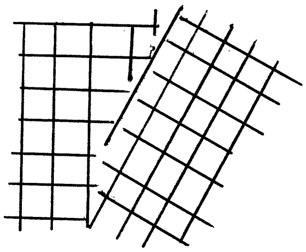
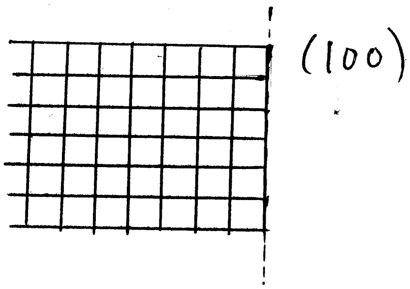
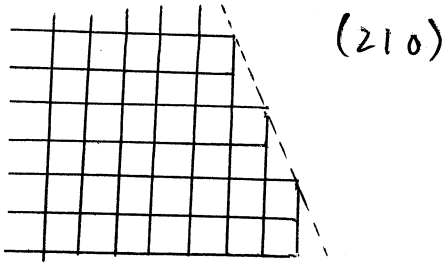
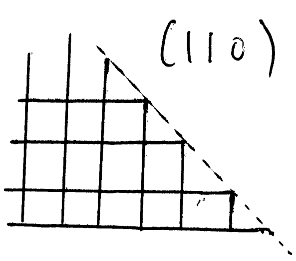
* Assumptions for bulk calculations on solids
- → infinite crystal
- → single ordered domain
- → technically: finite $L \times L \times L$ box with periodic boundary conditions, taking the limit $L \to \infty$ at the end

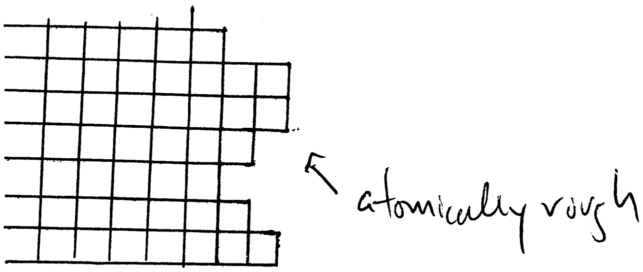
* All real crystals deviate from perfect crystallinity where the sample comes to an end
- → abutting another at a grain boundary
- → or abutting empty space at a crystal <u>surface</u>
- → the crystal may have a smooth surface, perfectly cleaved along a crystal plane, or a rough one.









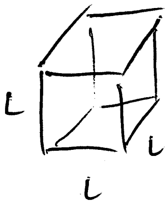


* Surfaces play an important role
  - → where the sample meets the outside world
  - → entry and exit point for all probes (incident photons, electrons, ...)
  - → locus of all crystal growth and dissolution
  - → venue for adatoms, bonding, catalysis
  - → open to more complex behaviours since the local symmetry is less than that of the full Bravais lattice

* Why have we generally ignored surface effects?
  - → small contribution to the bulk properties of a macroscopic sample

e.g. $N_V = \underset{\uparrow}{n} L^3$ = total number of atoms in a volume

number density of atoms



$N_s = 6nL^2\underset{\uparrow}{\lambda}$ = total number of atoms near the surface

length scale for a few atomic layers

relative contribution $\dfrac{N_s}{N_V} = \dfrac{6\lambda}{L}$ vanishes in the thermodynamic limit

→ on the other hand, the contribution becomes large on the nanoscale

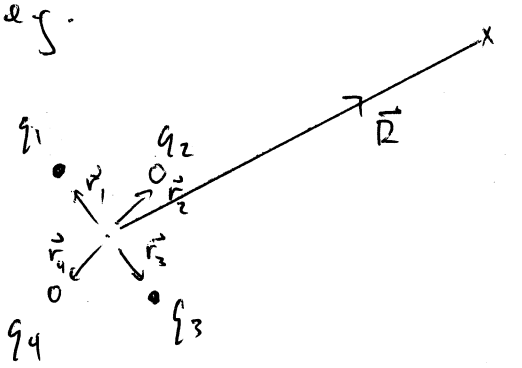
→ and chemistry is all "surface effects"

* Highly nontrivial distribution of surface charges and fields at a crystal's edge

→ over any coarse grained region in the bulk, the system is charge neutral

→ electrostatic potential determined by long-distance multipolar behavior

e.g.



potential at $\vec{R}$ given by

$$4\pi\varepsilon_0 \phi(\vec{R}) = \sum_i \frac{q_i}{|\vec{R}-\vec{r}_i|} = \frac{1}{R}\sum_i \frac{q_i}{|\hat{R}-\frac{1}{R}\vec{r}_i|}$$

$$=\frac{1}{R}\sum_i q_i\left(1-\frac{2\hat{R}\cdot\vec{r}_i}{R}+\frac{1}{R^2}|\vec{r}_i|^2\right)^{-\frac{1}{2}}$$

$$=\frac{1}{R}\sum_i q_i\left(1-\frac{2\hat{R}\cdot\vec{r}_i}{R}+\frac{a^2}{2R}\right)^{-\frac{1}{2}}$$

expand in $\frac{1}{R}$

high-symmetry configuration with

$\vec{r}_1 = \frac{a}{2}(-1,1)$ $q_1 = e$

$\vec{r}_2 = \frac{a}{2}(1,1)$ $q_2 = -e$

$\vec{r}_3 = \frac{a}{2}(1,-1)$ $q_3 = e$

$\vec{r}_4 = \frac{a}{2}(1,1)$ $q_4 = -e$

$$= \frac{1}{R} \sum_i q_i \left(1 + \frac{\hat{R}\cdot\vec{r}_i}{R} + \frac{3(\hat{R}\cdot\vec{r}_i)^2 - \frac{a^2}{2}}{2R^2} + \frac{5(\hat{R}\cdot r_i)^3 - 3(\hat{R}\cdot r_i)\frac{a^2}{2}}{2R^3} + \cdots \right)$$

$$= \frac{q_{tot}}{R}\left(1 - \frac{a^2}{4R^2}\right) + \frac{\hat{R}\cdot\vec{d}}{R^2} + \frac{3\hat{R}\cdot\overleftrightarrow{Q}\cdot\hat{R}}{2R^3} + \cdots$$

where $q_{tot} = \sum_i q_i$ monopole moment

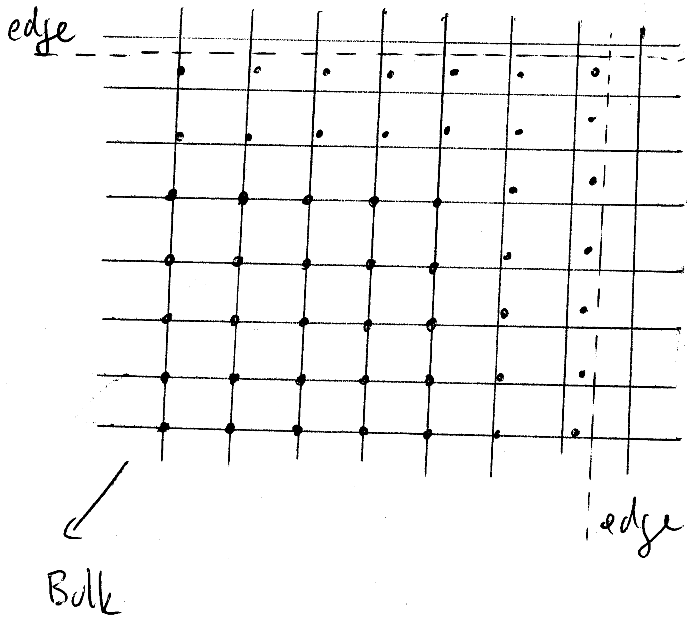
$\vec{d} = \sum_i \vec{r}_i q_i$ dipole moment

$Q_{\alpha\beta} = \sum_i r_{i,\alpha} r_{i,\beta} q_i$ qudrupole moment

charge neutrality and high-symmetry ensure that q_{tot} and $\vec{d}$ vanish; $\overleftrightarrow{Q}$ also vanishes in cubic symmetries; $\frac{1}{R^4}$ contribution identically zero if crystal has inversion symmetry ($\vec{r}_i \to -\vec{r}_i$)

$\Rightarrow$ potential may fall off as fast as $\frac{1}{R^5}$ at large distances

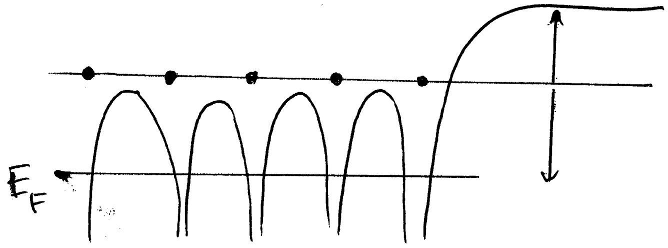
→ Significant deviations from the bulk Bravais lattice structure near edges



e.g. lattice relaxation

→ Leads to nonvanishing dipole contributions and potentially large electric fields in the vicinity of the surface

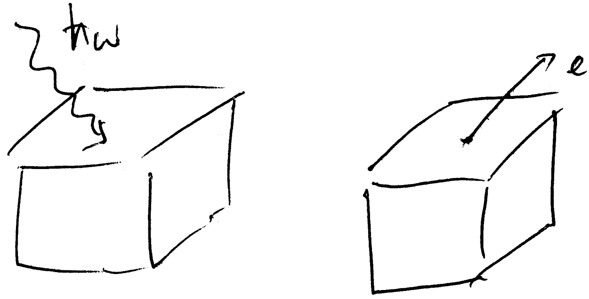
→ Work function of a metal is the energy required to remove an electron from the top of the fermi sea and transport it outside the crystal



$$W = -E_F + e\int \vec{E}\cdot d\vec{r}$$

* Work function is the confining potential for electrons in the solid

→ photoemission: kick out electrons with a beam of monochromatic light



→ ejected electron has a maximum kinetic energy

$$\frac{1}{2} m_e v_{\text{ejected}}^2 = \hbar\omega - W$$

→ $\omega = \frac{W}{\hbar}$ defines a sharp threshold for emission

→ thermionic emission: at high temperatures ($k_B T \sim W$) electrons can "boil off" from the surface

occupation inside $\dfrac{1}{e^{\beta(\epsilon_n(k)-\mu)}+1}$ where $\epsilon_n(k)$ represents the band structure

occupation outside $\dfrac{1}{e^{\beta\left(\frac{\hbar^2 k^2}{2m} + e\int \vec{E}\cdot dr - \mu\right)}+1}$

$$= \frac{1}{e^{\beta\left(\frac{\hbar^2 k^2}{2m} + W\right)}+1} \sim e^{-\beta W} e^{-\beta\frac{\hbar^2 k^2}{2m}}$$

at high temperatures

→ assume thermal equilibrium with dilute gas of electrons outside

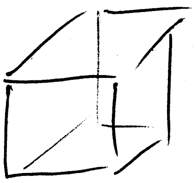
$$j = -2e \int_{k_x>0} \frac{d^3k}{(2\pi)^3} v_x \frac{1}{e^{\beta(E_n(k)-\mu)}+1} = e^{-W/k_BT}(-2e)\int_{k_x>0}\frac{d^3k}{(2\pi)^3}\frac{\hbar k_x}{m} e^{-\hbar^2k^2/2m}$$

↑ for n crossing the fermi level

$$= -\frac{em}{2\pi^2\hbar^3}(k_BT)^2 e^{-W/k_BT}$$

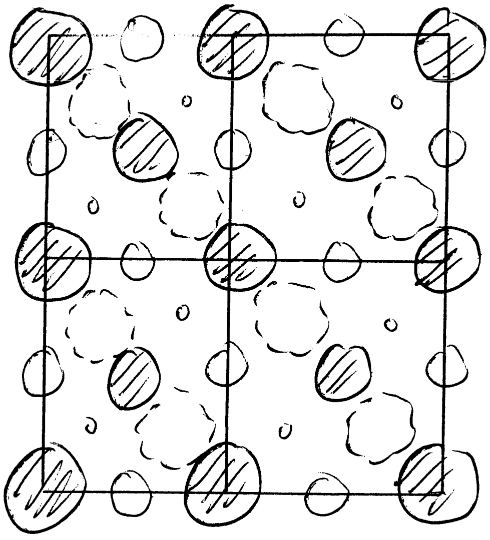
* Often important structural changes at the surface

e.g. crystalline silicon

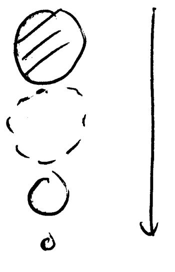


conventional unit cell

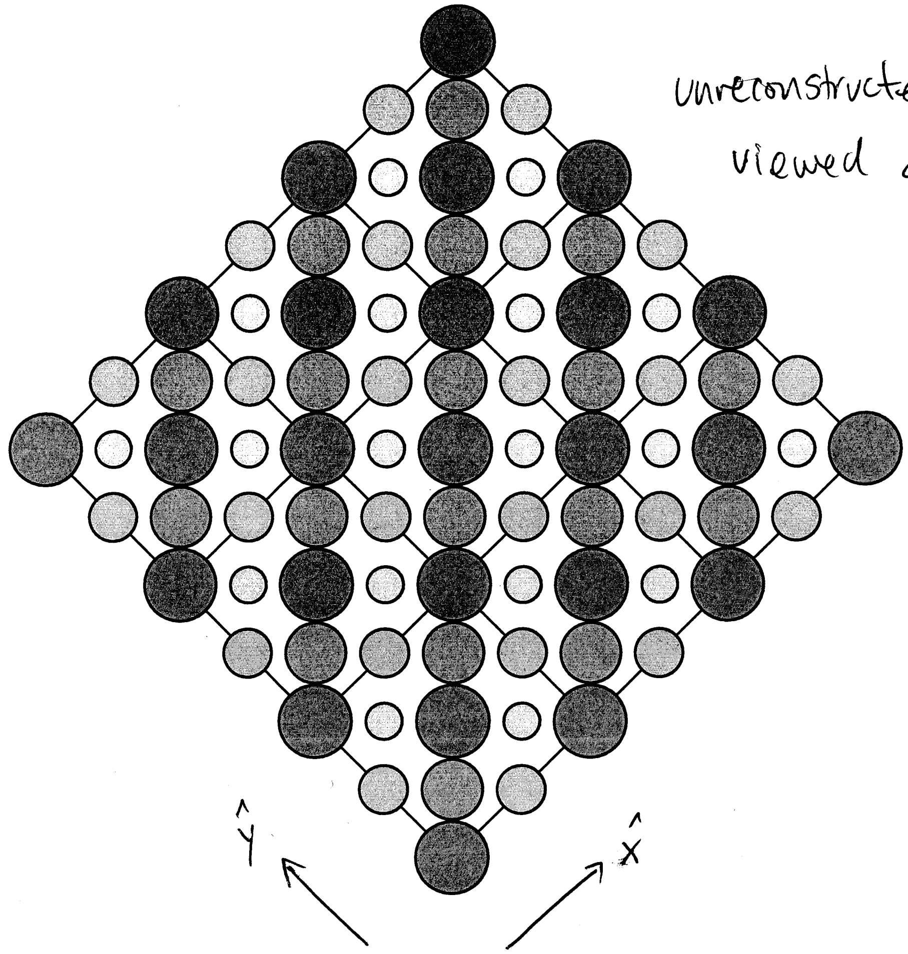
diamond structure (fcc + $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ basis)



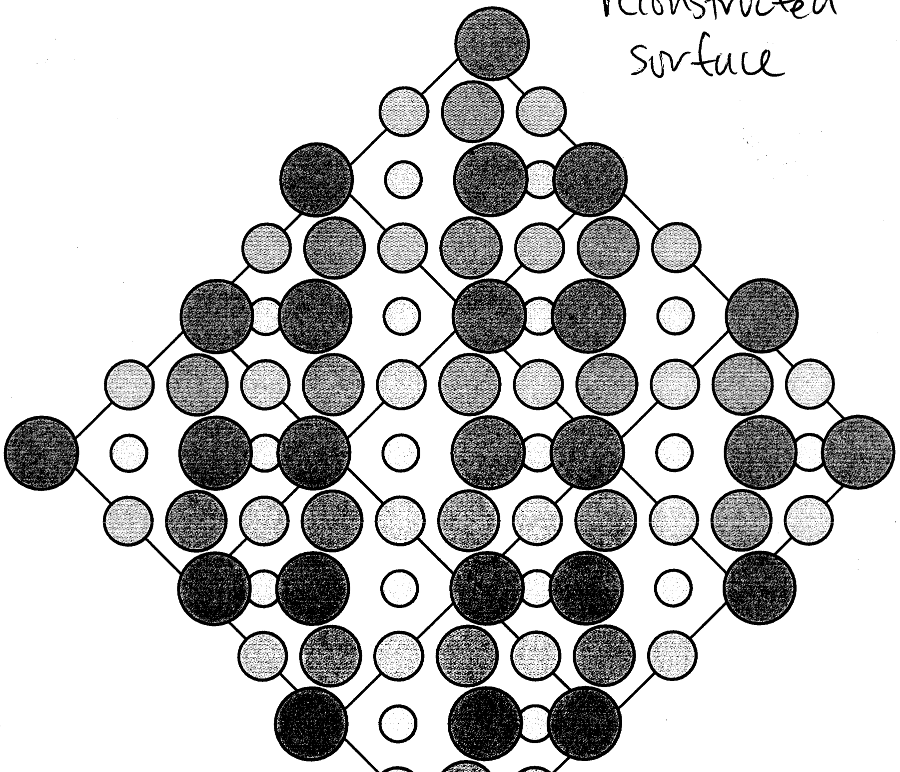
top-down view of cleaved (100) surface



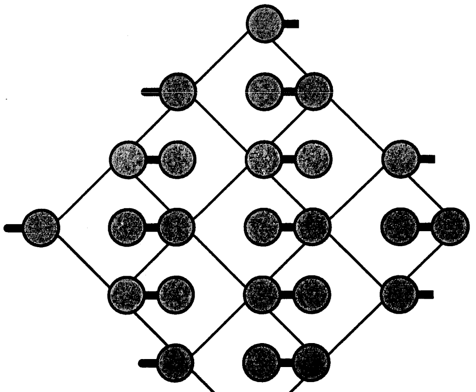
unreconstructed surface viewed at 45°



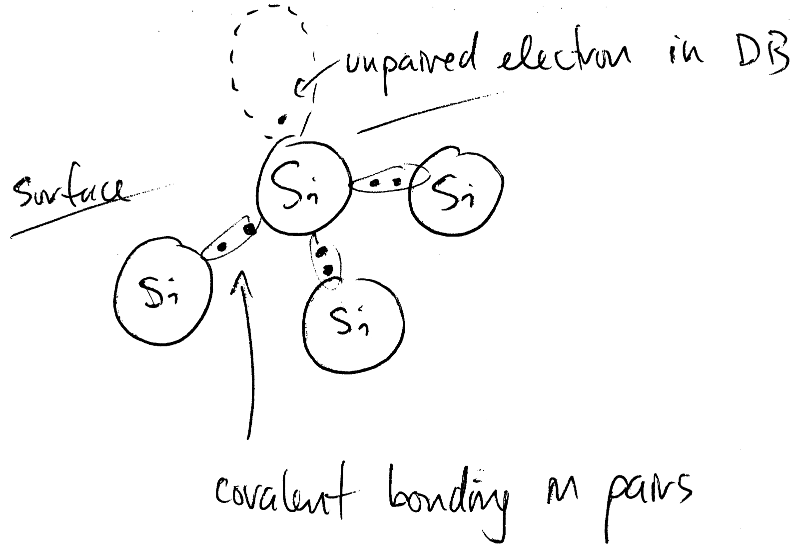
reconstructed surface



dimerization changes the periddicity of the surface

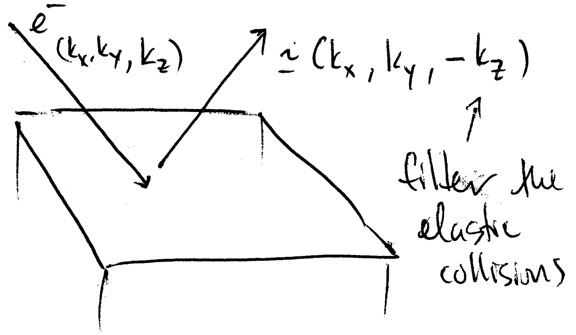


→ driven by energetics of dangling bond orbitals



* How to image the surface?

→ Low-energy electron diffraction (LEED)



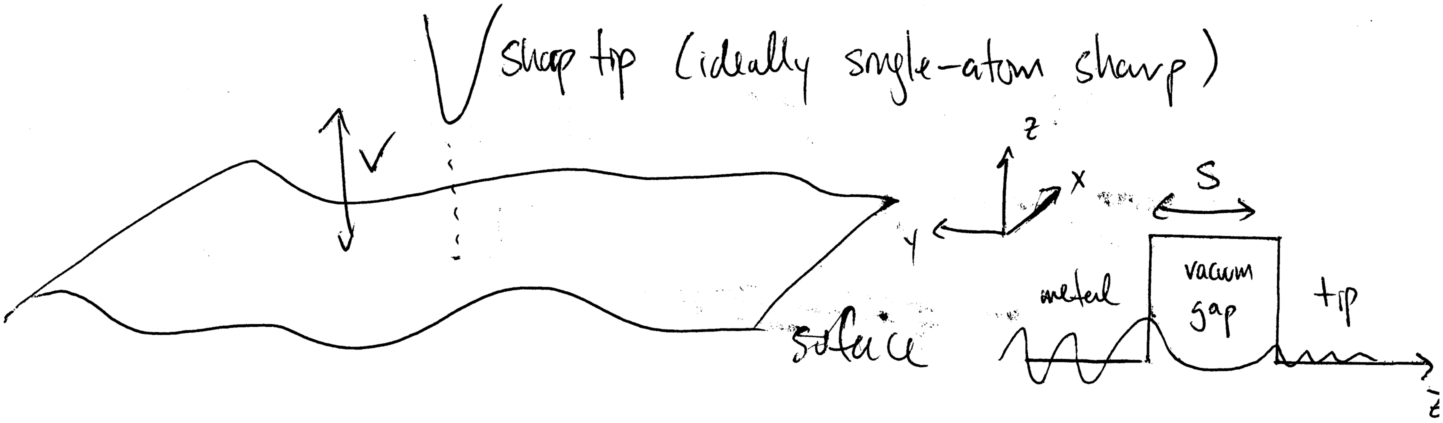
where k_z is arbitrary and (k_x, k_y) is a reciprocal lattice vector of the plane

→ wavelength $\lambda = 12.2\,\mathring{A}\left(\frac{E}{eV}\right)^{-\frac{1}{2}}$

so energies ~ 100 eV lead to $\lambda \sim \mathring{A}$

→ energies $\lesssim 10^3$ eV have huge cross-sections, so the electrons penetrate a few atomic distances at most (no Bragg scattering in $\hat{z}$ direction)

→ Scanning tunnelling Microscopy (STM)



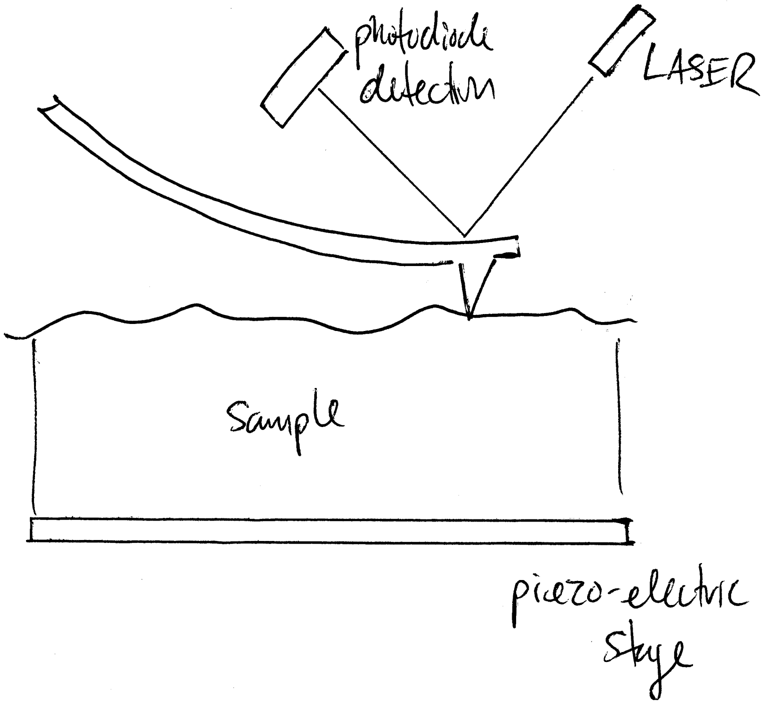
→ quantum tunnelling of electrons from sample to tip (or vice versa) due to an applied voltage

→ tip on a piezo-electric stage with raster scanning in xy and height adjustment in z

→ since the current is exponential in the separation s, typically run in constant current mode: feedback loop of adjusting V to maintain the current and measuring s(xy) to get a "height map"

→ measuring local DOS on the surface

→ atomic force microscopy: applicable to insulators, which have no LDOS.



→ Contact mode in which the cantilever is dragged across the surface and its deflection measured

→ noncontact mode in which the cantilever is suspended above the surface and driven to oscillate near its resonant frequency; van der Waals forces with the surface shift the resonance