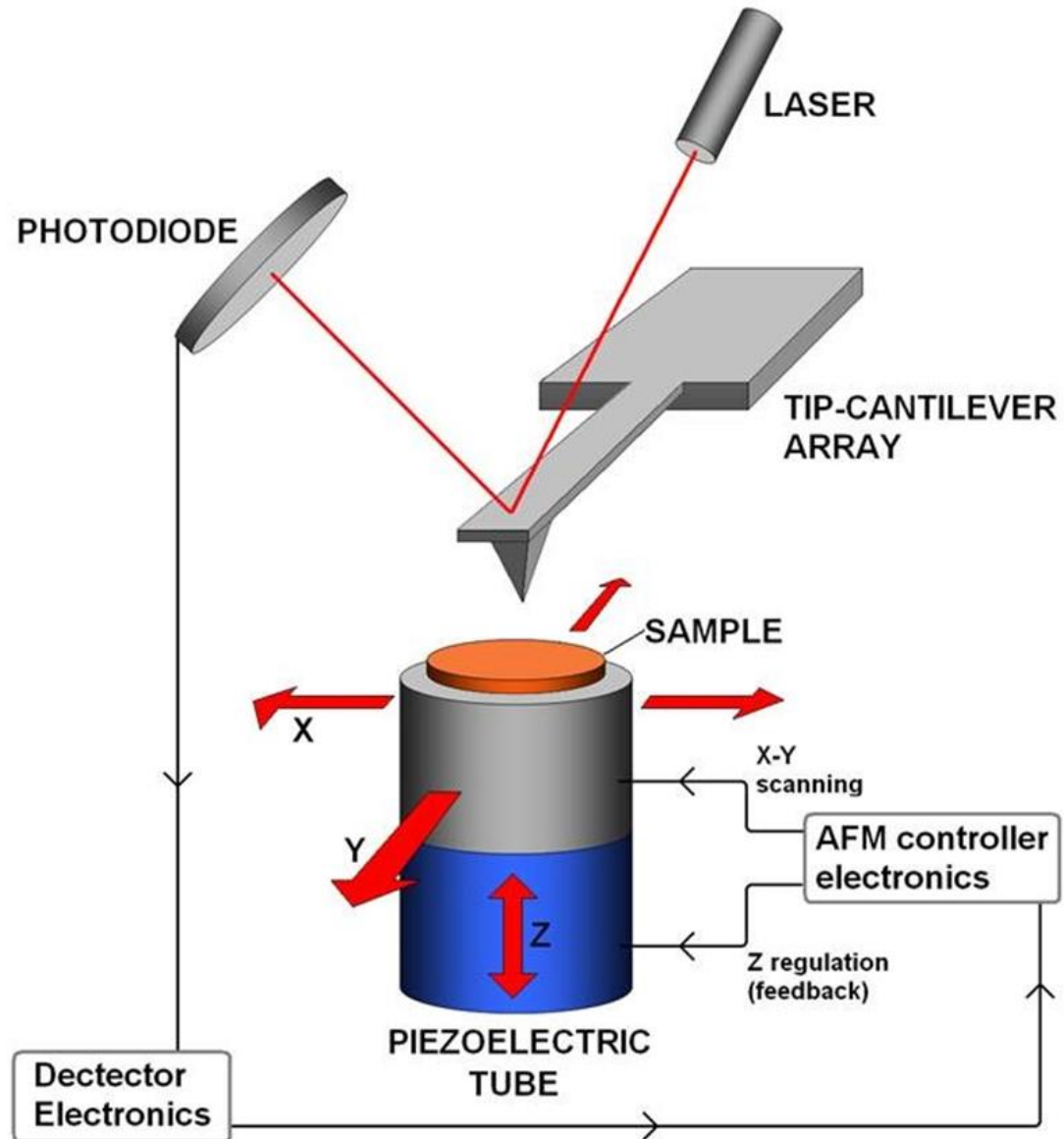
| | Optical Microscopy | SEM | TEM | AFM |
|---------------------|---------------------------|------------|------------|------------|
| Resolution | XY 200 nm | 2 nm | 0.1 nm | 1 nm |
| | Z 500 nm | NA | NA | 0.1 nm |
| Depth of focus | Poor | High | Moderate | High |
| Sample prep. | Simple | Moderate | Skilled | Simple |
| Works in Liquid? | Yes | Limited | No | Yes |
| Ambient Atmosphere | Variable | Vacuum | Vacuum | Variable |
| Damage to sample | Low | High | High | Low |
| Speed | Fast | Moderate | Slow | Moderate |
| Skill required | Low | Moderate | Advanced | Moderate |
| Data interpretation | Easy | Moderate | Moderate | Easy |

What is AFM?

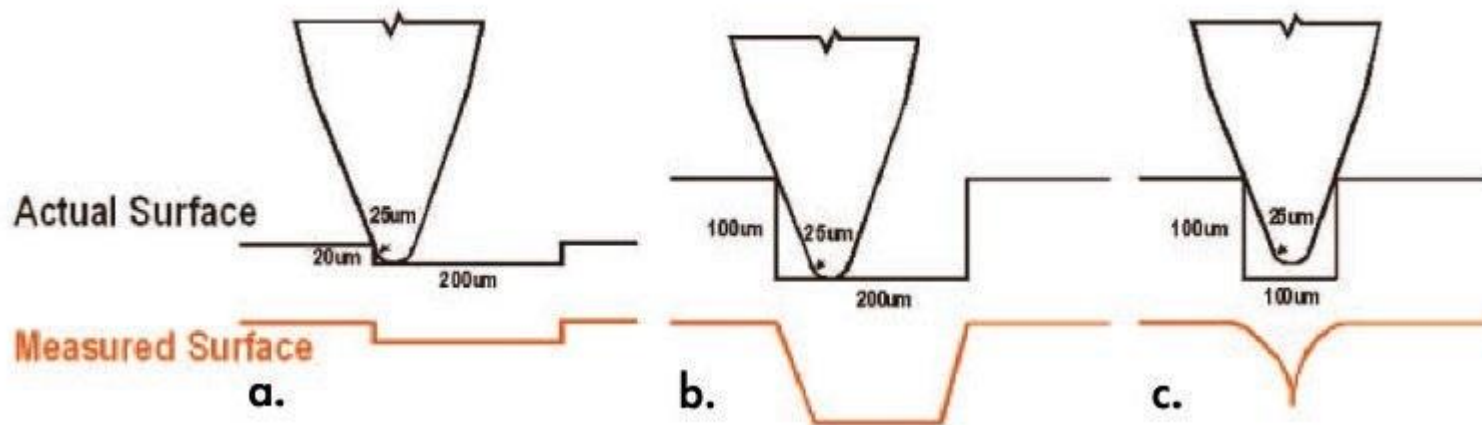
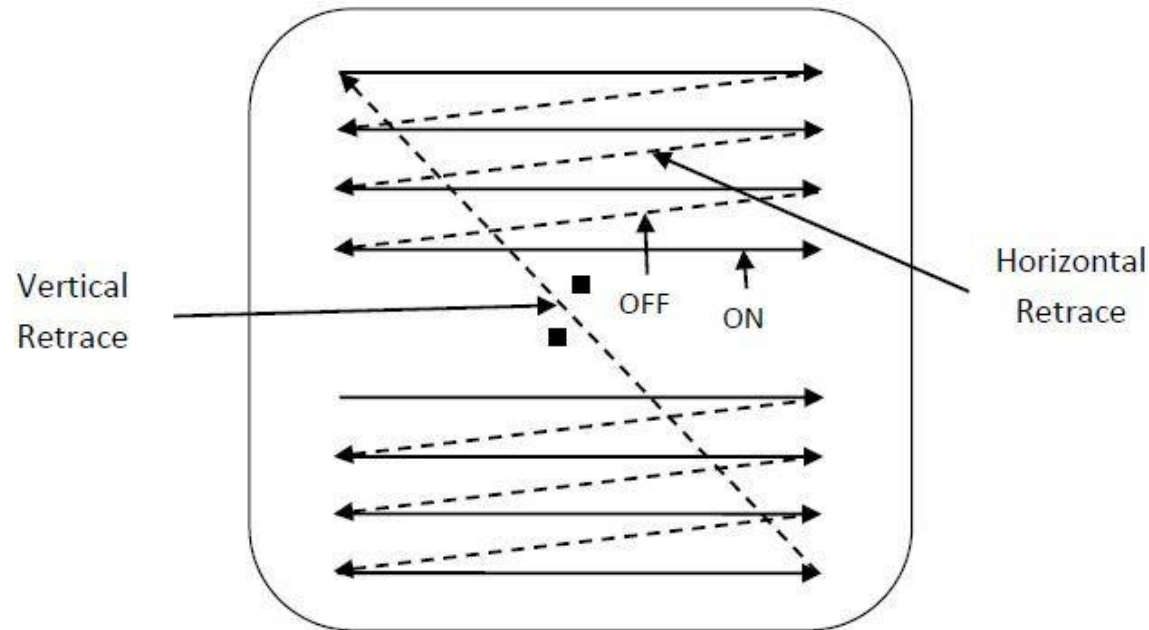
AFM images are surface property maps taken by sampling interactions occurring between surface and a sharp scanning tip ($R \geq 1\text{nm}$).



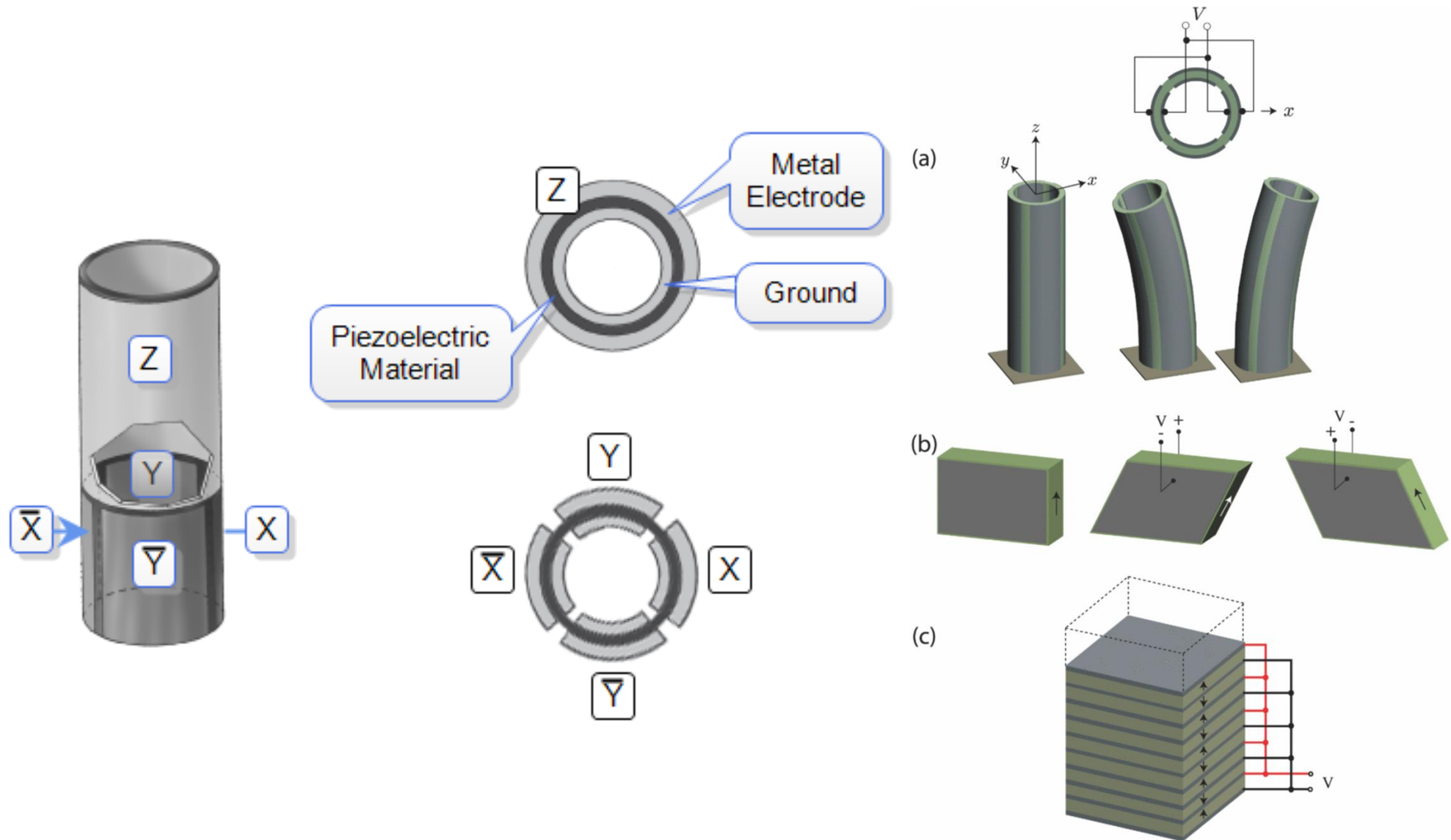
How AFM works?



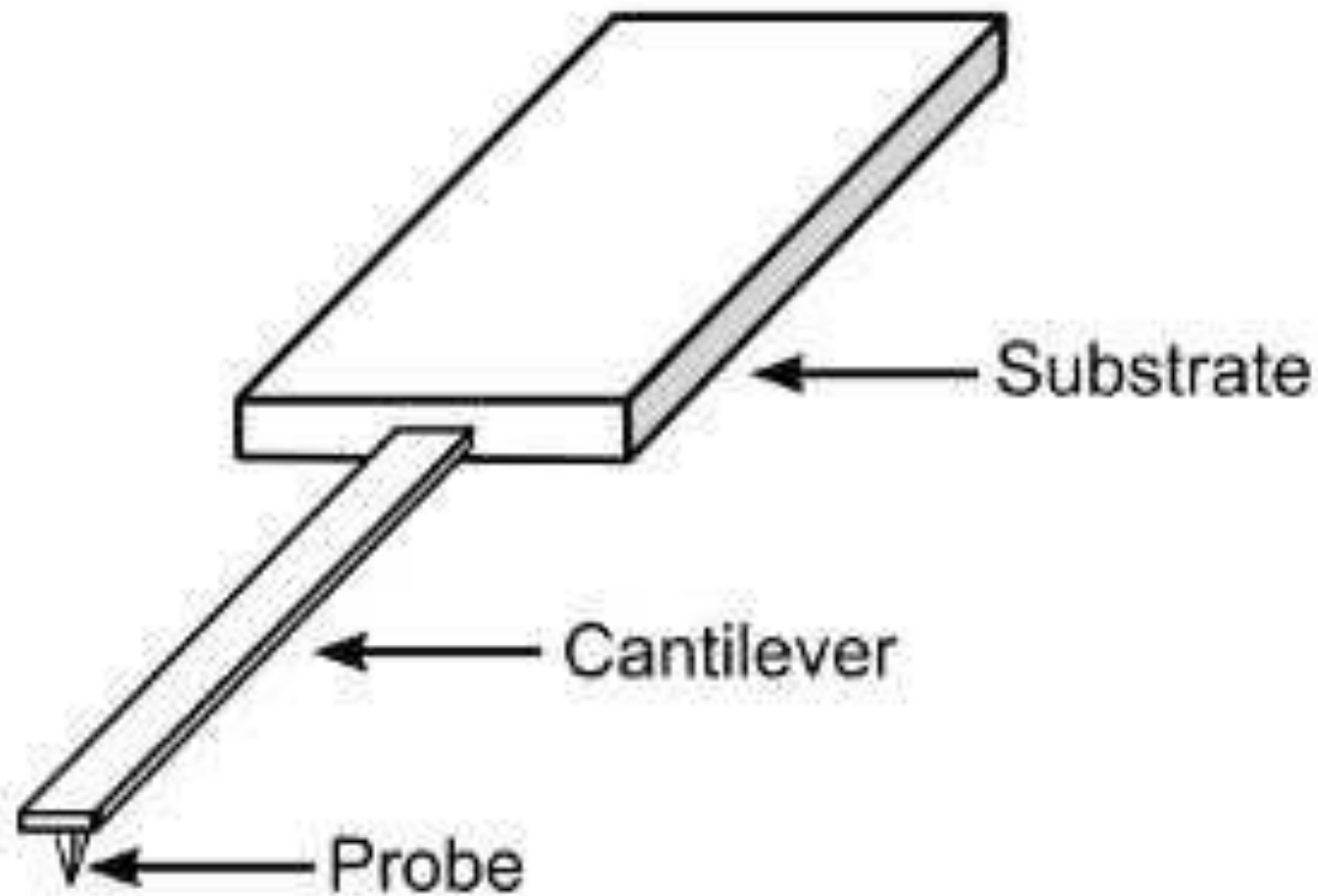
AFM = raster scanning + height profiling



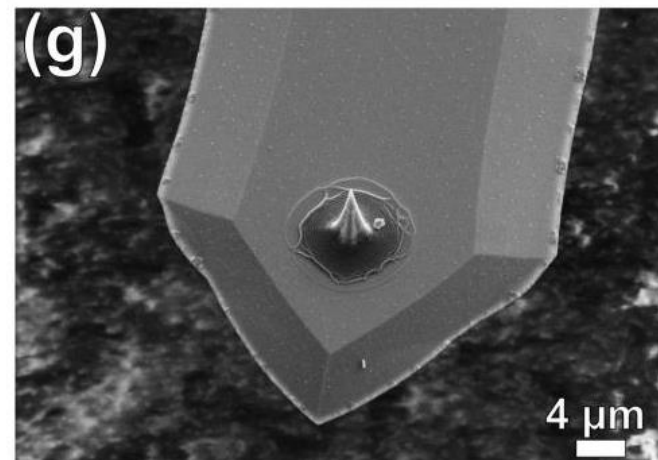
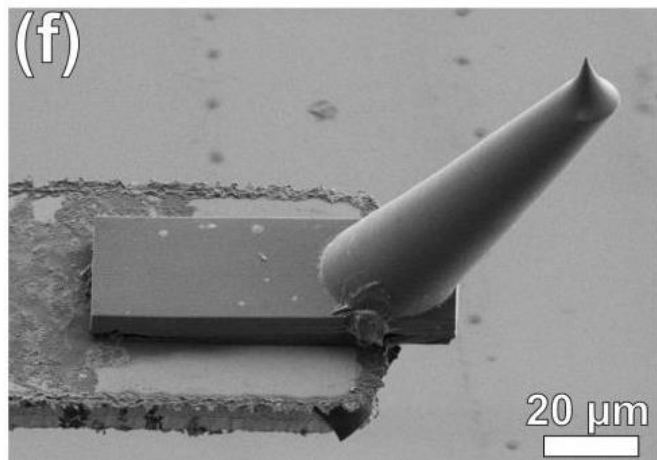
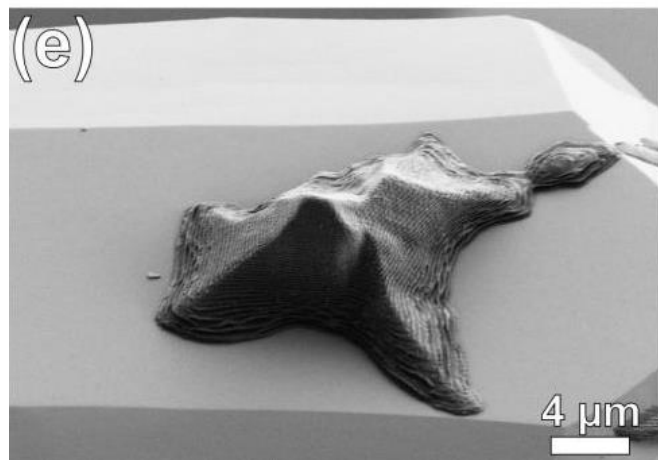
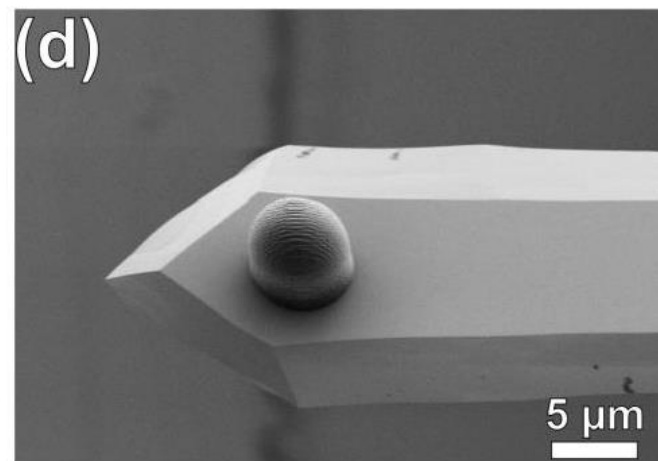
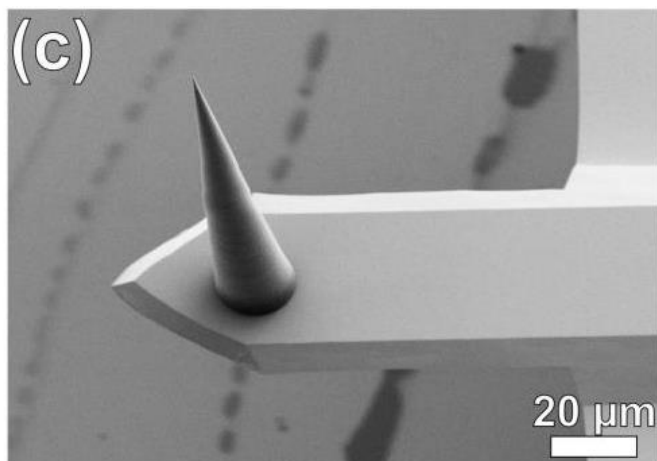
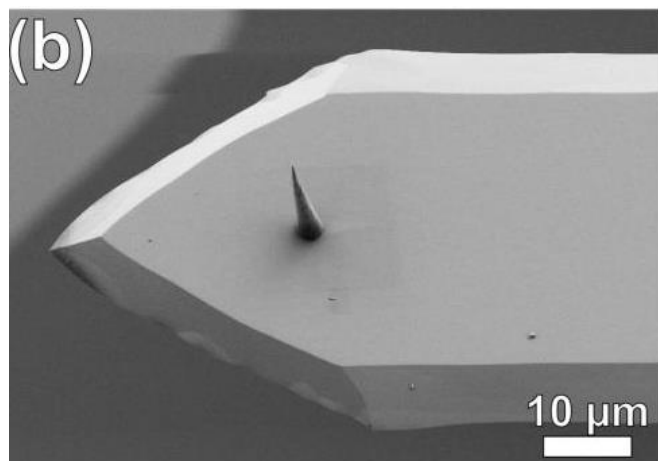
Piezoelectric scanner



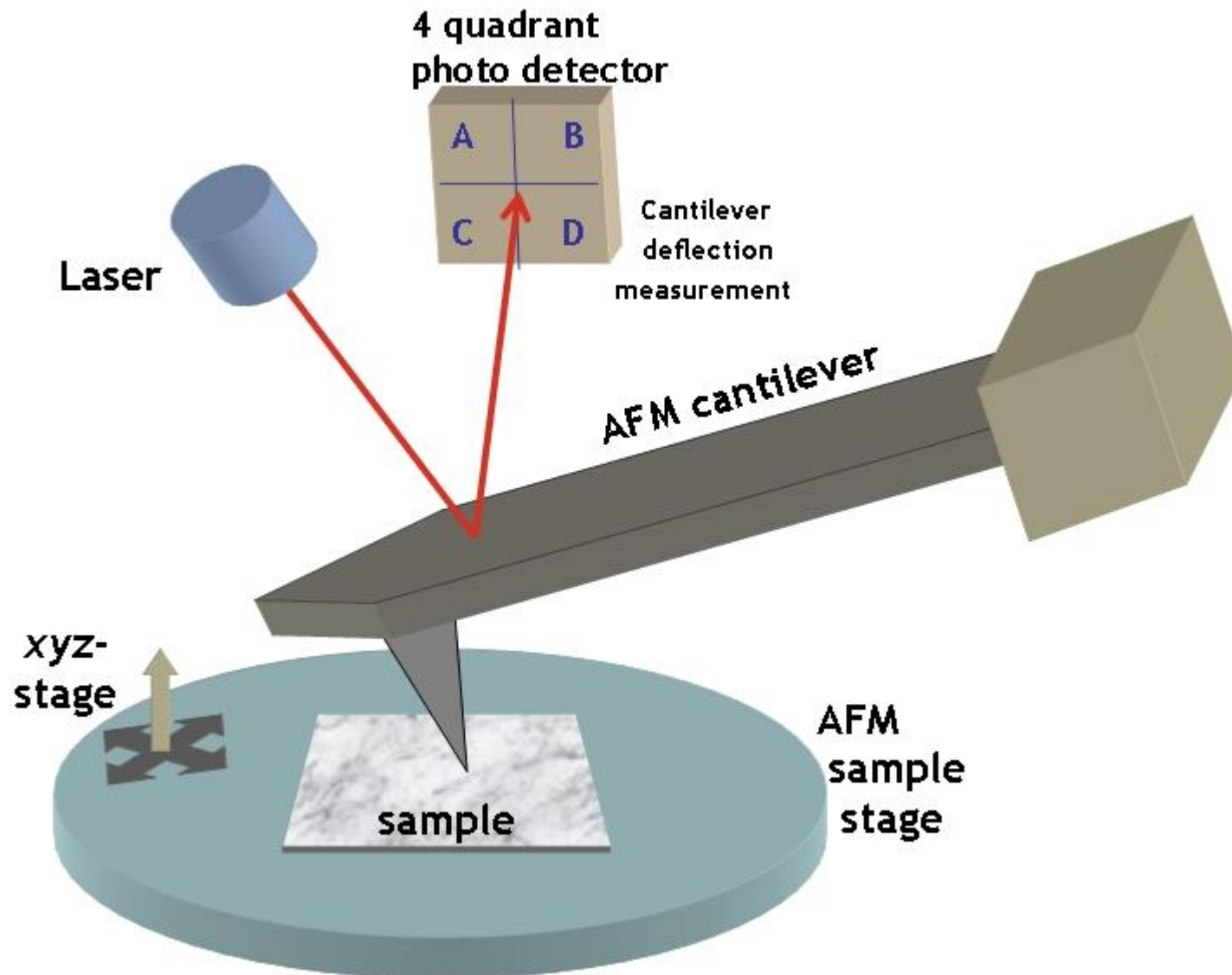
Scanning probe



Scanning tips



Detection of a lever deflection



Deflection modes

(normal) force constant

side view

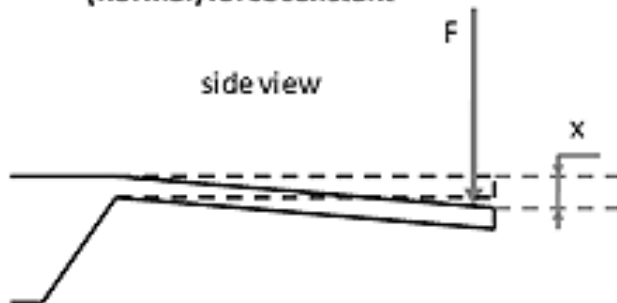


Fig. 1: Schematic side view of an AFM cantilever

lateral force constant

top view

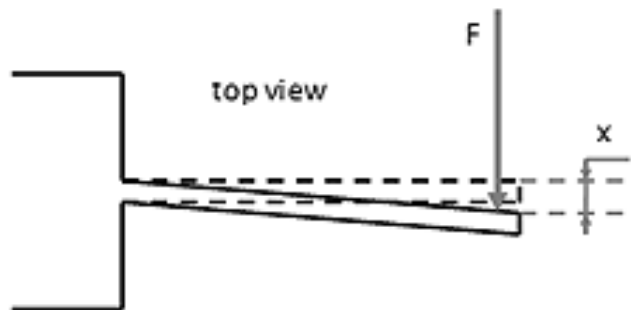


Fig. 2: Schematic top view of an AFM cantilever

torsional force constant

front view

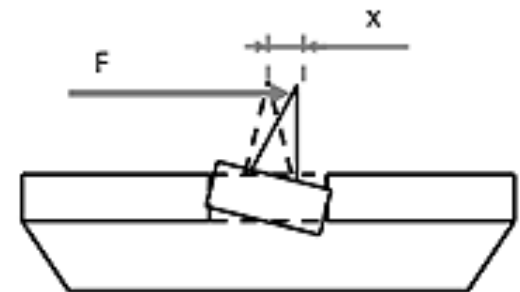


Fig. 3: Schematic front view of an AFM cantilever

Imaging modes

- **Contact** mode: repulsive tip-sample interaction due to close approach (less than 1 nm)
- **Tapping** mode: intermittent tip-sample contact due to tip oscillation (distance between 1 and 10 nm)
- **Non-contact** mode: attractive tip-sample interaction at a distance larger than 10 nm

Contact mode

| Advantage | Disadvantage |
|---|---|
| <ul style="list-style-type: none">• High scan speeds• Rough samples with extreme changes in vertical topography can sometimes be scanned more easily | <ul style="list-style-type: none">• Lateral (shear) forces may distort features in the image• In ambient conditions may get strong capillary forces due to adsorbed fluid layer• Combination of lateral and strong normal forces reduce resolution and mean that the tip may damage the sample, or vice versa |

Tapping mode

Advantage

- Lateral forces almost eliminated
- Higher lateral resolution on most samples
- Lower forces so less damage to soft samples or tips

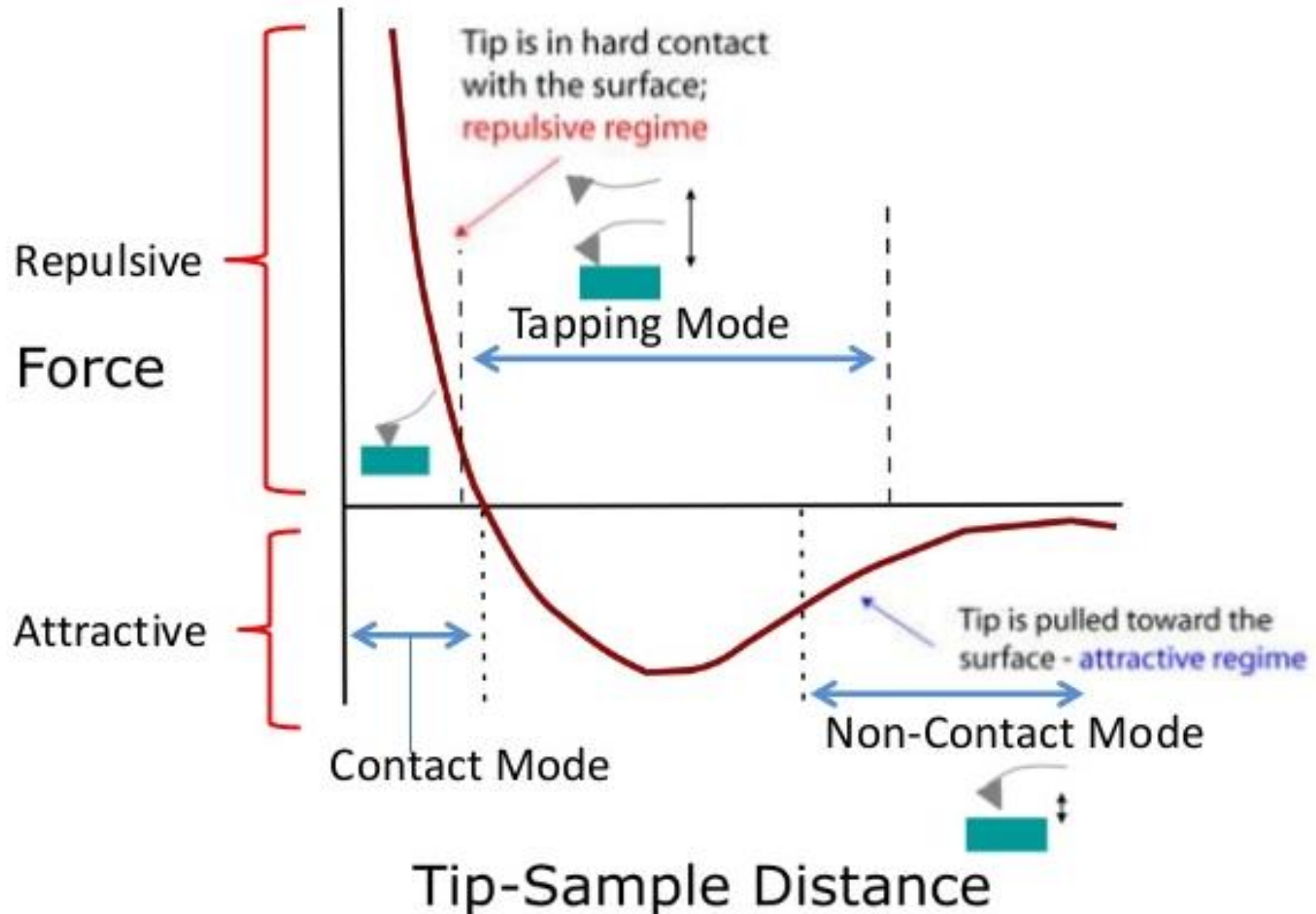
Disadvantage

- Slower scan speed than in contact mode

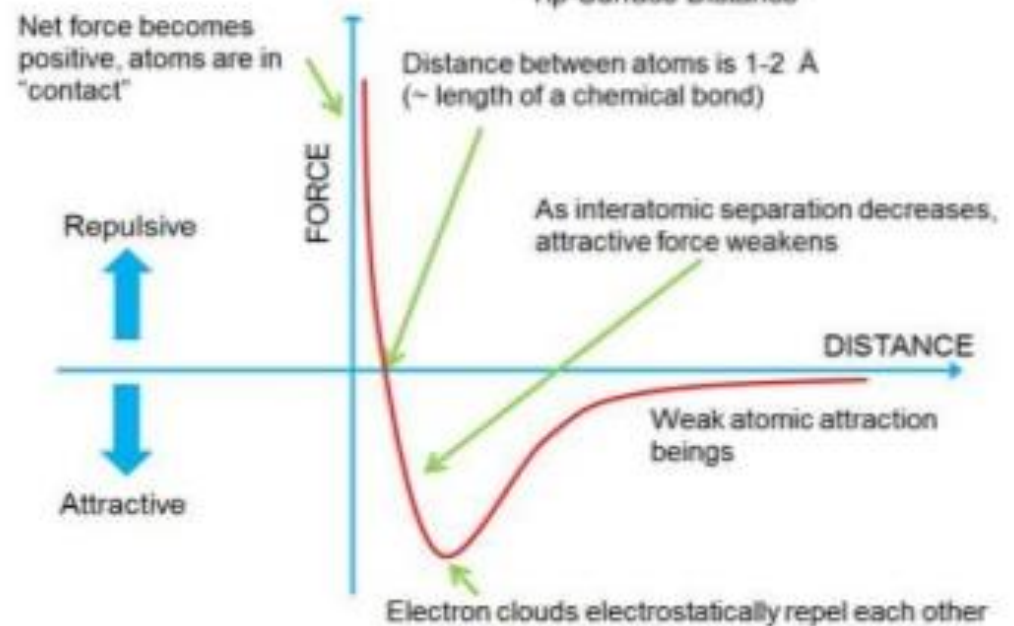
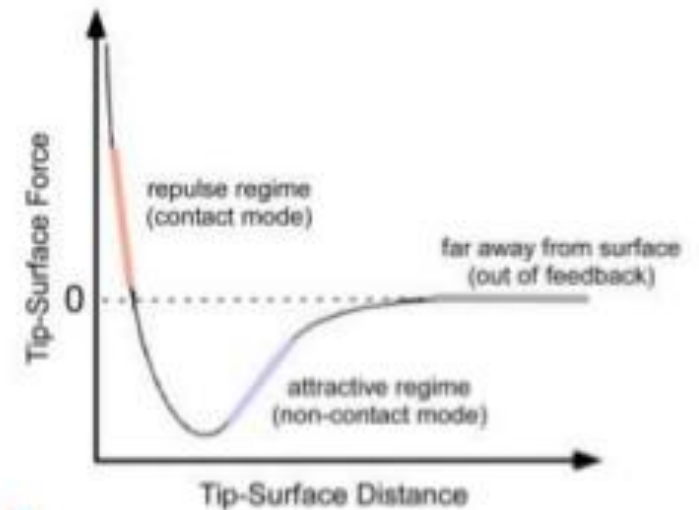
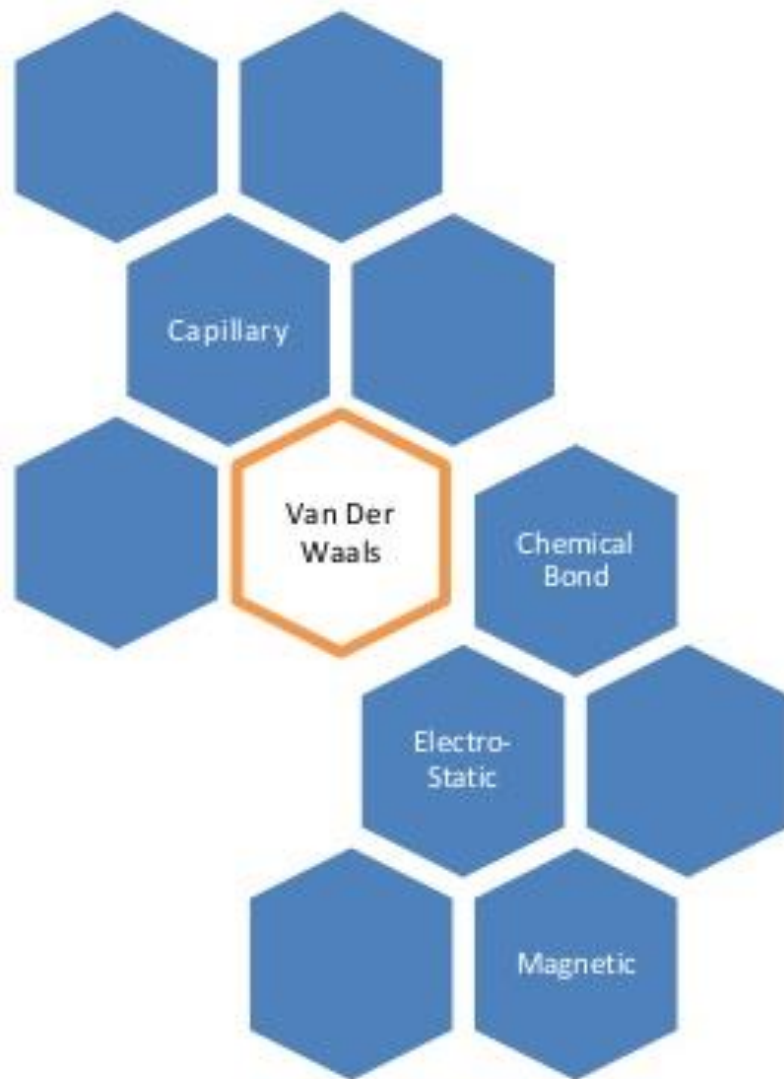
Non-contact mode

| Advantage | Disadvantage |
|---|--|
| <ul style="list-style-type: none">• Both normal and lateral forces are minimized, so good for measurement of very soft samples• Can get atomic resolution in a UHV environment | <ul style="list-style-type: none">• In ambient conditions the adsorbed fluid layer may be too thick for effective measurements• Slower scan speed than tapping and contact modes to avoid contacting the adsorbed fluid layer |

Imaging modes

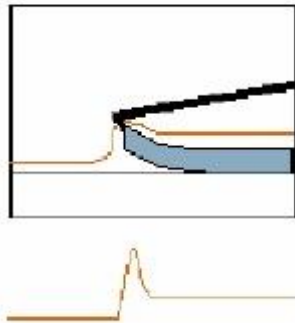


Tip-sample interactions



Imaging modes

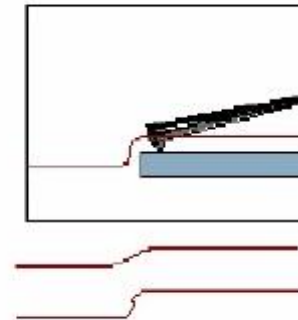
Contact



- Cantilever
- Force
- Friction
- Distance
- Damage
- Surface

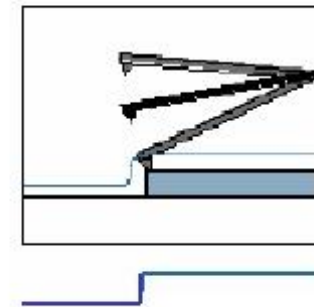
soft
1-10nN
large
<0.2nm
large
hard surface

Noncontact



hard
0.1-0.01nN
small
~ 1nm
small
soft or elastic surface

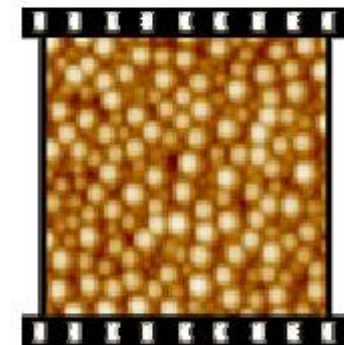
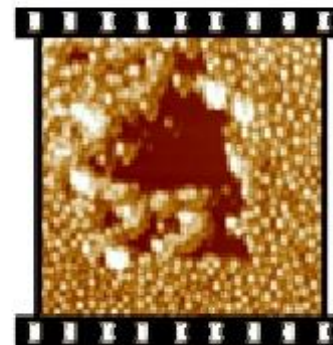
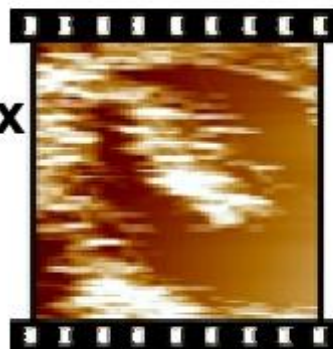
Vibrating (tapping)



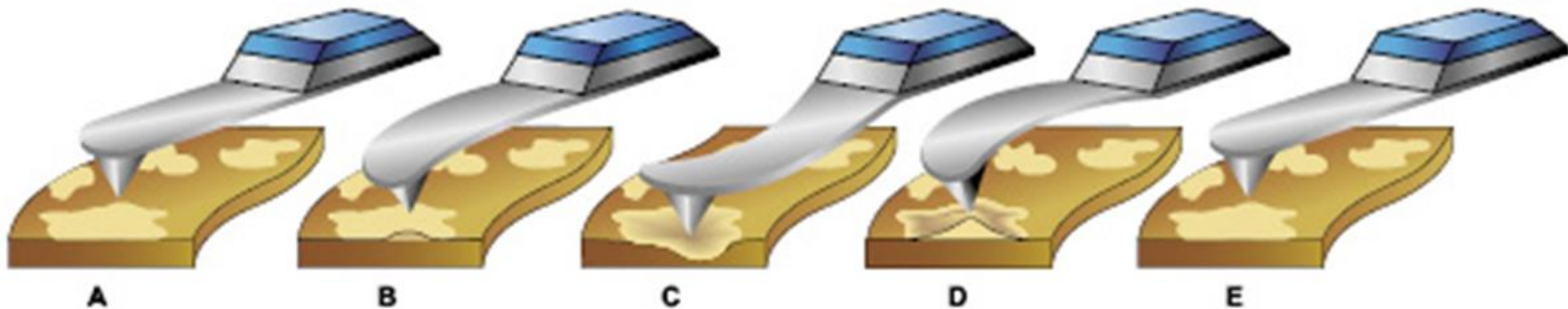
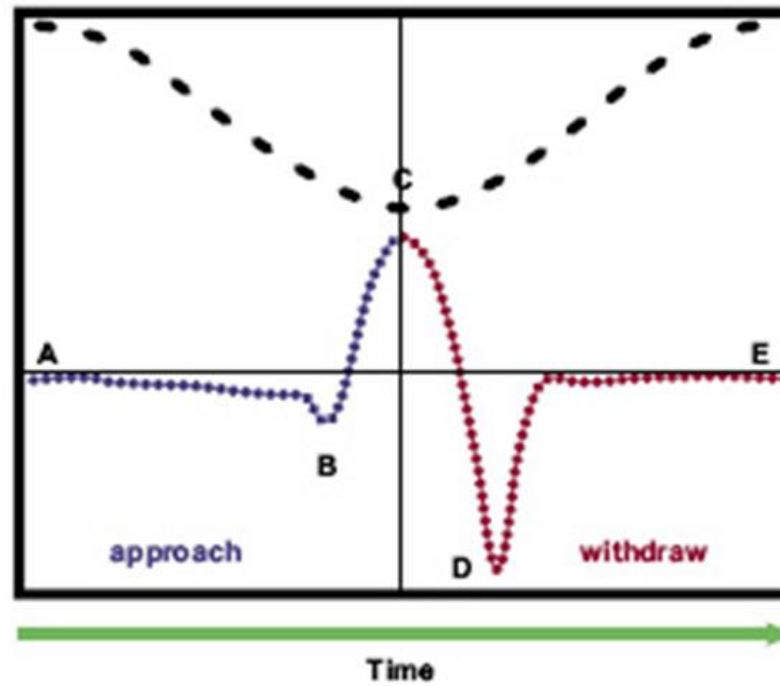
hard

small
>10nm
small

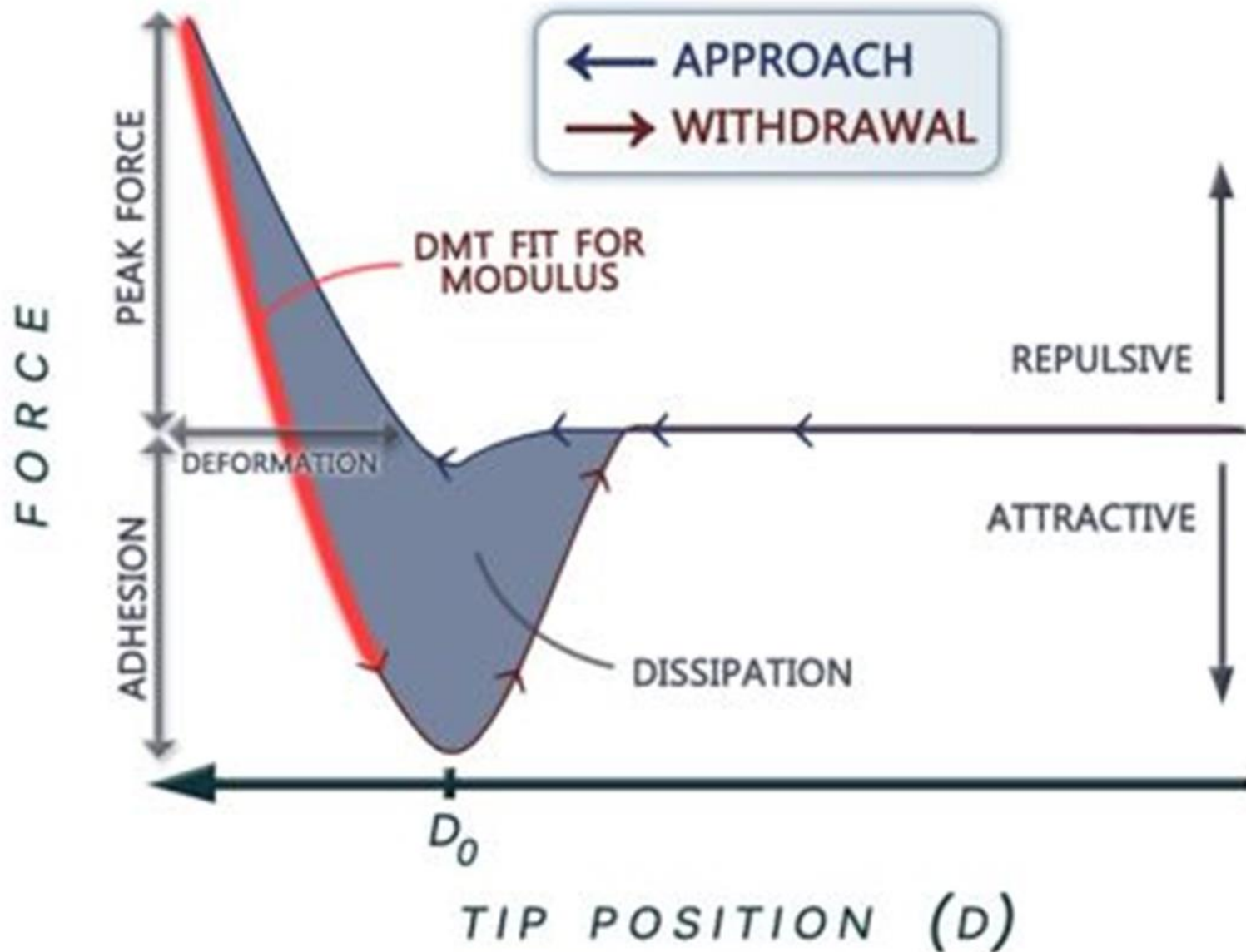
Polymer latex
particle on
mica



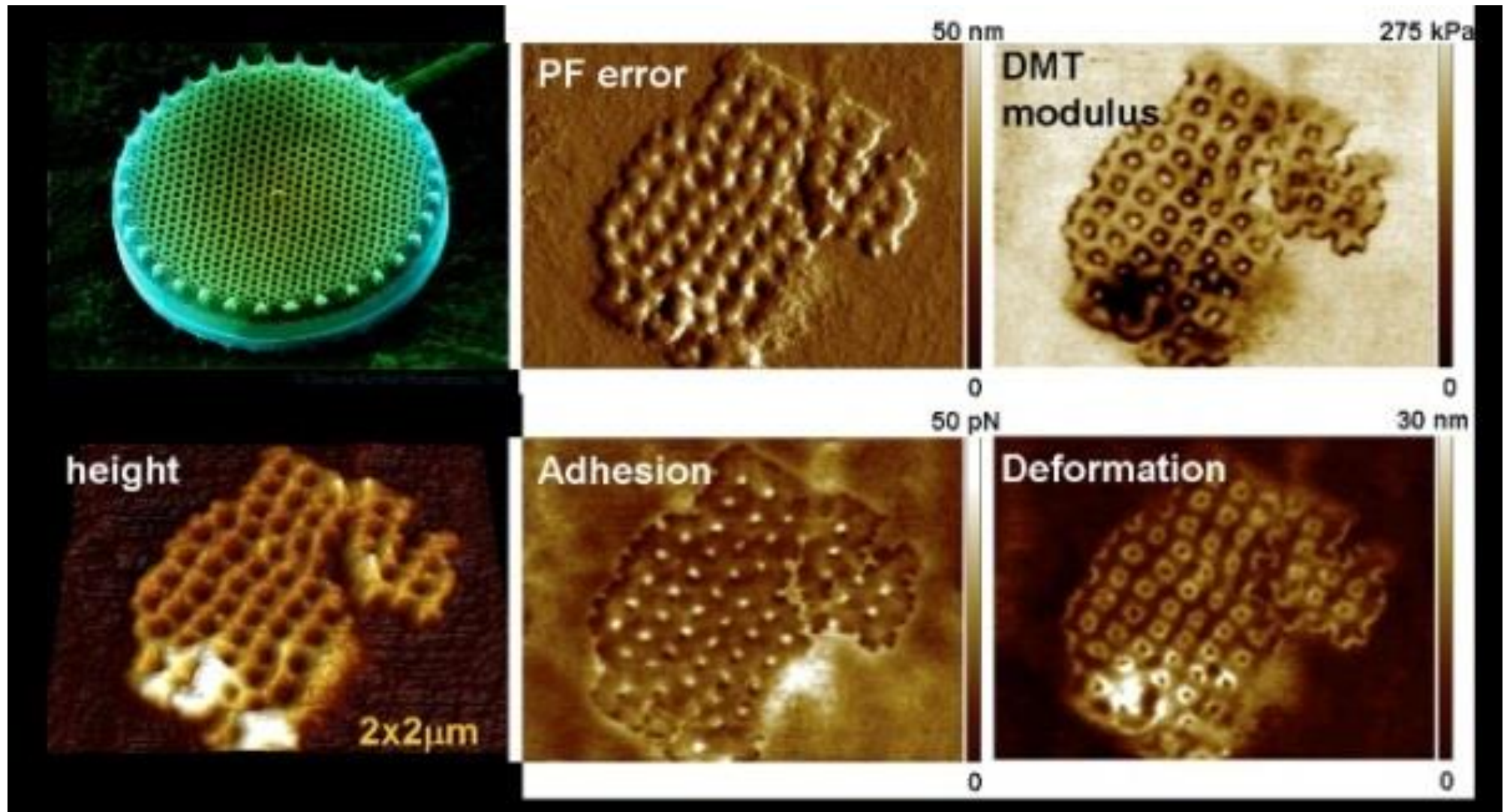
PeakForce AFM



Quantitative Nanomechanical Mapping



Quantitative Nanomechanical Mapping

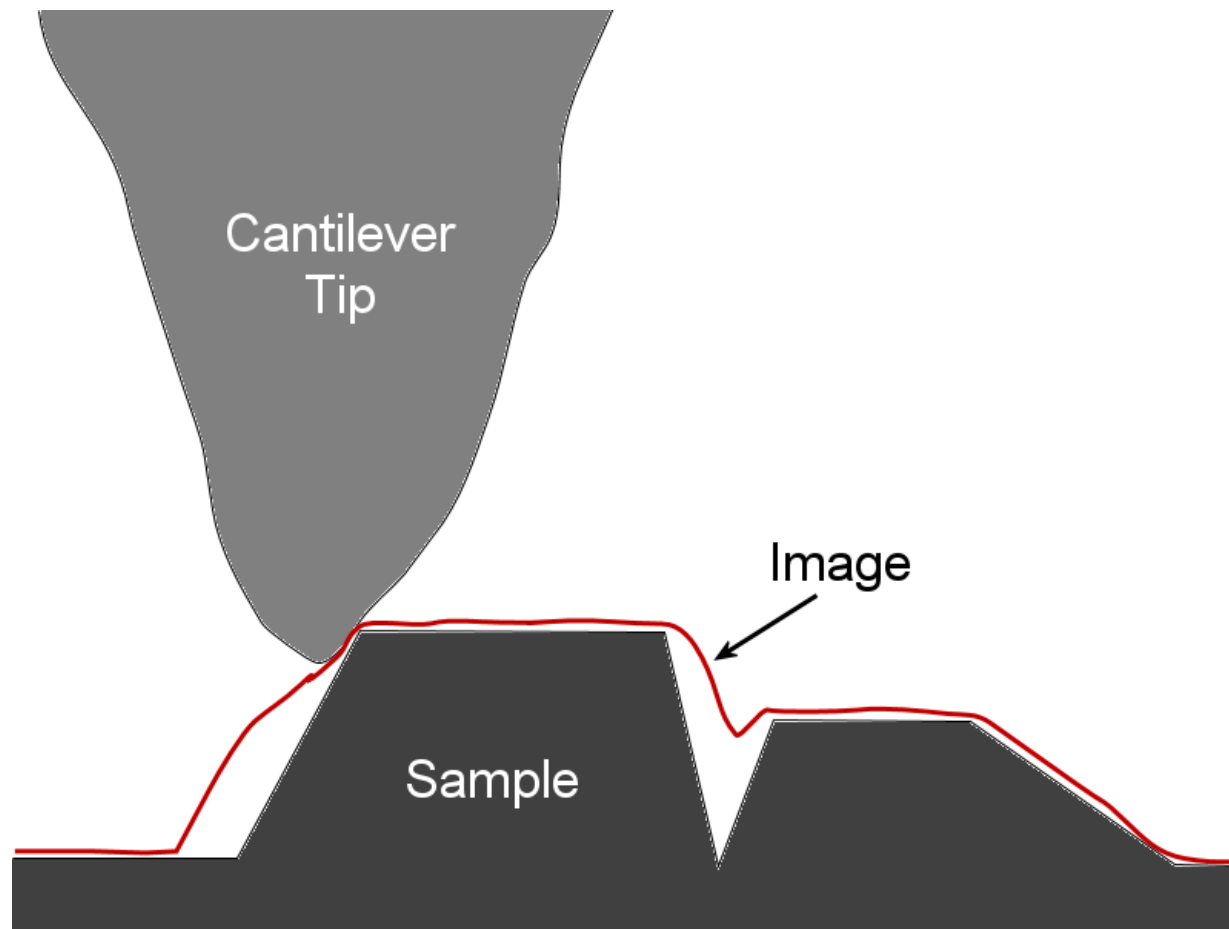


Measurement resolution

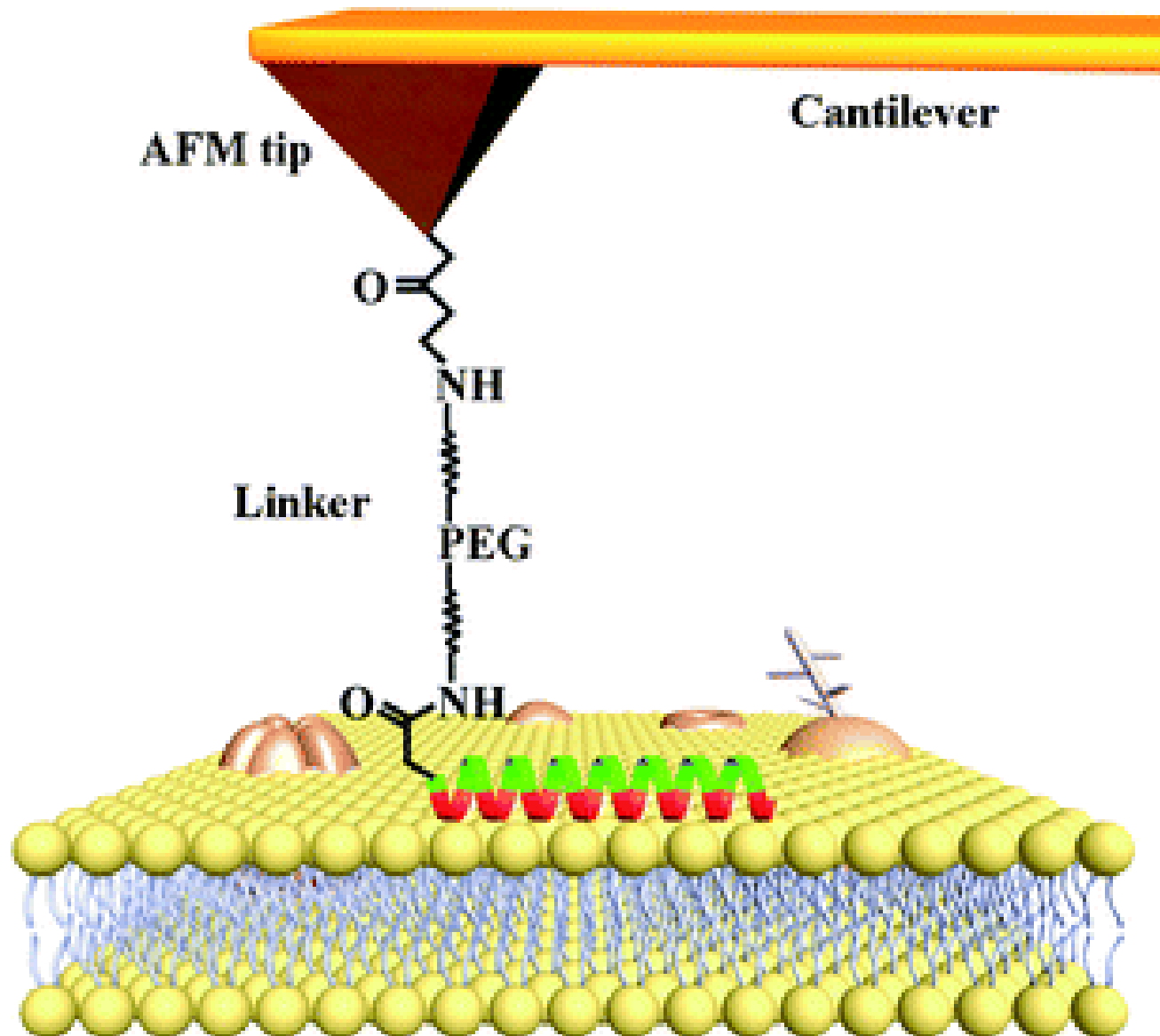
- . Scanning tip geometry
 - . Curvature radius, tip apex
- . External disturbances
 - . Thermal noise, acoustic vibrations, capillary forces
- . Scanner characteristics
 - . Sensitivity, linearity, stability, repeatability

What you get is **not** what you can see

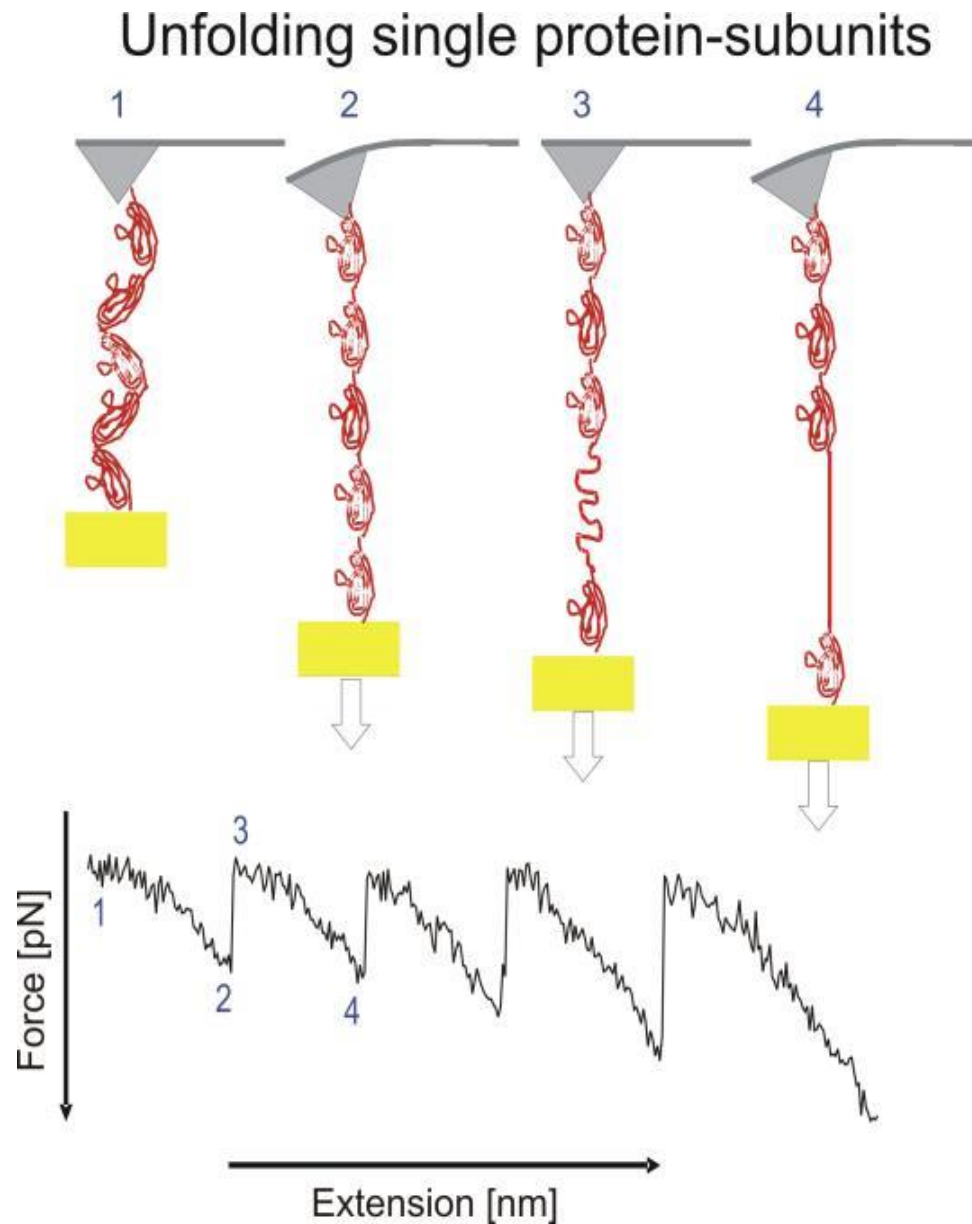
AFM images are convolution of surface topography and tip geometry



Tip functionalization



Atomic Force Spectroscopy



AFM @ WMil

Multimode 8 + Nanoscope V
(Bruker)

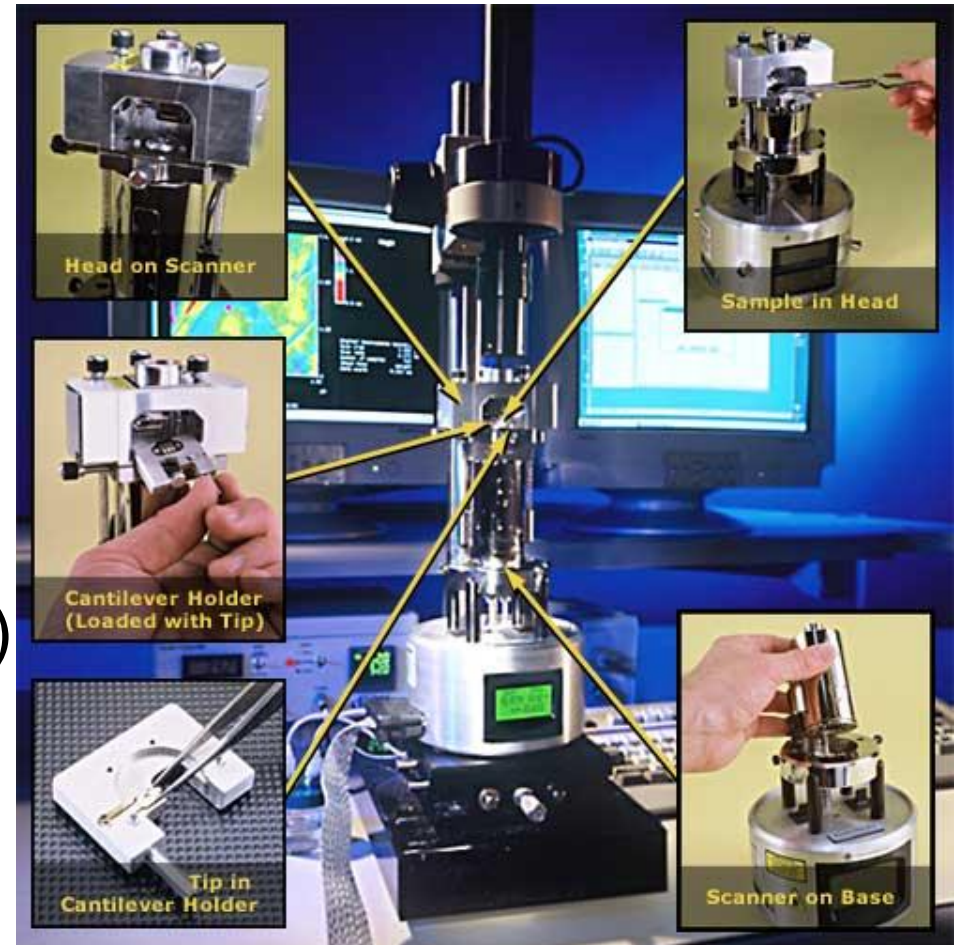
AFM + MFM + LFM + KPFM +
CAFM

Imaging in air/liquid

Modes: contact, tapping, peak-
force tapping

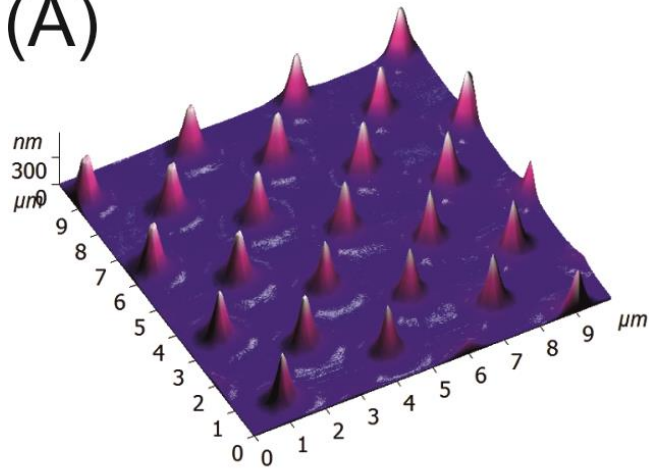
Tips: Scan-Asyst, SNL-10 (2 nm)

**What you get is not what you
could see: tip-surface
convolution**

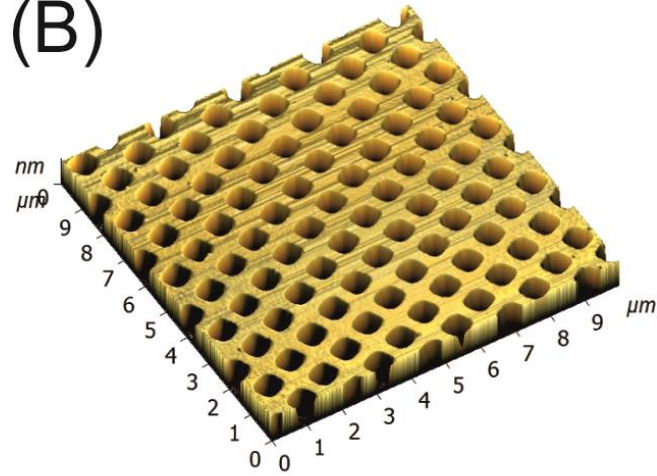


Silicon gratings

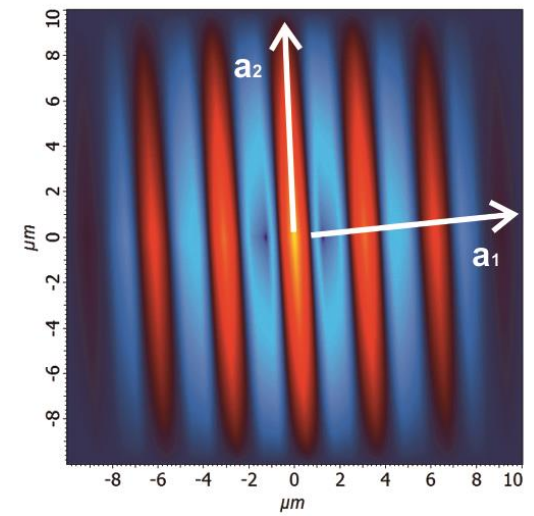
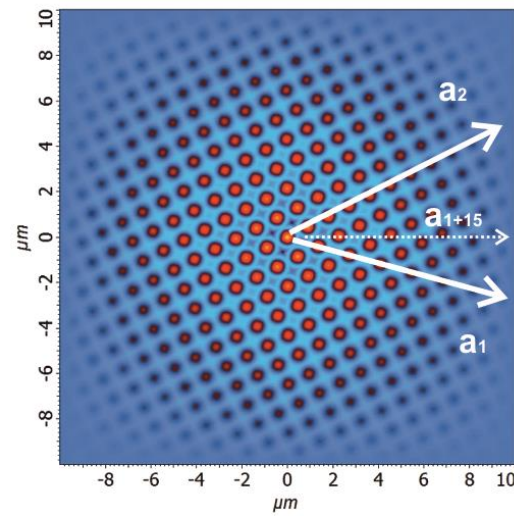
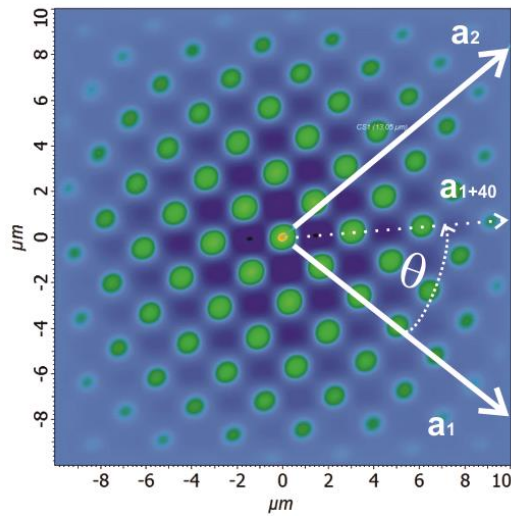
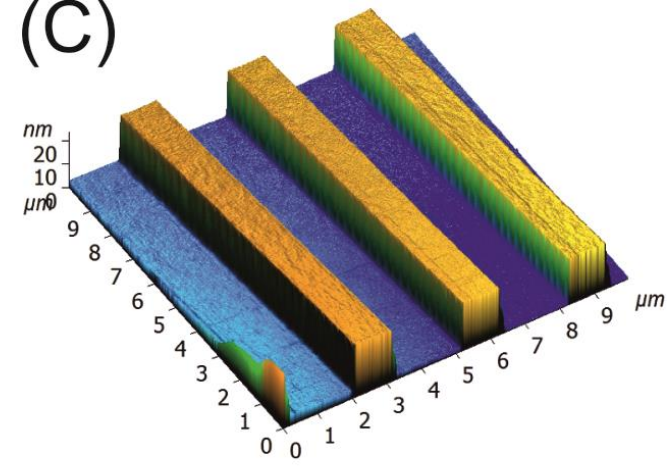
(A)



(B)



(C)

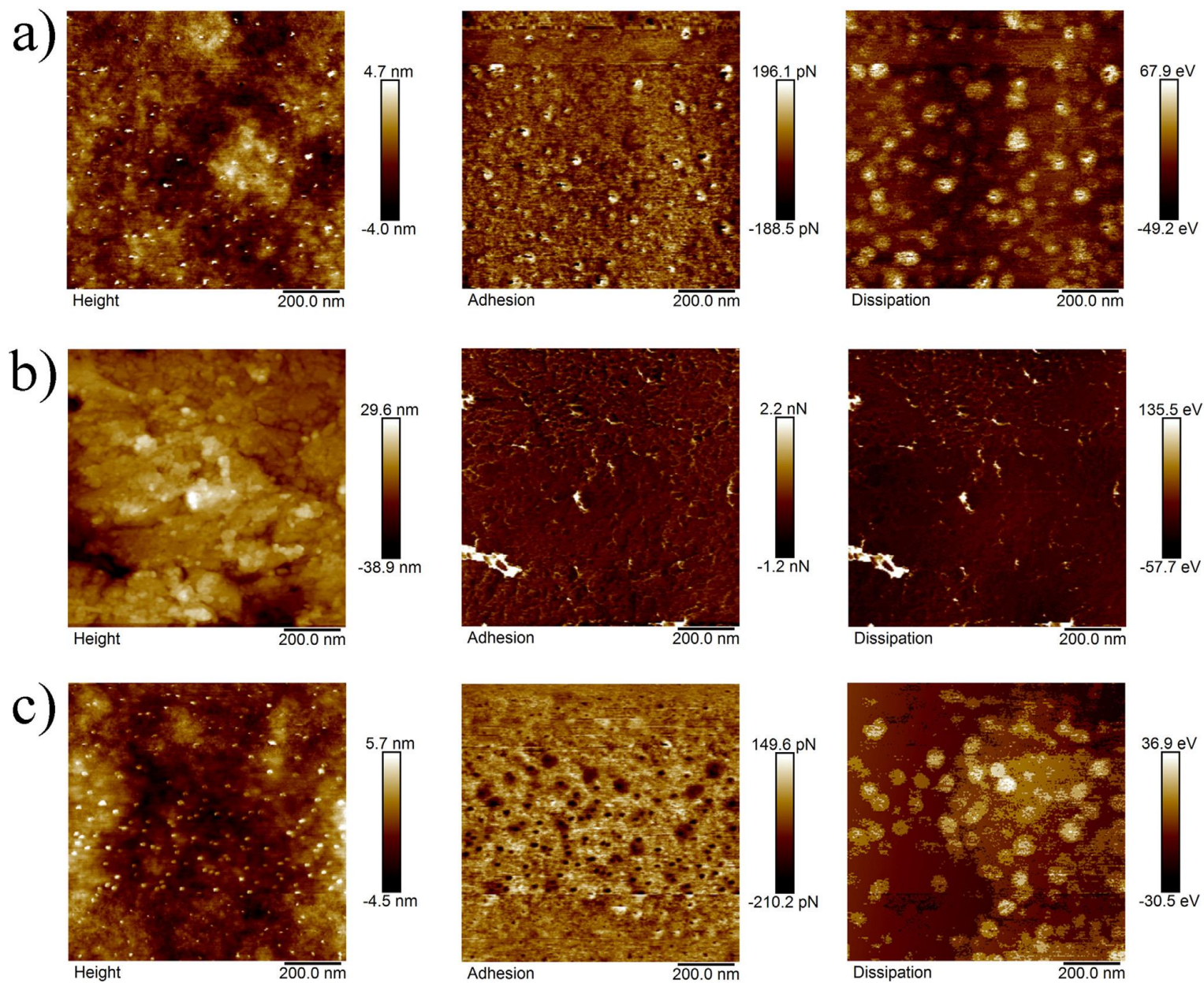


Nanomechanical verification of drugs

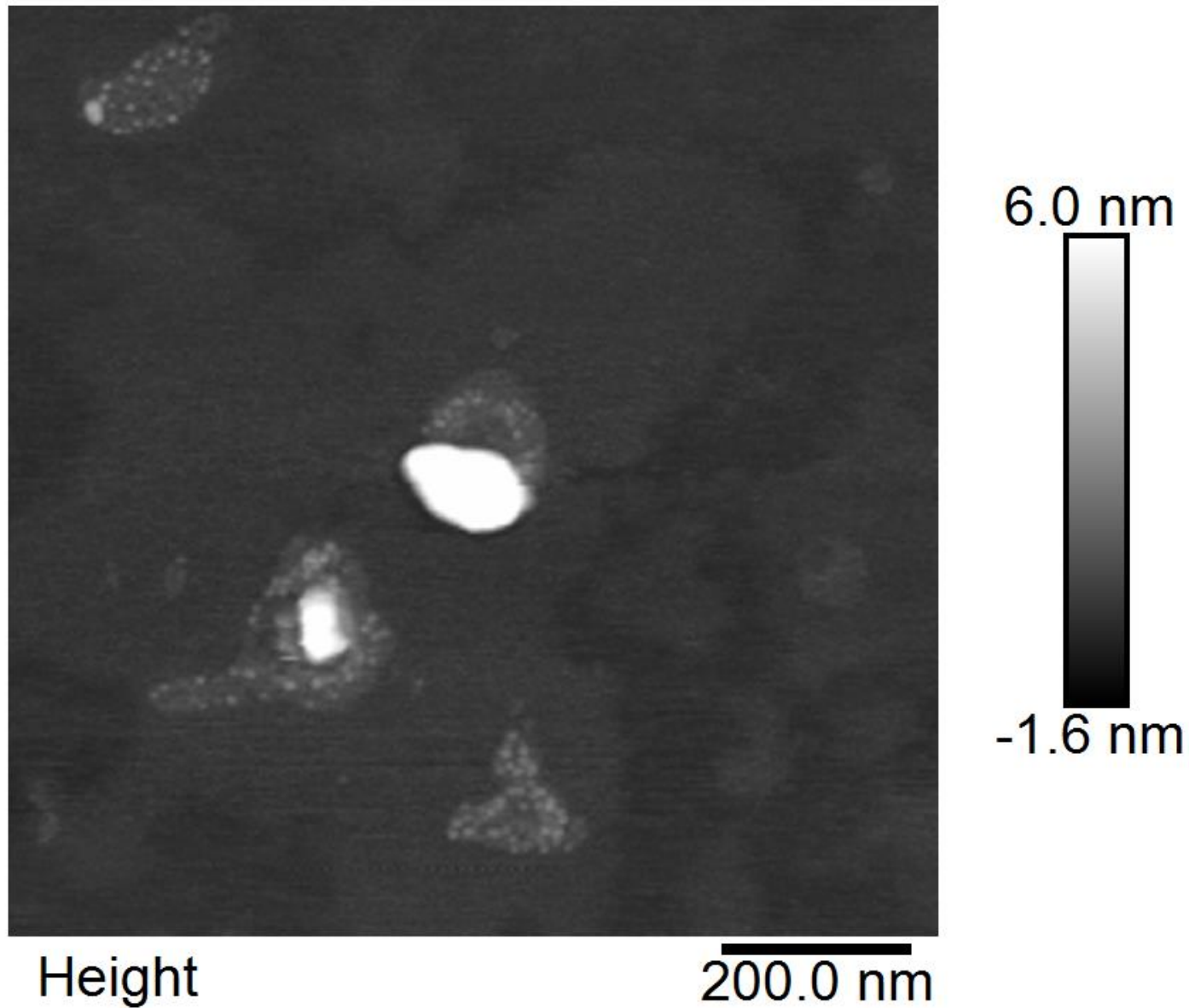


S. Wilczyński, M. Petelenz, M. Florek-Wojciechowska, S. Kulesza, Sz. Brym, B. Błońska-Fajfrowska, D. Kruk, *Verification of the authenticity of drugs by means of NMR relaxometry – Viagra® as an example*, Journal of Pharmaceutical and Biomedical Analysis, 135 (2017) 199

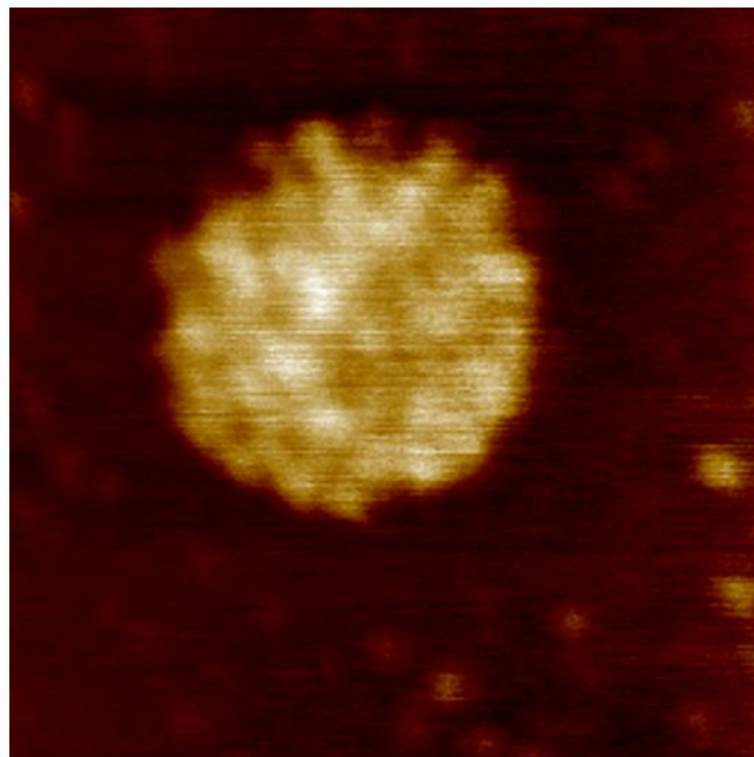
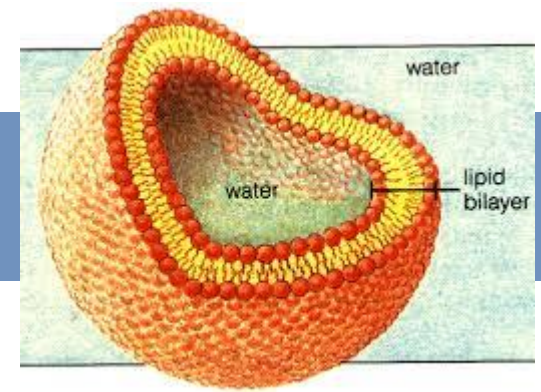
Pure sildenafil, Viagra[®], pseudo-Viagra



Cu-NPs embedded in glucose

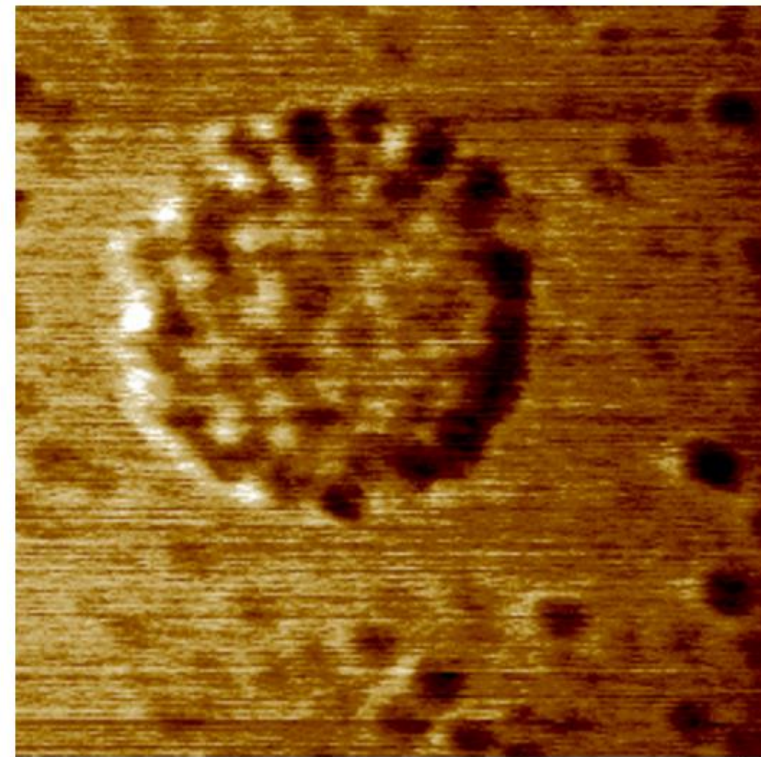
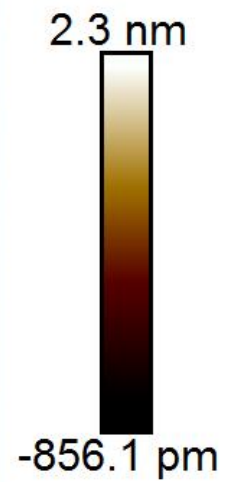


Liposomes



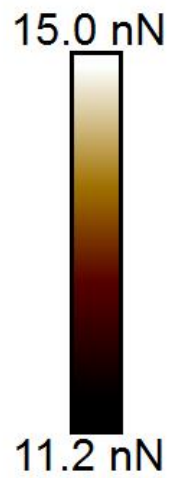
Height

100.0 nm

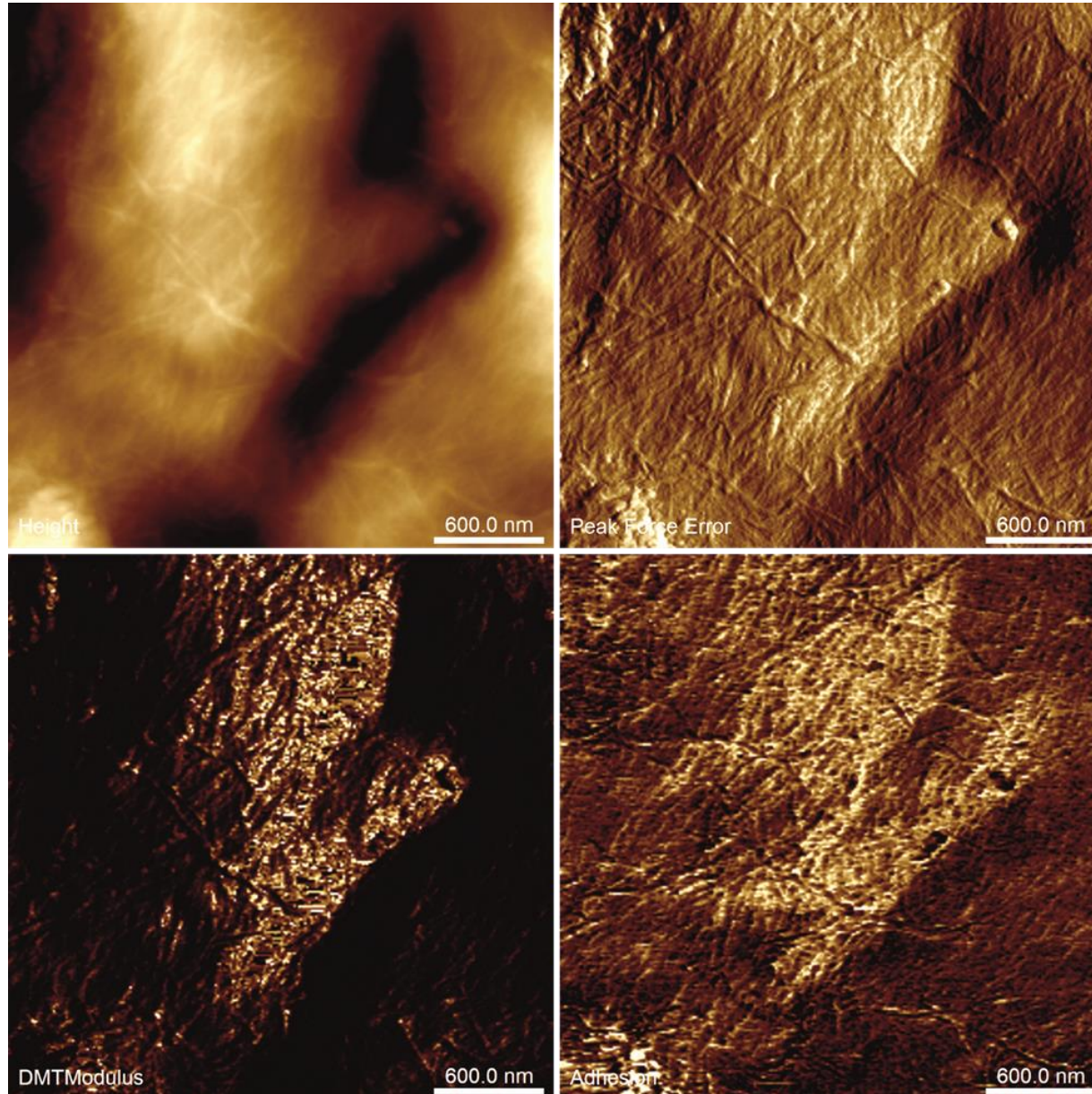


Adhesion

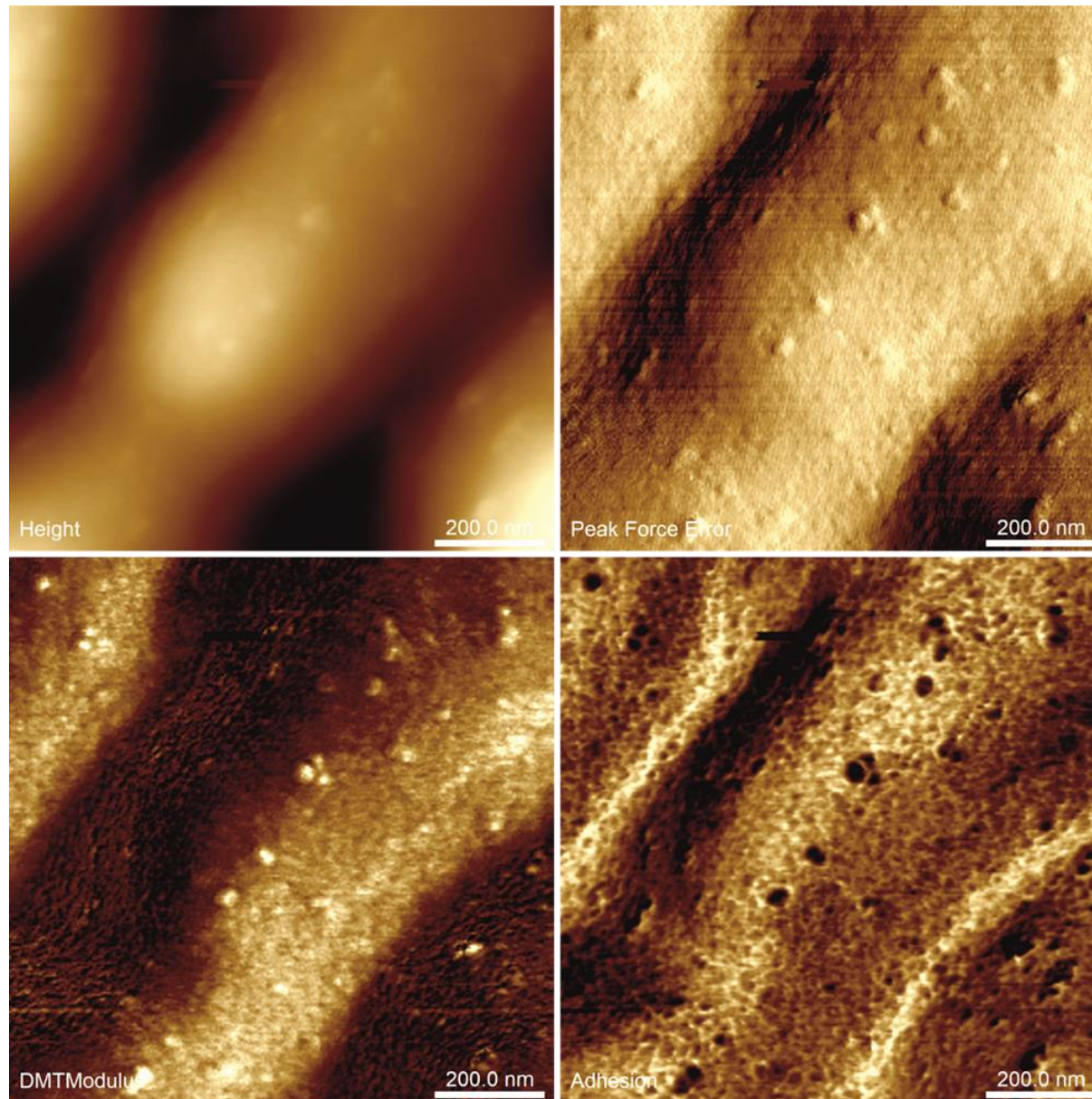
100.0 nm



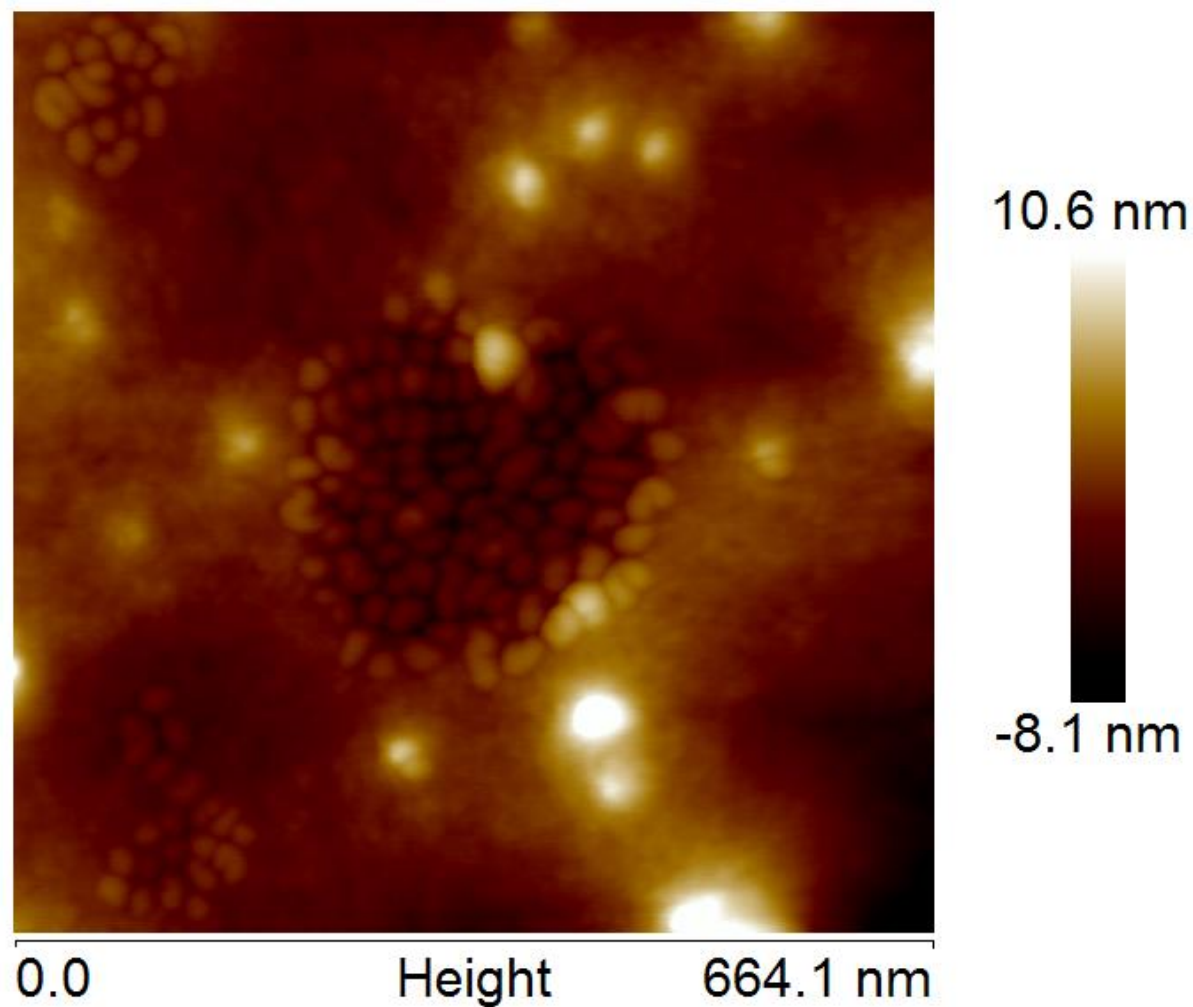
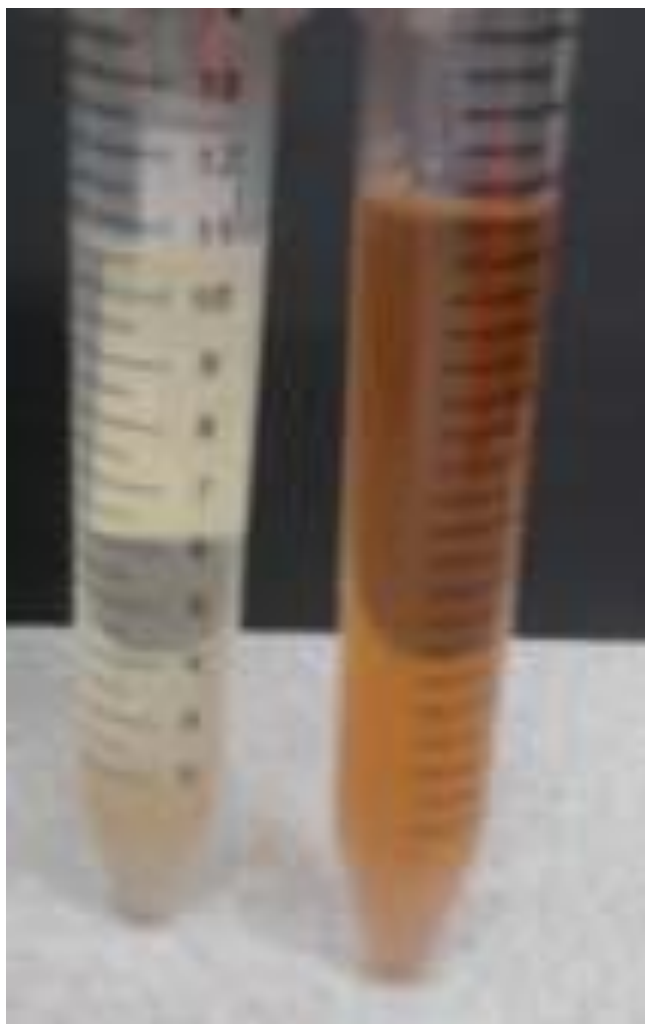
Dried squash of sugar beets without enzymes



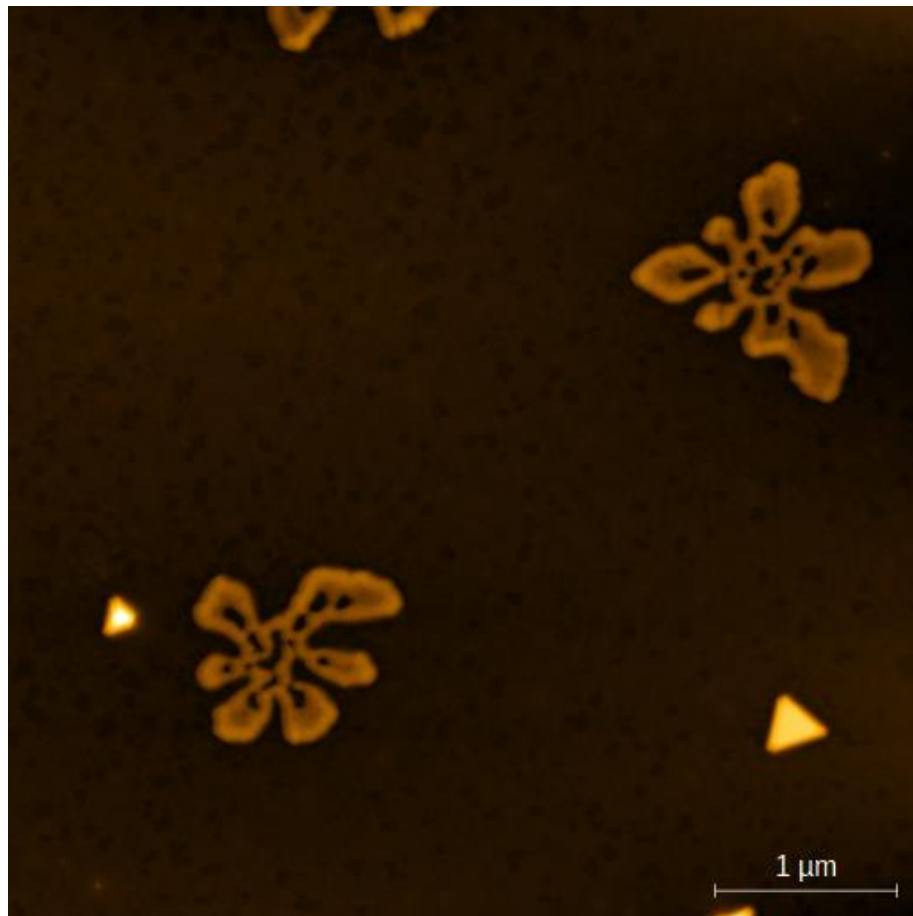
Dried squash of sugar beets with enzymes



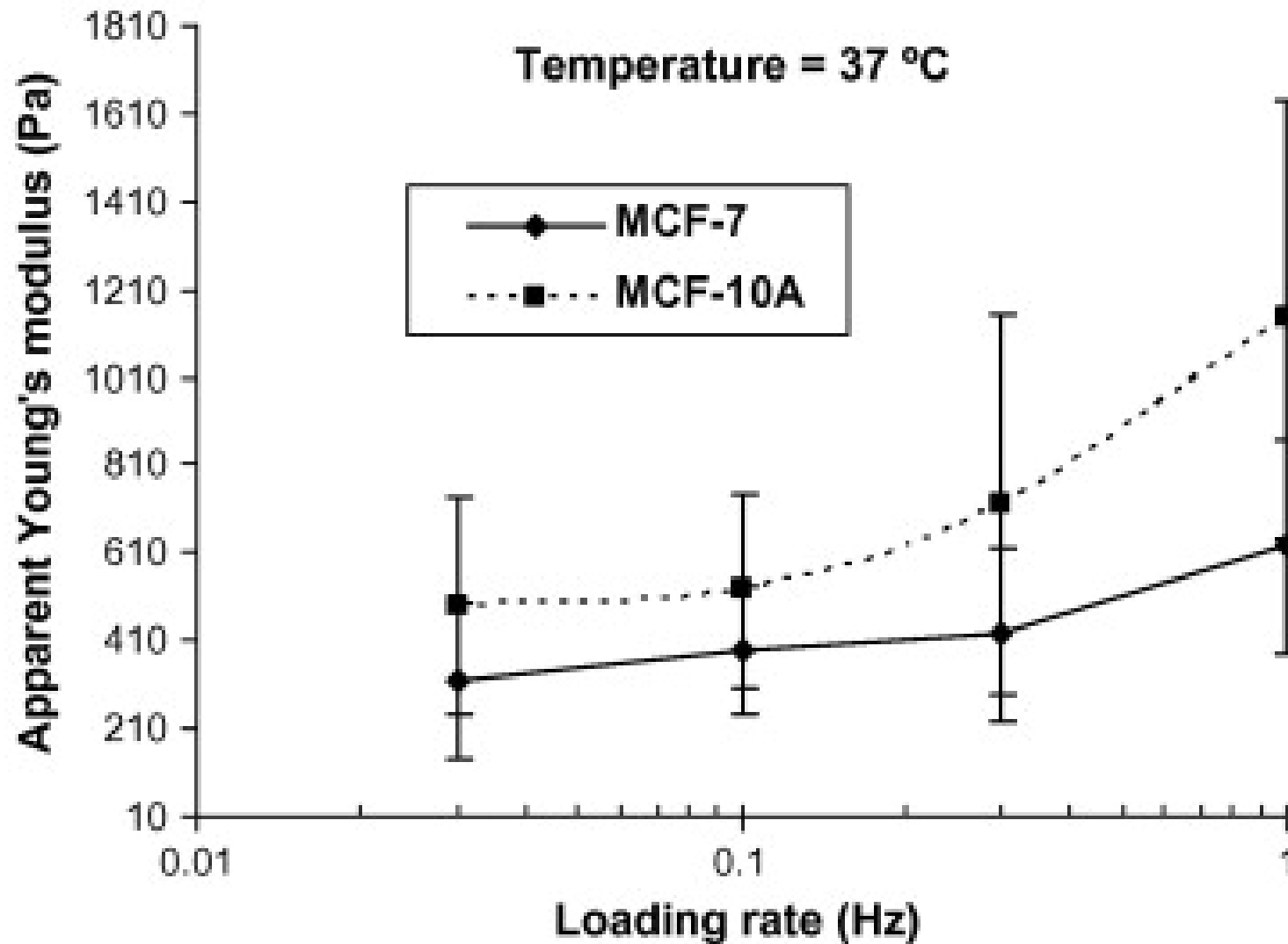
Ag-NPs and the extract of raspberry leaves



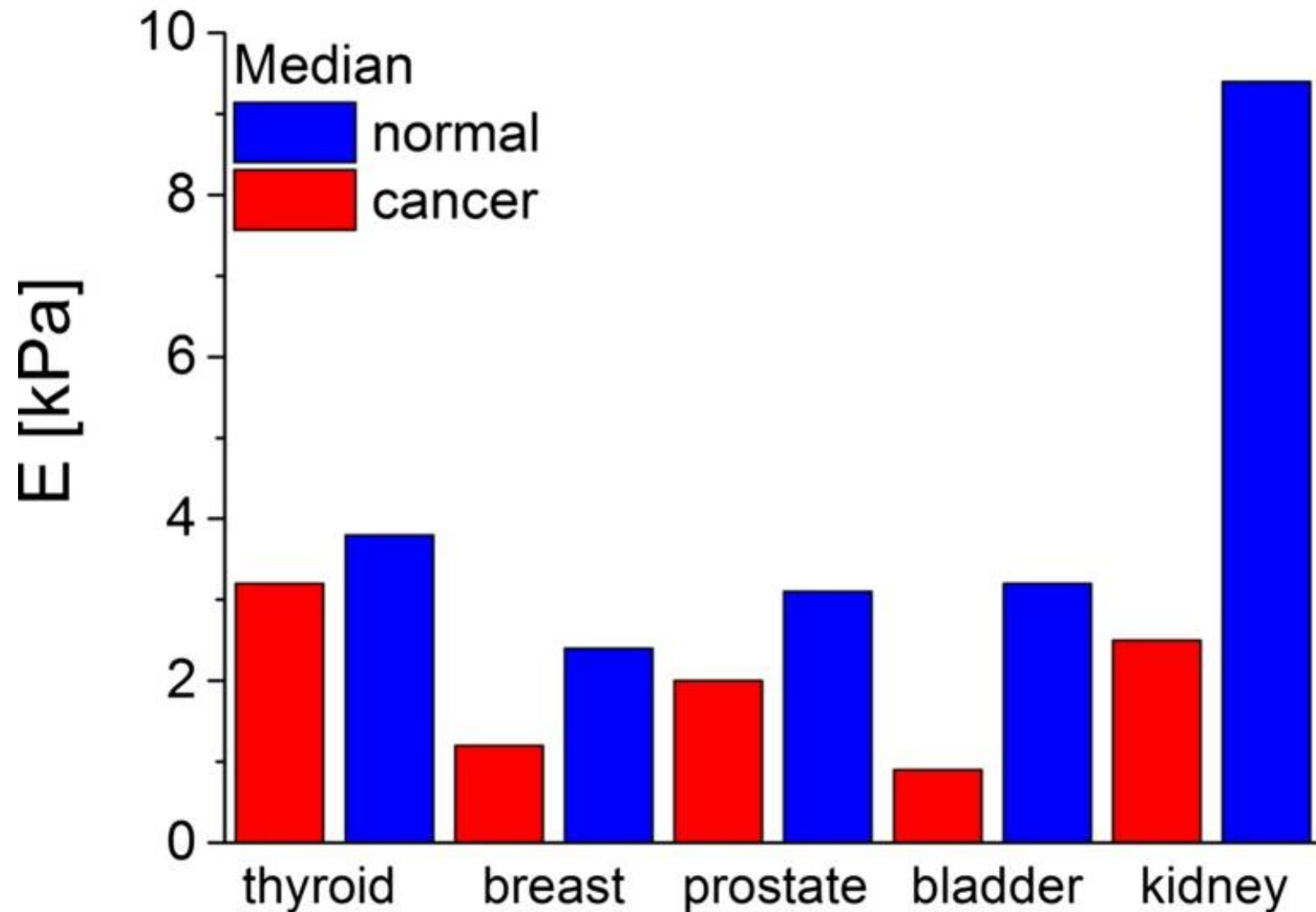
Sample contaminations



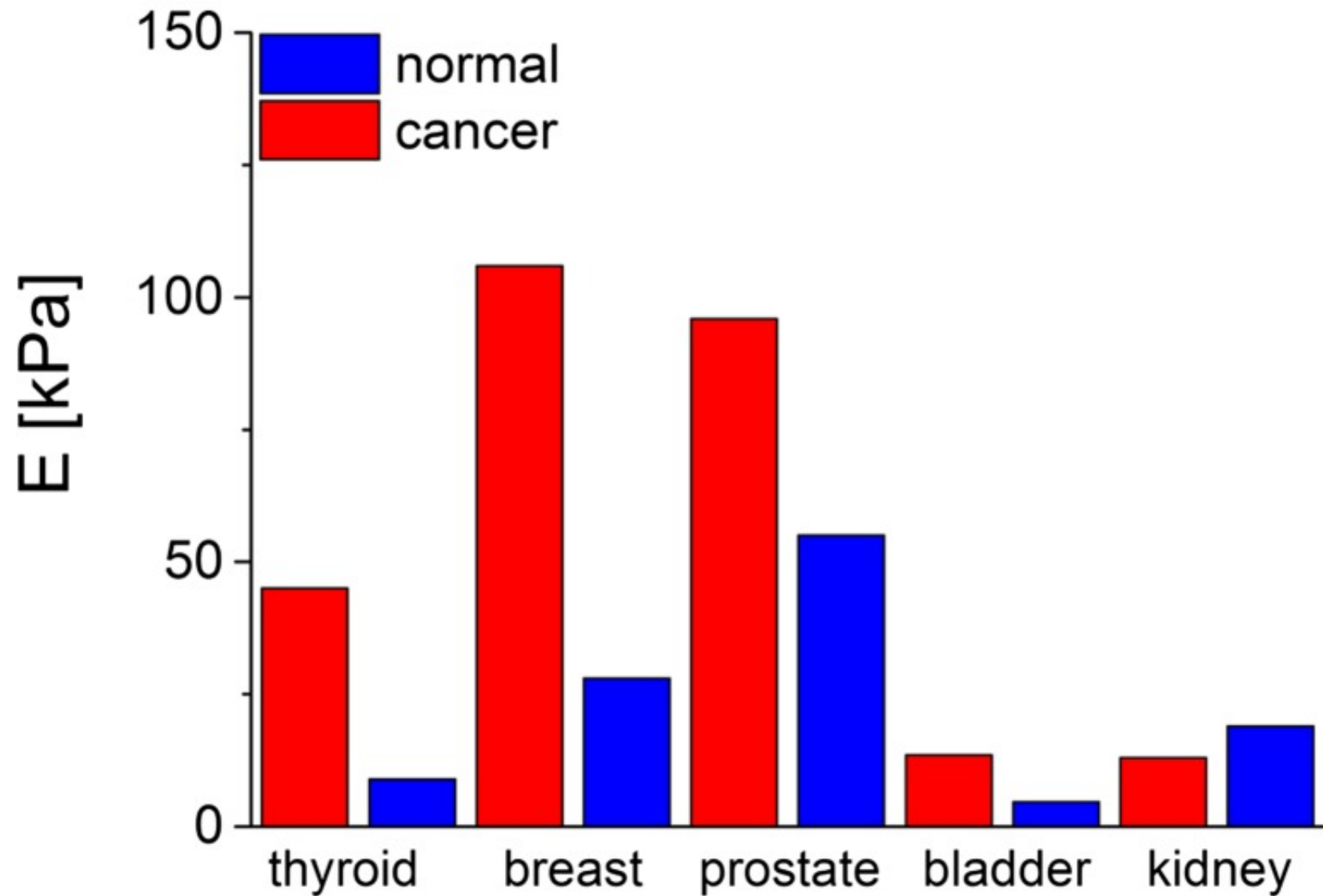
Malignant (MCF-10A) vs. nonmalignant (MCF-7) breast cancer



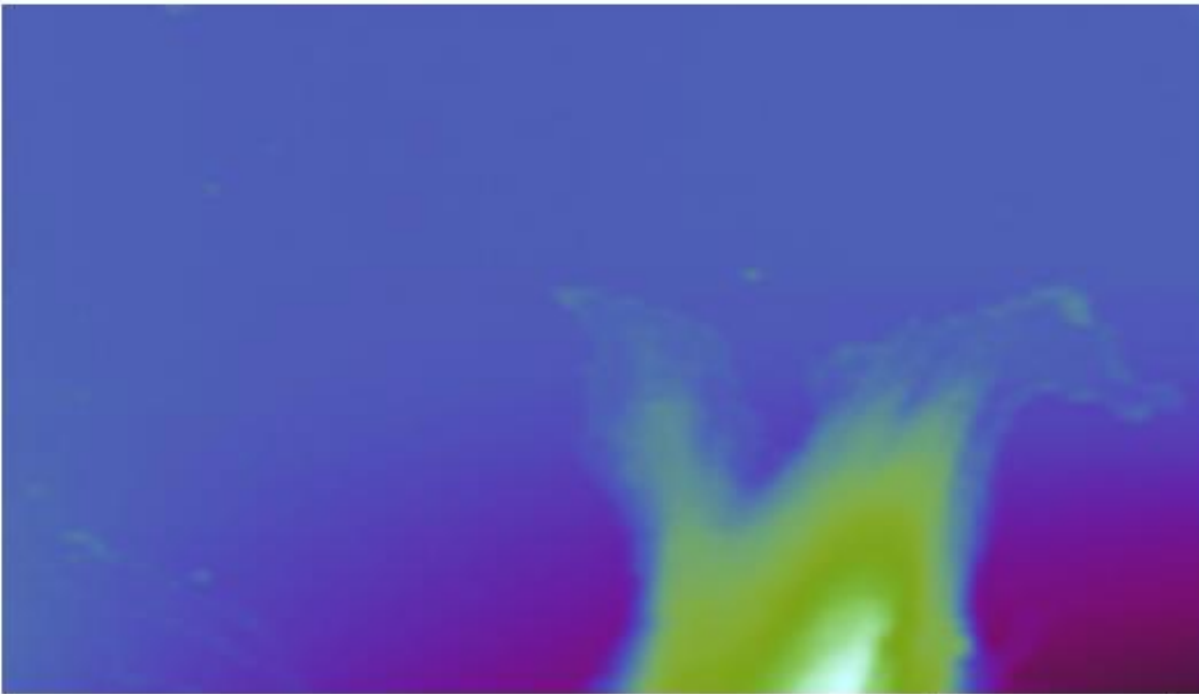
Elasticity of single cells



Elasticity of tissues

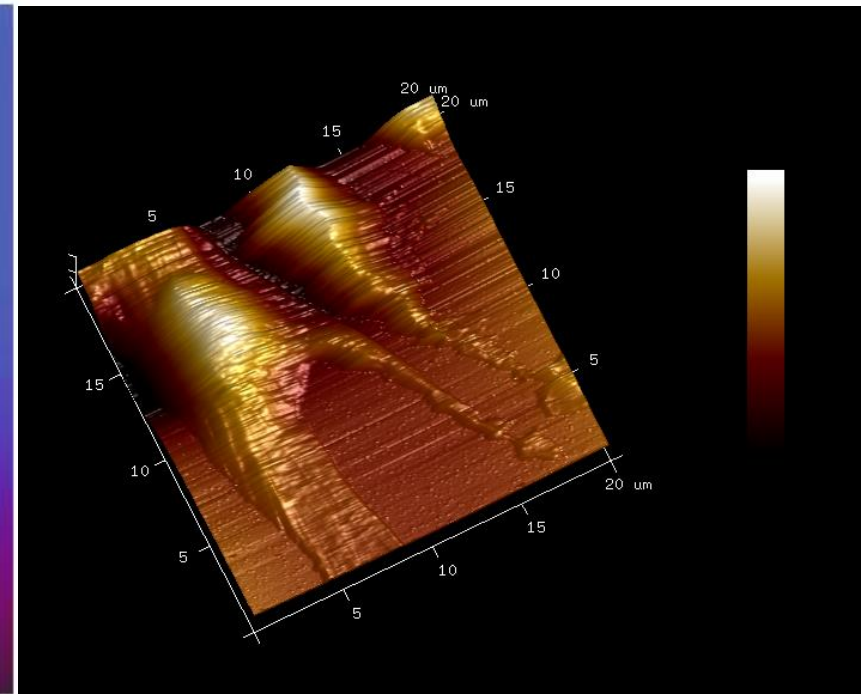


Stem cells

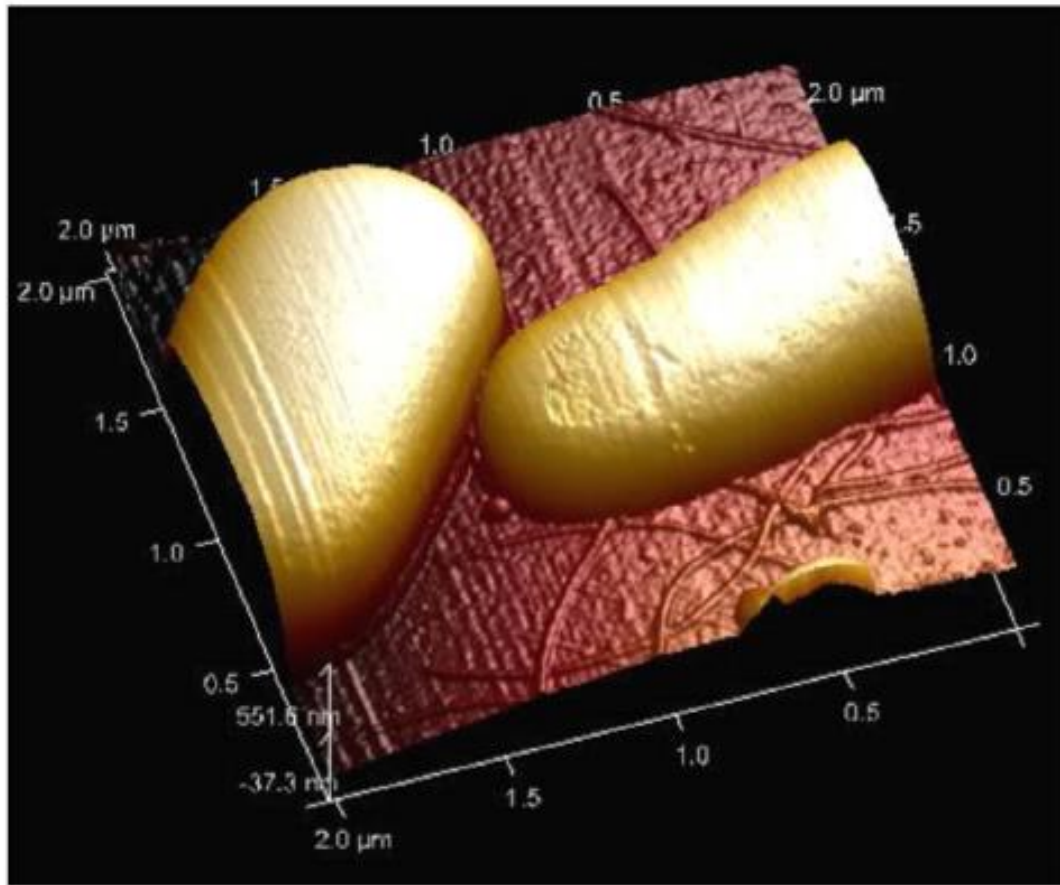


Height

20.0 μm

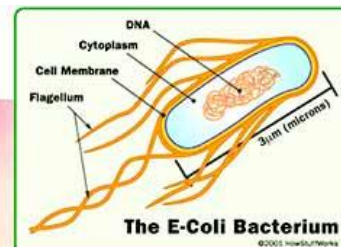
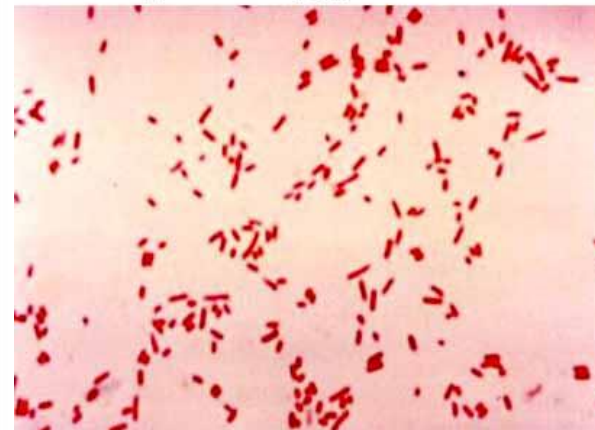


Rod-shaped Escherichia Coli



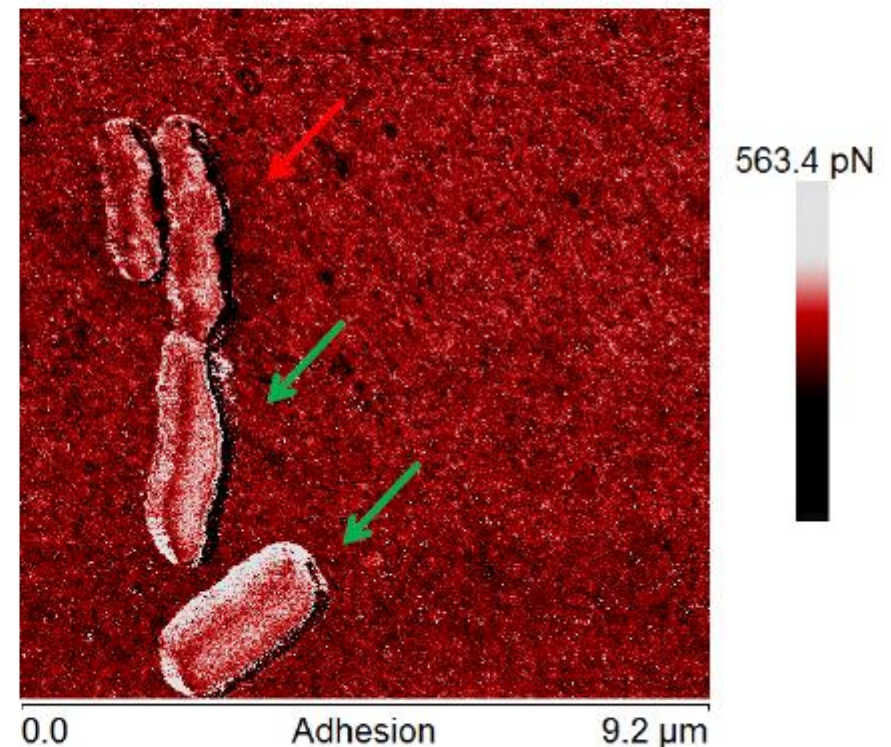
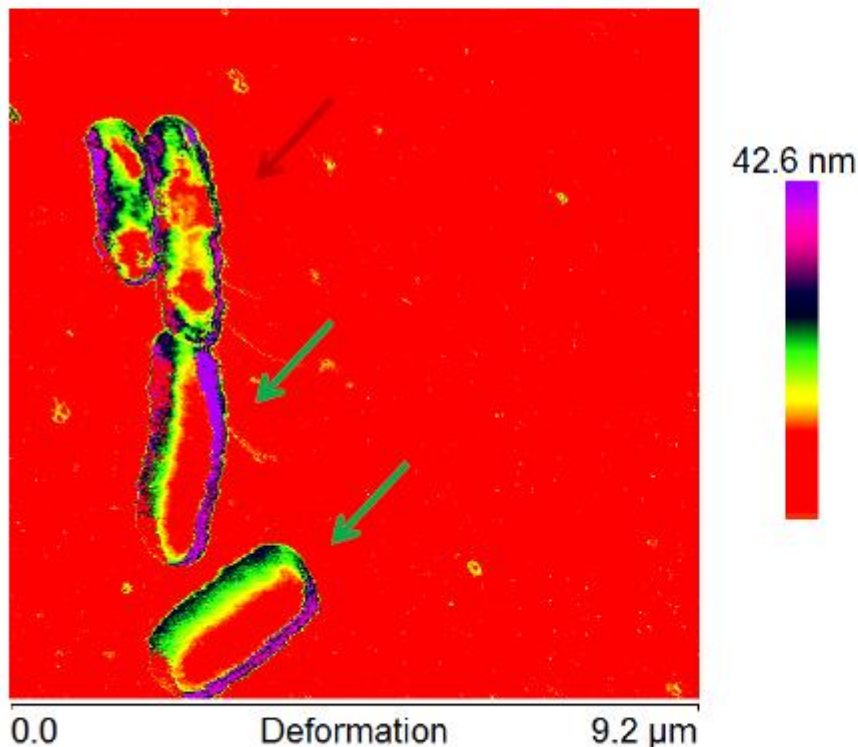
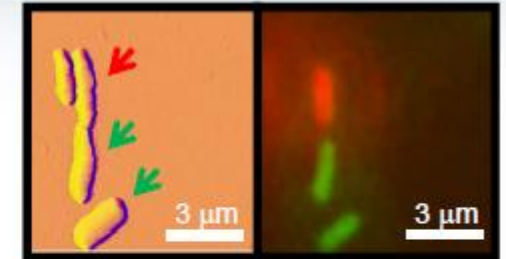
3D Topography image of live *E. coli* cells. AFM allows direct observation of the cellular envelope as well as other structures such as flagella and pili. Image was acquired on the Bruker FastScan™ AFM operated in TappingMode™ under fluid conditions (Image = 2 μ m).

Morphology of *E. coli*



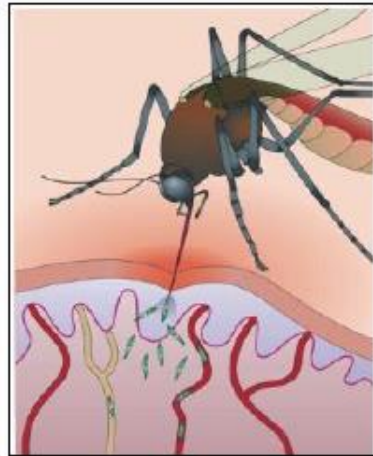
E. coli live vs. dead

- Live *E. coli* cells were fairly uniform in deformation (elasticity) while dead cells were more heterogeneous with areas of increased deformation (softer – less elastic).
- Live and dead cells showed no differences in adhesion.



Images were obtained on a BioScope™ Catalyst integrated with a Zeiss Axiovert 200 IOM and operated in PeakForce™ Tapping Mode in fluid. Images courtesy J. Shaw, Bruker-Nano Inc.

Red Blood Cells



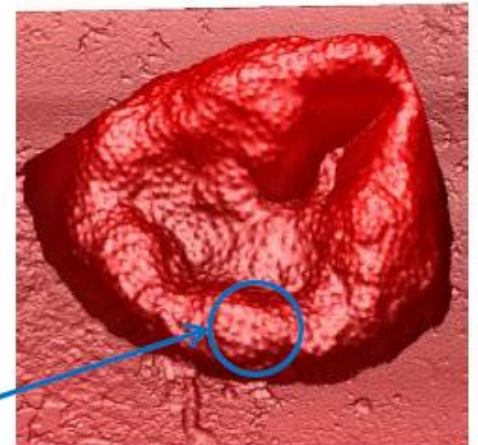
Anopheles mosquito



P. falciparum



Healthy RBC



Knobs

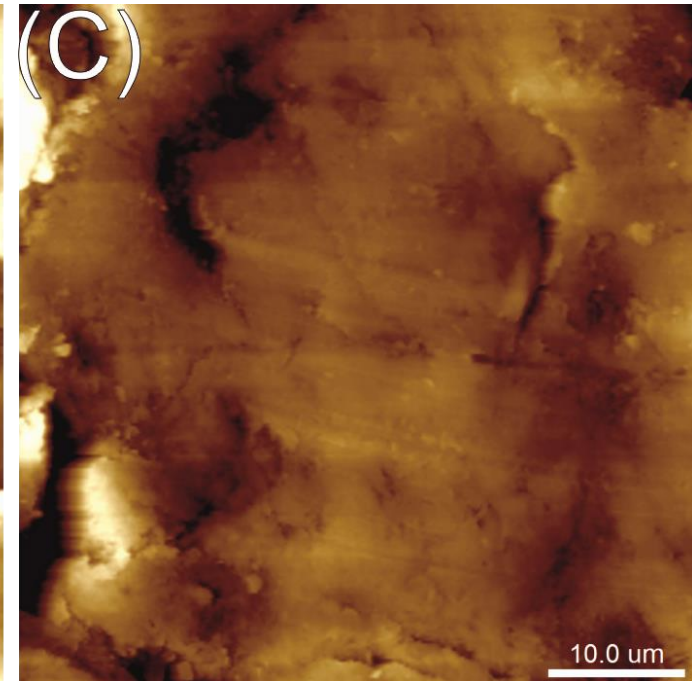
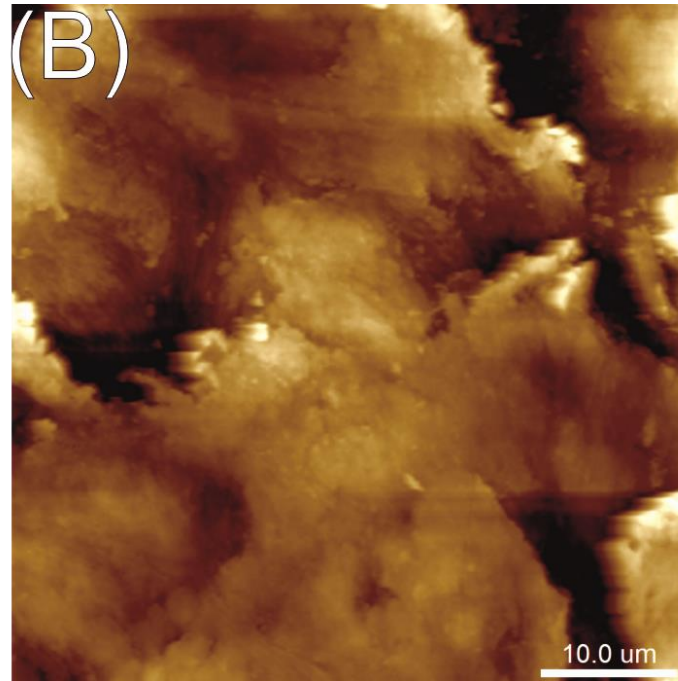
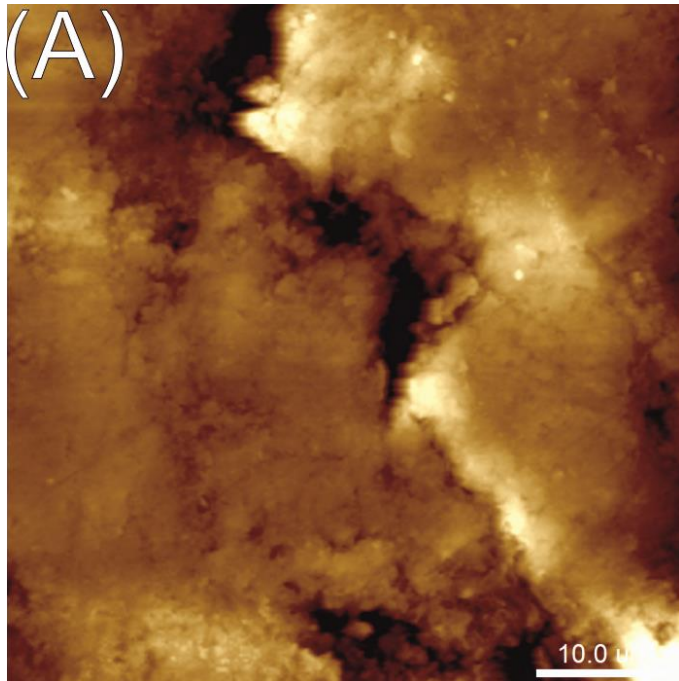
Infected RBC

Parasites enter bloodstream and infect RBCs.

As parasites multiply, the RBCs break open and infect more RBCs.

Infected RBCs are *misshapen* with *knob-like structures* on surface.

Human fingernails

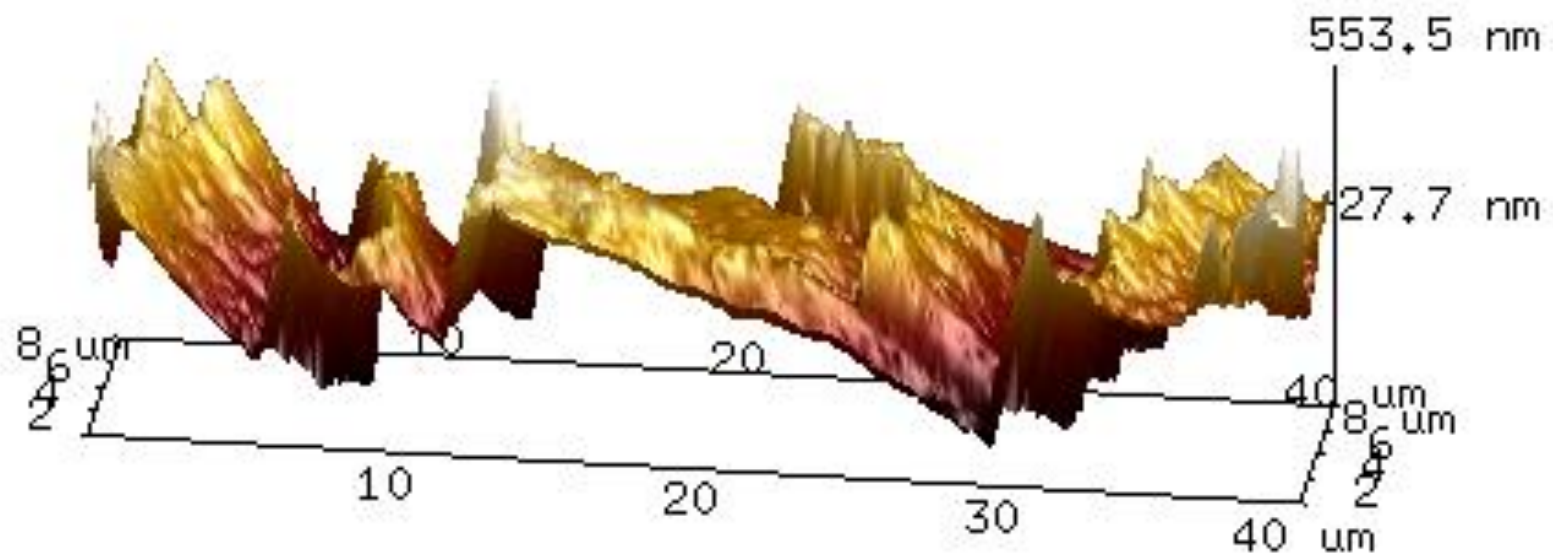


Human hair

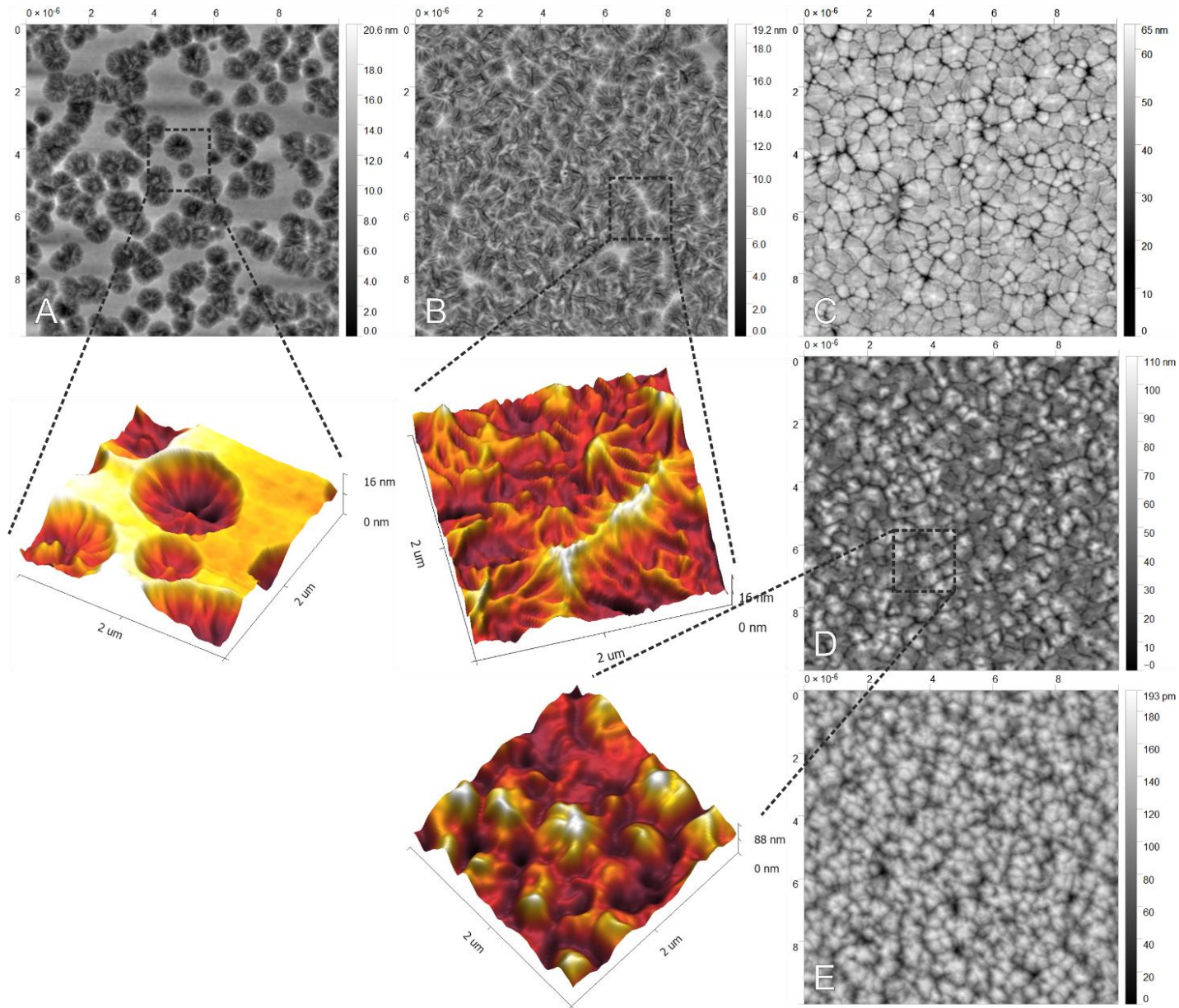


Height

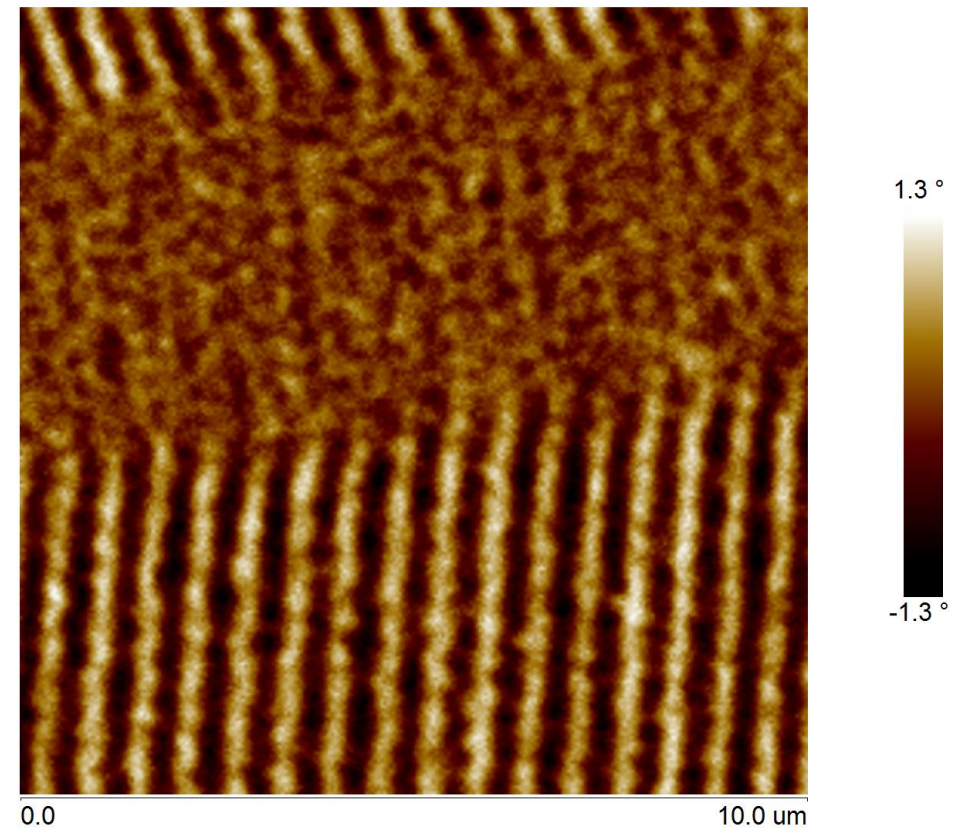
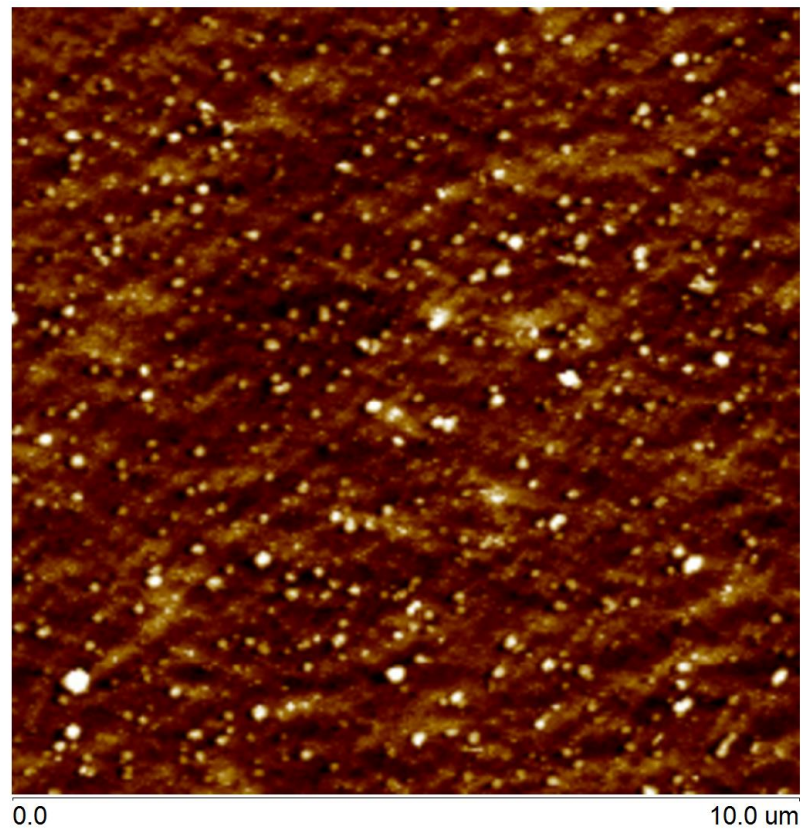
8.0 μm



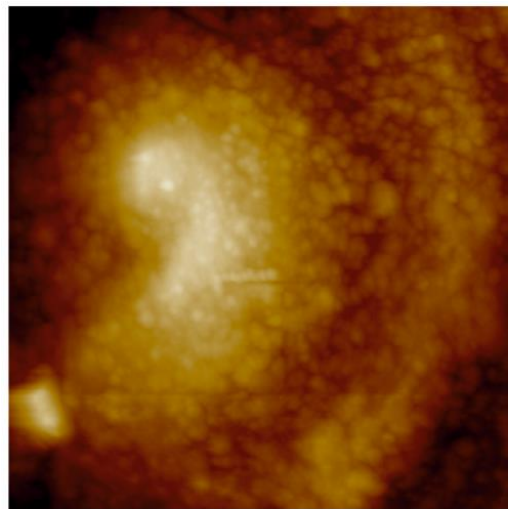
Hydrxyapatite (HAP)



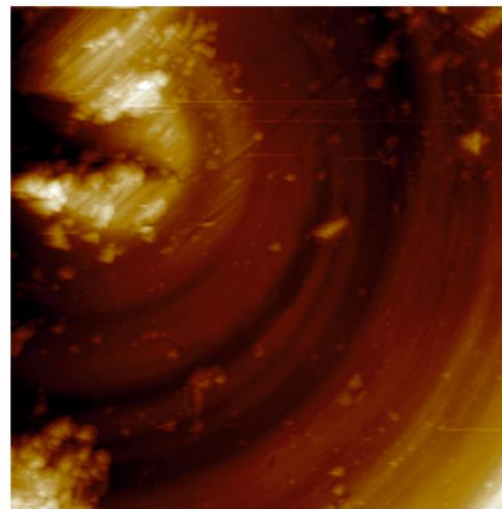
MFM – magnetic tape (VHS)



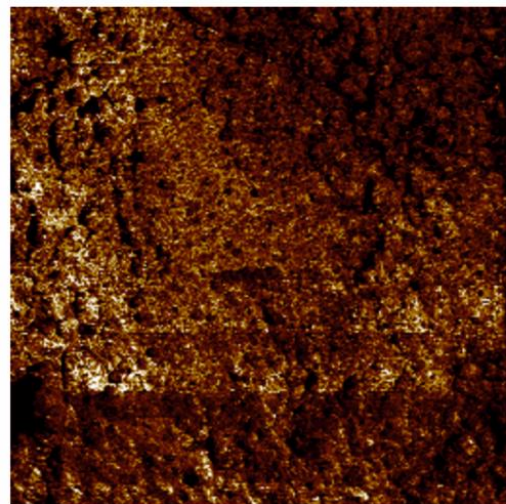
Ti dental implants



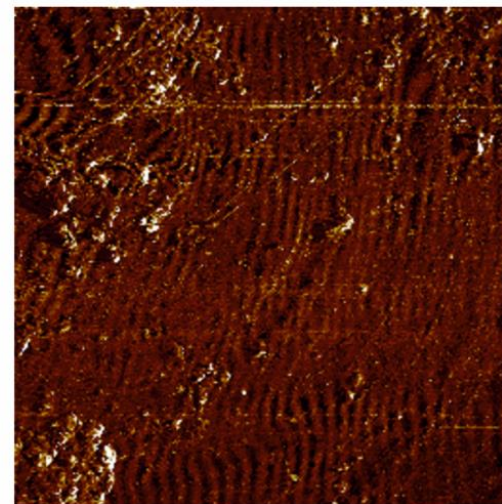
Height 10.0 μm



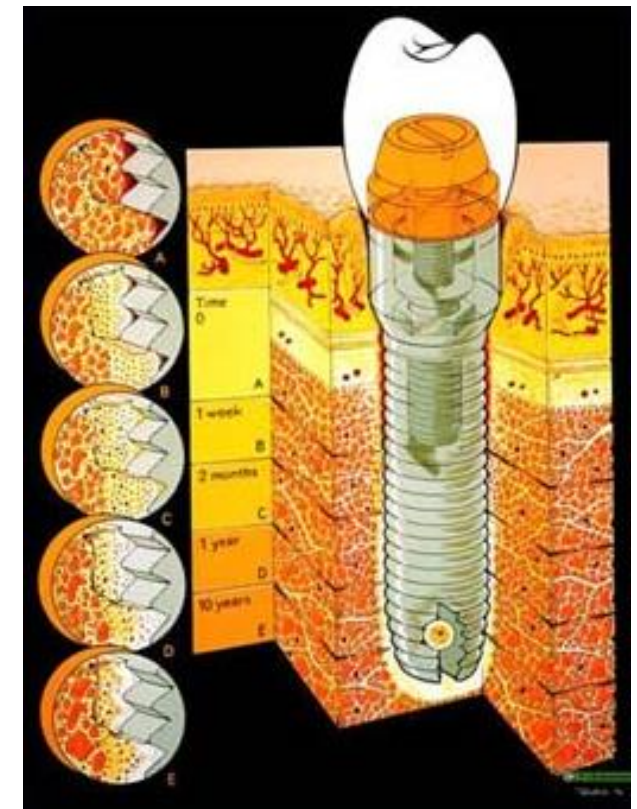
Height 10.0 μm



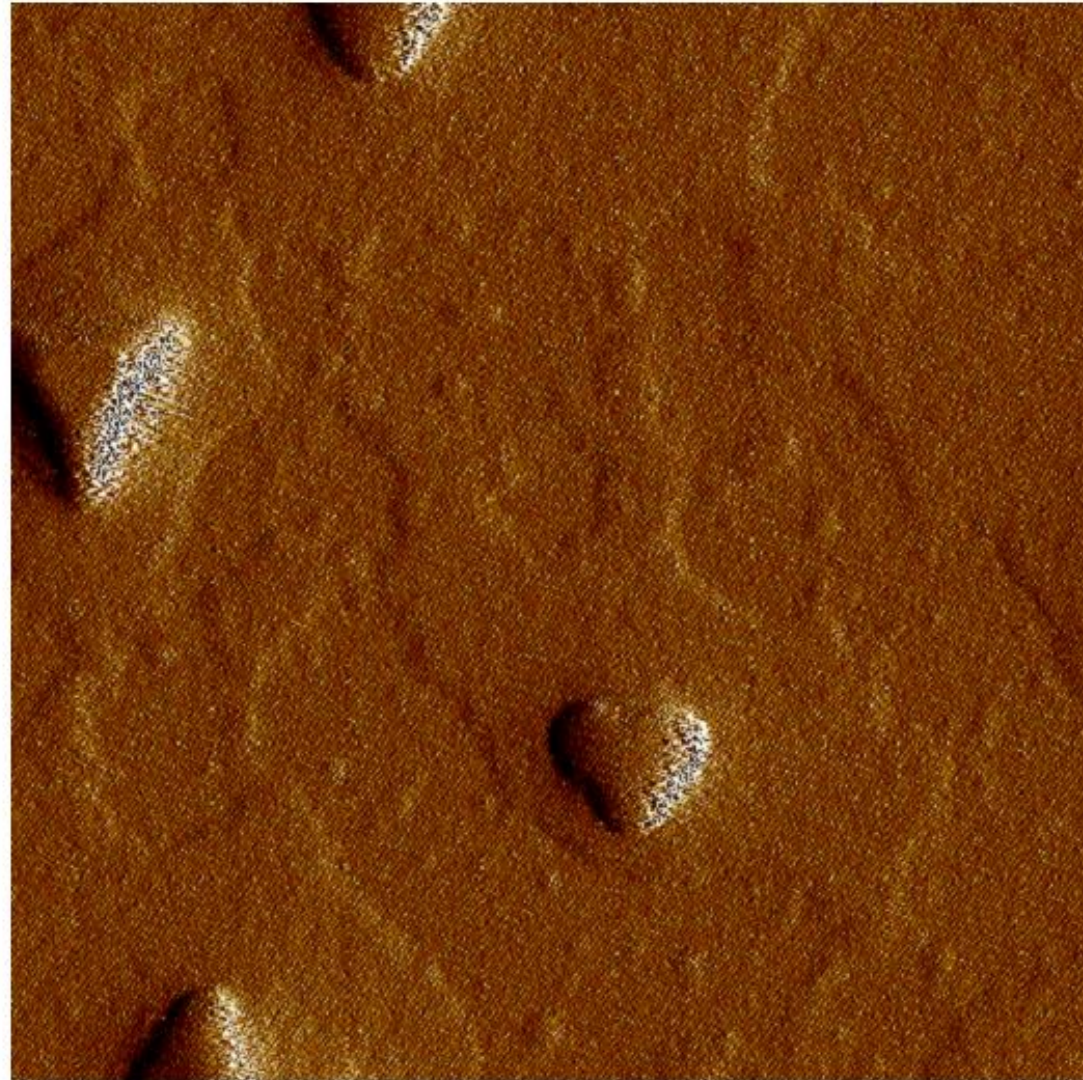
Adhesion 10.0 μm



Adhesion 10.0 μm



Thank you for your attention!



0.0 Peak Force Error 1.0 μm