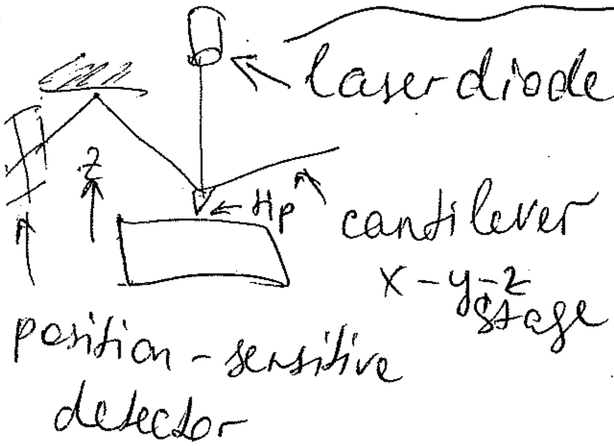
Lecture # 11

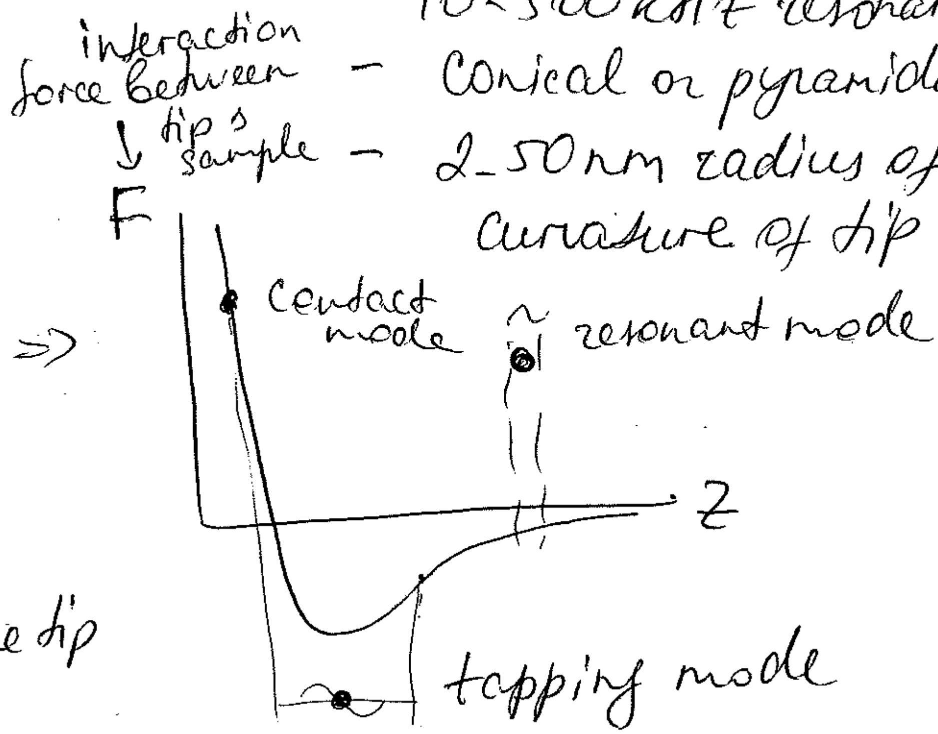
Atomic force microscopy



Typical cantilever:
- rectangular or V-shaped
- 50-250 μm length
- 0.01-100 $\frac{N}{m}$ stiffness
- 10-500 kHz resonance freq.
- Conical or pyramidal tip
- 2-50 nm radius of curvature of tip apex

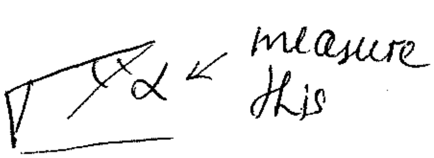
Modes:
- contact
- friction
- resonant
- tapping

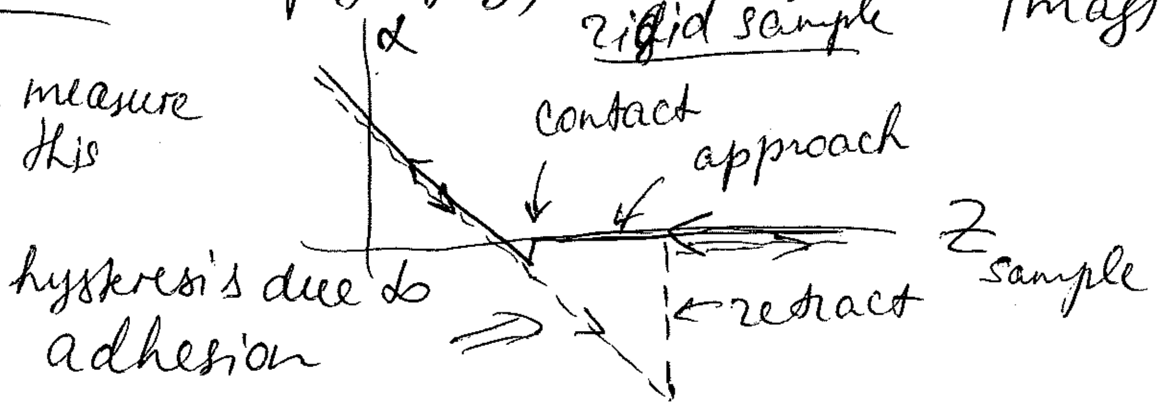
⇒



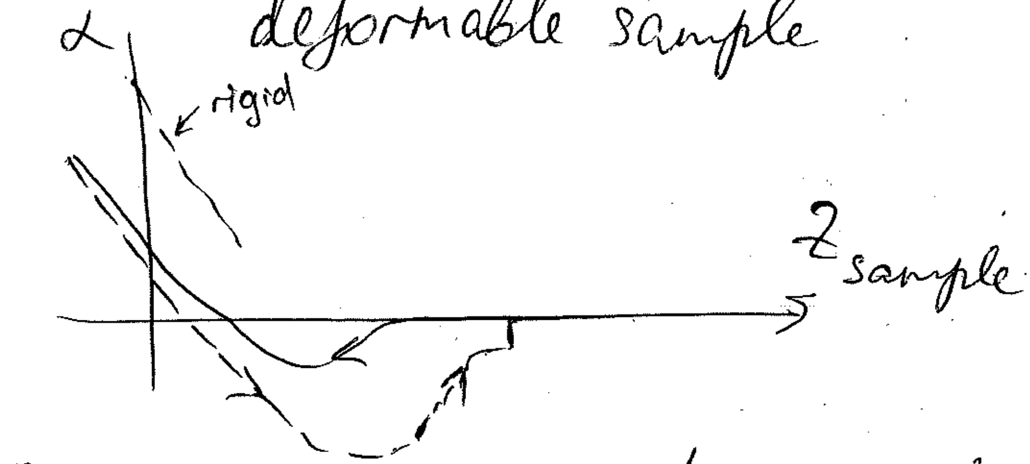
Resolution → depends on the tip shape & size

Contact mode: topography, elasticity & adhesion imaging





deformable sample



<u>Resonant mode:</u>

- drive cantilever ~~with~~ at a fixed frequency close to resonance and follow variations in amplitude & phase. Sample height is servo-controlled at a constant amplitude. Used in air.

<u>AM</u> - AFM $\Leftarrow$

amplitude modulated

- Dynamic mode - phase-locked loop which holds vibration amplitude & phase difference at certain values. Self-oscillations & their resonant freq. are monitored. $\Rightarrow$ <u>FM</u>-AFM freq. modulated

Typically used in UHV

General problem: find vibrational modes of a beam (cantilever) clamped at one end and subjected to a force field at the other. In a simple, one-mode, case $\Rightarrow$

$$\ddot{x} + 2\beta\dot{x} + \omega_0^2 x = \gamma\cos\omega t + \frac{f(D,t)}{m}$$

displacement of tip from equilibrium

ω_0 – resonant frequency $= \sqrt{\frac{K}{m}}$

$Q = \frac{\omega_0}{2\beta}$

quality factor

dissipation

~400 in air

~10,000 in UHV

~10 in water

γ – amplitude of excitation at frequency ω

$f(D,t)$ – tip-sample interaction

D: tip-sample separation when cantilever is not deflected

$x \ll D$

$\Rightarrow$ if $f(D,t) = f(D+x) =$
$= f(D) + f'(D)x \Rightarrow$

$$\ddot{x} + 2\beta\dot{x} + \underbrace{\left[\omega_0^2 - \frac{f'(D)}{m}\right]}_{=\omega_0'^2} x = \gamma\cos\omega t + f_0$$

resonance shifts!

Tapping mode $\Rightarrow$ seek solution $x = A\cos(\omega t - \varphi)$

Energy dissipated by tip-sample interaction over one cycle $U_{diss} = \oint f(D,t)\,dx = Am\gamma\left(\frac{2A\beta\omega}{\gamma} - \sin\varphi\right)$

If A is held constant when an image is scanned, the phase offset φ between excitation & oscillation of cantilever is a measure of U_{diss}.

Can do: elasticity measurements on a single molecule, magnetic measurements, electrical $\Rightarrow$ EFM (e.g. image working transistors), KFM, SCM, etc.

EFM: electric ~~field~~

KFM: Kelvin

SCM: Scanning capacitance

KFM $\Rightarrow$ apply voltage to the tip;

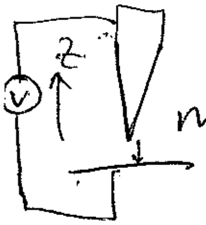
Since applied force is capacitive, $F \sim V^2$

$+ \sim V v \sin 2\omega t \Leftarrow$ Potential difference $= V + v \sin \omega t$

If cantilever is driven at $\omega \approx \frac{\omega_0}{2} \Rightarrow$ can measure signal at ω_0 and determine V which includes applied voltage and electrical characteristics of the sample.

Scanning tunneling microscopy (STM)

Binnig & Rohrer (1982) $\Leftarrow$ Nobel Prize in Physics 1986



measure tunneling current

$$I \sim \frac{e^2 V}{\hbar} \rho_s(r_0, E_F)\, \rho_t(E_F)$$

low V; Tersoff-Hamann theory

$\rho_s(r_0, E_F)$: DOS at the measured surface at tip position r_0

$\rho_t(E_F)$: DOS of the tip at energy E_F

$$\Psi(z) = \Psi(0)\, e^{-Kz}$$

$$K = \frac{\sqrt{2m(V-E)}}{\hbar} = \frac{\sqrt{2m\varphi}}{\hbar}$$

φ: work function of metal (W, Pt, Au, ...) $\sim 5\,eV$

$K \sim 1\,Å^{-1}$

$\Rightarrow$ high resolution in z!

$$I = \frac{2\pi}{\hbar} e^2 V \sum_{nm} |M_{nm}|^2 \delta(E_n - E_F)\, \delta(E_m - E_F),$$

$$M_{nm} = \frac{\hbar}{2m} \int_S dS \left(\Psi_n^* \vec{\nabla} \Psi_m - \Psi_m \vec{\nabla} \Psi_n^* \right)$$

Low V $\Rightarrow$ Tersoff - Hamann theory - applicable to metals only

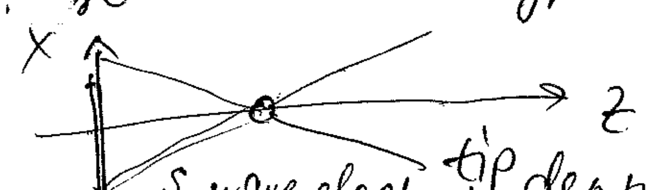
For semiconductors $\Rightarrow$ ($V \sim 1V$)

$$I = \int_0^{eV} \rho_s(r_0, E)\, \rho_t(r_0, -eV + E)\, T(E, eV, r_0)\, dE$$

$$\underset{\substack{\uparrow \\ \text{WKB}}}{T(E, eV) =} \exp\left[-\frac{2z\sqrt{m}}{\hbar} \sqrt{\frac{\varphi_s + \varphi_t}{2} + \frac{eV}{2} - E} \right]$$

For $eV < 0$ (negatively polarised surface) $\Rightarrow$ have T_{max} at $E = 0$, which corresponds to the electrons in the Fermi level of the surface. For $eV > 0$, T_{max} is at $E = eV$ $\Rightarrow$ electrons in the Fermi level of the tip.

<u>Resolution</u> $\Rightarrow$ depends on the tip & sample states $\Rightarrow$ assume that there is only one atom at the very end of the tip which participates in the tunnel current. Also assume S-type wave $|\Psi|^2 \sim \frac{e^{-2Kr}}{r^2}$, $r = \sqrt{x^2 + z^2}$



At $z \gg x \Rightarrow |\Psi|^2 \simeq \frac{e^{-2Kz}}{z^2} e^{-\frac{Kx^2}{z}}$ ⑥

FWHM of the Gaussian is $\Delta x = \sqrt{\frac{2z}{K}}$ $\Rightarrow$

If $K \simeq 1 Å^{-1}$ and z in Å, order of magnitude of the spatial resolution

$\Delta x \sim 1.4 \sqrt{z}$ Å

how small a feature can STM distinguish

In the Tersoff-Hamman theory, $z = d + R$

tip-sample distance

radius of curvature of the tip apex

the best resolution $\Rightarrow$ $\boxed{\text{Sub-pm vertical, sub-Å lateral}}$

$\sim 1.4 \sqrt{R}$ Å

this is not known accurately though

Contrast $\Delta z \simeq \frac{2}{K} e^{-2z\left(\sqrt{K^2 + \frac{\pi^2}{a^2}} - K\right)}$

how different the signal between two inequivalent positions

For large lattice periods, i.e. $a \gg \frac{\pi}{K}$; large contrast = large DOS difference $\Rightarrow$

high, almost z-independent contrast

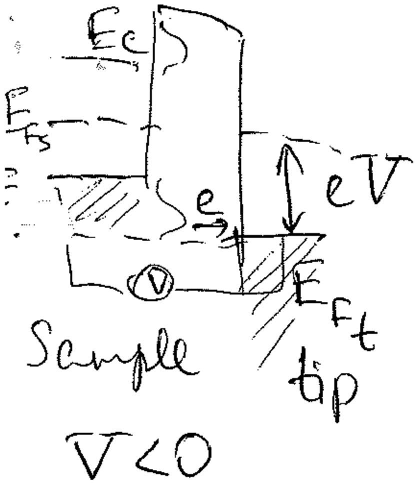
E.g. for $\Phi = 4eV$, $\Delta z \simeq 1.6$ Å at $a = 12$ Å

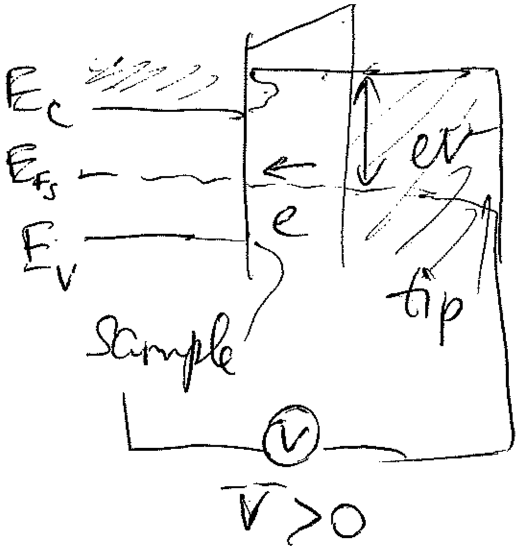
If $a < \frac{\pi}{K} \Rightarrow \Delta z \to e^{-\frac{\pi^2 z}{a^2 K}}$ ← exp decrease with tip-sample distance

STM spectroscopy

hold tip fixed above the surface; measure $I(V)$ $\Rightarrow$

get electronic structure of the surface at diff. energies





Generally, need UHV and <10K

Elastic current ⇔ electrons do not interact with surface ⇒ their energy is const.;

$\underbrace{\text{no coupling}}_{\text{electron - phonon}}$

In metals, $T(V) \sim aV \Rightarrow \frac{dI}{dV} \sim \rho_s(E)$

$$\frac{dI/dV}{I/V} = \frac{\rho_s(E)}{\frac{1}{eV}\int_0^{eV} \rho_s(E)\,dE}$$

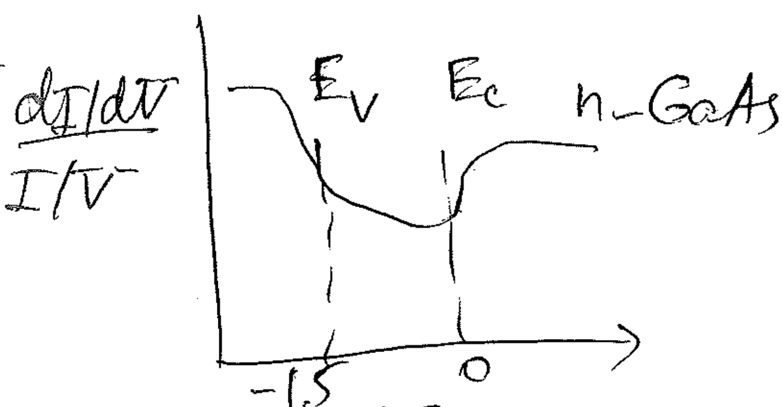
tip-sample distance at 0 bias

For $V < \varphi \Rightarrow z(V) = z_0\left(1 + \frac{|V|}{4\varphi}\right)$

$\underbrace{T(V)}_{max} = e^{-\frac{2\sqrt{2m}}{\hbar}\sqrt{\varphi - \frac{|V|}{2}}}$ keep const

$z\sqrt{1 - \frac{|V|}{2\varphi}} = z_0$

Example



$eV = E - E_F$

Inelastic current ⇒ $\frac{d^2I}{dV^2}$ ⇒ set the sample voltage

vibrational energy of a single bond

done on single molecules