# Introduction to Scanning Probe Microscopy

**Zhe Fei**

IOWA STATE UNIVERSITY

THE Ames Laboratory
Creating Materials & Energy Solutions
U.S. DEPARTMENT OF ENERGY

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# Outline



**Part 1 SPM Overview**

**Part 2 Scanning tunneling microscopy**

**Part 3 Atomic force microscopy**

**Part 4 Electric & Magnetic force microscopies**

**Part 5 Scanning near-field optical microscopy**

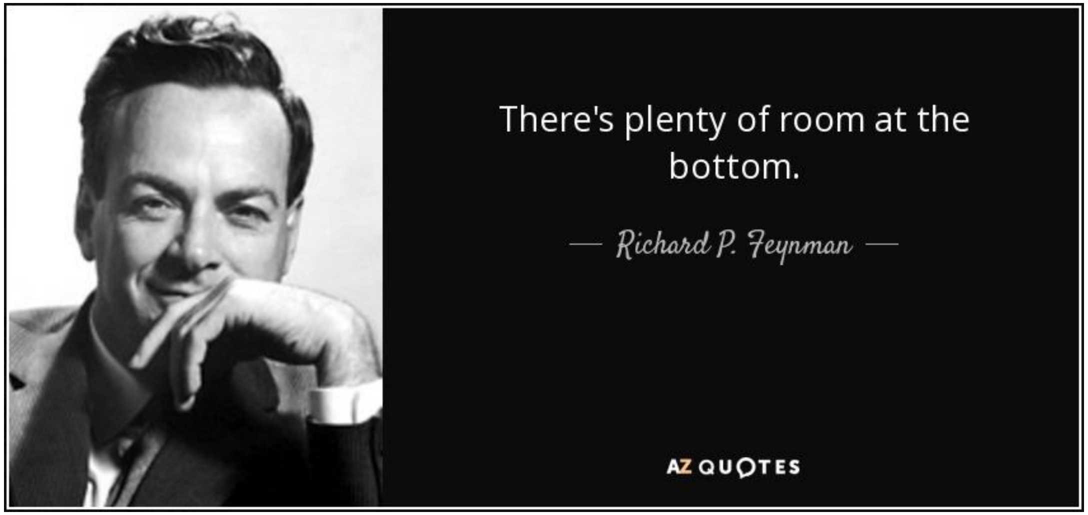
References:

Wikipedia & Fundamentals of scanning probe microscopy by V. L. Mironov

# 1. SPM overview

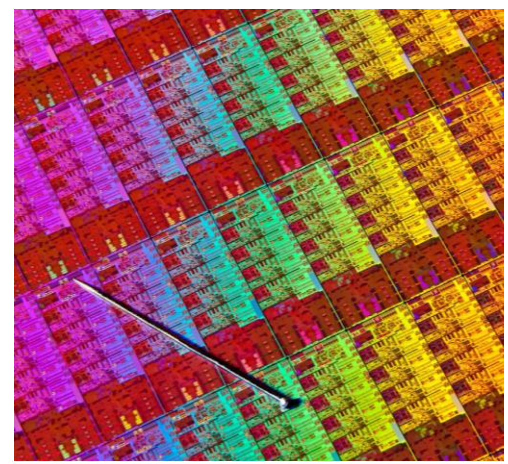
# SPM

In 1959, Richard Feynman gave a visionary talk about nanoscience and nanotechnology:




a new version at 1984 available

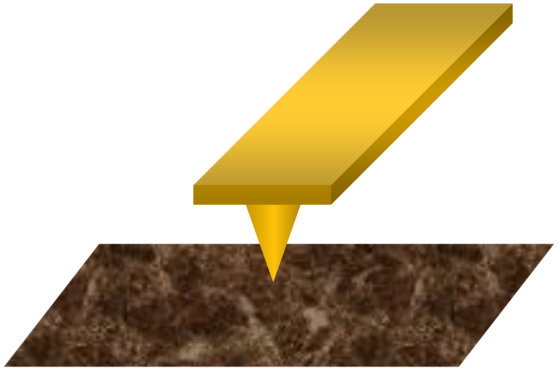
- ✓ laws of physics do not prevent manipulation of materials at the nano-/ atomic scale.
- ✓ Huge scientific and technological impact of going small.
- ✓ New techniques enabling nano-/ atomic scale.



# SPM



Scanning probe microscopy (SPM) is a branch of microscopy that forms images of surfaces using a physical probe that scans the specimen.



The most common SPMs are scanning tunneling microscopy (STM) and atomic force microscopy (AFM).

The Nobel Prize in Physics 1986 is awarded to STM (Gerd Binnig and Heinrich Rohrer) and Electron microscopy (Ernst Ruska).

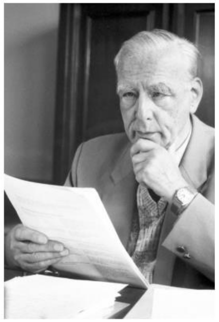


Photo from the Nobel Foundation archive.
Ernst Ruska

Photo from the Nobel Foundation archive.
Gerd Binnig

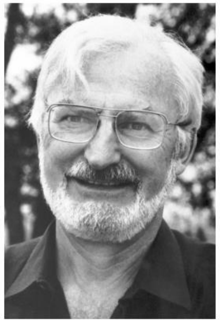
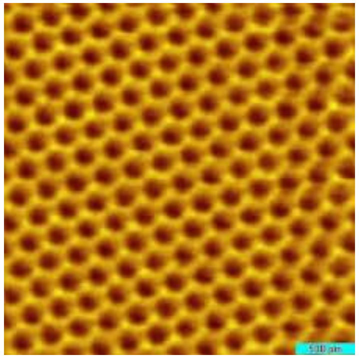


Photo from the Nobel Foundation archive.
Heinrich Rohrer

SPM often has very high resolution, can sometimes images atoms.



SPM could provide information about many physical properties (mechanical electronic, magnetic, optical …).

# General principle



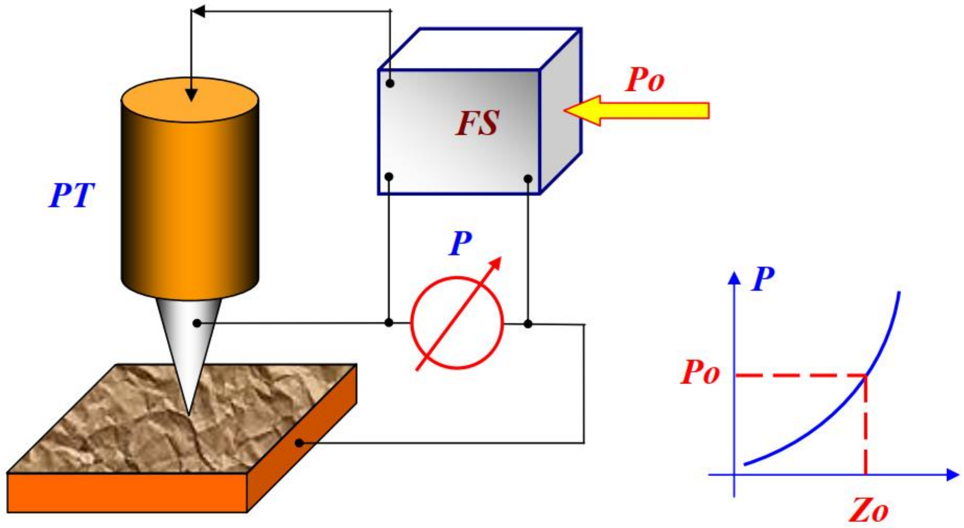
**Main components**

Physical tips

Feedback system (FS)

piezo transducer

Scanners & positioners




**Feedback system** (constant P mode)

P is a physical parameter that the **FS** monitors (e.g. tunneling current).

The **FS** keeps constant the value of the parameter P (equal to the preset $P_0$)

If the tip-sample distance changes, there is a change in the parameter P.

The transducer uses applied voltage $\Delta V$ to change the separation, bringing P back to $P_0$

Images record $\Delta V$ (x, y)

# Varieties



## Varieties

- AFM, atomic force microscopy[2]
  - Contact AFM
  - Non-contact AFM
  - Dynamic contact AFM
  - Tapping AFM
  - AFM-IR
  - CFM, chemical force microscopy
  - C-AFM, conductive atomic force microscopy[3]
  - EFM, electrostatic force microscopy[4]
  - KPFM, kelvin probe force microscopy[5]
  - MFM, magnetic force microscopy[6]
  - PFM, piezoresponse force microscopy[7]
  - PTMS, photothermal microspectroscopy/microscopy
  - SCM, scanning capacitance microscopy[8]
  - SGM, scanning gate microscopy[9]
  - SVM, scanning voltage microscopy[10]
  - FMM, force modulation microscopy[11]

- STM, scanning tunneling microscopy[12]
  - BEEM, ballistic electron emission microscopy[13]
  - ECSTM electrochemical scanning tunneling microscope[14]
  - SHPM, scanning Hall probe microscopy[15]
  - SPSM spin polarized scanning tunneling microscopy[16]
  - PSTM, photon scanning tunneling microscopy[17]
  - STP, scanning tunneling potentiometry[18]
  - SXSTM, synchrotron x-ray scanning tunneling microscopy[19]

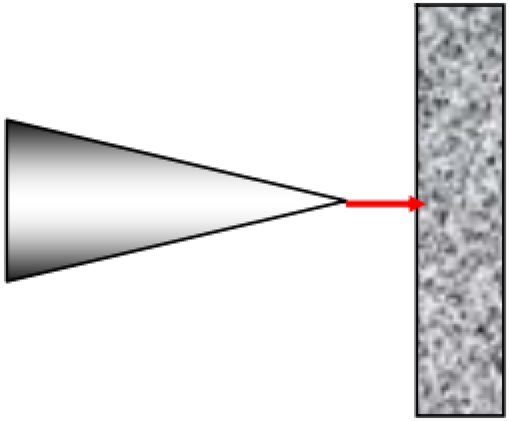
- FluidFM, fluidic force microscopy[20]
- FOSPM, feature-oriented scanning probe microscopy[21]
- MRFM, magnetic resonance force microscopy[22]
- NSOM, near-field scanning optical microscopy (or SNOM, scanning n
  - nano-FTIR, broadband nanoscale SNOM-based spectroscopy[24]
- SECM, scanning electrochemical microscopy
- SICM, scanning ion-conductance microscopy[25]
- SSM, scanning SQUID microscopy
- SSRM, scanning spreading resistance microscopy[26]
- SThM, scanning thermal microscopy[27]
- SSET scanning single-electron transistor microscopy[28]
- STIM, scanning thermo-ionic microscopy[29][30]

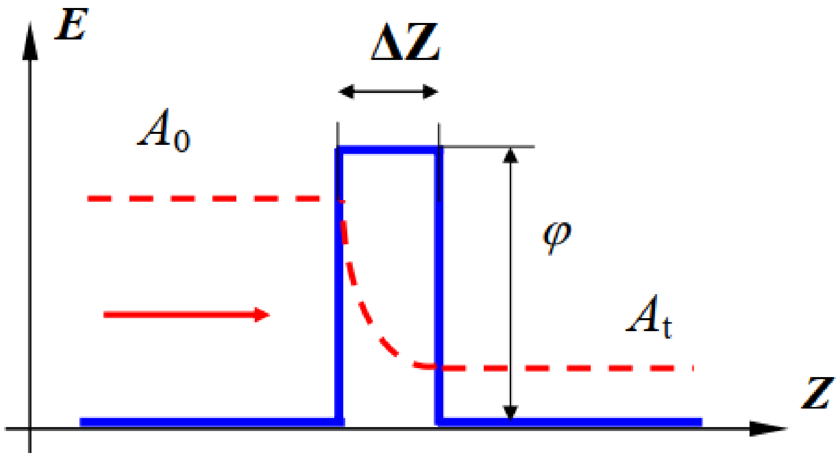
# 2. Scanning Tunneling Microscopy

# STM



Historically, the first microscope in the family of probe microscopes is the scanning tunneling microscope (STM).






The STM tip approaches the sample surface to distances of several Angstroms. This forms a tunnel transparent barrier, whose size is determined mainly by the values of the work function for electron emission from the tip ($\varphi_T$) and from the sample ($\varphi_S$).

$$\varphi^* = \frac{1}{2}(\varphi_T + \varphi_S).$$

$$W = \frac{|A_t|^2}{|A_0|^2} \cong e^{-k\Delta Z}$$

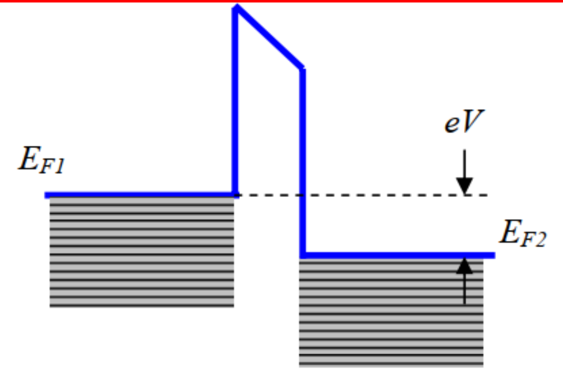
$$k = \frac{4\pi\sqrt{2m\varphi^*}}{h},$$ For two metals

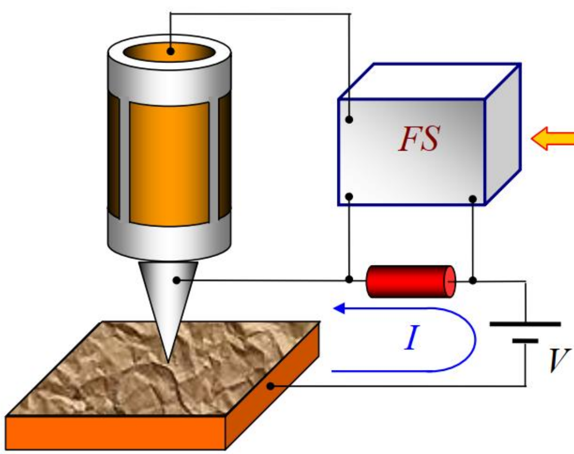
$W$ is the probability of electron tunneling, $A_0$, $A_t$ are the amplitude of the electron wave function, $k$ the attenuation coefficient; $\Delta Z$ the barrier width.

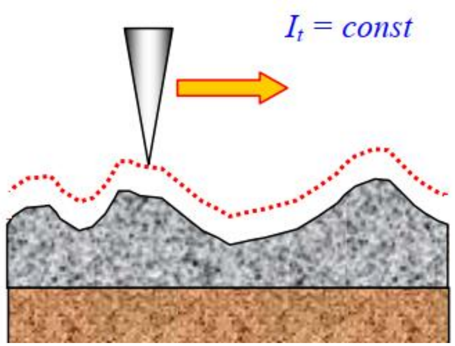
# STM modes

If a potential difference $V$ is applied to the tunnel contact, a tunneling current appears

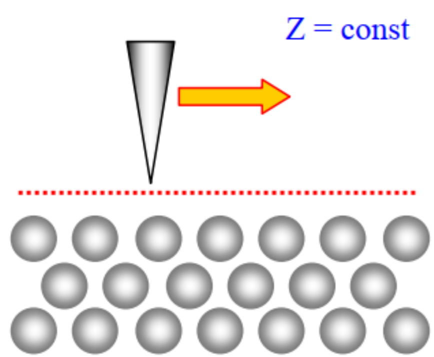
$$j_t = j_0(V)e^{-\frac{4\pi}{h}\sqrt{2m\varphi^*}\Delta Z},$$ (for small V)



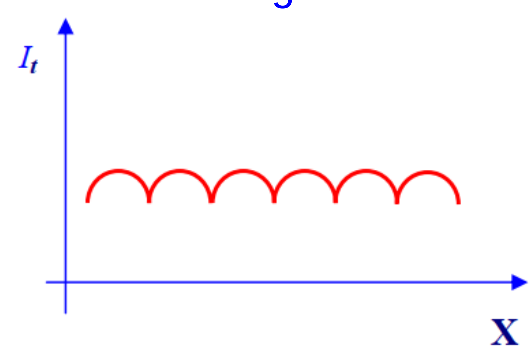




constant current mode


constant height mode



# STM resolution



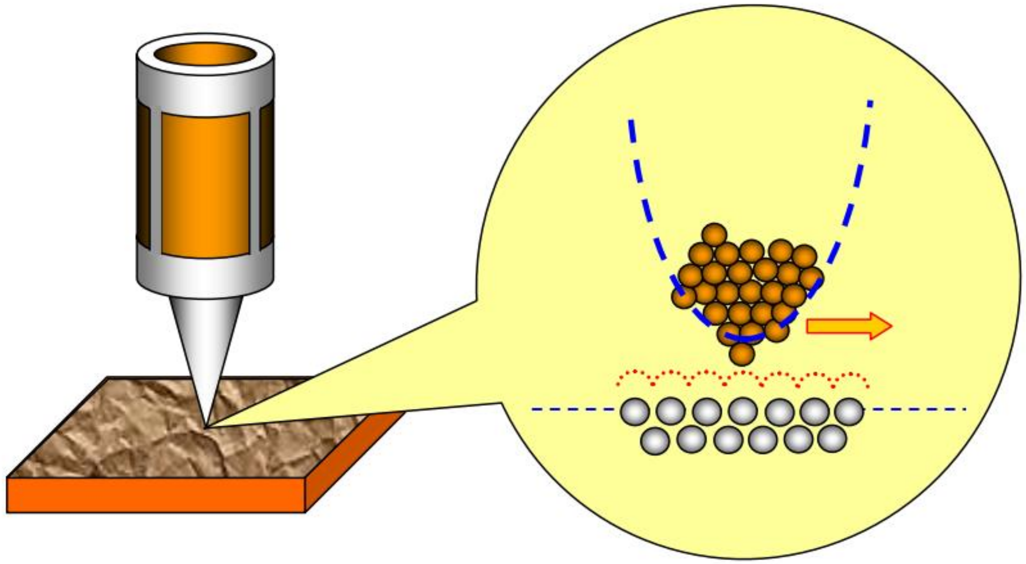
The high spatial resolution of the STM is due to the exponential dependence of the tunneling current on the tip-sample distance.

The vertical resolution can reach fractions of Angstrom.

The lateral resolution depends on the quality of the tip.

Normally, tip with a protruding atom gives an excellent lateral resolution.

Vacuum operation is required for atomic resolution.



# Work-function mapping



Measurement of the local work function with STM

$$j_t = j_0(V)e^{-\frac{4\pi}{h}\sqrt{2m\varphi^*}\Delta Z}$$ (for small V)

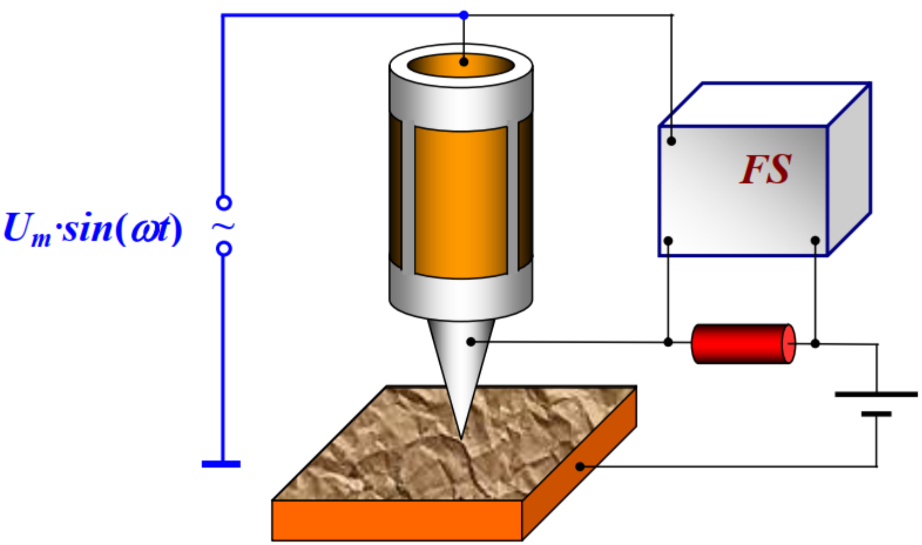
$$U(t) = U_0 + U_m \sin(\omega t).$$

$$\Delta Z(t) = \Delta Z_0 + \Delta Z_m \sin(\omega t)$$

$$I_t \cong I_0(V)e^{-\alpha\sqrt{\varphi^*}[\Delta Z_0 + \boxed{\Delta Z_m \sin(\omega t)}]}$$

$$I_t(\omega t) \cong I_o(V)e^{-\alpha\sqrt{\varphi}\Delta Z_0}\left[1 - \alpha\sqrt{\varphi}\boxed{\Delta Z_m \sin(\omega t)}\right].$$

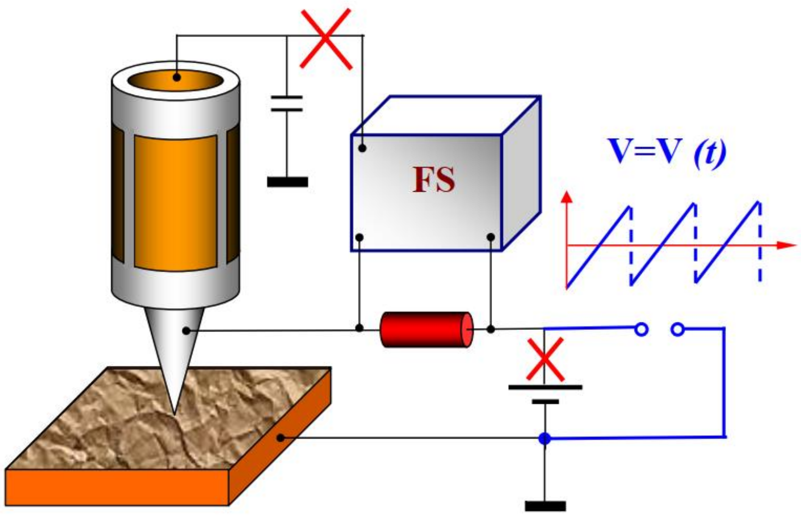
$$I_\omega = I_0\frac{2KU_m}{\hbar}\sqrt{2m\varphi^*(x,y)}.$$

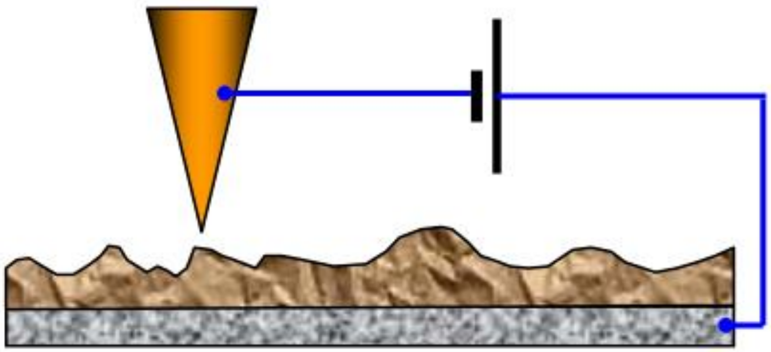


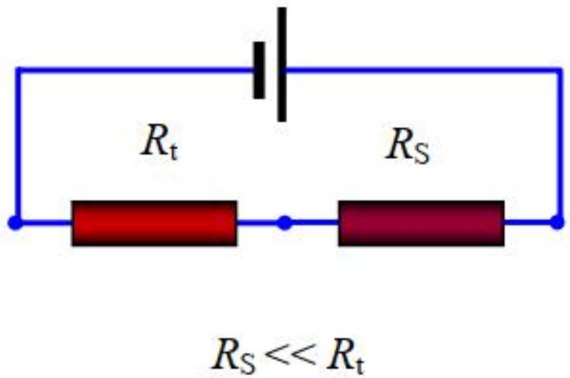
# Tunneling spectroscopy



Using STM it is possible to measure the tunnel I-V curves that give information on the local density of electron states (DOS).



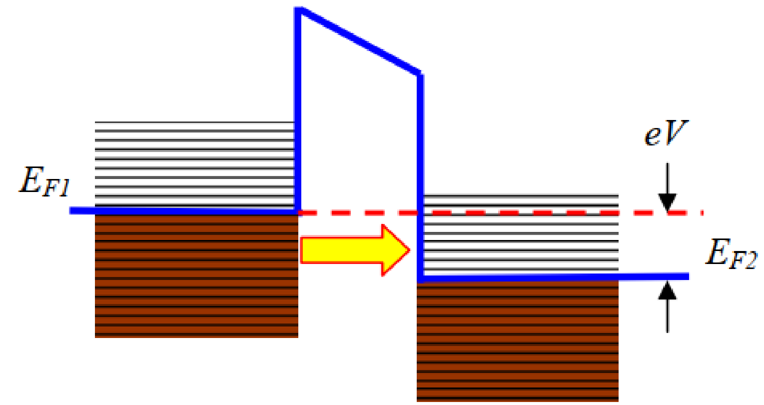





# Tunneling spectroscopy



The value of the tunneling current is defined by the bias voltage, the barrier transmission coefficient and the density of states near Fermi level.




$$dI = A \cdot D(E)\rho_P(E)f_P(E)\rho_S(E)(1 - f_S(E))dE\,,$$

*A* is a constant; *D(E)* the barrier transparency; *ρ(E)* is the density of states; *f(E)* is the Fermi distribution function.

$$I(V) = B\int_0^{eV}\rho_S(E)dE \qquad \rho_S(eV) \approx \frac{\partial I}{\partial V}\,.$$

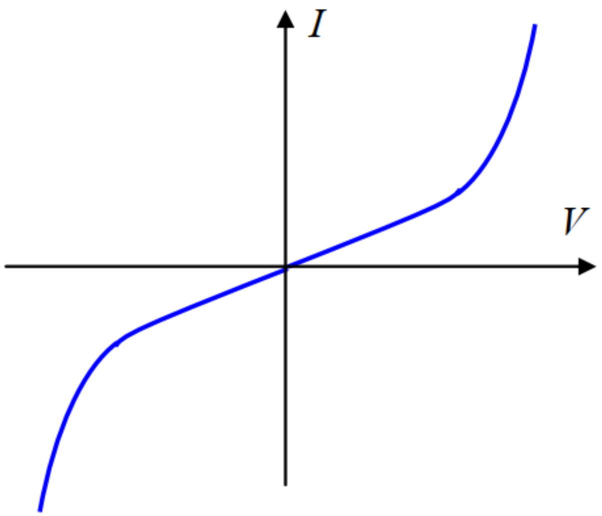
# STM metal



## Metal - metal tunneling junction

For small bias voltages, the dependence of the tunneling current on the bias voltage is linear.

$$j_t = j_0(V)\, e^{-\frac{4\pi}{h}\sqrt{2m\varphi^*}\,\Delta Z}$$



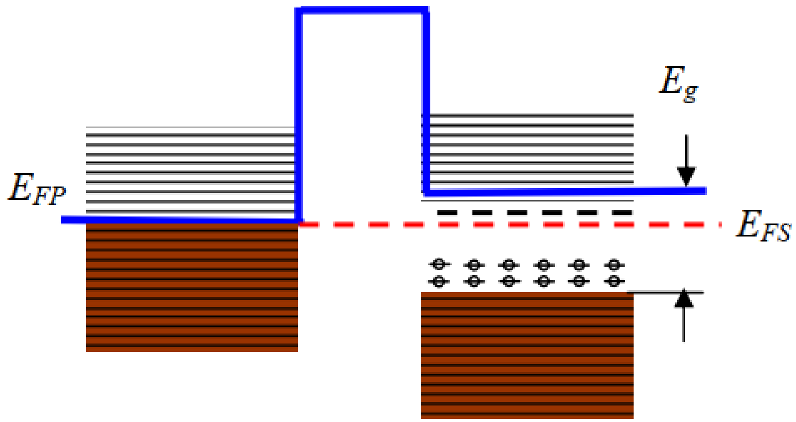

At very high voltages the barrier shape will strongly change, and the current will be described by the Fowler-Nordheim formula.

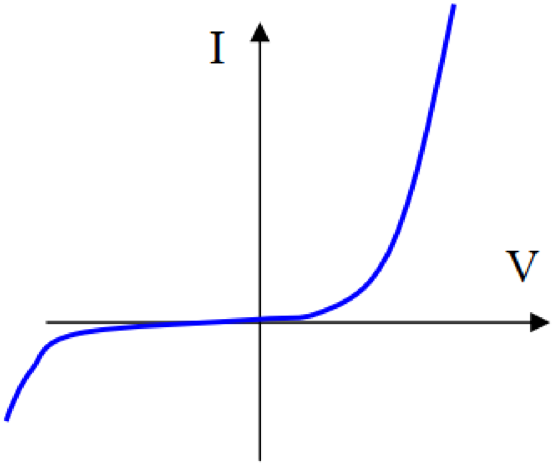
Metal-metal tunneling contact is nonlinear but it is normally symmetric.

# STM semiconductor



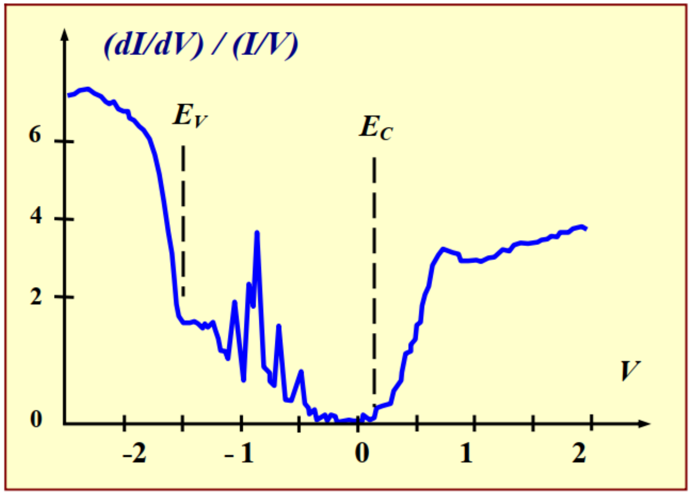
## Metal–semiconductor contact




Tunneling spectra can determine

- ✓ The edges of the conduction and valence band
- ✓ Impurity states inside the gap in

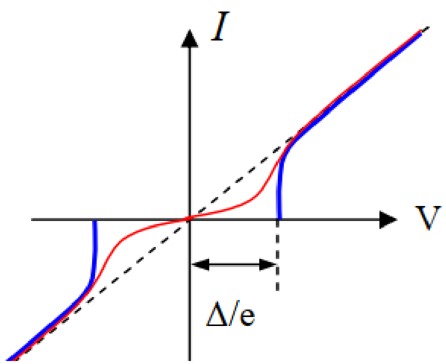


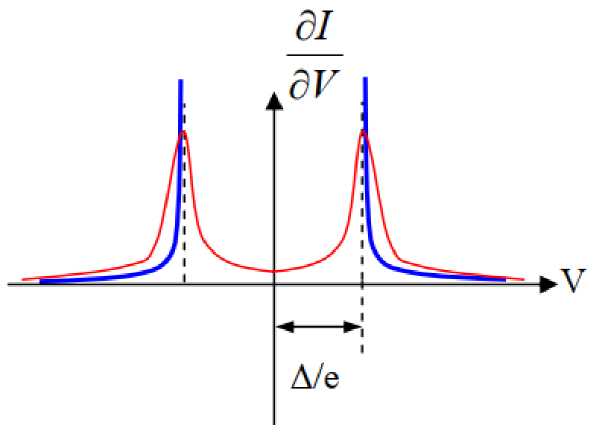

tunneling spectrum of a GaAs sample

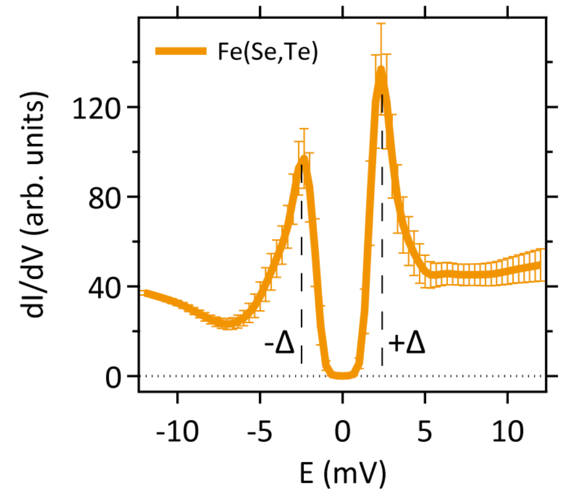
# STM superconductor

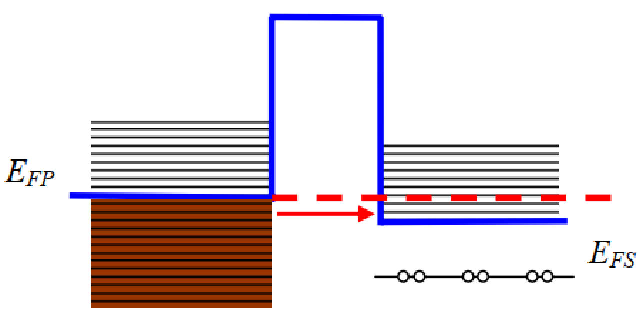


## Metal–superconductor contact

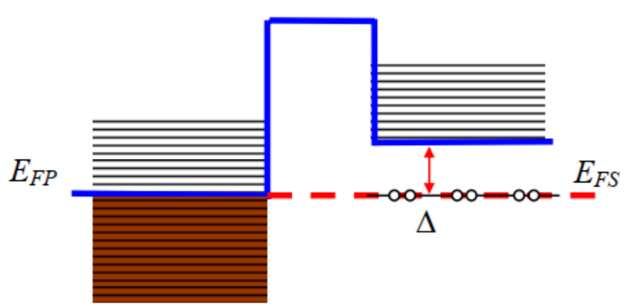


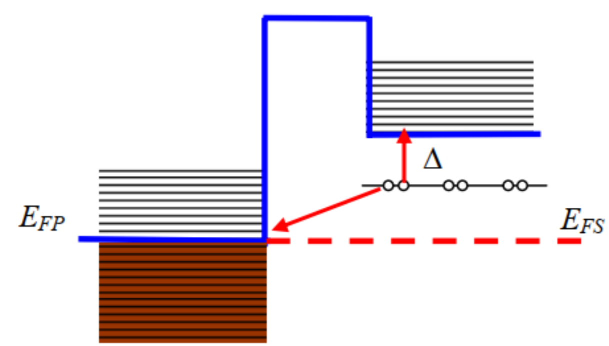




Finite DOS




1st Peak DOS




2nd Peak DOS

# 3. Atomic force microscopy

# AFM

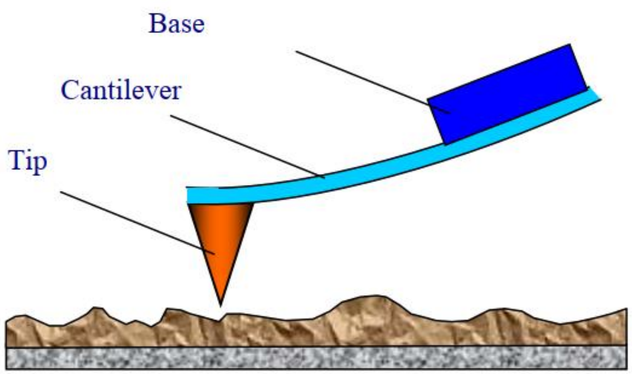
Atomic force microscope (AFM) was invented in 1986 by Binnig, Quate and Herber.

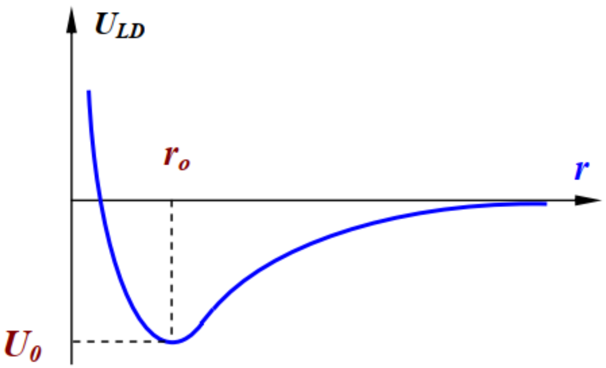
It measures the interactive force between a tip and the sample surface using special probes made by an elastic cantilever with a sharp tip on the end.

The interactive forces measured by AFM can be qualitatively explained by considering, for example, the van der Waals forces.

$$U_{LD}(r) = U_0\left\{-2\left(\frac{r_0}{r}\right)^6 + \left(\frac{r_0}{r}\right)^{12}\right\}.$$

Lennard-Jones potential
(for 2 atoms)



# Inter-molecule distance



Na - Hg

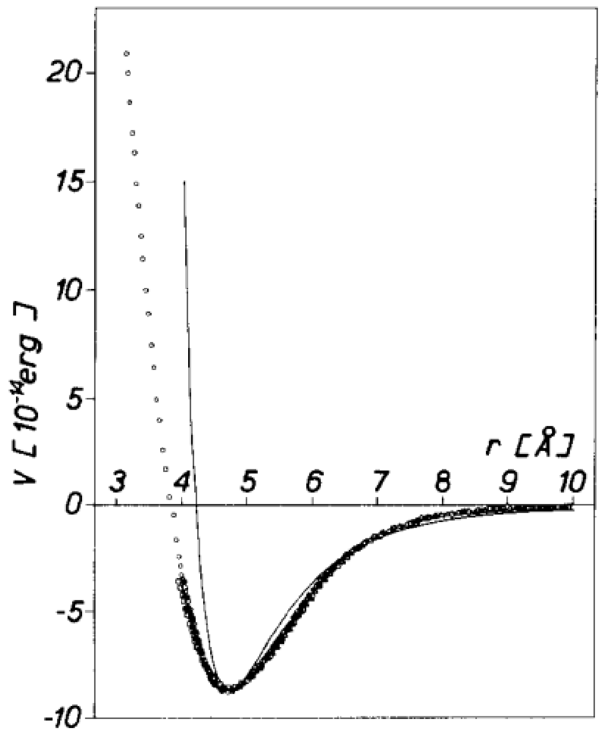
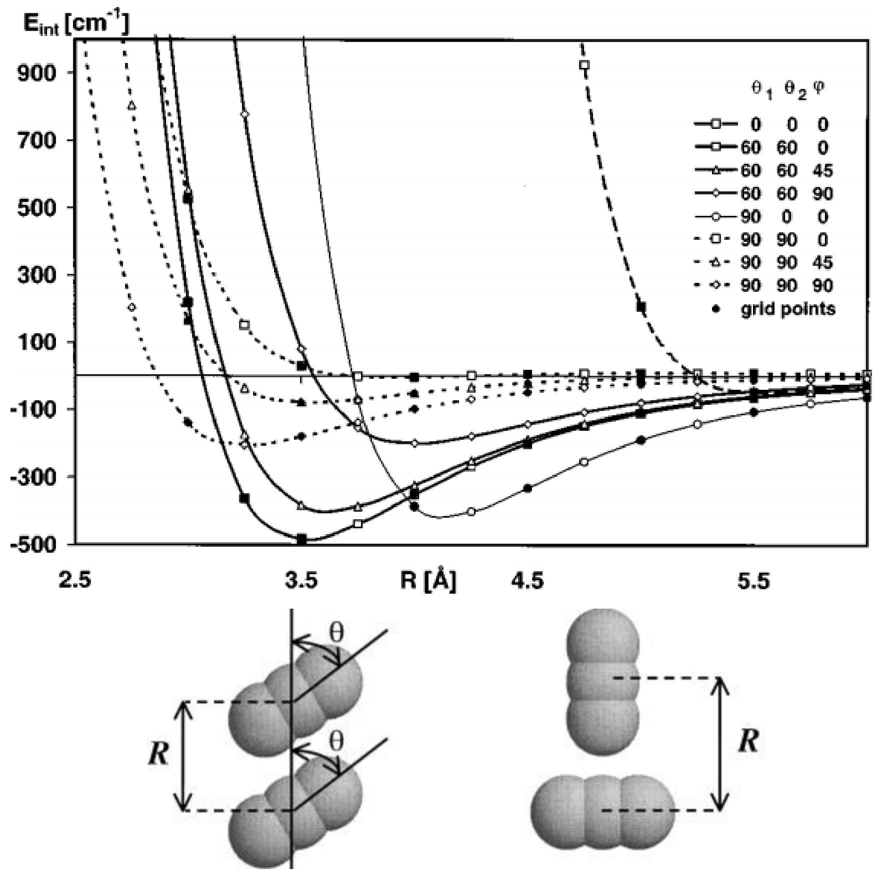



FIG. 8. The potential for Na–Hg. Each of the energies is designated by a different symbol (○ for $E=28.7\times10^{-14}$ erg; ◇ for $E=30.1\times10^{-14}$ erg; + for $E=31.3\times10^{-14}$ erg; △ for $E=34.5\times10^{-14}$ erg; and □ for $E=40.2\times10^{-14}$ erg).

Buck and Pauly, J. Chem. Phys. 54, 1929 (1971)

$CO_2 - CO_2$




Bukowski et al. J Chem. Phys. 110, 3785 (1999).

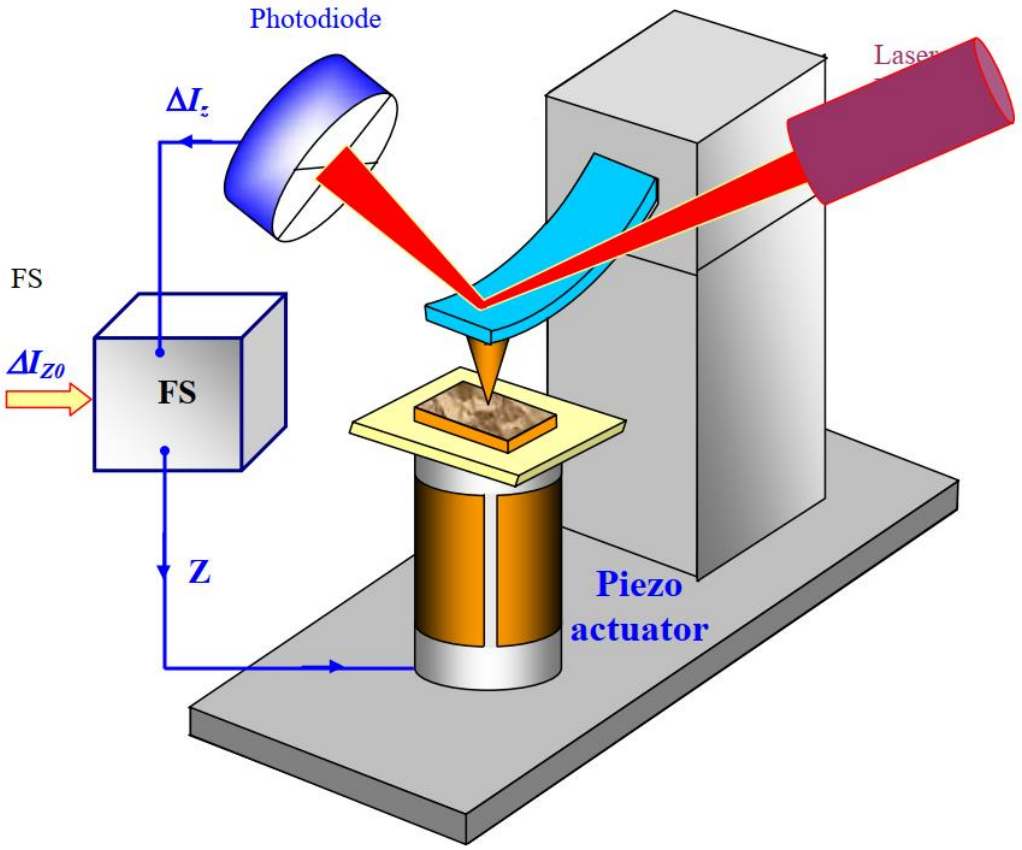
# Deflection-laser AFM



Acquisition of an AFM surface topography may be done by recording the small deflections of the elastic cantilever.

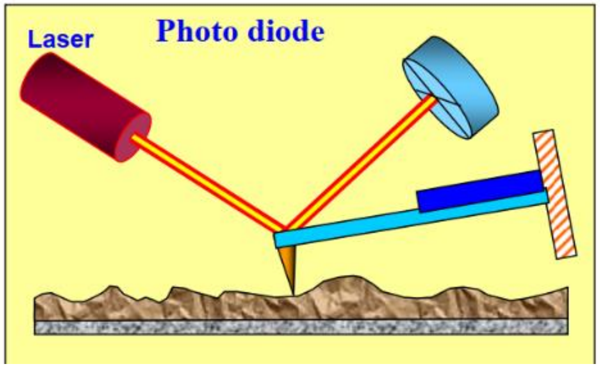
For this purpose optical methods are widely used in atomic force microscopy.

- ✓ Defection laser
- ✓ Position sensitive photodiode
- ✓ Feedback system
- ✓ Piezo scanner and positioner

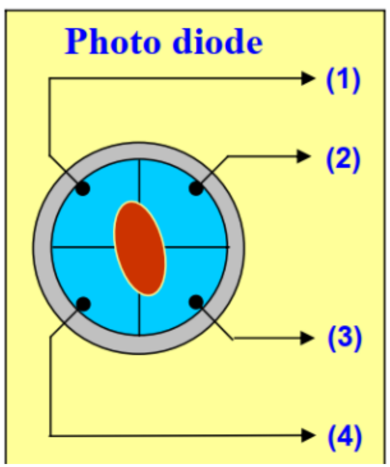


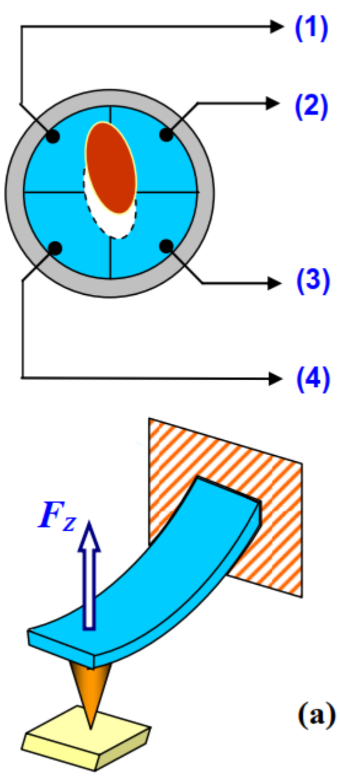
# Deflection-laser AFM



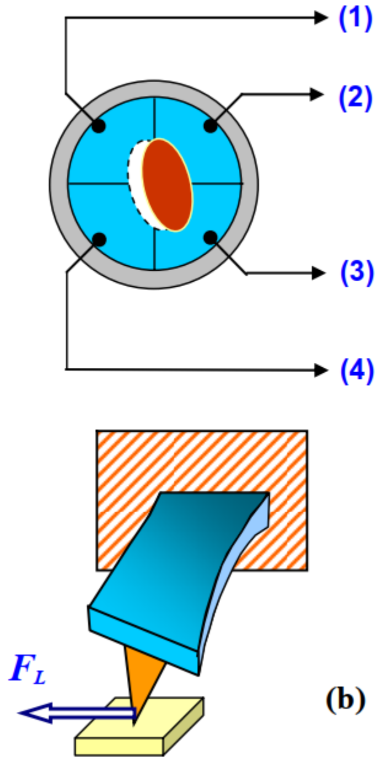



position-sensitive photodetectors



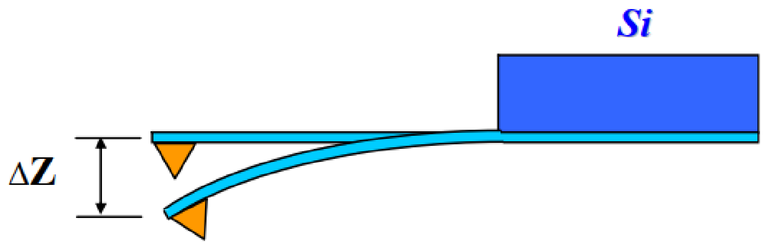

Attractive or repulsive forces

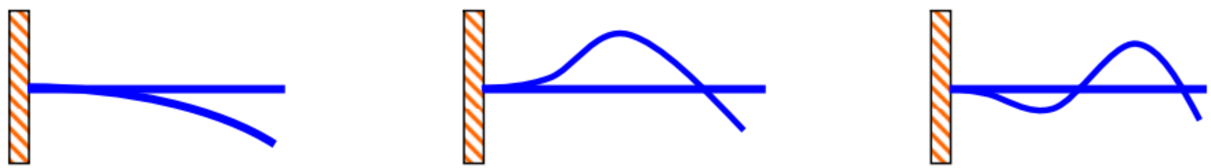



Lateral force

# AFM probes

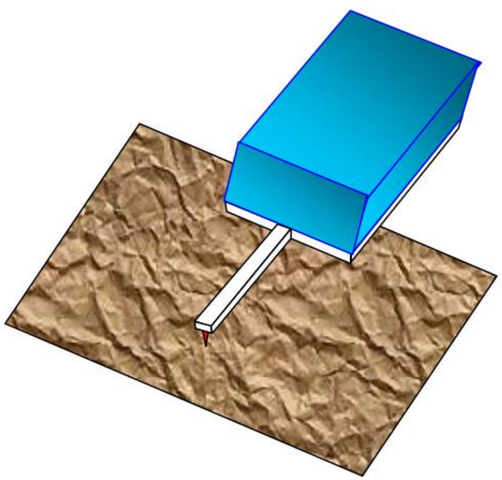
Probes are made of an elastic cantilever with a sharp tip on the end, typically by photolithography and etching of silicon or metal.

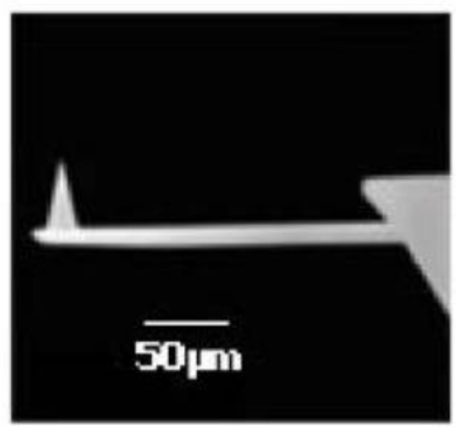


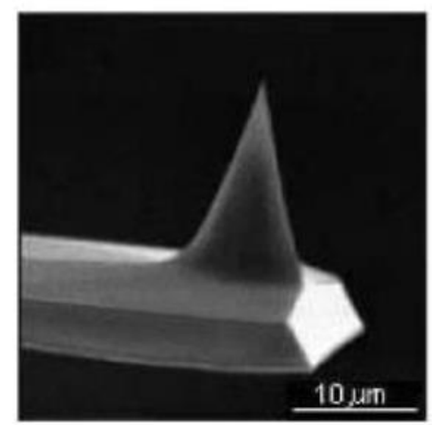



Fundamental mode

Higher-order modes





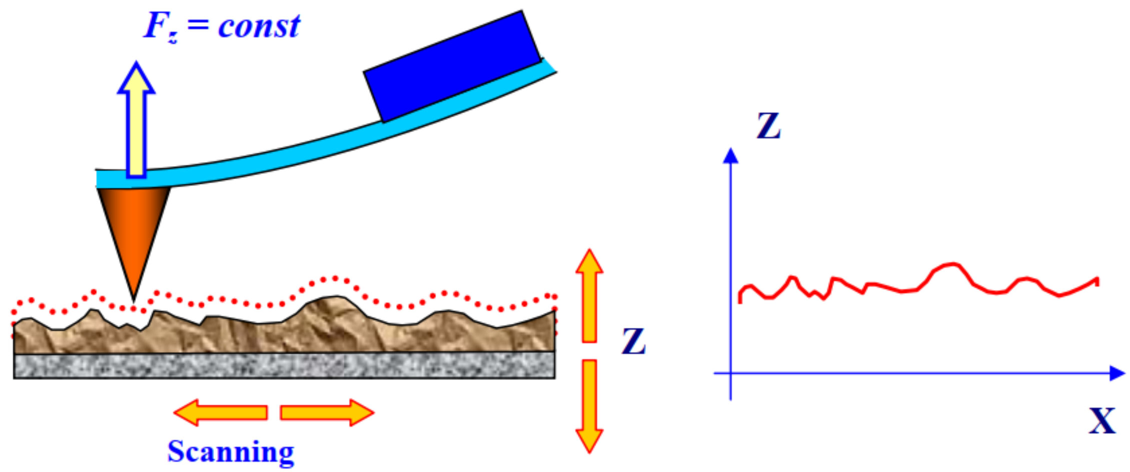



# AFM operation modes

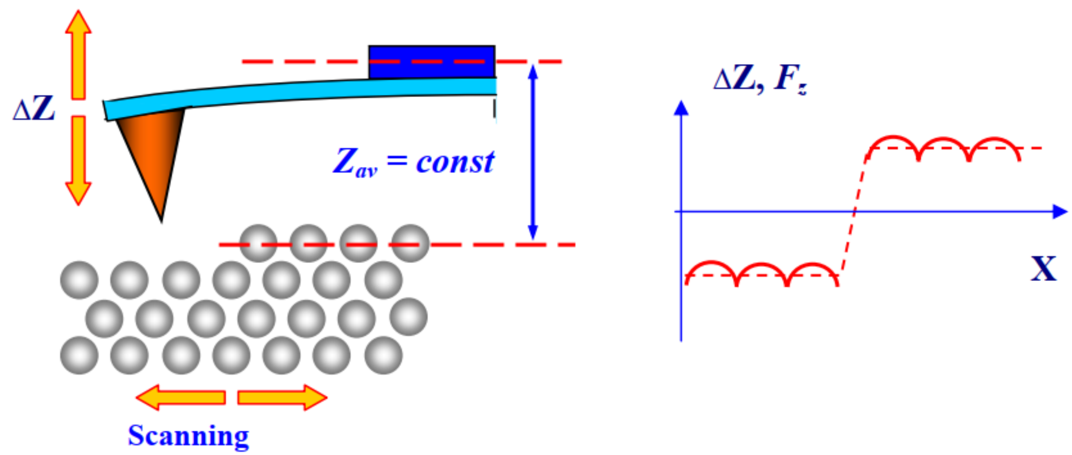


Contact mode AFM operates in the repulsive regime of the tip-sample interaction.

*constant force*




*constant distance*

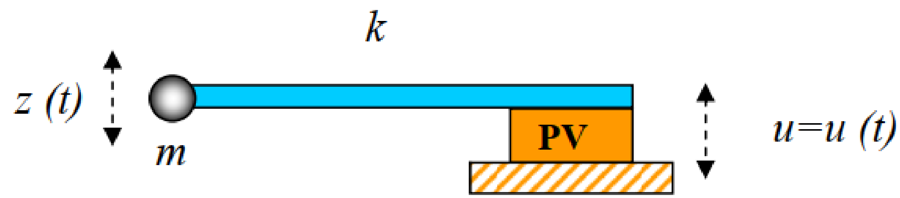



Contact mode is for samples with small roughness and it is good for clean and solid surface.

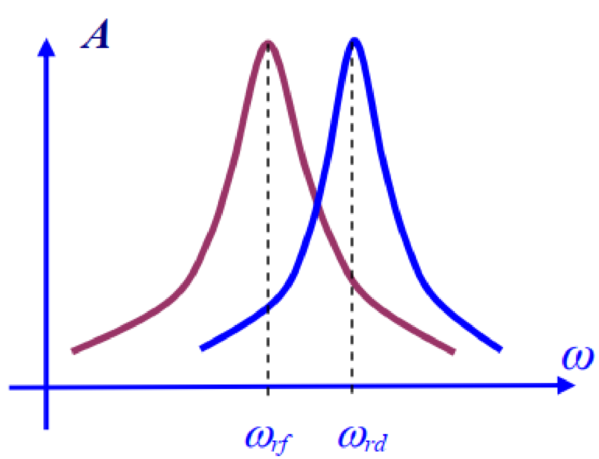
# AFM operation modes

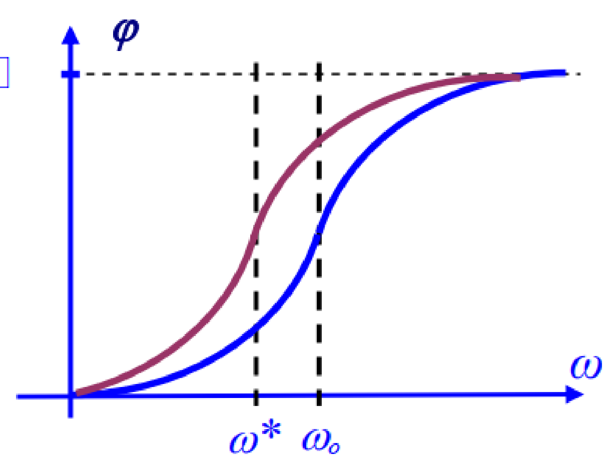


Contactless mode and tapping mode: both depends on *forced oscillations*




$$A(\omega)=\frac{u_0\omega_0^2}{\sqrt{(\omega_0^2-\omega^2)^2+\frac{\omega^2\omega_0^2}{Q^2}}}.\qquad \varphi(\omega)=arctg\left[\frac{\omega\omega_0}{Q(\omega_0^2-\omega^2)}\right].$$




Change of oscillation amplitude and phase due to tip-sample interactions

# AFM operation modes



Contactless mode and tapping mode: both depends on *forced oscillations*

Tapping mode: big oscillations, tip-sample distance < 1 nm.

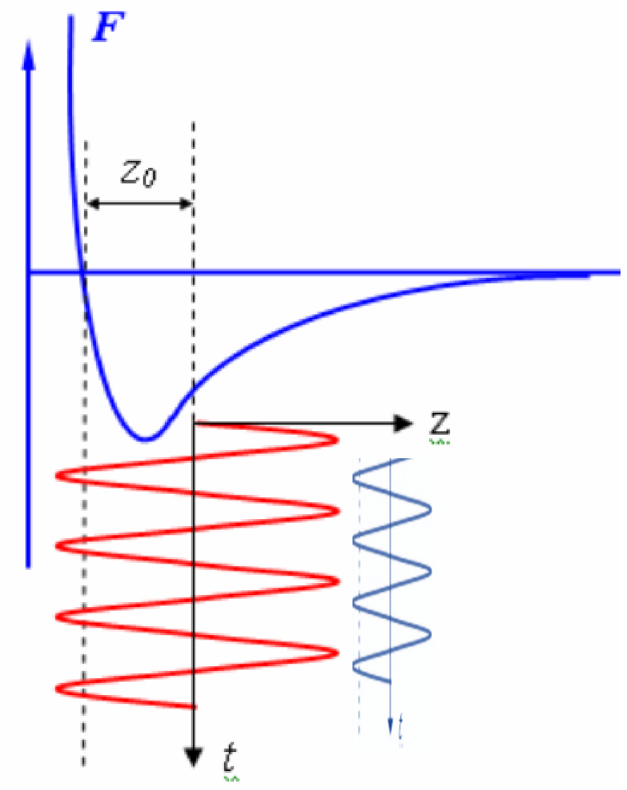
Contactless mode: small oscillations, tip-sample distance > 1 nm.

Both modes measure the amplitude and the phase of cantilever oscillations due to tip-surface interaction.

For tapping mode, sample local stiffness has essential influence on the amplitude and phase changes.

Contactless mode is used mainly for soft liquid surface, e.g. bio samples.

Tapping mode is more widely used in solid materials.

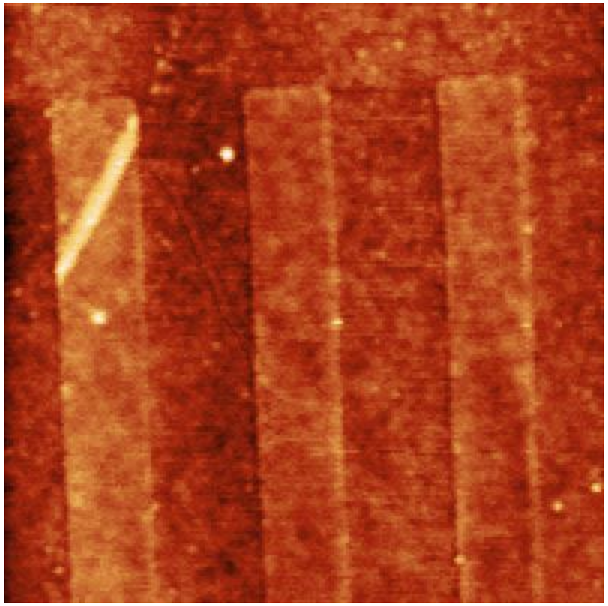



Tapping mode    Contactless mode

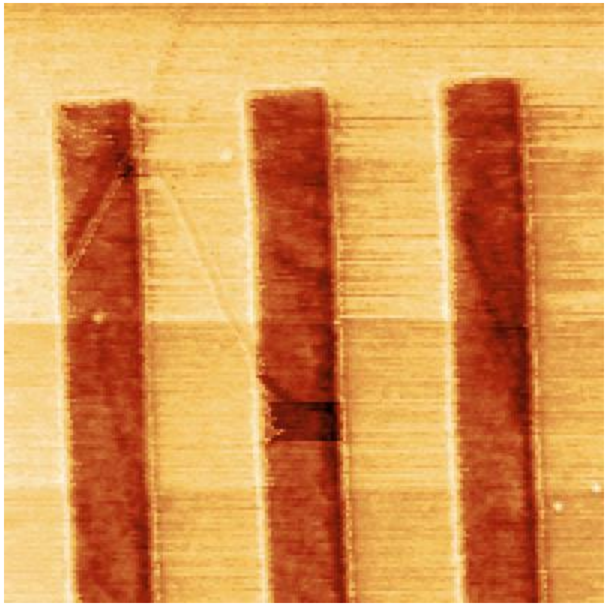
# AFM imaging



Tapping mode AFM images of a polythene film area surface.



Topography



Mechanical Phase
(energy dissipation)

Cantilever oscillations close to a resonant frequency

The AFM keeps the oscillations amplitude constant.

The voltage in the feedback loop is recorded as topographic AFM image of the sample.

The change of the cantilever oscillation phase is also recorded as "phase contrast image"

# 4. E & M force microscopy

THE Ames Laboratory
Creating Materials & Energy Solutions
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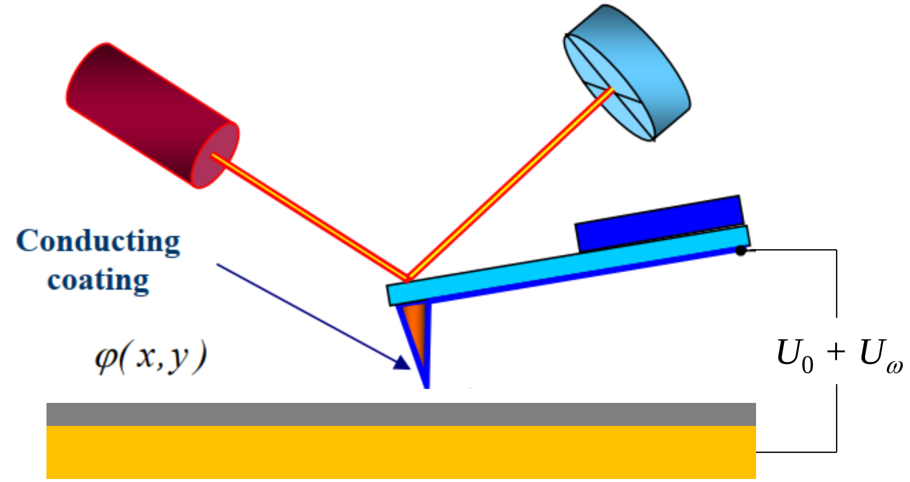
# Electric force microscopy

IOWA STATE UNIVERSITY

In EFM the electric tip-sample interaction is used to collect information on the sample properties

Conductive tips

Conducting substrates or samples




$$U = U_0 + U_1 \cdot sin(\omega t) - \varphi(x,y)$$

$$E = \frac{CU^2}{2}. \qquad \vec{F} = -grad(E)$$

$$F_z = -\frac{\partial E}{\partial z} = -\frac{1}{2}U^2\frac{\partial C}{\partial z} = -\frac{1}{2}\left[U_0 - \varphi(x,y) + U_1 sin(\omega t)\right]^2\frac{\partial C}{\partial z}.$$

$$F_{z(\omega=0)} = -\left\{\frac{1}{2}\left((U_0 - \varphi(x,y))^2 + \frac{1}{2}U_1^2\right)\right\}\frac{\partial C}{\partial z}$$ constant component;

$$F_{z(\omega)} = -\{(U_0 - \boxed{\varphi(x,y)}) \cdot U_1 sin(\omega t)\}\frac{\partial C}{\partial z}$$ component at frequency $\omega$; Measure contact potential difference (Kelvin probe microscopy)

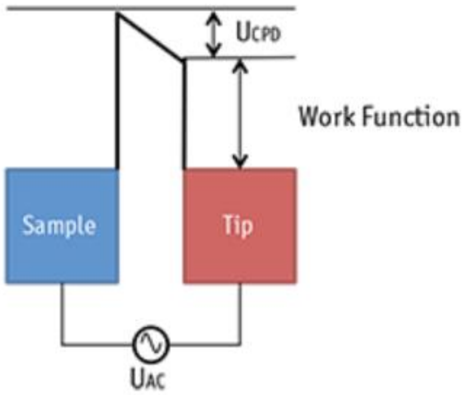
$$F_{z(2\omega)} = \left\{\frac{1}{4}U_1^2 cos(2\omega t)\right\}\boxed{\frac{\partial C}{\partial z}}$$ component at frequency $2\omega$. Measure capacitance derivative (scanning capacitance microscopy)

# Kelvin probe microscopy



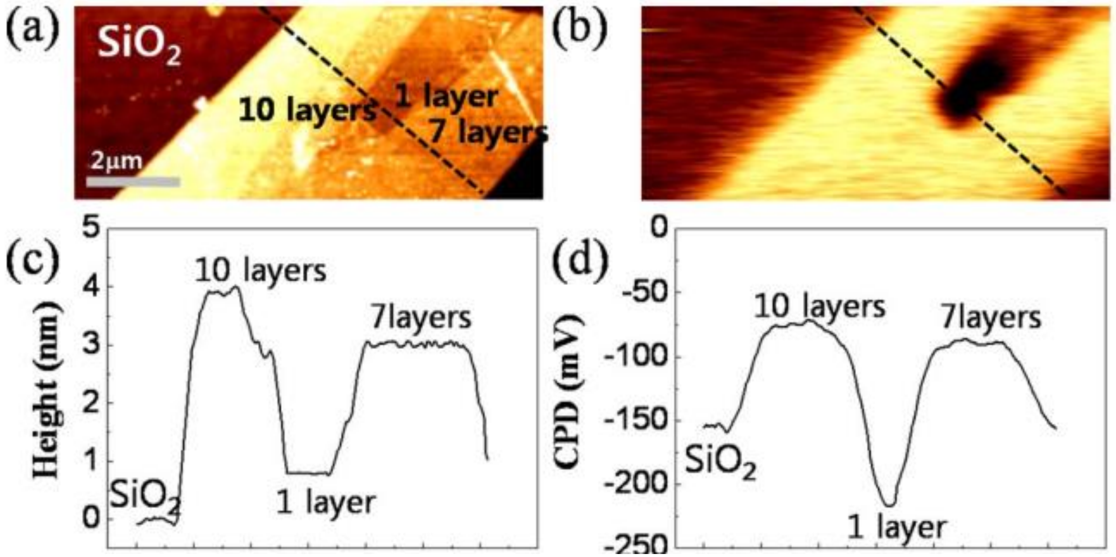
## Kelvin probe microscopy

$$F_{z(\omega)} = -\{(U_0 - \boxed{\varphi(x,y)}) \cdot U_1 \sin(\omega t)\}\frac{\partial C}{\partial z} \quad \text{component at frequency } \omega;$$




$\varphi$ is the contact potential difference (also $U_{CPD}$)

It is the difference of work function of tip *vs* sample




Lee et al. Appl. Phys. Lett. 95, 222107 (2009)

# Kelvin method



A Kelvin probe is a non-contact, non-destructive measurement device used to investigate surface properties of materials. It is a realization of "Kelvin method" with SPM.

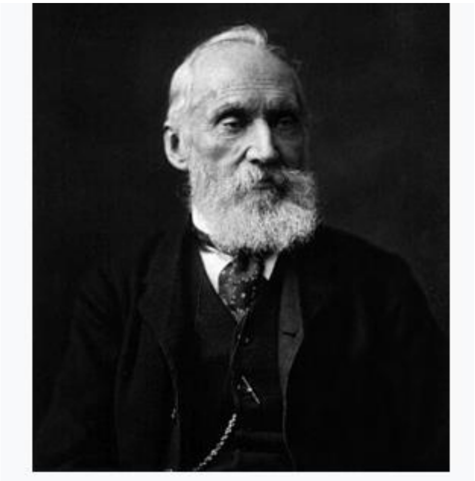
Nonnenmacher et al. APL 58, 2921 (1991)

The Kelvin method is a capacitive probe for measuring surface charge and surface potential.

Lord Kelvin. Philos. Mag. 46, 82-120 (1898).

Blott and Lee, J. Phys. E 2, 785-788 (1969).

The Kelvin method was first proposed by the renowned Scottish scientist Sir William Thomson (later known as Lord Kelvin), in the late 19$^{th}$ Century. He determines the absolution zero temperature.



Lord Kelvin

River Kelvin

# Magnetic force microscopy



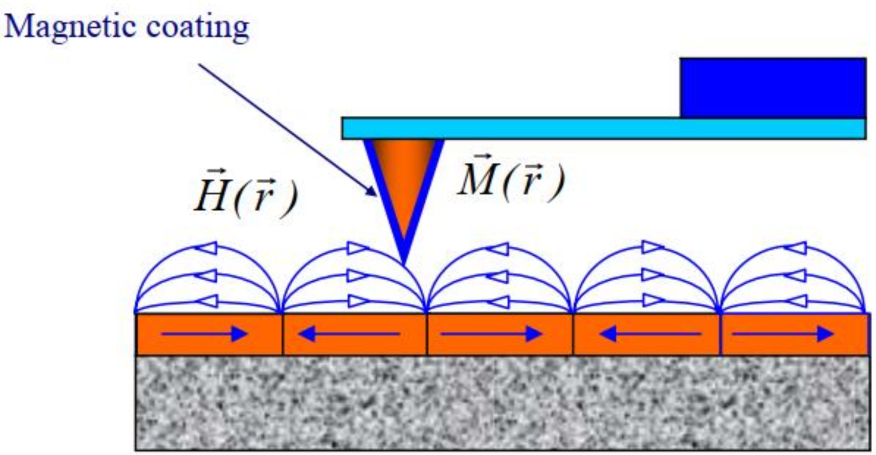
Magnetic force microscope (MFM) is invented for studying local magnetic properties.

magnetic energy of a dipole in a field

$$w = -(\vec{m} \cdot \vec{H}).$$

The force on the magnetic dipole

$$\vec{f} = -grad(w) = \vec{\nabla}(\vec{m} \cdot \vec{H})$$




Normally, only consider z component force if there is only $M_z$

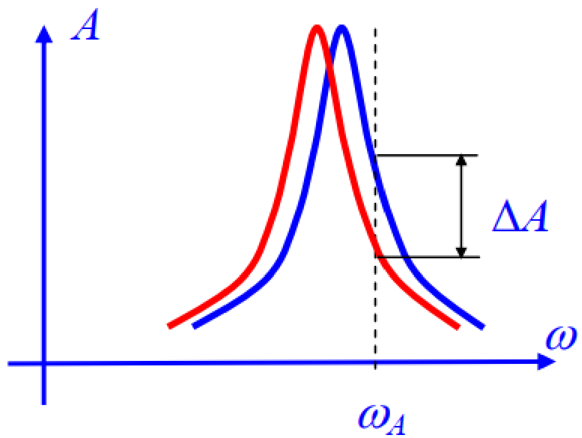
Real tips and samples are not dipoles, so integration is needed for quantitative simulation.

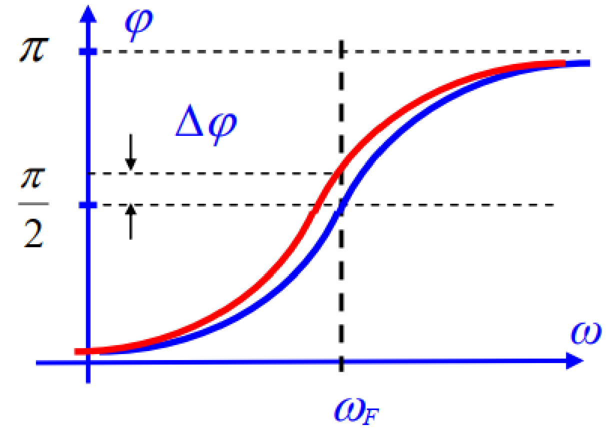
Static MFM technique measures directly the cantilever bending due to magnetic force.

# Magnetic force microscopy

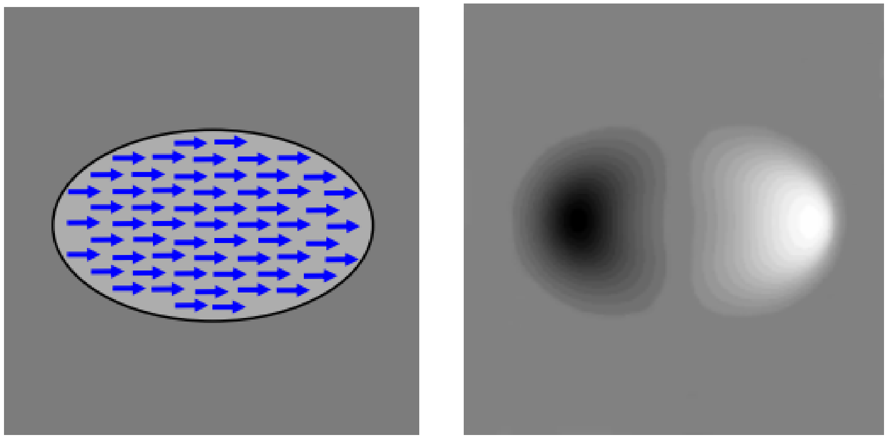


Dynamic MFM technique measures the change of resonance amplitude and phase, which are connected to the z derivatives of the magnetic force

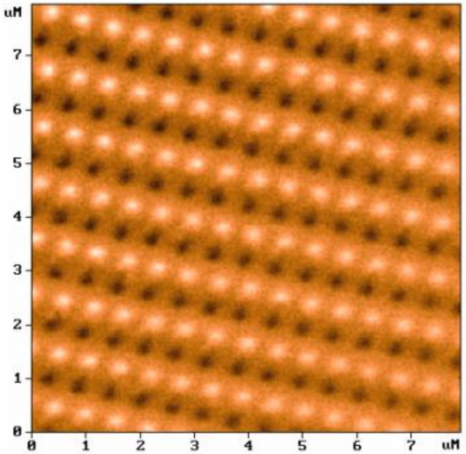



For repulsive force (positive), force gradient is negative, shift of frequency is positive



Modeling of a single magnetized particle




MFM image of an array of particles

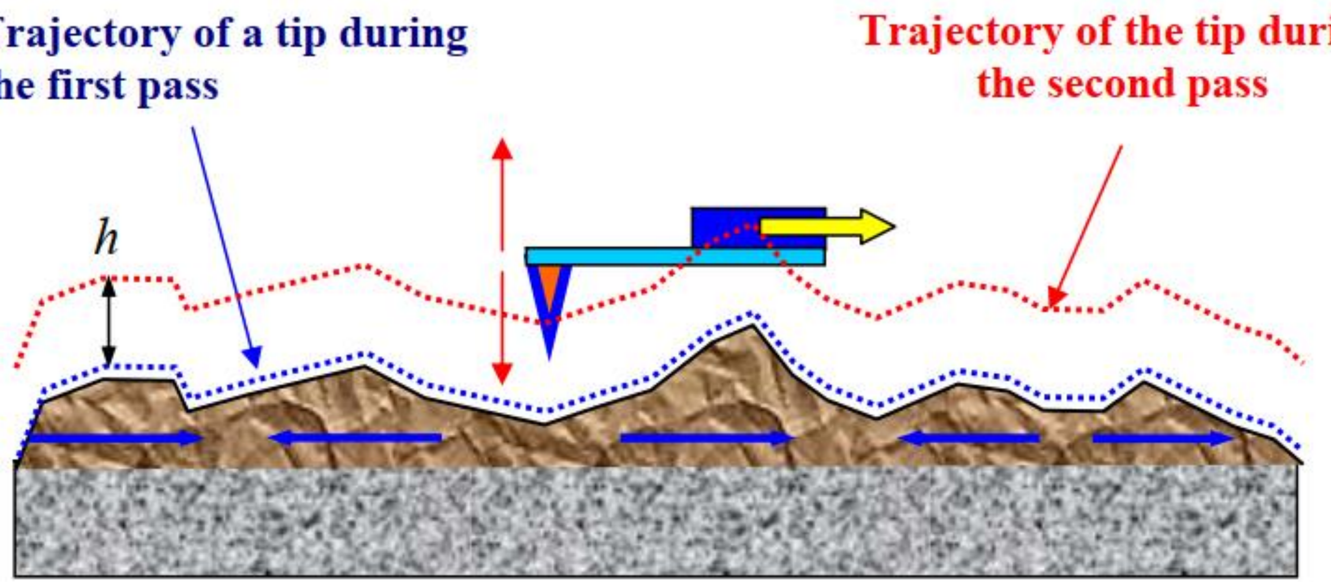
# Two step scanning



To avoid strong atomic force (topographic artifacts) and damage to the tip, normally 2-step scanning is used for both EFM and MFM.

During the first scanning, AFM topography is acquired.

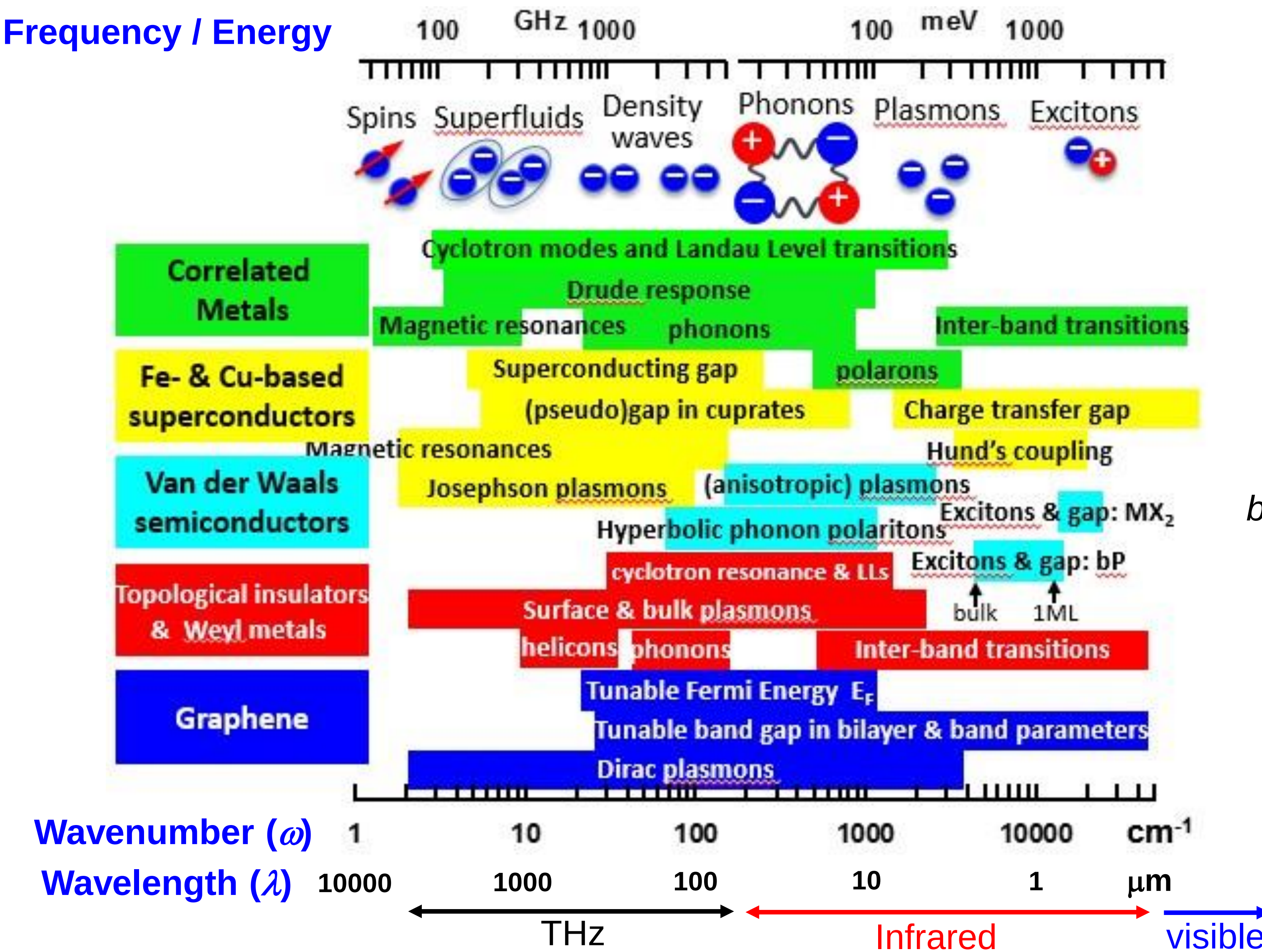
During the second scanning, the tip is slightly away from the substrate (many nanometers, depending on the sample roughness), no strong atomic force, so electrical or magnetic forces dominate.



# 5. Near-field optical microscopy

# Optical spectroscopy





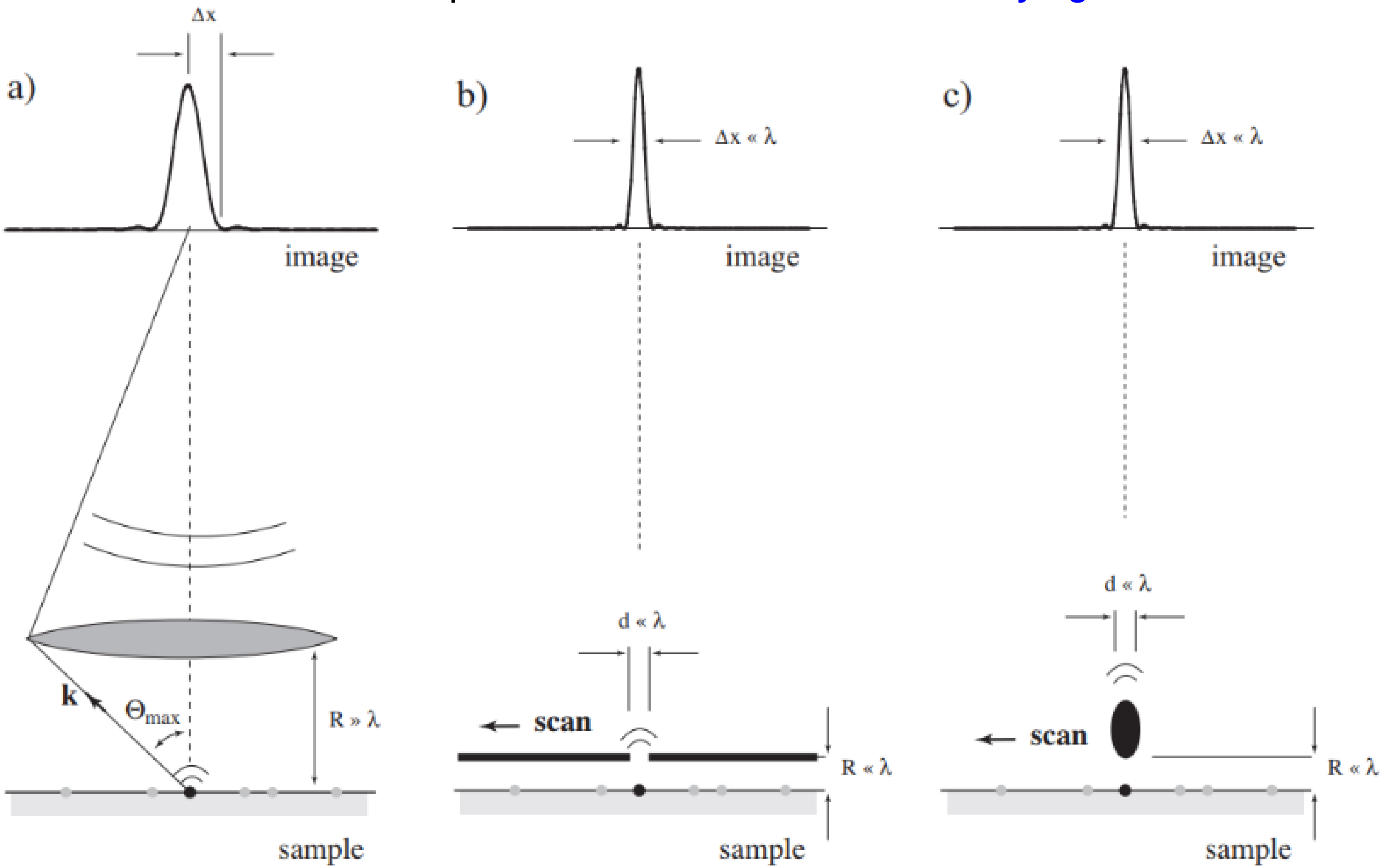

*by* Dimitri Basov

**Diffraction limit: $d \sim \lambda / 2$**

# SNOM



The core of near-field optics is about how to make a tiny light source.



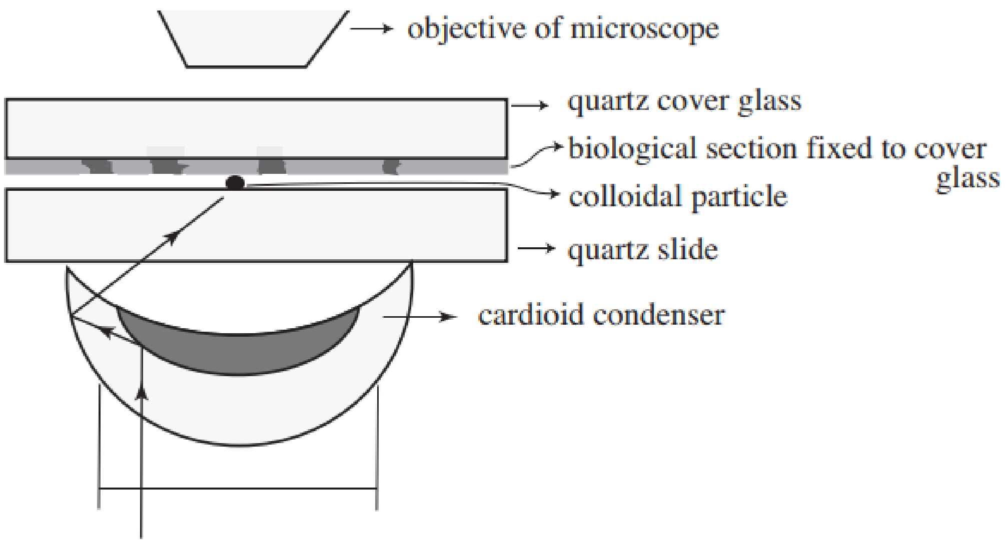

Diffraction limited | Aperture near-field probe | Scattering near-field probe

# Original ideas



In 1928, Irish scientist Edward Hutchinson Synge expressed his ideas of SNOM in his communications with Albert Einstein.

vides a sketch of the apparatus. Fig. 3a shows an adaptation of this sketch. Synge writes "*If a small colloidal particle, e.g. of gold, be deposited upon a quartz slide placed above a Zeiss cardioid condenser of NA 1.05, then, all rays of light from the condenser which reach the surface of the slide will be totally reflected by the surface, except those which strike the surface at the base of the particle. These will be scattered in all directions and if the objective of a microscope is suitably arranged above the slide, a proportion of the rays so scattered will come to a focus in the eye of an observer, or upon a photographic plate, or a*



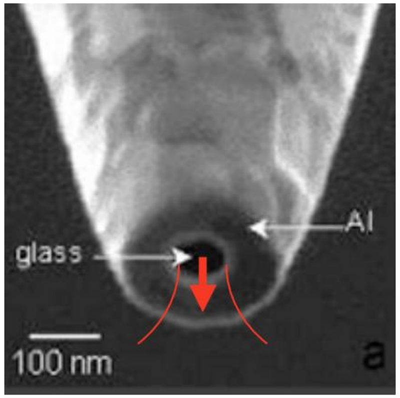
# Original ideas



In his reply, Einstein states that Synge's basic idea is correct but no use. Instead, he suggests of using the light that penetrates through a tiny hole in an opaque layer as a light source.

that time), Synge replies to Einstein's letter and states "*It was my original idea to have a very small hole in an opaque plate, as you suggest, and it was in this form that I had mentioned it to several people.*" In the same letter Synge suggests what later became the most standard way of fabricating aperture probes used in near-field optical microscopy: "*A better way could be, if one could construct a little cone or pyramid of quartz glass having its point P brought to a sharpness of order* $10^{-6}$ *cm. One could then coat the sides and point with some suitable metal (e.g. in a vacuum tube) and then remove the metal from the point, until P was just exposed. I do not think such a thing would be beyond the capacities of a clever experimentalist.*" In a following paragraph Synge states that he is

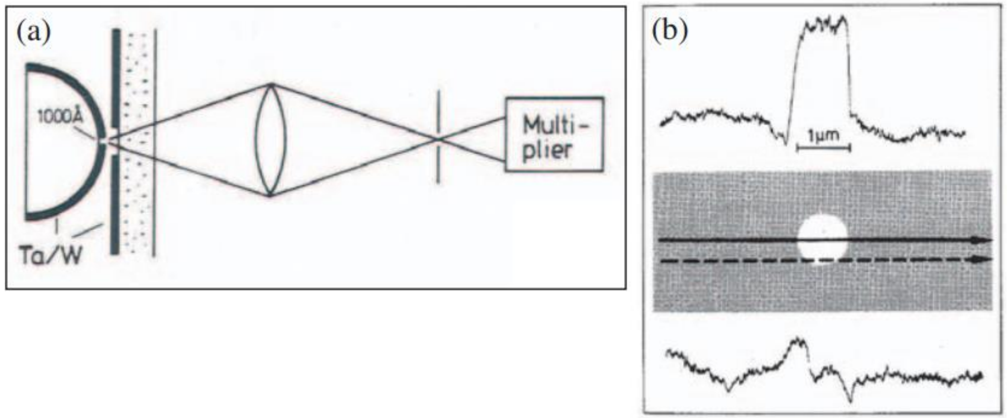
In his 1932 paper, Synge suggested the use of piezo-electric quartz crystals for rapidly and accurately scanning the specimen.



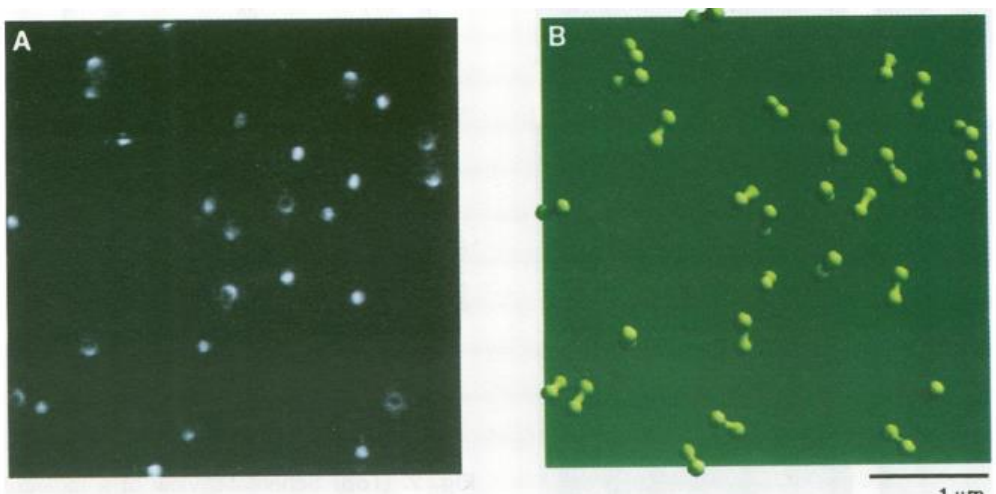
# Aperture SNOM

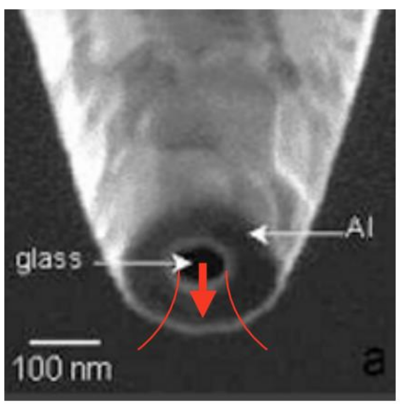


First aperture SNOM experiments performed by Dieter W. Pohl and Ulrich Ch. Fischer (1982-1983).




Later Eric Betzig and co-workers (1991) demonstrated single molecule detection with a-SNOM. This is the first demonstration of the modern version of a-SNOM.

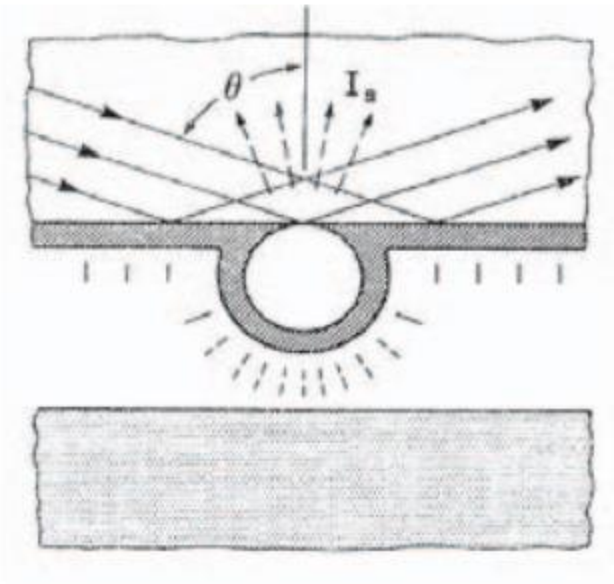


# Scattering SNOM



First scattering SNOM experiments also performed by Dieter W. Pohl and Ulrich Ch. Fischer (1988-1989) by using a gold coated nanoparticle as a scatter.




Particle probe

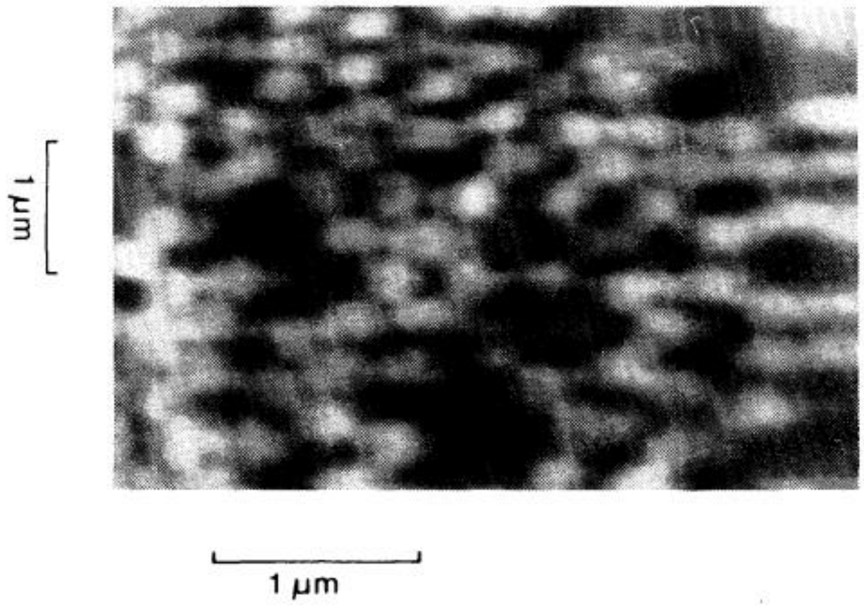


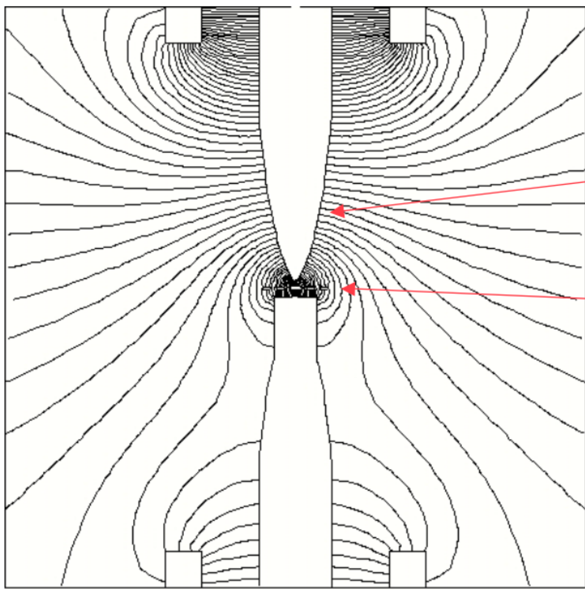

Image of holes in metal films

# Scattering SNOM



B. Knoll, F. Keilmann and students innovated the design of s-SNOM and make it popular.

## Near-field microwave imaging



coaxial cable from source

inner conductor sharpened to concentrate field lines

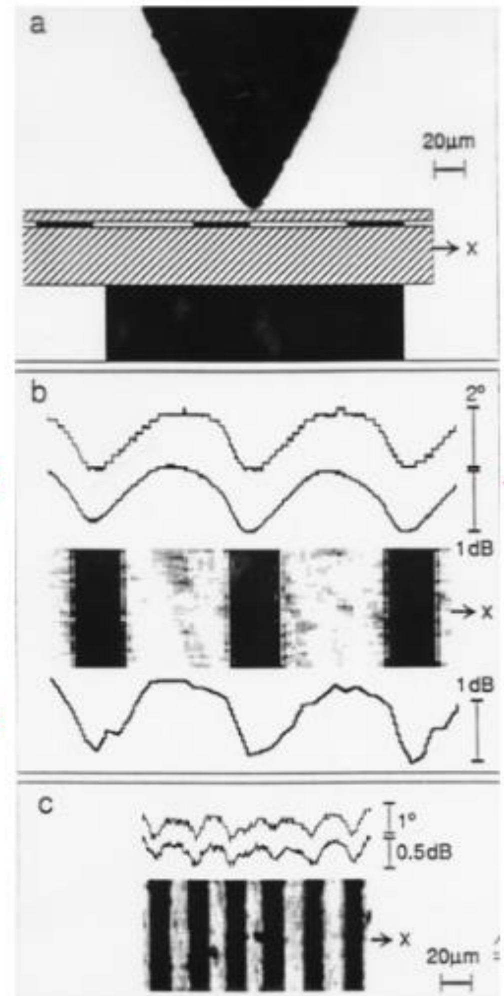
microstructured sample in "tip focus"

coaxial cable to receiver

B. Knoll and F. Keilmann, APL 70, 2667-2669 (1997).

700 MHz

7 MHz




wavelength

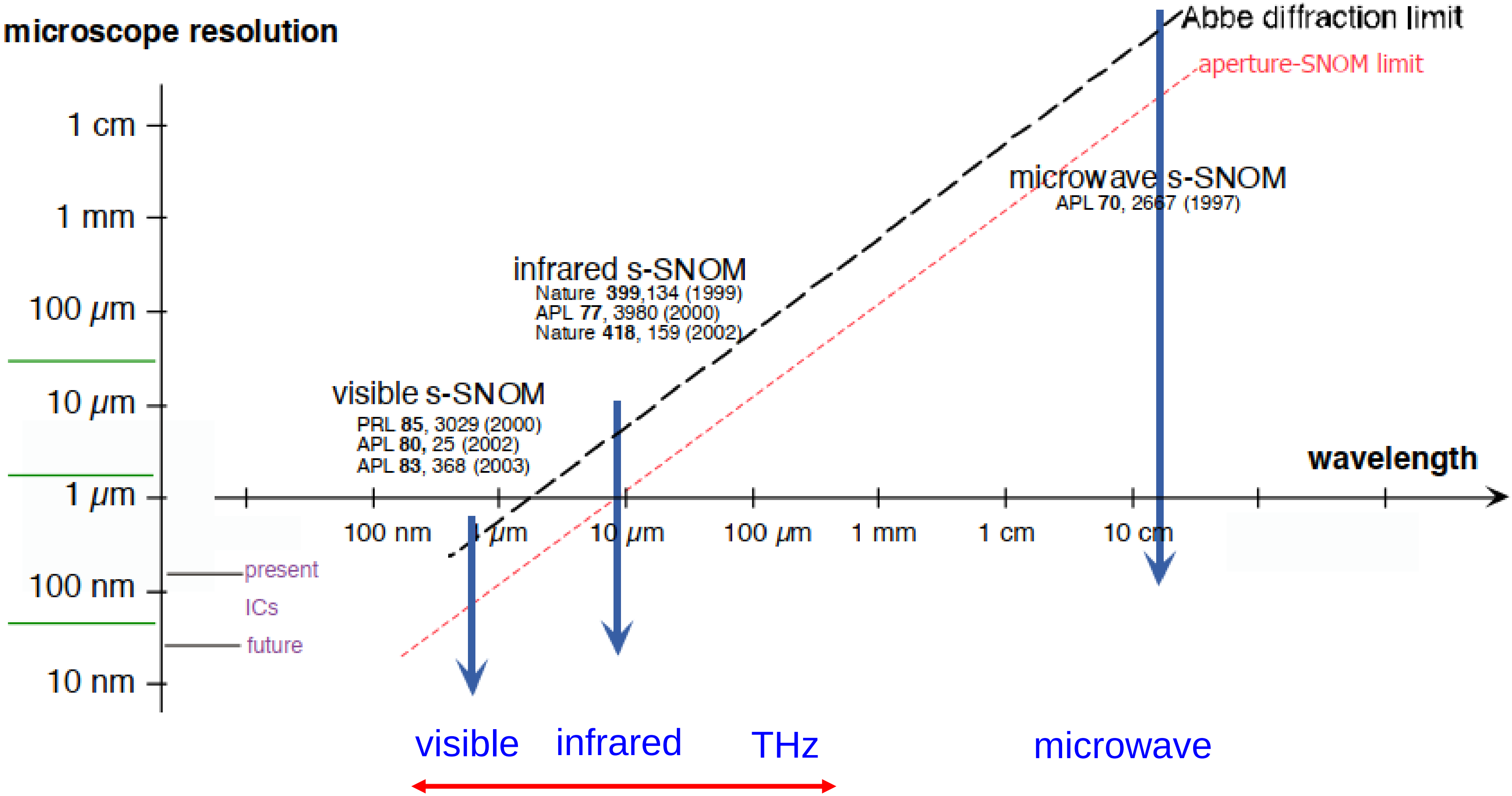
43 cm

4.3 m

# Scattering SNOM



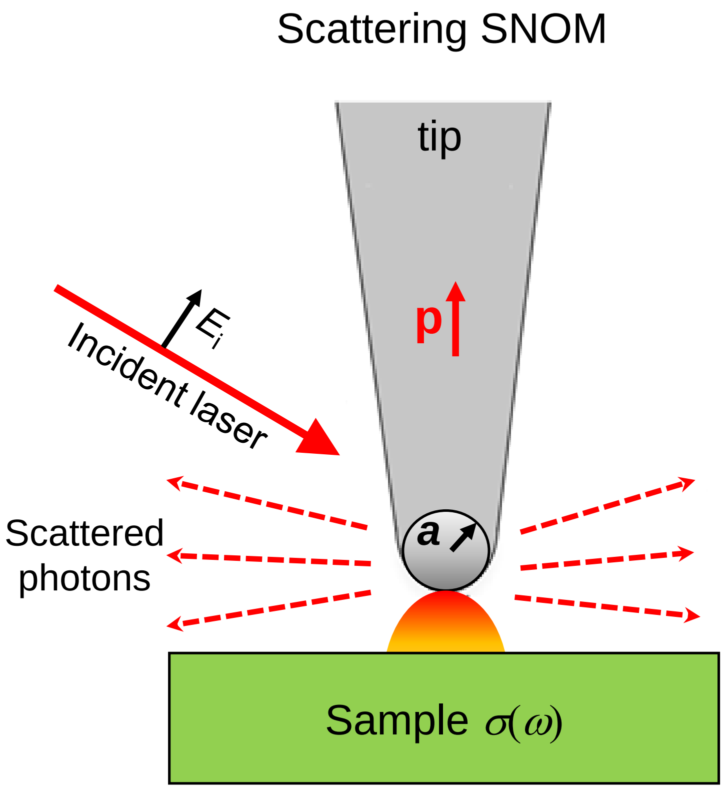
B. Knoll, F. Keilmann and students innovated the design of s-SNOM and make it popular.




One s-SNOM apparatus works for the entire range from visible to THz

# Principles of s-SNOM






Knoll & Keilmann Nature (1999)
Knoll et al. APL (1997)

✓Strong field enhancement 10-100 x

✓High spatial resolution ~ 10 nm

✓Finite momenta 0 – 0.2 nm$^{-1}$

✓Sensitive to $\sigma(\omega)$ and **E**

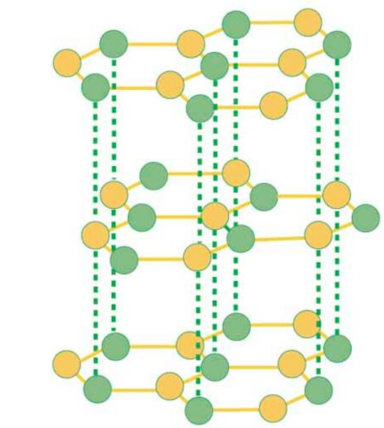
Capable of probing conductivity, phonons, plasmons, excitons, magnons

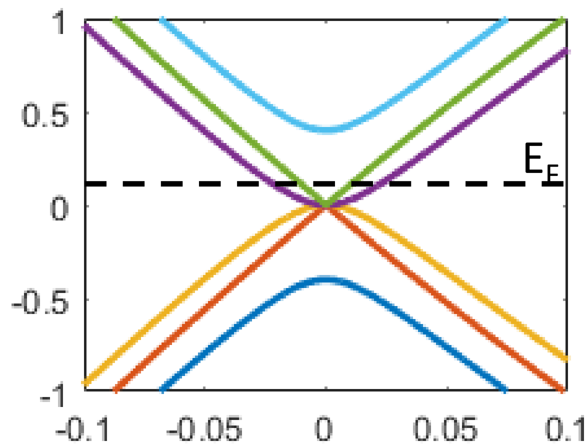
by imaging and spectroscopy with ~10 nm resolution.

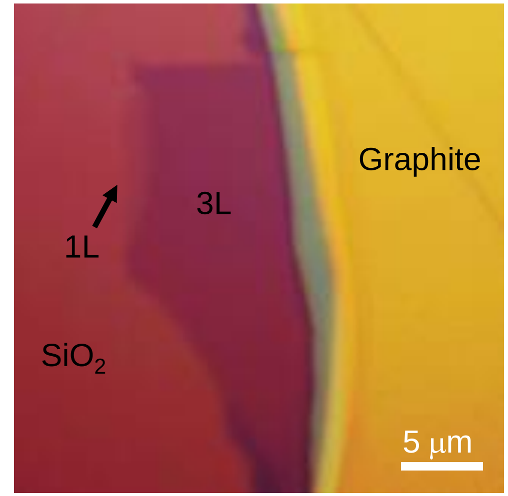
# Trilayer graphene

## Conductivity mapping

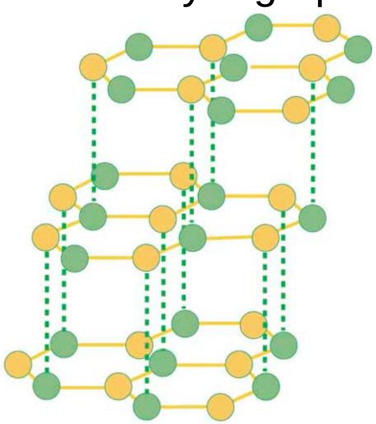
ABA trilayer graphene

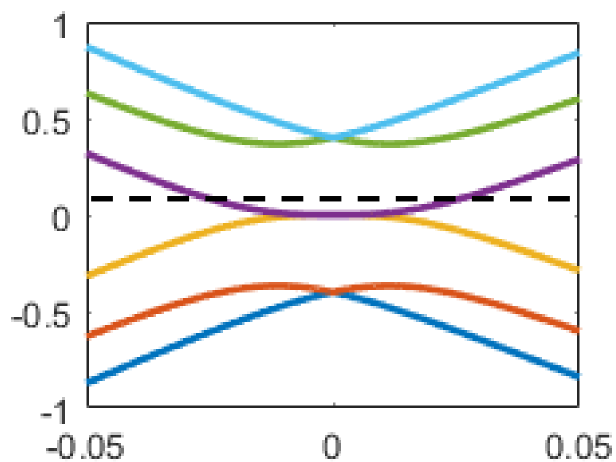


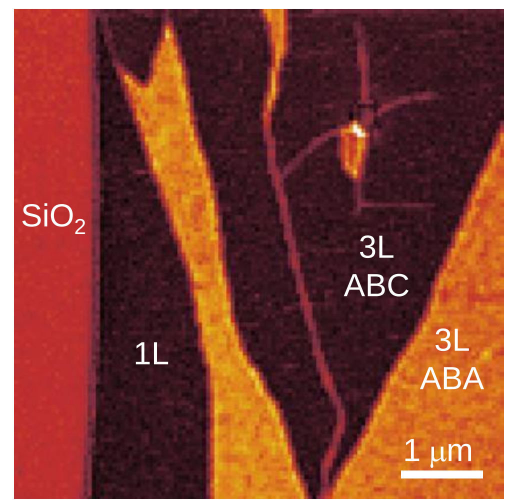



ABC trilayer graphene





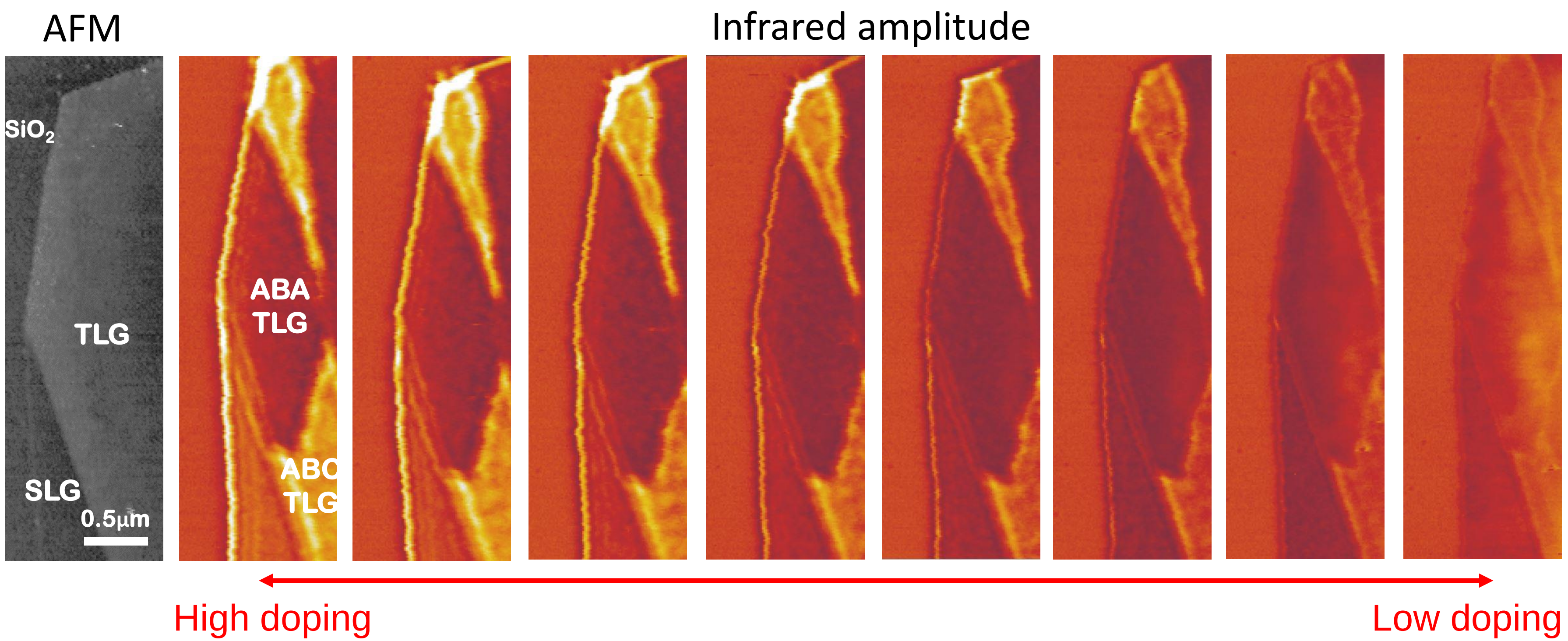




Conductivity mapping

**Work in progress**

# Trilayer graphene

## Plasmon imaging



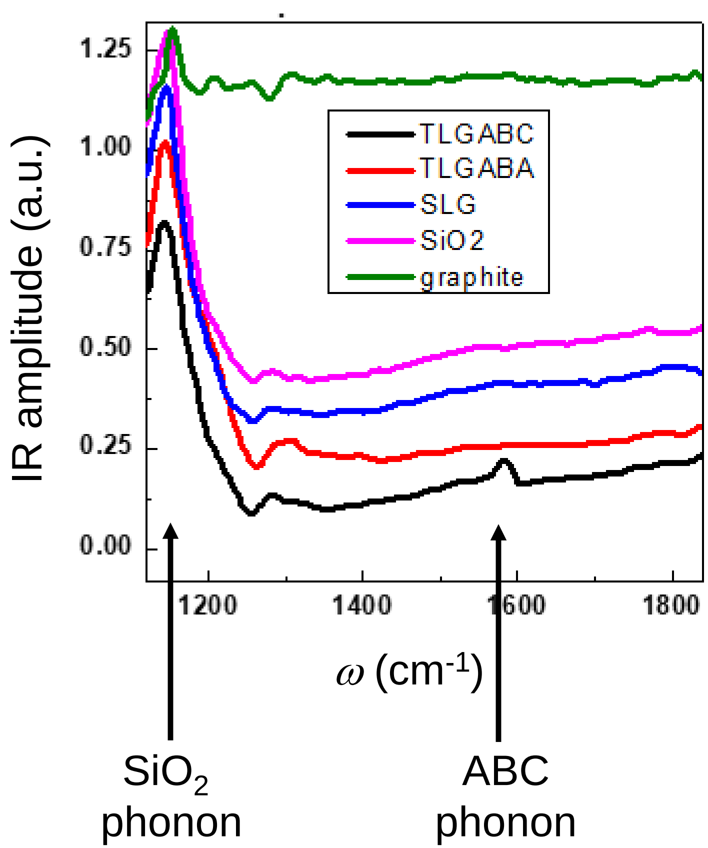

Images shown plasmon interference fringes close to the edges and boundaries.

**Work in progress**

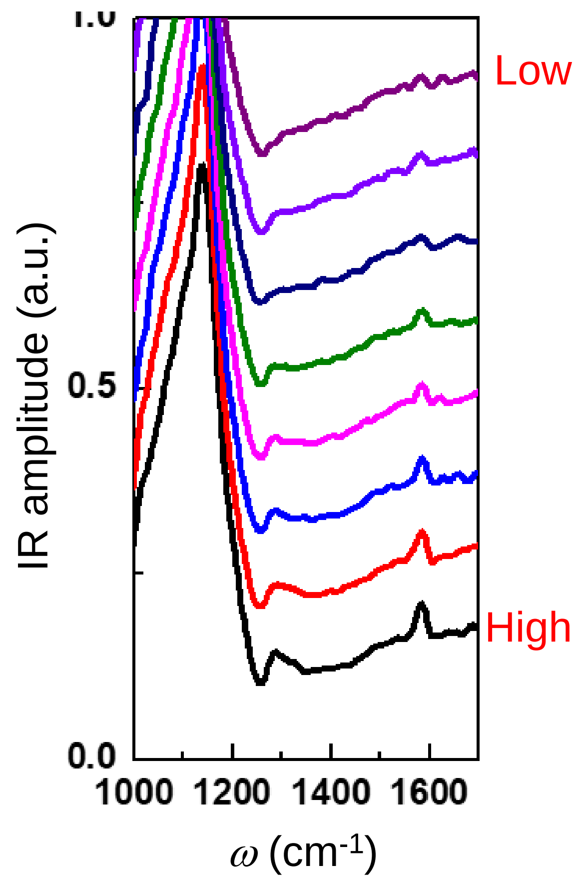
# Trilayer graphene



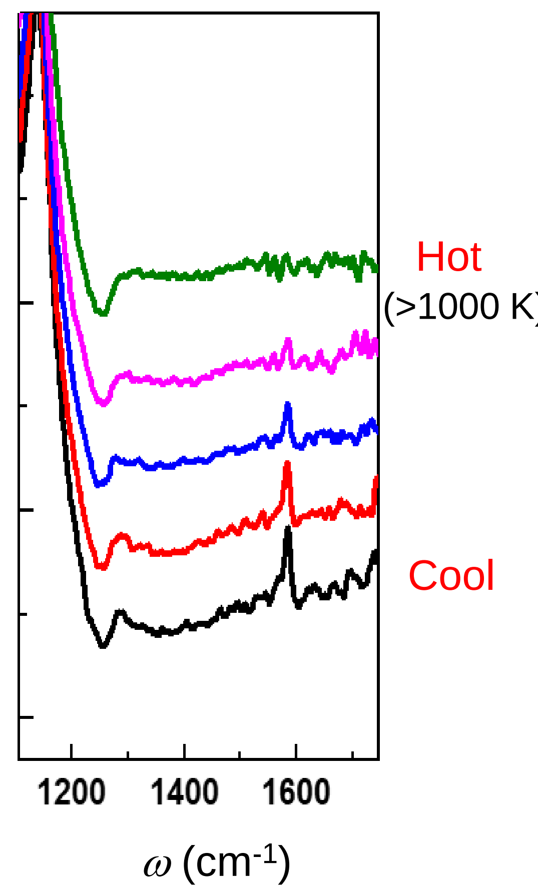
## Phonon spectroscopy




### Doping dependence




### T dependence




**Work in progress**

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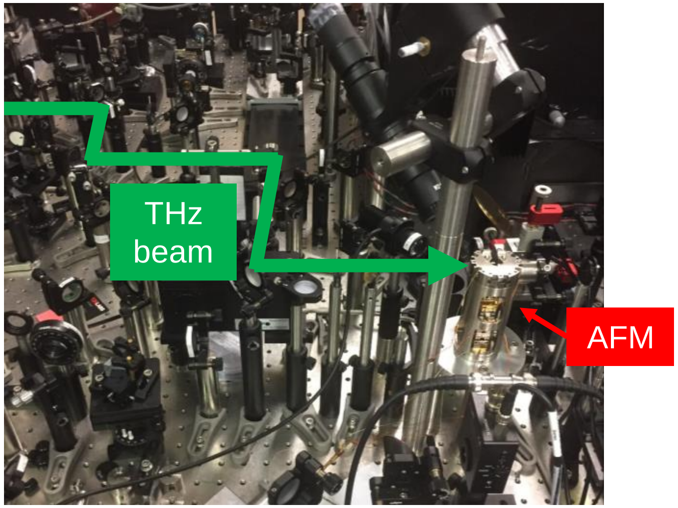
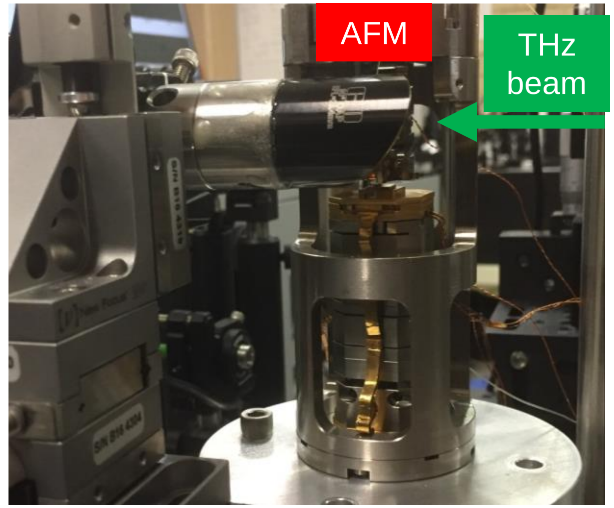
# THz s-SNOM

IOWA STATE UNIVERSITY

Nanoscope testing platform



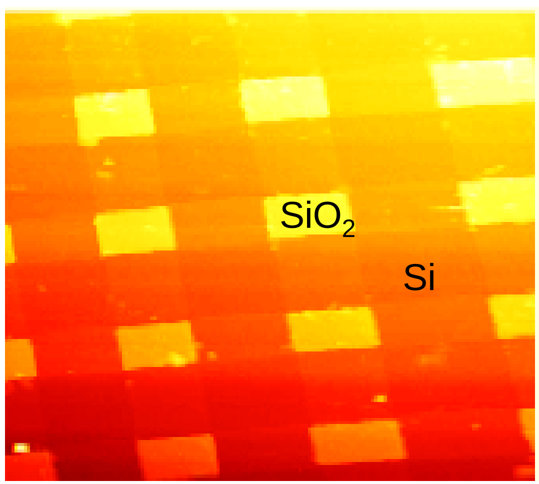

Nanoscope



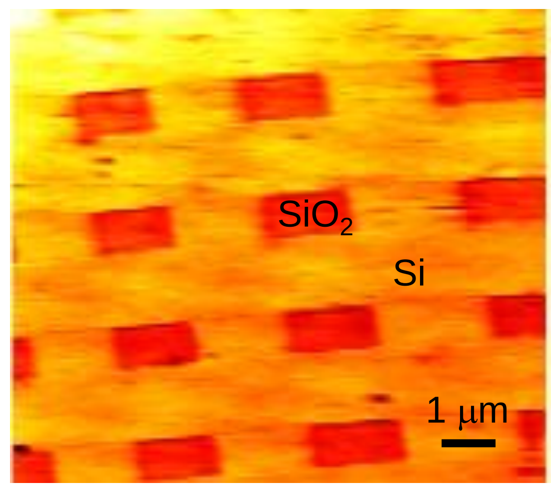

Cryostat

Test scanning THz s-SNOM

W.M. KECK FOUNDATION




Topography



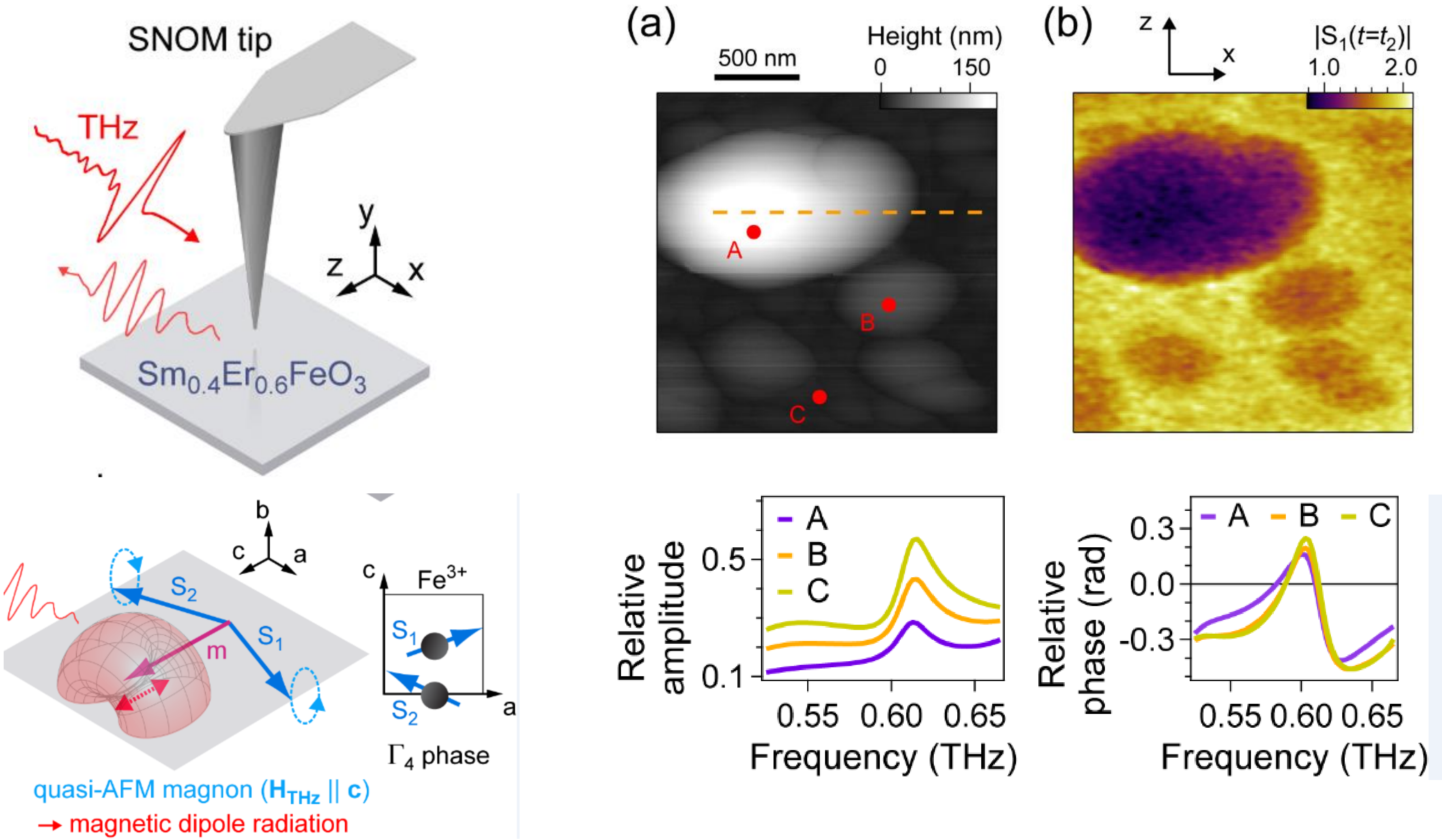

THz amplitude

$\lambda \sim 300\mu m$

Resolution < 100nm

# Magnons

THz near-field studies of magnons in a rare-earth orthoferrite (**with Jigang's group**).

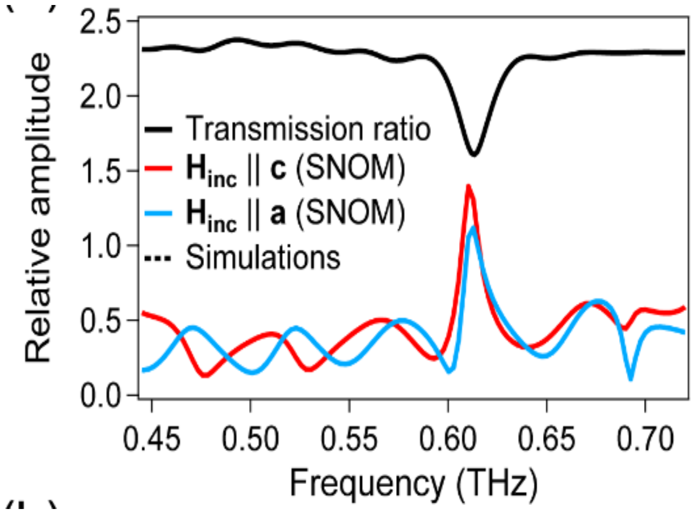



**Manuscript in preparation**

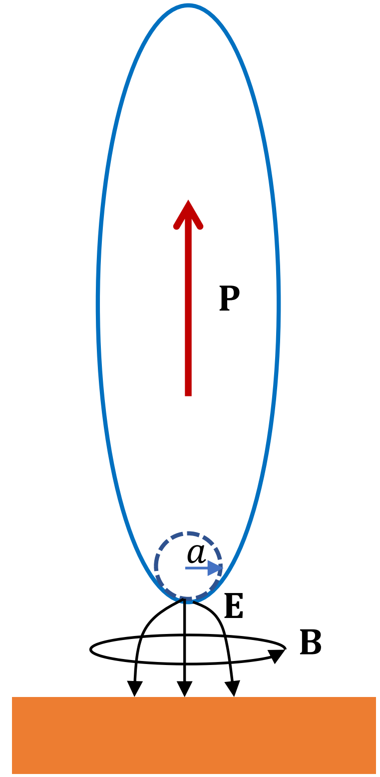
# Magnons



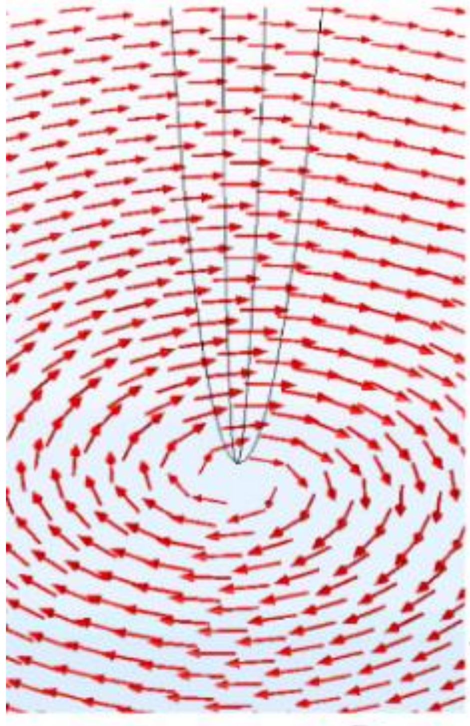
No magnetic anisotropy observed → consistent with near-field optics.




Rotating sample by 90 degrees




**H field**



Simulation by Thomas Koschny

**Manuscript in preparation**

**Thank you very much!**