Aalto University
School of Science

Lecture 1:
Introduction to scanning probe microscopy

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Outline

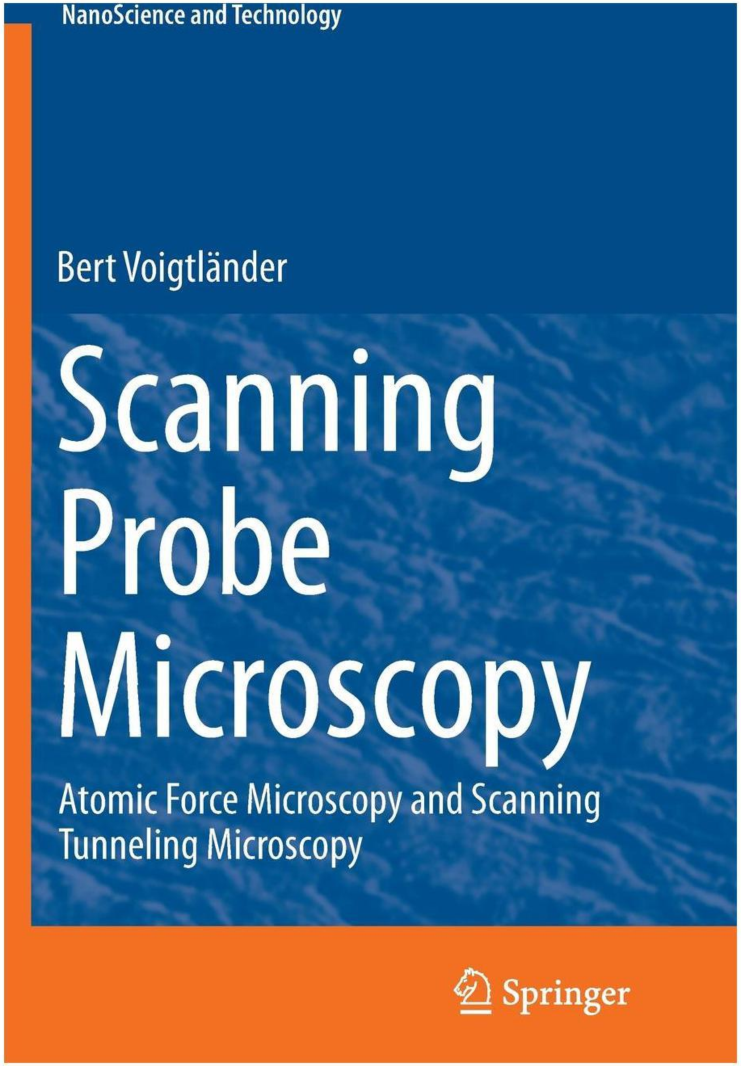
Learning outcomes:

- 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

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


NanoScience and Technology

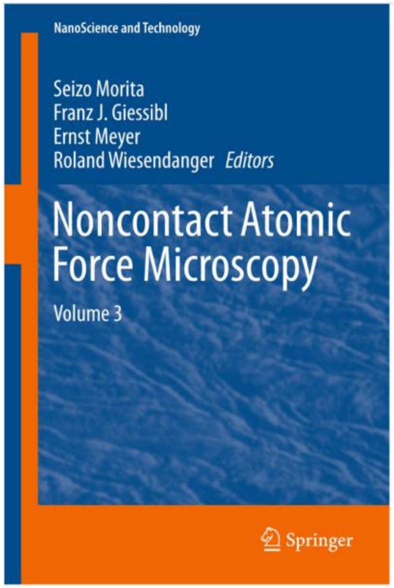
Bert Voigtländer

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&

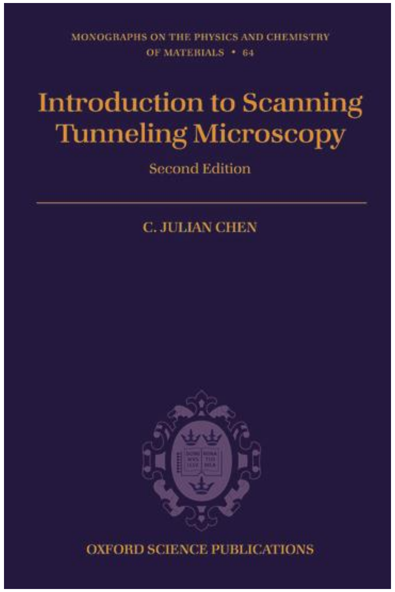

NanoScience and Technology

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

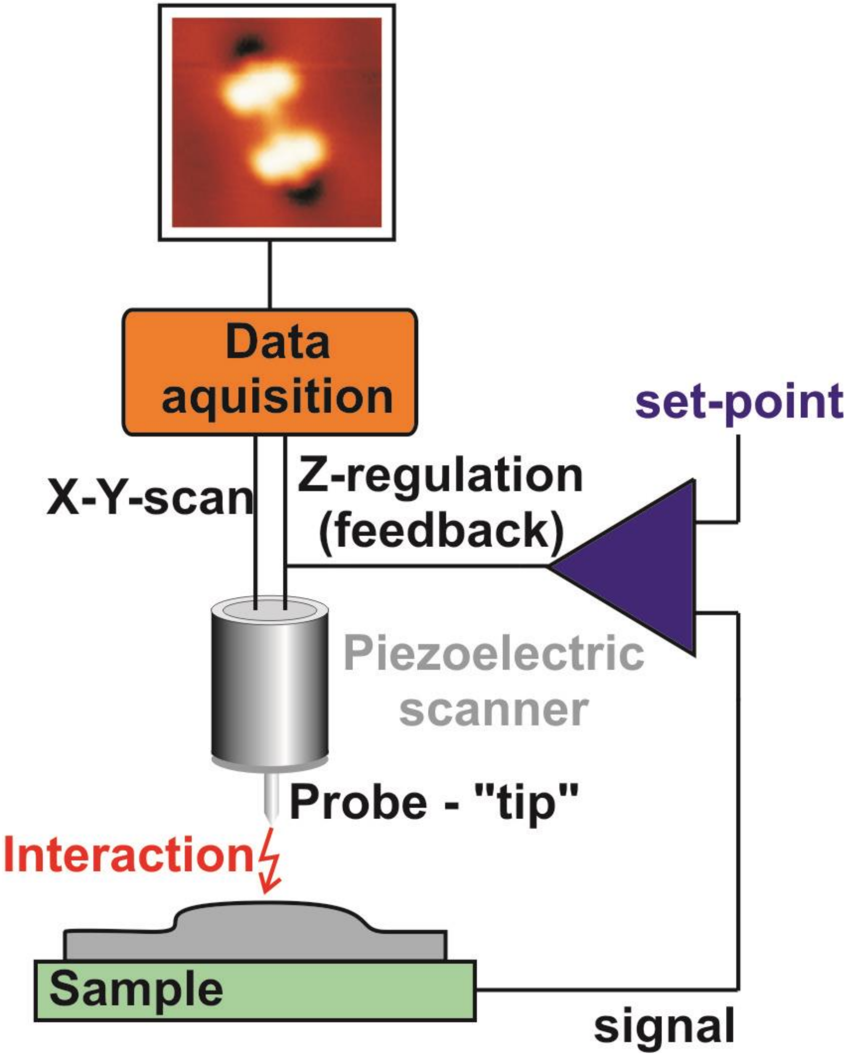
Second Edition

C. JULIAN CHEN

OXFORD SCIENCE PUBLICATIONS

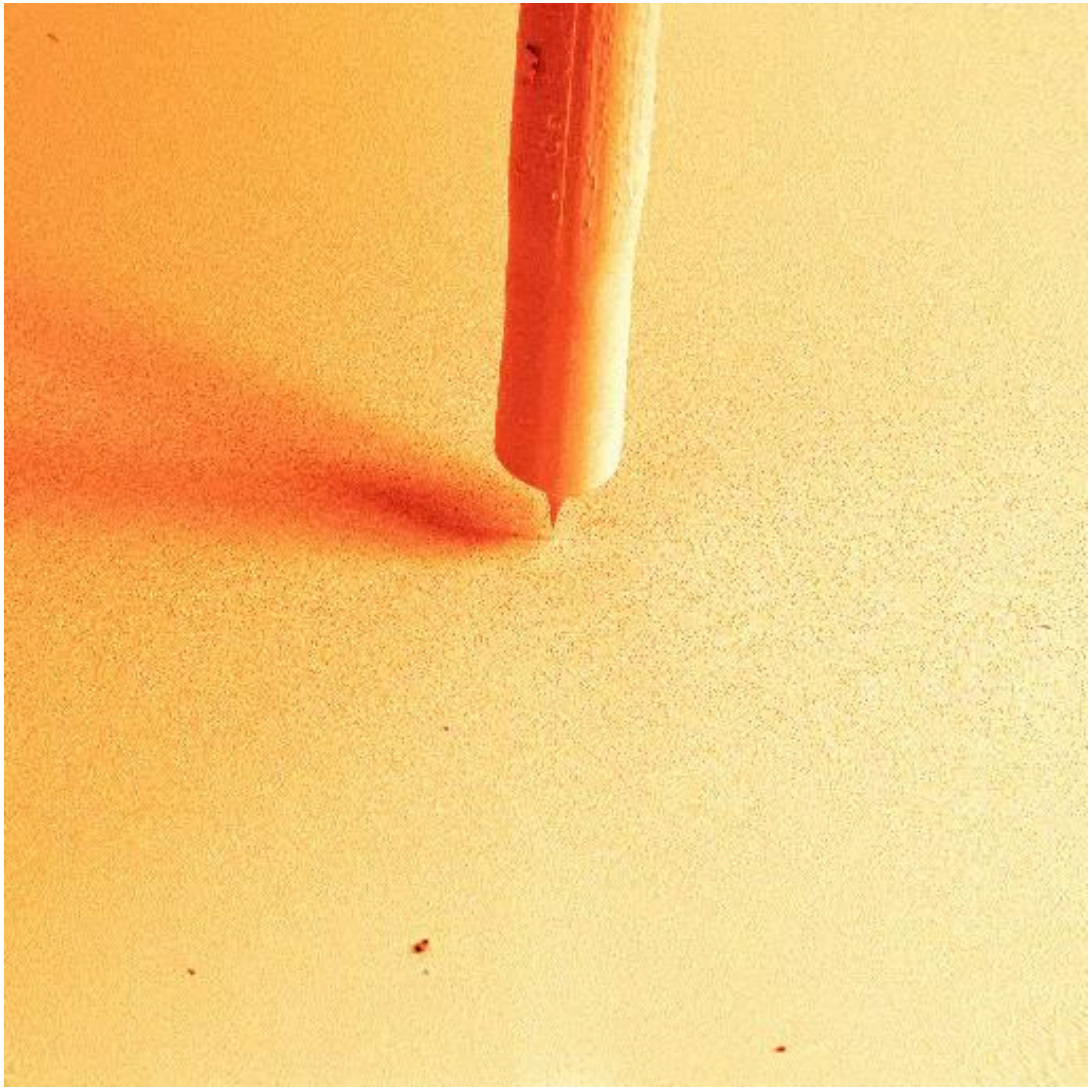
https://www.springer.com/gp/book/9783319155876

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)

STM / AFM topographic mode



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

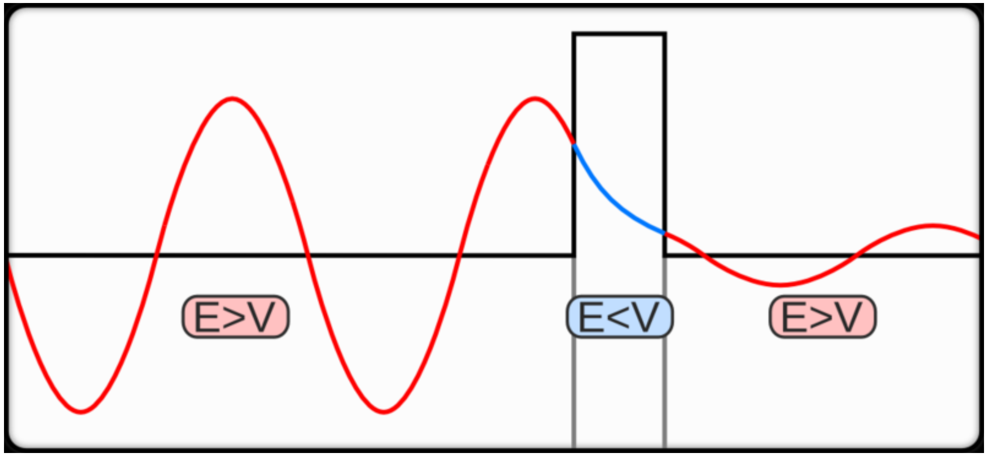
$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+V(x)\psi=E\psi$$

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

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

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

x=0 x=d



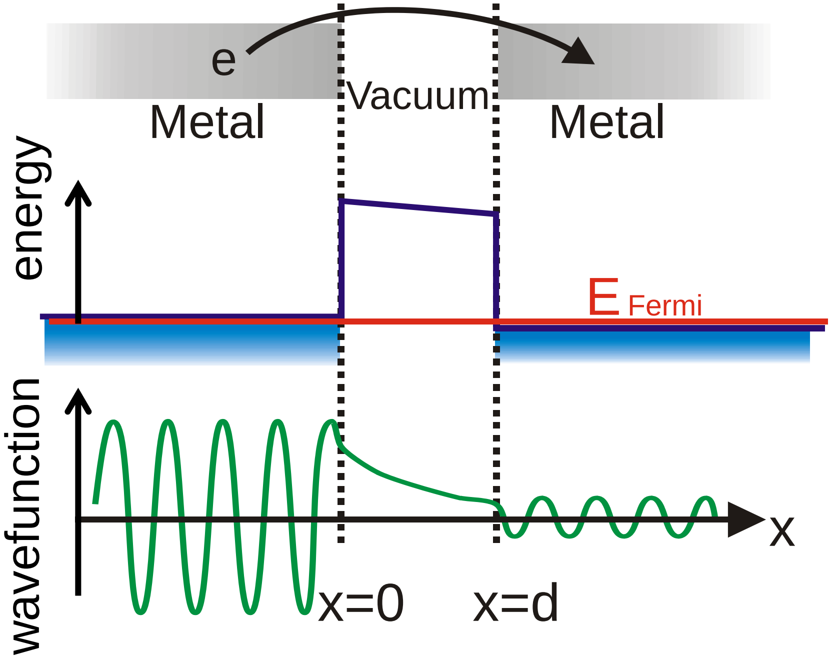
$$\psi = F\exp(\kappa x)+G\exp(-\kappa x)$$

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

- 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



- If the barrier is large, i.e. $\kappa d >> 1$, then transmission probability

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

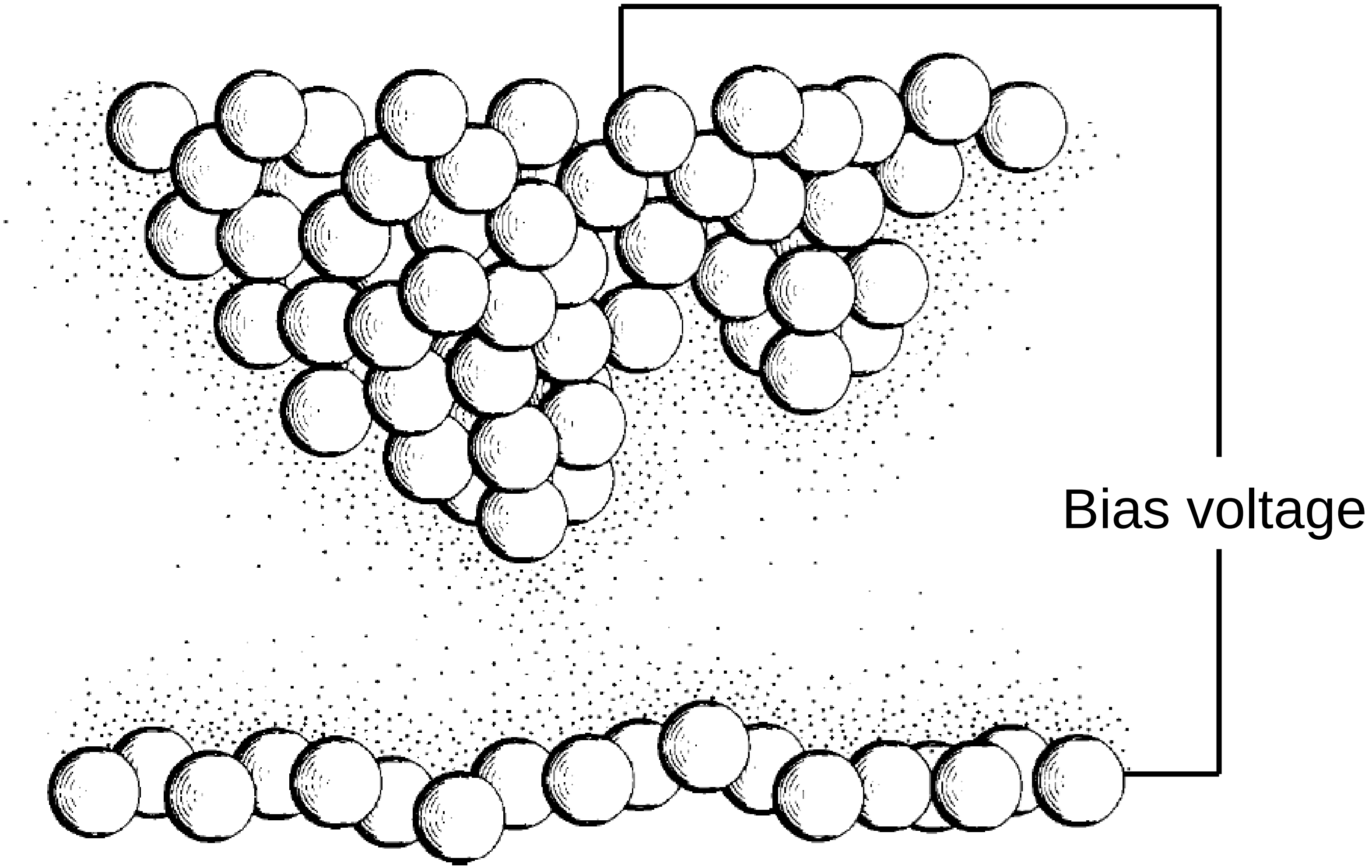
and the current

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

with

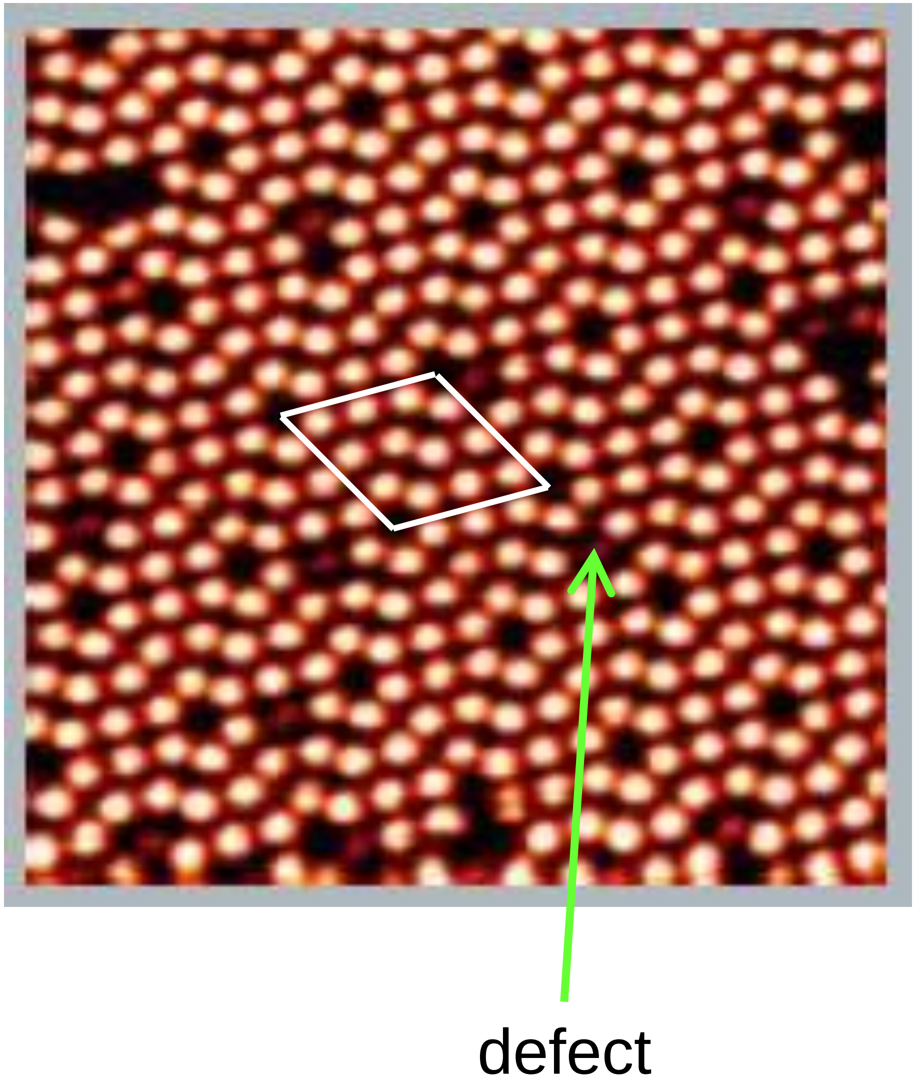
$$\kappa = \left(\frac{2m}{\hbar^2}(V_0 - E)\right)^{1/2}$$

- $\kappa = 1.1$ 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

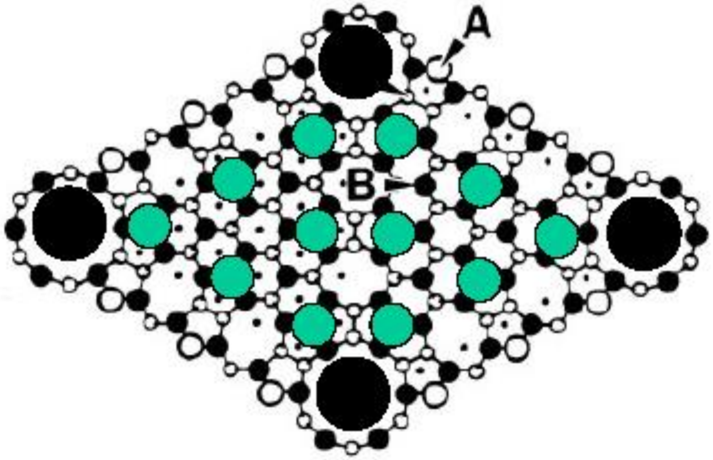


- Typical bias voltage from a few mV to a few V (limited by the onset of field emission)
- Typical currents from a few pA to a few nA (tunneling conductance << conductance quantum ≈ 1/12.9kΩ)

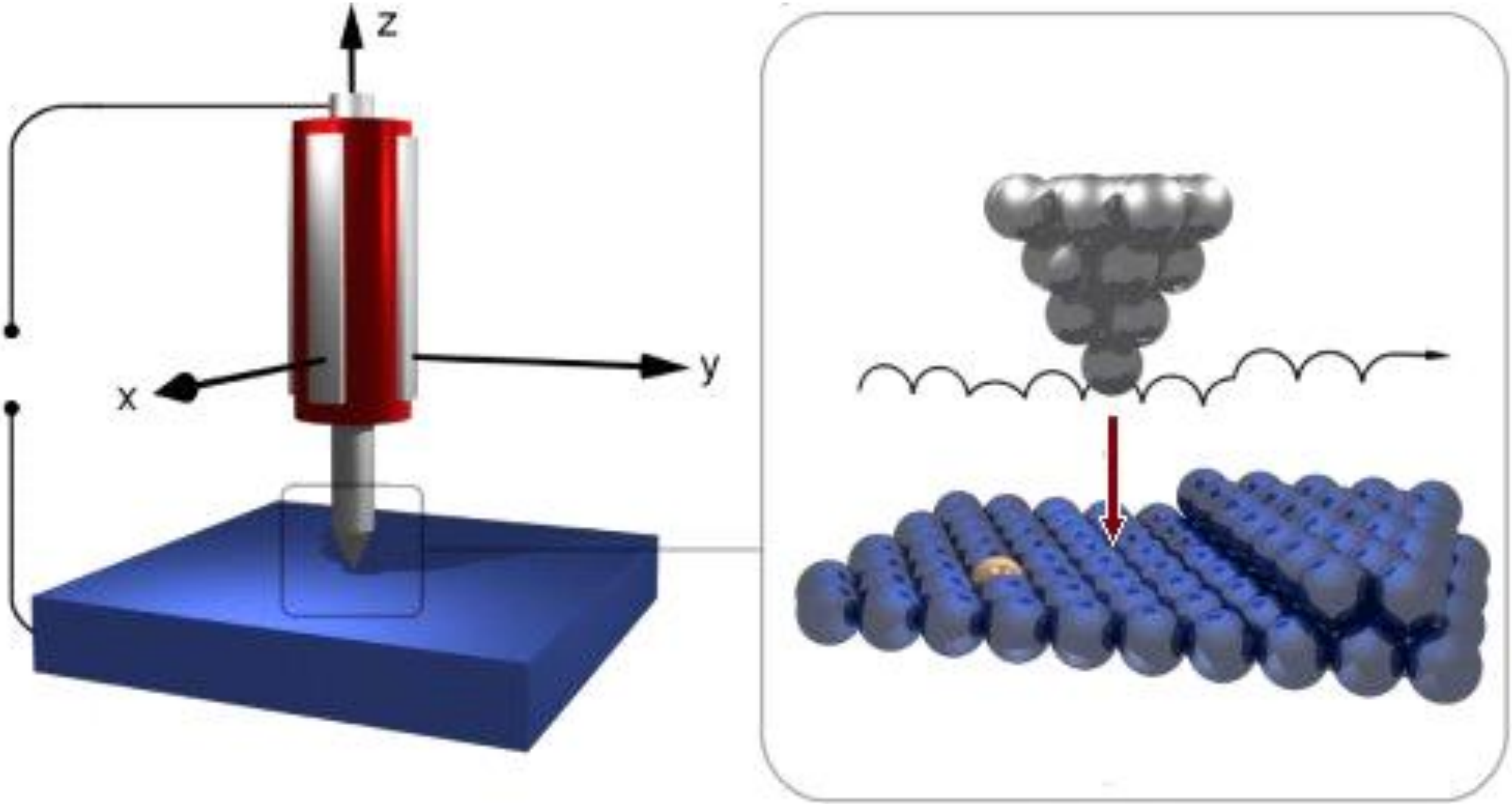
Si(111) 7×7 reconstruction



- STM topography of Si(111) 7×7 reconstruction both atoms and defects visible
- First surface structure determination by STM



STM topographic mode



S. Woedtke, Ph. D. Thesis, Kiel, 2002.

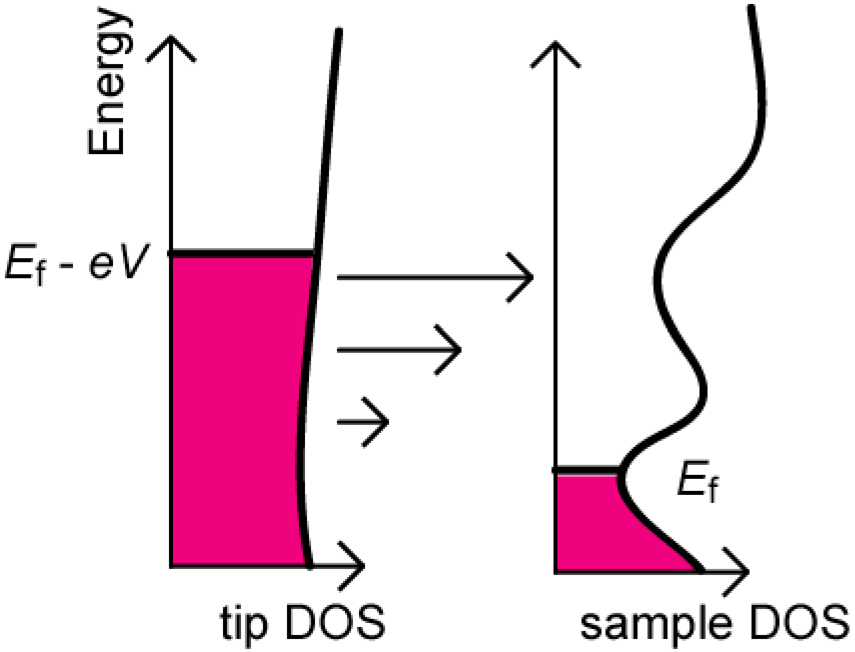
Measuring LDOS

If ρ_{tip} and T energy independent (at least close to the Fermi level):

$$\mathrm{d}I/\mathrm{d}V_{\mathrm{b}}(V_{\mathrm{b}},x,y) \propto \rho(eV_{\mathrm{b}},x,y) = \mathrm{LDOS}(eV_{\mathrm{b}},x,y)$$

What is LDOS?

$$\mathrm{LDOS}(eV_{\mathrm{b}},x,y) = \sum_{\delta E} \left|\psi_i(E_i,x,y)\right|^2$$

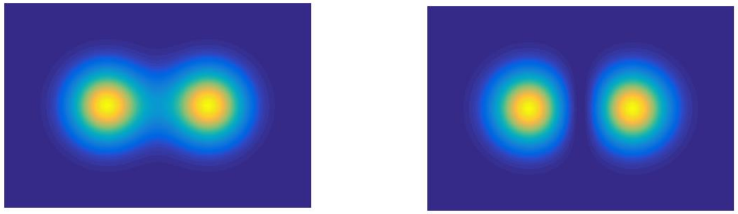


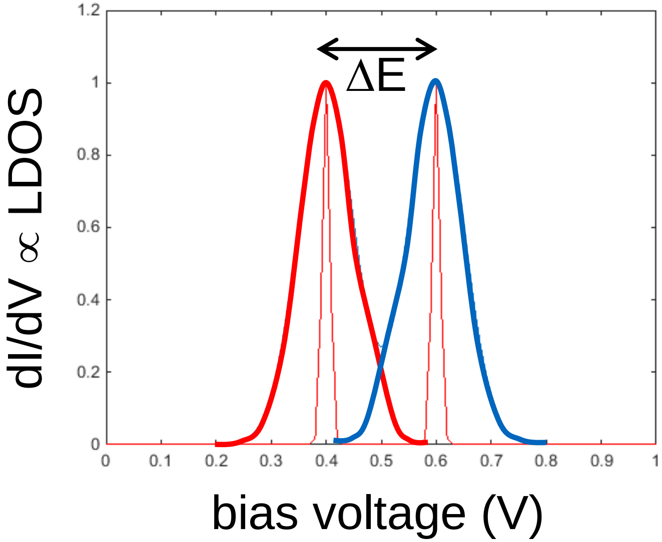
→ STM maps the (integrated) **constant** density of states surface of the sample

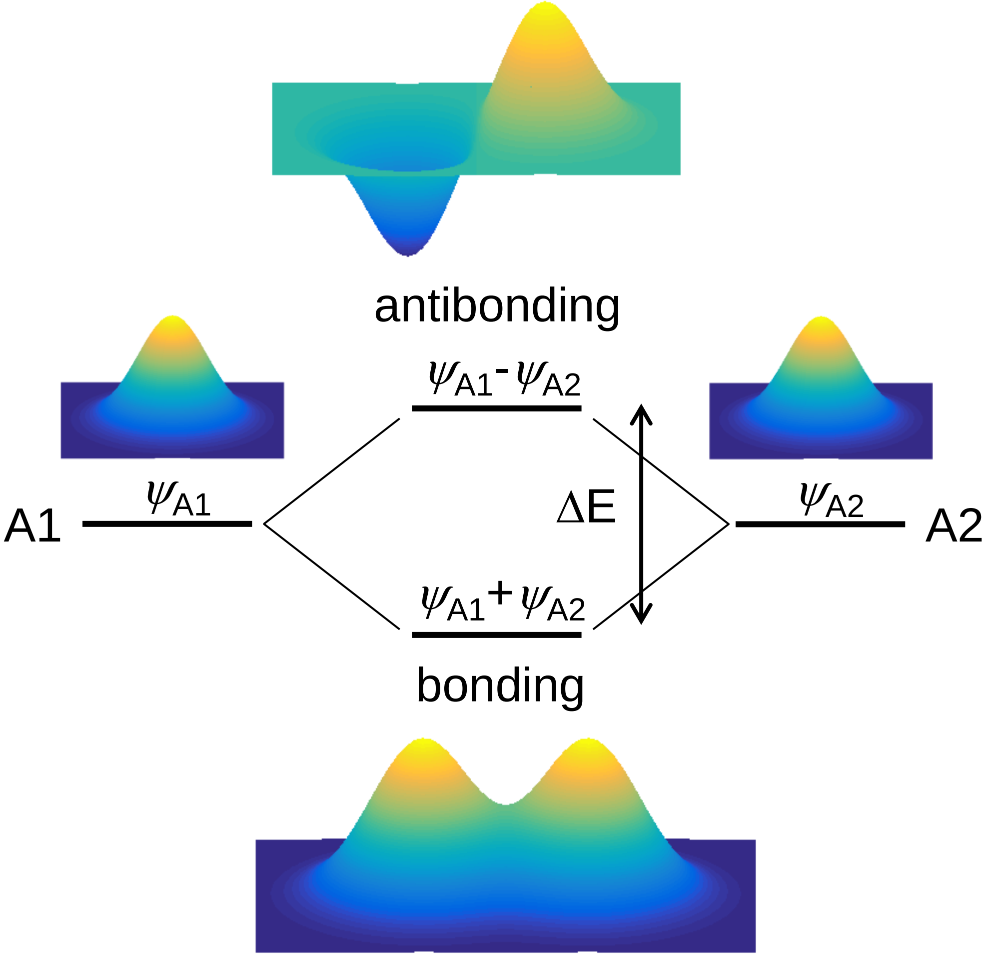
→ dI/dV spectroscopy gives the local density of states

LDOS example: two atoms making a molecule

dI/dV maps (proportional to ψ^2)







antibonding

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

A1 ψ_{A1}

ΔE

ψ_{A2} A2

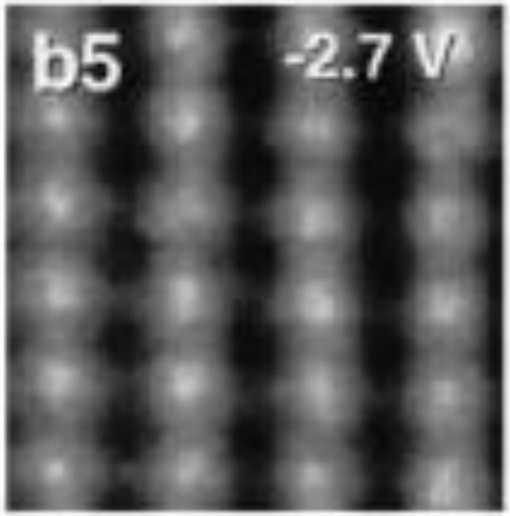
$\psi_{A1} + \psi_{A2}$

bonding

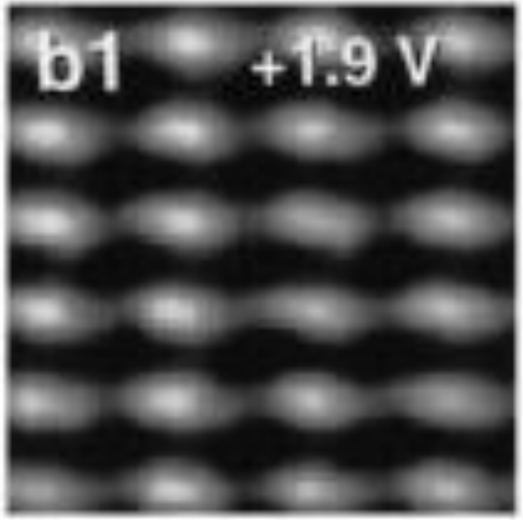
- What determines the energy and spatial resolution?

Real example 1: semiconductor surface

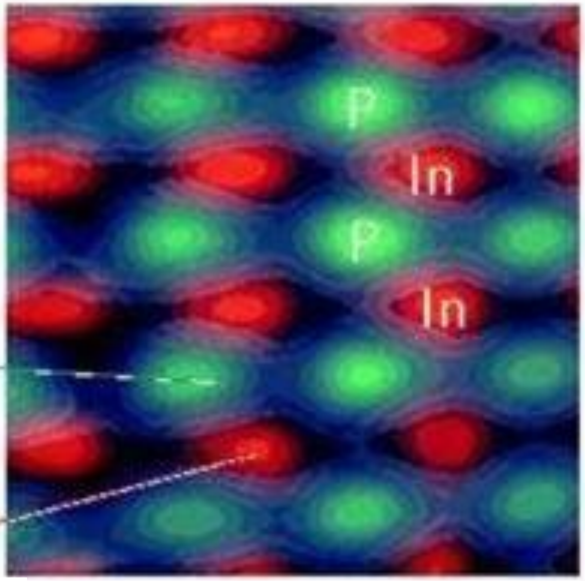
occupied

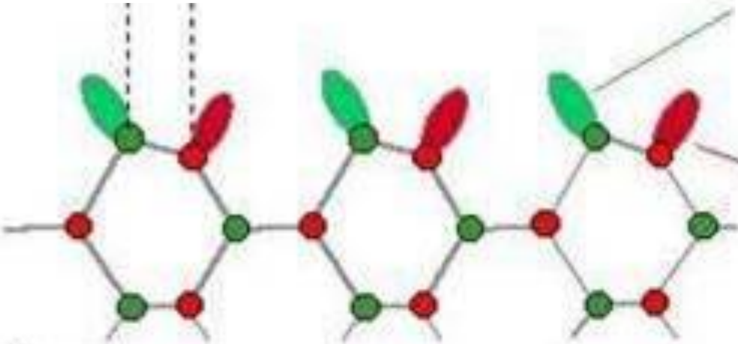


empty



two superimposed STM images of the occupied and empty density of states





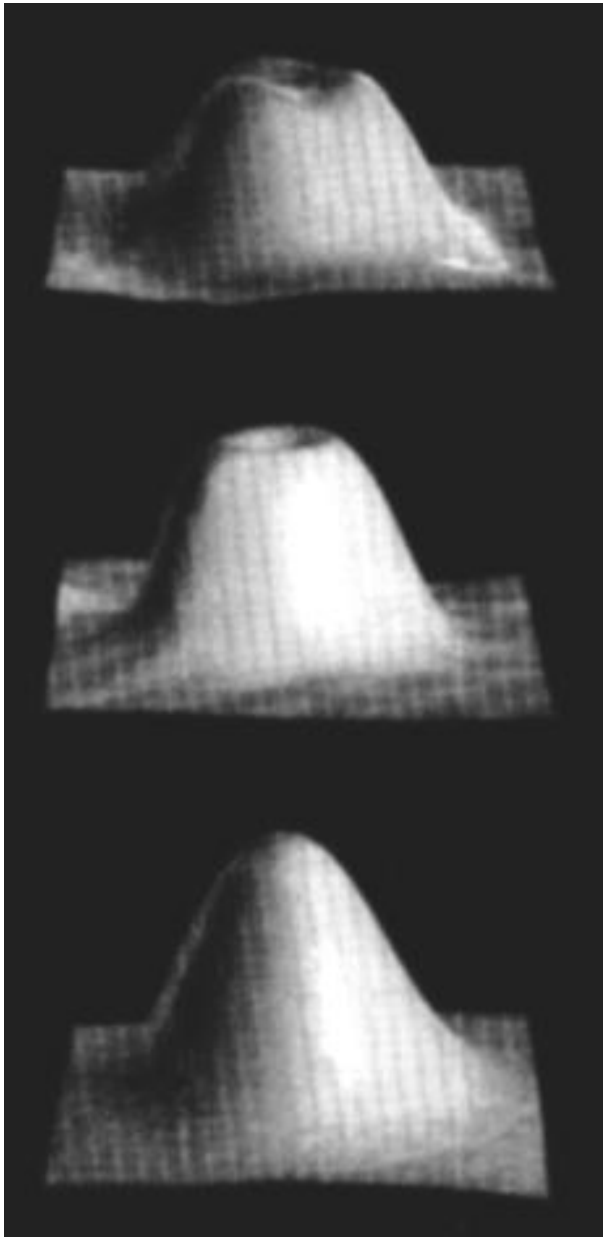
occupied dangling bond

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

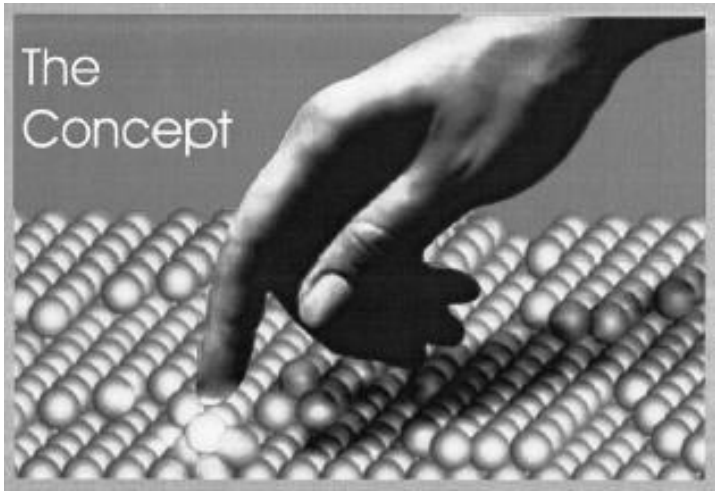
P.S. Weiss, D.M. Eigler, *Phys. Rev. Lett.* **71**, 3139 (1993).

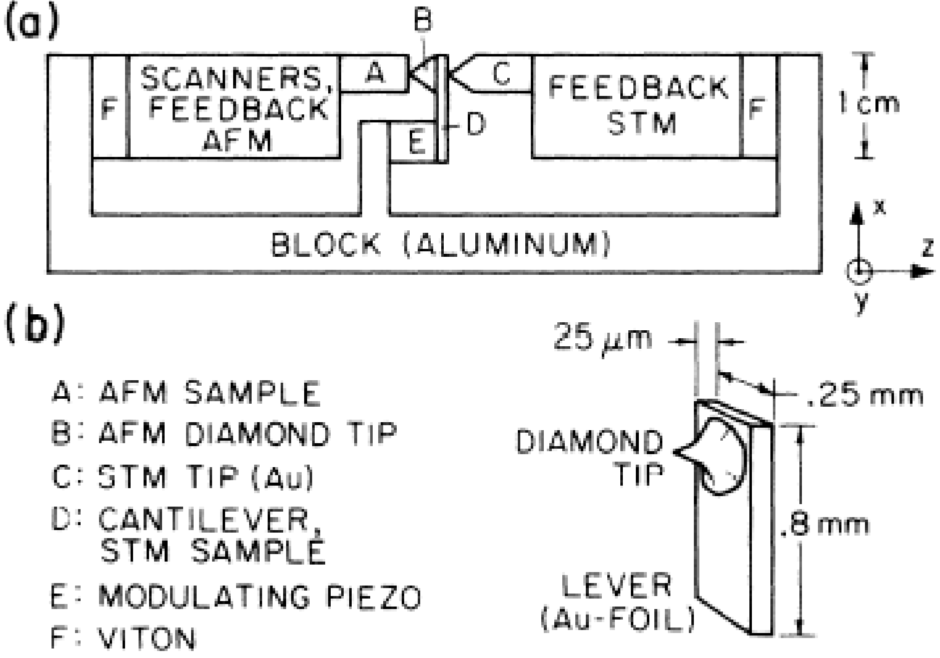
Reasons for the success of STM

- 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*

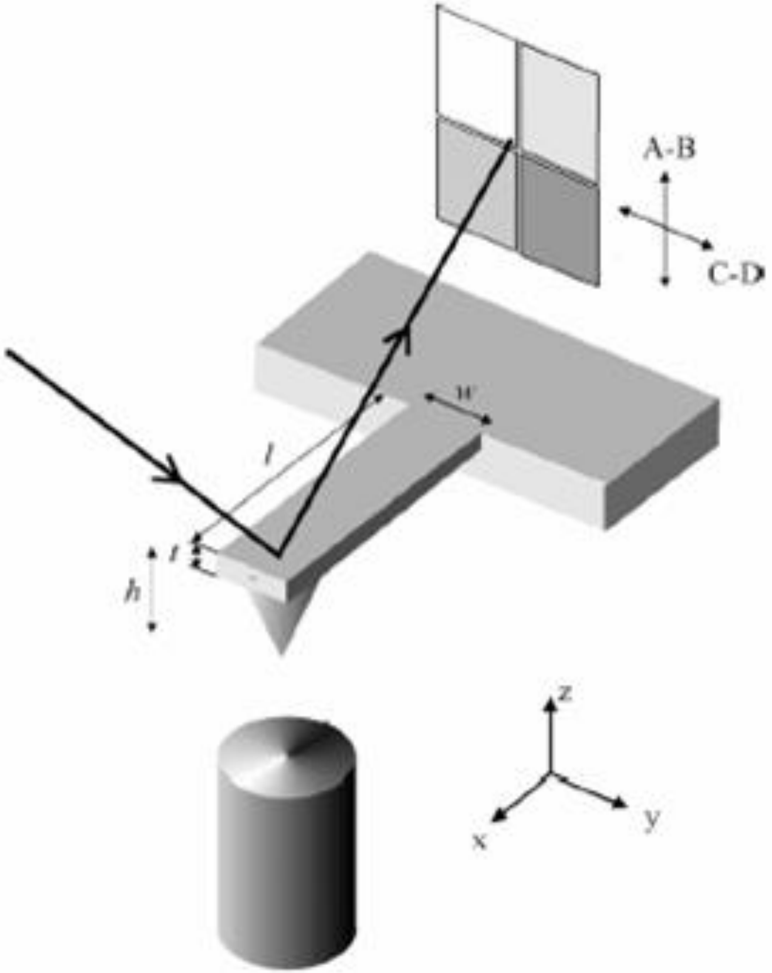




G. Binnig, C.F. Quate, C. Gerber, *Phys. Rev. Lett.* **56**, 930 (1986).

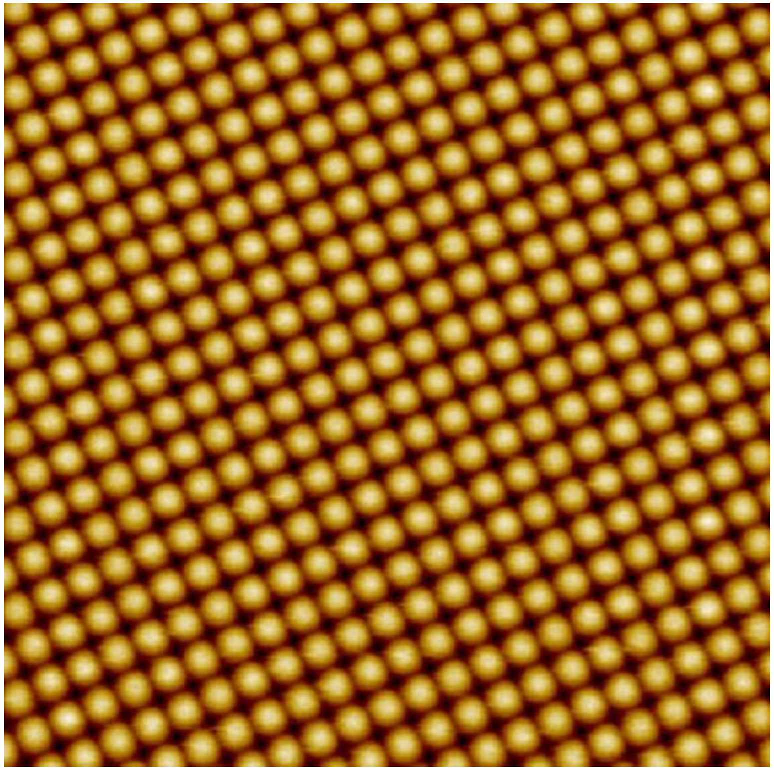
Bending of a cantilever

- 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



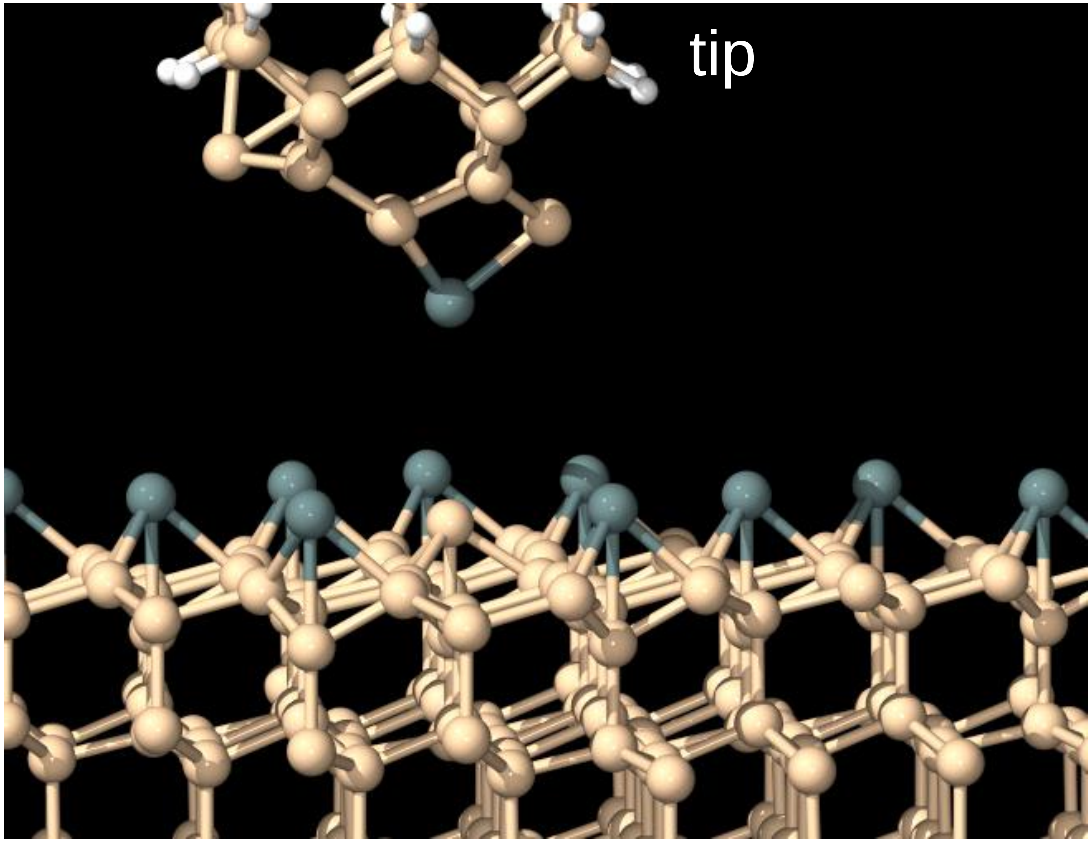
Atomic resolution imaging on bulk insulators

- Image on a cleaved KBr surface
- Only bromine ions are visible
- Insulating substrate, i.e. STM would not be possible



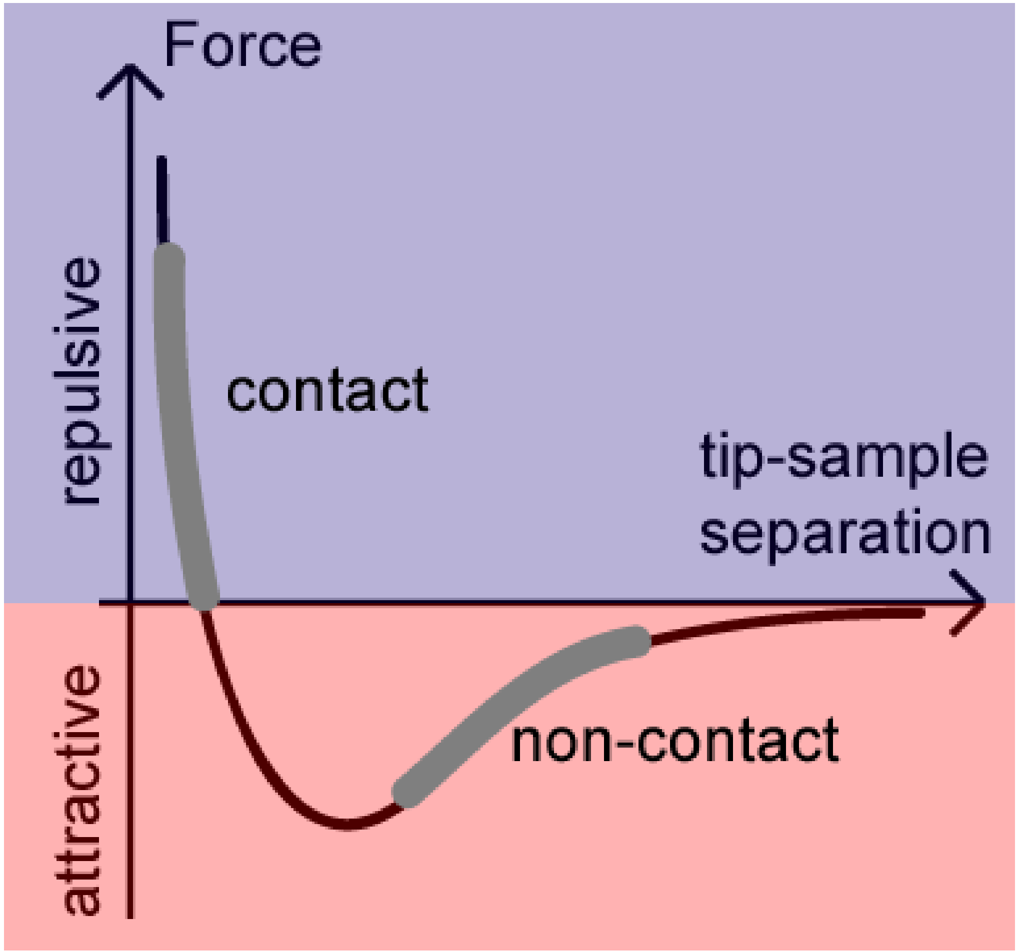
AFM principles

- 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)



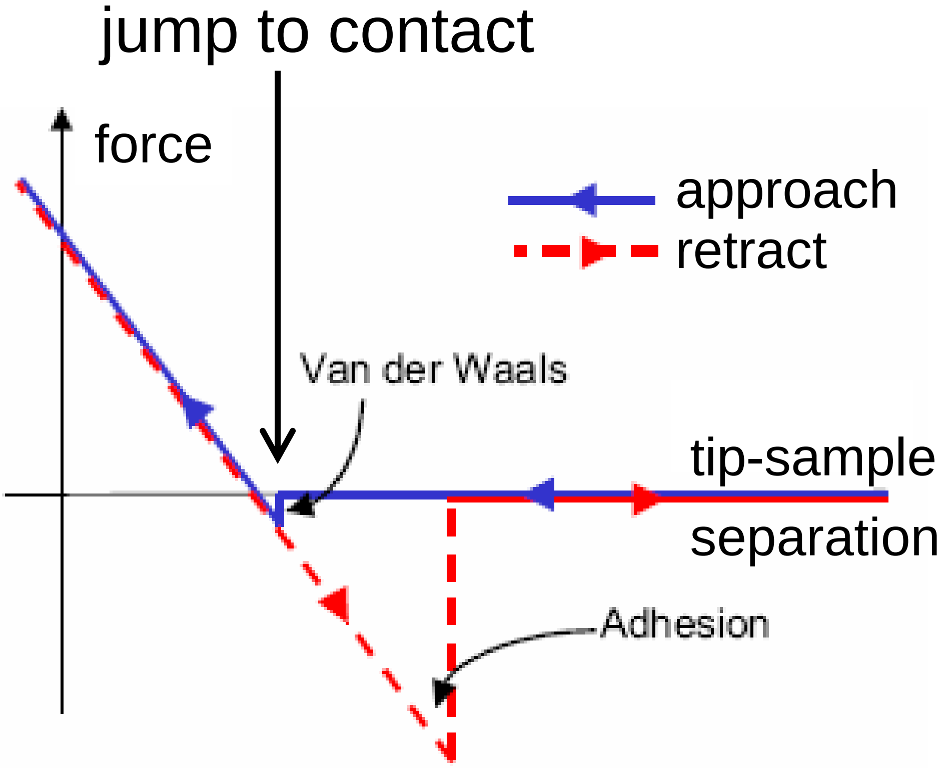
Different modes

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

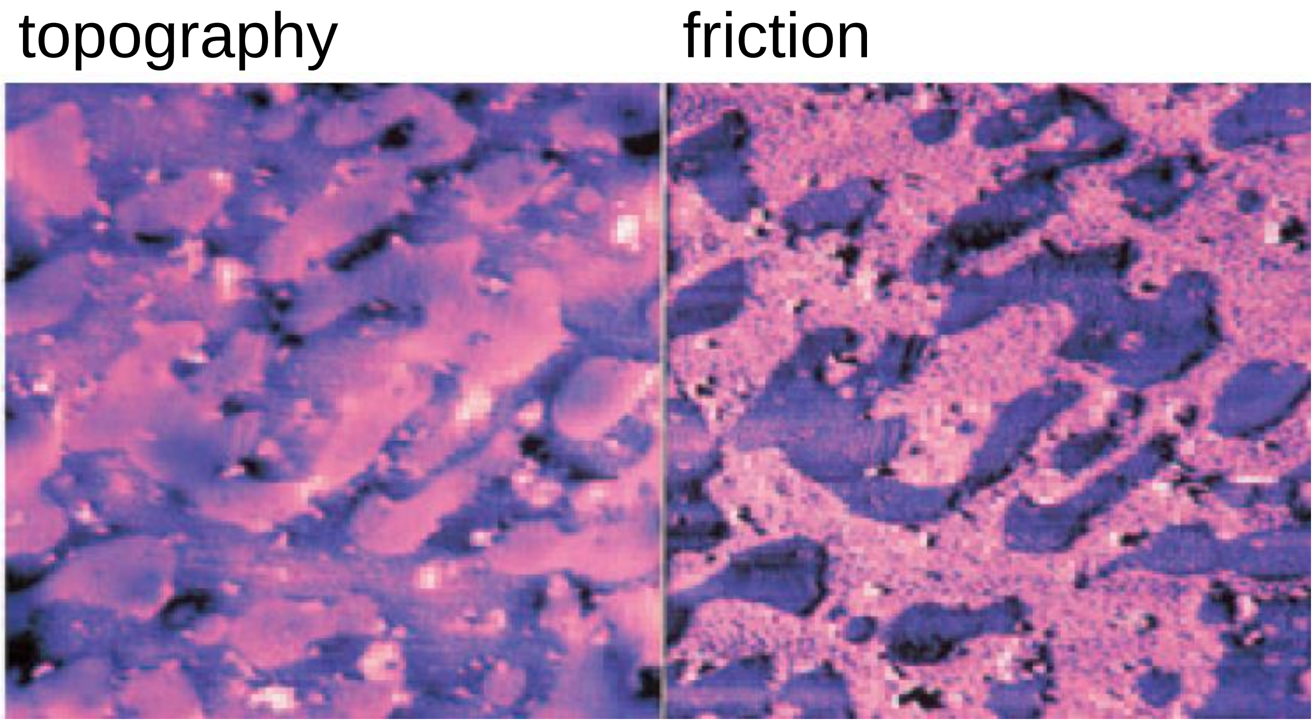


Contact mode

- 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

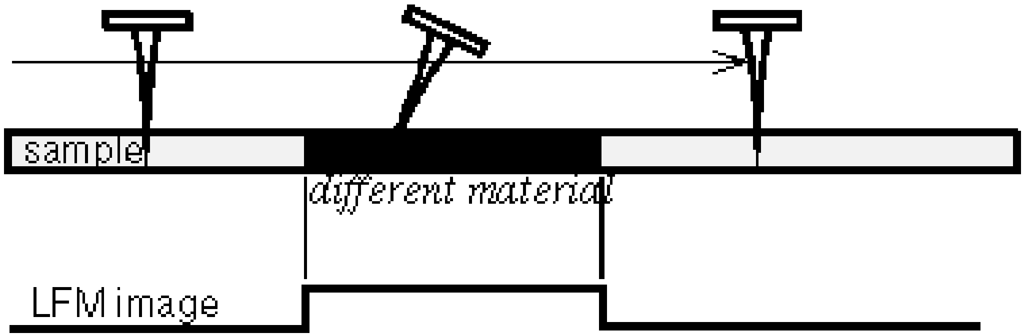


Example on contact mode AFM



topography

friction

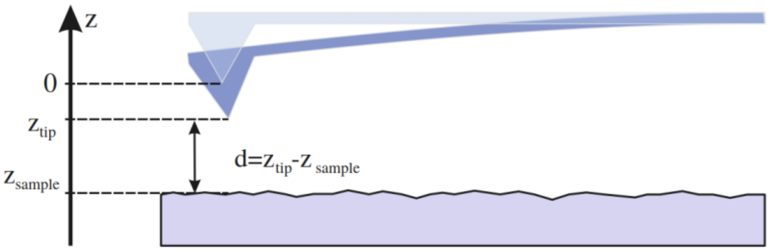


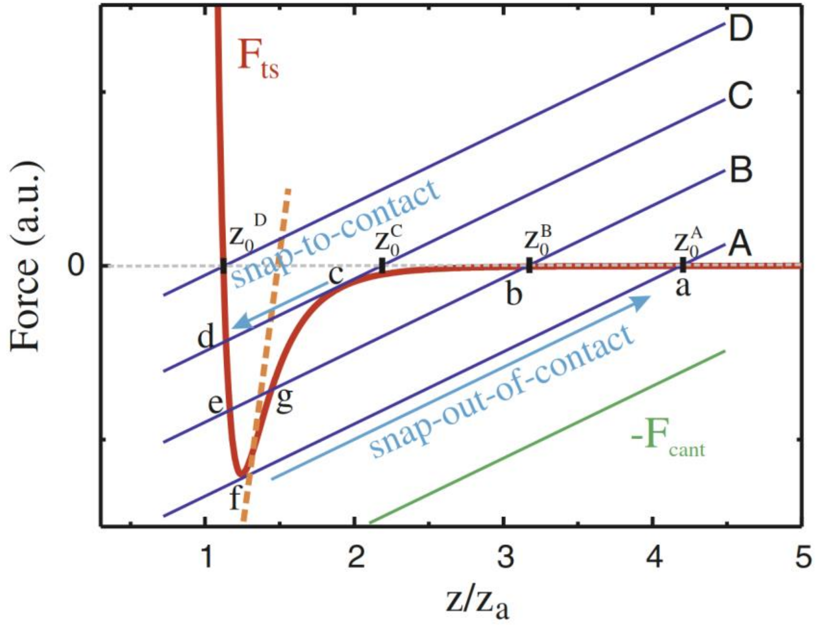
Static mode approach curve

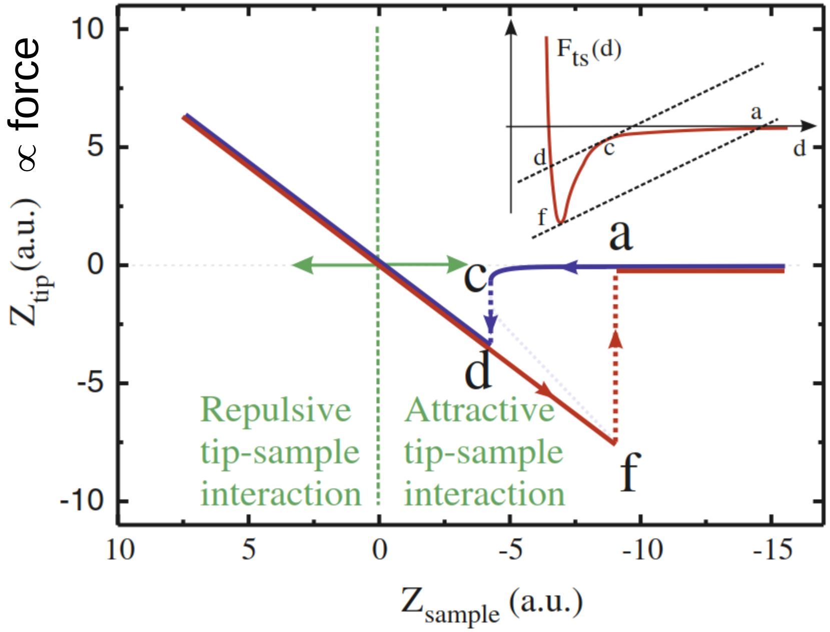
- Instability occurs if

$$\frac{\partial F_{ts}(z)}{\partial z} > k$$

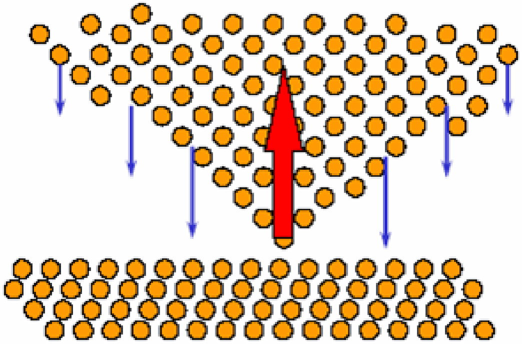
where *k* is the cantilever spring constant and F_{ts} is the tip-sample interaction force







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

→ this is not good

- How to avoid it?

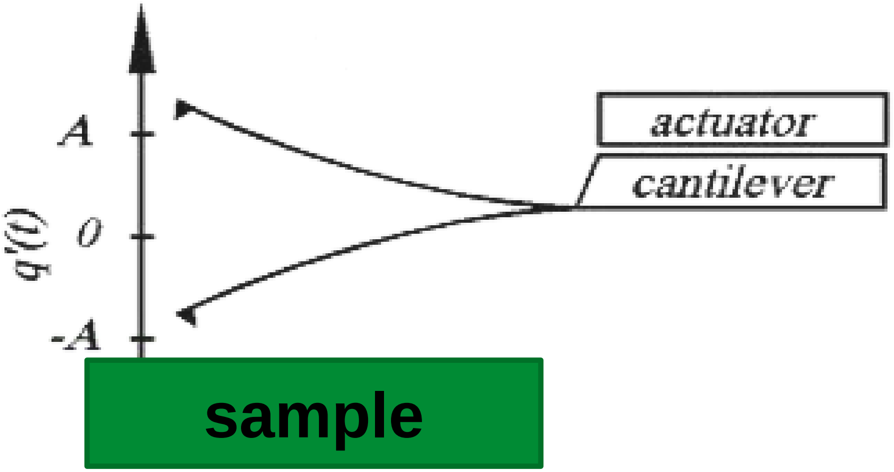
- If the cantilever oscillates, stability condition is modified
- Largest restoring force (oscillation amplitude *A*) is *kA*

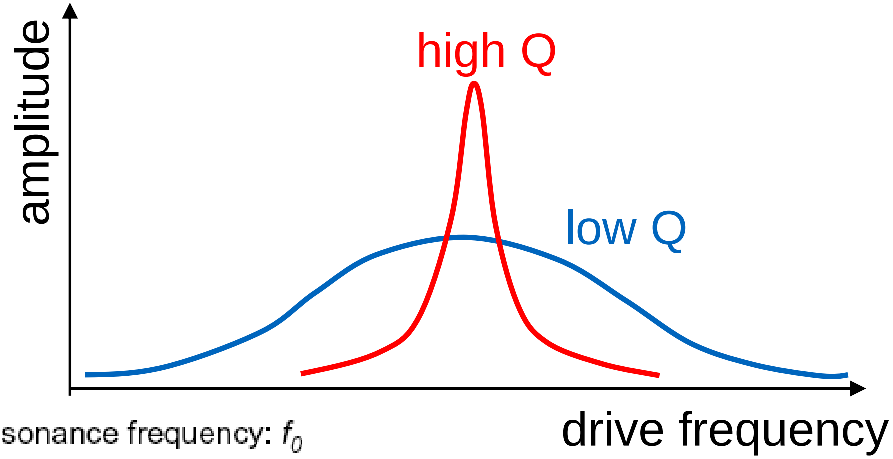
$$kA > -F_{ts}$$

- 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”)





Resonance frequency: f_0

Width of resonance curve (FWHM): Γ

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

- 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

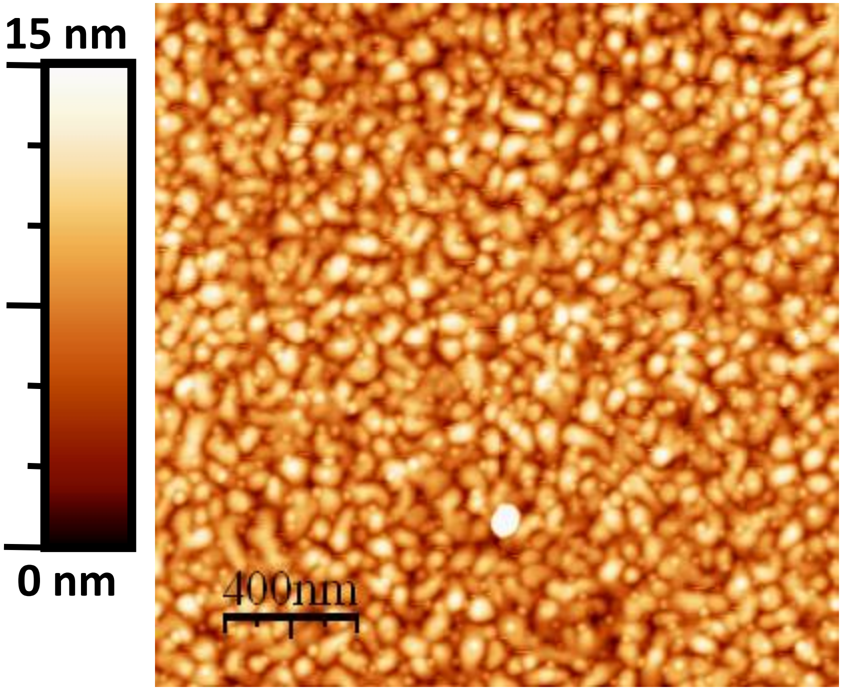
Tapping mode

- 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

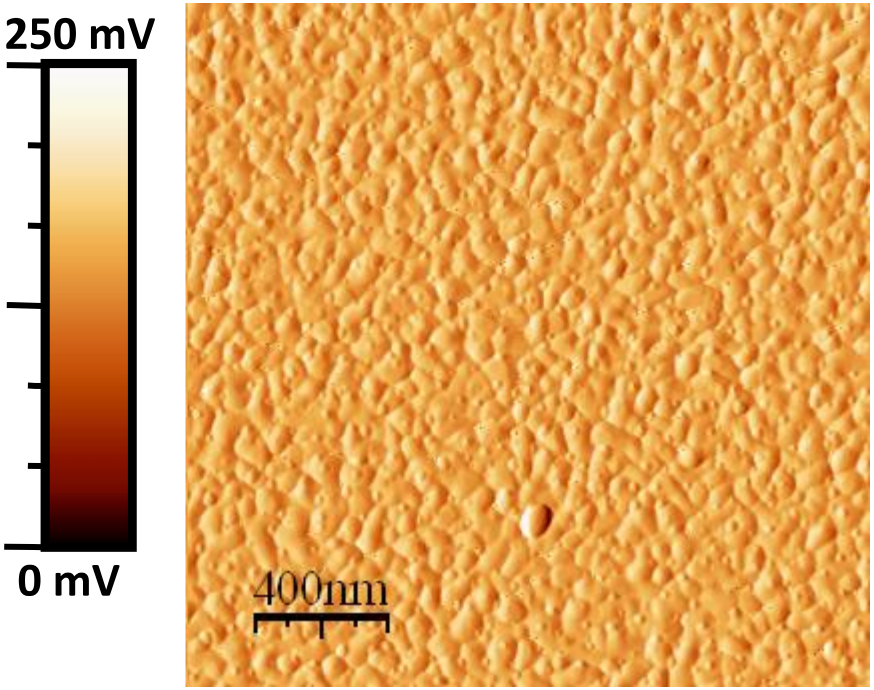
Q. Zhong et al. *Surf. Sci. Lett.* **290**, L688 (1993).

Typical AFM images

Polycrystalline Au layer



topography



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

New imaging modes

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

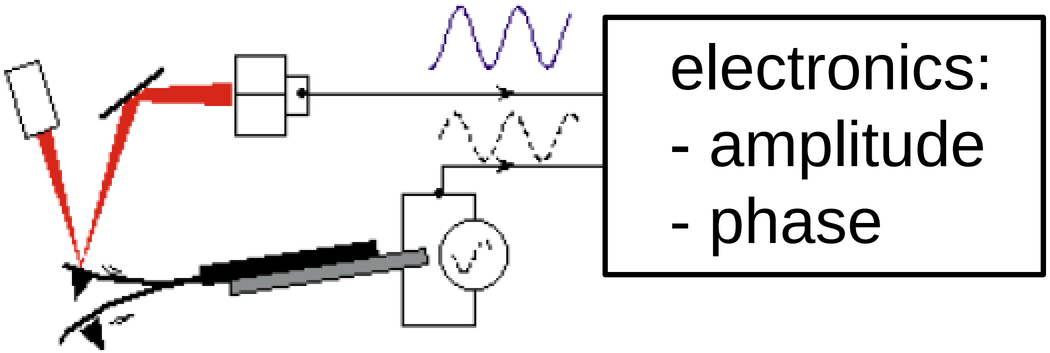
Phase imaging

Tapping mode :

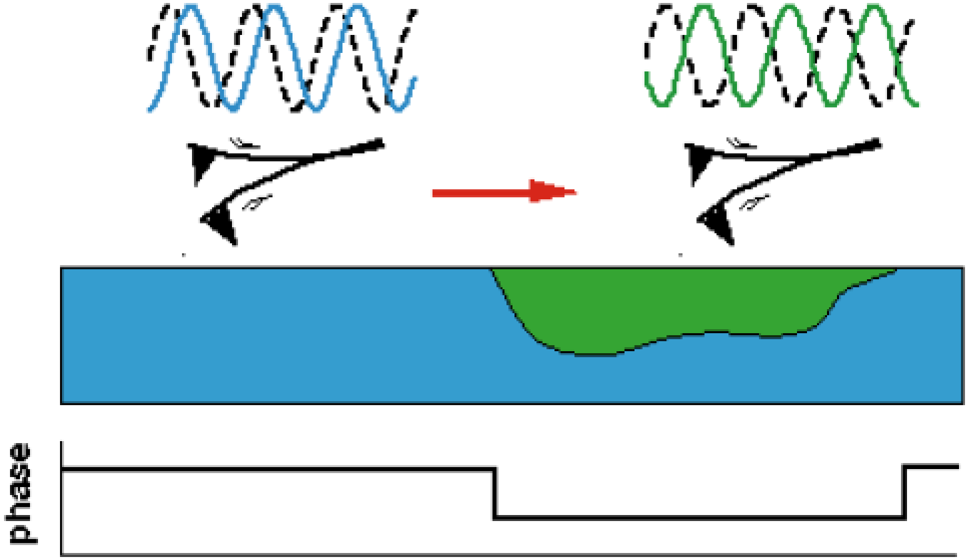
- measure the amplitude and the phase difference between excitation and oscillation

Gives:

- Contrast
- Information on elastic properties

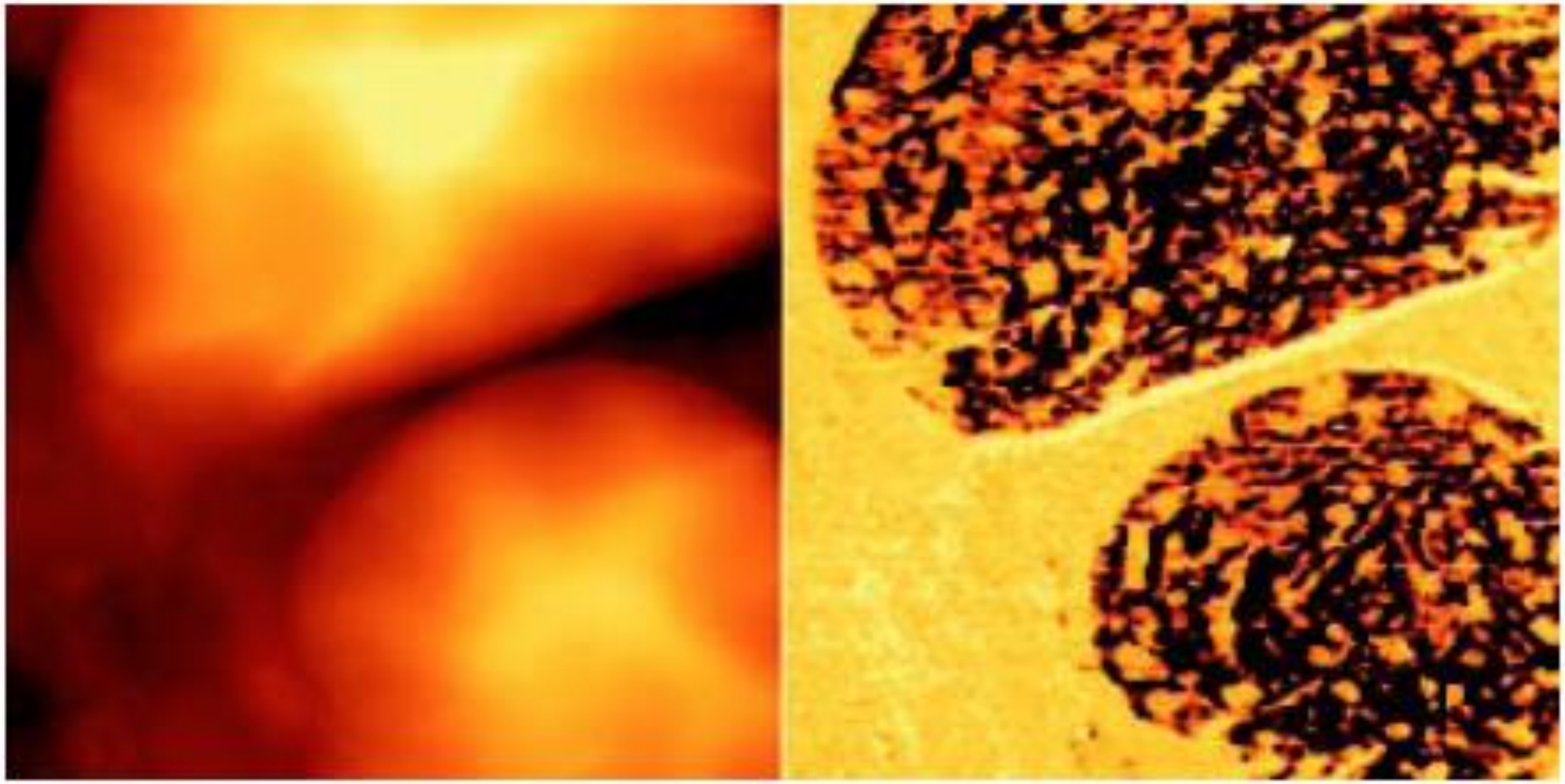


electronics:
- amplitude
- phase



Phase contrast

Composite polymer in a polymer matrix

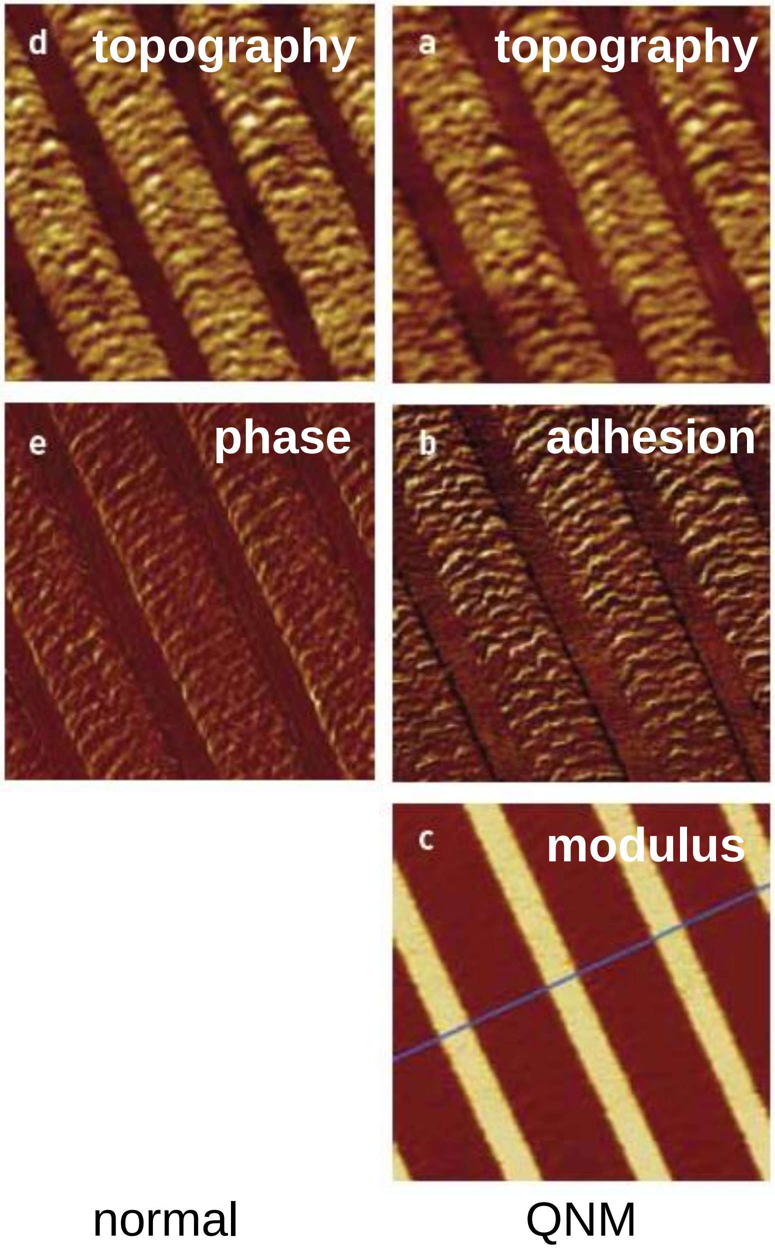


tapping mode AFM topography

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



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?

- 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)

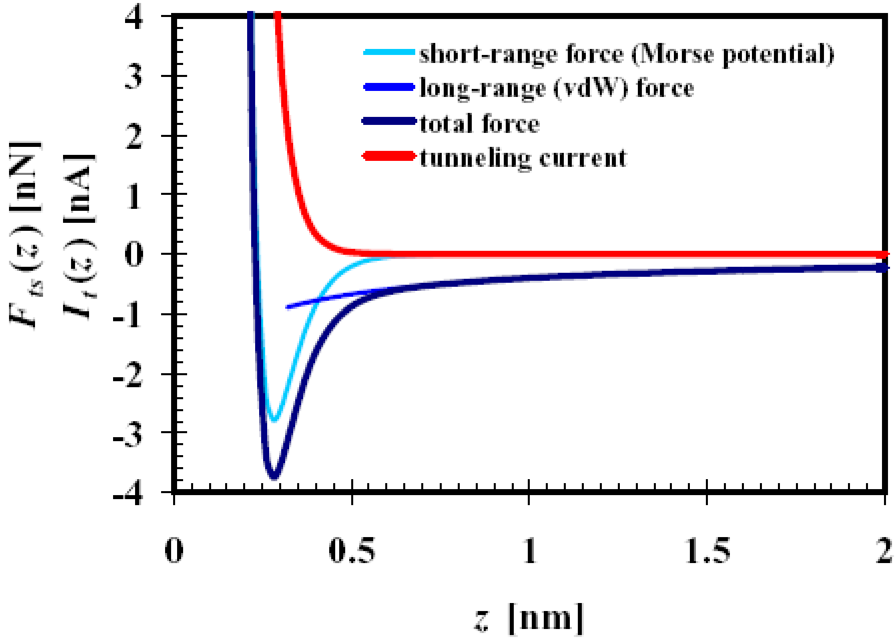
F.J Giessibl, *Rev. Mod. Phys.* **75**, 949 (2003)
W.A. Hofer, A.S. Foster, A.L. Shluger, *Rev. Mod. Phys.* **75**, 1287 (2003)

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

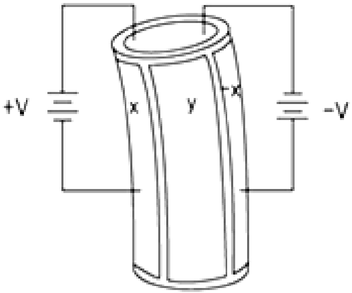


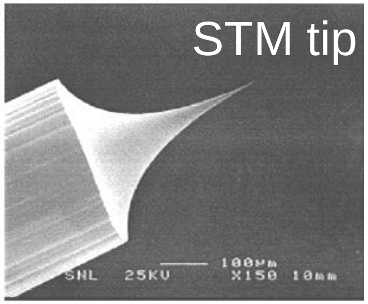
What about AFM – is the resolution poorer or better than in STM?

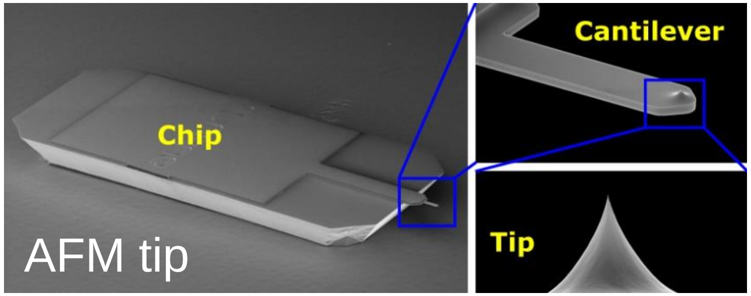
- it depends…which force are we sensitive to:
  - force has to have atomic scale contrast
  - has to have significant contribution to the total force gradient
  - chemical forces – interaction between the last atom of the tip and the molecule
- STM probes LDOS near the Fermi level (“electronic structure”)
- AFM is more sensitive to the total electron density (”geometry”)

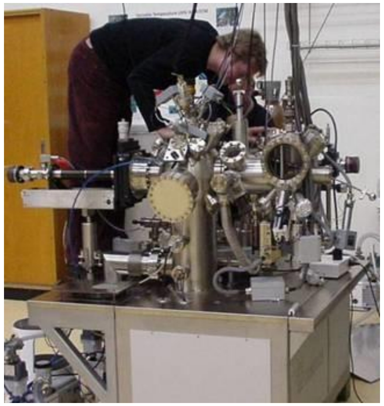
Practical aspects

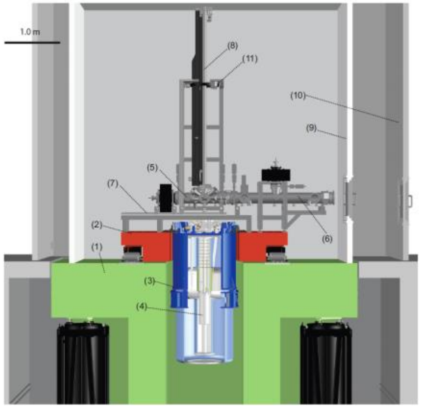
- Precise positioning
  - piezoelectric elements
- Sharp tip
  - STM tip etching or cutting
  - AFM micromachined tips
- Vibration isolation
  - rigid design
  - eddy-current damping
- ambient or UHV



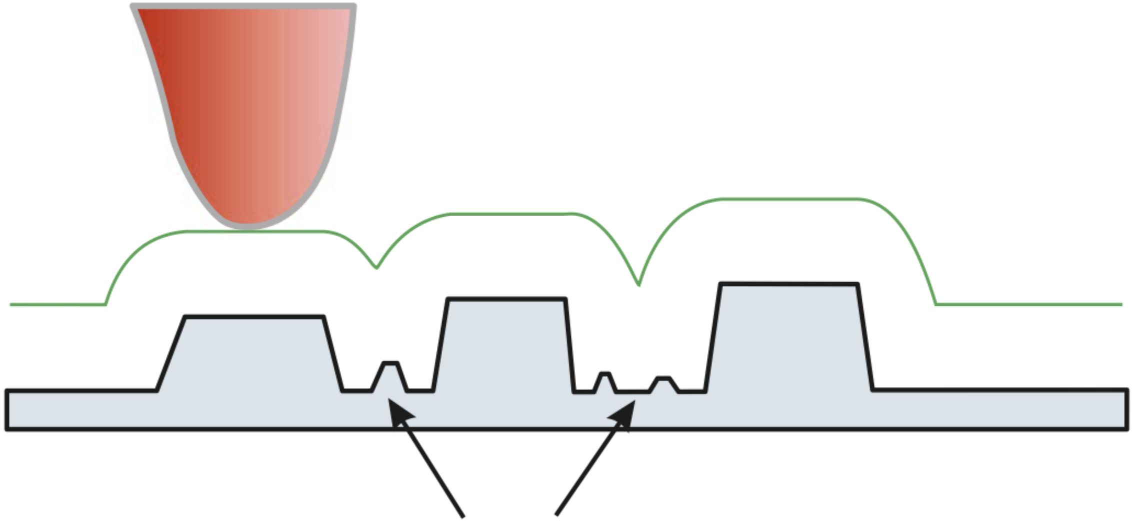




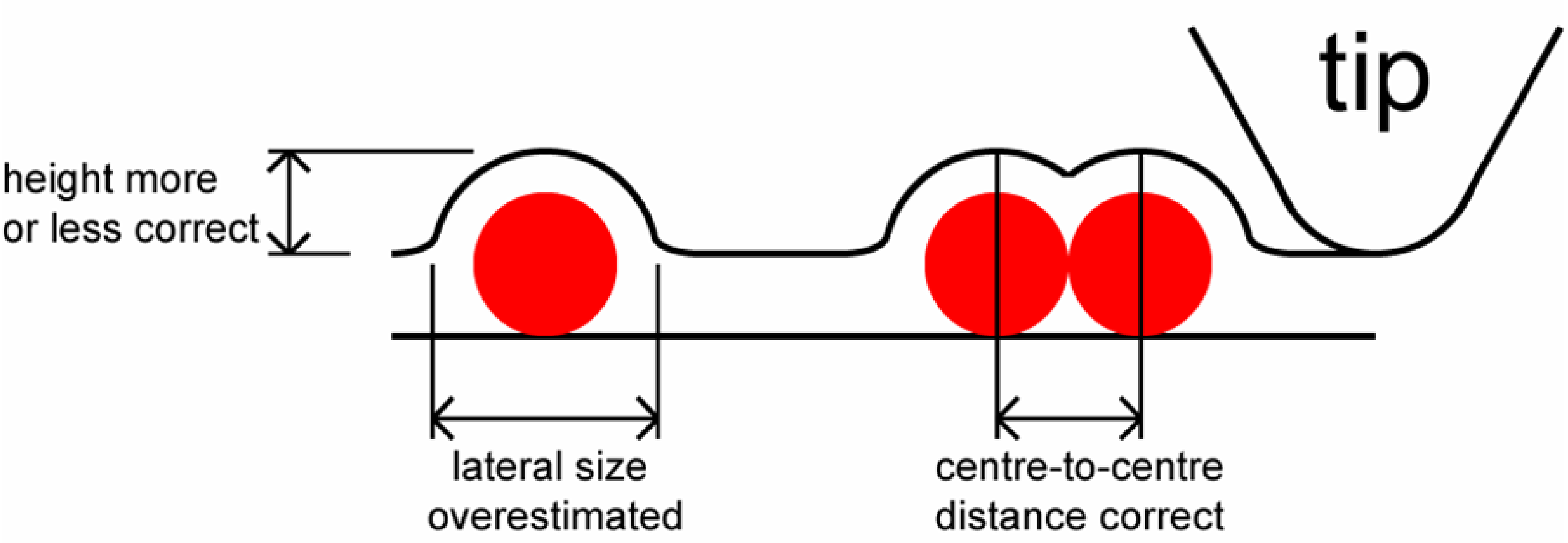




tip-size effects: convolution

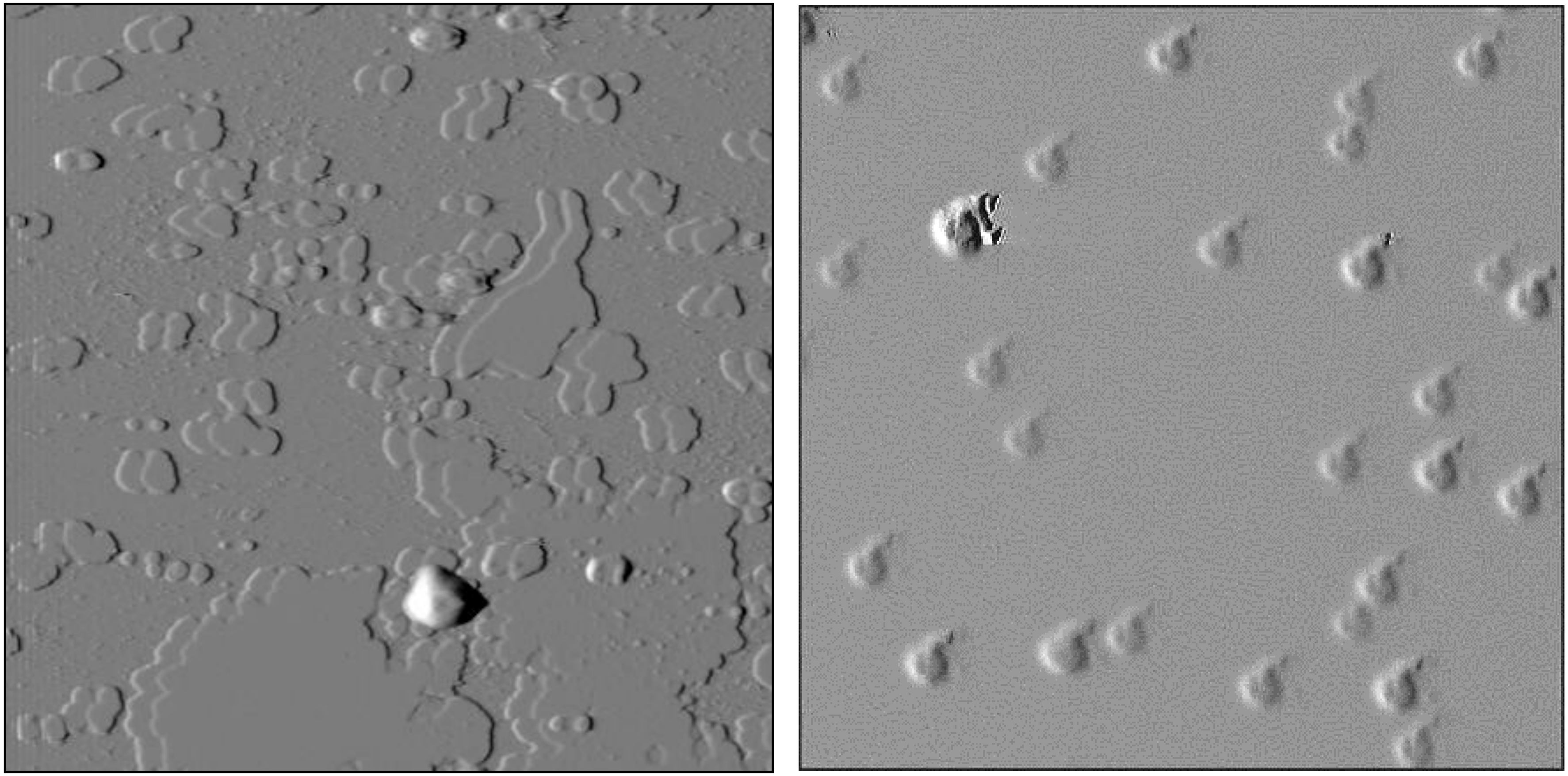


Dead zones: not imaged by a blunt tip



Tip artifacts

- All features have a uniform shadow or the same shape/orientation



Double tips

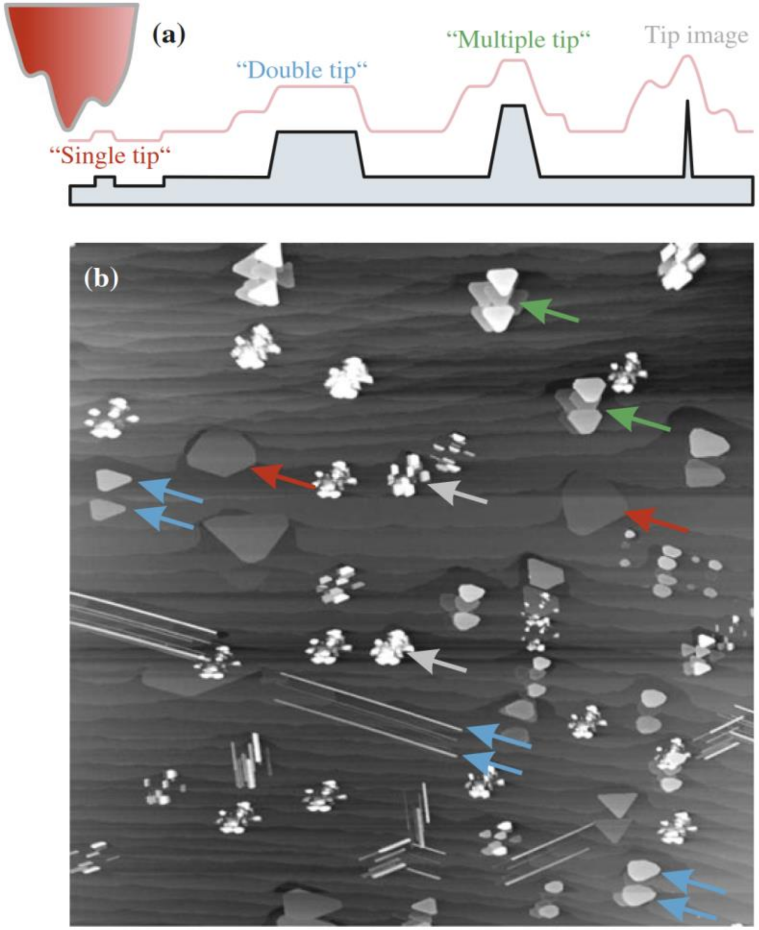
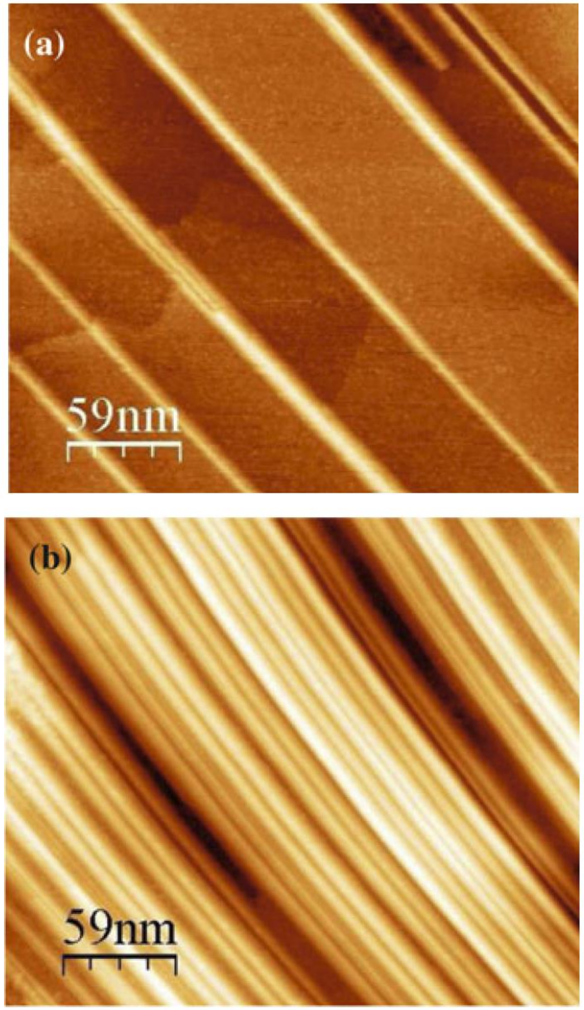


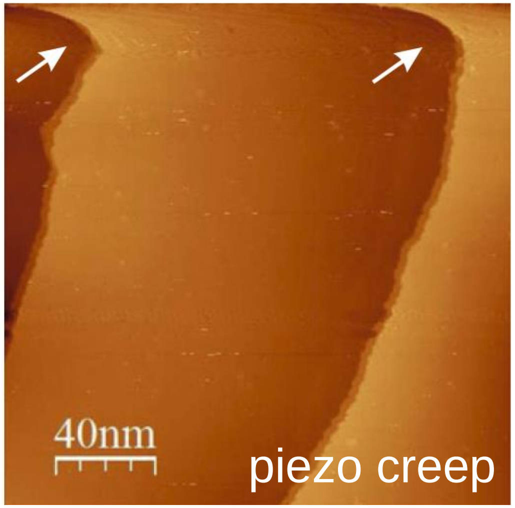
Fig. 8.3 **a** Sketch of a double (multiple) tip giving rise to doubled (multiple) imaging of surface features. The *light red line* shows the trace of the tip above the surface. **b** Example of silicide nano islands and nano wires imaged. The higher the structures imaged, the stronger is the tendency 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*)

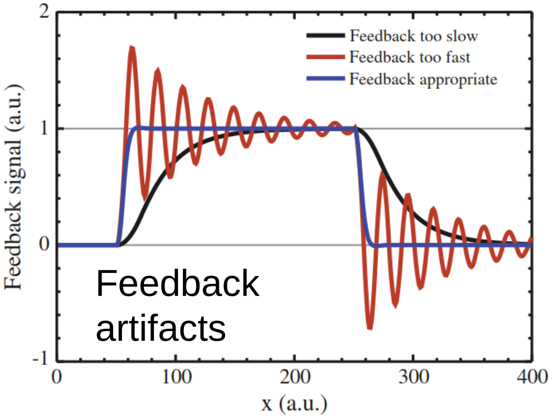
Fig. 8.4 STM image of 5 Å yttrium deposited on Si(110). **a** Silicide nanowires imaged with a sharp tip. **b** The same surface imaged with a blunt tip leads to much higher apparent coverage due to multiple images of the silicide nanowires

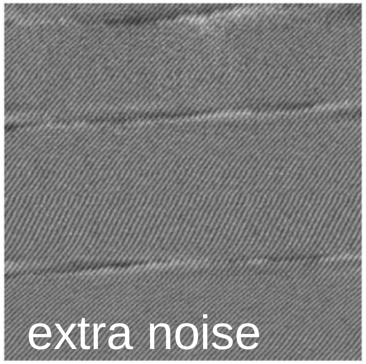


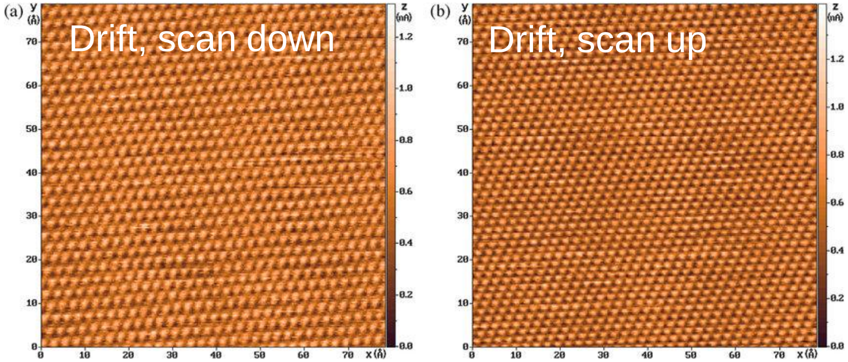
Creep / drift / noise / feedback

- **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)





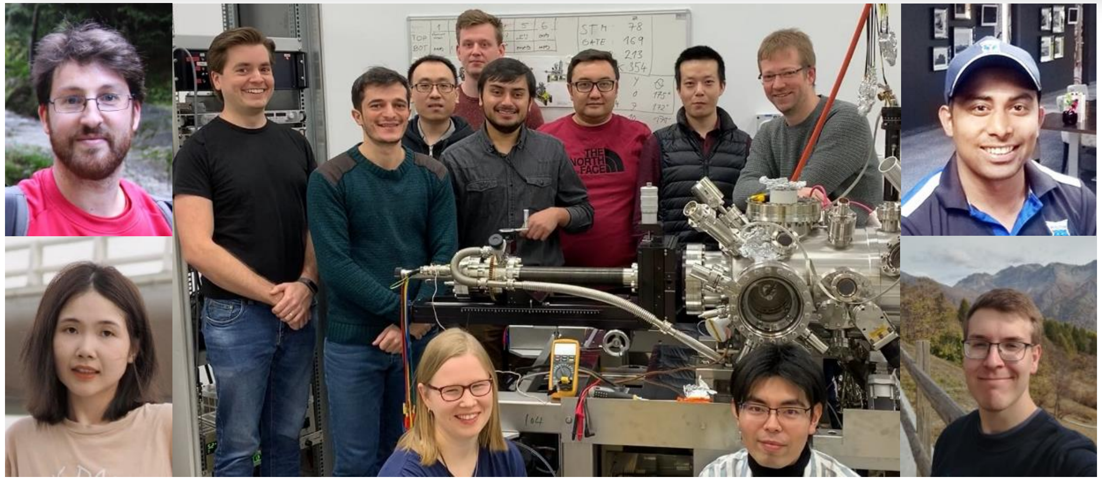
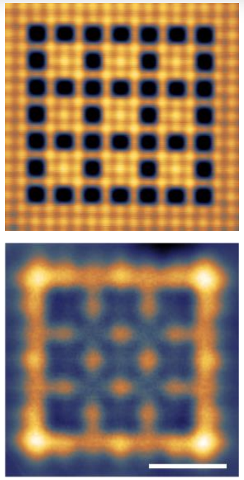
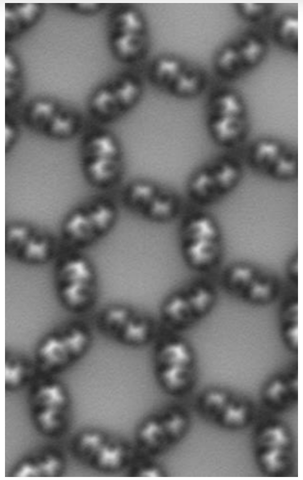
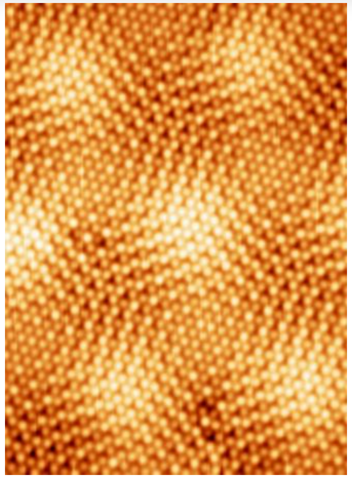
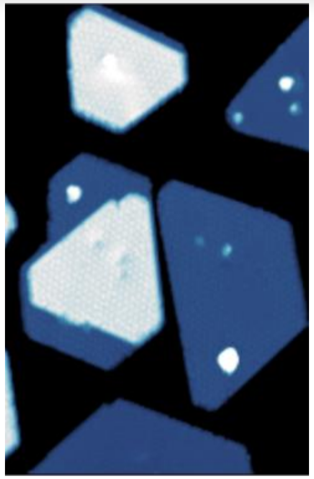




Aalto University
School of Science

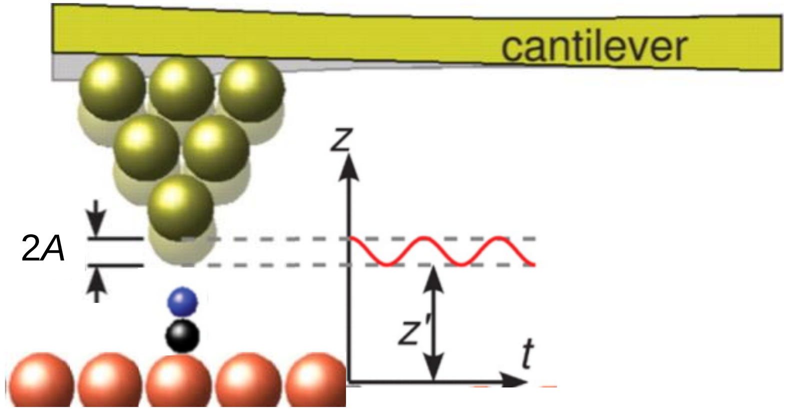
Lecture 2:
Materials at the atomic scale

Peter Liljeroth (peter.liljeroth@aalto.fi, @AaltoAtoms)

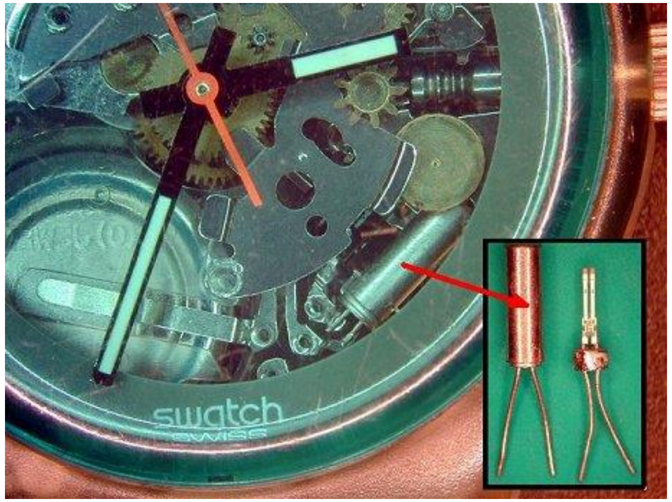






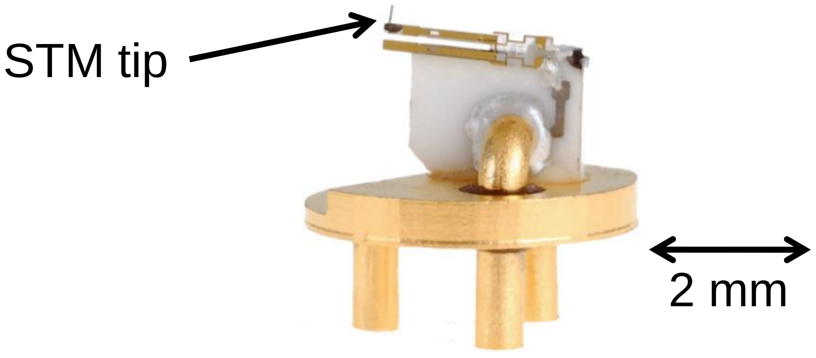
Simultaneous STM and AFM

- Frequency modulation non-contact AFM (nc-AFM)
- Very stiff cantilever
  - k = 1800 N/m
  - f_0 ~ 30 kHz
  - small oscillation amplitudes << 1 Å
  - All electrical detection



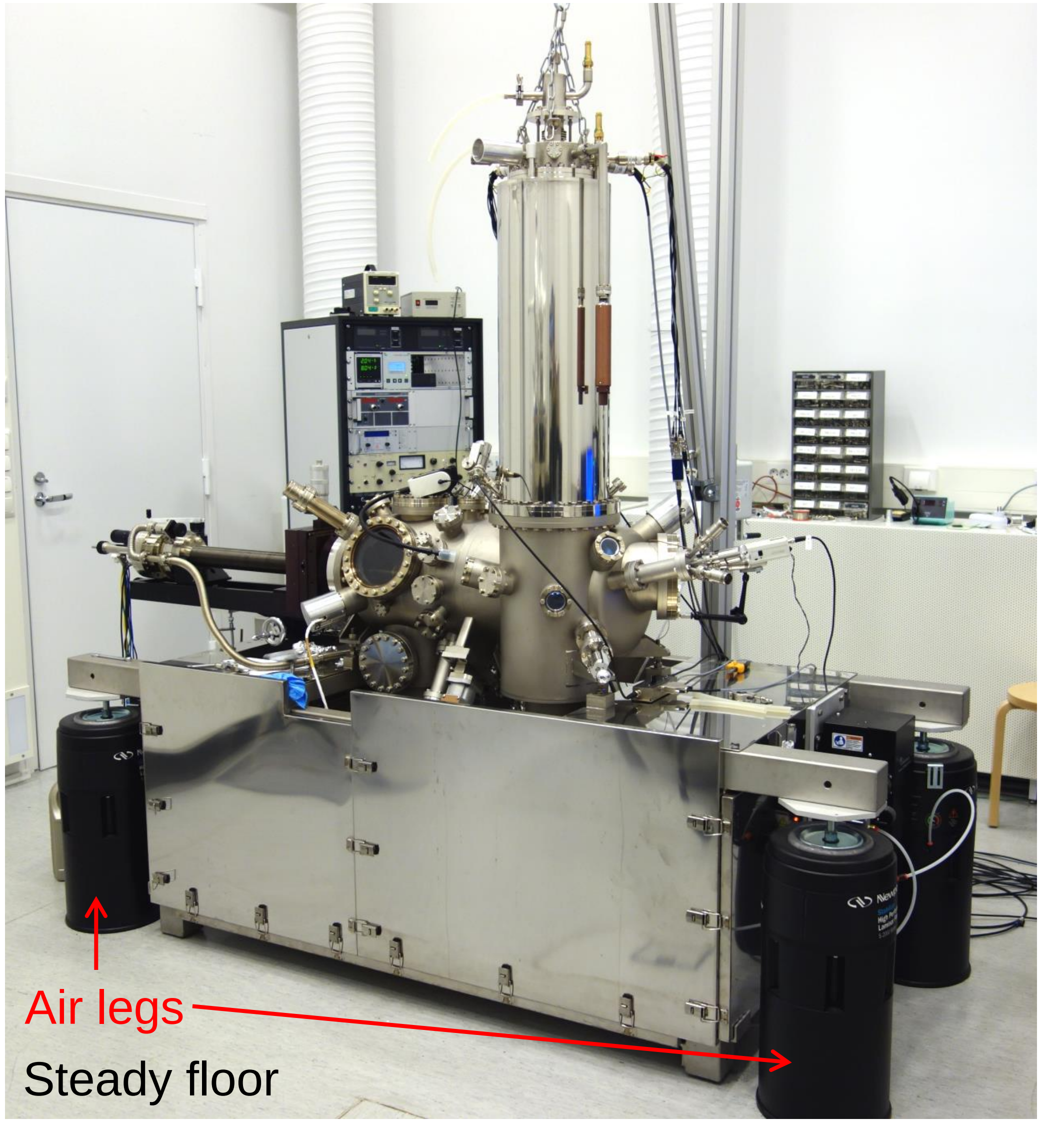
- **STM with an additional data channel giving the short-range tip-sample interaction**

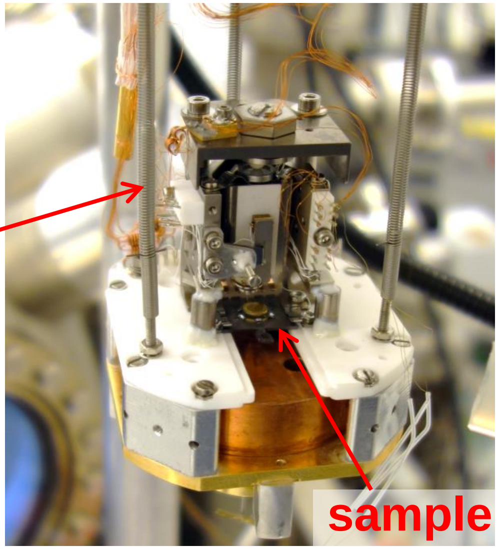




Details: F.J. Giessibl, Rev. Mod. Phys. 75, 949 (2003)

In the lab...



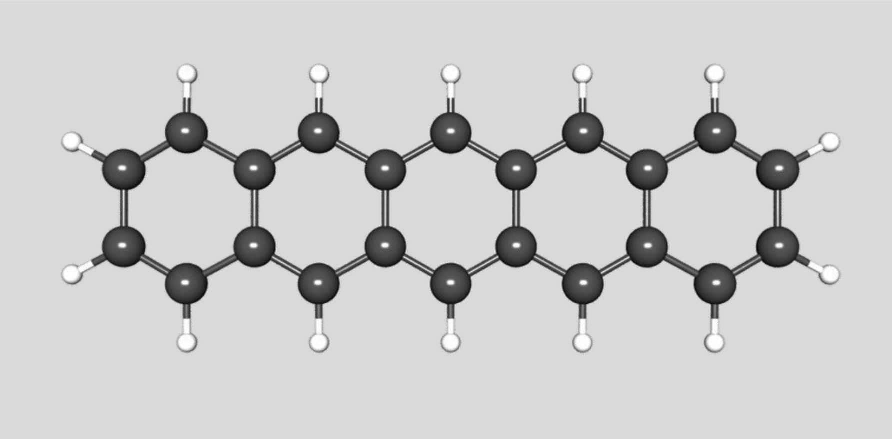


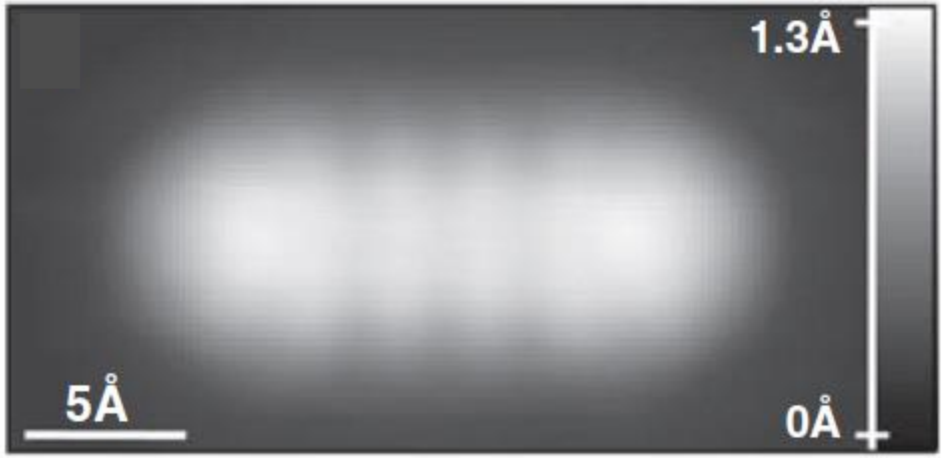
Spring suspension + eddy-current damping

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

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

STM of a molecule

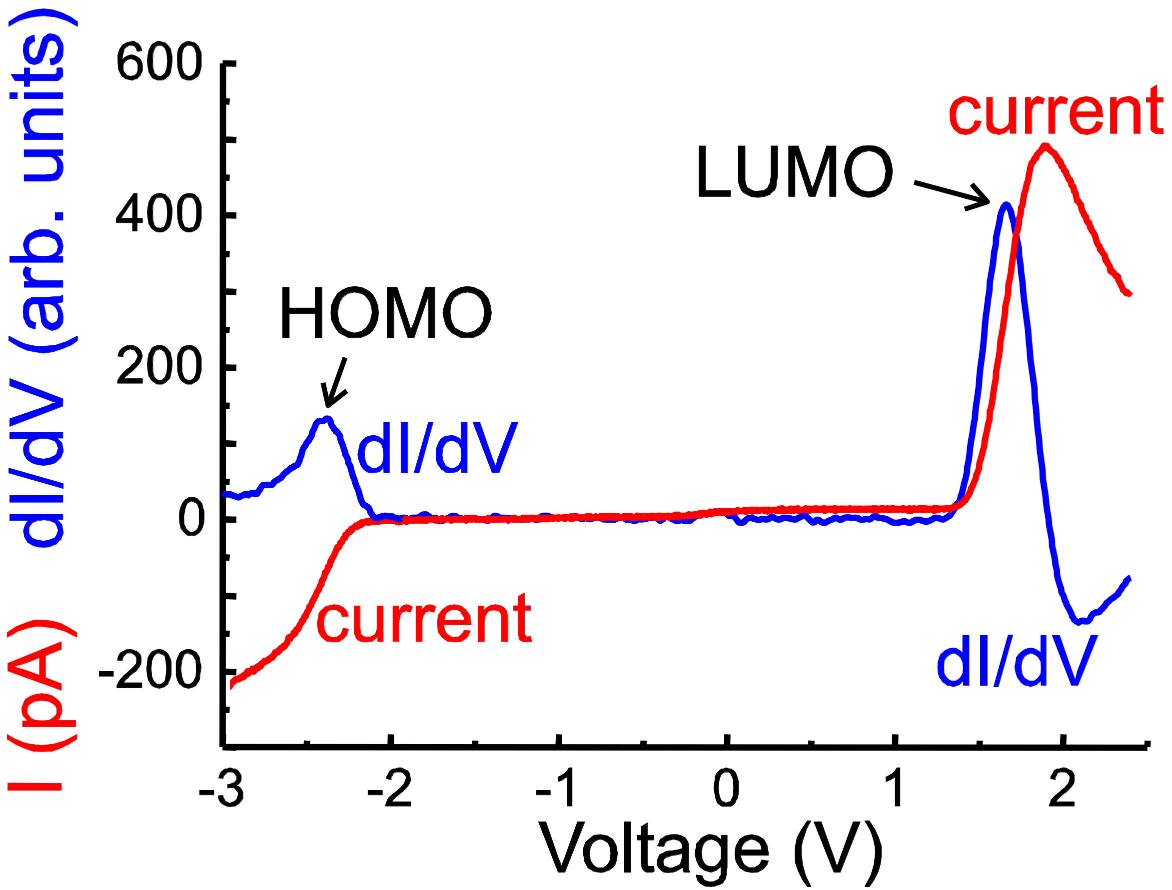


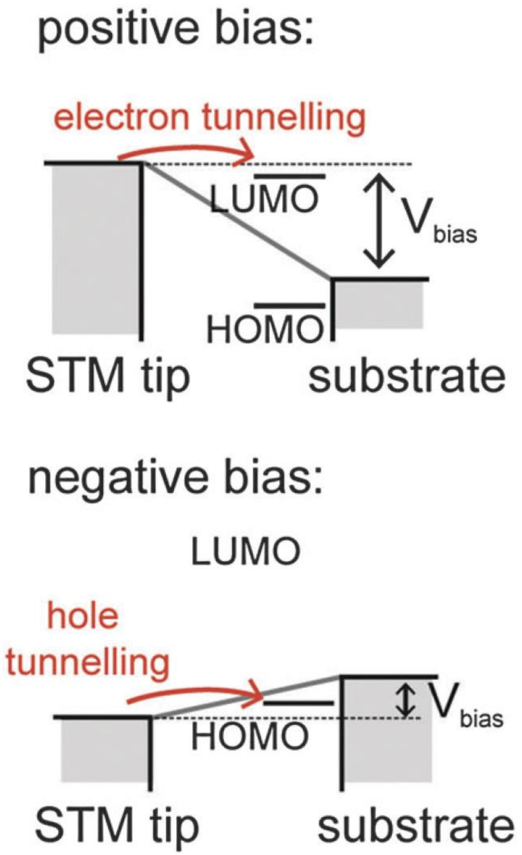


- Where are the atoms?
- Measure current – this is not directly related to the positions of the atoms
- this measurement in the HOMO-LUMO gap of the molecule: modification of the tunneling barrier

→ no atomic scale contrast

Pentacene: spectroscopy



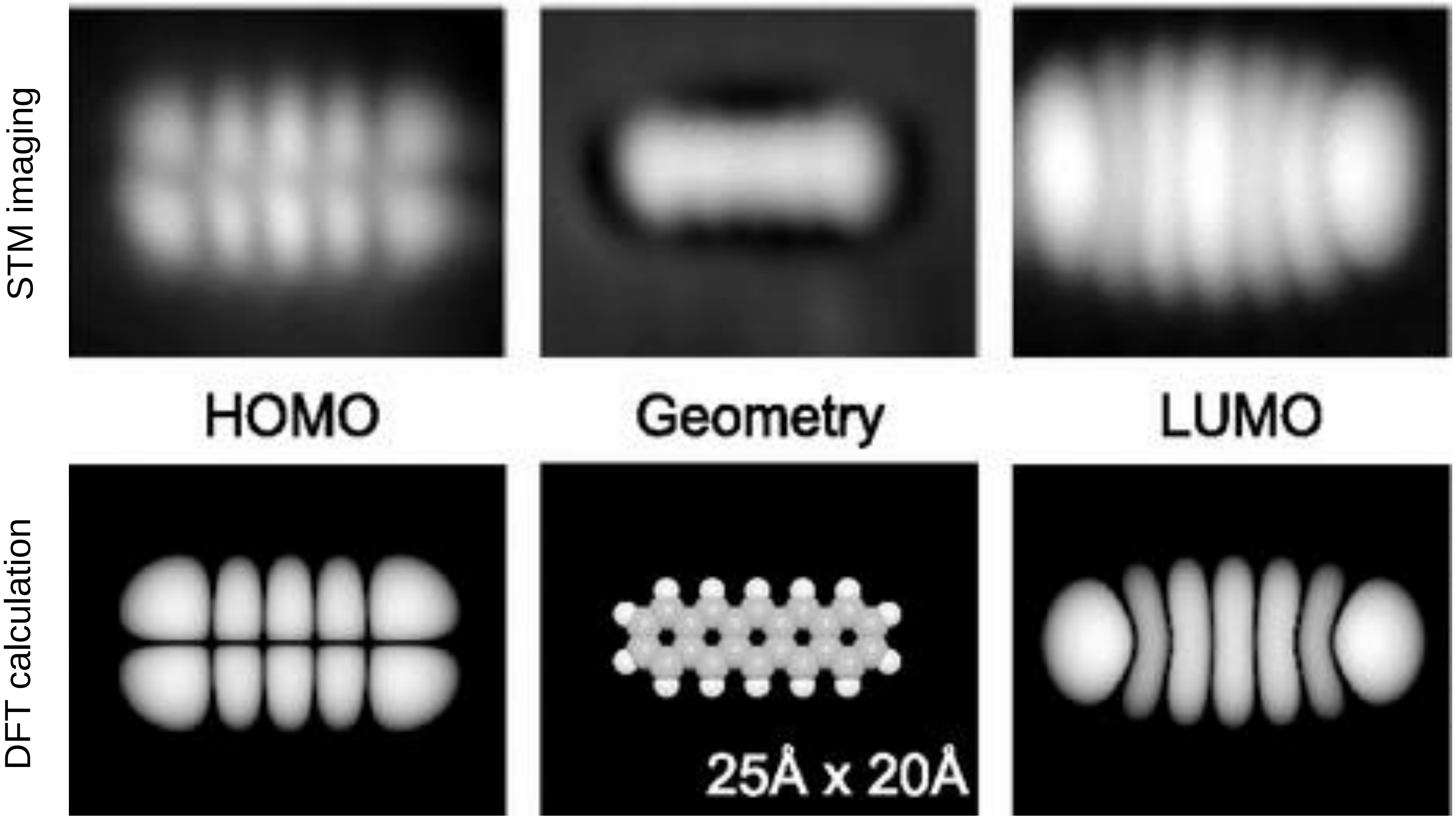


- Energies of molecular orbitals can be studied
- Their wavefunctions can be imaged directly

$$dI / dV_{bias} \propto \text{LDOS}\ (E = V_{bias})$$

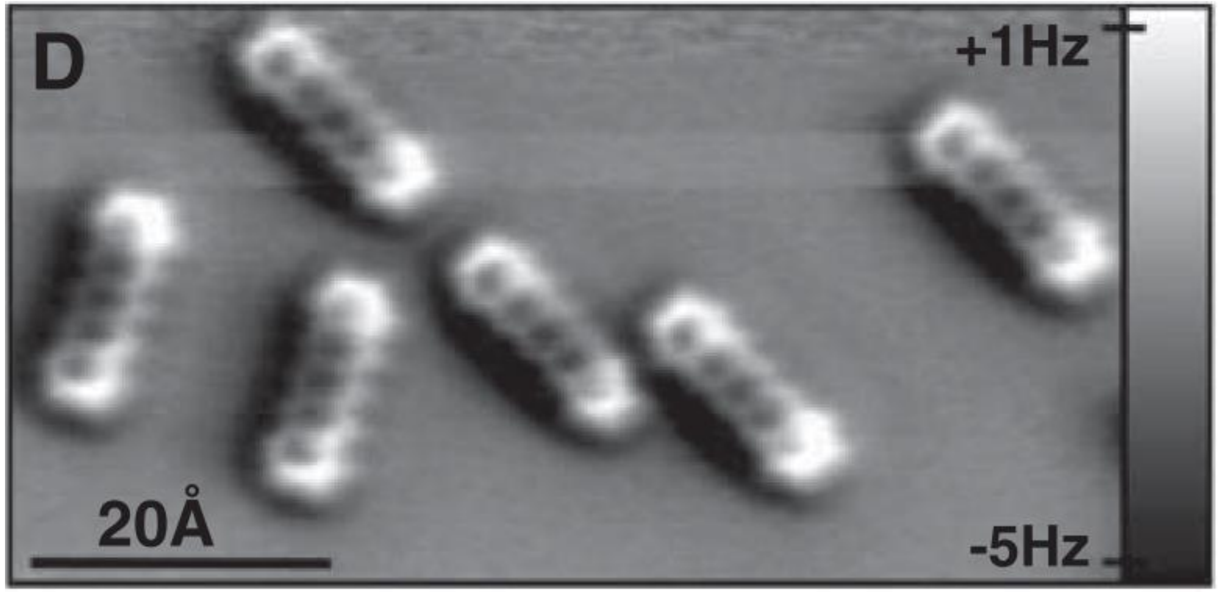
$$= \sum_{\Delta E} \left|\psi_i(E, r)\right|^2$$

Pentacene: molecular orbitals

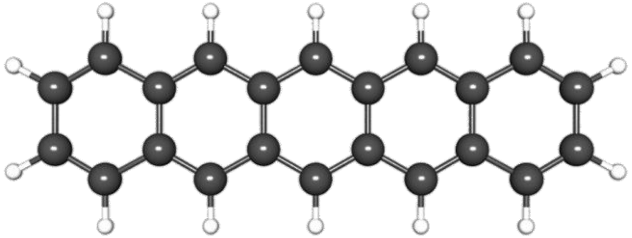


J. Repp et al. Phys. Rev. Lett. 94, 026803 (2005)

Atomic resolution on molecular systems

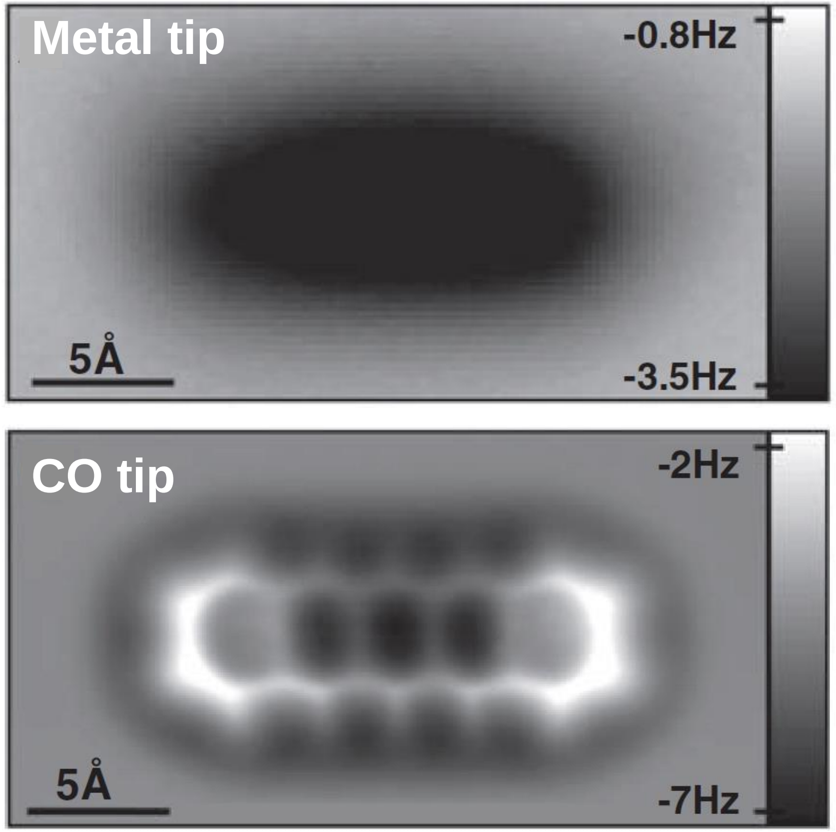


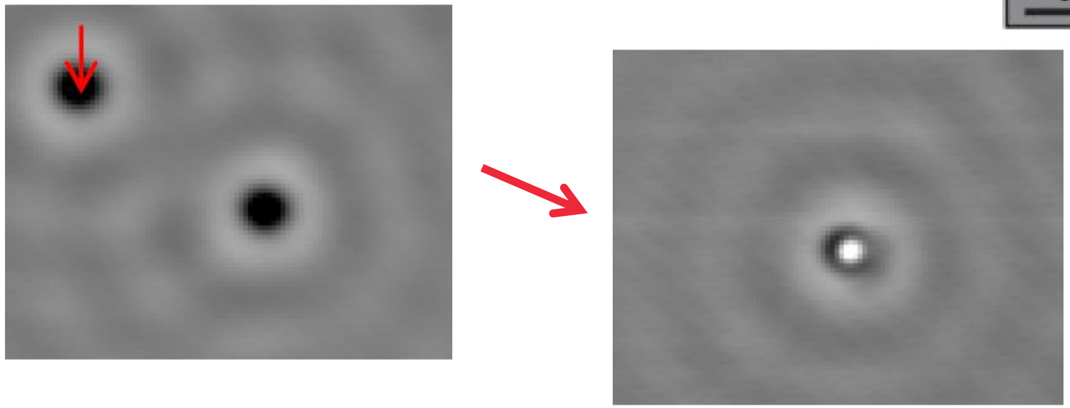
- Best possible STM/AFM with the QPlus sensor
- Where are the atoms?
- Metallic tips are reactive – large attractive forces between the tip and sample causes the molecule to be moved before reaching atomic resolution
- Sudden tip change!



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

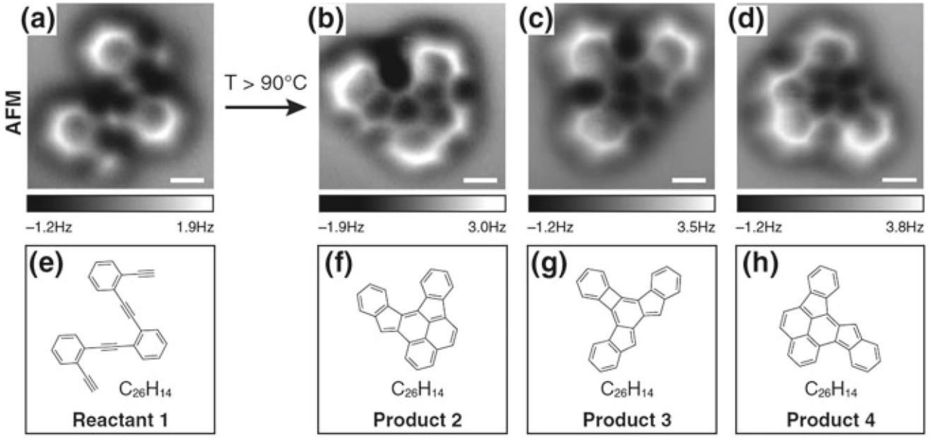




Science 325, 1110 (2009).

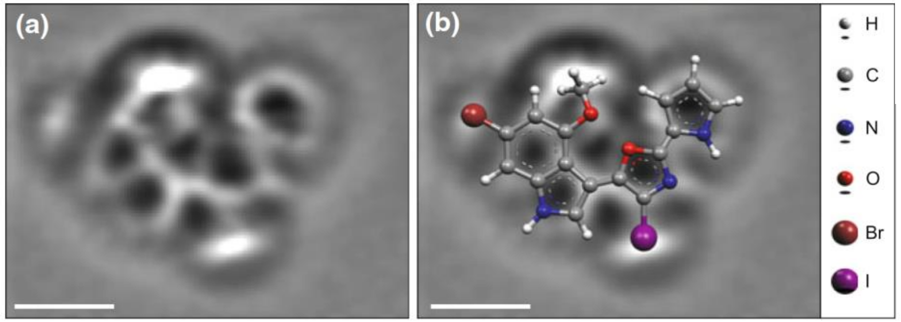
What can you do with it?

- Identify molecules
- Follow on-surface reactions
- Characterize nanostructures



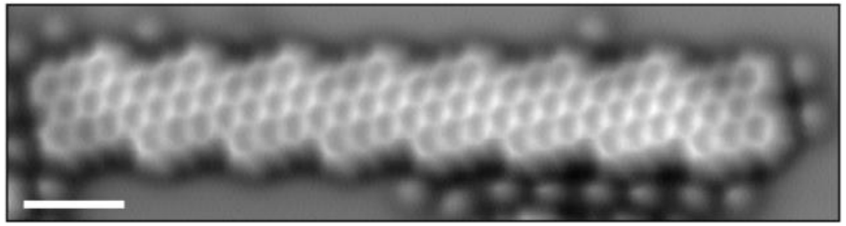
Fischer and Crommie groups (UC Berkeley)
D.G. De Oteyza et al. Science 340, 1434 (2013)

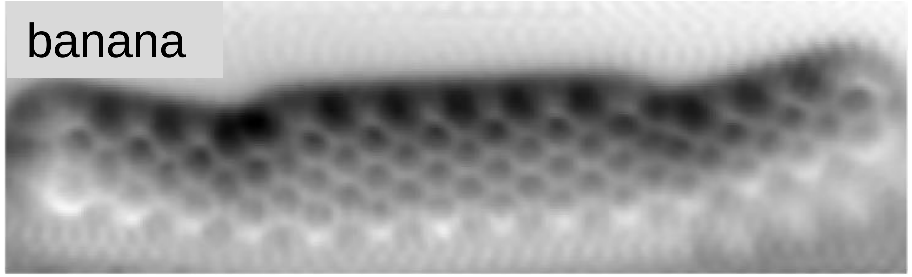
Breitfussin A or B



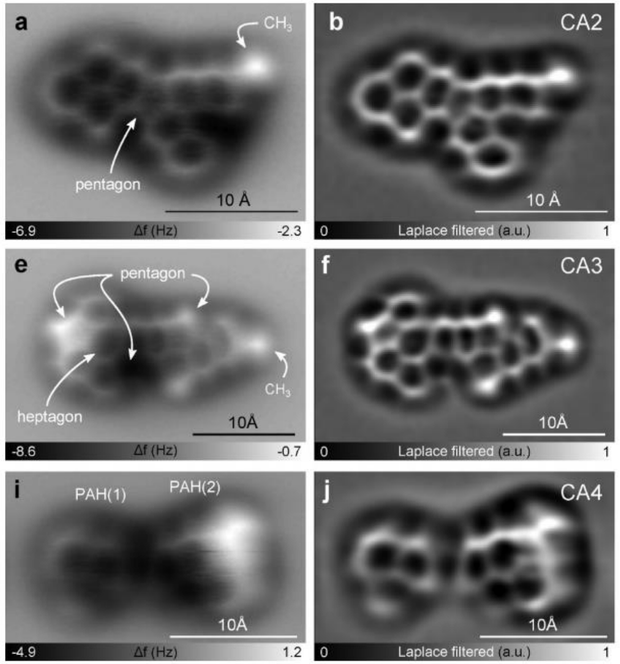
L. Gross group (IBM Zurich)
K.Ø. Hanssen, Angew. Chem. Int. Ed. 51, 12238 (2012)

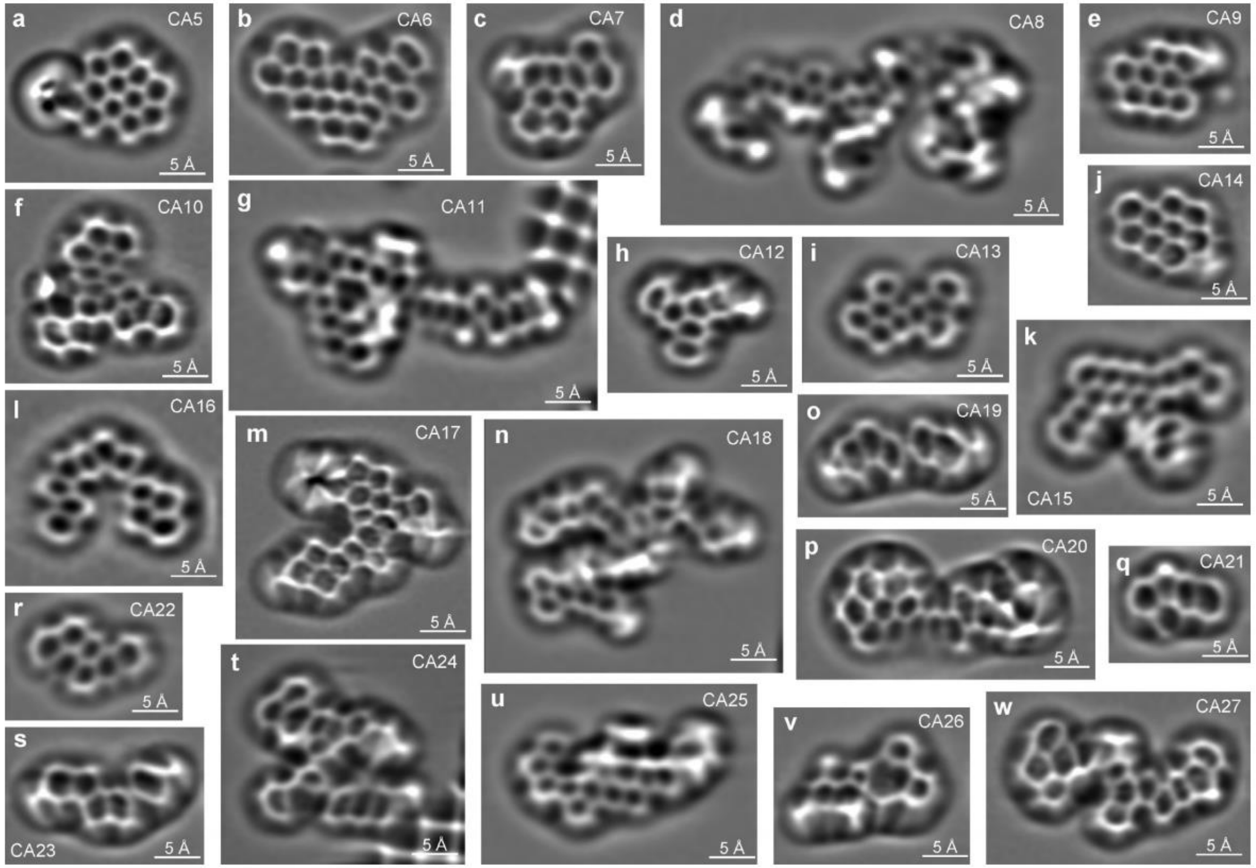
F. Schulz et al. J. Phys. Chem. C 123, 2896 (2017)
P. Jacobse et al. Nat. Commun. 8, 119 (2017)





Complicated but more or less 2D





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Unraveling the Molecular Structures of Asphaltenes by Atomic Force Microscopy

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