Modification of graphite surfaces for the adsorption of molecular motors

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Chapter 2

Scanning Tunneling Microscopy

This chapter outlines the basic working principle of the scanning tunneling microscope (STM) and describes the sample preparation performed prior to the measurements described in this thesis.
Applications of the scanning tunneling microscope (STM) were discussed in the previous chapter, illustrating the importance of this tool also in the field of molecular nanomachines. The possibilities of the STM were first explored in 1981, when Binnig and Rohrer built a microscope based on electron tunneling. Their invention made it possible to visualize conducting and semi-conducting surfaces with atomic resolution.\(^1\) In 1986, just 5 years after their revolutionary invention, Binnig and Rohrer received the Nobel Prize in Physics due to the wide range of potential applications in several scientific research areas of this scanning probe technique.

### 2.1 Quantum tunneling

Quantum tunneling is the non-classical penetration of small particles through a barrier.\(^3\) Consider a system in which an electron, which simultaneously behaves as a particle and a wave, is incident with energy \(E\) upon a potential barrier of height \(\Phi\) and width \(d\). In classical physics it is not possible for an electron to overcome the barrier when \(\Phi > E\). Yet, according to quantum mechanics, there is a possibility that this electron (described by a wave function \(\psi\)) penetrates the barrier or even “tunnels” through it. This phenomenon is referred to as quantum tunneling. The system can be described by the stationary Schrödinger equation:

\[
\hat{H}\psi = -\frac{\hbar^2}{2m_e} \frac{d^2\psi}{dx^2} + \Phi(x) = E\psi
\]

where \(\hbar\) is the reduced Planck constant, \(m_e\) the electron rest mass, \(x\) the displacement in the \(x\)-direction and \(\hat{H}\) the one-dimensional Hamiltonian. The solutions of the Schrödinger equation for a one-dimensional rectangular barrier are extensively discussed in several textbooks.\(^3\) A schematic representation of an incoming wave \(\psi\) penetrating the potential barrier is depicted in Figure 2.1a. When the wave approaches the barrier from the left at \(x = 0\) it will be partly reflected in zone I and the incoming and reflected wave are therefore superimposed in this zone. Inside the barrier, zone II, the amplitude of \(\psi\) exponentially decreases with increasing \(x\). At the right side of the barrier (zone III), \(\psi\) continues with lower amplitude and thus lower probability density. The tunnelling current \(I_t\) can be expressed as:

\[
I_t \propto e^{-2\kappa d}
\]

where \(\kappa\) is the reciprocal decay length for all tunneling electrons given by:

\[
\kappa = \sqrt{\frac{2m(\Phi - E)}{\hbar}}
\]
These derivations are based on the fundamental model of an electron passing through a one-dimensional potential barrier and offer a first approach to tunneling between two conducting surfaces. The working principle of a STM is based on the tunneling process between the tip and the sample (Figure 2.1b). When the STM tip is carefully brought to within 1 nm of the conducting sample, a tunneling current can be measured between the STM tip and the sample. The exponential dependence of the tunneling current on the thickness of the tunnelling barrier provides the basis for the astonishing resolution of the STM. By an increase in the tunneling gap of 1 Å the tunnelling current decreases roughly by an order of magnitude.

Figure 2.1 Two schematic representations of quantum tunneling. a) Representation of a one-dimensional rectangular potential barrier with height $\Phi$ and width $d$. The turquoise line represents the wave function $\psi$ of an electron traveling from zone I to III through the potential barrier. In zone I ($x < 0$), the incoming wave travels with energy $E < \Phi$ from left to right. Within the barrier, zone II ($0 \leq x < d$), the wave function $\psi$ decays exponentially and is transmitted with a lower amplitude (lower probability) in zone III ($x \geq d$). b) Schematic energy diagram of the sample and the STM tip when they are in tunneling contact. A negative bias applied to the sample causes the Fermi levels to shift with respect to each other. This results in an electron flow from the filled states of the sample into the empty states of the tip. The work functions $\Phi_{\text{sample}}$ and $\Phi_{\text{tip}}$ represent the minimum energy barriers that electrons would need to overcome to leave the sample and the tip, respectively.

The monitored tunneling current during the acquisition of STM data does not only depend on $\kappa$ and the tip-sample distance but also on the tip radius and the applied bias voltage. Foremost, the tunneling current acquired during the STM measurements depends on the density of states (DOS) of the tip and the sample. The exact geometry of the tip apex is unknown and thereby also the orbitals at the end of the tip. Tersoff and Hamann assumed a system wherein the wave function of the tip atom closest to the surface is described as a spherical $s$-orbital (Figure 2.2a). The dependence of the tunneling current can be expressed as:

$$I_t \propto V_{\text{bias}}\rho_{\text{tip}}(E_F)\rho_{\text{sample}}(r_0, E_F)e^{-2kd} \tag{2.1.4}$$
where $V_{\text{bias}}$ is the bias applied between the tip and the sample, $\rho_{\text{tip}}(E_F)$ is the DOS of the tip at the Fermi level and $\rho_{\text{sample}}(r_0,E_F)$ is the local density of states (LDOS) of the sample at the position of the tip $r_0$ (Figure 2.2a) at the Fermi level. We can see from equation 2.1.4 that for a constant DOS of the tip, i.e. constant $\rho_{\text{tip}}(E_F)$, the STM probes the LDOS of the sample. Therefore, the tip follows the contour of $\rho_{\text{sample}}(r_0,E_F)$ when the system is operating in constant current mode.

![Figure 2.2 Schematic representations of an STM tip during measurements. a) Schematic representation of the geometry of the STM tip according to Tersoff and Hamann. The tip is assumed to be locally spherical with radius R. The center of the curvature is labeled as $r_0$, where $d$ is the distance of the tip apex and the surface. b) Schematic representation of the STM operating in a constant current mode. The dashed line represents the pathway of the tip, which follows the contour of the LDOS of the surface in order to keep $I_t$ constant.]

### 2.2 STM in practice

During the STM measurements a conducting tip is brought close to a conducting surface. Once the tip is close enough to the surface for a tunneling current to be present, the tip is moved across the surface line by line in the x- and y-directions by a piezo actuator. Via the piezoelectric tube, the x-y-z positions of the tip are precisely controlled. When the system is operating in constant current mode, the feedback loop is used to vertically adjust the z-position of the scanning tip to maintain the tunneling current constant (Figure 2.2b). The feedback loop is disabled when measuring in the constant height mode, where the vertical position of the tip remains constant and the tunneling current is measured in dependence of the x- and y-position of the tip. The advantage of this mode is that it can be used at higher scanning speeds. However, there is a higher risk of tip-crashing in case of large variations in sample height. Therefore, the research described in this thesis was exclusively executed in constant current mode.
2.2.1 STM at the solid/liquid interface

The STM experiments described in this thesis were performed under ambient conditions at the solid-liquid interface (Figure 2.3). Because of the presence of the liquid, no vacuum barrier separates the tip and the sample making the measurements slightly more difficult. While in ultra-high vacuum (UHV) solely the tunneling current is measured, the tunneling current measured at the solid-liquid interface can have a component caused by the conductance of the used solvent. Therefore, non-conducting solvents are commonly used in order to prevent background current. Furthermore, it is preferable to use nonvolatile solvents i.e. \( n \)-tetradecane, \( n \)-octanoic acid, decamethyltetrasiloxane or 1-phenyloctane, to prevent desiccation of the sample and to maintain the equilibrium between the molecules adsorbing on the surface and dissolving in the solution. The STM tip, mechanically cut from a platinum/iridium wire (often in a 90/10 ratio, respectively), was submersed in the solvent while scanning.

![Figure 2.3 Schematic representation of a STM setup operating at the solid-liquid interface.](image)

**Figure 2.3** Schematic representation of a STM setup operating at the solid-liquid interface. The tip, connected to a piezoelectric tube, is in tunneling contact with the conducting surface. The feedback loop is used to control the position of the tip with high accuracy by using precisely regulated voltages to deform the piezo.

2.2.2 Sample preparation

Preparation of the STM samples is carried out via a drop casting method, meaning that the solutions were dripped onto the substrate. Prior to the deposition of the solutions, the highly-oriented pyrolytic graphite (HOPG) substrate was exfoliated using the scotch tape method.\(^9\) Graphite is the most commonly used atomically flat conductive surface for the study of adlayers (which are layers of physisorbed organic molecules)\(^10\) at the solid-liquid interface and is therefore the substrate of choice in this thesis. This surface is of particular interest also due to the possible commensurate adsorption of \( n \)-alkanes on it.\(^11\)\(^-\)\(^13\) Furthermore, it is cheap and easy to prepare. The solutions were all prepared with viscous, high boiling point solvents to prevent a coffee-ring effect upon drying.\(^14\) Various adlayes were used in order to adsorb the molecular motors on the surface, which will be described in the upcoming chapters.
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Figure 2.4 Schematic representation of the sample preparation via the drop casting method.

After drop casting the solution containing the adlayer molecules at temperatures at or above room temperature on a HOPG crystal, the sample was, in case the adlayers were robust enough, rinsed with the solvent and dried prior to the deposition of the motor molecules. Figure 2.4 shows the deposition of adlayer molecules (turquoise) on a HOPG crystal and the subsequent deposition of molecular motor molecules (orange).

2.3 References