Aalto University
School of Science

Introduction to scanning probe microscopy

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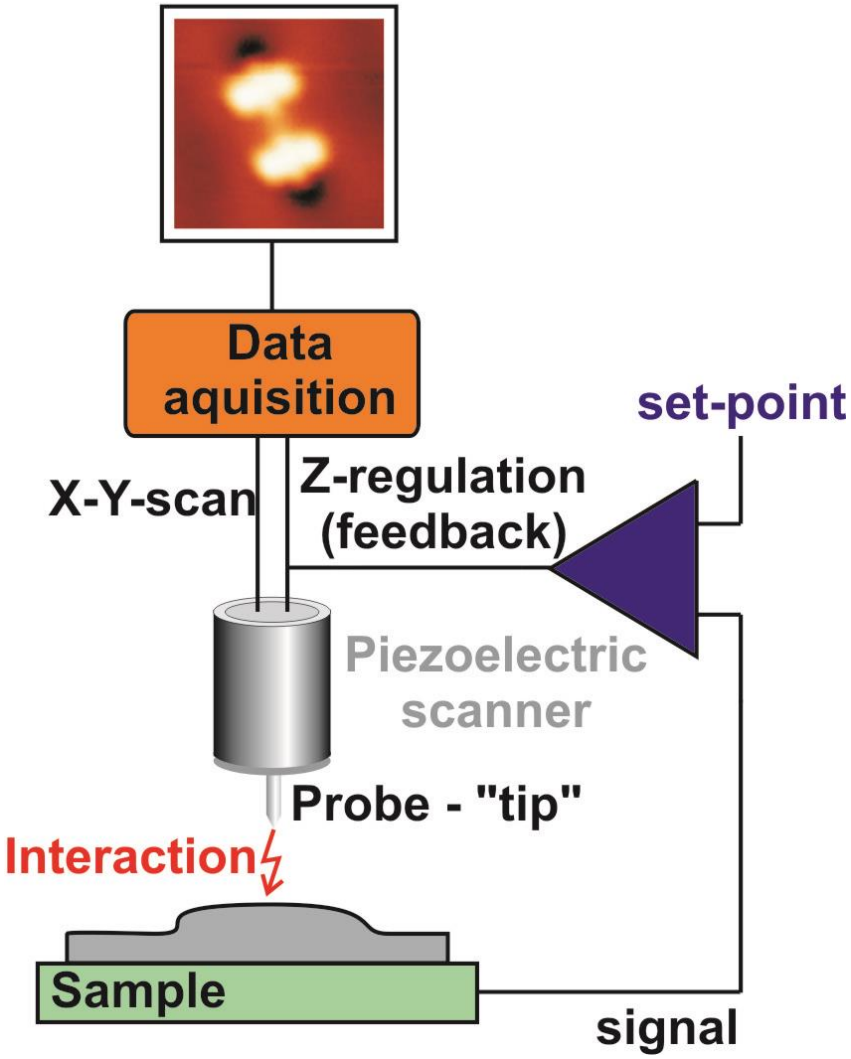
Outline

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

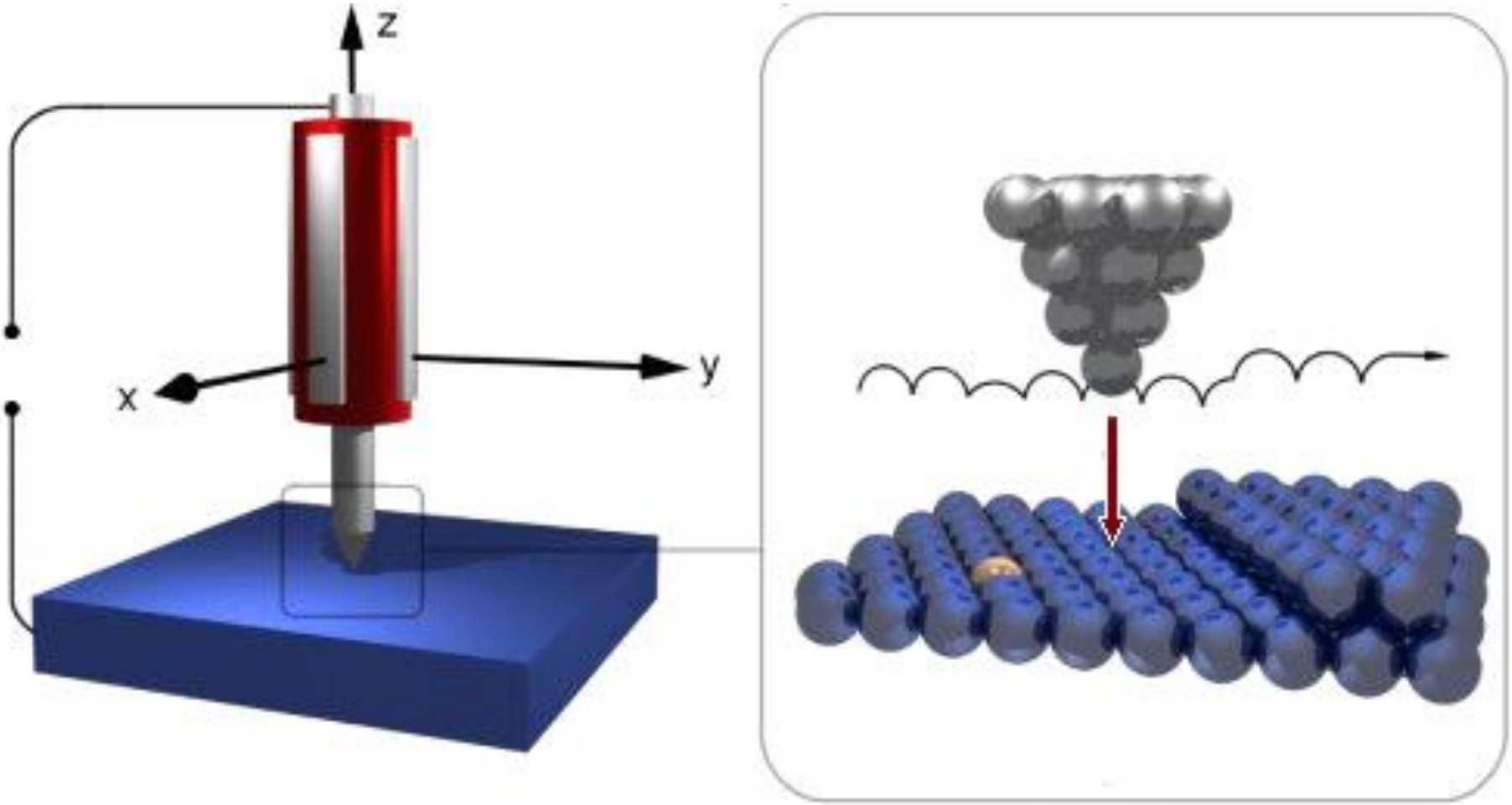
- **Lecture 1**: Introduction to STM and AFM
- **Lecture 2**: Atomic-scale materials science using STM and AFM

General principle of scanning probe microscopy



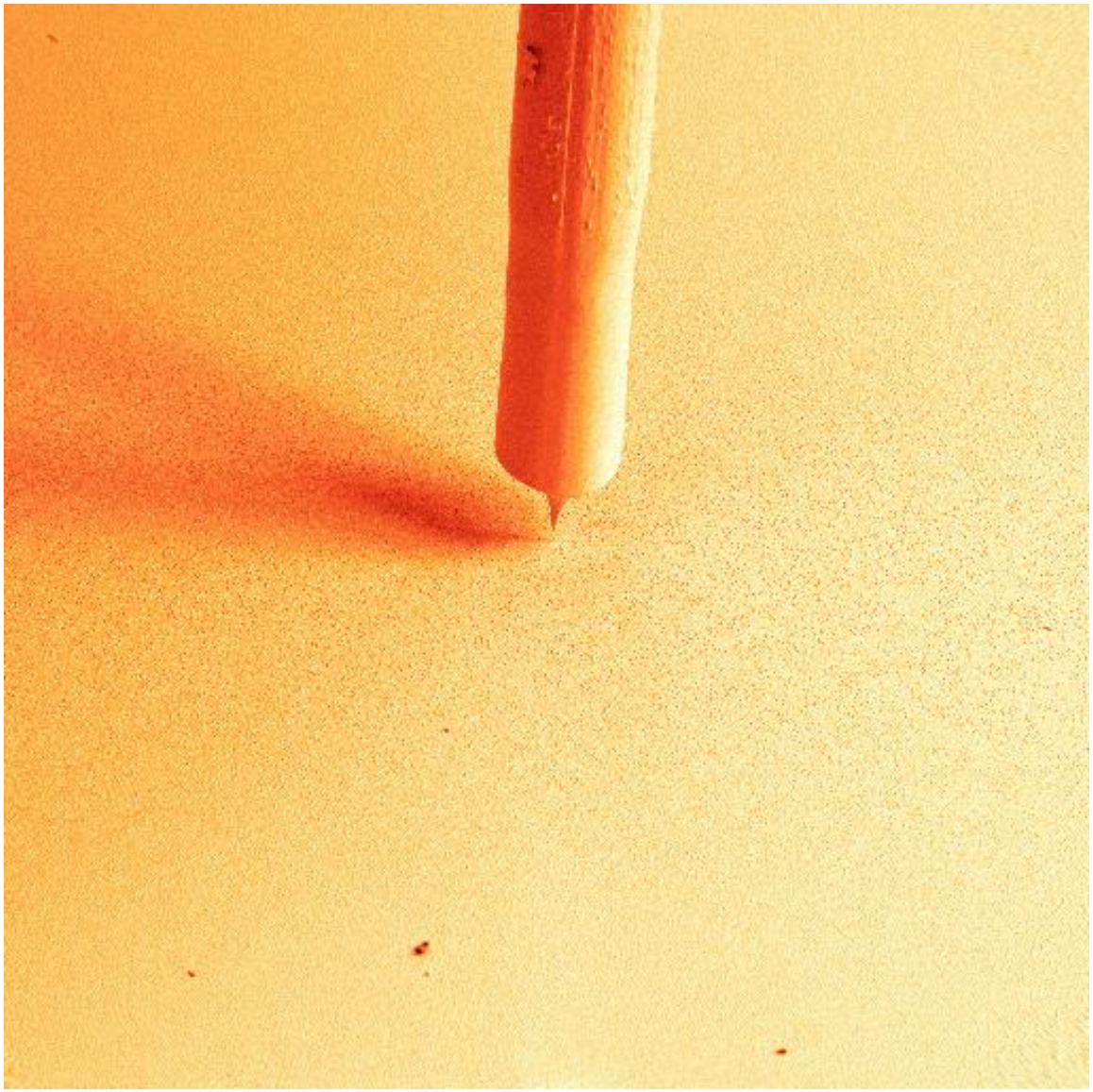
- Measure some interaction between a sharp probe and the sample
- **Scanning**: Move sample or tip while keeping this interaction constant (feedback) or while keeping height constant
- **Spectroscopy**: Change something (*z*, voltage, etc.) while keeping *x* and *y* constant (feedback off)

STM topographic mode



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

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

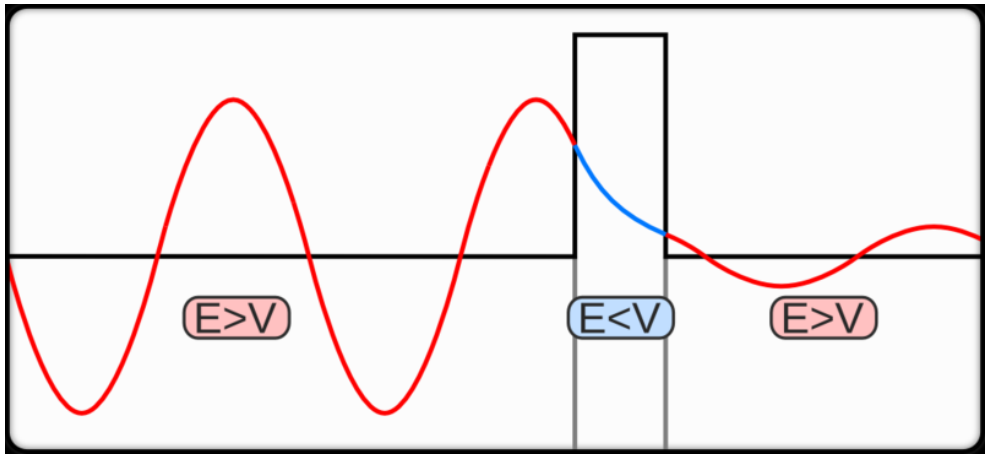
$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+V(x)\psi=E\psi$$

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

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

x=0 x=d

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



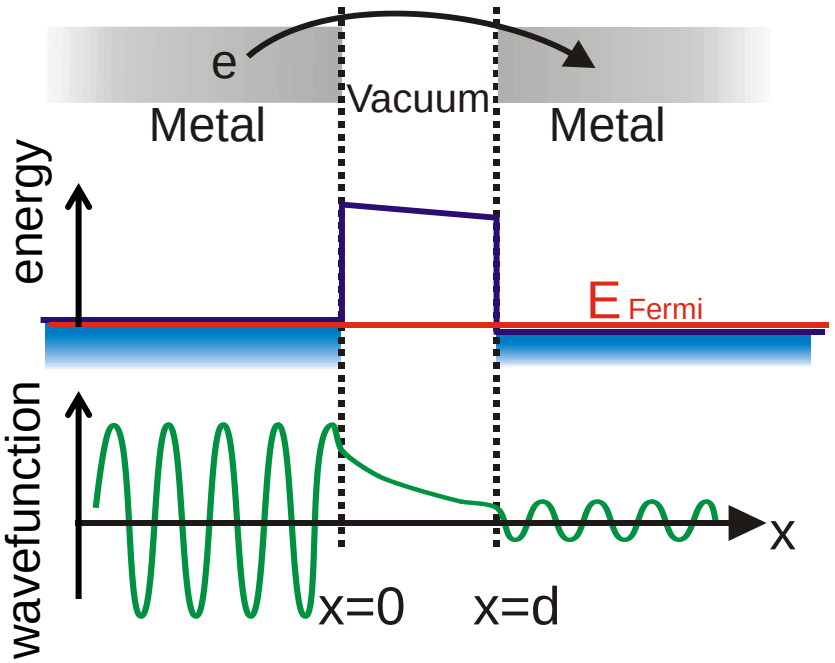
$$\psi = F\exp(\kappa x)+G\exp(-\kappa x)$$

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

- ψ and $\mathrm{d}\psi/\mathrm{d}x$ 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

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

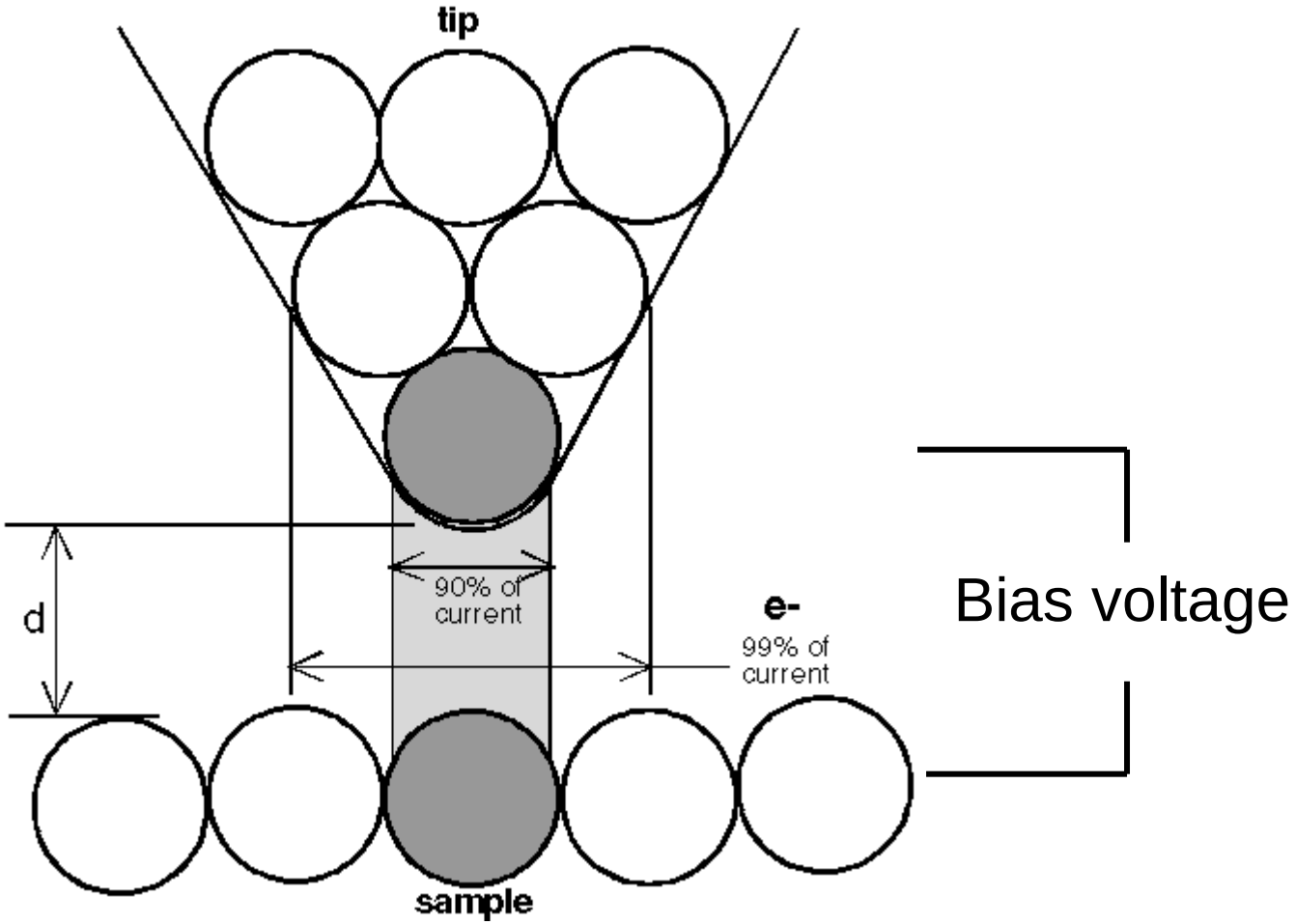
and the current

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

with

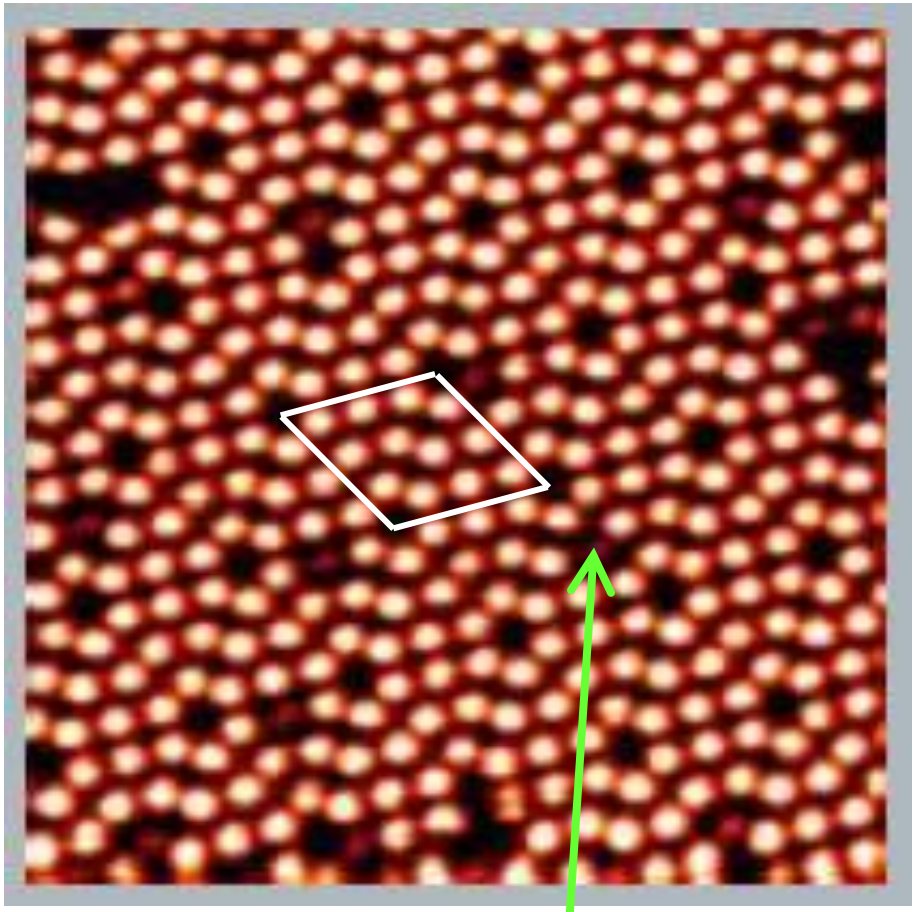
$$\kappa = \left(\frac{2m}{\hbar^2}(V_0 - E) \right)^{1/2}$$

- κ = 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



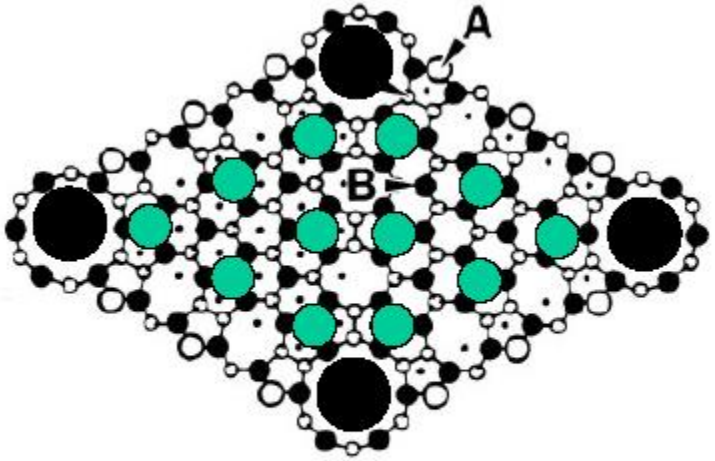
- Typical bias voltage from a few mV to a few V
  (limited by the onset of field emission)
- Typical currents from a few pA to a few nA
  (tunneling resistance >> resistance quantum ≈ 12.9kΩ)

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



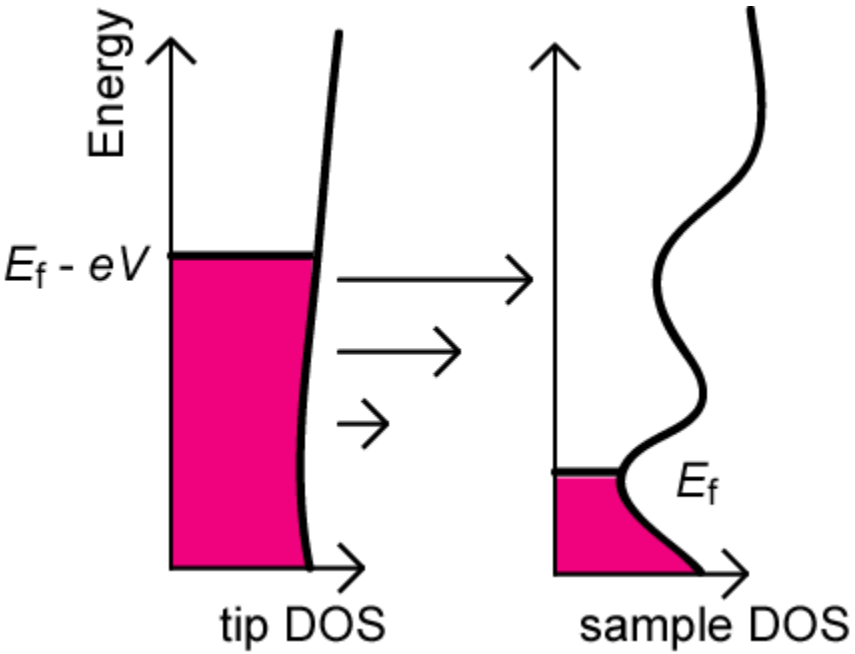
Measuring LDOS

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

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

What is LDOS?

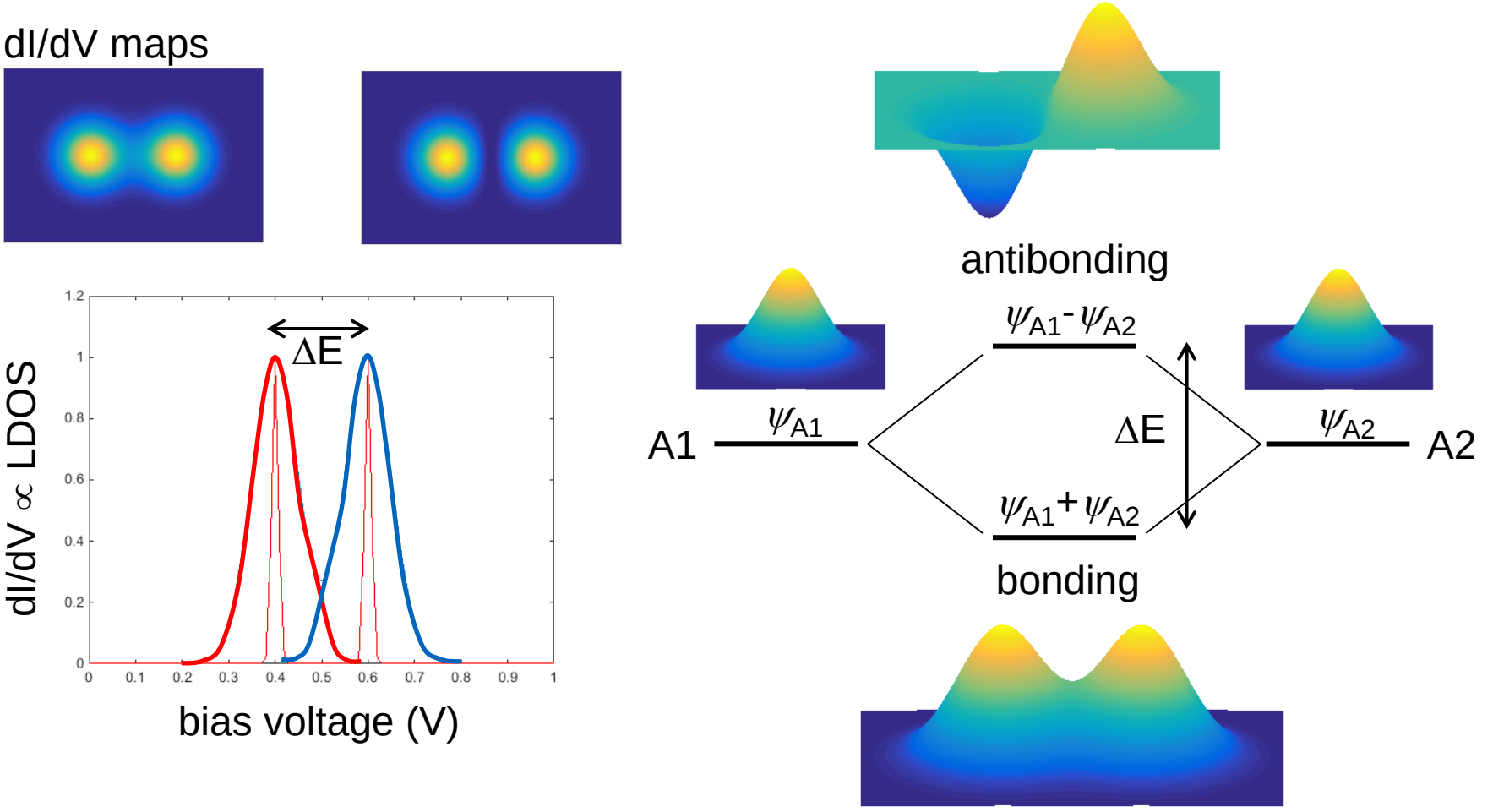
$$\mathrm{LDOS}\left(eV_\mathrm{b}, x, y\right) = \sum_{\delta E} \left|\psi_i\left(E_i, x, y\right)\right|^2$$



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

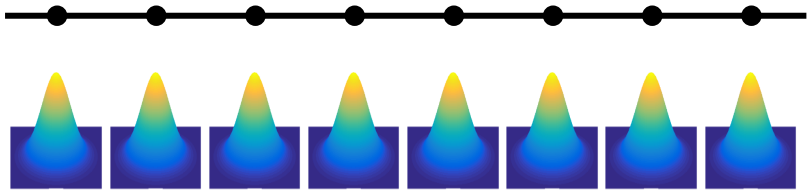
→ d*I*/d*V* spectroscopy gives the local density of states

LDOS example 1: two atoms making a molecule

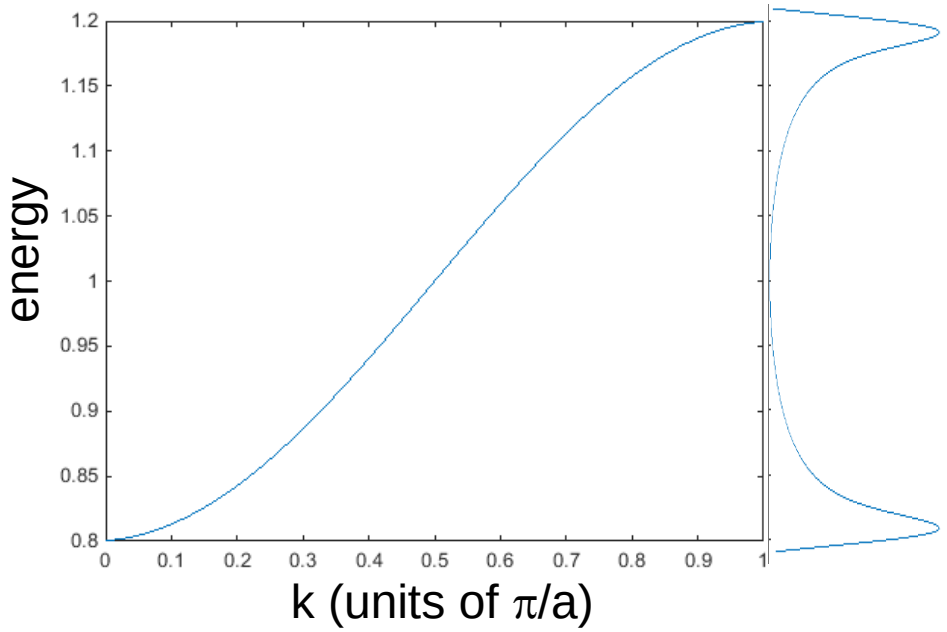


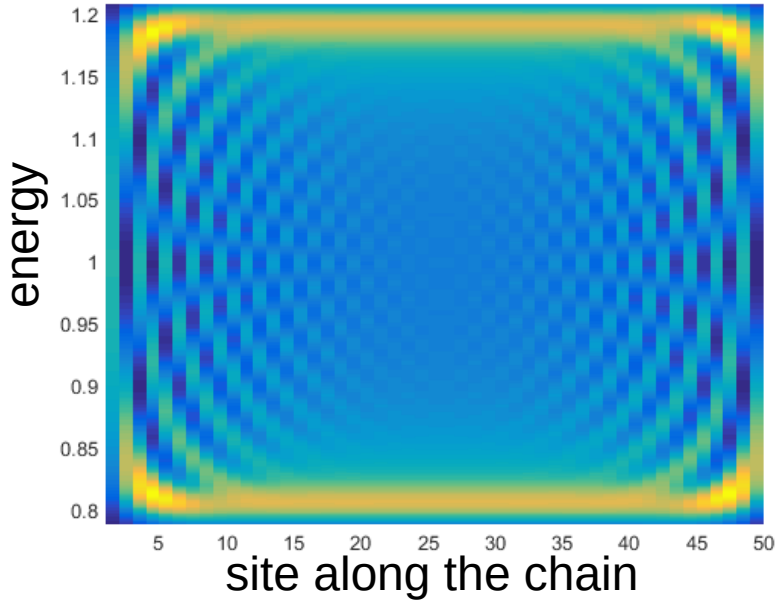
- What determines the energy and spatial resolution?

LDOS example 2: atomic chain



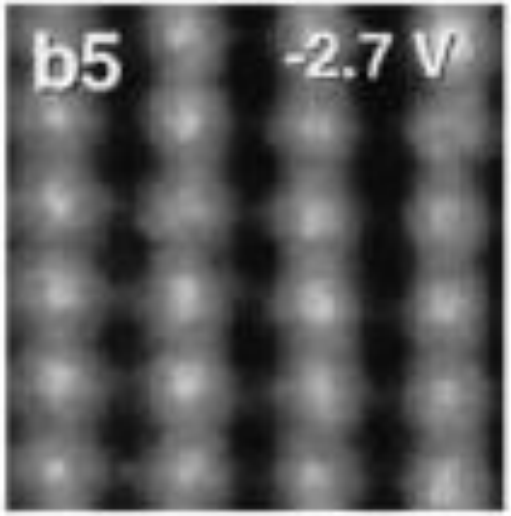
- Tight binding chain with cos(ka) dispersion
- Bottom of the band – maximally bonding wavefunction
- Top of the band – maximally antibonding wavefunction
- LDOS $\propto \psi^2$
- LDOS oscillations close to the ends



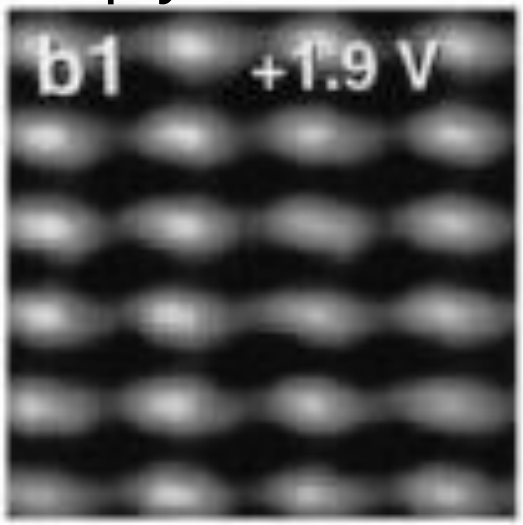


Example 1: semiconductor surface

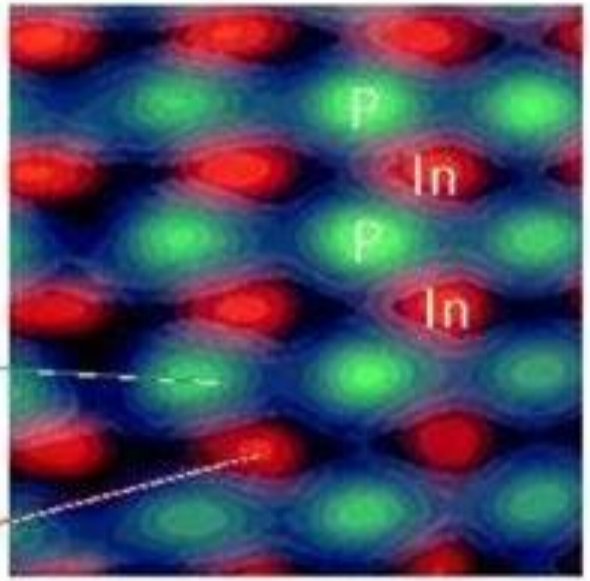
occupied

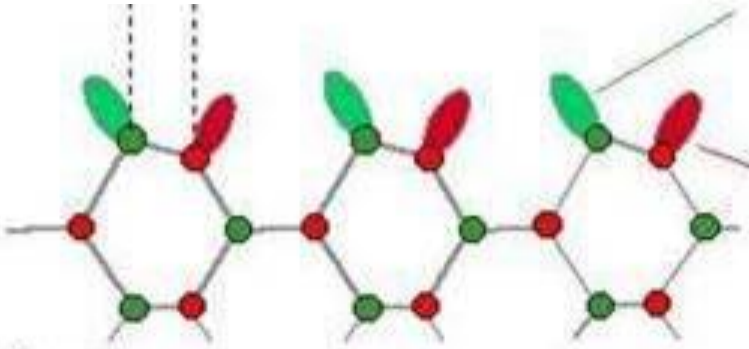


empty



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





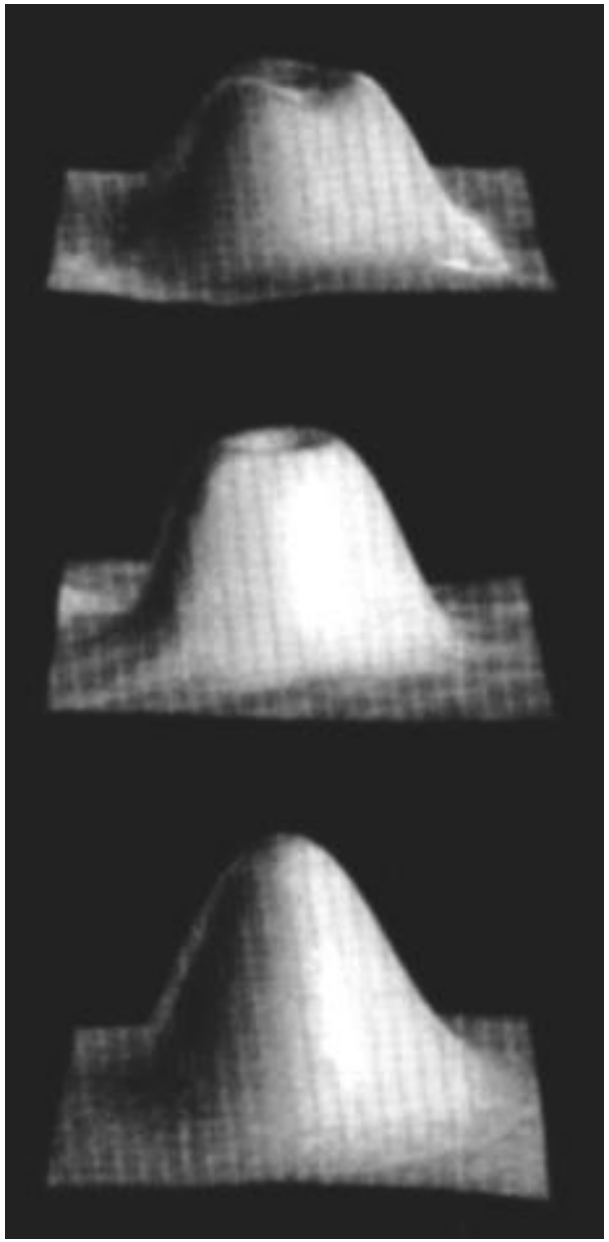
occupied dangling bond

empty dangling bond

side view

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

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

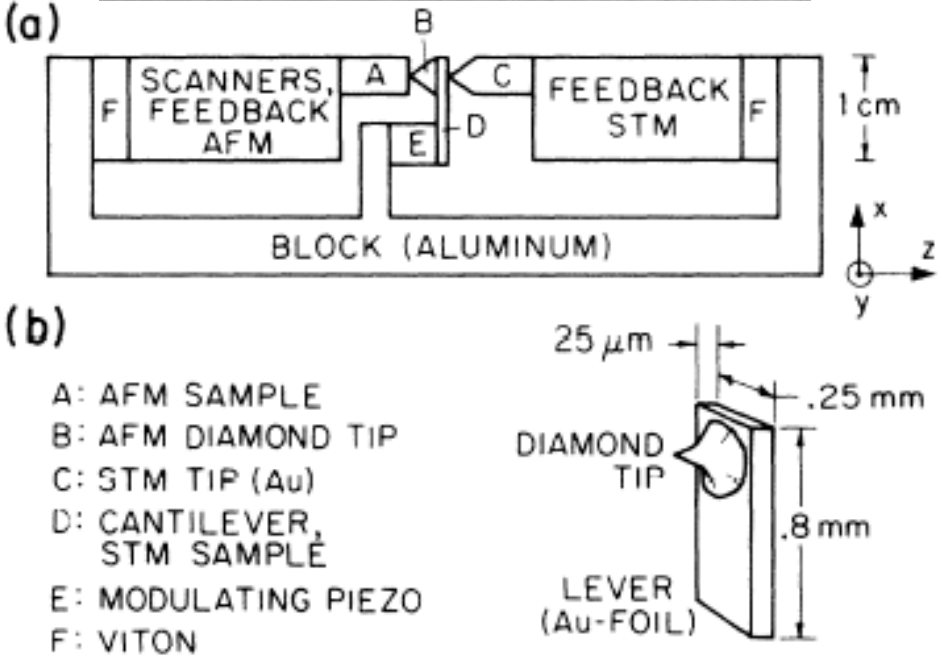
P.S. Weiss, D.M. Eigler, *Phys. Rev. Lett.* **71**, 3139 (1993).

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

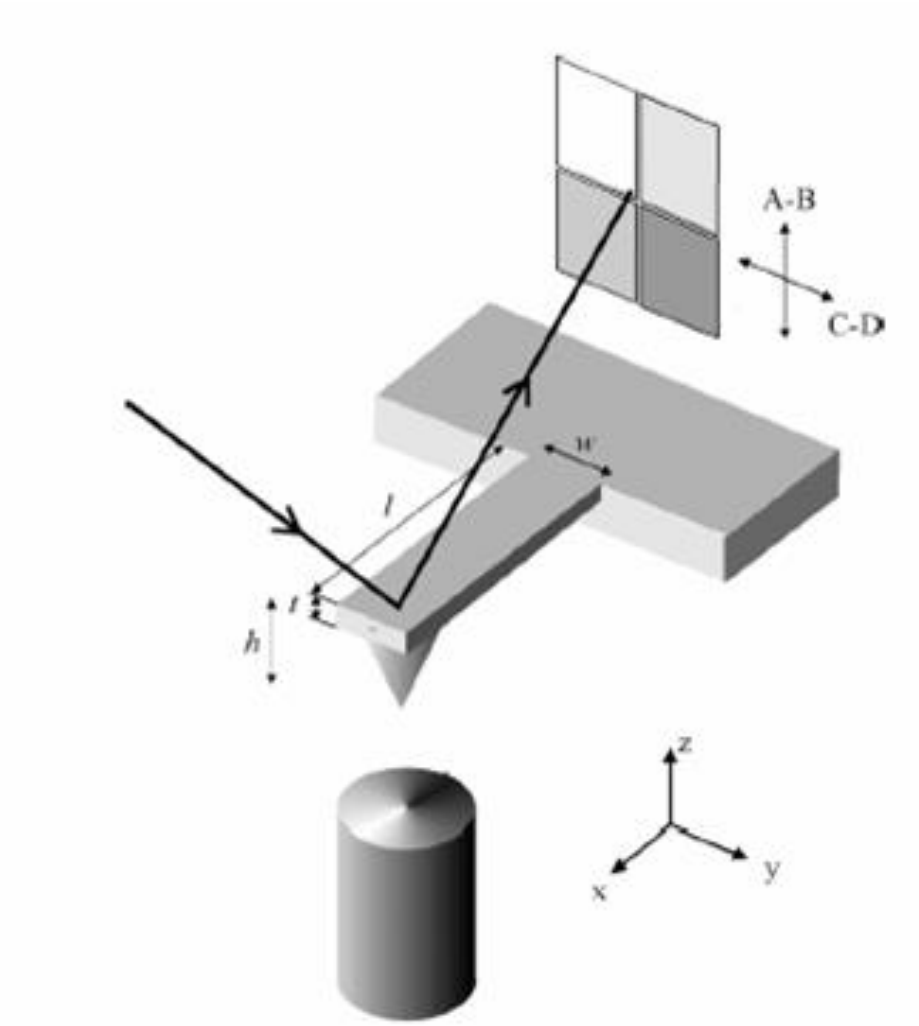
- Invented in 1986 by G. Binnig, C. Gerber, and C. Quate (IBM Zurich)
- Idea is to measure a force due to a very small contact with a sample
- Typical forces in pN - nN range
- Based on detecting the bending of a cantilever – Hooke's law: $F = -kx$



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

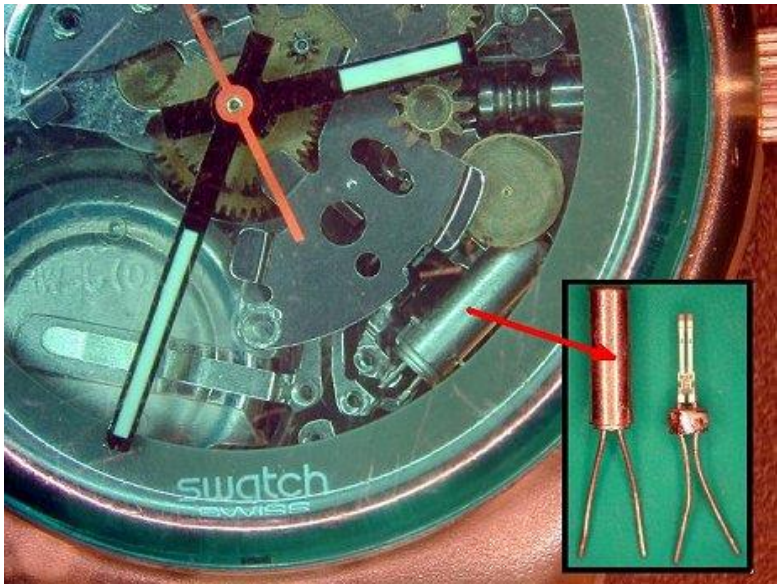
Bending of a cantilever

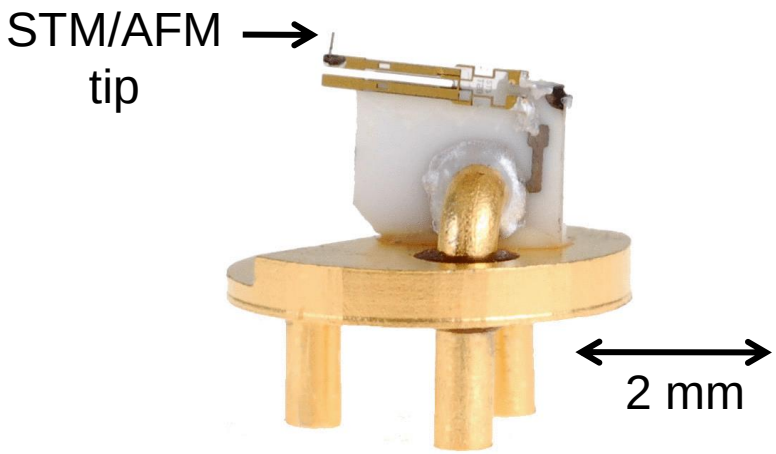
- Optical detection the most common
- four-field detector can measure both the normal deflection (A-B) and torsional bending (C-D), i.e both normal and lateral force components can be measured



qPlus force sensor

- Very stiff cantilever (k=1800 N/m)
- Small oscillation amplitudes (<< 1 nm, record ~0.1Å)
- Sensitive to short-range forces
- Practical advantage: all electrical force detection
- **Simultaneous STM and AFM**

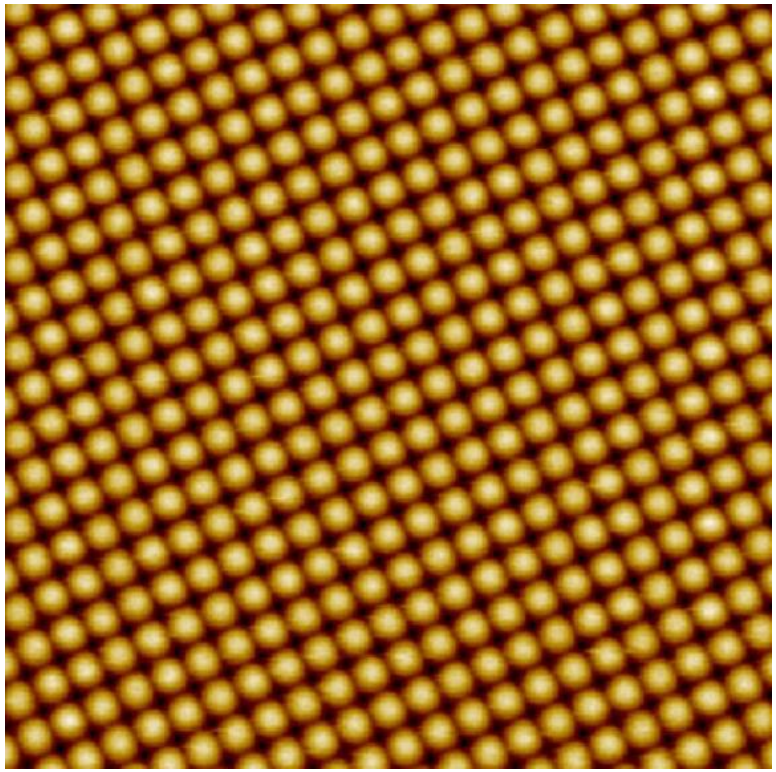




F.J. Giessibl, *Rev. Mod. Phys.* **75,** 949 (2003)

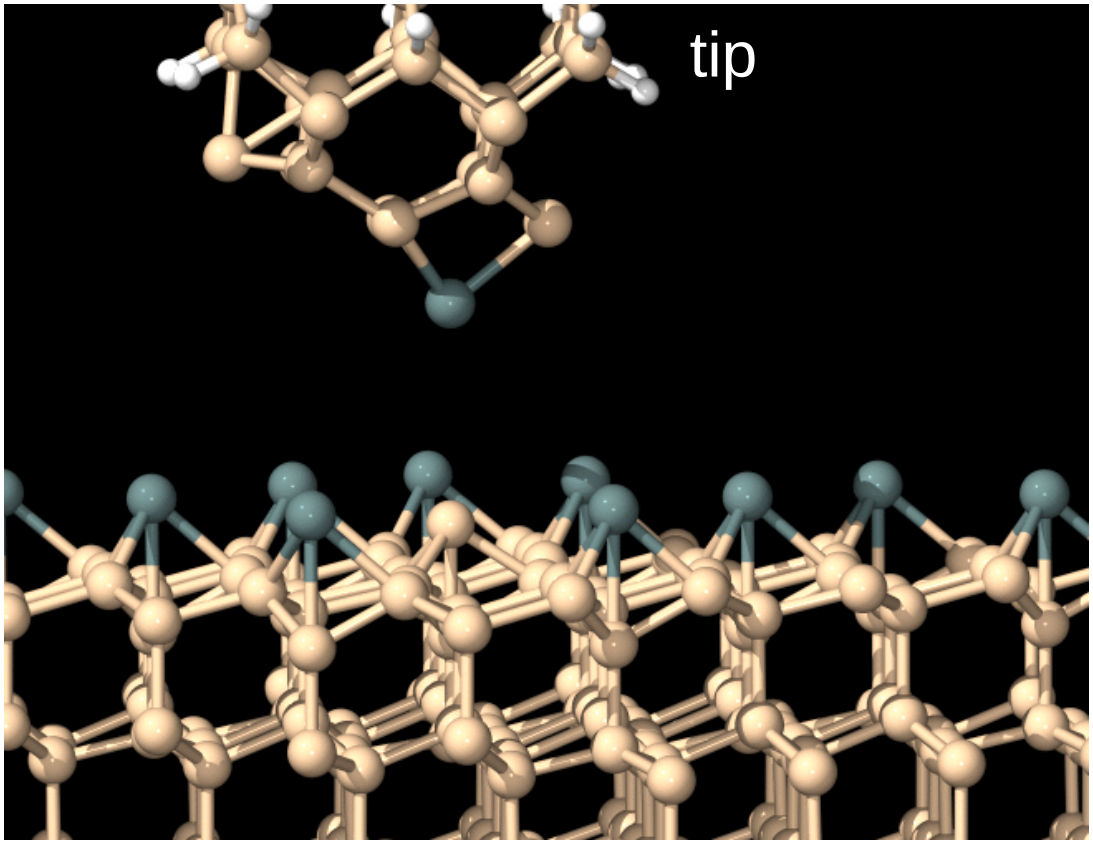
Atomic resolution imaging on bulk insulators

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



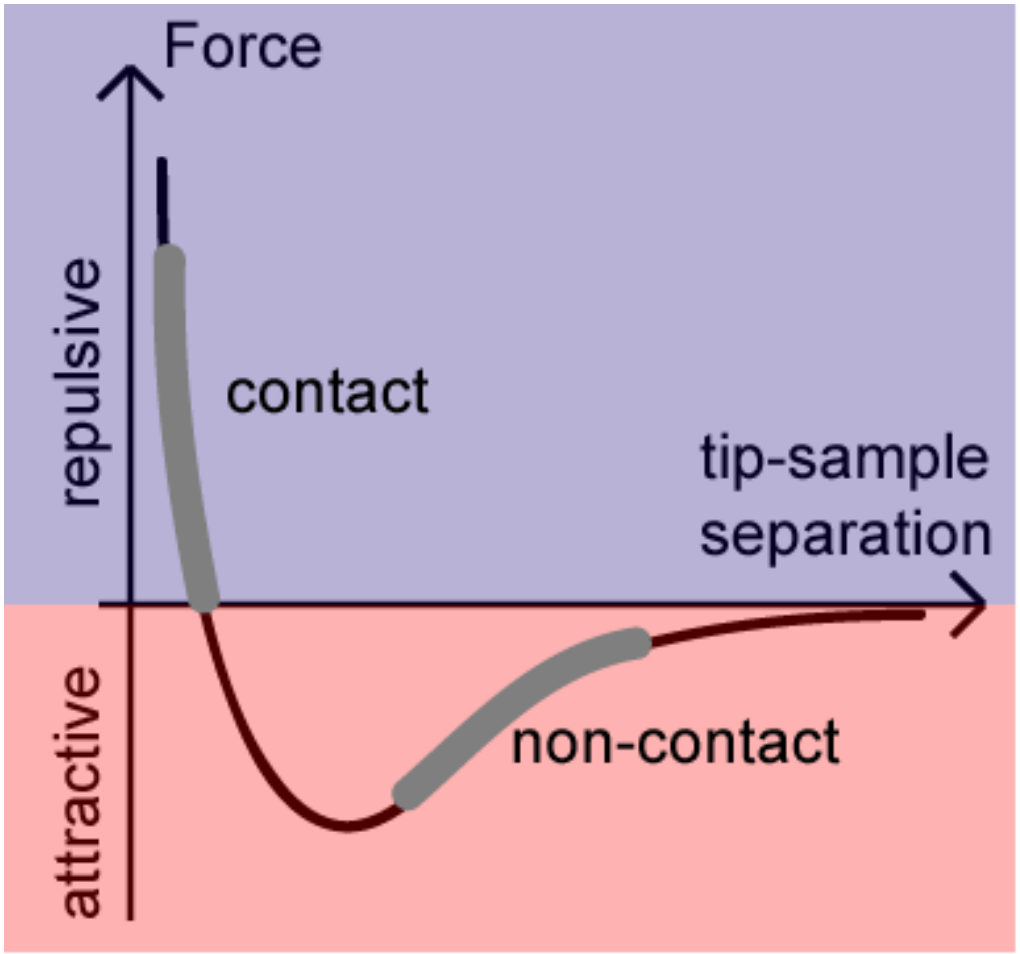
AFM principles

- 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)

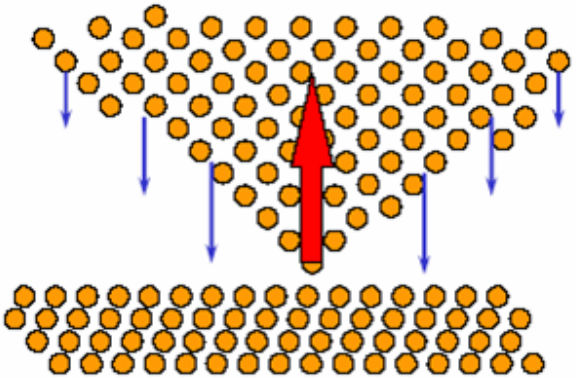


Different modes

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



Jump-to-contact – problem



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

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

- If the cantilever oscillates, stability condition is (net force has to be negative)

$$kA > -F_{ts}$$

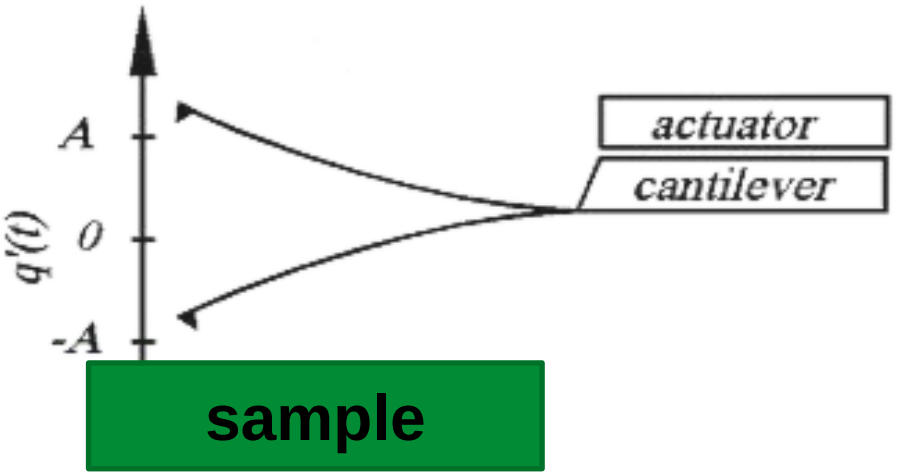
- For stable amplitude feedback, it is required

$$\frac{k}{2} A^2 > \Delta E_{ts} \frac{Q}{2\pi}$$

- Solution: larger amplitudes or stiffer cantilevers

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

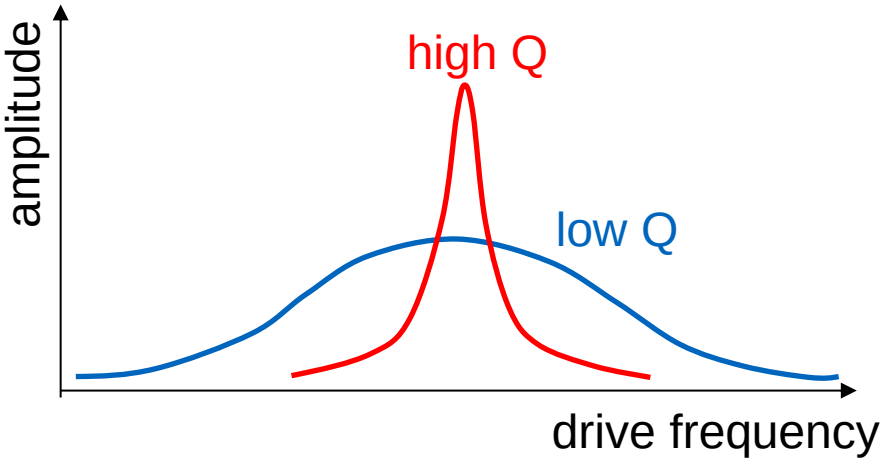
Dynamic modes ("non-contact AFM")



- Vibrating cantilever (externally driven)
- avoids jump to contact problem
- low Q (air or liquid)

  ⇒ amplitude modulation
- high Q (vacuum)

  ⇒ 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).

What kind of forces are there in AFM?

Short range:

- Chemical bonding (attractive)
- Pauli repulsion

Different model potentials:

- Lennard-Jones

$$V_{LJ} = -4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{6} - \left(\frac{\sigma}{r}\right)^{12}\right)$$

- And others, e.g. short-range chemical binding (Morse potential), more complicated potentials that take into account the asymmetry of the chemical bond (Stillinger-Weber etc.)

What kind of forces are there in AFM?

Long range:

- Van der Waals (for a spherical tip)

$$V_{vdW} = -\frac{A_H R}{6z}$$

  where A_H is the Hamaker constant and R the tip radius

- Electrostatic (notice force, not potential), only valid at small z

$$F_{es} = -\frac{\pi\varepsilon_0 R V_b^2}{z}$$

- Force related to the potential

$$F = -\nabla V$$

Total force

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

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

- 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)

What is the frequency shift Δf ?

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

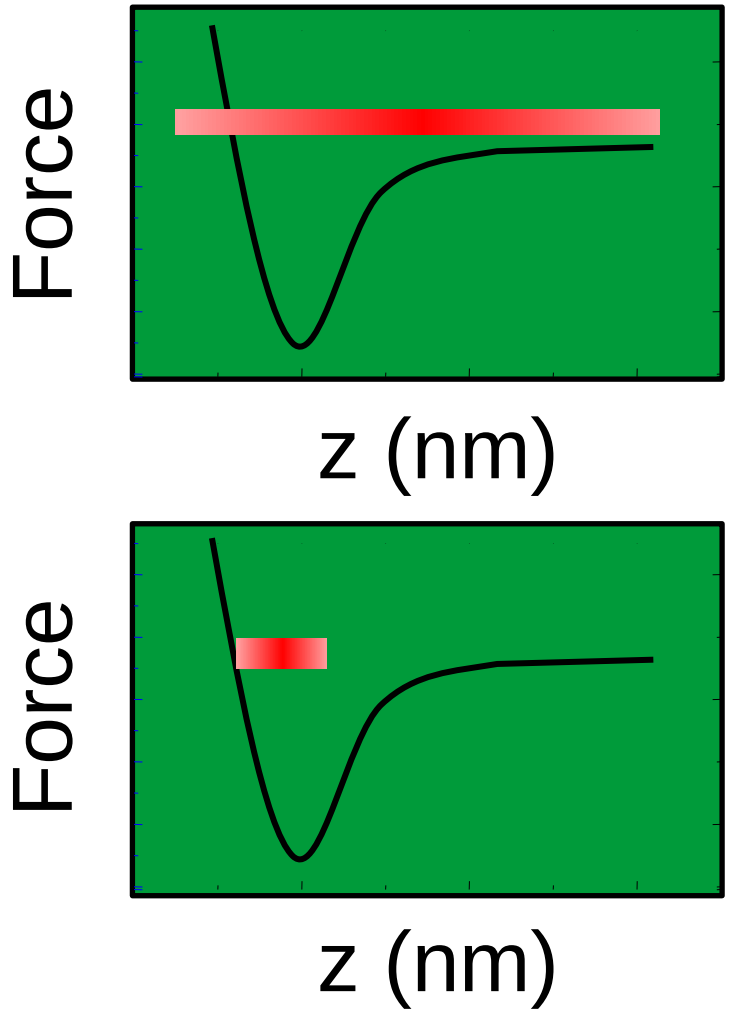
$$f = f_0 + \Delta f$$

- 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

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

What does finite tip oscillation amplitude mean?

- Frequency shift depends on the tip-sample forces ”averaged” over the oscillation amplitude
- Maximum contribution of short-range forces with small amplitudes $\Rightarrow$ Small amplitudes with stiff cantilevers



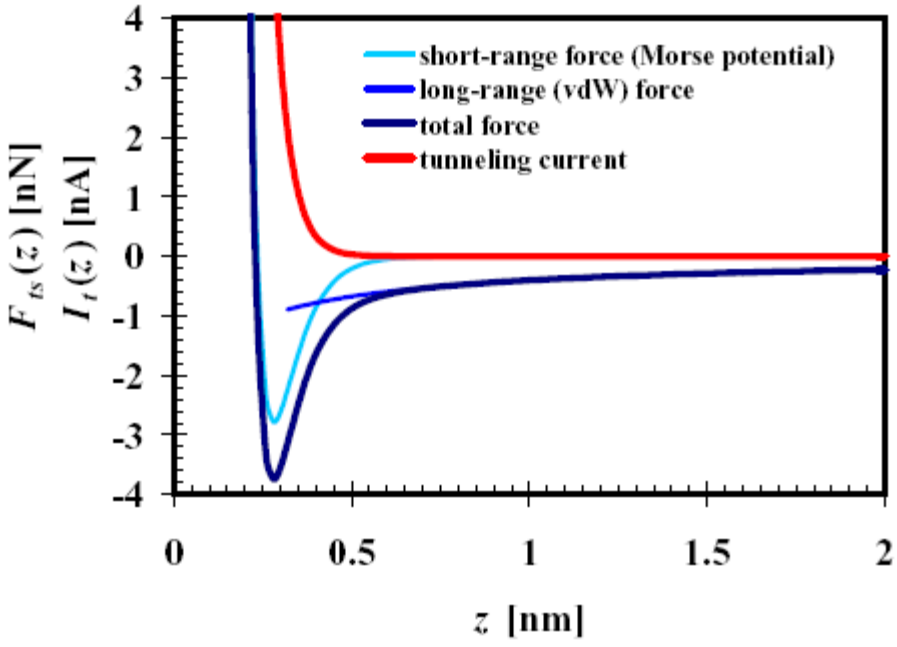
F.J. Giessibl, *Rev. Mod. Phys.* **75**, 949 (2003).

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”)