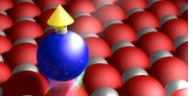


2.1 Surfaces and Ultra High Vacuum (UHV)

The characterization of a solid surface or of supported nanostructures on the atomic level requires that the surface or the nanostructure composition remains unchanged over the duration of the experiment.
According to the kinetic theory of gases, the flux (arrival rate) I of molecules impinging on a surface from the environment is given by the expression:

$$I = \frac{p}{\sqrt{2\pi m k_B T}}$$

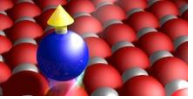
where p is the pressure, m the mass of the molecule, and T the temperature. Defining the density of one monatomic layer as $n_0 = 10^{15}$ atoms/cm^2, the time necessary to form a monolayer of molecules of mass 28 a.u. (N_2, CO) at room temperature, assuming a sticking coefficient of 1, is given by:

$$\tau = \frac{n_0}{I}$$

At atmospheric pressure, $p = 1013$ mbar, the arrival rate is I = 3 x 10^{23} cm^{-2} s^{-1} (1 mbar = 100 Pa = 100 N/m^2).

Estimate τ for atmospheric pressure and for pressures typical of low vacuum ($p = 1$ x 10^{-3} mbar), high vacuum ($p = 1$ x 10^{-6} mbar), ultra-high vacuum ($p = 1$ x 10^{-9} mbar), extremely high vacuum ($p = 1$ x 10^{-12} mbar).

What is the required pressure if we accept that only 1% of the surface is contaminated during the measurements that are performed in A) 1 hour, B) 10 hours?



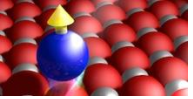
2.1 Surfaces and Ultra High Vacuum (UHV) - Solution

Pressure p (mbar)	**Molecular density** n (cm^{-3})	**Flux** I ($cm^{-2}\ s^{-1}$)	**Monolayer formation time** τ
1013 (atmospheric pressure)	2×10^{19}	3×10^{23}	3 ns
1×10^{-3}	2×10^{13}	3×10^{17}	3 ms
1×10^{-6}	2×10^{10}	3×10^{14}	3 s
1×10^{-9}	2×10^{7}	3×10^{11}	3000 s ~ 1h
1×10^{-12}	2×10^{4}	3×10^{8}	3×10^{6} s ~ 85h ~ 3 days

The table provides also the values of molecular densities for comparison.

A pressure of the order of 10^{-11} mbar is needed for having max 1% of the surface contaminated in 1 hour, and of the order of 10^{-12} mbar in 10 hours (both in the worse case hypothesis of a sticking coefficient of 1).

A pressure in the very low 10^{-10} mbar is the standard base pressure in UHV setups.



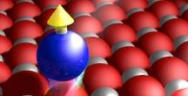
2.2 Bardeen model, expression for tunneling current

The tunneling current from tip to sample in terms of discrete states is given by

$$I_{\text{tip}\to\text{sample}} = \frac{4\pi e}{\hbar}\sum_{i,f}\left|M_{fi}\right|^2 \delta\left(E_f - E_i\right)$$

Use the definition of the Dirac delta function $\int_{-\infty}^{\infty} F(\varepsilon)\delta\left(\varepsilon - E_f\right)d\varepsilon = F\left(E_f\right)$ applied to $F(\varepsilon) = |M(\varepsilon)|^2\,\delta(\varepsilon - E_i)$ to obtain the intermediate expression for the current

$$I_{\text{tip}\to\text{sample}} = \frac{4\pi e}{\hbar}\int_{E_{F,\text{sample}}}^{E_{F,\text{tip}}} \rho_{\text{t}}(\varepsilon)\rho_{\text{s}}(\varepsilon)\,|M(\varepsilon)|^2 d\varepsilon$$



2.2 Bardeen model, expression for tunneling current - Solution

$$I_{\text{tip}\to\text{sample}} = \frac{4\pi e}{\hbar}\sum_{i,f}\left|M_{fi}\right|^2 \delta\left(E_f - E_i\right)$$

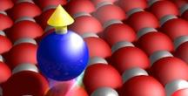
$$\int_{-\infty}^{\infty}|M(\varepsilon)|^2\,\delta(\varepsilon - E_i)\delta\left(\varepsilon - E_f\right)d\varepsilon = \left|M\left(E_f\right)\right|^2\delta\left(E_f - E_i\right)$$

$$\rho(E) = \sum_n \delta(E - E_n)$$

Using the definition of the density of states to transform the sum into integral, $\rho(\varepsilon) = \sum_n \delta(\varepsilon - E_n)$

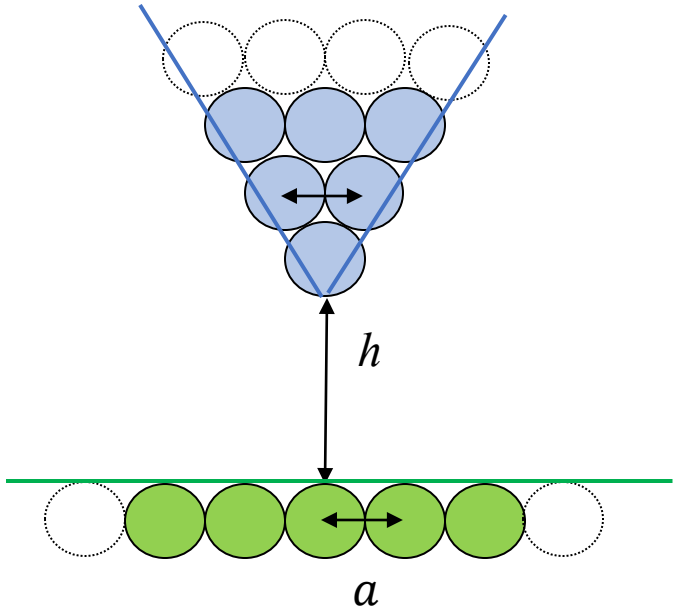
and considering the energy window between the two Fermi levels

$$I_{\text{tip}\to\text{sample}} = \frac{4\pi e}{\hbar}\sum_{i,f}\left|M\left(E_f\right)\right|^2\delta\left(E_f - E_i\right) = \frac{4\pi e}{\hbar}\int_{E_{F,\text{sample}}}^{E_{F,\text{tip}}}|M(\varepsilon)|^2\,\delta(\varepsilon - E_i)\delta\left(\varepsilon - E_f\right)d\varepsilon = \frac{4\pi e}{\hbar}\int_{E_{F,\text{sample}}}^{E_{F,\text{tip}}}\rho_{\text{t}}(\varepsilon)\rho_{\text{s}}(\varepsilon)\,|M(\varepsilon)|^2 d\varepsilon$$



2.3 STM lateral resolution

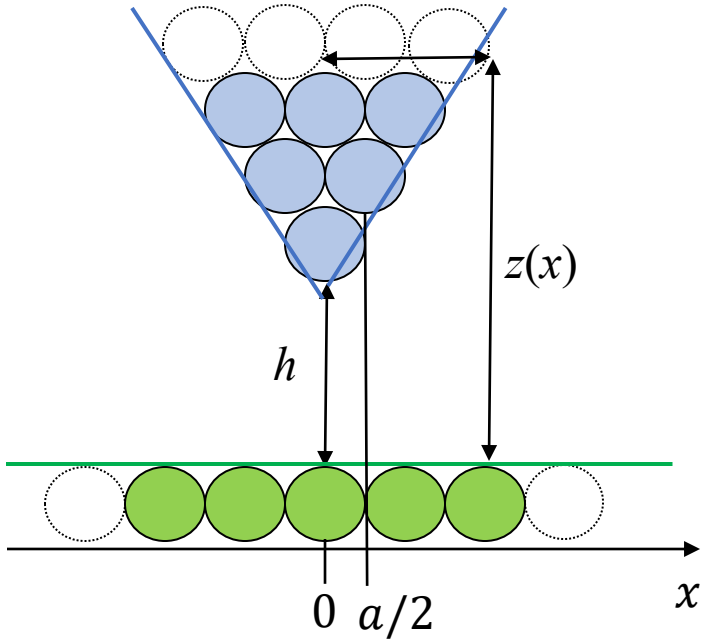
We want to evaluate the lateral resolution of an STM tip in the simplified unidimensional model sketched in the figure.



Calculate the total tunneling current assuming that electrons can tunnel only perpendicularly to the surface and assuming both tip and surface as having a spatially constant DOS. What is the contribution of the apex atom with respect to the total current? Consider that the distance between the atoms in the surface and in the tip is $a = 2$ Å.

Hints:
express the distance between the tip and the surface as a function of the horizontal coordinate x;
consider the tip as an equilateral triangle.

2.3 STM lateral resolution - Solution



$$z(x) = h + x\sqrt{3}$$

$$I(x) \propto \exp(-2\kappa\, z(x))$$

$$I_{tot} \propto 2\int_0^{\infty} e^{-2\kappa\, z(x)}\, dx = \frac{e^{-2\kappa h}}{\kappa\sqrt{3}}$$

$$I_{apex} \propto 2\int_0^{a/2} e^{-2\kappa\, z(x)}\, dx = \frac{1 - e^{-\kappa a\sqrt{3}}}{\kappa\sqrt{3}}\, e^{-2\kappa h}$$

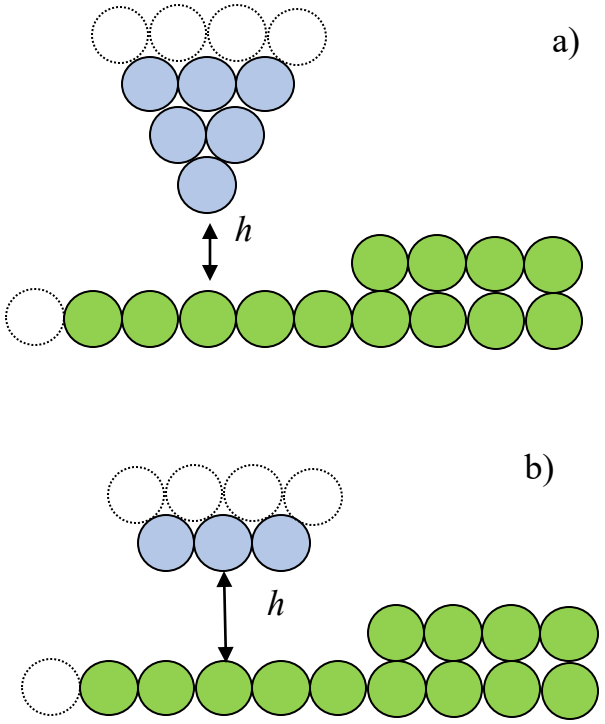
with $\kappa \sim 1$ Å^{-1} and $a = 2$ Å, I_{apex}= 97% I_{tot}

→ almost all the tunneling current is due to the apex atom

2.4 Effect of tip shape on lateral resolution

Consider the two cases sketched in the figure.

Using the results of the previous exercise, trace the step profile measured by the STM when the tip is moved along the surface in constant current mode

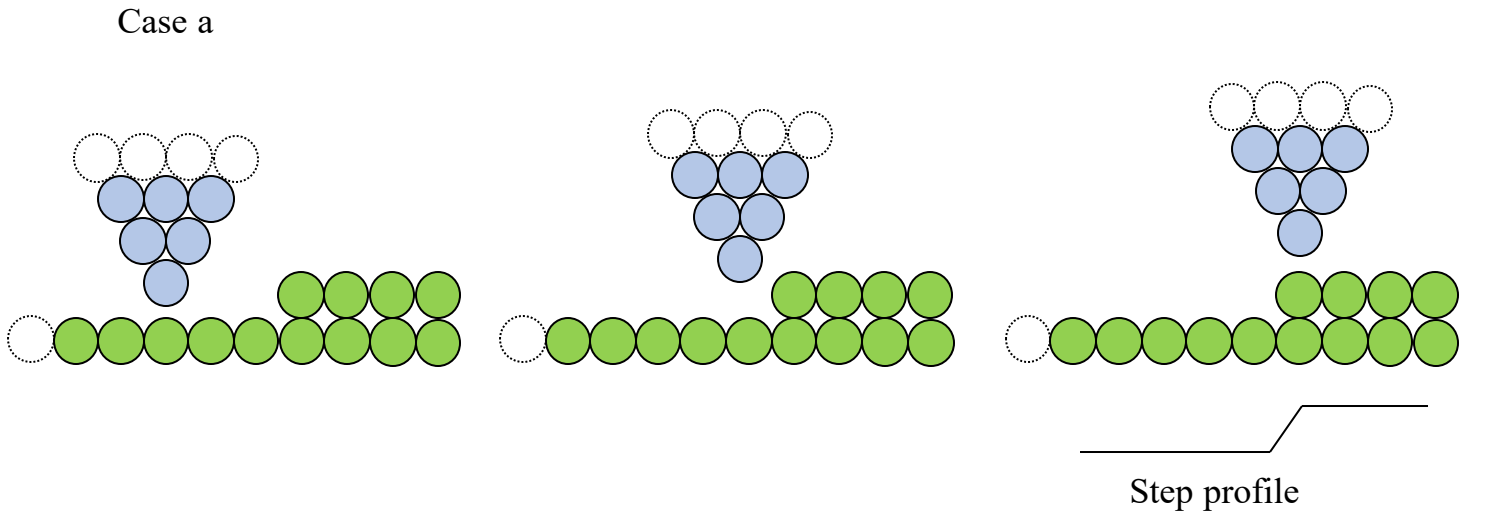


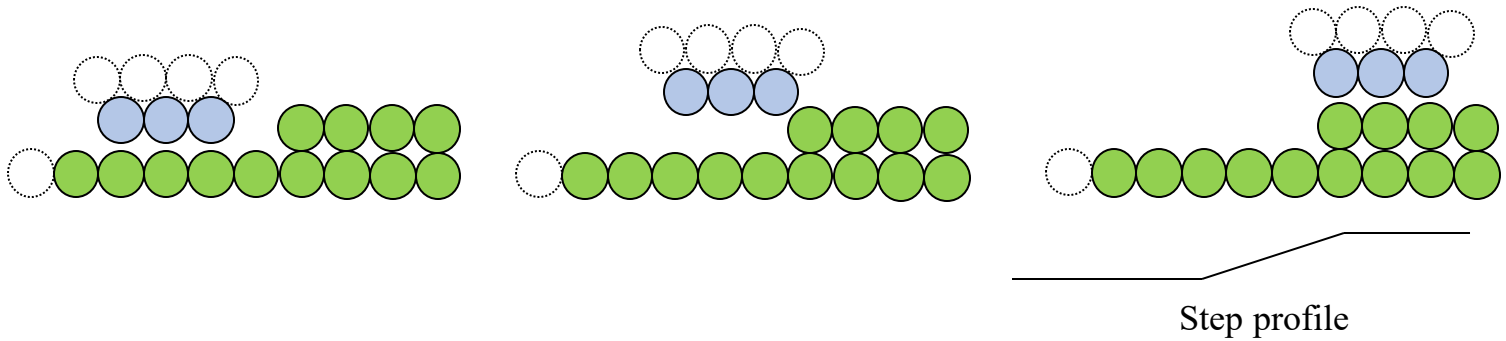
2.4 Effect of tip shape on lateral resolution - Solution

When the tip moves close to the surface only the apex atom and the surface atom closest to the tip contribute to the tunneling current

In case b) the tunneling current on the terraces is given by the three apex atoms. This implies that only when the three apex atoms have climbed the step, the tunneling current on the two terraces is the same. Thus, the step is seen with a very smooth profile with a width comparable to the tip size.

Indeed, in general the recorded topography is the **convolution** of the surface features and tip atomic structure





2.5 STM tips and DOS at Fermi level

We have seen in the lecture that standard STM tips are made from W or from PtIr alloys (for example $Pt_{90}Ir_{10}$).

Using the calculated orbital-resolved DOS for Pt and Ag shown in the figures below, estimate the relative contribution of s, p and d states to the total DOS at the Fermi level, indicated by the dotted line.

Pt

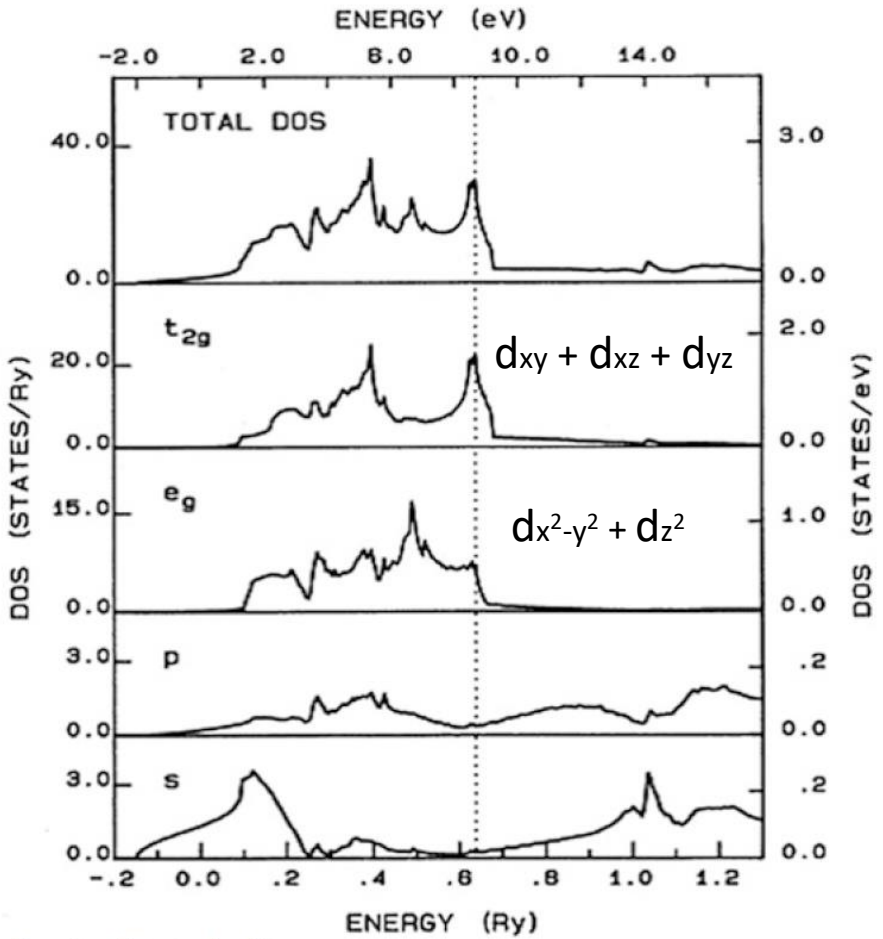


Fig. 6.21 Density of states for Pt

Ag

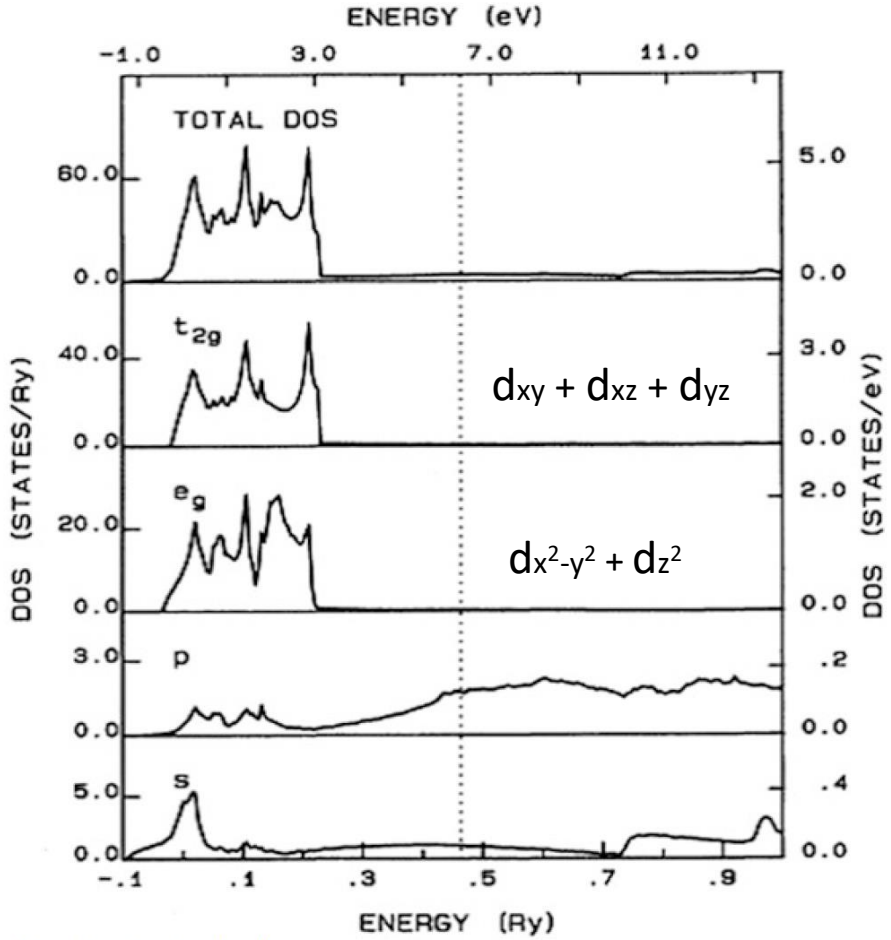
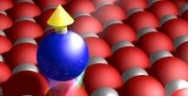


Fig. 5.21 Density of states for Ag

Handbook of the Band Structure of Elemental Solids, D. A. Papaconstantopoulos



2.5 STM tips and DOS at Fermi level - Solution

Pt		(states/eV)
	s	< 0.02
	p	~ 0.02
	d	$\sim 0.5 + 1.5 = 2$
	tot	2.04

s $<$ 1%
p $\sim$ 1%
d $\sim$ 98%

Ag		(states/eV)
	s	~ 0.07
	p	~ 0.13
	d	0
	tot	~ 0.20

s $\sim$ 35%
p $\sim$ 65%
d $\sim$ 0%

In general, material with high d density of states at the Fermi level are chosen as materials to produce tips, for example W, as well as PtIr alloys, where the role of Ir is to make the material less soft.

In particular, z-oriented orbitals of p and of d states increase the corrugation measured in STM images, leading more easily to high resolution images.

For some specific applications, different materials might be used, for example Au tips for their plasmonic properties, and Cr or MnNi tips for their magnetic properties. Tip functionalization with molecules (p.e. CO) leads to special tip-surface interaction and resolution.

2.5 STM tips and DOS at Fermi level – Solution - Supplement

Supplement: Why in the orbital-resolved DOS presented in the figures of the exercise the d states are separated into two?

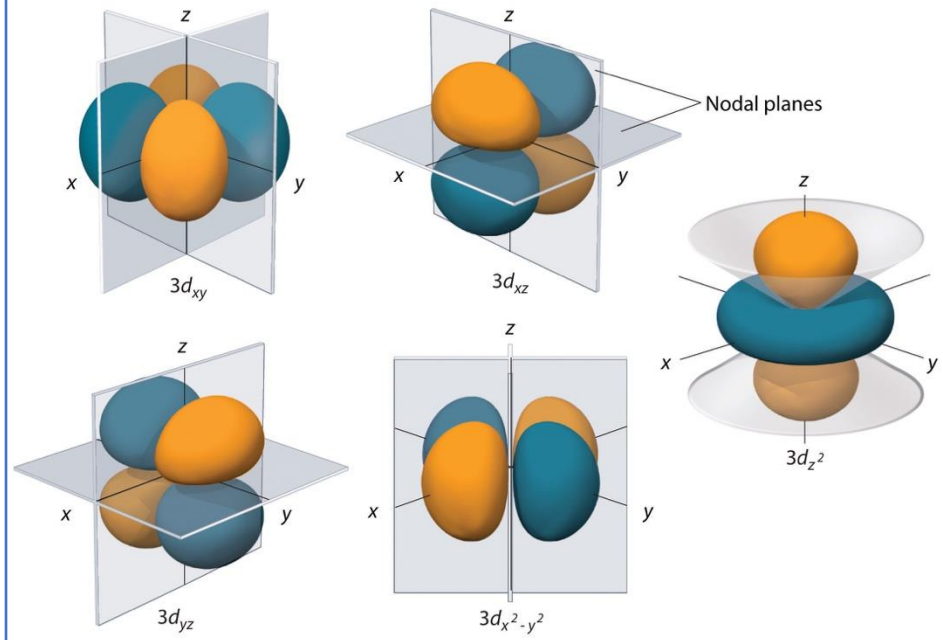
In a octahedral crystal field, the degeneracy of the five d orbitals of a transition metal atom is partially lifted. This is due to the orientation of the different d orbitals, and to the position of the surrounding negative charges due to the presence of the nearest neighbor atoms in the crystal. It's the crystal field splitting.

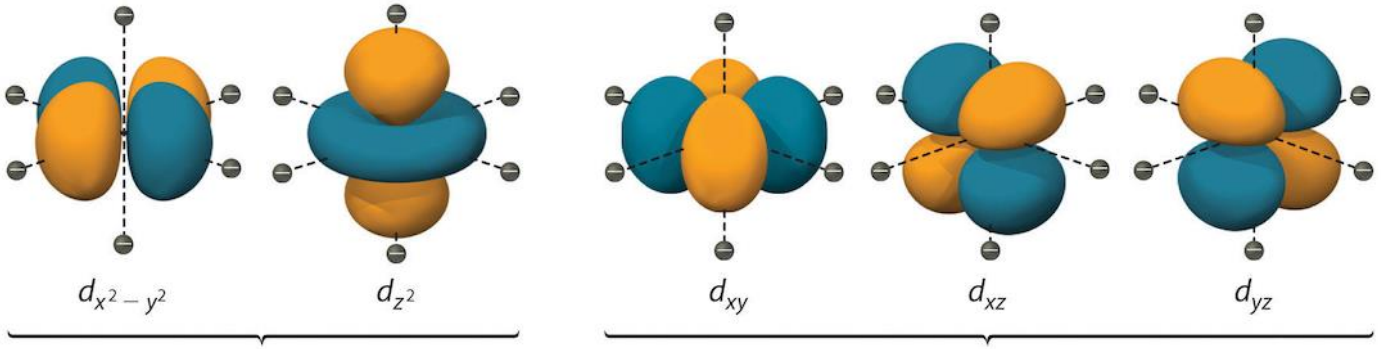
For the $d_{x^2-y^2}$ and d_{z^2} orbitals, the surrounding charges are aligned with the "lobes" of the orbitals, i.e with the regions in space where the probability of finding the electrons is high, resulting in some repulsion. As a consequence the energy of the states derived from these 2 orbitals is higher.

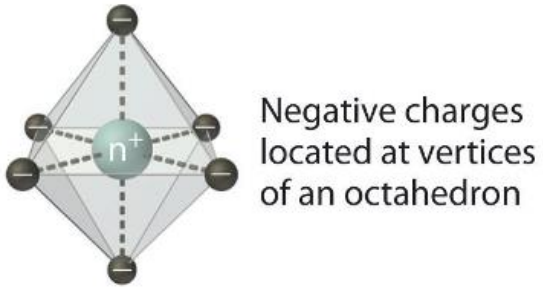
For the d_{xy} , d_{xz} and d_{yz} orbitals, the surrounding charges are not aligned with the "lobes" of the orbitals, so there is no repulsion. This lowers the energy of these 3 states.

When analyzed in the frame of group theory, the wave functions for these two groups fall into different symmetry groups, designated by e_g (2 states) and t_{2g} (three states).

The lobes of d_{xy} , d_{xz} and d_{yz} orbitals are at 45° with respect to the axes (check the nodal planes), while for $d_{x^2-y^2}$ and d_{z^2} the lobes are aligned with the x and y axes







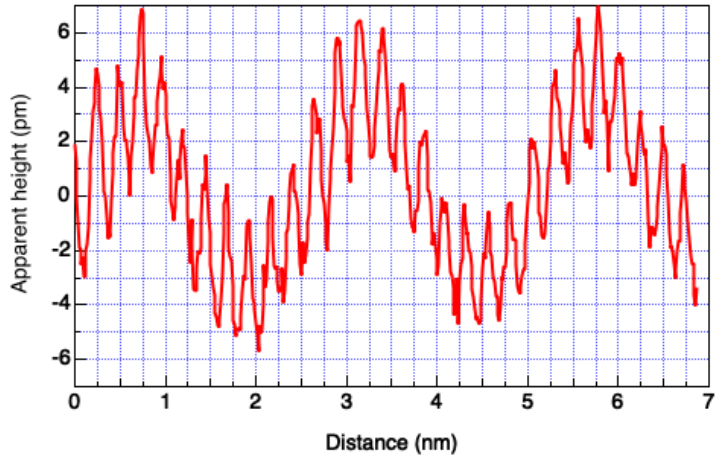
2.6 Graphene on Ir(111): moiré and atomic resolution

Graphene can be grown on surfaces by chemical vapor deposition. (We will discuss this technique in the upcoming weeks.)

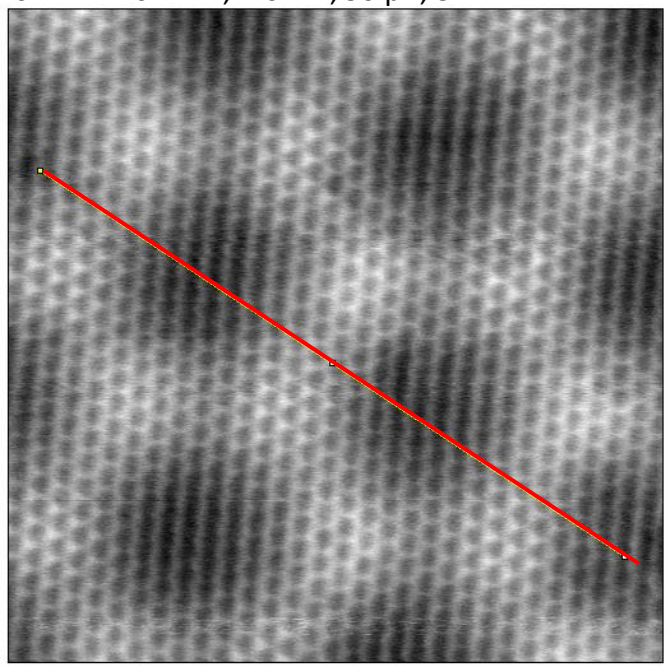
One example is graphene / Ir(111). STM images reveal a superstructure that can be viewed as a moiré, i.e. a regular pattern resulting from the superposition of two lattices having slightly different surface lattice parameters:
Ir(111) atomic nearest-neighbor distance = 2.715 Å
graphene lattice parameter = 2.45 Å

From the STM image and the line profile, estimate:

- the moiré periodicity
- the apparent moiré corrugation
- the apparent graphene atomic corrugation
- the noise level



6.4 nm x 6.4 nm, -20 mV, 50 pA, 5 K

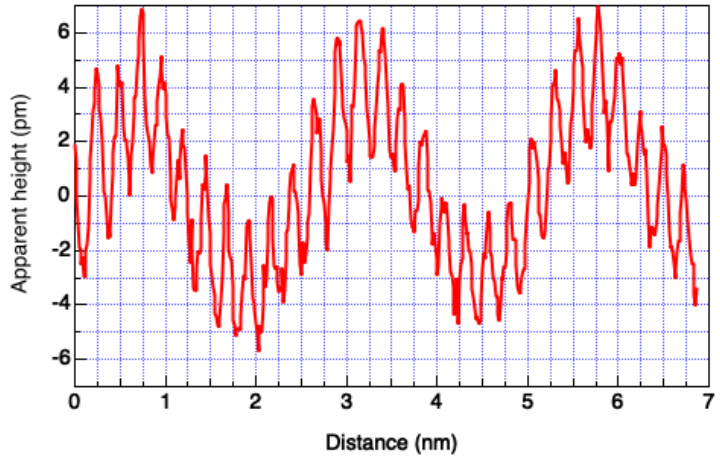


DOI: 10.1088/1367-2630/10/4/043033
N'Diaye *et al* ., *New J. Phys.* **10**, 043033 (2008)

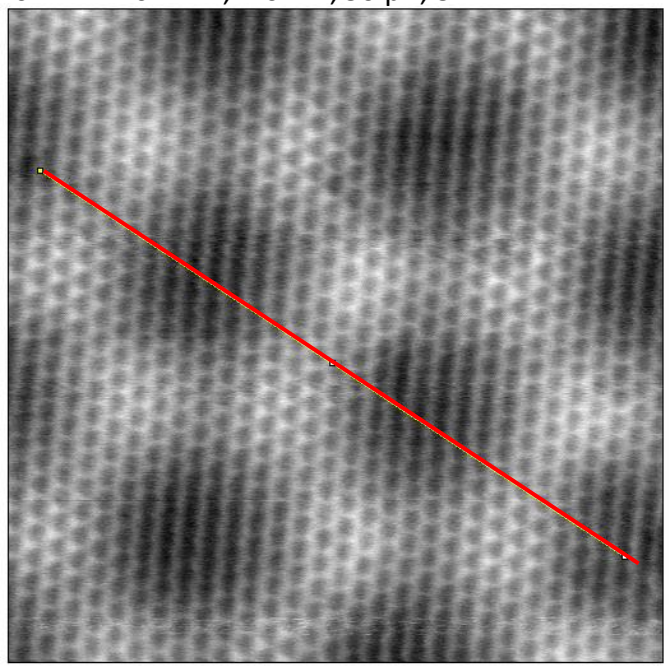
LNS lab

2.6 Graphene on Ir(111): moiré and atomic resolution - Solution

- moiré periodicity: ~ 2.5 nm. (It corresponds to a 9.32 x 9.32 incommensurate structure)
- apparent moiré corrugation: from +5 pm to -5 pm → ~ 10 pm
- apparent graphene atomic corrugation: from +6 pm to +1 pm → ~ 5 pm
- noise level: of the order of 1 pm



6.4 nm x 6.4 nm, -20 mV, 50 pA, 5 K



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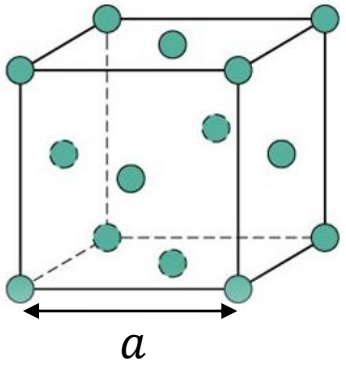
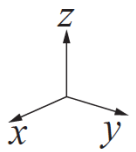
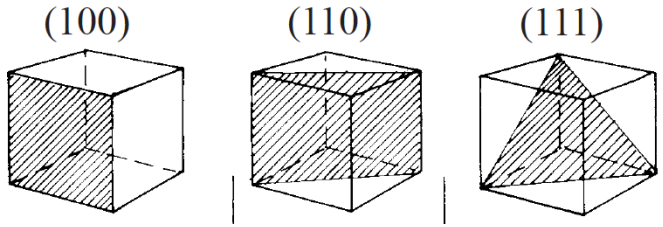
2.7 Atomic resolution and lattice parameters

Silver (Ag) crystallizes in a monoatomic face-centered cubic (fcc) structure (one atom in each corner of the cube, and one atom at the center of each face, see sketch).





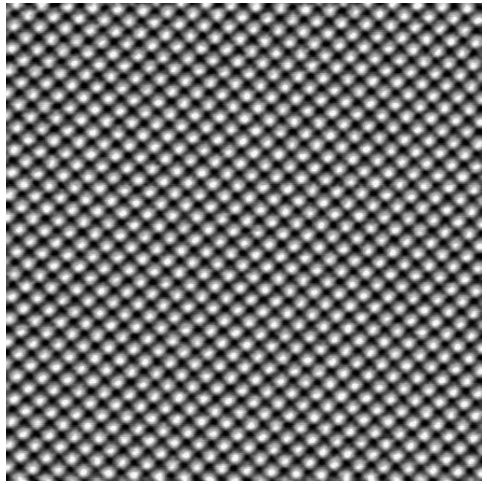


Two different Ag single crystals, oriented along low-Miller index faces, have been measured by STM: atomically resolved images of the two surfaces are shown in **1** and **2**.

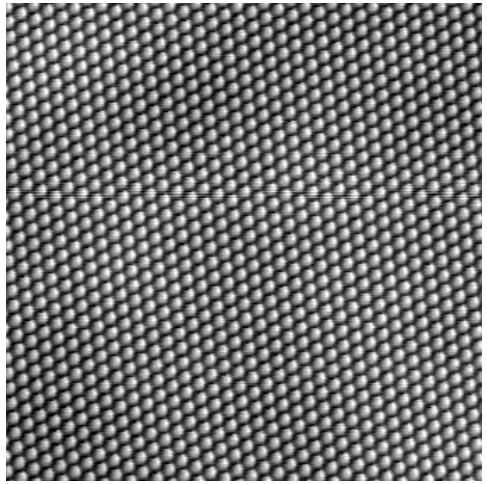
a) Considering the crystal structure and the low-Miller index orientations shown in the sketch, determine what is the orientation of the two crystals.

b) Knowing that the Ag lattice parameter (the side of the cube) is $a = 0.409$ nm, determine the distance between nearest-neighbor atoms on the two surfaces.

1



2



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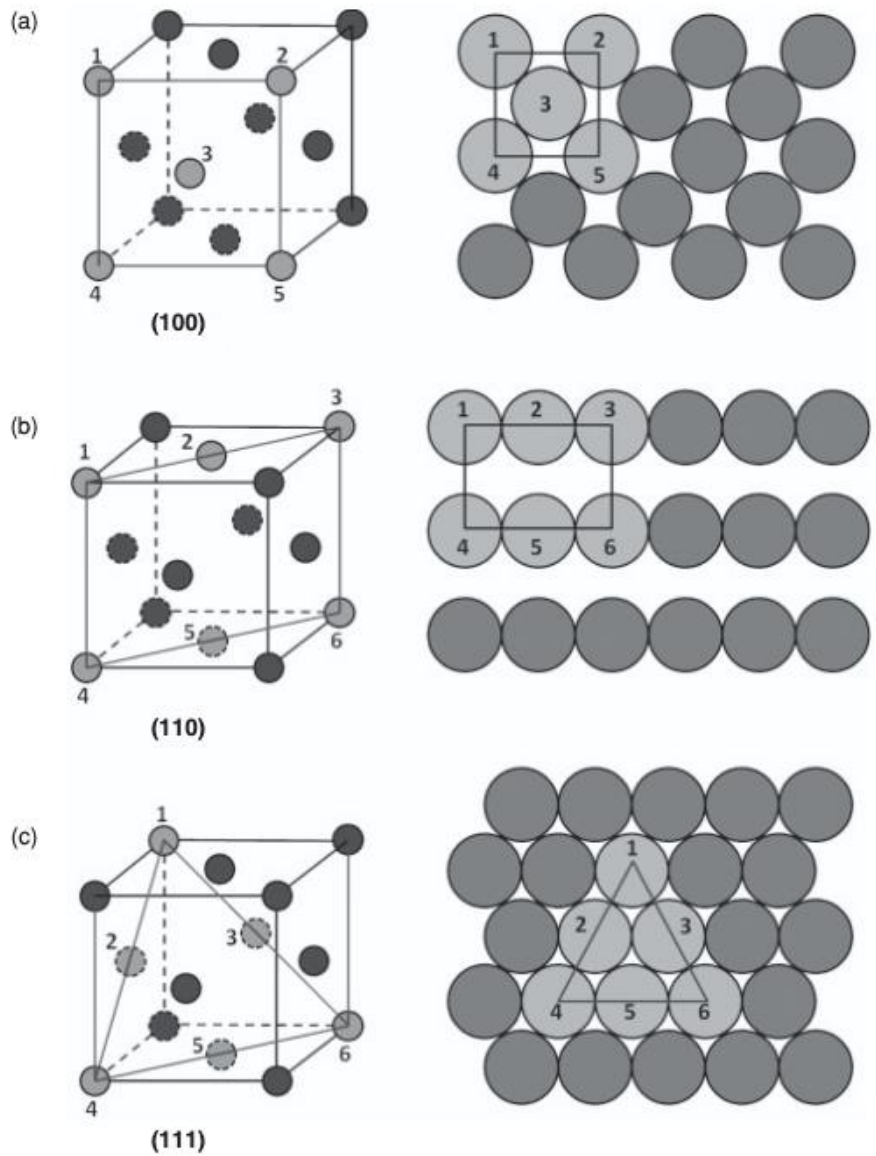
2.7 Atomic resolution and lattice parameters

a) Image **1**: square surface lattice; image **2**: hexagonal surface lattice. Comparing with the planes shown in the figure, we deduce that image **1** is acquired on a (100)-oriented crystal, and image **2** on a (111)-oriented crystal.

b) On the (100) surface: $d_{nn} = a\frac{\sqrt{2}}{2} = 0.289$ nm

On the (111) surface: $d_{nn} = a\frac{\sqrt{2}}{2} = 0.289$ nm

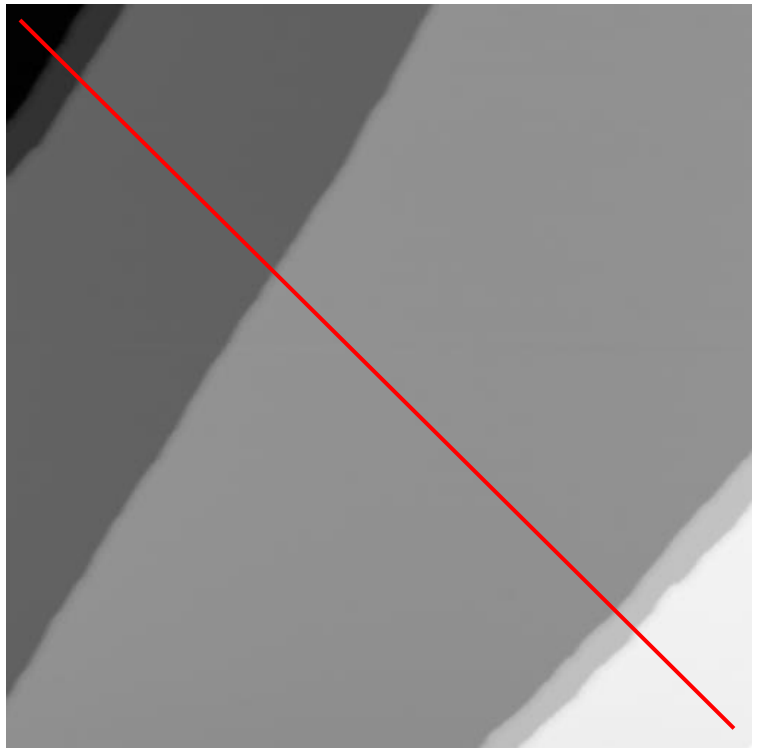


2.8 Step height and lattice parameters

We measure another Ag single crystal.
We obtain large scale images where adjacent terraces are visible.

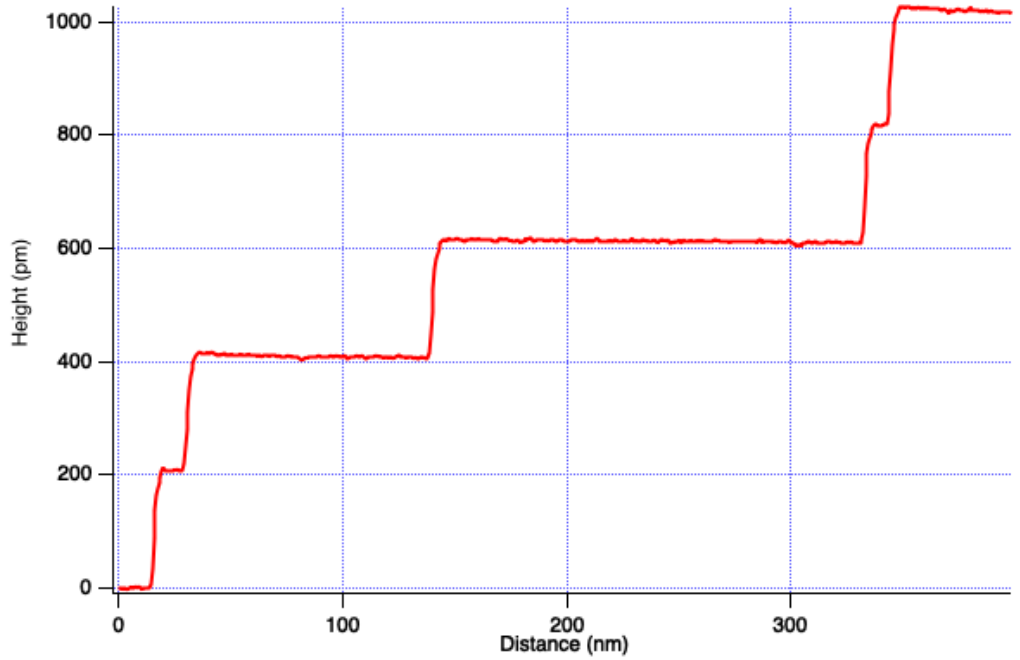
Is it possible to determine the crystal orientation?
If yes, which one is it?

lowest terrace



highest terrace

line profile corresponding to the red line on the STM image



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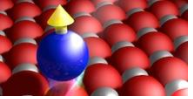


2.8 Step height and lattice parameters - Solution

In a fcc crystal, the distance between adjacent planes is (considering of course all the planes, also the ones that originate from the fact that the crystal is not simple cubic, but face-centered cubic):

for (100): $d = \frac{a}{2} = 204$ pm

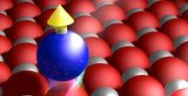
for (110): $d = a\frac{\sqrt{2}}{4} = 144$ pm

for (111): $a\frac{\sqrt{3}}{3} = 236$ pm

From the line profile, we see that each step corresponds to slightly more than 200 pm, indicating that the crystal is (100)-oriented.

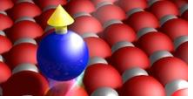
Note: experimentally, the procedure is the opposite. A know crystal is used to calibrate the piezotube (how many angstroms per volt are spanned). In fact, although these values are specified, they depend on the temperature and can change with time (aging).

Atomic steps are used to calibrate z; atomic resolution (or surface reconstructions) are used to calibrate x and y.



2.9 STM *vs* AFM

Which classes of materials can be investigated easily by AFM and not by STM? Why?



2.9 STM *vs* AFM - Solution

With AFM one can investigate non-conducting samples, i.e., insulators and intrinsic wide-band gap semiconductors. These materials are not easily accessible to STM since there are no states at the Fermi level. Therefore, it is not possible to obtain a tunneling current at low bias.

It is possible to measure semiconductors with STM by using high enough bias (several eV), such that the Fermi level of the tip is aligned with the top of the valence band, or with the bottom of the conduction band.