An introduction to surface microscopy probes
SPM is ubiquitous in modern research

**Physics**
- *Science* 343(6169), 390-392 (2014)

**Nanotechnology/chemistry**

**Materials**
  doi:10.1038/nmat4384
Advantages

- High resolution
- Local, no requirement for periodicity
- Can probe a number of characteristics, depending on the mode
- Beautiful data

*ACS Nano, 2013, 7 (2), pp 1652–1657*
SPM: elegant physics + smart engineering

Physics – what are we measuring when we put a probe so close to a surface?

Engineering – how do we position the probe and measure the signal?
SPM in generic terms

- Positioner
- Transducer
- Probe
- Signal

Electronics/Computer:
- Noise reduction (vibrational + electronic)
- Probe deflection and raster scan generation
- Feedback loop
- Data storage
The signal determines the acronym

AFM, atomic force microscopy
- Contact AFM
- Non-contact AFM
- Dynamic contact AFM
- Tapping AFM
BEEM, ballistic electron emission microscopy
CFM, chemical force microscopy
C-AFM, conductive atomic force microscopy
ECSTM, electrochemical scanning tunneling microscope
EFM, electrostatic force microscopy
FluidFM, fluidic force microscope
FMM, force modulation microscopy
FOSPM, feature-oriented scanning probe microscopy
KPFM, kelvin probe force microscopy
MFM, magnetic force microscopy
MRFM, magnetic resonance force microscopy
NSOM, near-field scanning optical microscopy (or SNOM, scanning near-field optical microscopy)

PFM, Piezoresponse Force Microscopy
PSTM, photon scanning tunneling microscopy
PTMS, photothermal microspectroscopy/microscopy
SCM, scanning capacitance microscopy
SECM, scanning electrochemical microscopy
SGM, scanning gate microscopy
SHPM, scanning Hall probe microscopy
SICM, scanning ion-conductance microscopy
SPSM, spin polarized scanning tunneling microscopy
SSM, scanning SQUID microscopy
SSRM, scanning spreading resistance microscopy
SThM, scanning thermal microscopy
STM, scanning tunneling microscopy
STP, scanning tunneling potentiometry
SVM, scanning voltage microscopy
SXSTM, synchrotron x-ray scanning tunneling microscopy
SSET, Scanning Single-Electron Transistor Microscopy

STM – basic schematic

- Positioner
- Preamplifier
- Probe
- Tunneling current
- Surface
- Noise reduction (vibrational + electronic)
- Electronics/computer
  - Probe deflection and raster scan generation
  - Feedback loop
  - Data storage
TUNNEL EFFECT

All the animations and explanations on www.toutestquantique.fr
STM: the elegant physics part

Q. How do we describe the electrons in the tip/gap/sample region?

A. With quantum mechanics.

Regions I and III

\[ -\frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} = E \Psi(x) \]

Region II

\[ -\frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} = (U - E) \Psi(x) \]
STM: the importance of the gap (qualitative)

Increasing the gap decreases the probability of tunneling.
STM: Bardeen’s approach

The derivation is not straightforward, but the results are really useful.

Fermi’s Golden Rule gives the probability for an electron in state $\Psi$ to tunnel to state $\chi$:

$$w = \frac{2\pi}{\hbar} |M|^2 \delta(E_\Psi - E_\chi)$$

$M$ is a tunneling matrix element found from the Bardeen surface integral in the gap between the tip and sample:

$$M = -\frac{\hbar^2}{2m} \int_{\Sigma} (\chi^* \nabla \Psi - \Psi^* \nabla \chi) \cdot dS$$


STM: Bardeen’s approach

At a bias voltage $V$, the tunneling current $I$ depends on the density of states ($\rho$) of both the tip and the sample, considered in the energy interval from 0 to $eV$:

$$I = \frac{4\pi e}{\hbar} \int_0^{eV} \rho_s(E_F - eV + \epsilon)\rho_t(E_F + \epsilon)|M|^2 d\epsilon$$
Tunneling current in STM depends importantly on two factors

1. The local density of states (LDOS)
   - States in the tip and sample both contribute to the LDOS
   - The number of accessible states depends on the magnitude of the bias voltage
   - Signal depends on either filled or empty states in the sample, depending on the sign of the applied bias voltage

2. The tip-sample separation
   - The tip must be angstroms from the surface, and the tunneling current drops off rapidly as the separation increases
Tersoff and Hamann used Bardeen’s approach in the context of STM, and found that under certain conditions (low temperature, low bias) STM conductance is proportional to the sample local density of states at the centre of the tip. This is great, because we can calculate the sample LDOS to predict what STM images should look like for specific systems. Comparing this to experimental data helps us understand STM images.
STM: the engineering part

- How do we make an atomically sharp tip?
- How do we hold the tip within angstroms of the surface?
- How do we measure a picoamp signal?
- How do we continually move the tip across the surface and measure a useful signal?
- How do we calibrate our images and know what we’ve measured?
STM tips 1: electrochemical etching

- Tungsten wire
- Etchant (KOH, NaOH)
- Ring electrode (platinum)
STM tips 2: mechanically formed

Commercial pre-cut PtIr tips
(US$22 each, 6 mm long)


STM tips: cartoon comparison

**TUNGSTEN**

**PT/IR**

Watch out for double tip artefacts!
Double tip = trouble

Simultaneous tunneling through two protrusions of the tip (a “double tip”) can create a doubled image, like the one shown at right.

MacLeod/Lipton-Duffin, unpublished raw data
Sn on Pd(111), 30 nm image
STM tips: choosing your type

Tungsten tips: oxidize more quickly than PtIr. Well-defined apex shape means they can be sharpened/conditioned with sputtering/e-beam. Crashes often fatal.

PtIr tips: slow to oxidize. Poorly-defined apex shape means they can be unstable. Can be conditioned with controlled crashes/voltage pulses. Quick to fabricate.
Piezoelectric materials

No applied field

Field applied

Field applied

positive charge symmetry centre  negative charge symmetry centre
Piezoelectric actuators

The angstrom-scale control (and sometimes the coarse control) of the STM tip is accomplished with piezoelectric actuators.

https://commons.wikimedia.org/wiki/File:Slip-stick_actuator_operation.svg

"Piezomotor type inchworm" by LaurensvanLieshout - Own work. Licensed under CC BY-SA 3.0 via Commons
https://commons.wikimedia.org/wiki/File:Piezomotor_type_inchworm.gif#/media/File:Piezomotor_type_inchworm.gif
Preamplification

Tunneling currents are tiny!
\[ pA = 0.000000000001 \text{ A} \]

- Preamplifiers amplify the tunneling current as close to the tip as possible.
- Typical gains are \(10^7 - 10^9\)
- Tradeoffs must be made
  - gain and bandwidth
  - gain and maximum measurable current

http://dberard.com/home-built-stm/electronics/
The small signals in STM are very susceptible to electrical noise. All cables must be carefully shielded, ground loops avoided, and shielding the whole apparatus also helps.

How can we tell if we’ve got noise?

- Acquire forward and back scan
- Change scan speeds
It is possible to collect forward and reverse scan images because of the way STM images are collected, which is a serial acquisition technique known as raster scanning.

Most microscopes will allow for the acquisition of data in the forward and reverse directions. Most will also allow for a variety of starting positions (any corner) and vertical scanning rather than horizontal.
Constant height imaging

In STM, the tunneling current is determined by the LDOS, the voltage and the tip-sample separation. For a fixed voltage and LDOS, the current changes according to tip-sample separation.

(Some controllers cannot actually do this.)

Video at:
Constant current imaging

In STM, we usually set the current to a specific value, then reposition the tip to maintain this value as the tip is scanned across the surface (at a fixed voltage).

Video at: http://www.ntmdt.com/spm-principles/view/constant-current-mode
The feedback loop

The measured tunnel current is compared to the set point, and the tip position is corrected according to a PID loop. Note that not every STM controller uses all three terms in the correction.
Tuning the feedback loop

Ideal tracking

Overdamped

Underdamped

“soft focus”

Au on mica, MacLeod, unpublished raw image, 250 nm lateral scale

Au on mica, Tiffany Hua, unpublished raw image, 400 nm lateral scale
Vibrational noise

(a) Atomic resolution of Si(111)
(b) Atomic resolution of Cu(110)
(c) Atomic resolution of Au(111)
(d) Line profiles from images (a-c)
(e) Which noise profile will allow for atomic resolution on all surfaces?
Vibrational noise

Key issues:
- Building noise must be low
- Slow-response damping stages typically pass only low frequencies (but may amplify these frequencies!)
- Instruments are designed to have high eigenfrequencies


Image artefacts and distortions

**Piezo creep (raster)**
Cu(111) (overheated), Lipton-Duffin and MacLeod, unpublished raw image, 20 nm lateral scale

**Drift (vertical)**
TMA+fullerene, MacLeod, unpublished raw image, 30 nm lateral scale

**Spontaneous tip change**
TMA on HOPG, MacLeod, unpublished raw image, 20 nm lateral scale
Calibration and epitaxy

Good technique: include an unknown structure and a calibration lattice in the same image. Correct the image to the known lattice.

Autocorrelation of an image with two lattices can reveal their commensurability (or lack thereof).
Extensions of STM: $dI/dV$, CITS

Recall: 
\[ I \propto \int_0^{eV} \rho_s((E_F - eV + \epsilon)\rho_t(E_F + \epsilon)d\epsilon \]

So for constant tip LDOS:
\[ \frac{dI}{dV} \propto \rho_s(E_F - eV) \]
Extensions of STM: manipulation
Extensions of STM: manipulation

STM can be used to move atoms around
- Needs to be low temperature (4 K) for the atoms to stay put
- Neat quantum effects
- Less fashionable than it used to be

*Physics Today 46 (11), 17-19 (1993).*
Extensions of STM: electron injection

Tunneling electrons can induce chemical reactions.

Review: MacLeod et al. ACS Nano, 2009, 3 (11), pp 3347–3351

Dissociation by Tunneling Electrons


Extensions of STM: inelastic tunneling spectroscopy

Vibrations of adsorbates can lead to inelastic contributions to tunneling current – this can show up in the second derivative of current.
Atomic force microscopy

Typical Van der Waals force curve

Contact mode
Tapping mode
Non-contact mode

http://upload.wikimedia.org/wikipedia/commons/6/67/AFM_contact_ICM_and_NCM.jpg

"AFM (used) cantilever in Scanning Electron Microscope, magnification 1000x" by Materialscientist
Atomic force microscopy

Advantages:
- Conducting samples are not required – works on any material (including biomaterials)
- Images can be acquired quickly (depends on the mode, resolution)
- AFM is very widely used, and AFMs are very widely available

Most common AFM modes


Video at: http://www.ntmdt.com/spm-principles/view/intermittent-contact-mode

Video at: http://www.ntmdt.com/spm-principles/view/non-contact-mode
Q-plus
Other resources

NT-MDT SPM Principles:  http://www.ntmdt.com/spm-principles

Hyperphysics:  http://hyperphysics.phy-astr.gsu.edu/hbase/hph.html

STM Tutor:  http://www2.fkf.mpg.de/ga/research/stmtutor/stmindex.html
Summary

STM is a blend of elegant physics and clever engineering

• Tunneling current signal reveals LDOS and topography (physics)

• High resolution depends on engineering (noise, tips, positioning)
What next?

Applying STM to the study of self-assembled molecules in 2D.