Chapter 2

Scanning Probe Microscopy (SPM)

Since scanning force microscopy (SFM) has stemmed from the STM-based technology a brief description of the first SPM, the scanning tunneling microscope (STM) and its applications is presented. Then, we give an account for forces relevant to SFM. Finally, the SFM technique is explained with emphasis on the modes of operation that will be employed in the next chapters.

2.1 Scanning Tunneling Microscopy (STM)

Binnig et al.[1] achieved the first successful combination of vacuum tunneling and scanning capability.

The principle of the STM is straightforward. A bias voltage $V$ is applied between a sharp metal tip and a conducting sample. Bringing tip and sample surface within a separation $s$ of a few Ångstroms, their wave functions overlap and a finite probability exists that electrons will cross the barrier $\phi$ between the surfaces. The resulting tunneling current, $J_t$, is

$$J_t \propto C(V) \exp(-A\phi^{1/2}s)$$

(2.1)

where $C(V)$ contains information about the electron density of tip and sample, $A = 1.025 \text{Å}^{-1}\text{eV}^{-1/2}$. Note that the tunneling current varies exponentially with the distance. With barriers $\phi$ (work functions) of a few electronvolts a 1 Å decrease in the tip-sample separation will increase the current by almost one order of magnitude. Thus, the tunneling current can be used to probe physical properties locally at the sample surface as well as to control the separation between tip and sample.

In fig. 2.1 a simplified schematic drawing of a STM is shown. The probe tip is attached to a piezodrive, which consists of three mutually perpendicular piezoelectric transducers. By applying a sawtooth voltage on the x-piezo and a voltage ramp on the y-piezo the tip scans the $xy$ plane. Scanning the tip over the sample surface while keeping the tunneling current constant by means of a feedback loop that is connected to the z-piezo, the tip
will remain at a constant distance from the sample surface (eq. 2.1) and will follow the surface contours. Monitoring the vertical position \( z \) of the tip as a function of the lateral position \((x, y)\), one can get a two-dimensional array of \( z \) positions representing an equal tunneling-current surface.

Alternatively, in the constant height mode\(^1\), a metal tip can be scanned across a surface at constant height and constant bias voltage while the current is monitored. In this case, the feedback keeps the average current constant. There are advantages inherent in both modes; the former produces contrast directly related to electron charge density profiles, while the latter provides for faster scan rates not being limited by the response time of the \( z \)-piezo. The constant height mode is not suited for rough surfaces.

We note that if different materials are present in the sample, the tunneling current will be in general different for each of them (for a given bias voltage). Thus, the height data may not be a direct representation of the topography of the sample surface. In fact, if we assume that the electronic structure of the tip remains constant, the STM contrast is convolution of the electronic structure of the sample and the tunneling barrier height.

\(^1\)This mode is also called variable current mode.

**Figure 2.1: Schematic drawing of the scanning tunneling microscope**
2.1. Scanning Tunneling Microscopy (STM)

Figure 2.2: Rijksuniversiteit Groningen (State University of Groningen) and Material Science Center logo’s. Gold mounds and pits made by applying voltage pulses of +5.0 V and duration of 300 ns. Although the lateral size of the mounds can reach 500 Å (average about 200 Å) their height rarely exceeds 20 Å. Pits have much smaller size of less than 100 Å with a depth of only a few Å. The substrate is atomically flat gold (atomic steps can be clearly seen) made from gold wire melted in an oxyacetylene torch to give gold balls with (111)-oriented facets.
(related to the surface work function). For a surface with a uniform work function, a constant-current graph is qualitatively related to the surface topography.

To achieve atomic resolution, vibration isolation is essential. Apart from an external damping system (usually a set of suspension strings) one can make use of the inherent structural damping of a rigid STM.

Although the atomic resolution capability of STM directly in real space has become its most important feature, STM is not simply an imaging method for surface structures. One can perform spectroscopy measurements, $J_t - s$, $J_t - V$, $s - V$ characteristics and their derivatives, to determine the local (in space and energy) surface energy of states $N(E, r)$ and the barrier heights $\phi(r)$.

An important application of STM is in the field of surface modification. STM-based fabrication of nanometer-scale structures are motivated by the smallness of the features which can directly be written onto solid substrates. Various methods have been used to attain surface modification. In fig. 2.2 we present the fabrication of nanostructures on a gold(111) substrate treated with alkanethiols, via a gold tip by applying short voltage pulses. We observe both mounds and pits. In many cases, during the same pulse both a mound and a pit appear at almost the same location. Mamin et al. [2] demonstrated the formation of gold mounds using a gold tip and substrate. They showed that in ambient conditions the process is fast, reliable and reproducible. Chang et al. [3] applied the process in high vacuum. They observed the formation of both mounds and pits with almost equal probability. The process is believed to be local field evaporation of tip and/or sample atoms. In our configuration we performed the experiment in air and the gold substrate is covered by a self assembled monolayer (SAM) of alkanethiols [4] making the Au surface (much more) chemically inert. The appearance of both mounds and pits with roughly equal probability compares to the situation in vacuum.

An important aspect for STM measurements is the tip-sample interaction effects. The role of atomic forces in tunneling, discovered by Teague [6], has proven essential for the interpretation of STM images. Dürig et al. [5] were the first to investigate short-range interatomic forces using the STM configuration. These developments paved the way to the invention of scanning force microscope\(^2\) (SFM) [7] which is capable of monitoring directly the interatomic forces.

\section{2.2 Forc}es

Forces that can act between a tip and surface are the physical basis of scanning force microscopy. Many types of forces\(^3\) can arise if two bodies come into proximity: van der

\(^2\) It is also called Atomic Force Microscope (AFM)

\(^3\) Actually, all these types of interatomic forces have electromagnetic and/or quantum-mechanical origin. The classification is useful since their calculation from first principles has proven to be quite cumbersome even in very simple systems. We also note that this classification of intermolecular and surface forces is empirical and there can be cases where two normally distinct interactions are strongly coupled,
Waals force, ion-ion core repulsion, capillary forces, adhesion, friction, forces originating from physisorption, ionic, covalent and metallic bonds etc\(^4\).

**Van der Waals Interaction**

Van der Waals forces are significant for distances of a few Ångstroms to a few hundred Ångstroms, and they can be attractive or repulsive (they are always attractive between identical atoms). There are three contributors to the van der Waal force: orientation forces i.e. interactions between permanent dipoles (or “multipoles”); induction forces e.g. forces between a dipole with an induced dipole (molecules with permanent multipole moments can induce moments in otherwise nonpolar molecules); and dispersion forces which are of purely quantum mechanical origin. Dispersion forces arise from the instantaneous polarization due to fluctuations in the charge distribution of atom: thus at certain moment a dipole exists and induces a dipole in another atom. This component of the van der Waals force is always present between all types of atoms or molecules.

The potential energy for two molecules due to van der Waals forces, to first order is

\[
U_{vdw} = -\frac{C_{vdw}}{r^6}
\]  

(2.2)

where \(C_{vdw} = C_{orient} + C_{ind} + C_{disp}\), and \(r\) the distance.

Usually the dispersion contribution is the dominant one. If we assume that the interaction is isotropic, additive and nonretarded, the interaction potential between macroscopic bodies can be readily calculated. Simple power laws result and the Hamaker constant \([9]\), \(A_H\), specific for the materials can be defined. The interaction energy between two flat surfaces at a separation \(D\) is \(-\frac{A_H}{12\pi D^2}\) per unit area and between a sphere of radius \(R\) and a flat surface is \(-\frac{A_H R^6}{6D}\) for \(R \gg D\). The Hamaker constant is \(A_H = \pi^2 C_{vdw} \rho_1 \rho_2\), where \(\rho_1\) and \(\rho_2\) are the numbers of atoms per unit volume.

**Ion-ion Repulsion Forces**

These forces are only present if the distance between two bodies is smaller than the equilibrium distance of an adatom on either of the two bodies. When two atoms are brought closely together their electron clouds overlap strongly. This leads to incomplete screening of nuclear charges, which causes coulombic repulsion. The ion-ion forces are very short range (\(\approx 1 \text{ Å}\)) and can be described by a power law \((U \propto r^n)\) where \(n\) is greater than 9, or by an exponential function.

A successful interatomic potential that is widely used in simulations is the Lennard-Jones potential which combines both long and short-range forces:

\[\text{or some types of forces can be counted twice.}\]

\(^4\)We mention only types of forces that are most relevant in the systems investigated in this thesis and in understanding the principle of operation of SFM. For a detailed overview on intermolecular and surface forces the book of Israelachvili [8] is recommended.
\[ U_{LJ} = \left( \frac{C_1}{r} \right)^{12} - \left( \frac{C_2}{r} \right)^6 \] (2.3)

The first term is repulsive and corresponds to short-range ion-ion repulsion. The second term is attractive and long-range and corresponds to van der Waals attraction.

**Friction and Adhesion**

Friction is the resistance to motion that exists when a solid object is moved tangentially with respect to the surface of another that it touches, or when an attempt is made to produce such motion. The friction between two surfaces is strongly related to their adhesion. Adhesion, in its turn, depends on the type of interatomic interactions and therefore strongly depends on the fundamental properties of the two solids, both bulk and surface, and on the state of their surfaces. Adhesion should be seen in connection with elastic and plastic deformation of solids and various continuous theories that treat adhesive contact have immerged (e.g. JKRS [10], DMT [11]). However, a generic microscopic understanding of friction and adhesion and their relation is still lacking.

### 2.3 Scanning Force Microscopy (SFM)

Like the STM, the SFM [7] relies on a scanning technique to produce high resolution images of sample surfaces. However, unlike STM, the physical magnitude monitored is not tunneling current but the interaction force between the tip and sample. This is accomplished by attaching the tip to a cantilever-like spring and detecting its deflections due to forces acting on the tip. Since interatomic forces are always present when two bodies come into close proximity, the SFM is capable of probing surfaces of both conductors and insulators on an atomic scale. Since its invention by Binnig et al. in 1986, different modes of operation have been introduced and various detecting schemes for the cantilever’s displacements have been employed (for reviews see ref. [12, 13]). The so-called contact mode, where ion-ion repulsion force is monitored, combined with a -laser beam deflection-detecting technique [14] is the most widely used.

In fig. 2.3 we present a schematic drawing of a SFM. A sharp tip at the end of a cantilever is brought into contact with a sample surface via the z-piezo extension (either the sample or the tip can be scanned\(^5\)). The repulsive force \( F \) causes the cantilever to deflect vertically according to Hooke’s law \( F = k \Delta z \), where \( k \) is the spring constant and \( \Delta z \) the vertical displacement of the cantilever. \( \Delta z \) is monitored by the laser beam deflection technique. The back of the cantilever has to be a mirror-like reflecting surface. A laser beam (coming from a laser diode) is reflected off the rear side of the cantilever and the beam deflection is monitored with a position-sensitive detector (PSD) (split photodiode with two parts: top (T) and bottom (B)). The voltage difference from the top and bottom

\(^5\)In fig. 2.3, we assume that the sample is scanned. We note that in almost all schematic drawings in this thesis, the tip is assumed to be scanned.
photodiodes, \( V_T - V_B \), provides the SFM signal which is sensitive measure of the cantilever vertical deflection. During scanning via the x, y-piezo’s the z-piezo is connected to a feedback system. The feedback loop is used to keep the differential detector signal at a constant value \( V_0 \) by adjusting the vertical z position of the sample to achieve (almost) constant deflection \( \Delta z_0 \) of the cantilever. \( \Delta z_0 \) corresponds to a constant force \( F_0 \), \( F_0 = k\Delta z_0 \). The output signal of the feedback circuit \( U_z \) (z-piezo signal) is recorded as a function of \((x,y)\) coordinates which are determined by the voltages \( U_x \) and \( U_y \) applied to the x and y-piezodrives. The two-dimensional array \( U_z(U_x,U_y) \) can be transformed to ”topography” \( z(x,y) \), provided that the piezo coefficients are known. This mode of SFM operation is called constant force or constant cantilever deflection mode and is analogous to constant current mode in STM.

**Figure 2.3:** *Schematic drawing of the scanning force microscope.*

Similarly to constant height mode in STM, if the feedback is used to keep only the
average force constant and the cantilever deflection is monitored (and therefore the force) one can obtain two-dimensional arrays of the force variation \(F(x,y)\).

SFM images in the constant force mode in the contact regime correspond to ”equiforce” surfaces. Ciraci et al. [15] applied the Hellmann-Feynman theorem for derivation of atomic forces in real space and showed that SFM measurements in the contact regime are expected to probe primarily the ion-ion repulsion force and consequently to directly probe the positions of the ion cores. We note that STM measurements probe the local surface electronic structure near the Fermi level which can be different from the geometric arrangement of the ion cores (topography). SFM measurements in the constant height mode are more difficult to interpret since they are not equiforce surfaces. However for small scannings the variation of the forces is usually negligibly small and the measurements can be interpreted similarly to the constant force mode.

The most crucial component of a SFM is the cantilever. The deflection should be sufficiently large for ultralow forces (0.1 nN). Therefore, the spring constant should be as low as possible (lower than 1 N/m). On the other hand, the resonance frequency of the cantilever must be high enough (10 to 100 kHz) to minimize the sensitivity to mechanical vibrations (e.g. vibrational noise from the building ~ 100 Hz, frequency of the corrugation signal up to a few kHz). The resonant frequency of a spring loaded with an effective mass \(m\) is

\[
\omega_0 = \left(\frac{k}{m}\right)^{1/2}
\]

Thus, in order to sustain a high resonance frequency, while reducing the spring constant, it is necessary to reduce the mass and therefore the geometrical dimensions of the cantilever. Microfabrication techniques are usually employed for the production of cantilever beams with integrated tips. The shape of the cantilevers is either rectangular or V-shaped. The opening angle of the tips and their apex should be as small as possible allowing penetration into deep troughs on the surface and high resolution.

### 2.4 Friction Force Microscopy (FFM)

If a tip and sample surface are in contact and in relative motion with respect to one another, the cantilever is expected to bend and/or twist in response to friction force. In fig. 2.4 the tip is scanned perpendicular to the long axis of the cantilever and a split photodiode with four quadrants is used. Due to the cantilever twisting opposite to the direction of scanning the laser beam will be reflected out of the plane defined by the incident beam and the vertically reflected beam from an untwisted cantilever. The voltage difference between the right and left segments of the photodiode, \(V_{A+B} - V_{C+D}\), is proportional to cantilever torsion, which, in turn, is a measure of the lateral force.

We have already mentioned that a microscopic theory of friction is still lacking. Experiments with macroscopic bodies are difficult to quantify since the real area of contact is unknown. Further, adhesion is difficult to measure since elastic relaxation of the higher
asperities when the load is removed breaks the adhesive contact of the lower junctions. Therefore, single asperity experiments are extremely useful to study friction. Mate et al. [16] used the FFM to demonstrate stick-slip process with atomic periodicity on a graphite sample. This behaviour was also detected in mica [17]. The FFM technique has had an immense impact on the field of tribology (for a review see ref. [18]).

Figure 2.4: Schematic drawing of probing friction forces with a SFM. Normal and Lateral forces can be simultaneously measured.

2.5 Force-Distance Curves (Force Spectroscopy)

SFM can measure the force as a function of vertical distance at a particular location on the sample surface. Experimentally, the cantilever deflection $z_t$ versus the position of the sample $z_s$ is measured. The force $F$ can then be determined by multiplying $z_t$ with the spring constant $k$, $F = k z_t$. If we neglect elastic deformations of the sample and the tip, the interaction distance $D$ between tip and sample is given by $D = z_t - z_s$. Thus, we can determine the force-distance curve ($F_d$ curve) or force profile $F(D)$.

In fig. 2.5 we show a typical surface force. As the sample approaches towards the cantilever tip, the cantilever follows the attractive force till point A. At this point the gradient of the attractive force exceeds the spring constant $k$ which leads to an instability.

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We assume that the sample is mounted on the z-piezo drive.
resulting in a jump to contact to point B. On further approach due to ion-ion core repulsion the sample just pushes the cantilever and force increases steeply. On reversing the direction of the sample, the spring will extend from point B to point C. At this point a second instability occurs because the force gradient has again become equal to the spring constant of the cantilever and the tip jumps out of contact at point D. Point C corresponds to the position of maximum adhesive force (called usually pull-off force). We can see that SFM Fd-curves suffer from hysteresis and discontinuities. This is a direct consequence of the low spring constant of the cantilever. If a sufficiently stiff cantilever [19] is used or a feedback mechanism to compensate for the change of the force gradient [20, 21], the cantilever instability can be avoided\textsuperscript{7}.

\textbf{Figure 2.5:} Schematic diagram of a usual surface force profile. At points of instability the force gradient becomes equal to the spring constant of the cantilever.

\textbf{References}


\textsuperscript{7}Cantilever instability and the resulting hysteresis are due solely to the compliance of the measurement system. Of greater interest is the adhesion hysteresis of the direct tip-sample contact.


