Lecture 1: Introduction to scanning probe microscopy

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Outline

Learning outcomes:

■ Understand the basic principles of scanning probe microscopies (scanning tunnelling microscopy and atomic force microscopy)

■ Get insight into how to study the geometric and electronic structure of surfaces using scanning probe microscopies

■ Be familiar with how to apply scanning probe microscopies to study the properties of nanomaterials

■ **Lecture 1**: Introduction to STM and AFM

■ **Lecture 2**: Atomic-scale materials science using STM and AFM

Additional reading

A?

https://link.springer.com/book/10.1007/978-3-662-45240-0

NanoScience and Technology

Bert Voigtländer

Scanning Probe Microscopy

Atomic Force Microscopy and Scanning Tunneling Microscopy

Springer

https://global.oup.com/academic/product/introduction-to-scanning-tunneling-microscopy-9780199211500?cc=fi&lang=en&

NanoScience and Technology

Seizo Morita
Franz J. Giessibl
Ernst Meyer
Roland Wiesendanger *Editors*

Noncontact Atomic Force Microscopy

Volume 3

Springer

MONOGRAPHS ON THE PHYSICS AND CHEMISTRY OF MATERIALS • 64

Introduction to Scanning Tunneling Microscopy

Second Edition

C. JULIAN CHEN

OXFORD SCIENCE PUBLICATIONS

https://www.springer.com/gp/book/9783319155876

General principle of scanning probe microscopy
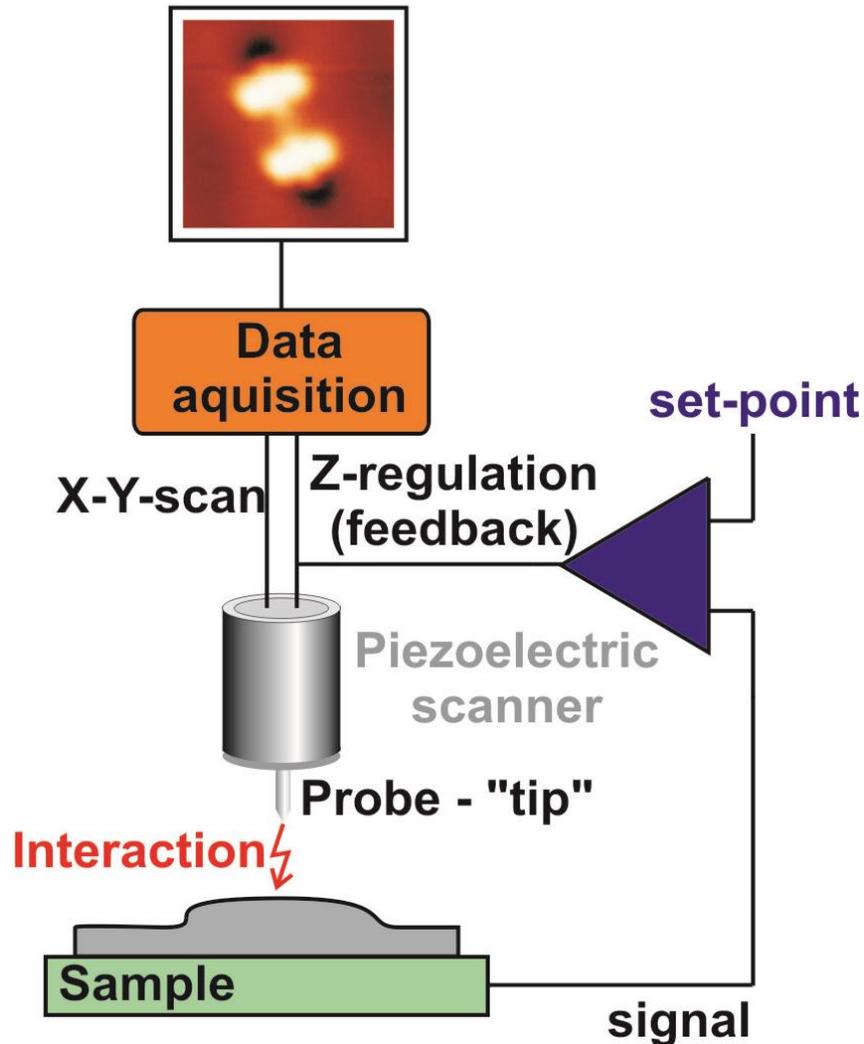
- Measure some interaction between a sharp probe and the sample

- **Scanning**: Move sample or tip while keeping this interaction constant (feedback) or while keeping height constant

- **Spectroscopy**: Change something (z, voltage, etc.) while keeping x and y constant (feedback off)
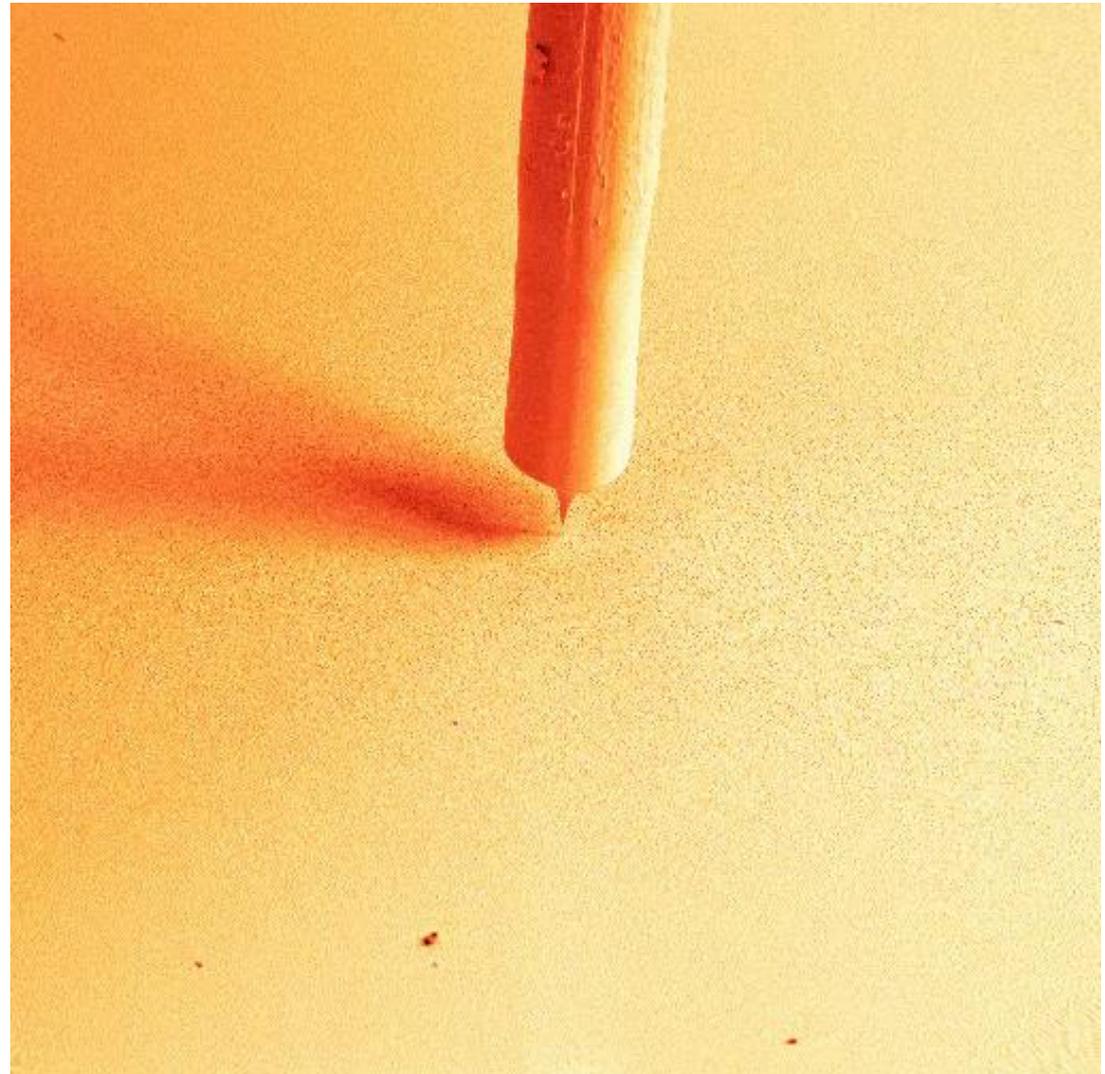
Functional nanostructures at
surfaces Forschungszentrum Jülich

Concepts: check-up

- Schrödinger equation
- Tunneling
- Density of states
- Fermi level
- Molecular orbital / wavefunction
- Van der Waals interaction
- Pauli repulsion

Tunnelling - Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi = E\psi$$

$$\psi = A\exp(ikx) + B\exp(-ikx)$$

$$\psi = C\exp(ikx)$$

$k = (2mE)^{1/2}/\hbar$

x=0 x=d

E>V   E<V   E>V
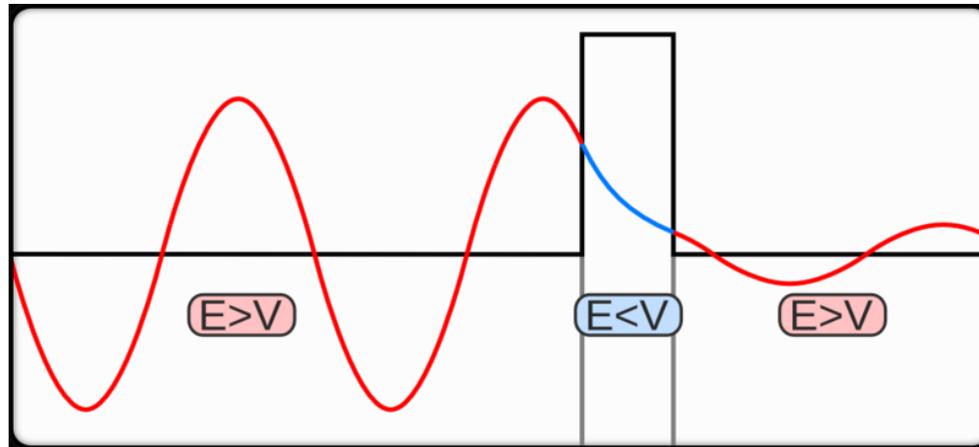
$$\psi = F\exp(\kappa x) + G\exp(-\kappa x)$$

$\kappa = (2m(V_0-E))^{1/2}/\hbar$

- ψ and dψ/dx must be continuous

- Transmission probability given by $T = |C|^2/|A|^2$

$$T = \left[1 + \frac{V_0^2 \sinh^2(\kappa d)}{4E(V_0 - E)}\right]^{-1}$$

Tunnelling continued

energy

Metal | Vacuum | Metal

e

E_{Fermi}

x

wavefunction

x=0   x=d
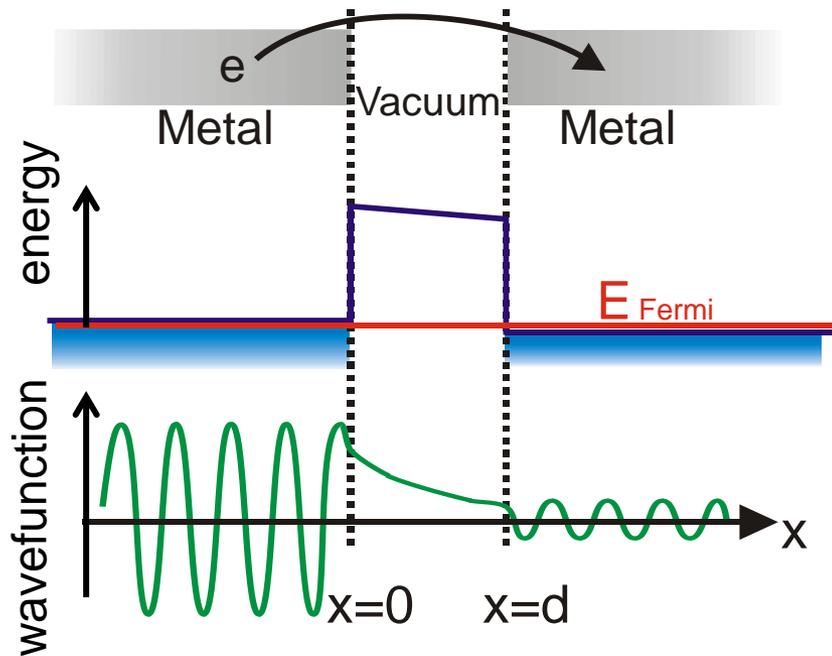
- If the barrier is large, i.e. $\kappa d \gg 1$, then transmission probability

$$T \approx 16E(V_0 - E)/V_0^2 \exp(-2\kappa d)$$

and the current

$$I(d) = I_0 e^{-2\kappa d},$$

with

$$\kappa = \left(\frac{2m}{\hbar^2}(V_0 - E)\right)^{1/2}$$

- $\kappa = 1.1$ Å^{-1} for barrier height of 4.5 eV
- If d changes by 1 Å, current changes by a fraction of $\exp(-2*1.1) = 0.11$
- If d changes by 1 pm, current changes ~2%
  - still measurable
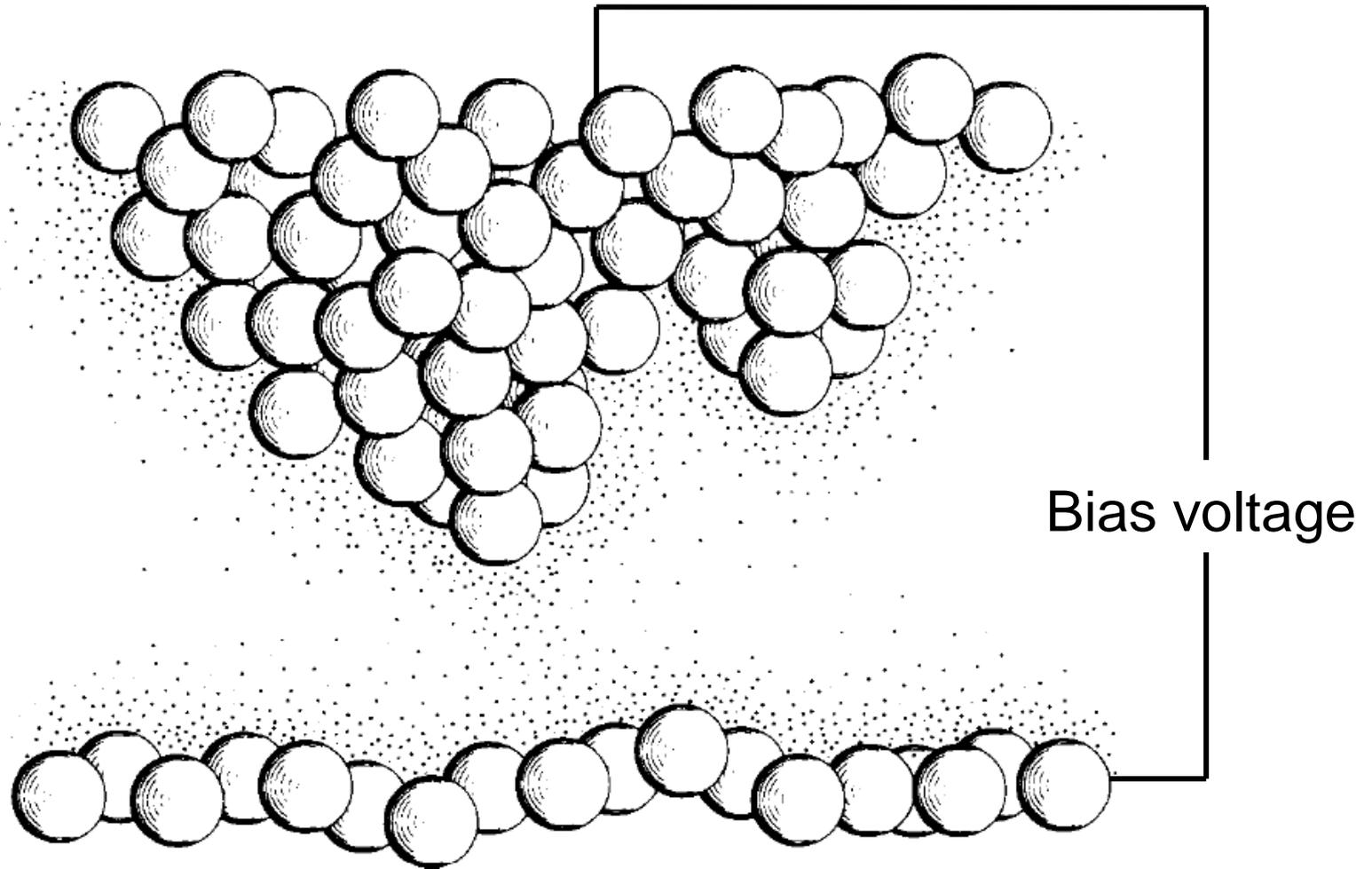
Bias voltage

- Typical bias voltage from a few mV to a few V (limited by the onset of field emission)
- Typical currents from a few pA to a few nA (tunneling conductance << conductance quantum ≈ $1/12.9k\Omega$)

Si(111) 7×7 reconstruction
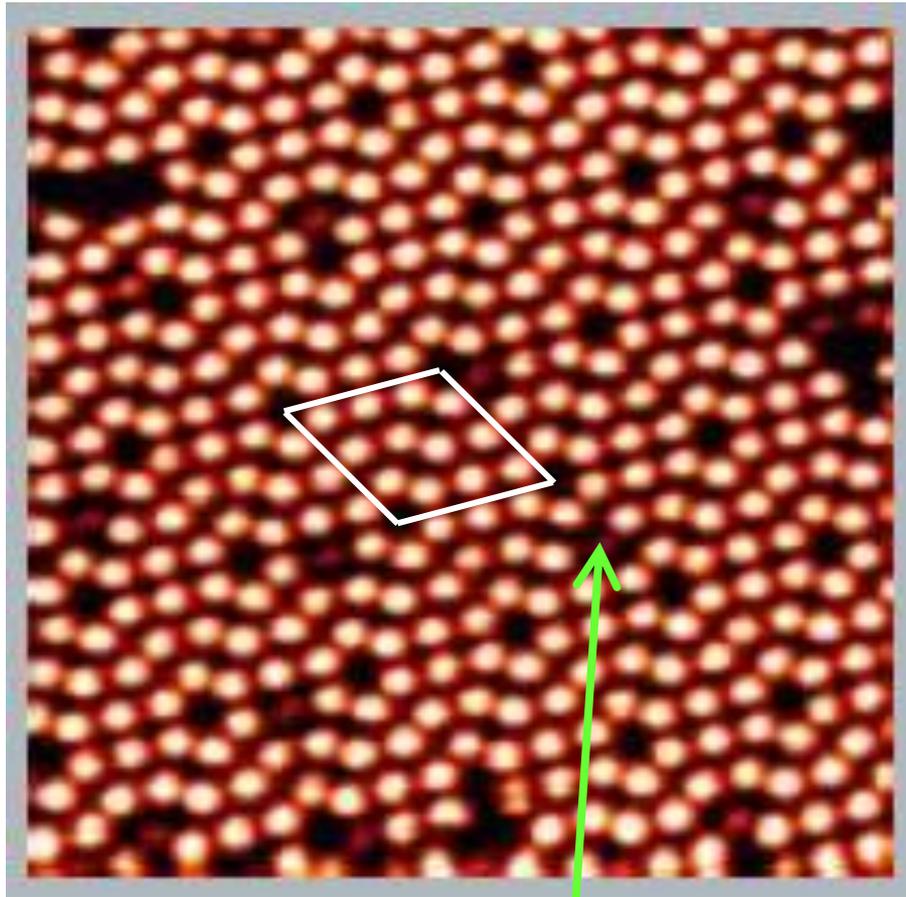
defect

- STM topography of Si(111) 7×7 reconstruction both atoms and defects visible
- First surface structure determination by STM
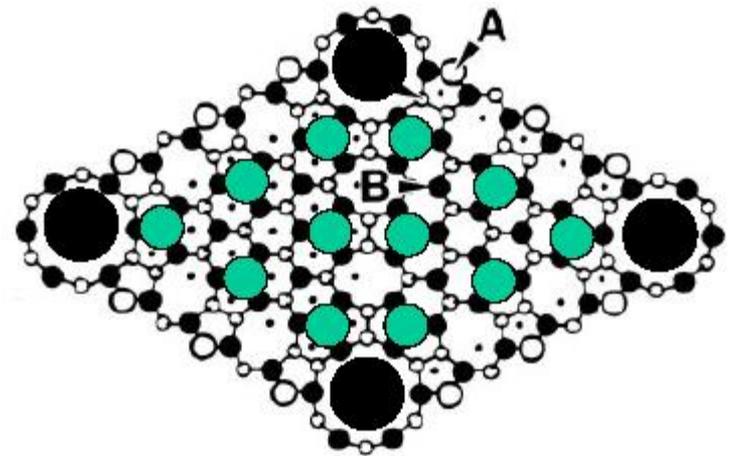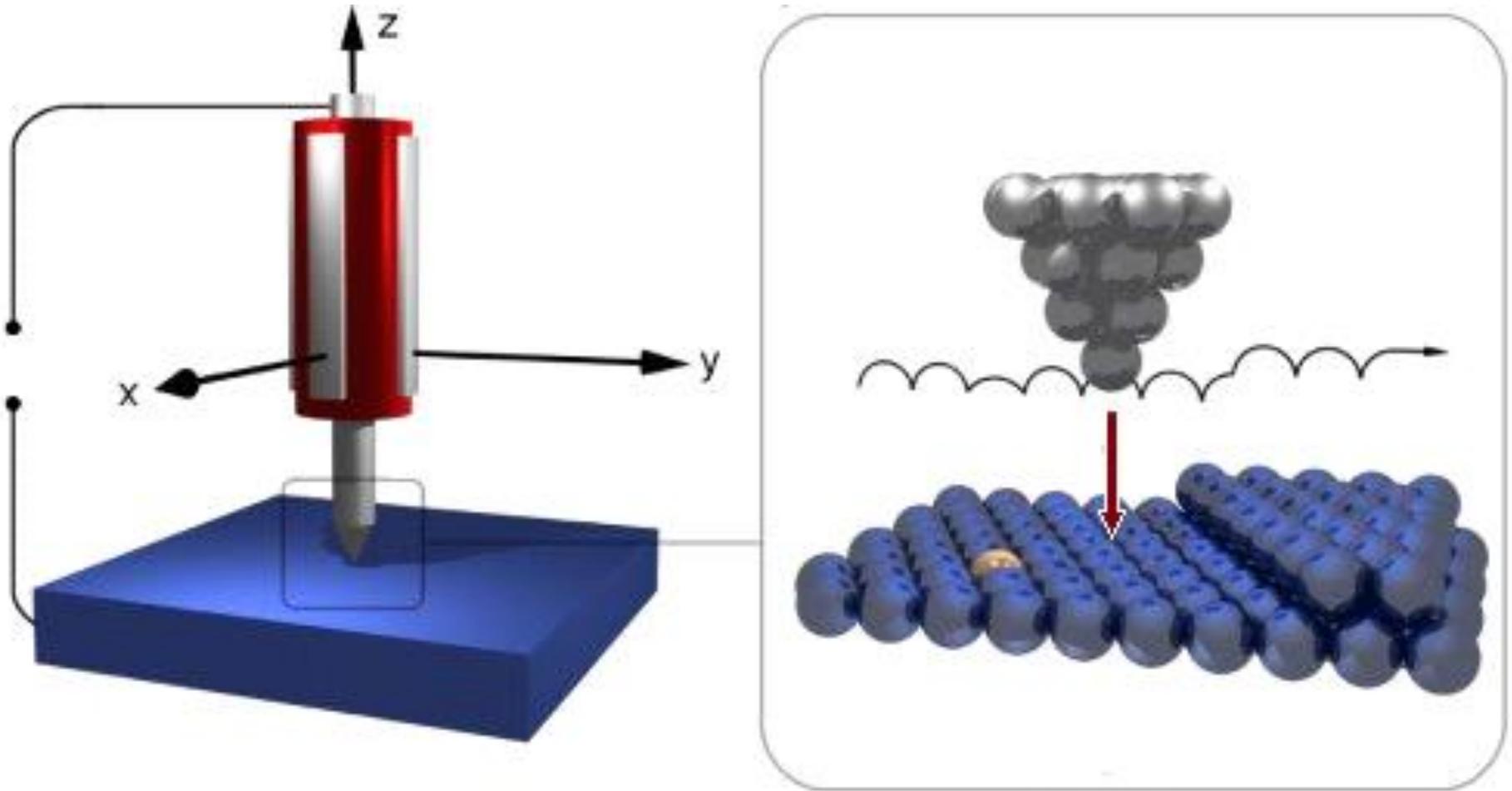
If ρ_{tip} and T energy independent (at least close to the Fermi level):

$$\mathrm{d}I / \mathrm{d}V_b (V_b, x, y) \propto \rho(eV_b, x, y) = \mathrm{LDOS}(eV_b, x, y)$$

What is LDOS?

$$\mathrm{LDOS}(eV_b, x, y) = \sum_{\delta E} |\psi_i(E_i, x, y)|^2$$
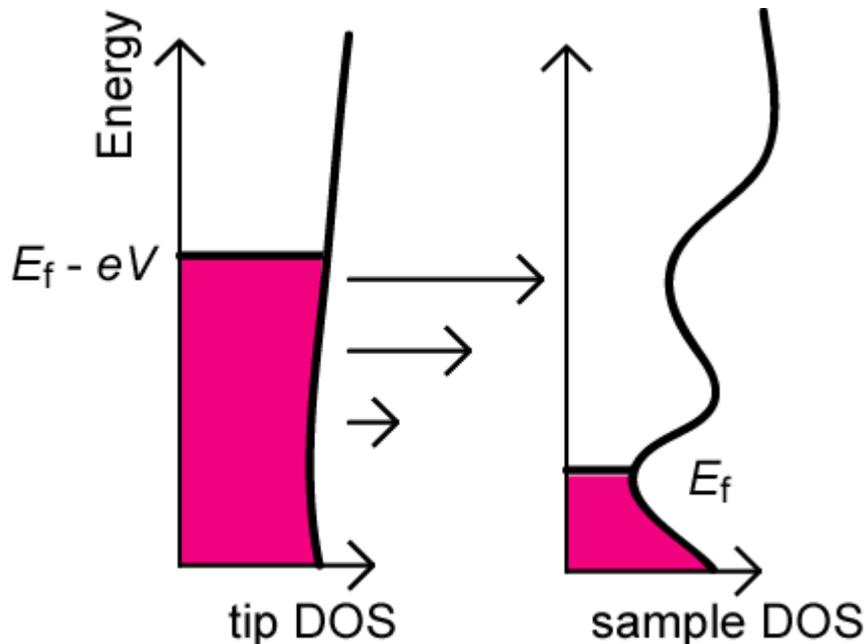
→ STM maps the (integrated) **constant** density of states surface of the sample

→ dI/dV spectroscopy gives the local density of states

LDOS example: two atoms making a molecule

dI/dV maps (proportional to ψ^2)

ΔE

dI/dV $\propto$ LDOS

bias voltage (V)

antibonding

$\psi_{A1} - \psi_{A2}$

A1 —— ψ_{A1}

ΔE

ψ_{A2} —— A2

$\psi_{A1} + \psi_{A2}$

bonding
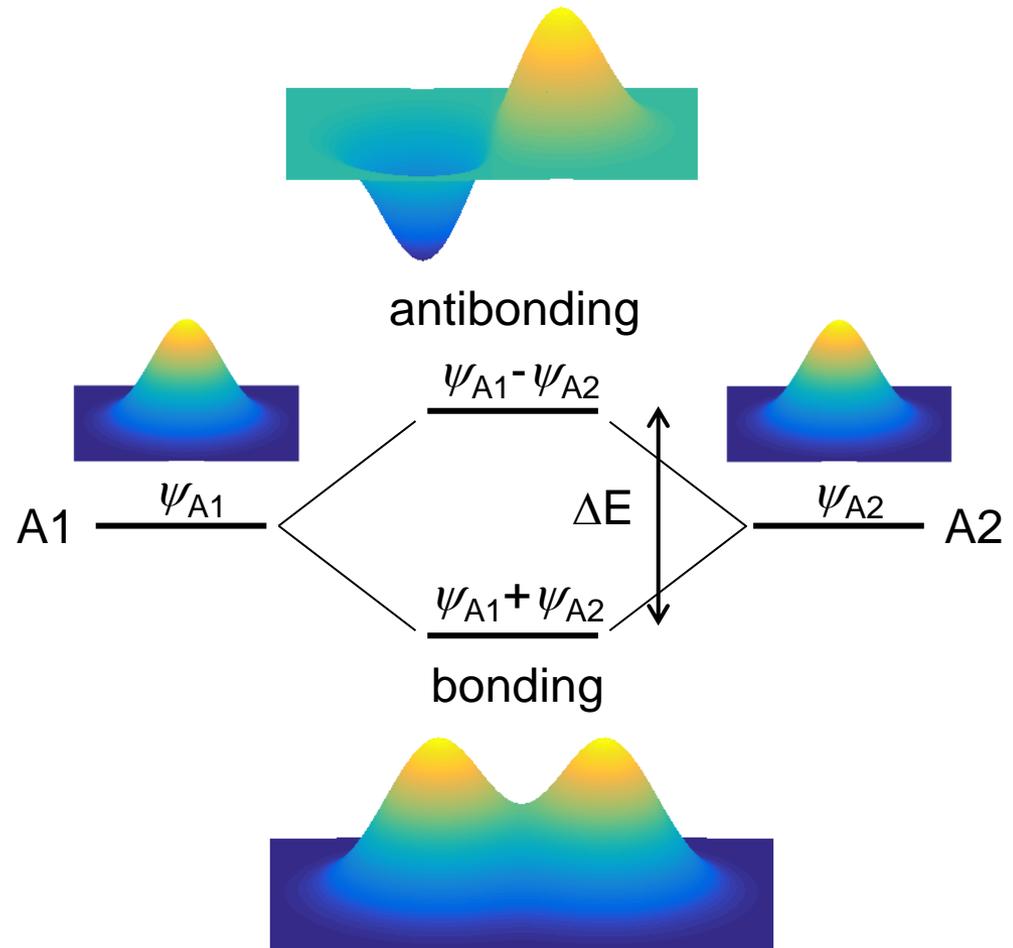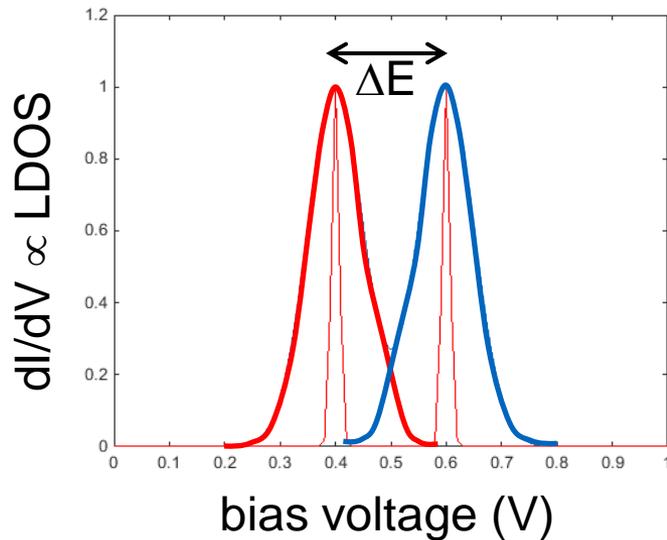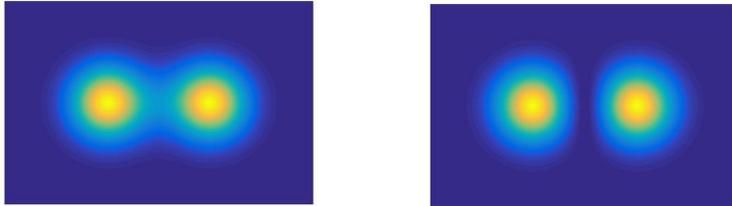
■ What determines the energy and spatial resolution?

Real example 1: semiconductor surface A?

occupied

empty

b5   -2.7 V

b1   +1.9 V
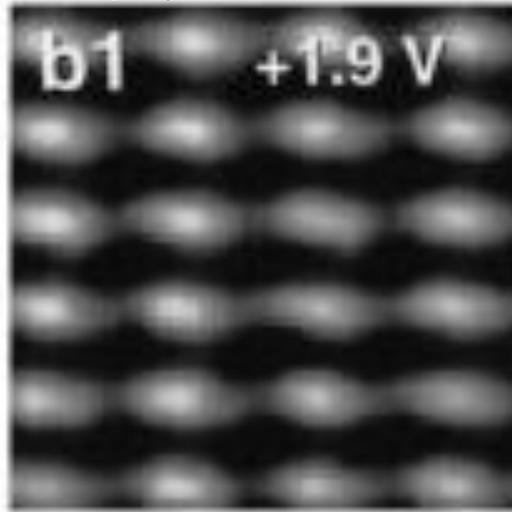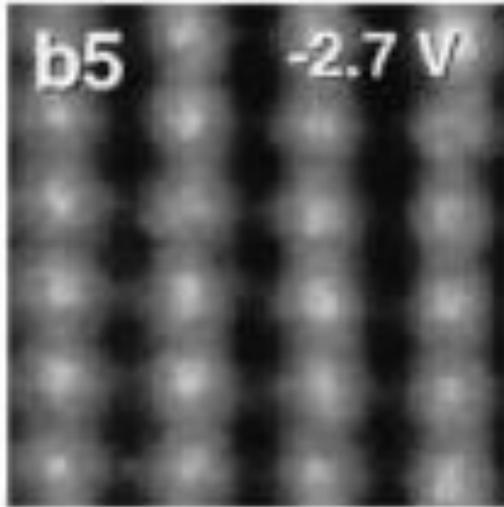
two superimposed STM
images of the occupied and
empty density of states
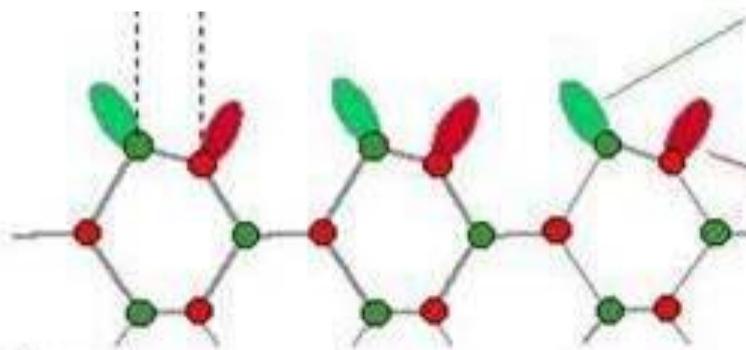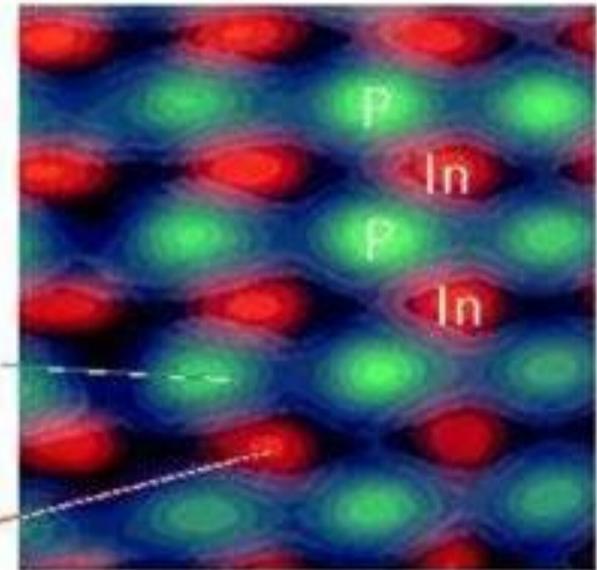
occupied
dangling bond

empty
dangling bond

side view

Ebert et al. Surf. Sci. 271, 587 (1992)

Real example 2: benzene on Pt(111)
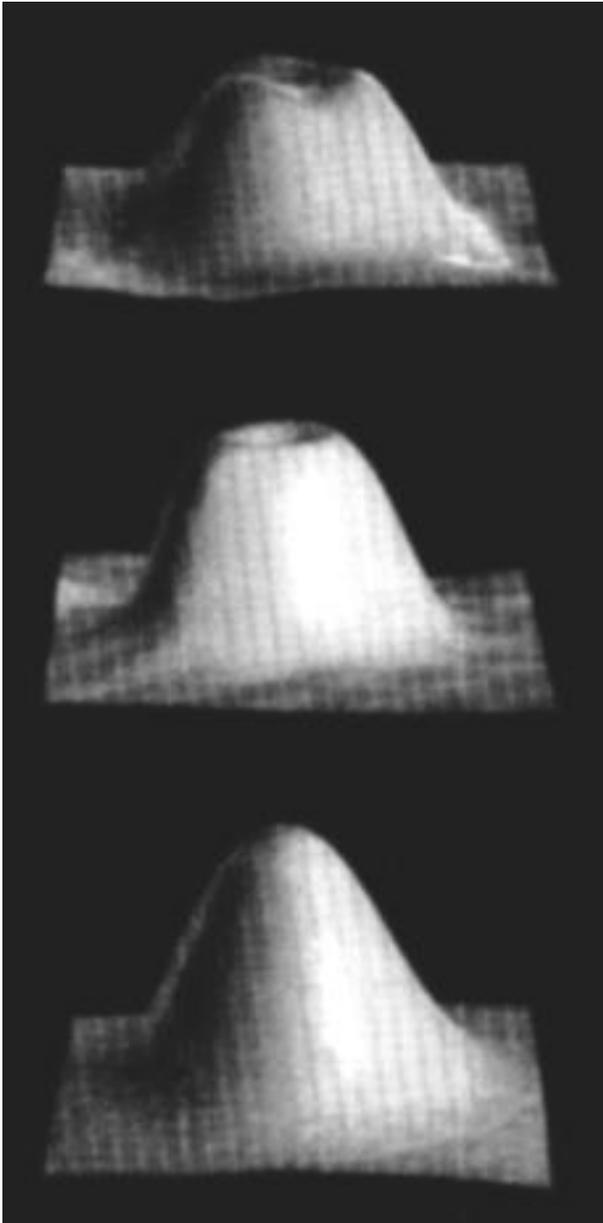
3 different adsorption sites – 3 different topographies

- STM does not measure atomic positions directly
- The measured current is related to the local density-of-states (LDOS)
- STM height/shape generally not equal to atom / molecule / thing size / shape

P.S. Weiss, D.M. Eigler, *Phys. Rev. Lett.* **71**, 3139 (1993).

Reasons for the success of STM

- As a consequence of the strong distance dependence of the tunneling current, it is likely that a single atom carries the main part of the current leading to very high spatial resolution

- Tunneling current monotonic function of the tip-sample distance, which makes feedback control simple

- Tunneling currents are sufficiently high to be measured "without difficulty"

- Possibility of carrying out electronic spectroscopy with atomic resolution

AFM background

- Invented in 1986 by G. Binnig, C. Gerber, and C. Quate (IBM Zurich)

- Idea is to measure a force due to a very small contact with a sample

- Typical forces in pN - nN range

- Based on detecting the bending of a cantilever – Hooke's law: $F = -kx$

The Concept

(a)

SCANNERS, FEEDBACK AFM | A | B | C | FEEDBACK STM | F
F | | D | E | | | 1 cm

BLOCK (ALUMINUM)

x
z
y

(b)

25 μm
.25 mm

DIAMOND TIP

A: AFM SAMPLE
B: AFM DIAMOND TIP
C: STM TIP (Au)
D: CANTILEVER, STM SAMPLE
E: MODULATING PIEZO
F: VITON

.8 mm

LEVER (Au-FOIL)

G. Binnig, C.F. Quate, C. Gerber, *Phys. Rev. Lett.* **56**, 930 (1986).

Bending of a cantilever

A?
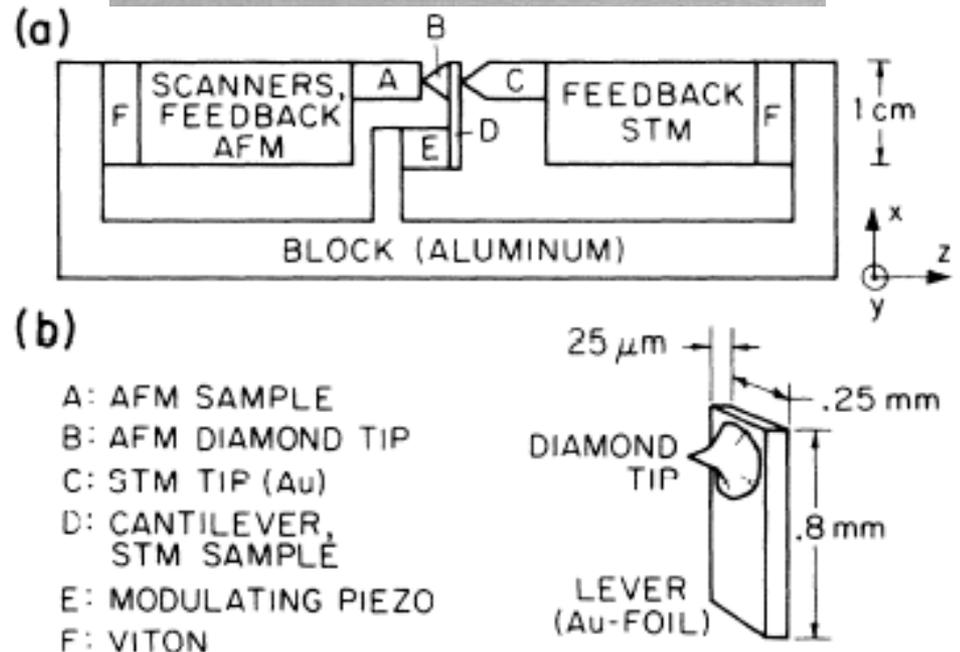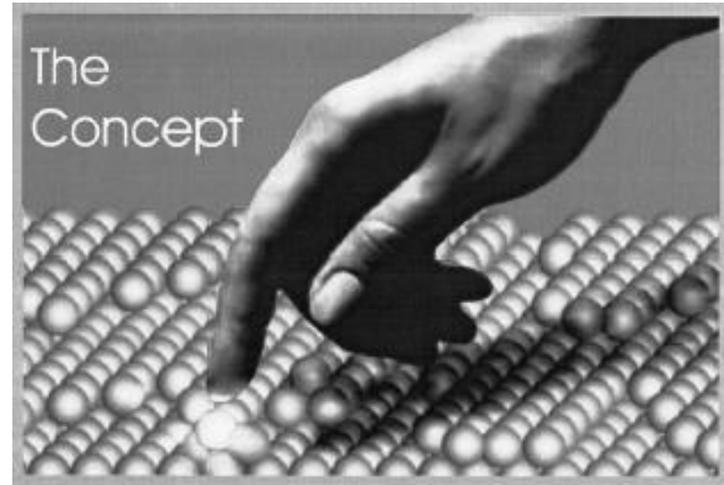
- Optical detection the most common

- four-field detector can measure both the normal deflection (A-B) and torsional bending (C-D), i.e both normal and lateral force components can be measured
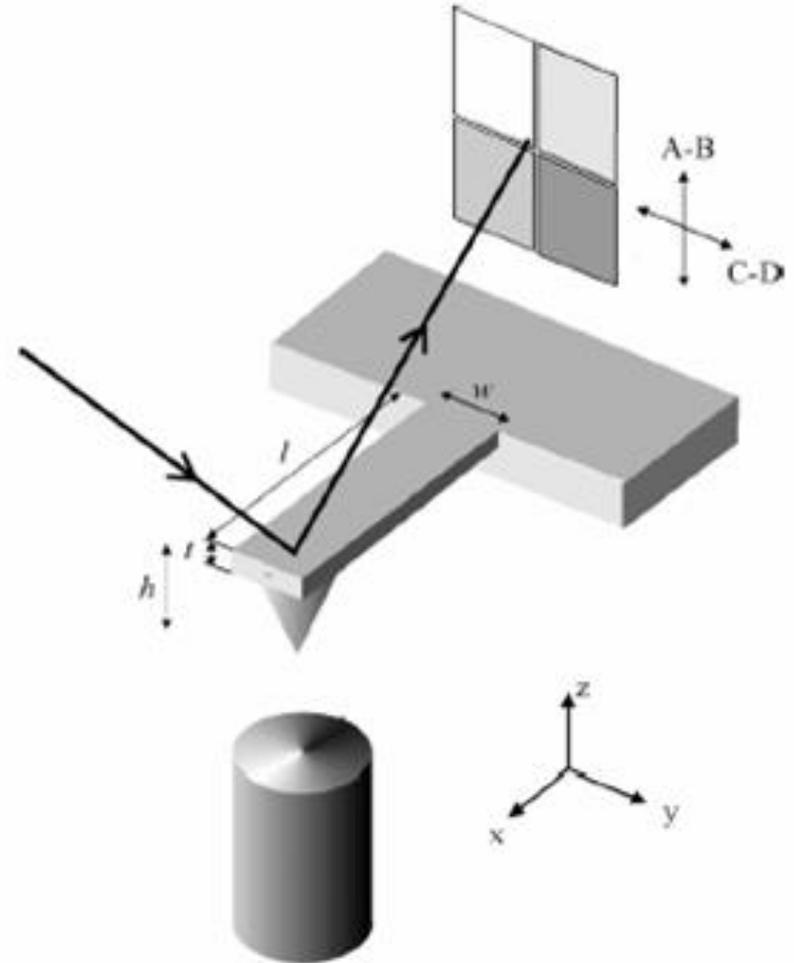
Atomic resolution imaging on bulk insulators

- Image on a cleaved KBr surface

- Only bromine ions are visible

- Insulating substrate, i.e. STM would not be possible
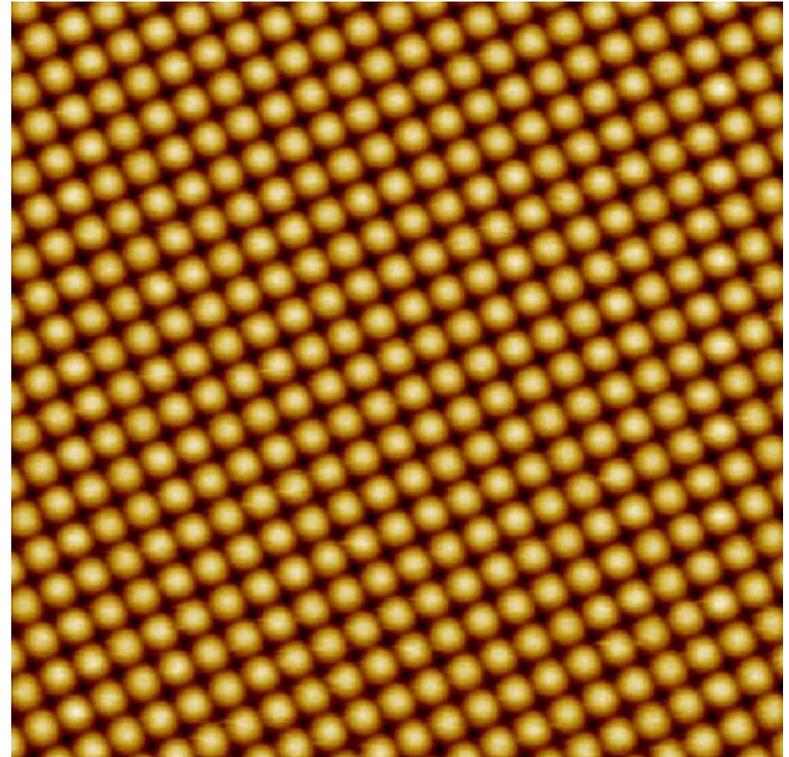
AFM principles

- Force or derivatives used as the feedback signal
  - Contact- and non-contact AFM, tapping mode etc.
- Both long and short range forces contribute (unlike in STM)
  - van der Waals
  - electrostatic forces
  - magnetic forces
  - capillary forces
  - short range binding (attractive) and Pauli exclusion (repulsive)

tip
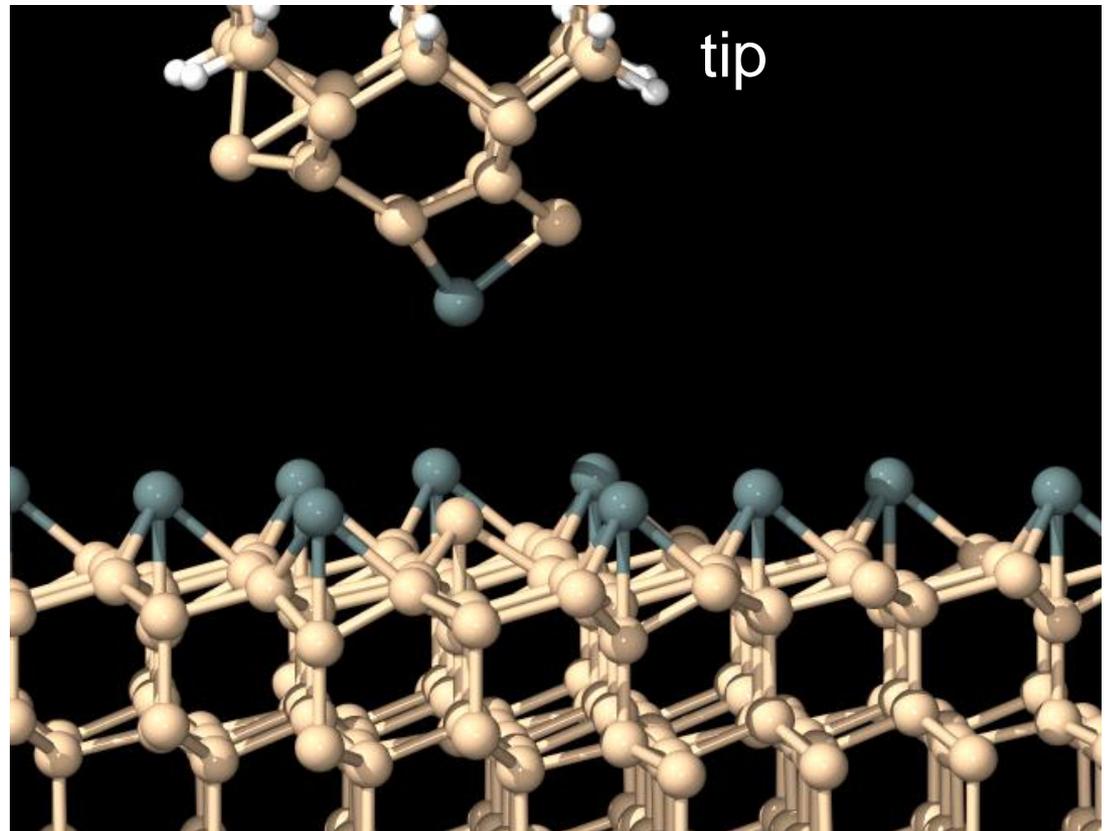
sample

Different modes

A?

- Contact mode
  - friction
- Non-contact mode (dynamic mode, frequency modulation)
  - frequency shift
  - damping
- Tapping mode (Intermittent contact, amplitude modulation)
  - frequency fixed
  - amplitude measured
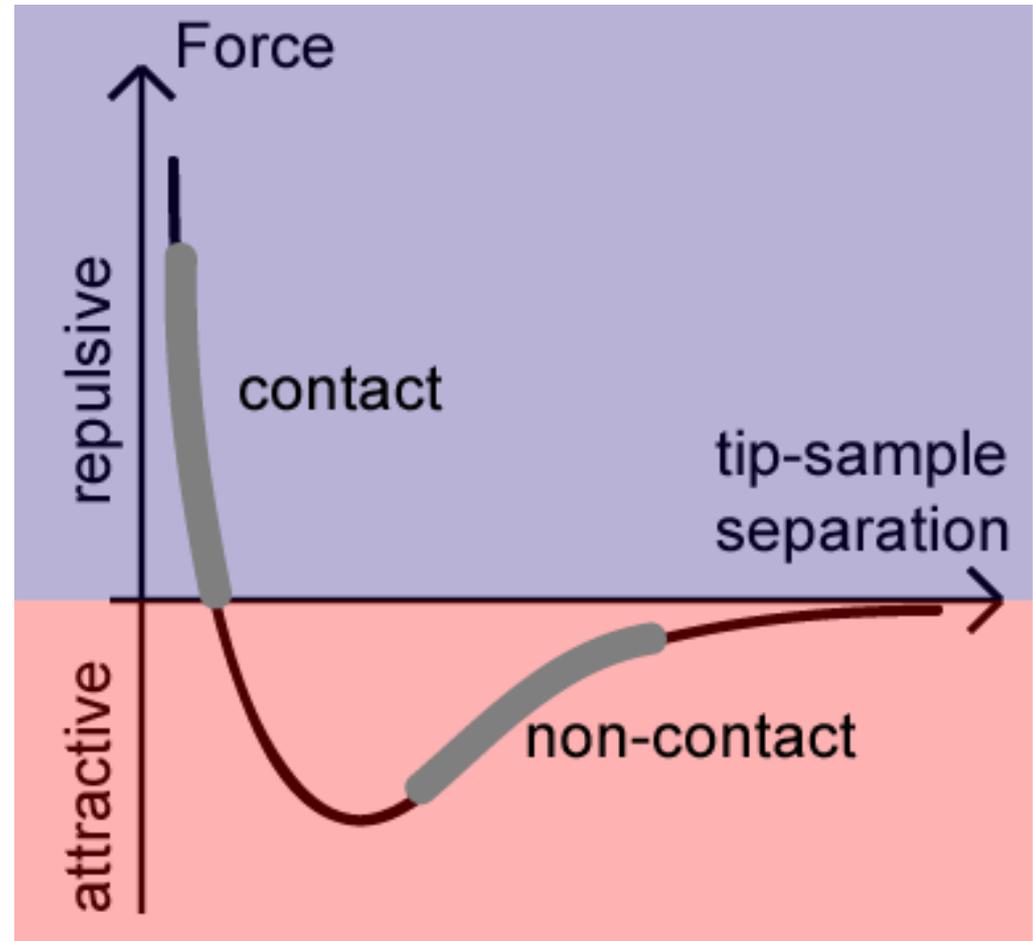
Contact mode

- Tip in "contact" with the sample
- Deflection of the cantilever (force) is the feedback parameter
- Simplest to interpret
- Damage to tip or sample possible
- Lateral force on the sample
- True atomic resolution is not possible

jump to contact

force

approach

retract

Van der Waals

tip-sample

separation

Adhesion
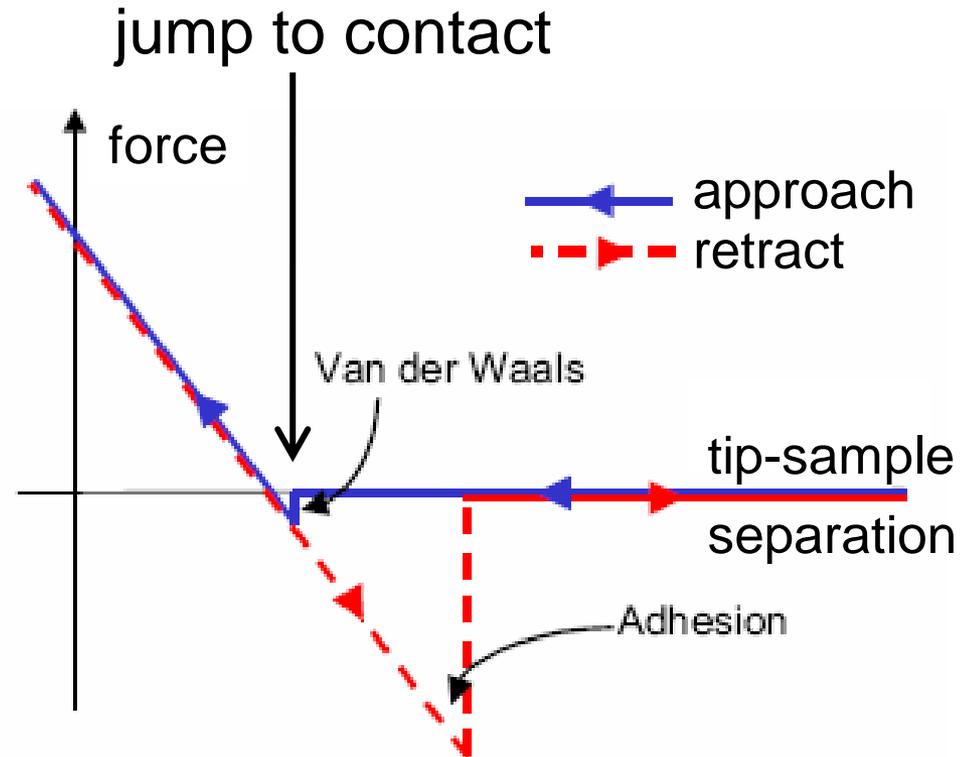
Example on contact mode AFM

topography

friction
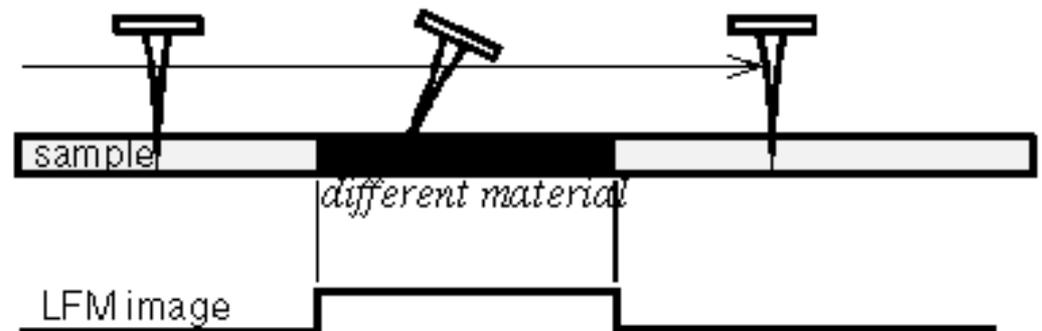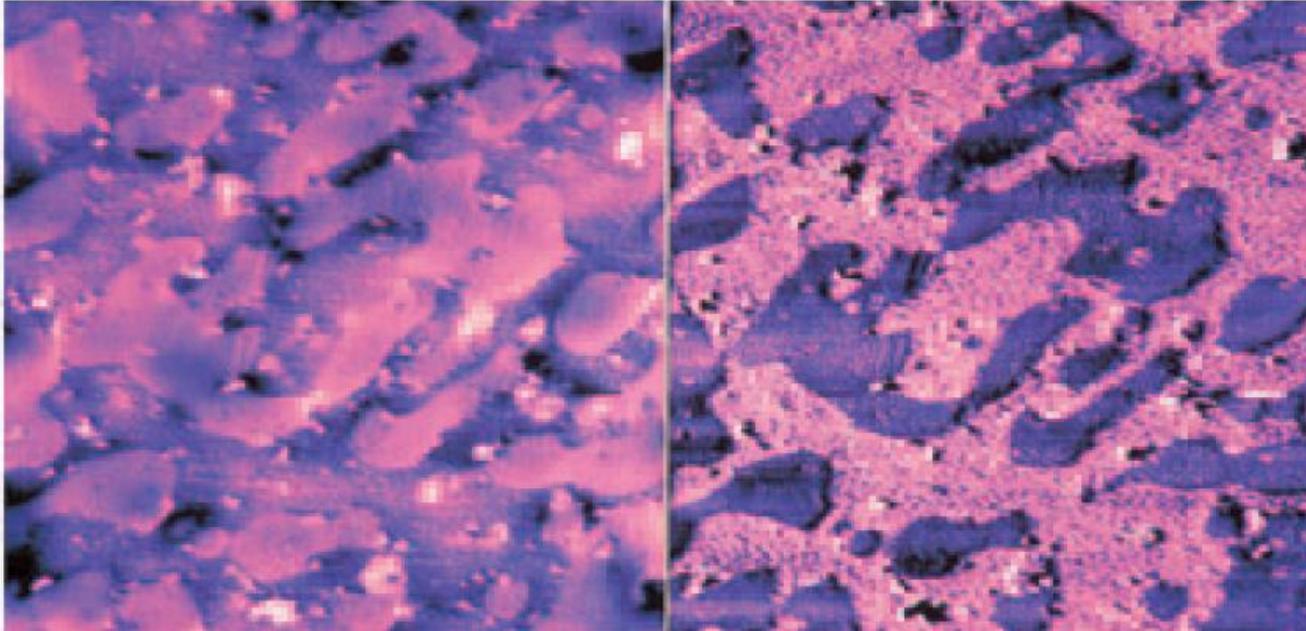
- Instability occurs if
$$\frac{\partial F_{ts}(z)}{\partial z} > k$$

where k is the cantilever spring constant and F_{ts} is the tip-sample interaction force
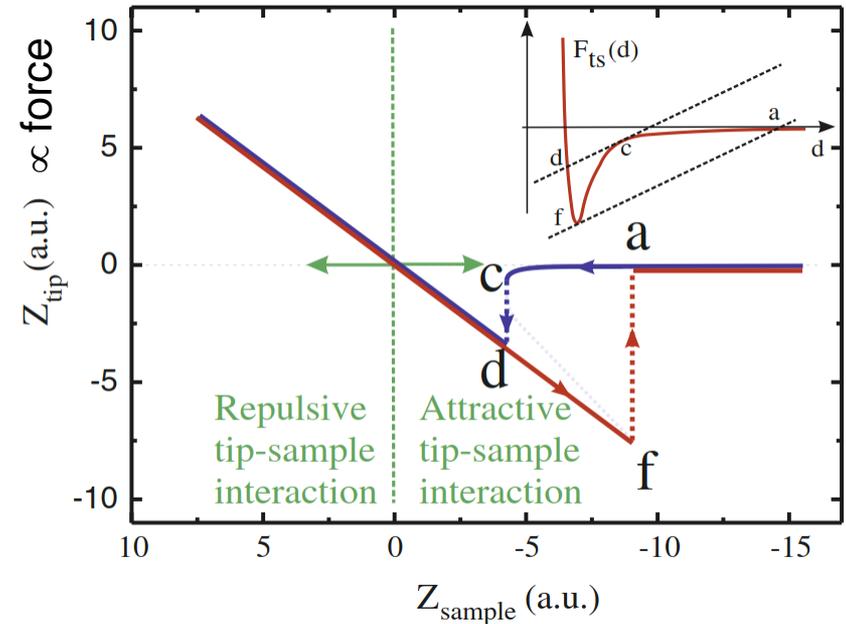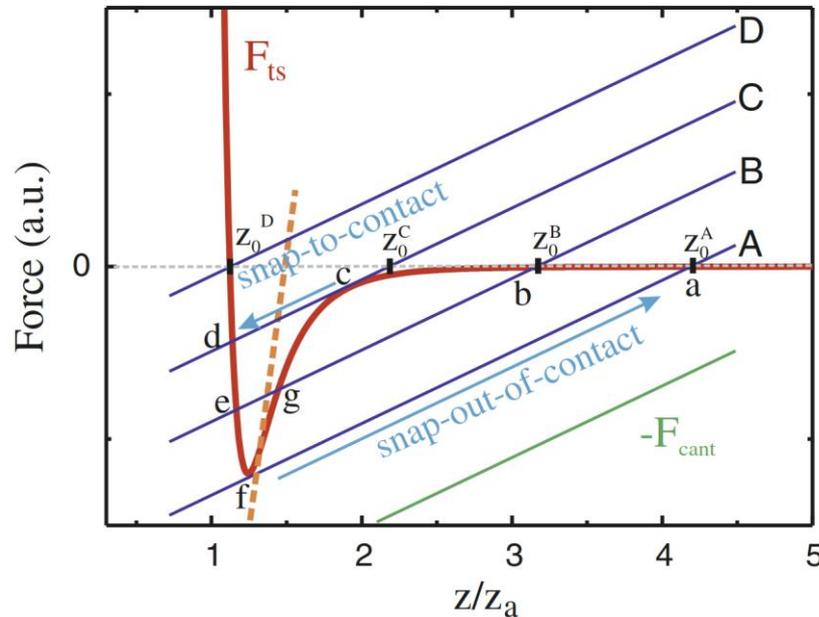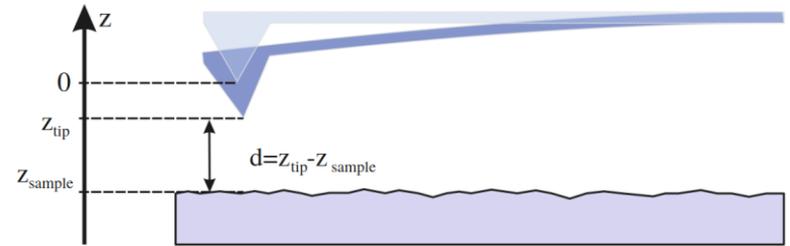
What to do about snap-to-contact?

- The instability occurs when attractive overcomes the restoring force of the cantilever

$$k < -k_{ts} = \frac{\partial F_{ts}}{\partial z}$$

- If there is snap-to-contact

$\rightarrow$ this is not good

- How to avoid it?

- If the cantilever oscillates, stability condition is modified

- Largest restoring force (oscillation amplitude A) is kA

$$kA > -F_{ts}$$

- Solution: use dynamic modes (cantilever oscillates) with larger amplitudes or stiffer cantilevers

F.J. Giessibl, *Rev. Mod. Phys.* **75**, 949 (2003).
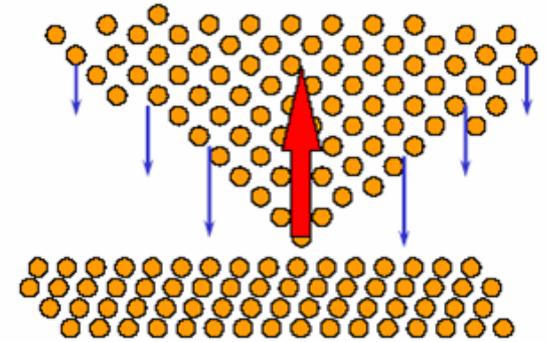
Dynamic modes ("non-contact AFM")
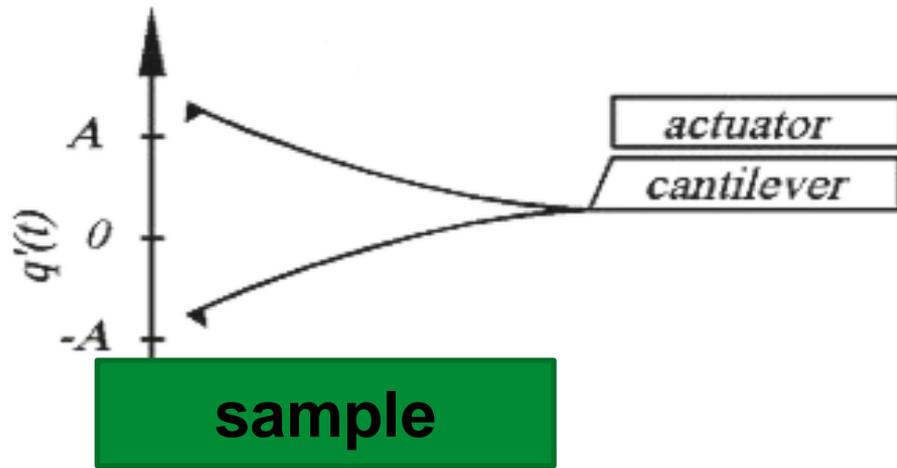
- Vibrating cantilever (externally driven)
- avoids jump to contact problem
- Time constants:
  - Amplitude changes: $\tau \propto Q/f_0$
  - Frequency changes: $\tau \propto 1/f_0$
- low Q (air or liquid)
  $\Rightarrow$ amplitude modulation
- high Q (vacuum)
  $\Rightarrow$ frequency modulation

Resonance frequency: f_0
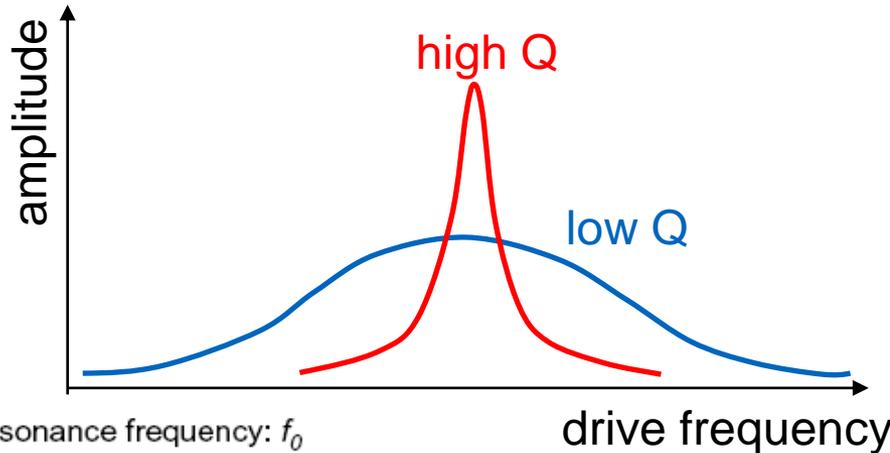
Width of resonance curve (FWHM): Γ

Q-factor: $Q = \dfrac{2\pi \cdot f_0}{\Gamma}$

Tapping mode

- Amplitude of the cantilever oscillation monitored
- Also called intermittent contact mode
- closest point of cantilever oscillation is in-contact, hence "tapping"
- amplitude larger than in non-contact mode
- works very well in ambient; the oscillation amplitude larger than the thickness of a possible contamination layer
- minimum lateral force on the sample
- mode of choice for ambient AFM

Q. Zhong et al. *Surf. Sci. Lett.* **290**, L688 (1993).

Typical AFM images

A?

Polycrystalline Au layer

15 nm

0 nm

400nm

topography

250 mV

0 mV

400nm
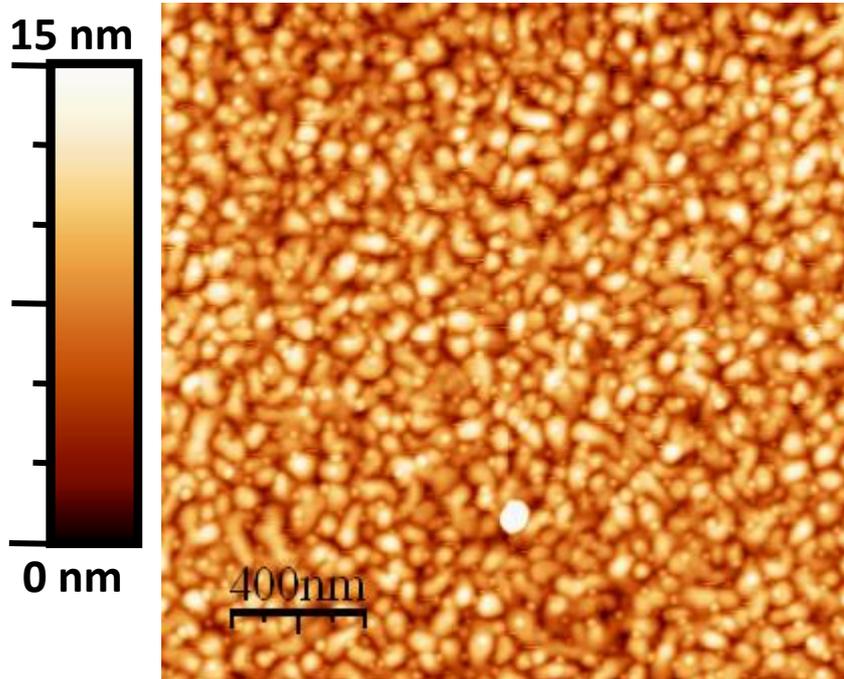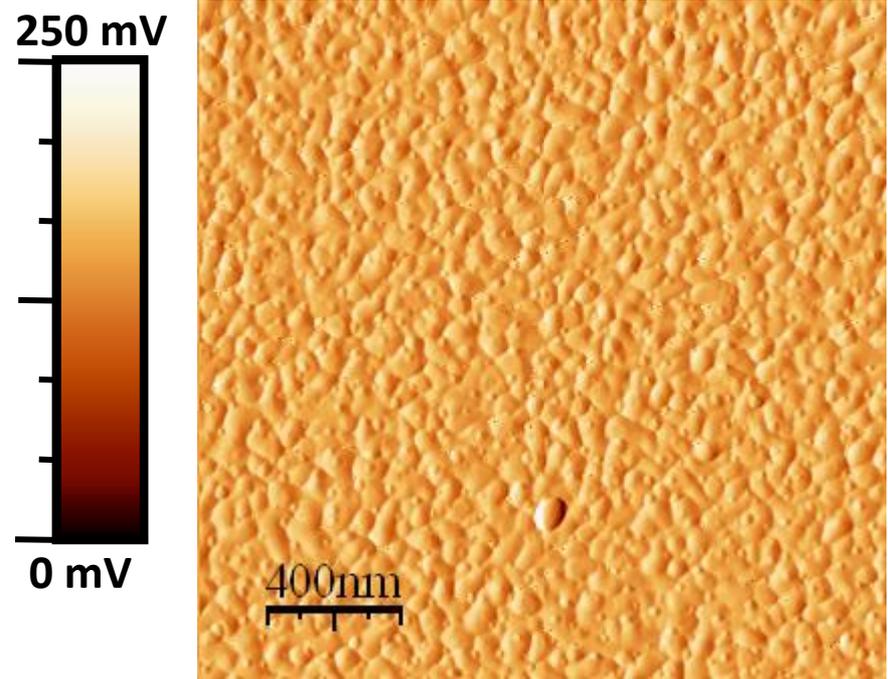
amplitude image;
difference between
the actual amplitude
and the set-point

New imaging modes

- Derivatives of the tapping mode
- Phase imaging
- Peak force imaging

Phase imaging

A?

Tapping mode :

- measure the amplitude and the phase difference between excitation and oscillation

Gives:

- Contrast

- Information on elastic properties

electronics:
- amplitude
- phase

phase

Phase contrast

A?
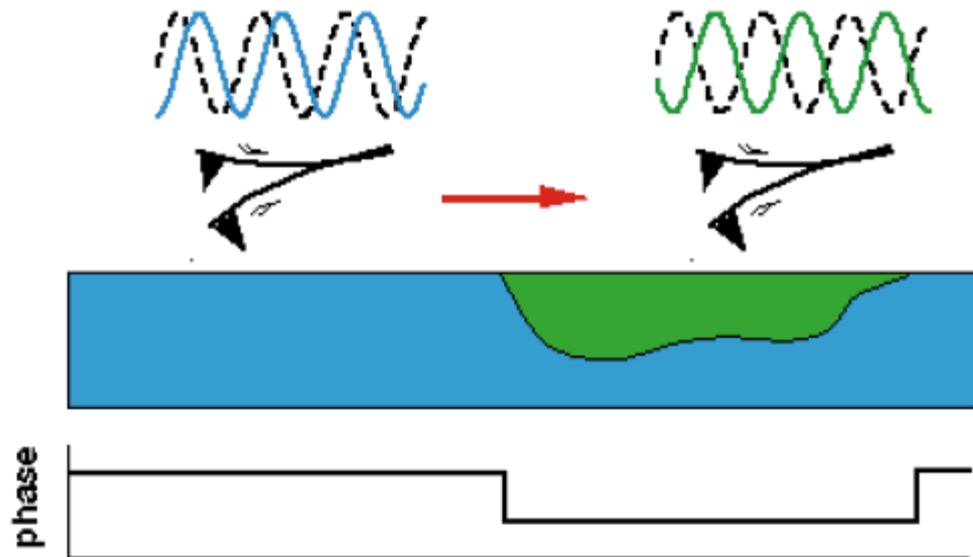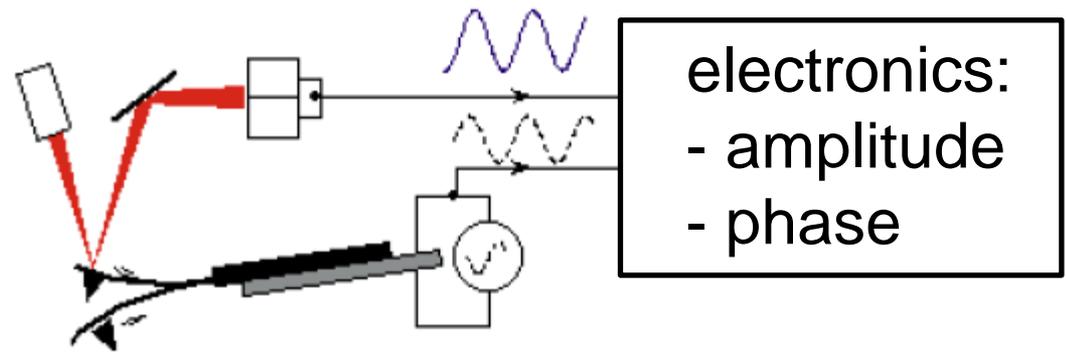
Composite polymer in a polymer matrix
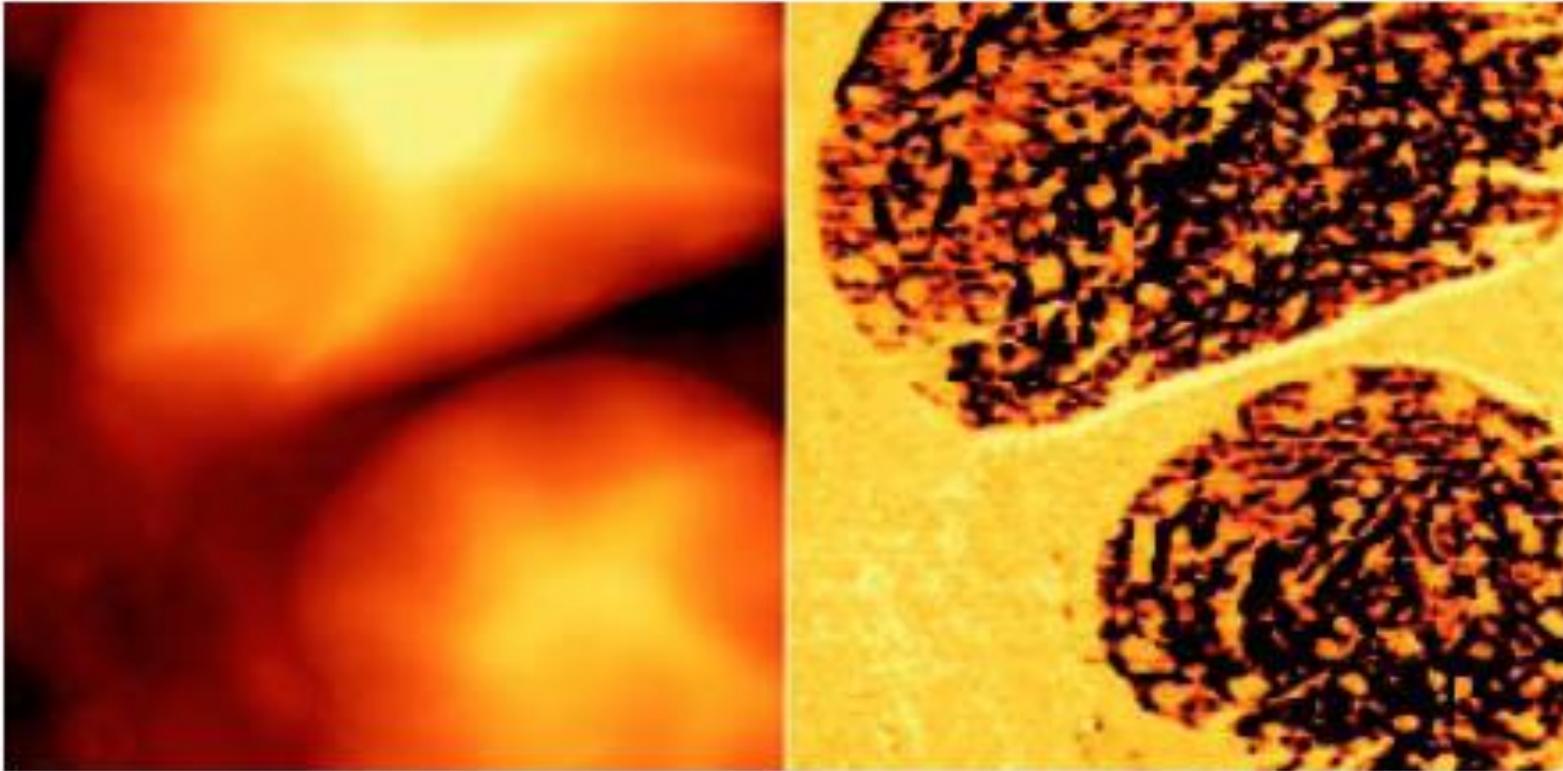
tapping mode AFM
topography

phase image; phase
difference between
the excitation and
oscillation signals

Peak force QNM from Bruker (Veeco)

- "Quantitative nanomechanical property mapping"
- based on the tapping mode
- map modulus and adhesion simultaneously with topography
- take a force curve (force – distance curve at each point of the topograph
- values of modulus can be calibrated
- other approaches to simultaneous imaging and force spectroscopy exist

d topography   a topography

e phase   b adhesion

c modulus

normal   QNM

Non-contact AFM
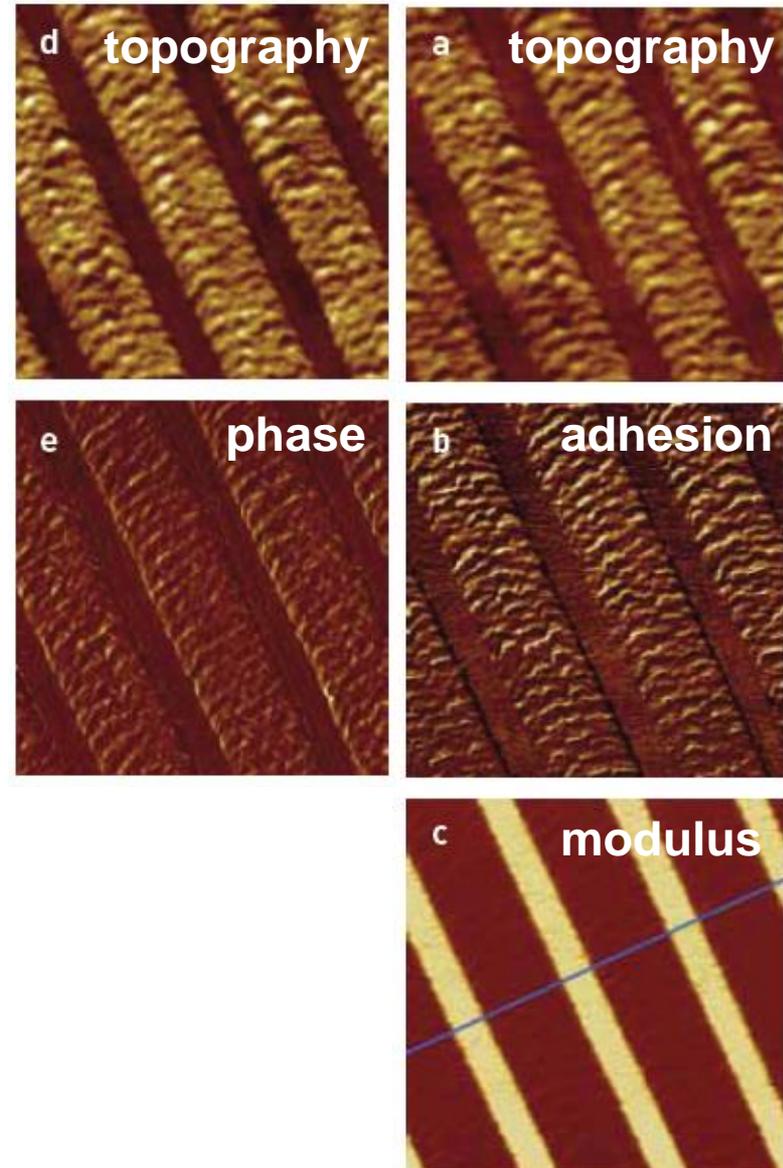
- Frequency-modulation AFM

- Oscillate the cantilever, measure the frequency shift Δf

- Force on the tip cause a shift of the cantilever oscillation frequency (f_0 natural frequency, k the spring constant)

$$f = f_0 + \Delta f$$

- If the tip-sample interaction is not too strong and the tip oscillation amplitude is small ($k_{ts} << k$ and $k_{ts} = \partial^2 V_{ts}/\partial z^2$ is constant over oscillation cycle) then the frequency shift Δf is related to the vertical force gradient

$$\Delta f = -\frac{f_0}{2k}\frac{\partial F_{ts}}{\partial z}$$

- Goal: Make a controlled single-atom contact with the sample so that it has a significant effect on the measured Δf

What forces are there in AFM?

A?

- Total force measured in AFM – most components decay more slowly than tunneling current and have no atomic corrugation:

$$F_{\text{total}} = F_{\text{vdW}} + F_{\text{es}} + F_{\text{magn}} + F_{\text{capillary}} + \boldsymbol{F_{\textbf{chemical}}} + \ldots$$

- Long range: van der Waals, electrostatic, (magnetic)

- **Short range: chemical bonding and Pauli repulsion**

- What is the effect of tip oscillation amplitude?

  – Most sensitive to forces that have a similar length scale to the tip oscillation amplitude

  – Use of small amplitudes difficult (detection and need to use stiff cantilevers)

F.J Giessibl, *Rev. Mod. Phys.* **75**, 949 (2003)
W.A. Hofer, A.S. Foster, A.L. Shluger, *Rev. Mod. Phys.* **75**, 1287 (2003)

Advantages with AFM

- insulators
- in principle, atomic resolution on any surface
- any force can be used as feedback signal
- minimum lateral force (tapping mode) for delicate samples
- force measurements on single-molecule level
- etc.

Problems with AFM

- non-monotonic force

- All forces contribute

- both long and short range contributions

- jump to contact in static mode

- can be avoided with an oscillating cantilever with a sufficient amplitude

- tip has to be included in modelling which makes it difficult
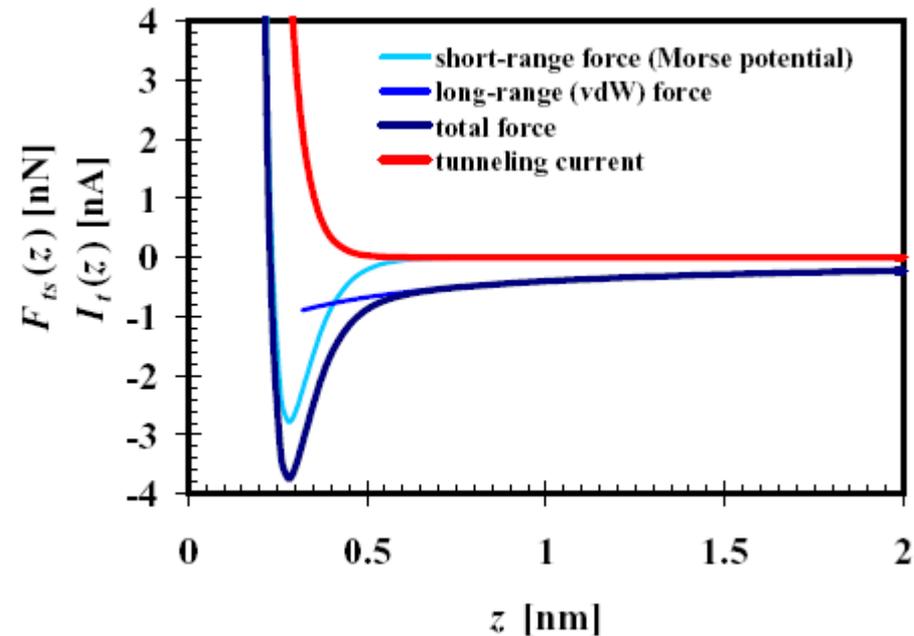
What about AFM – is the resolution poorer or better than in STM?

- it depends…which force are we sensitive to:

  - force has to have atomic scale contrast

  - has to have significant contribution to the total force gradient

  - chemical forces – interaction between the last atom of the tip and the molecule

- STM probes LDOS near the Fermi level ("electronic structure")

- AFM is more sensitive to the total electron density ("geometry")

Practical aspects

- **Precise positioning**
  - piezoelectric elements
- **Sharp tip**
  - STM tip etching or cutting
  - AFM micromachined tips
- **Vibration isolation**
  - rigid design
  - eddy-current damping
- **ambient or UHV**

STM tip

STM tip

Cantilever

Chip

AFM tip

Tip
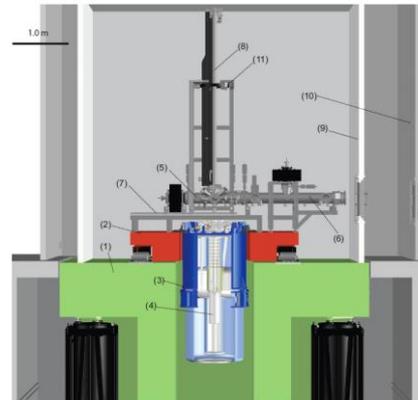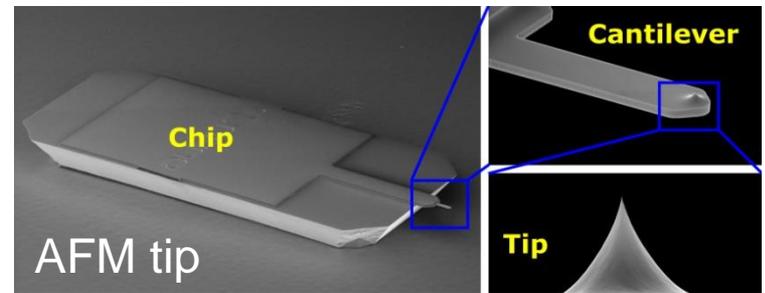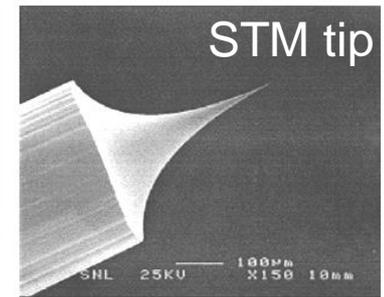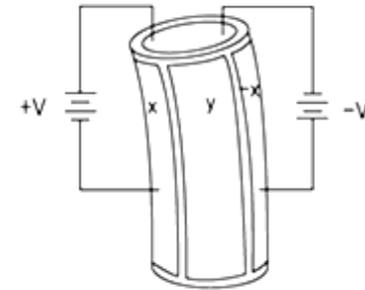
tip-size effects: convolution

A?

Dead zones: not imaged by a blunt tip

tip

height more
or less correct

lateral size
overestimated

centre-to-centre
distance correct
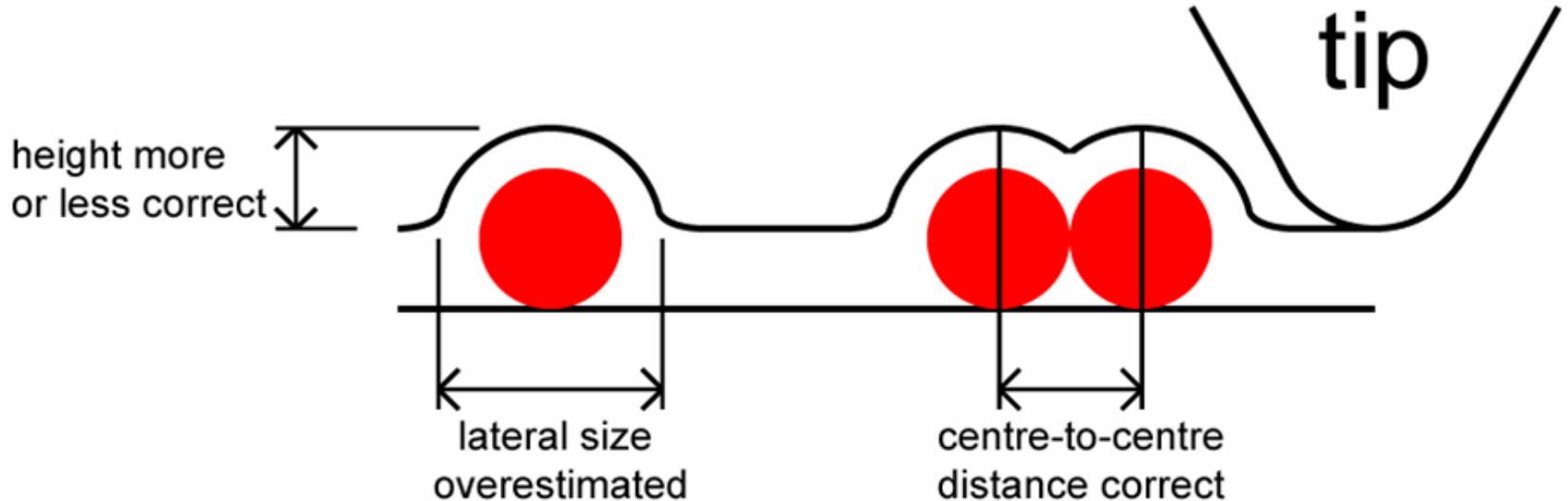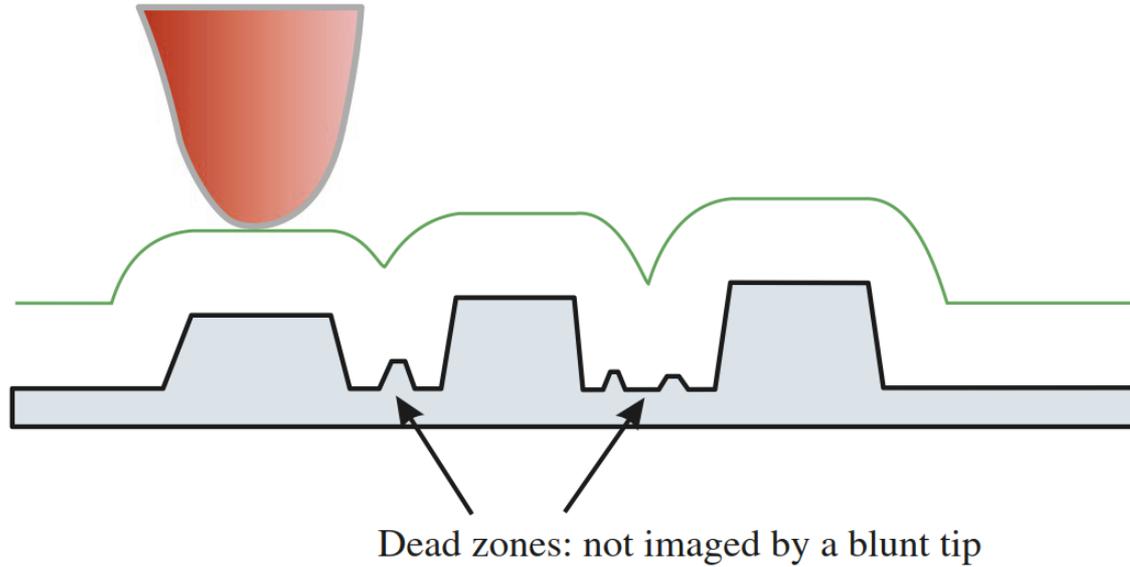
Tip artifacts

■ All features have a uniform shadow or the same shape/orientation
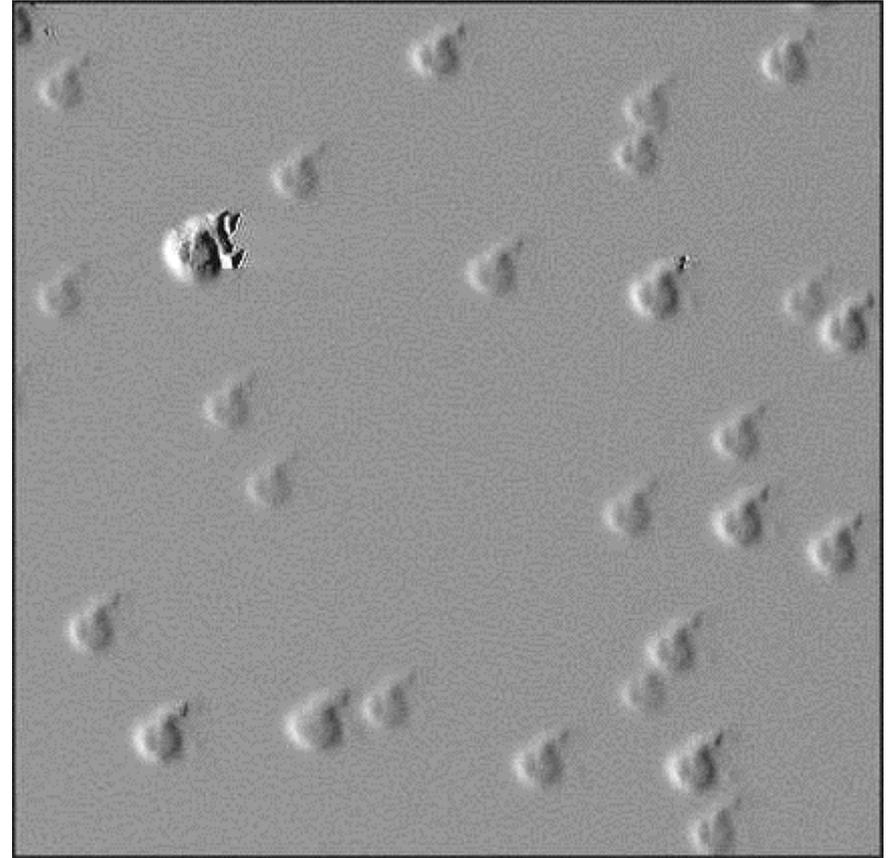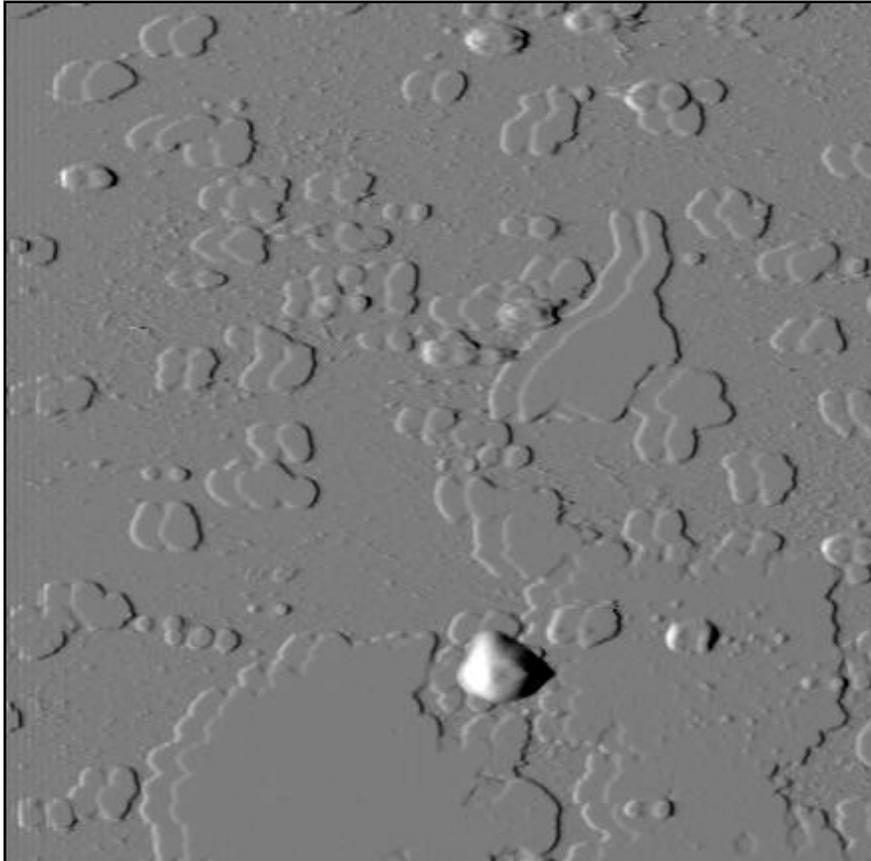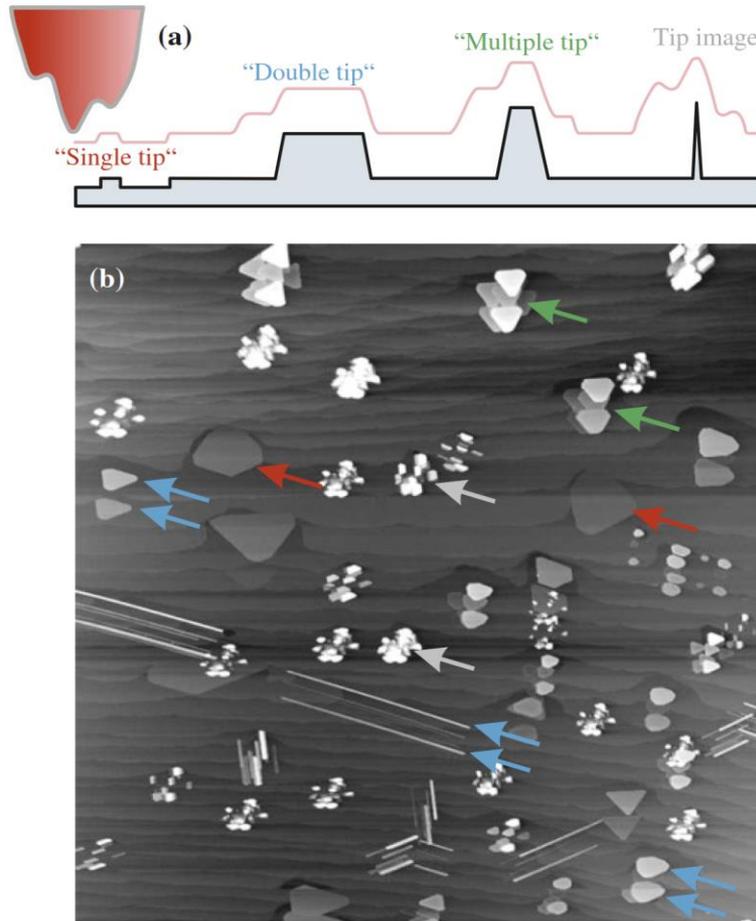
Fig. 8.3 **a** Sketch of a double (multiple) tip giving rise to doubled (multiple) imaging of surface features. The *light red line* shows the trace of the tip above the surface. **b** Example of silicide nano islands and nano wires imaged. The higher the structures imaged, the stronger is the tendency towards double (multiple images). For structures of one atomic height a single tip apex images (*red arrows*), somewhat higher structures are imaged by a double tip apex (*blue arrows*). Even higher structures are imaged by even more micro tips (*green arrows*). Narrow and high structures result in an image if the tip structure instead of the surface feature (*gray arrows*)

Fig. 8.4 STM image of 5 Å yttrium deposited on Si(110). **a** Silicide nanowires imaged with a sharp tip. **b** The same surface imaged with a blunt tip leads to much higher apparent coverage due to multiple images of the silicide nanowires
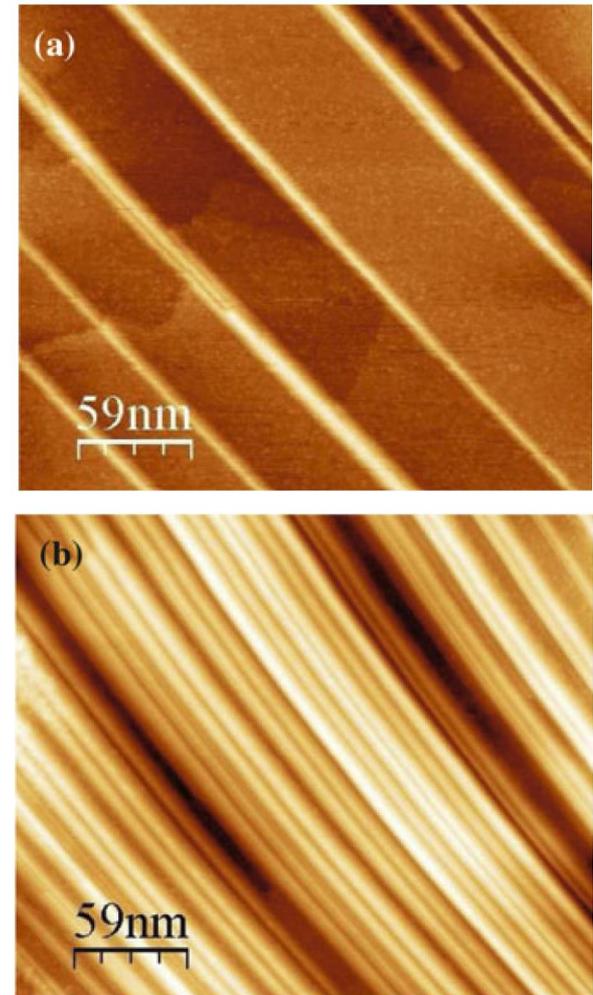
Creep / drift / noise / feedback

- **Creep:** setting a voltage on the piezo actuators, the new position is not reached instantaneously, but is only reached asymptotically. If this creep is not yet finished this leads to an image

- **Feedback "ringing":** If the feedback is too slow this will lead to blurred images; if the feedback is too fast this may lead to a feedback overshoot

- **Noise** with a high amplitude at a specific frequency will show up as stripes superimposed onto the true topography of the surface

- **Drift:** tip moves w.r.t. the sample (usually in a certain direction)

40nm

piezo creep

Feedback artifacts

extra noise

Drift, scan down

Drift, scan up
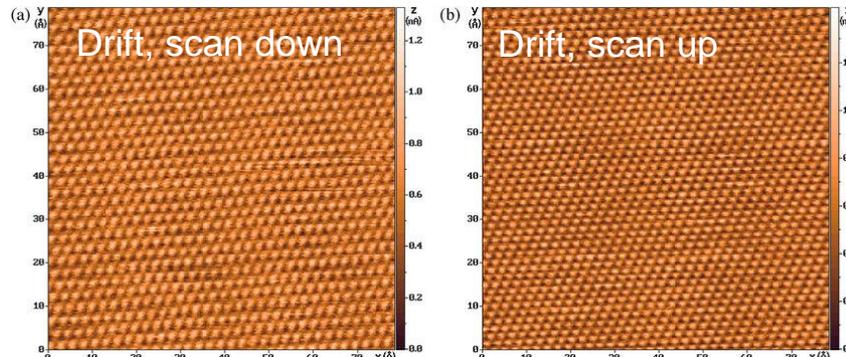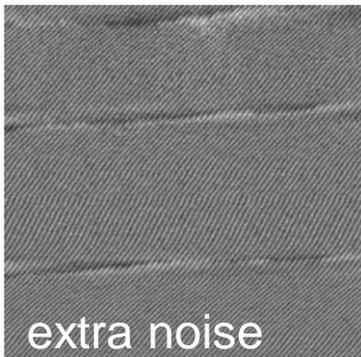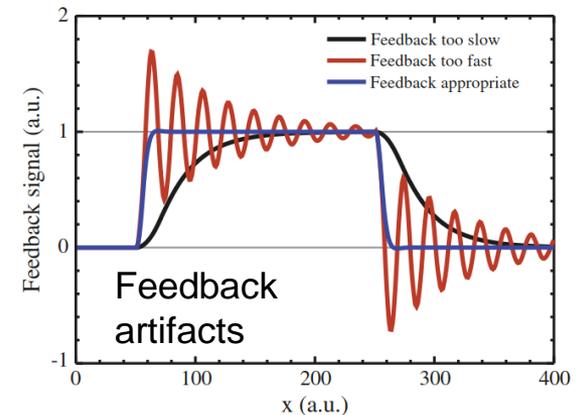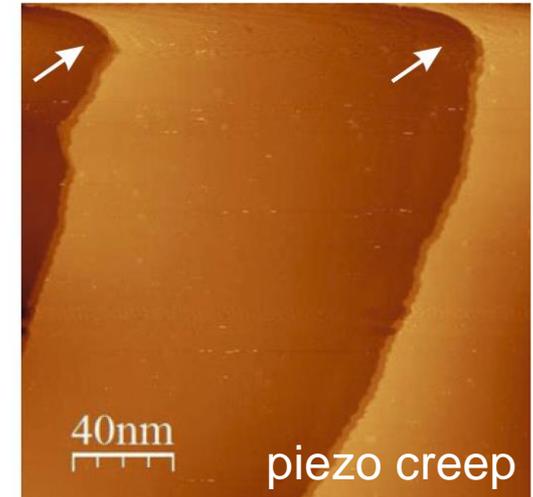
Lecture 2:
Materials at the atomic scale

Peter Liljeroth

peter.liljeroth@aalto.fi

http://physics.aalto.fi/groups/stm/

In the lab...

Spring suspension + eddy-current damping

sample
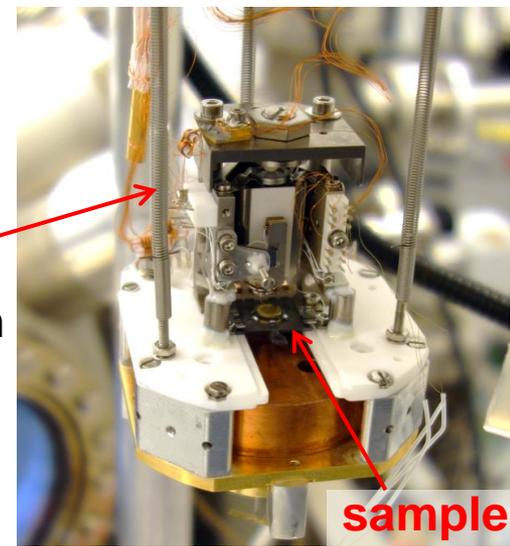
- Ultrahigh vacuum ($< 10^{-10}$ mbar)
- Low temperature ($T = 5K$)
- Cost ca. 0.5 M€

- noise level ~1 pm
- drift < 1nm / day (1 nm ~ 3 atoms)

Air legs
Steady floor

Simultaneous STM and AFM

A?

- Frequency modulation non-contact AFM (nc-AFM)

- Very stiff cantilever
    - $k = 1800$ N/m
    - $f_0 \sim 30$ kHz
    - small oscillation amplitudes << 1 Å
    - All electrical detection

- **STM with an additional data channel giving the short-range tip-sample interaction**

STM tip

2 mm
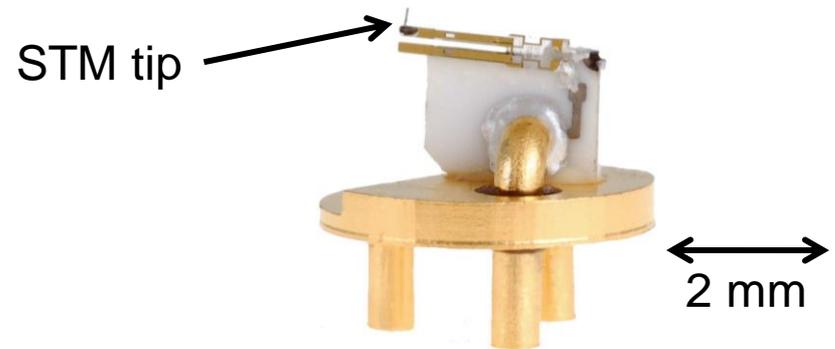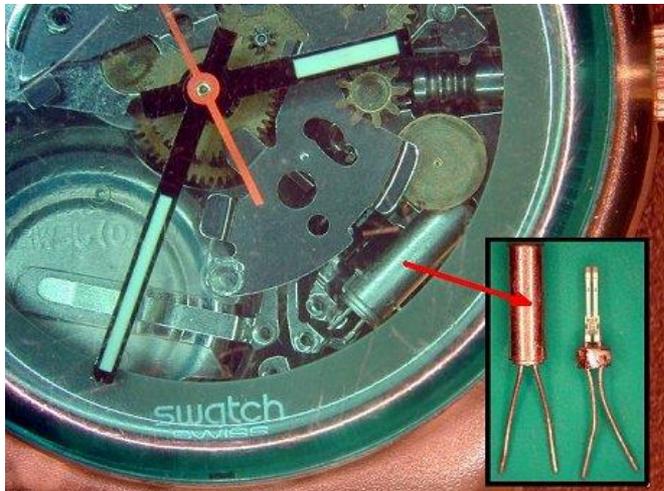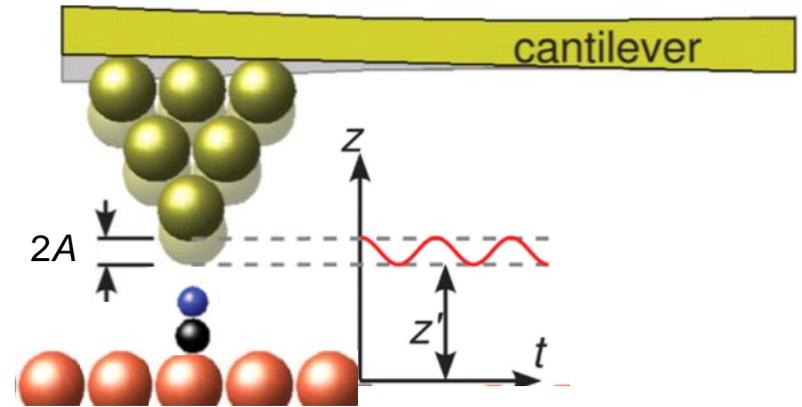
Details: F.J. Giessibl, Rev. Mod. Phys. 75, 949 (2003)
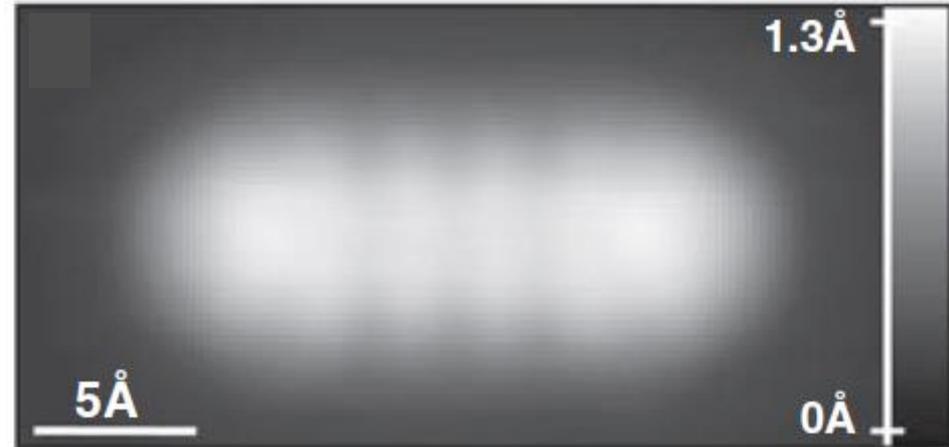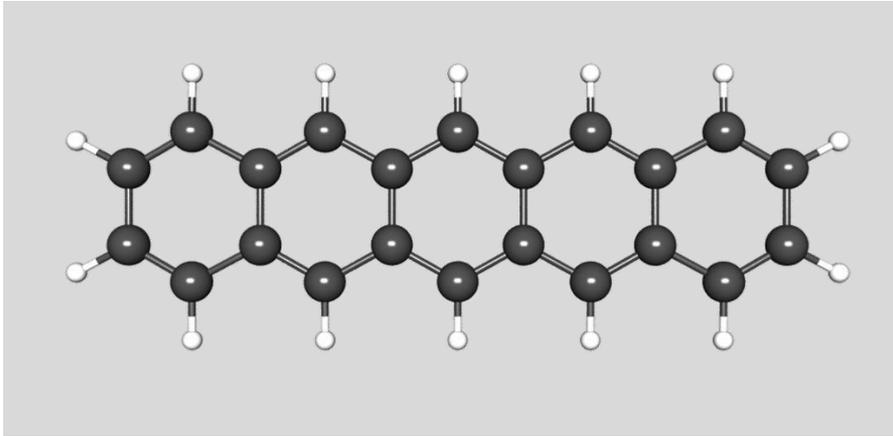
■ Where are the atoms?

■ Measure current – this is not directly related to the positions of the atoms

■ this measurement in the HOMO-LUMO gap of the molecule: modification of the tunneling barrier

$\rightarrow$ no atomic scale contrast

Pentacene: spectroscopy

positive bias:

electron tunnelling

LUMO V_{bias}

HOMO

STM tip   substrate

negative bias:

LUMO

hole tunnelling

HOMO V_{bias}

STM tip   substrate
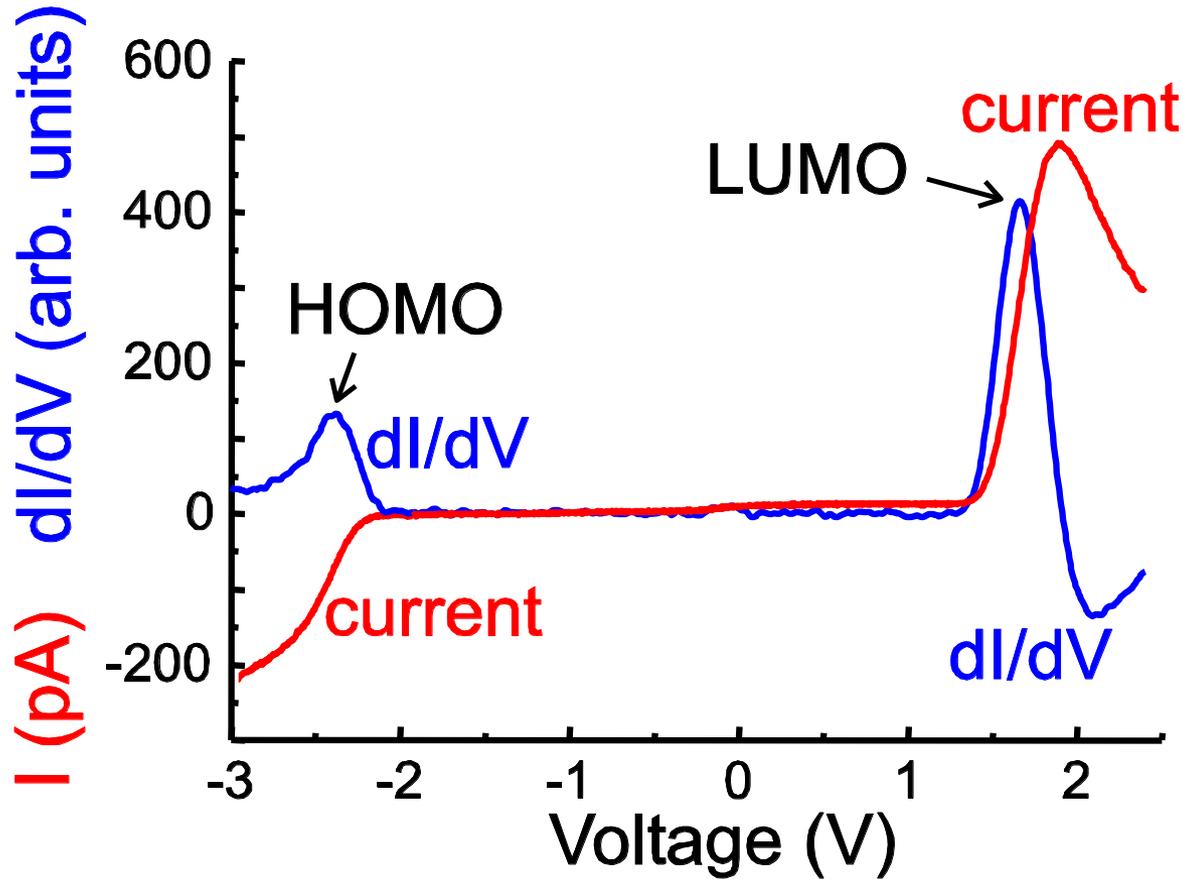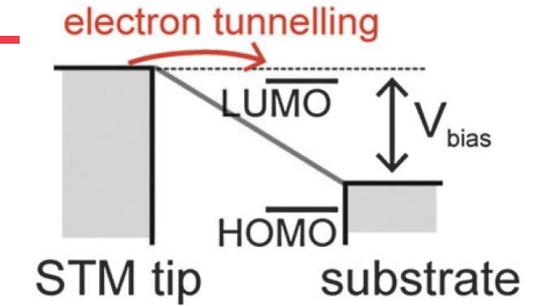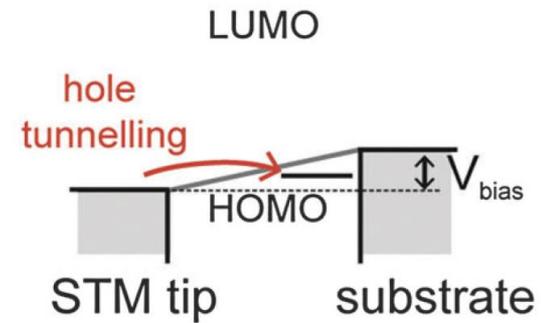
$dI / dV_{bias} \propto \mathrm{LDOS}\, (E = V_{bias})$

$$= \sum_{\Delta E} \left| \psi_i (E, r) \right|^2$$

- Energies of molecular orbitals can be studied

- Their wavefunctions can be imaged directly

Pentacene: molecular orbitals

A?

STM imaging

HOMO Geometry LUMO

DFT calculation

25Å x 20Å

Atomic resolution on molecular systems
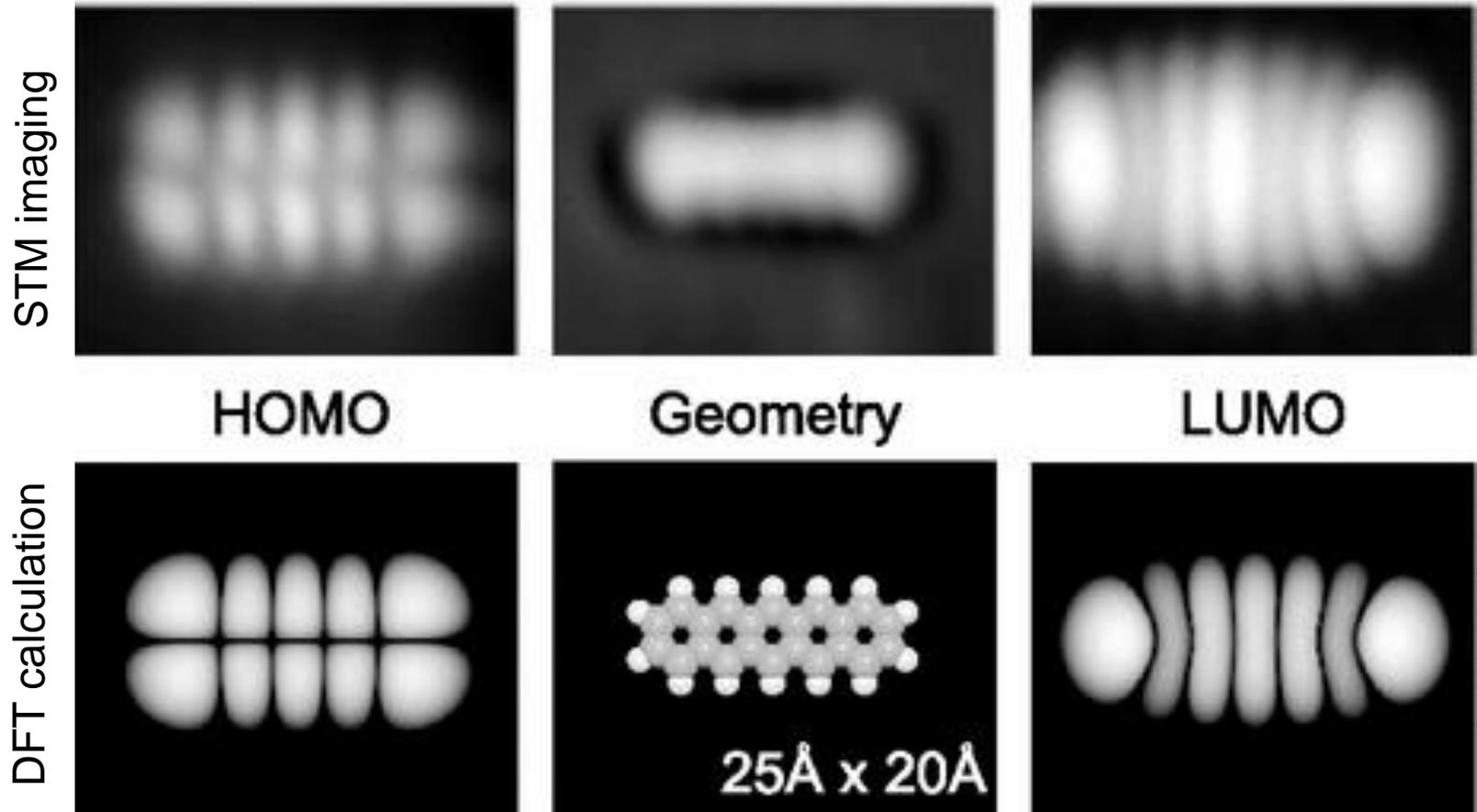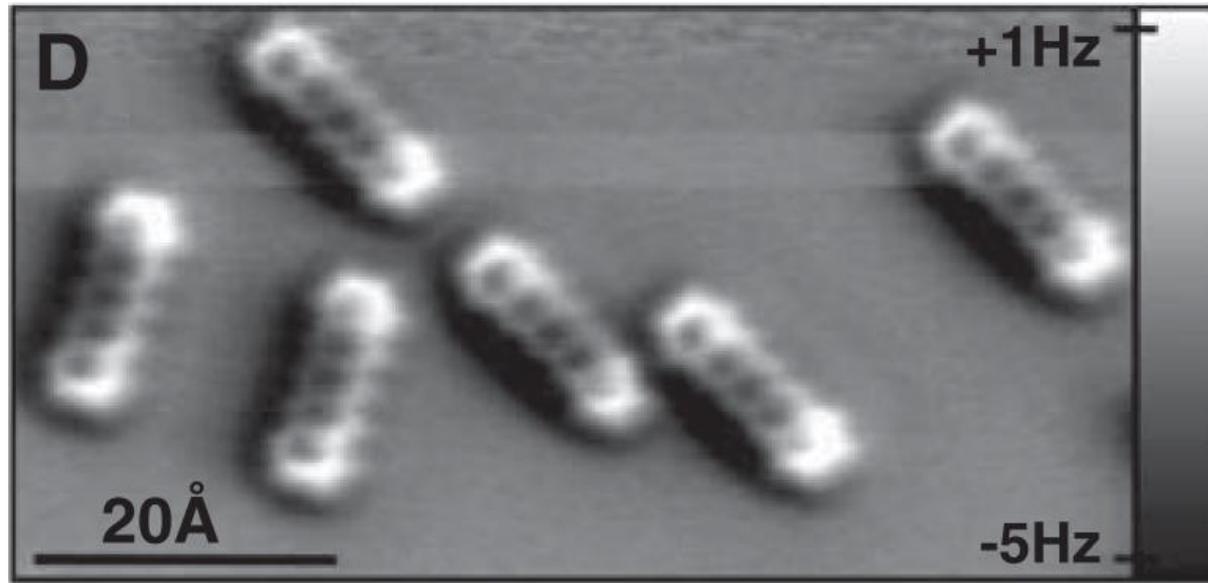
- Best possible STM/AFM with the QPlus sensor

- Where are the atoms?

- Metallic tips are reactive – large attractive forces between the tip and sample causes the molecule to be moved before reaching atomic resolution

- Sudden tip change!
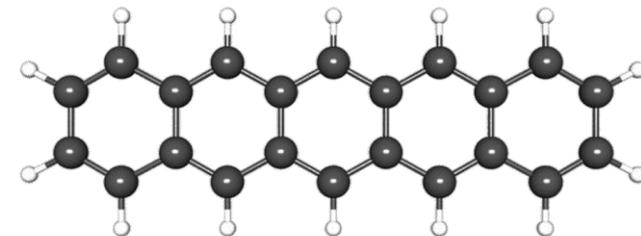
What happened?

- Tip apex was made non-reactive tip by accidental pickup of a CO molecule

- Can be done on-purpose in a controlled way

- Allows atomic resolution imaging under Pauli repulsion

Metal tip
-0.8Hz
5Å
-3.5Hz

CO tip
-2Hz
5Å
-7Hz

Science 325, 1110 (2009).
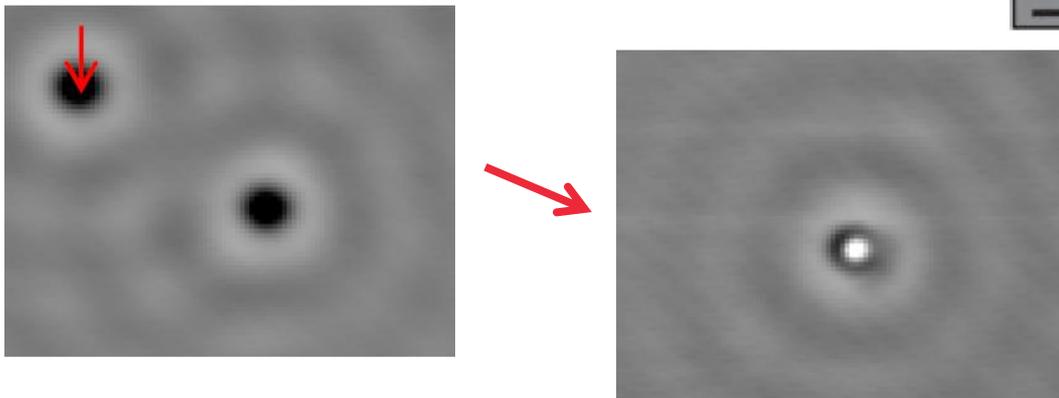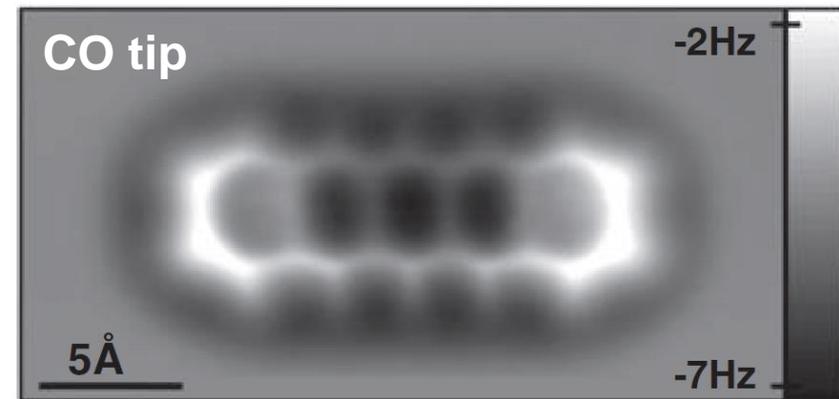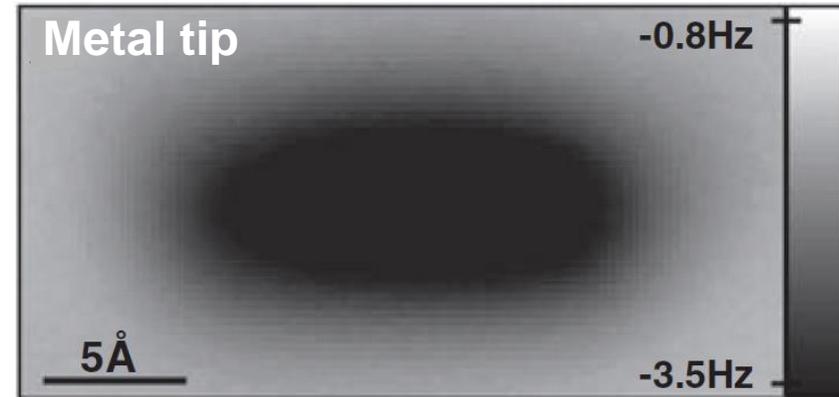
What can you do with it?

A?

- Identify molecules
- Follow on-surface reactions
- Characterize nanostructures
- All essentially flat...

Breitfussin A or B

H, C, N, O, Br, I
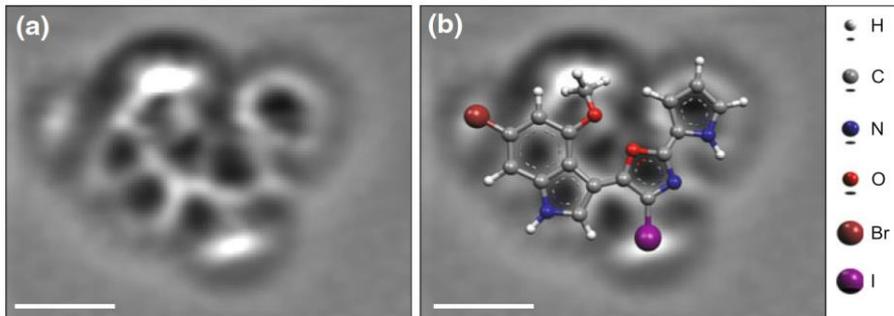
L. Gross group (IBM Zurich)
K.Ø. Hanssen, Angew. Chem. Int. Ed. 51, 12238 (2012)
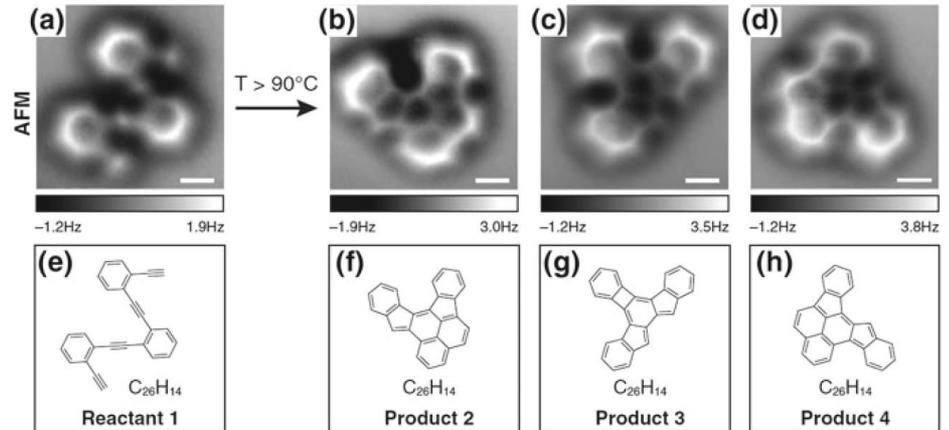
Fischer and Crommie groups (UC Berkeley)
D.G. De Oteyza et al. Science 340, 1434 (2013)

$C_{26}H_{14}$ Reactant 1

$C_{26}H_{14}$ Product 2

$C_{26}H_{14}$ Product 3

$C_{26}H_{14}$ Product 4

$T > 90°C$

−1.2Hz / 1.9Hz −1.9Hz / 3.0Hz −1.2Hz / 3.5Hz −1.2Hz / 3.8Hz

F. Schulz et al. J. Phys. Chem. C 123, 2896 (2017)
P. Jacobse et al. Nat. Commun. 8, 119 (2017)

banana
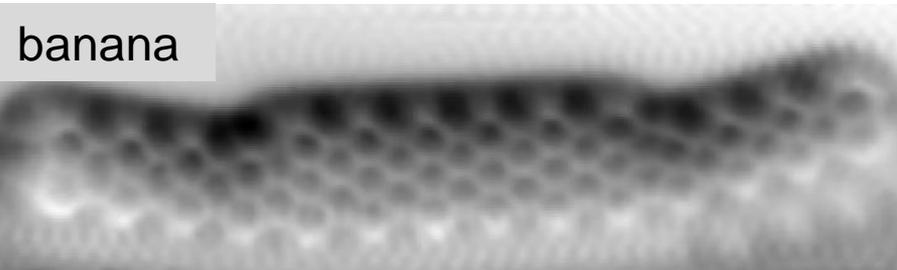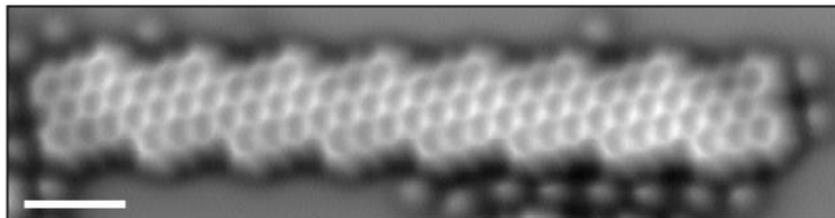
Complicated but more or less 2D
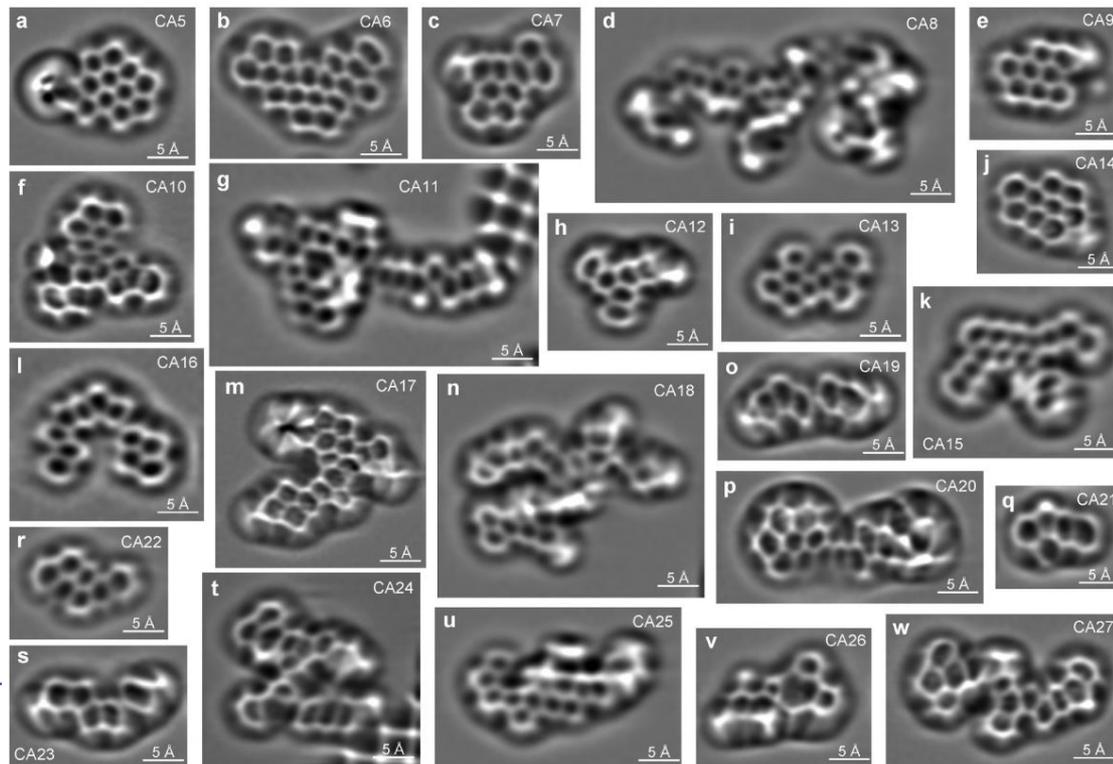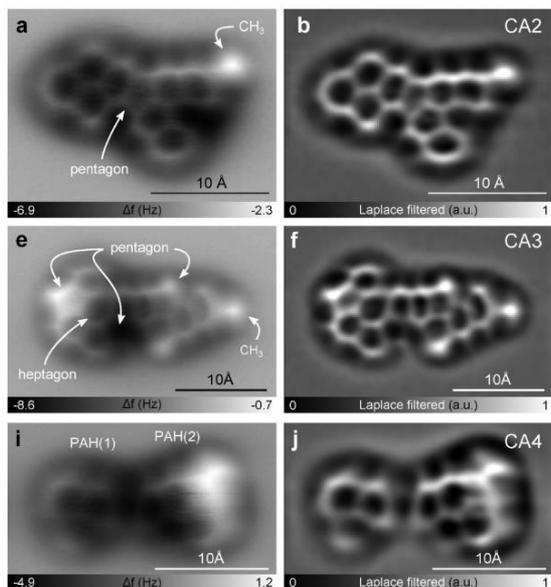
Unraveling the Molecular Structures of Asphaltenes by Atomic Force Microscopy

Bruno Schuler,*,[†] Gerhard Meyer,[†] Diego Peña,[‡] Oliver C. Mullins,[§] and Leo Gross*,[†]

[†]IBM Research — Zurich, Säumerstrasse 4, 8803 Rüschlikon, Switzerland

Why not 3D?

- Imaging is not a problem, pictures come out
- What are we looking at?

What can we do?

A?
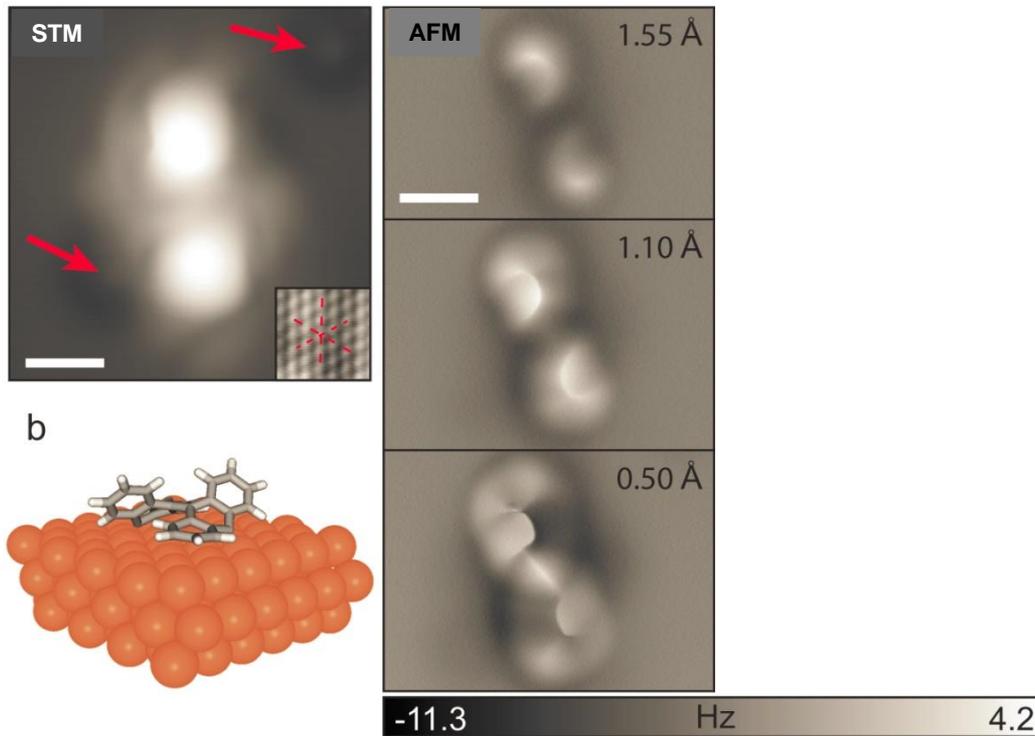
- Human interpretation is difficult, even for expert operator

- Lack of intuition on 3D structures, with tip flexibility

- Especially for unknown molecules (or unknown orientation)

- AFM with CO-tips can be very effectively and accurately modelled

- "Probe-particle model"
  - P. Jelinek, J. Phys.: Condens. Matter 29, 343002 (2017)
  - http://ppr.fzu.cz/index.php

- Machine learning with synthetic data?

More complicated cases – how to tell where the atoms are?

■ Combine AFM experiments with machine learning

■ AFM images can be simulated with high-accuracy
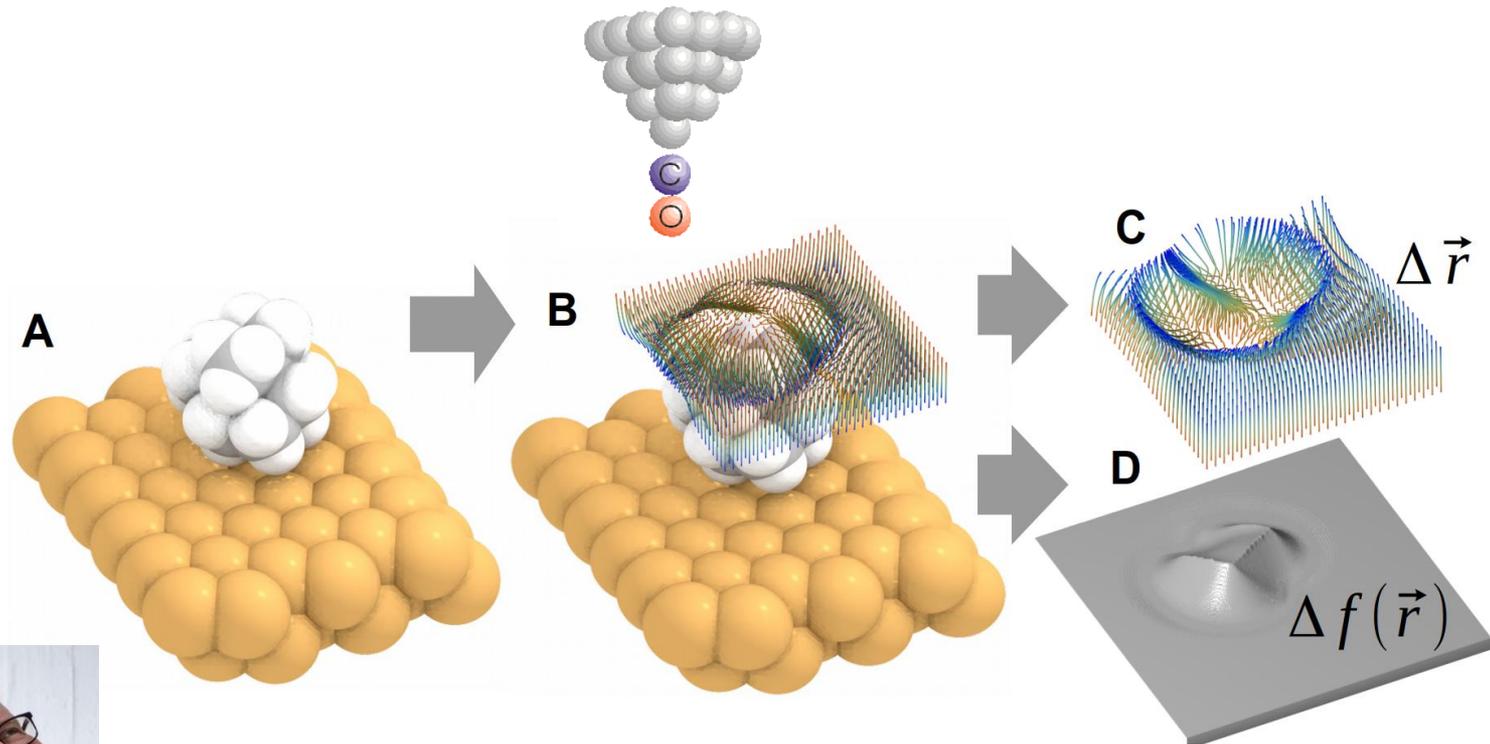
Machine learning + AFM simulations
Prof. Adam Foster

Machine learning infrastructure

- Use machine learning to go in the other direction
- Image recognition problem - train a convolutional neural network on database of 3D AFM simulations of 134,000 molecules.
- Use image descriptors (a representation of where the atoms are in each molecule)

AFM measurement

A familiar representation of atoms as spheres with radii equal to their van der Waals (vdW) radii.
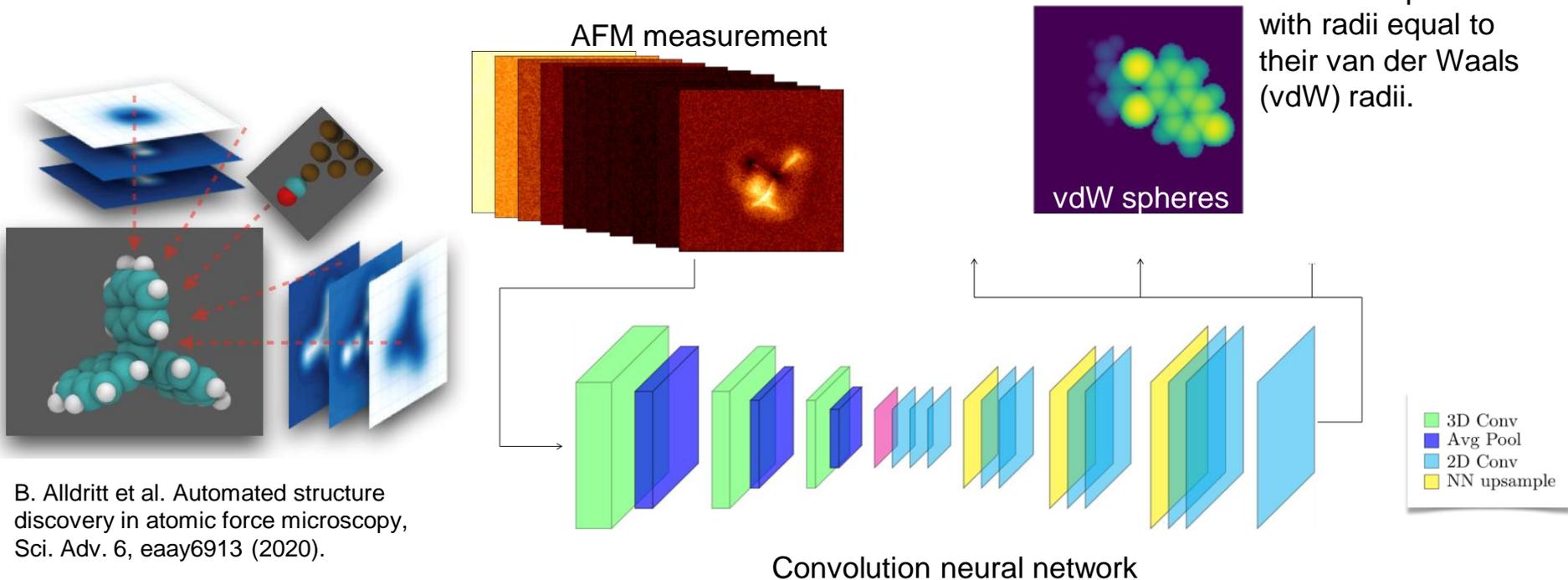
vdW spheres

3D Conv
Avg Pool
2D Conv
NN upsample

B. Alldritt et al. Automated structure discovery in atomic force microscopy, Sci. Adv. 6, eaay6913 (2020).

Convolution neural network

Training

■ Image recognition problem - train a convolutional neural network on database of 3D AFM simulations of 134,000 molecules.
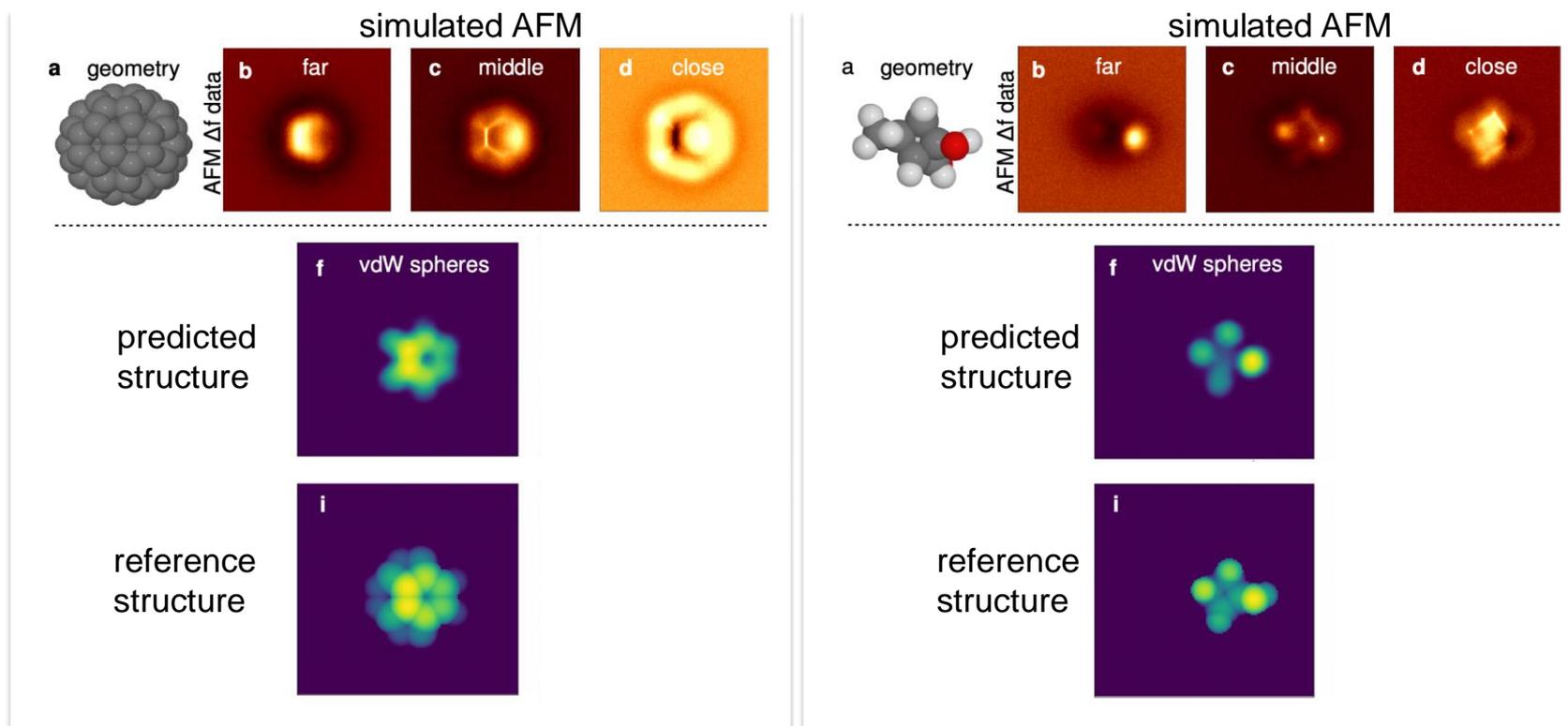
Does it work in practice - camphor

- Deposit camphor (C10H16O) molecules on Cu(111) surface
- Expect a variety of adsorption configurations
- Repeated AFM experiments on characteristic configurations
- Run the resultant datasets through the machine learning infrastructure and predict the configuration

Gustaf Komppa (1867 – 1949)
Chemistry professor in Otaniemi 1908–1937
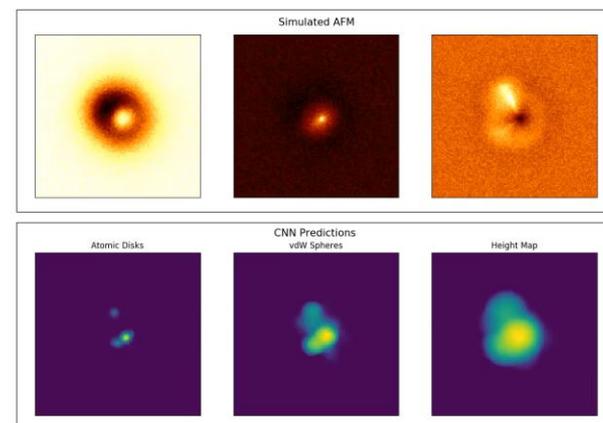
Camphor on Cu(111)

- Several different configurations found
- Identification by STM
- Some represent non-stable (rotating) adsorption structures ("pinwheel no. 2")
- Take a full set of constant-height Δf images on each configuration
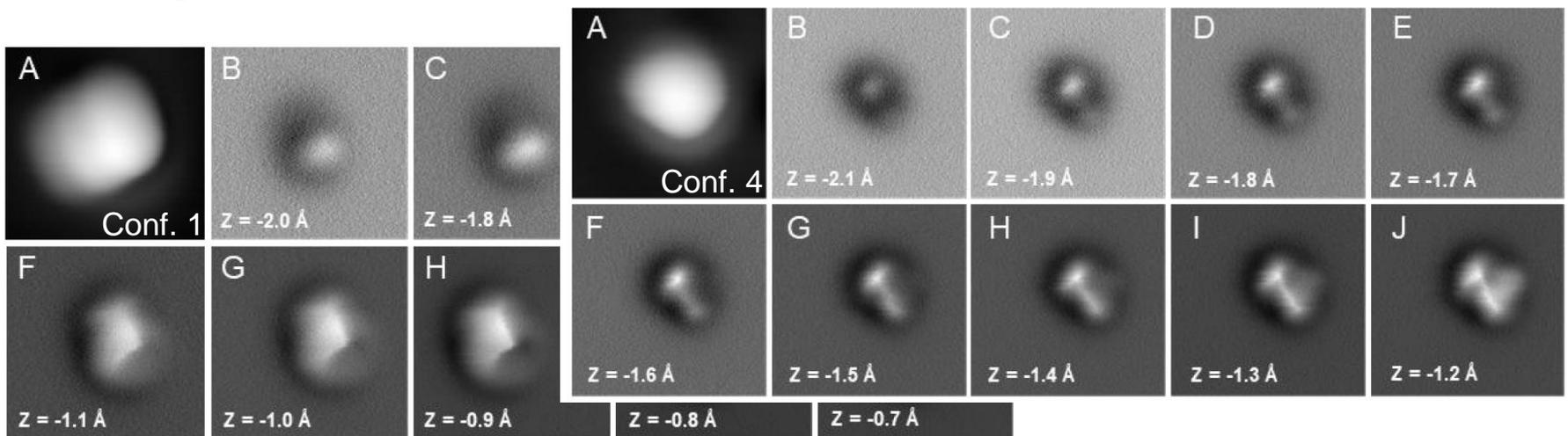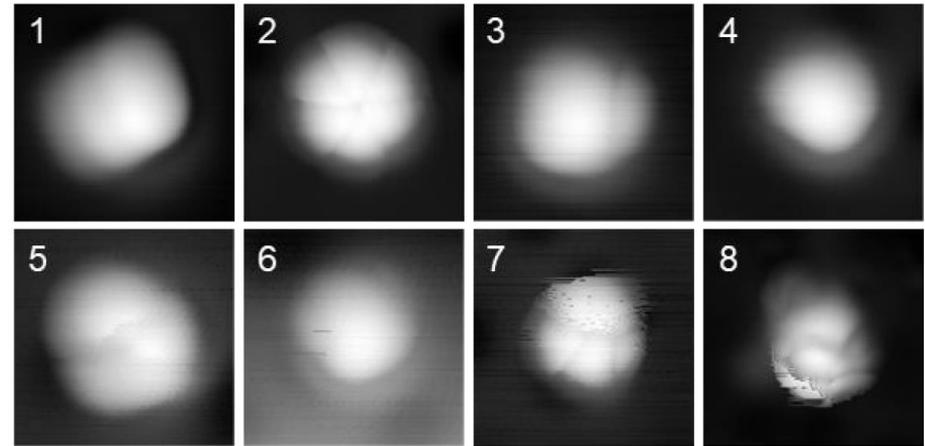
Full experimental data set
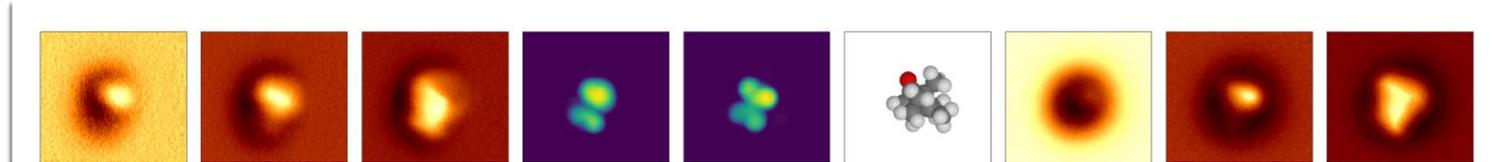
Present status:

- We can identify adsorption structure of a known molecule
- Not a trivial task
- Target molecules are usually not completely unknown

$\Rightarrow$ How to incorporate some knowledge of the molecule into the model?

AFM measurement   Descriptor prediction   Descriptor match   Molecular configuration   Simulated images

B. Alldritt et al. Automated structure discovery in atomic force microscopy, Science Advances 6, eaay6913 (2020).

Conclusions

A?
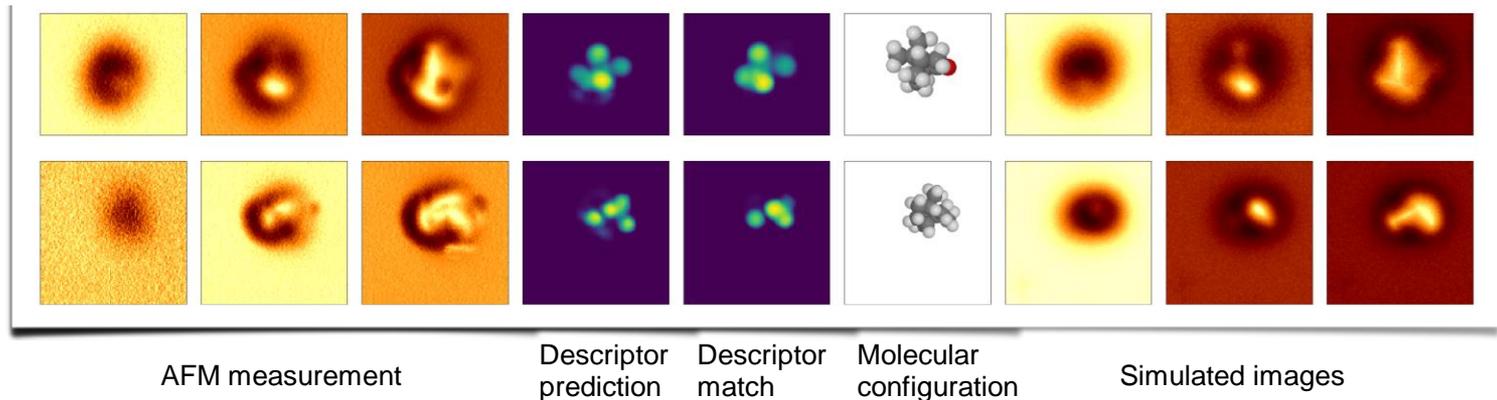
- AFM gives beautiful images
- Machine learning can help with 3D molecules
  - Training with synthetic data
- **Currently**: identify adsorption structure of a known molecule
- **To do**: towards complete structural characterization of single molecules (atom positions, type, functional groups, electrostatic potentials)
- **Future directions**: more complicated large molecules, look at surfaces of viruses ...

SCIENCE ADVANCES | RESEARCH ARTICLE

CONDENSED MATTER PHYSICS

Automated structure discovery in atomic force microscopy

Benjamin Alldritt[1]*, Prokop Hapala[1]*, Niko Oinonen[1]*, Fedor Urtev[1,2]*, Ondrej Krejci[1], Filippo Federici Canova[1,3], Juho Kannala[2], Fabian Schulz[1†], Peter Liljeroth[1‡], Adam S. Foster[1,4,5‡]
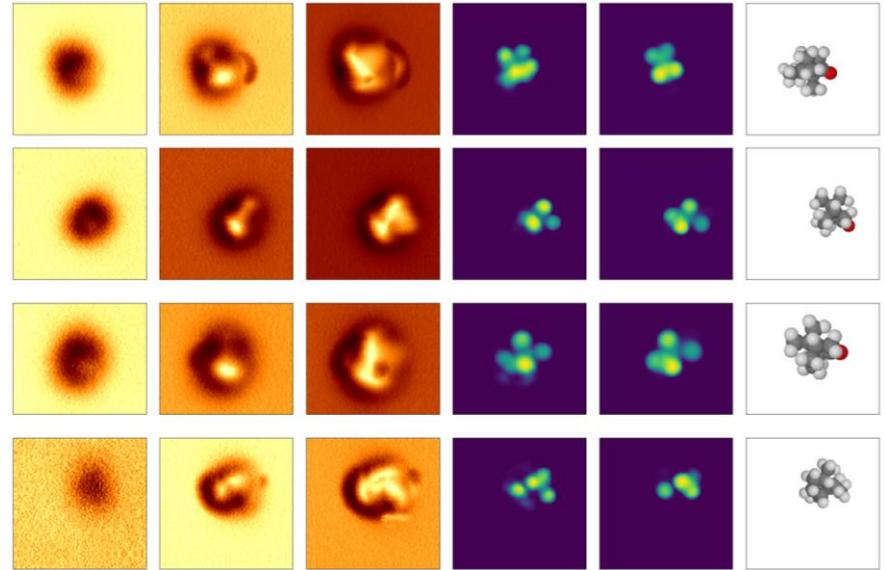
Alldritt *et al., Sci. Adv.* 2020; **6** : eaay6913