Manipulating Atoms and Molecules

• Moving atoms with the STM
• Unwinding proteins with an AFM
• Using an AFM tip as pen
Scanning Tunneling Microscopy (STM)

- Electrons tunnel from the yellow surface atoms to the blue tip atoms (or vice versa), even though they don’t have enough energy to get into the vacuum gap between tip and sample.
- The tunneling probability is 100x lower when retracting the tip by an atom diameter!
STM sees contours of equal **charge density at the electron energy** $E$ (here $E \approx E_{\text{Fermi}}$). The charge density is proportional to the square of the wave function $\psi(z)$.

The wave function $\psi(z)$ decays exponentially: $\psi(z) \propto \exp(-kz)$

The decay constant $k$ is related to the momentum $p=\hbar k$ and the energy $\Delta E=p^2/2m$:

$$k = \frac{\hbar}{2m} \sqrt{2m\Delta E} \approx 5 \text{ nm}^{-1} \left(\frac{\Delta E}{\text{eV}}\right)^{\frac{1}{2}} \approx 10 \text{ nm}^{-1} \text{ for } \Delta E \approx 4\text{eV} \text{ (typical work function)}$$

Moving the tip up from $z$ to $(z+\Delta z)$ causes the charge density to drop by the factor:

$$|\psi(z+\Delta z)|^2 / |\psi(z)|^2 = \exp(-2k\Delta z) \approx e^{-4} \approx 10^{-2} \text{ for } \Delta E \approx 4\text{eV}, \Delta z \approx 0.2\text{nm (1 atom)}$$
Moving Atoms with the STM

Lateral force < Tip force < Surface force

Need loosely-bound atoms which diffuse easily.
⇒ Works only at low temperature (< 10 K).
Building a Quantum Corral

Crommie and Eigler
Unwinding Proteins with an AFM Tip

Figure 1 | Applications of the scanning force microscope (SFM). a | The principal SFM components. Laser light is focused onto the back of a cantilever that ends with a nanometre-scale tip. The reflection and corresponding position of the tip is detected by a position-sensitive photodiode. A piezo-electric scanner moves the sample in all directions, enabling the tip to scan topography or to extend molecules attached to the surface. b | Diagrams and force curves showing the mechanical unfolding of repeating immunoglobulin-like domains. As the distance between the surface and tip increases (from state 1 to state 2), the molecule extends and generates a restoring force that bends the cantilever. When a domain unfolds (state 3), the free length of the protein increases, relaxing the force on the cantilever. Further extension again results in a restoring force (state 4). The last peak represents the final extension of the unfolded molecule before detachment from the SFM tip (state 5).
AFM measures contours of equal **force**. When approaching a solid, the AFM tip encounters two forces: First, it is attracted to the surface by the **van der Waals force**, which is caused by the electric attraction between oscillating dipoles in the tip and at the surface. When the tip touches a surface atom, it is repelled by **Pauli repulsion** which prevents atoms from overlapping.
Using an AFM Tip as Pen

As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a danger in the market. They tell me by which you can write the Lord’s Prayer on the head of a pin. But that’s nothing; that’s the most primitive, halting step in the direction I intend to discuss. It is a staggering small world that is below. In the year 2050, when they look back at this age, they will wonder why it was not until the year 1950 that anybody began seriously to move in this direction.

Richard P. Feynman, 1959
Figure 2.5. (a) A schematic representation of the STM patterning of SAMs. (i) Normal STM imaging of the SAM with tip bias $V_b$; (ii) Removal of SAM by applying a pulse $V_p$ to the gold substrate; (iii) The same as (ii) in solution of conjugated oligomers; (iv) insertion of conjugated oligomers in the patterned sites. (b) STM image of dodecanthiol and conjugated oligomeric patterned SAMs. (i) The STM image after consecutive pulsing at three different locations indicating insertion of molecules (two peaks) and one pit without insertion. (ii) The same region imaged a few minutes later showing adsorption into the remaining pit. (iii) A programmed pattern consisting of circles tracing out a rectangle. (iv) The resulting image of the patterned dodecanthiol SAM after chemisorption of the conjugated oligomers showing the produced rectangular frame.
Atomic Scale Doping

STM-based fabrication of phosphorous dopant nanostructures. Each STM image shows the same region of the surface.

1) Passivating a silicon surface with H.
2) Activating specific regions by desorbing H with electric pulses from a STM tip. Panel a) with dangling bonds bright.
3) Selective adsorption of phosphine on the activated regions. Panel b) with black arrows showing PH, white arrows PH$_2$, gray arrows dangling bonds.
4) Incorporate phosphorus by annealing 5 s at 350°C. Panel c) with white arrows for ejected silicon atom chains, black arrows for incorporated phosphorous.