5. Scanning probe microscopies

5.1 General concept behind scanning techniques

- Computer controls (x,y)-movement of tip over surface
- At each raster point signal is converted to pixel intensity to generate image
- 3D scanner based on piezoelectric materials (PbZrTiO₃, PZT)
- Vibrational isolation is crucial
- Alternative mode: fixed (x,y), vary probe mode: spectroscopy
5.2 Scanning Tunneling Microscopy (STM)

5.2.1. General idea

- Binning, Rohrer, Gerber and Weibel 1982, 1986 NP for Binning and Rohrer
- Bring two metals close to each other and measure tunneling current

Tunneling is a convolution of tip and sample states
- Tunneling highly sensitive to tip-sample distance
- Dominated by electrons at $E_F$, which see the lowest barrier
- Semiconductors have no states at $E_F$. Need much higher voltages to tunnel into valence/conduction band

Negative tip bias: Probe empty substrate states
Positive tip bias: Probe filled substrate states
5.2.2. Setup

- Monoatomically “sharp” tip (W, Pt/Ir) rastered over surface
- Electronics control voltage (0-3 V) and measure current (1 pA – 10 nA)
- Typical “resistance” of the gap is ~10^7 – 10^10 Ω. Typical tip-sample separation is ~2-5 Å
- Since tunneling current decreases rapidly with distance:
  i) Very good vertical resolution
  ii) If tip is sufficiently sharp, most \( I_t \) will go through pinnacle atom. Good lateral resolution

- Modes of operation:
  - Constant height (CH)
  - Constant current (CC)
  - Spectroscopy (STS)

- Spectroscopy mode has potential to map out electronic structure with atomic precision (resolve “location” of individual electronic states)
5.2.3. Tunnel theory

i) 1D quantum mechanical tunneling

Rectangular barrier ($\kappa d >> 1$):

\[ T \sim \exp(-2\kappa d) \]

\[ \kappa = \frac{(2m\Phi)^{\frac{1}{2}}}{\hbar} = 0.51 \text{ [eV]^{\frac{1}{2}}} \]

\[ \kappa \approx 1-2 \text{ Å}^{-1} \text{ for typical metals} \]

ii) Bardeen transfer hamiltonian

\[ H = -\hbar^2\Delta/(2m) + V_S + V_T \]

Fermi’s golden rule:

\[ I = 2e \sum_{k'=\text{empty}}^{k'=\text{empty}} T_{kk'} = 2e \sum_{k'\text{occ}} T_{kk'} \frac{2\pi}{\hbar} |M_{kk'}|^2 \delta(\varepsilon_k - \varepsilon_{k'}) \]

and $M_{kk'} = \langle \psi_k | V_T | \phi_{k'} \rangle$ Bardeen matrix element

\[ T \rightarrow 0K: \quad I = \frac{4\pi e v}{\hbar} \int_0^{\varepsilon_F} d\varepsilon \int \frac{d^2 k}{(2\pi)^2} \int \frac{d^2 k'}{(2\pi)^2} |M_{kk'}|^2 \rho_k^{\text{tip}}(\varepsilon) \rho_{k'}^{\text{sample}}(\varepsilon) \]

Tersoff-Hamann Approximation:
- Limit of low bias (constant matrix-element)
- Single tip atom at \( R_o \), with s-like DOS

\[
I \sim \int_0^{eV} d\varepsilon \, \rho_{\text{sample}}(\varepsilon, R_o)
\]

- Practical evaluation:
  - Compute \( \rho_{\text{tot}}(x, y, z) = \int d\varepsilon \, \rho_{\text{sample}}(\varepsilon, x, y, z) \)
  - Solve \( \rho_{\text{tot}}(x,y,R_o) = \rho_o \)
  - Plot \( R_o(x,y) \) to simulate constant current mode

“Real tips” – Bardeen matrix elements:
- Compute \( M_{kk'} = \langle \psi_k | V_T | \phi_{k'} \rangle \)

\[
M_{kk'} = -\frac{\hbar^2}{2m} \int dS \left( \psi_k^*(r) \nabla \phi_{k'}(r) - \phi_{k'}^*(r) \nabla \psi_k^*(r) \right)
\]

iii) Landauer-Büttiker formula
- View tunneling as a scattering problem
- General relation between current and conductance:
  \[
  I = \int_0^{eV} dE \, G(E)
  \]
- Exploit LB-formula to relate \( G \) to transmission coefficient:
  \( G(E) = 2e/h \, T/R \approx 2e/h \, T(E) \)

iv) “Exact” tunnel theory: Keldysh Green’s functions
- Current operator in 2\text{nd} quantization:
  \[
  \hat{j}_{ij} \sim \hat{\alpha}_i^+(t+)\hat{\alpha}_j(t) + \hat{\alpha}_j^+(t+)\hat{\alpha}_i(t)
  \]
- Identify with Keldysh Green’s functions
  \[
  I = \langle \hat{j}_{ij} \rangle \sim G_{ji}^+(\tau) - G_{ij}^+(\tau)
  \]
5.2.4. STM applications

Static:
- Mesoscopic surface structure (domains, terraces, steps)
- Atomic-resolution images (reconstructions, adsorbate geometries)
- Alloy surface composition (chemical contrast)
- Magnetic domains (magnetic tip)
- Electronic structure (STS)

Dynamic:
- Adsorbate vibrations
- Diffusion (tip-induced!)

Manipulation:
- Atomic jumps under influence of high electric field
- Atom dragging, e.g. due to VdW forces between tip and sample
- Tip-induced chemistry (bond dissociation)

Current challenges:
- high-pressure/reactor STM (Frenken, Besenbacher, Wintterlin, Salmeron,…)
- variable T-STM (Frenken, Bowker, Ramsey,…)
- inelastic STM (Ho,…)

Pt(111), (1µm x 1µm)

Fe on Cu(111), “quantum corral”
5.2.5. Pros and cons

+ “Real space” images
  Excellent lateral (< 1 Å) and vertical (< 0.1 Å) resolution
  Information about surface unit cell, symmetry
  Works in principle in air/liquid/UHV
  Some spectroscopic information (STS) for composition fingerprinting
  Atom manipulation

- Image is convolution of tip and surface electronic structure – not truly a topographic measurement
  Highly sensitive to noise (electrical, vibration)
  Highly sensitive to tips (dull tips, multiple tips)
    → no “routine” images
  Works only for conductive samples (metals, semiconductors) – though can tunnel through thin insulators (< 20-30 Å)
5.3 Atomic Force Microscopy (AFM)

3.3.1. General idea

- Binnig, Quate, Rohrer (1986) as a spin-off of STM
- Relies on forces between a sharp tip (< 100 Å diameter) and surface at very short distances
- Tip is supported on a flexible cantilever

- Hooke’s law: \( F(x) = -kx \)
  If \( k_{\text{Tip}} < k_{\text{Surf}} \): cantilever bends

- Modes of operation:
  Contact mode (\( x < 5\text{Å} \)): strong forces due to Pauli repulsion
  Non-contact mode (10Å < \( x < 100\text{Å} \)): weak forces due to van-de-Waals attraction
  Intermittent (tapping) mode

  and constant height or constant force scans
5.3.2. Signal measurement and cantilever instrumentation

- "beam bounce method" (contact-mode)
- piezoelectric cantilever (resistance change)
- AC driven oscillating cantilever, constant resonance frequency (non-contact, tapping mode)

- Cantilever/tip material: Si$_3$N$_4$, BN
- Fabricated by thin film growth on etched Si wafer
- Shape of etch pit determines tip shape: pyramidal, conical (~50Å diameter).
- Tip shape (aspect ratio) determines resolution
5.3.3. AFM applications and variants

- mesoscopic surface structure, particularly of soft materials
- Magnetic force microscopy (MFM): magnetic structure
- Lateral force microscopy (LFM): friction/tribology, but must acquire simultaneous AFM and LFM images to deconvolute twisting due to surface roughness
5.3.4. Pros and cons

+ True topographic imaging
Non-contact or tapping mode cause minimum damage to soft/fragile samples
Not limited to conducting samples
  → especially powerful for biological, organic and polymer samples
Works in air/liquid/UHV
Commercial tips and cantilevers
Related AFM techniques can measure other physical properties:
  hydrophobicity, magnetism, electrostatic charge, friction, elastic modulus

- Tip shape convolutes into image
Typical lateral resolution only ~50Å (is steadily improving though)
Highly sensitive to noise (vibrations)
Highly sensitive to tips (dull tips)
  → no “routine” images
Presence of water (capillary action) may distort image
“Chemically blind”

Screw dislocation in a single-crystal of a long-chain alkane (14µm x 14µm)