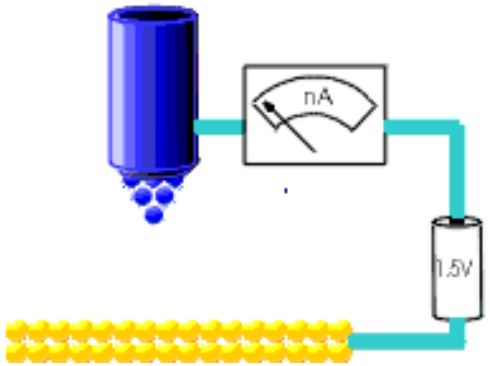
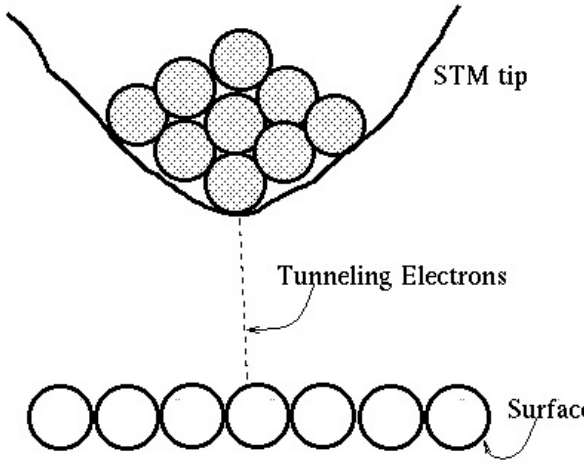
Lecture 6 Scanning Tunneling Microscopy (STM)

- General components of STM;
- Tunneling current;
- Feedback system;
- Tip --- the probe.



Brief Overview of STM

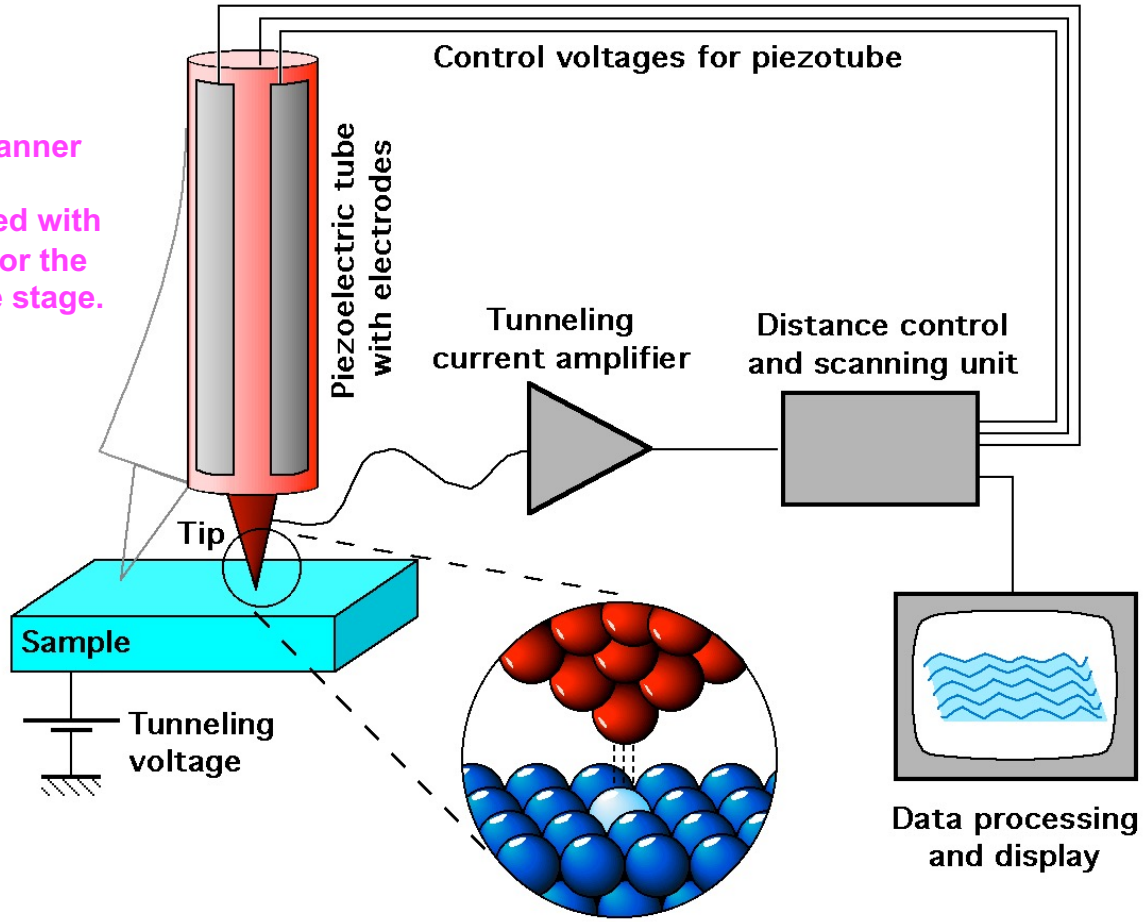
The Scanning Tunneling Microscope



The Scanning Tunneling Microscope (STM) was developed by Gerd Binnig and Heinrich Rohrer at IBM. When a metal tip is brought near a conducting surface, electrons can tunnel from the tip to the surface or vice–versa. Because the tunneling probability is exponentially dependent on the distance the contours of the surface can be mapped out by keeping the current constant and measuring the height of the tip. In this way, atomic resolution can be obtained. For their work, Binnig and Rohrer shared the 1986 Nobel Prize.

Basic components of STM:

The scanner can be mounted with the tip or the sample stage.



Five basic components:

1. Metal tip,
2. Piezoelectric scanner,
3. Current amplifier (nA),
4. Bipotentiostat (bias),
5. Feedback loop (current).

- Tunneling current from tip to sample or vice-versa depending on bias;
- Current is exponentially dependent on distance;
- Raster scanning gives 2D image;
- Feedback is normally based on constant current, thus measuring the height on surface.

Inventors of STM

The Nobel Prize in Physics 1986

Nobel Laureates Heinrich Rohrer and Gerd Binnig

Brief History of STM

- The first member of SPM family, scanning tunneling microscopy (STM), was developed In 1982, by Gerd Binnig and Heinrich Rohrer at IBM in Zurich created the ideas of STM (Phys. Rev. Lett., 1982, vol 49, p57). Both of the two people won 1986 Nobel prize in physics for their brilliant invention.

Nobel Laureates Heinrich Rohrer and Gerd Binnig (B. 1947)

STM is really small in size.

STM Tips

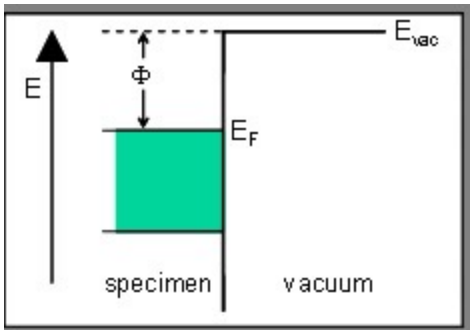
- STM tip should be conducting (metals, like Pt);
- STM plays with the very top (outermost) atom at the tip and the nearest atom on sample; so the whole tip is not necessarily very sharp in shape, different from the case of AFM, where spatial "contact" is necessary and crucial for feedback.
- **How do we obtain these wonderful tunneling tips where only one atom is at the top?**

  Answer: really easy to obtain such tips, simply by cutting a thin metal wire using a wire cutter --- *there is always a single atom left over at the very top.*

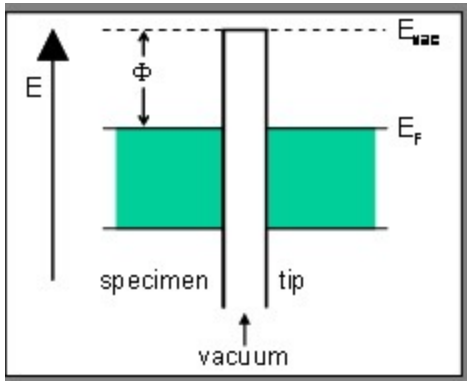
Tunneling Current

a result of the overlap of tip and sample electron wavefunctions

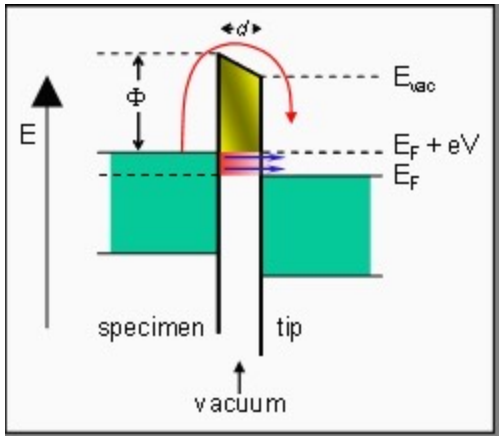
Two requirements: 1. small distance --- electron wavefunction overlap
2. bias --- for net current flow.



In a metal, the energy levels of the electrons are filled up to a particular energy, known as the 'Fermi energy' E_F. In order for an electron to leave the metal, it needs an additional amount of energy Φ, the so-called 'work function'.

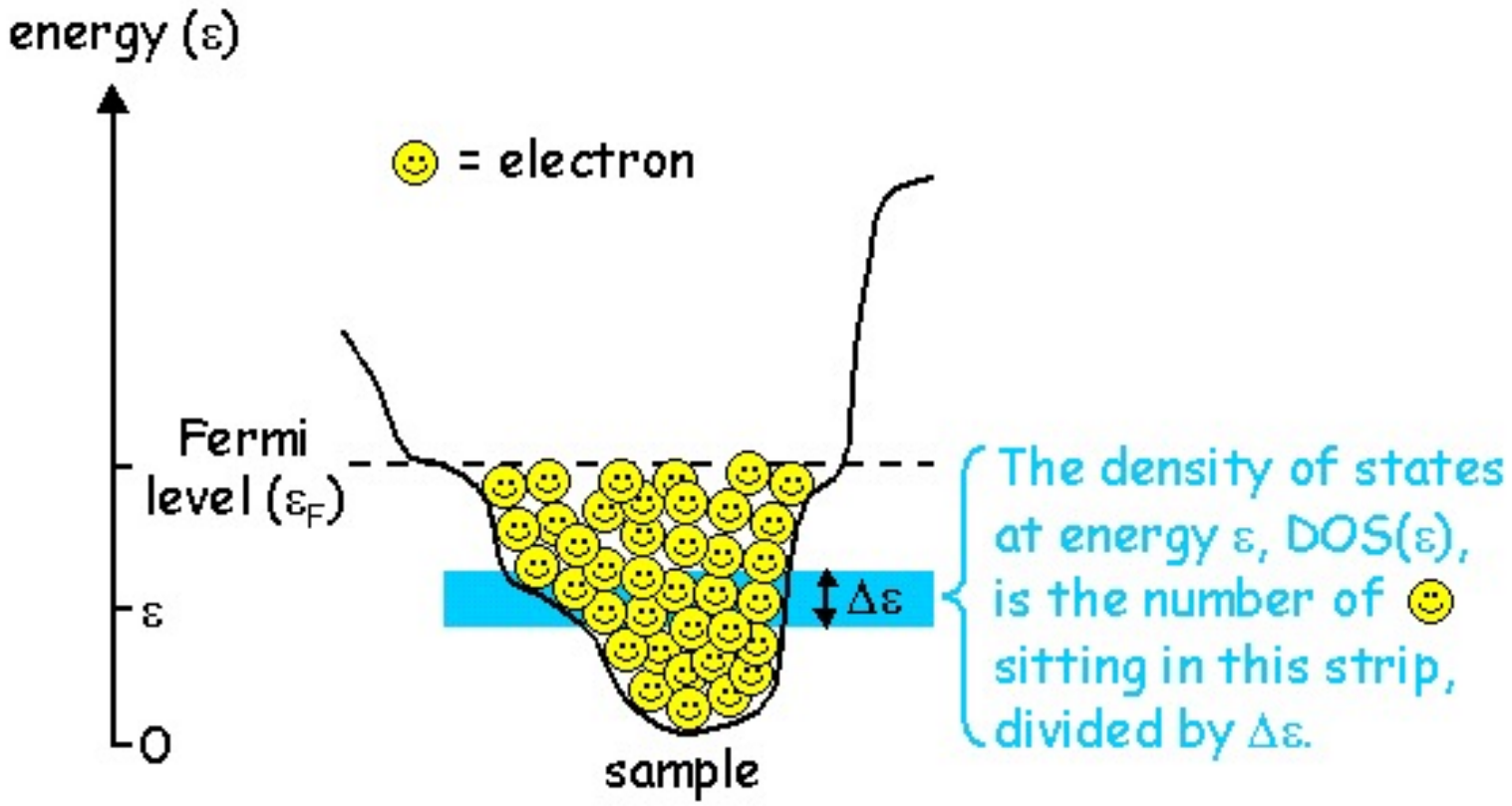


When the specimen and the tip are brought close to each other, there is only a narrow region of empty space left between them. On either side, the electrons are present up to the Fermi energy. They need to overcome a barrier Φ to travel from tip to specimen or vice versa.



If the distance d between specimen and tip is small enough, electrons can 'tunnel' through the vacuum barrier. When a voltage V is applied between specimen and tip, the tunneling effect results in a net electron current. In this example from specimen to tip. This is the tunneling current.

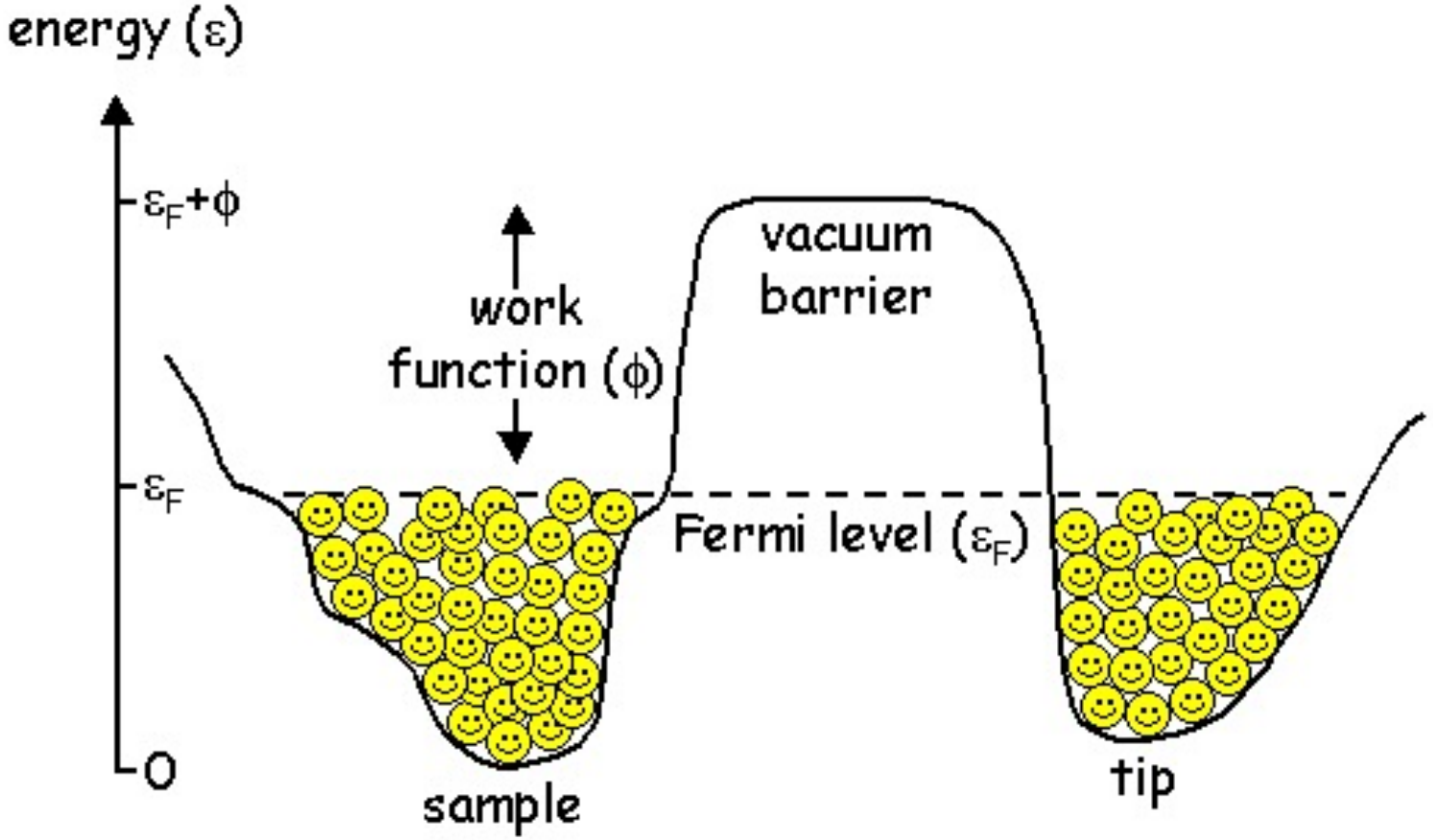
Electron density of states: Fermi level



Electron density of states: Fermi level

- The electrons fill up the energy valley in the sample until there are no more electrons.
- The top energy level at which electrons sit is called the Fermi level, ε_F.
- For every energy ε, the density of states is the number of electrons sitting within $\Delta\varepsilon$ of ε, divided by $\Delta\varepsilon$. So, for the energy shown above as a blue strip, DOS(ε) is approximately 7 / $\Delta\varepsilon$.

Tip and Sample: lined up exactly under zero bias

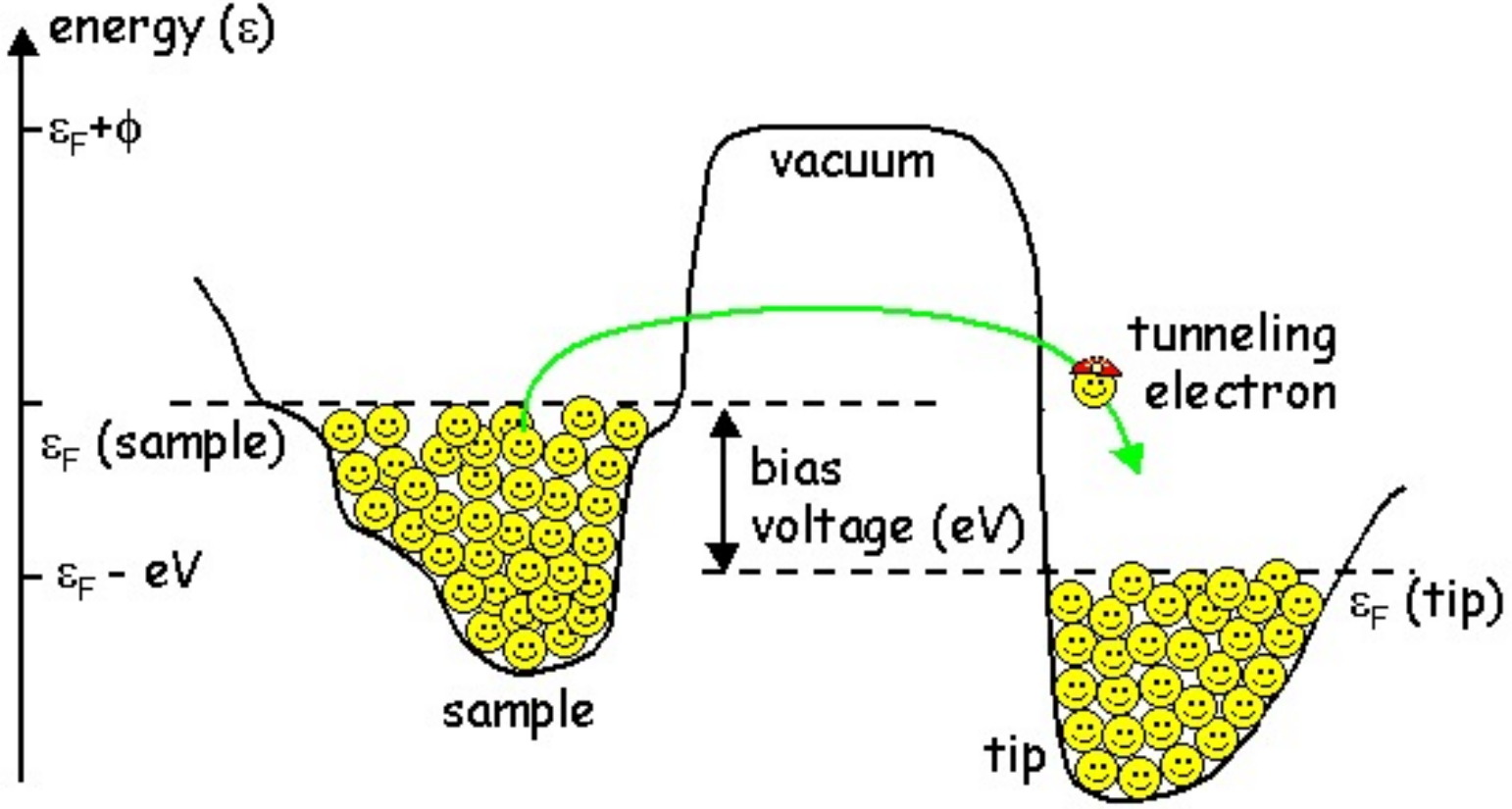


The electrons in the tip and the sample are sitting in two separate valleys, separated by a hill which is the vacuum barrier.

Electron density of states: Fermi level

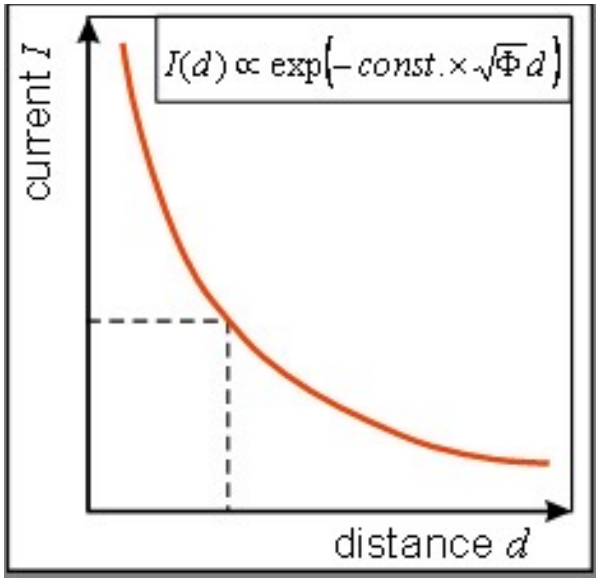
- Electrons are happy sitting in either the tip or the sample, i.e. they're sitting in nice energy valleys.
- It takes energy to remove an electron into free space. We can think of the vacuum around the tip as an energy hill that the electron would need to climb in order to escape. The height of this energy hill is called the work function, ϕ.
- In order to bring an electron up and *over* the vacuum energy barrier from the tip into the sample (or vice versa), we would need to supply a very large amount of energy.
- Climbing hills is hard work!
- Luckily for us, quantum mechanics tells us that the electron can tunnel right *through* the barrier. Note: *this only works for particles (with both wave and particle characteristics, i.e., wave-particle duality), not for macroscopic objects*. **Don't you try walking through any closed doors!** ☺
- As long as both the tip and the sample are held at the same electrical potential, their Fermi levels line up exactly. There are no empty states on either side available for tunneling into! This is why we apply a bias voltage between the tip and the sample.

Tunneling current at bias



By applying a bias voltage to the sample with respect to the tip, we effectively raise the Fermi level of the sample with respect to the tip. Now we have empty states available for tunneling into.

Tunneling Current



$$I(d) = const \tan t \times eV \exp\left(-2\frac{\sqrt{2m\Phi}}{\hbar} d\right)$$

Φ: the work function (energy barrier),
e: the electron charge,
m: the electron mass,
h: the Planck's constant,
V: applied voltage,
d: tip-sample distance.

Next page: Φ of common metals.

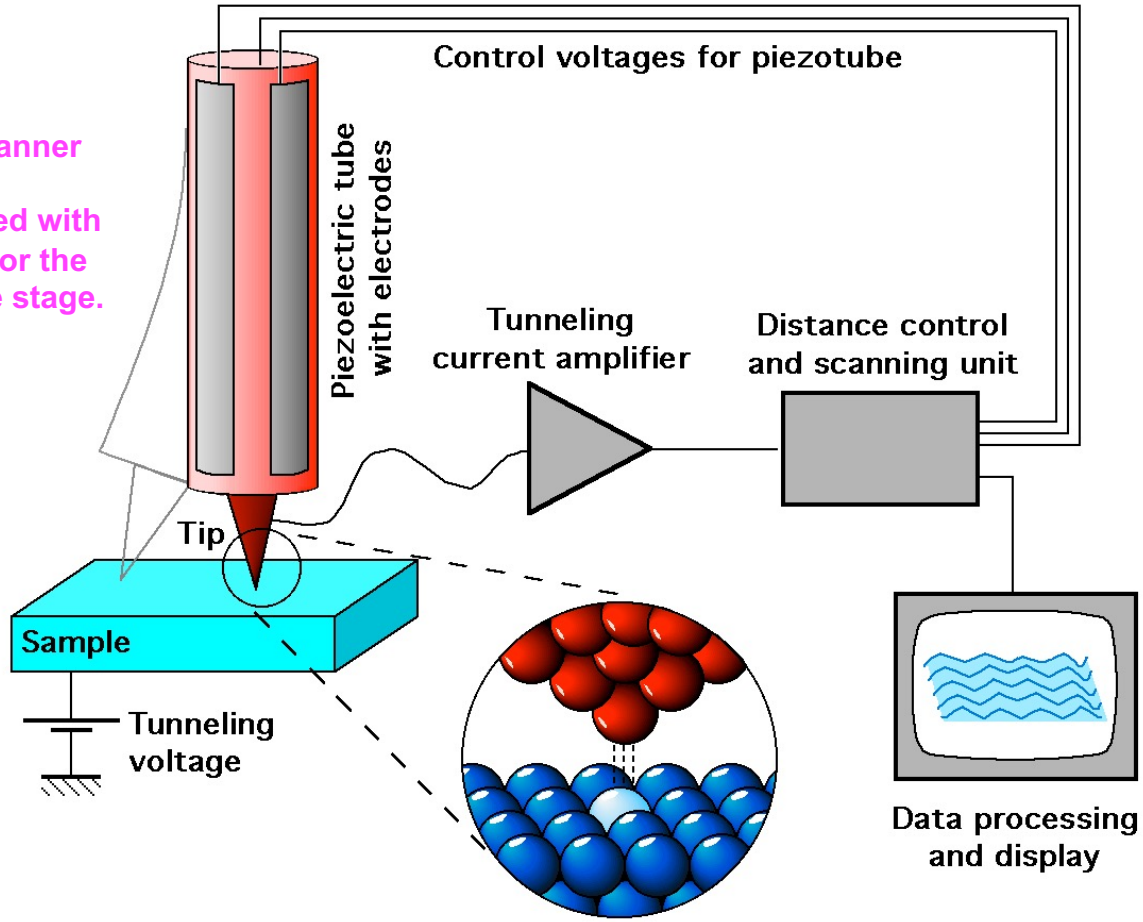
- A thin metal tip is brought in close proximity of the sample surface. At a distance of only a few Å, the overlap of tip and sample electron wavefunctions is large enough for an electron tunneling to occur.
- When an electrical voltage *V* is applied between sample and tip, this tunneling phenomenon results in a net electrical current, the 'tunneling current'. This current depends on the tip-surface distance *d*, on the voltage *V*, and on the height of the barrier Φ:
- This (approximate) equation shows that the tunneling current obeys Ohm's law, i.e. the current *I* is proportional to the voltage *V*.
- The current depends exponentially on the distance *d*.
- For a typical value of the work function Φ of 4 eV for a metal, the tunneling current reduces by a factor **~10** for every **0.1** nm increase in *d*. This means that over a typical atomic diameter of e.g. **0.3 nm**, the tunneling current changes by a factor **~1000**! *This is what makes the STM so sensitive.*
- The tunneling current depends so strongly on the distance that it is dominated by the contribution flowing between the last atom of the tip and the nearest atom in the specimen --- single-atom imaging!

Work Function of Common Metals

Metal	Φ(eV) (Work Function)
Ag (silver)	4.26
Al (aluminum)	4.28
Au (gold)	5.1
Cs (cesium)	2.14
Cu (copper)	4.65
Li (lithium)	2.9
Pb (lead)	4.25
Sn (tin)	4.42
Chromium	4.6
Molybdenum	4.37
Stainless Steel	4.4
Gold	4.8
Tungsten	4.5
Copper	4.5
Nickel	4.6

Basic components of STM:

The scanner can be mounted with the tip or the sample stage.



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- Tunneling current from tip to sample or vice-versa depending on bias;
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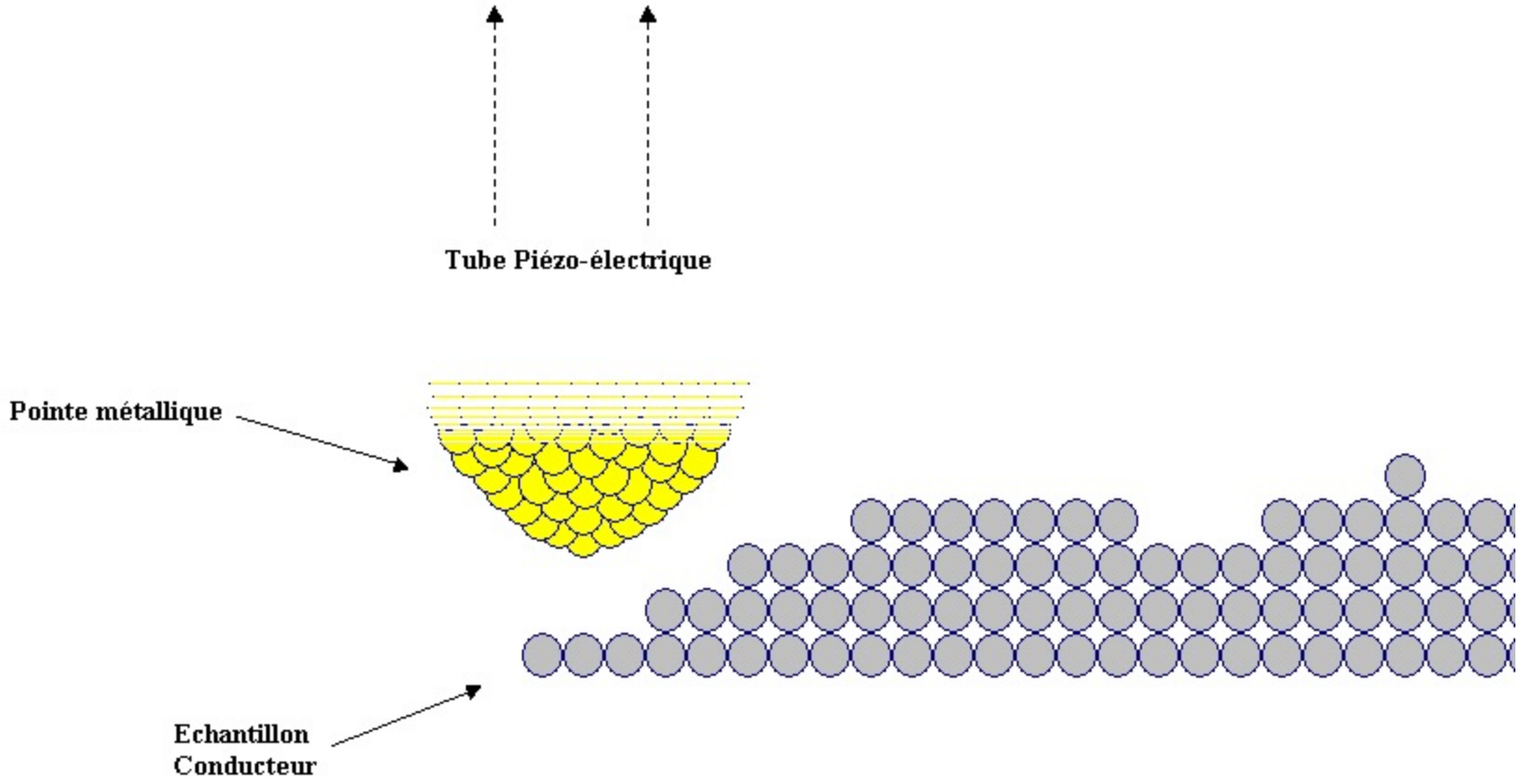
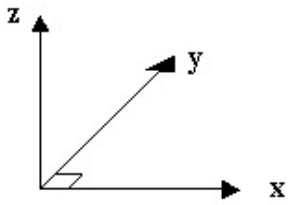
Feedback based on Tunneling Current

- The principle of the STM is based on the strong distance dependence of the quantum mechanical tunneling effect.
- Maintaining a constant tunneling current by adjusting the height with a piezo-electric crystal, and monitoring the piezo voltage while scanning, allows one to image a surface, under ideal conditions, to atomic resolution. (If the tip is scanned over the sample surface while an electronic feedback loop keeps the tunneling current constant (*constant current mode*), the tip height follows a contour of constant local density of electronic states and provides information on the topography of the sample surface **if the surface is composed of the same atoms**.)
- Most of the tunneling current flows through a single protruding atom on the tip and thus sub-angstrom resolution in z can be achieved on a clean surface with a sharp tip.
- The x-y resolution is somewhat larger.

STM: constant current mode



Raster Scanning of STM: 2D imaging

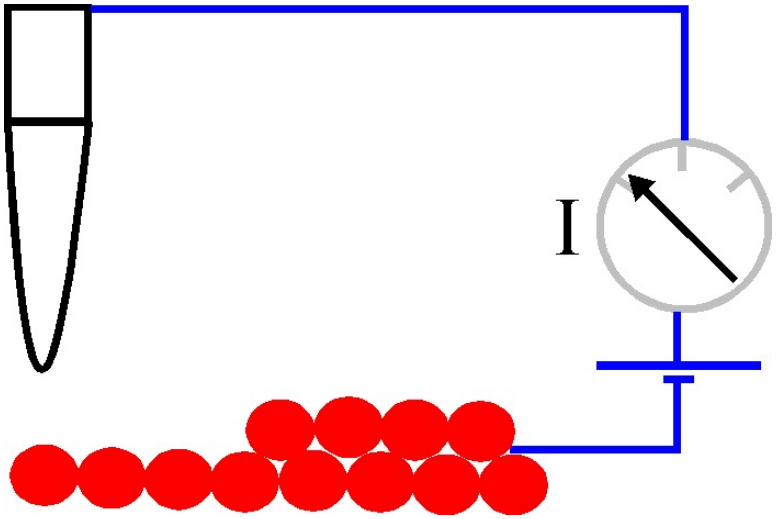


Scan $\Delta Z(x)$

(voir animation précedente)

Constant height mode

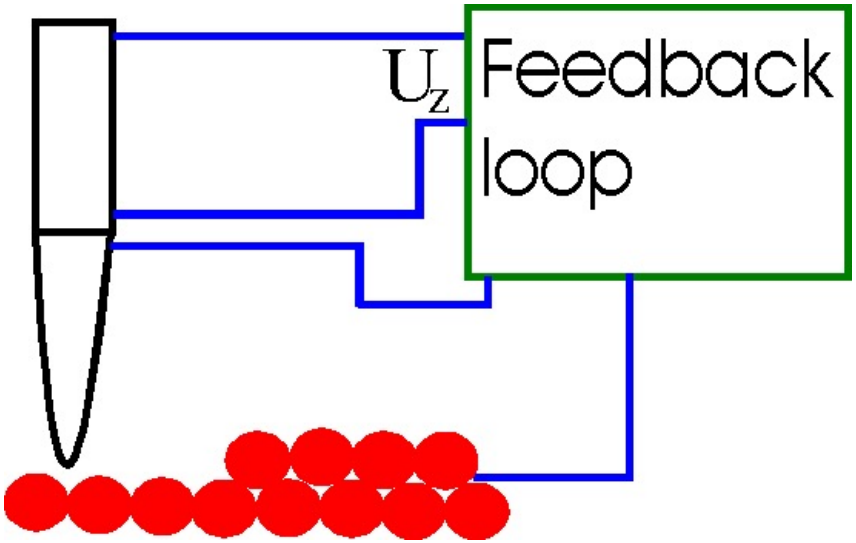
Tell if same atoms



Imaging the different surface atoms (due to their different work functions), revealing the surface composition or defects.

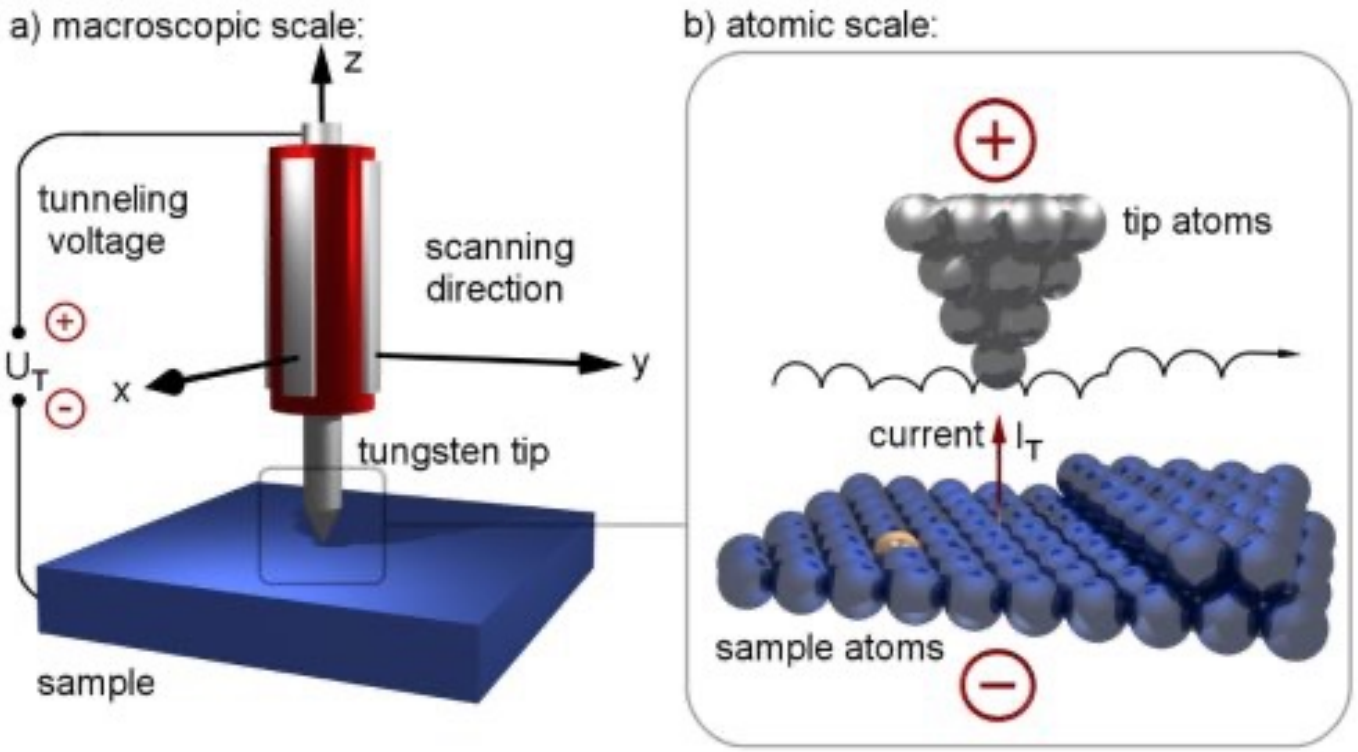
Constant current mode

Tell heights for the same atoms



Imaging the surface topography at atomic resolution if the surface is composed of the same atoms, *i.e., the only factor affecting the tunneling current is the distance.*

Scanning resolution of STM

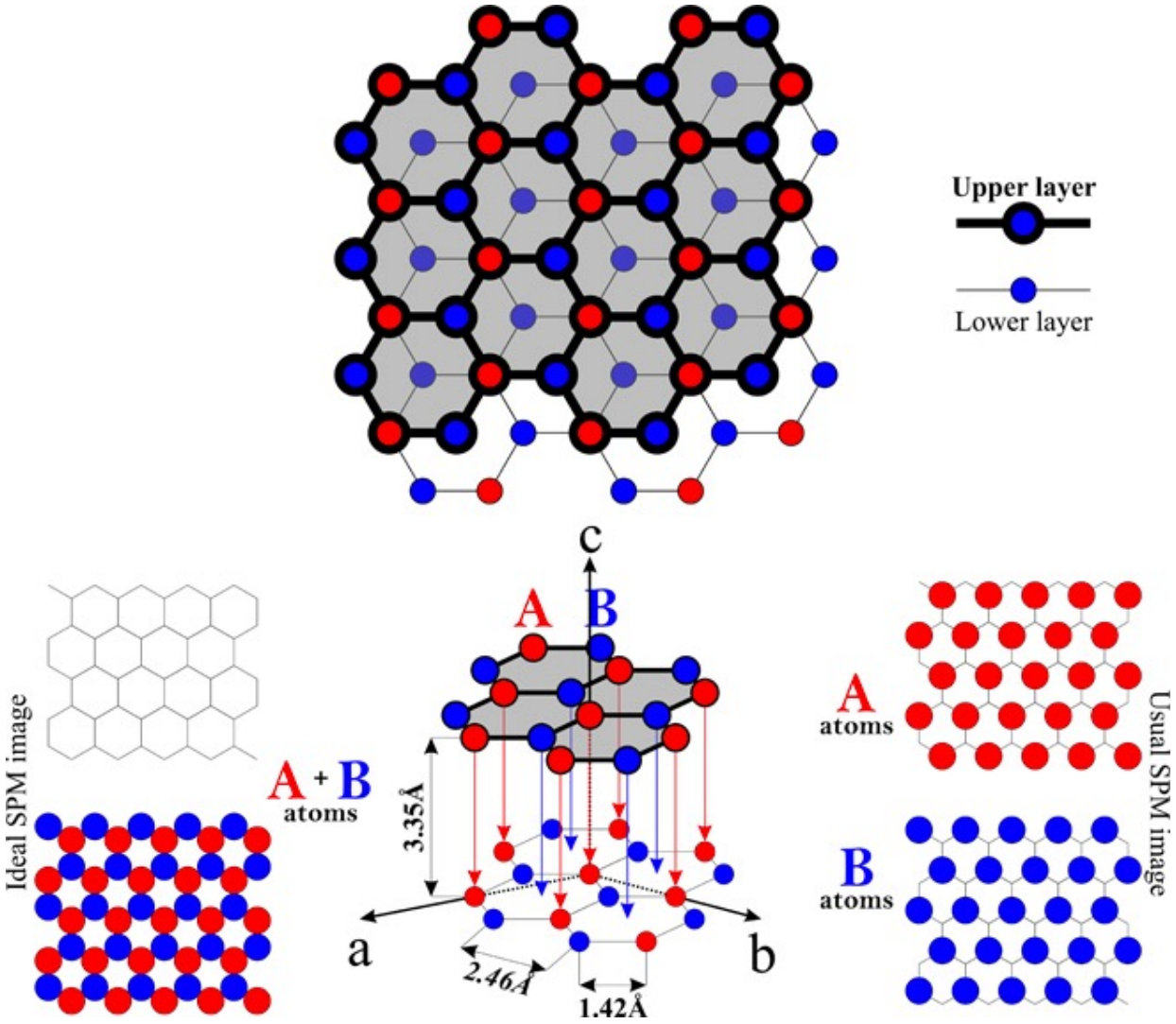


STM does NOT probe the nuclear position directly, but rather it is a probe of the **local density of electronic states,** ***i.e., the size of the whole atom dominated by the electron cloud.***

Principle of scanning tunneling microscopy: Applying a negative sample voltage yields electron tunneling from occupied states at the surface into unoccupied states of the tip. Keeping the tunneling current constant while scanning the tip over the surface, the tip height follows a contour of constant ***local density of states.***

Factors affecting the resolution

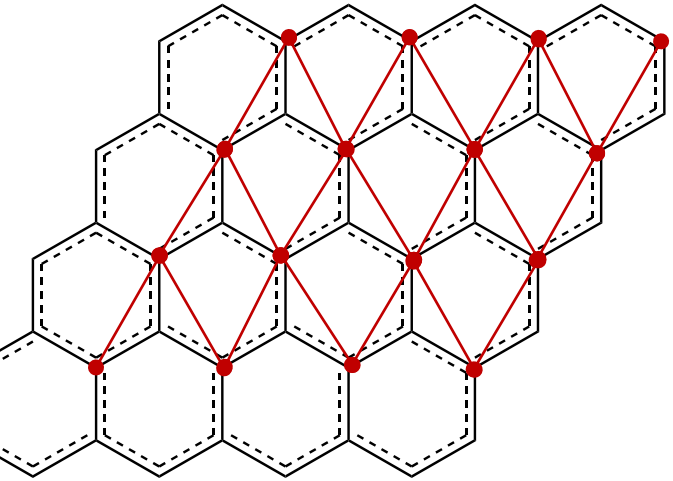
- One of the factors affecting resolution is *corrugation*, i.e. how much the electron density of surface atoms varies in height above the surface.
- *Graphite has a large corrugation, and is very planar, and thus is one of the easiest materials to image with atomic resolution. (see next slide for example)*
- STM does NOT probe the nuclear position directly, but rather it is a probe of the **local density of electronic states** , so STM images do not always show the position of the atoms. STM imaging depends on the nature of the surface and the magnitude and sign of the tunneling current. *For example, if you have Cu and Si on the same surface, under the same condition, the current with Cu is much higher .*
- Since STM images the outermost atom on sample surface, UHV is normally required to assure no surface contamination (e.g., coverage of air molecules or water) so as to image single atoms or at atomic resolution.

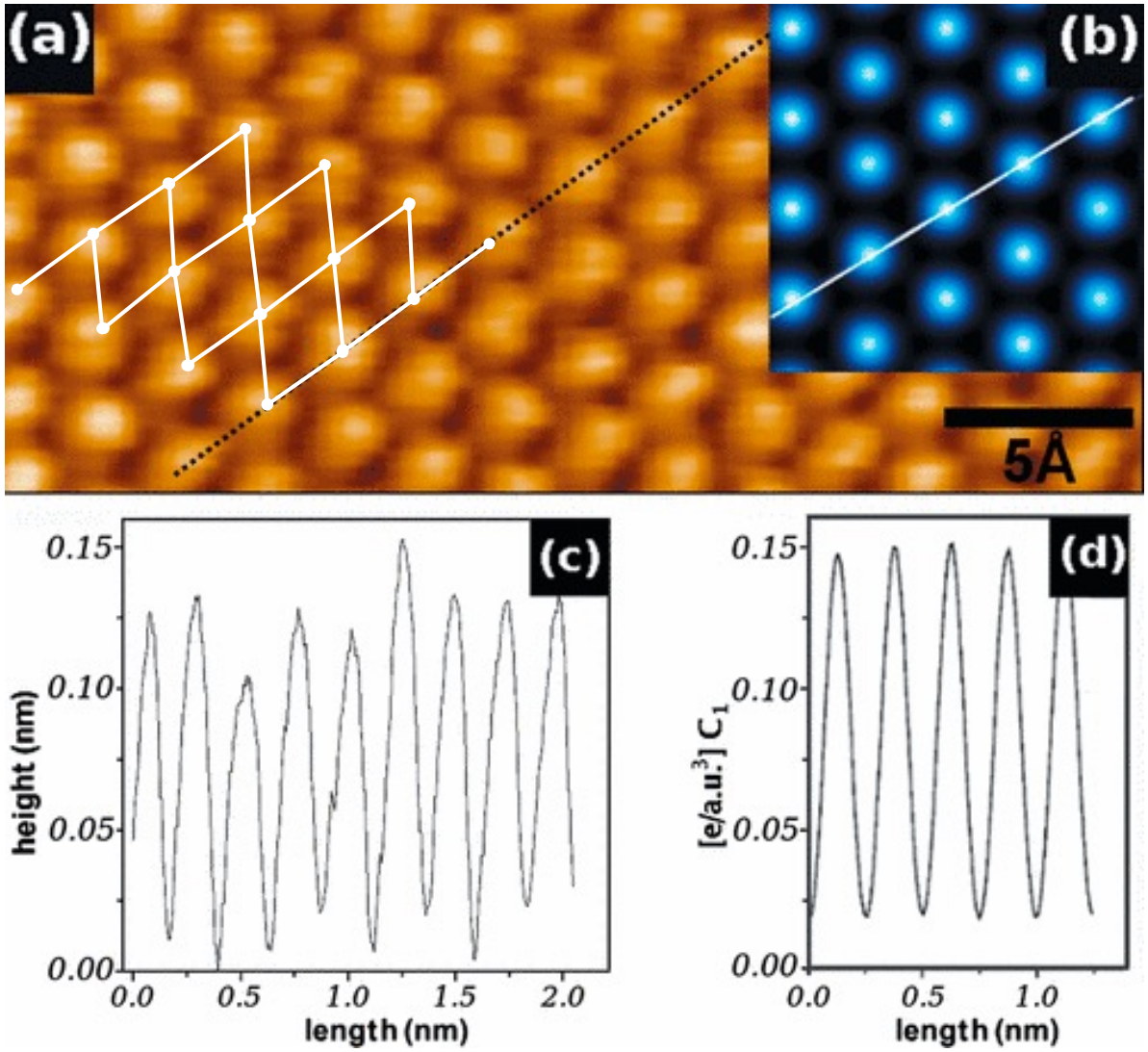


Copied from: http://nanoprobes.aist-nt.com/apps/HOPG%20info.htm

6 carbons in a ring can be classified into 3 A (α) and a B (β) atoms according to their positions relative the lower layer of graphene. B (β) atoms , not sitting atop an atom underneath, gives high tunneling current（“visible”）when imaged under constant height mode, as seen from above result.

constant current mode



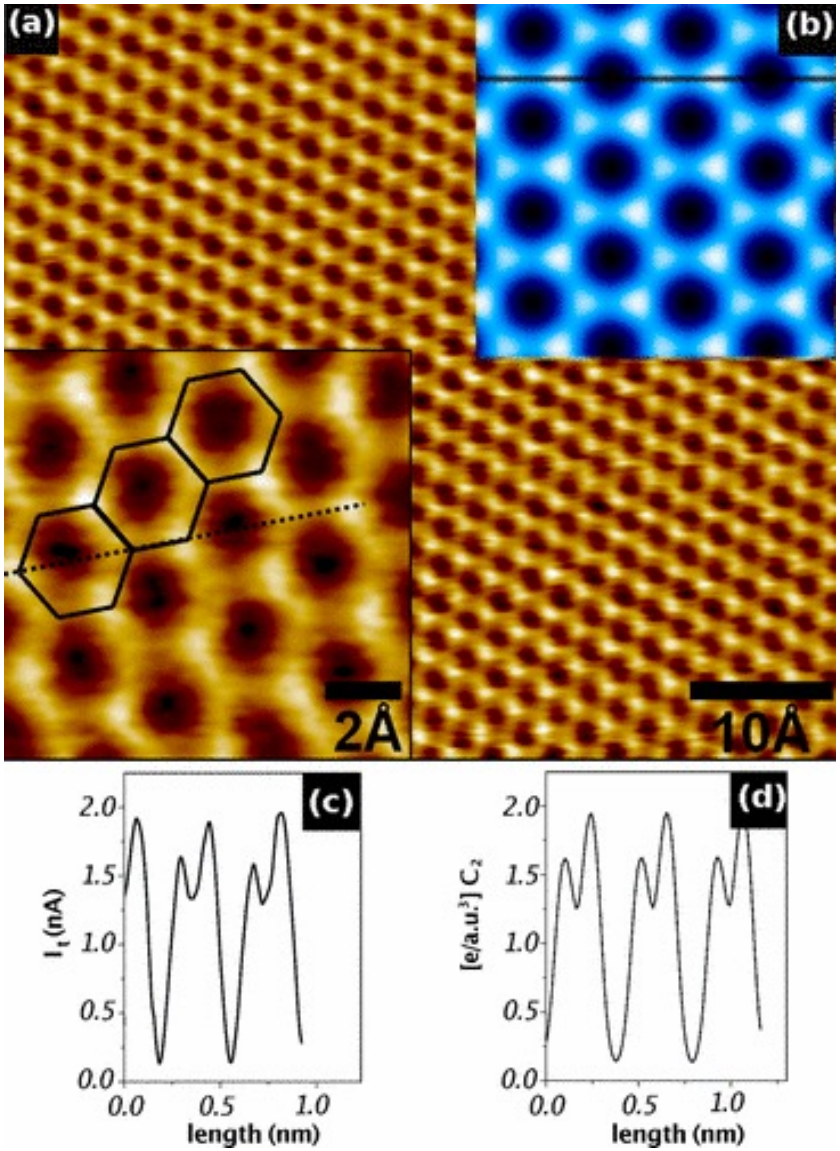


(a) (Color online) Experimental STM image of HOPG at constant-current mode, Vb=−50 mV. (b) Calculated STM image at constant-height mode, Vb=−50 mV, and tip-surface distance of 1.2 Å. The triangular structure is visualized in both images. (c) And (d) line profiles along the lines indicated in Figs. 1(a) and 1(b), respectively.

https://journals.aps.org/prb/abstract/10.1103/PhysRevB.79.205431#fulltext

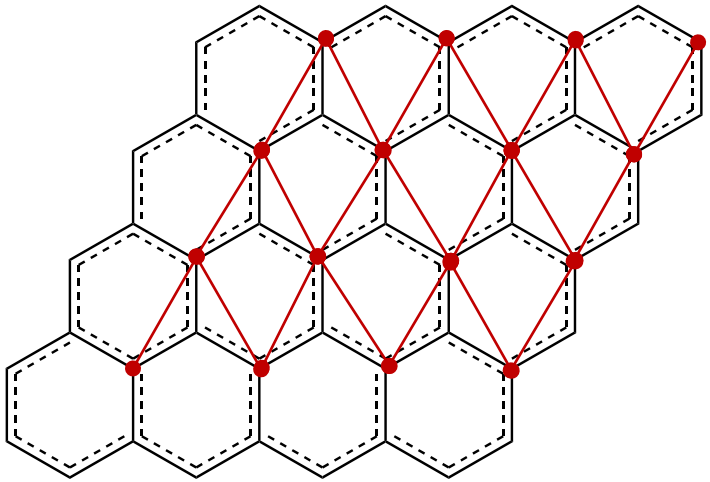
Constant height mode

The 3 β atoms show brighter (higher current) than the 3 α atoms, when imaged under the same height.



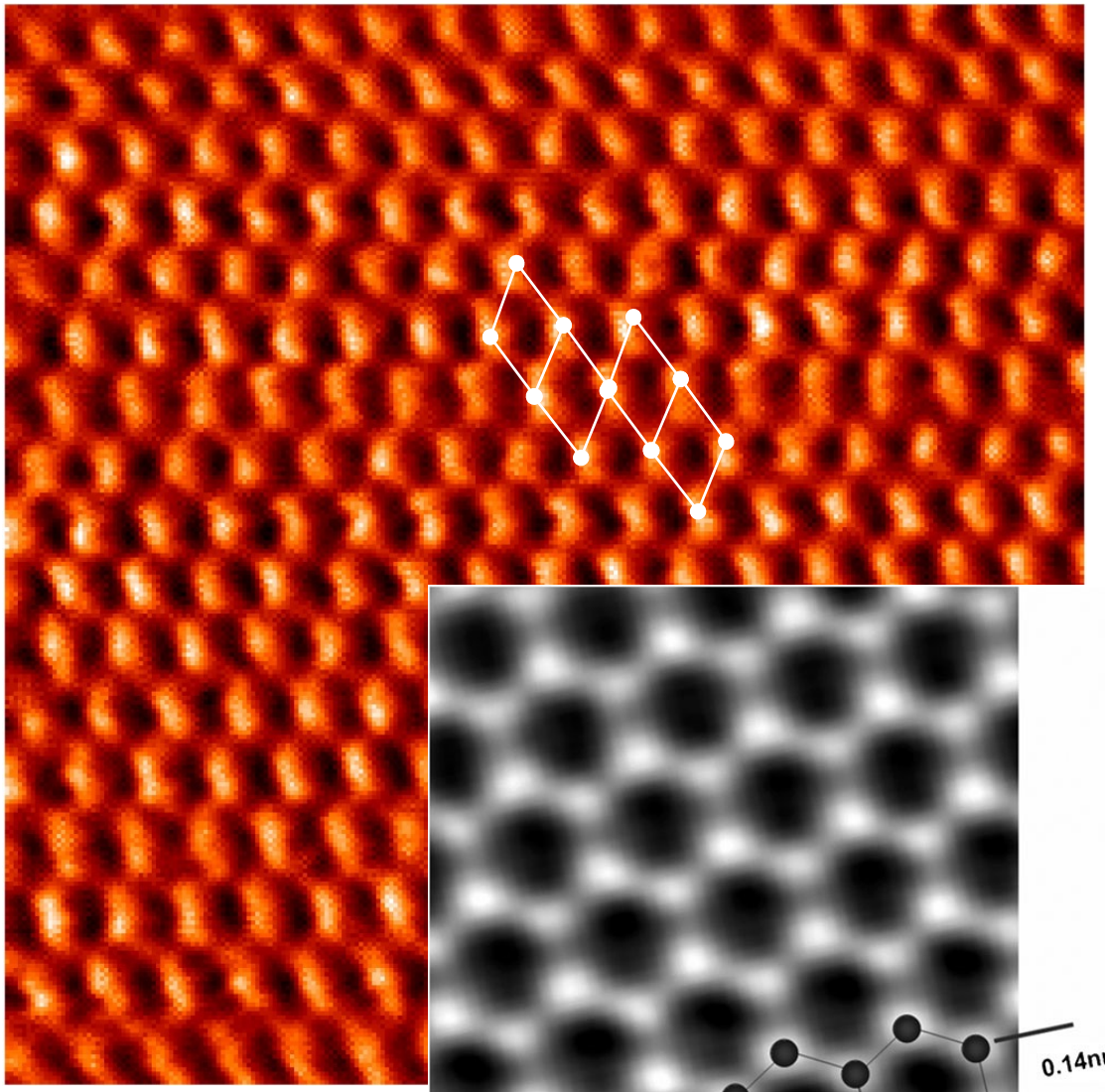
(a) (Color online) Experimental STM image of HOPG at constant-height mode, Vb=−300 mV. (b) Calculated STM image at constant-height mode, Vb=−300 mV, and tip surface distance of 1.2 Å. Both images reveal the hexagonal atomic structure which is compound by α and β atoms. (c) And (d) are line profiles along the lines indicated in (a) and (b), respectively.

STM image of highly oriented pyrolytic graphite (HOPG)



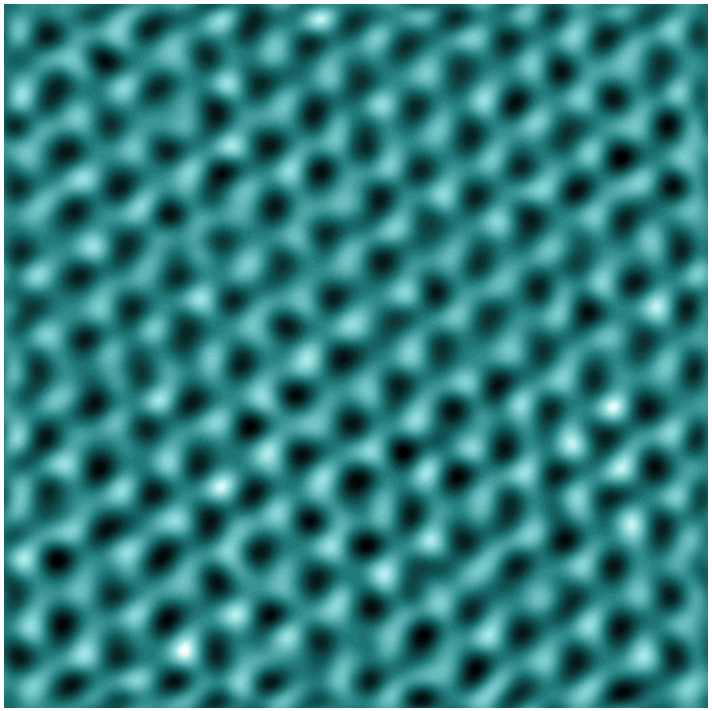
Among the 6 carbons in a ring, only the 3 β atoms can be imaged under constant current mode, since these 3 carbons give much higher tunneling current, which in turn is due to their much higher higher local density of states, resulting in so called “giant corrugations” (enormous apparent heights of atoms).

(0001) 5x5 nm, in constant current mode

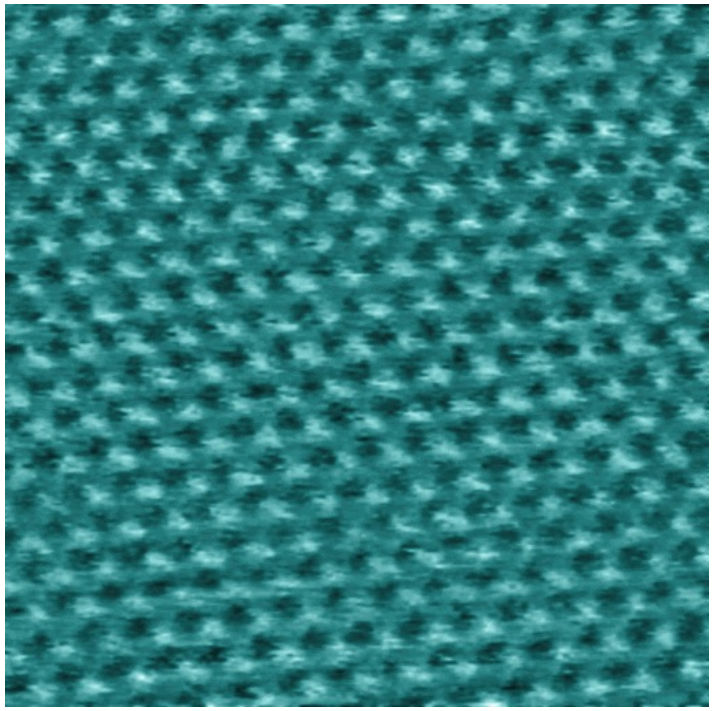


Compared to TEM imaging

Graphite surface: temperature dependence (thermal agitation of electrons)



77 K 29 Å x 29 Å



295 K 37 Å x 37 Å

Imaged in Constant height mode

Brief Overview of STM

- In the scanning tunneling microscope the sample is scanned by a very fine metallic tip; the scanning can be controlled in 3D by a piezo-scanner either bound to the tip or attached under the sample stage.
- The sample is positively or negatively biased so that a small current, the "tunneling current" flows if the tip is in close proximity to the sample. This feeble tunneling current is amplified and measured.
- With the help of the tunneling current the feedback electronic keeps the current between tip and sample constant. If the tunneling current exceeds its preset value, the distance between tip and sample is increased, if it falls below this value, the feedback decreases the distance. This is the constant current mode for STM, and similarly one can have the constant height mode using the same feedback system.
- The tip is scanned line by line above the sample surface following the topography of the sample.

Brief Overview of Tunneling Current

- The tunneling current flows across the small gap that separates the tip from the sample, a case that is forbidden in classical physics but that can be explained by the better approach of quantum mechanics.
- The tunneling current ***I*** has a very important characteristic: it exhibits an exponentially decay with an increase of the gap d: $I = c*V*e^{-(k*d)}$; k and c are constants, V is the bias.
- **Very small changes in the tip-sample separation induce large changes in the tunneling current!**
- This has the consequence that: The tip-sample separation can be controlled very exactly.
- The tunneling current is only carried by the *outermost* tip atom; the atoms that are second nearest carry only an negligible amount of the current: **The sample surface is scanned by a single atom!**

Brief Overview of STM

https://www.youtube.com/watch?v=HE2yE8SvHmA

More about STM imaging of HOPG (0111) surface

Basically, the highly oriented pyrolytic graphite (HOPG) crystal is formed by layers of honeycomb atomic array of carbon atoms with interatomic distance of 1.42 Å (a single layer is called graphene). The layers are held together by van der Waals forces and they present an ABAB stacking sequence. This stacking sequence gives rise to a 4-carbon atom unit cell with two nonequivalent atomic sites: the α-type-sites, atoms with neighbors directly above and below in adjacent layers, and the β-type-sites, atoms without such neighbors [15] (in what follows α and β atoms, respectively).

The widely accepted theory for STM image formation of Tománek *et al.* [12] predicts, for low-bias voltages, that only β atoms are visible as a consequence of the asymmetry in the interlayer interaction in the bulk graphite. Such asymmetry occurs due to the higher local density of states (LDOS) of the β atoms compared with α atoms near the Fermi level. This (often called triangular) electronic surface structure has a unit cell length of about 2.46 Å corresponding to the periodicity of the lattice, and it is usually reported in the STM experiments.[1,2] I

https://journals.aps.org/prb/abstract/10.1103/PhysRevB.79.205431#fulltext