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Scanning Probe Microscopy – Investigating the World Down Under

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1. Introduction

Investigating the physical and (bio)chemical properties of materials at the micro and nano scale is not a trivial exercise. The emergence of Scanning Probe Microscopy (SPM) as a versatile and powerful group of techniques for manipulation and visualisation of surfaces and interfaces has been driven by the need for material characterisation at these small length scales. The relative maturity and increasing topicality of SPM is evidenced by the growing body of literature including many monographs. SPM instruments are now well established in many fields of science yielding a wealth of information in the physical, chemical and biological disciplines.

2. SPM Family Tree

SPM is a large family of microscopy techniques with Scanning Tunneling Microscopy (STM) being the first to be developed by Binnig *et al.* [1]. The abbreviated family tree is shown in figure 1 below. Within this family Scanning Force Microscope/y (SFM) constitutes a group for which the interaction is a force acting between a probe, consisting of a lever and a tip (see figure 2), and the surface. The interaction in the case of the Scanning Tunneling Microscope/y (STM) and its sibling, scanning tunneling spectroscopy (STS), is electron tunneling, while in the case of scanning thermal microscopy (SThM), the “interaction” is the thermal radiative transport of energy between surface and probe.

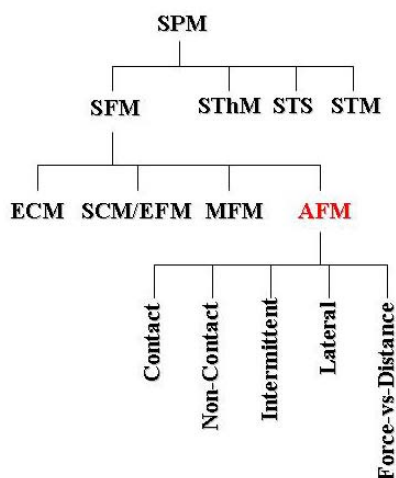


Figure 1 – The SPM Family Tree

The SFM branch (described in greater detail in section 3 below) is the largest and most popular, in terms of usage and installed instrumental capacity. It includes some variants, which are currently less commonly used, such as electrical conductance microscopy (ECM), scanning capacitance (or capacitive, or electrostatic force) microscopy (SCM/EFM), and magnetic force microscopy (MFM).

Finally, there is the atomic force microscope/y (AFM) subgroup. This sub-branch includes the most widely used technique(s). Thus it merits further sub-division into its various operational modes. Contact – the dominant interaction is generally short-range (tip in contact with surface), usually the net force is repulsive. Non-contact – the net interaction is longer-range and the tip and surface may be separated from 1 to hundreds of nm. Intermittent contact (or tappingTM) – the lever is stimulated to oscillate at an eigen-frequency with an amplitude so that the tip enters the short-range force-field of the surface. Lateral force – in contact mode, but the mapping parameter is responsive to the lateral, ‘frictional’, force component resulting from torsional twisting or buckling of the lever. Force-vs-distance (F-d) – forces acting between the tip and surface are detected at various separation distances and when the surface and tip are in contact. This mode is further discussed in section 5 below.

3. How the SFM Works

The heart of the SFM is a cantilever with tip. The SFM has the advantage of using a tip with a radius of curvature between 1 and 100 nm, which enables the measurement of local interactions with high spatial resolution. As the probe is brought into close proximity or contact with a surface, the cantilever bends, buckles and twists as it senses the local attractive/repulsive forces. Because the cantilever and tip are characterized by spring constants and geometry (see figure 2), a detailed study of the surface under investigation can be made. Mate *et al.*, [2], have demonstrated that the tip will respond to in-plane as well as out-of-plane force components. The three familiar expressions for force constants of deformation - arising from the simple bending (k_N), torsion (k_T) and longitudinal buckling (k_L) of the beam - are shown in equations 1.1 – 1.3 below [Warmack *et al.*, 3; Gibson *et al.*, 4; Ogletree *et al.*, 5]. The expressions assume that the deformation of the lever can be described by the lowest order modes of a long thin beam. The k_T and k_L modes are stimulated by force components acting along the x - and y -directions, respectively, with reference to a coordinate system anchored in the probe as shown in figure 2. There will be an additional contribution to the displacement in the x -direction of the tip apex, arising from transverse bending of the lever. The corresponding force constant is shown in equation 1.4. For completeness it is also noted that shear deformation of the lever and tip, and simple bending of the tip, may also contribute. The force constants $k_{C_{sx}}$ (equation 1.5) and $k_{C_{sz}}$ (equation 1.6) refer to shear deformation of the cantilever in the x - and z -directions, respectively. Tip bending (k_{Tb}) and shear (k_{Ts}) may also be present and need to be taken into account.

$$k_N = \frac{Et^3w}{4L^3} \quad 1.1 \quad k_T = \frac{Gwt^3}{3Lh^2} \quad 1.2$$

$$k_L = \frac{k_N L^2}{3h^2} \quad 1.3 \quad k_{Cb} = \frac{k_N w^2}{t^2} \quad 1.4$$

$$k_{C_{sx}} = \frac{G_x t w}{L} \quad 1.5 \quad k_{C_{sz}} = \frac{G_z t w}{L} \quad 1.6$$

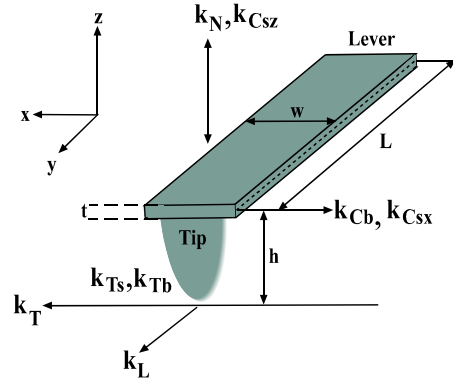


Figure 2 – A schematic representation of a ‘beam-shaped’ cantilever with a tip attached at the free end, where w = width of lever, L = length of lever, t = thickness and h = height of tip.

Because of the small distance between the tip and the surface, specific physical and chemical interactions can be measured. The resolution of these interactions depend very much on the shape of the tip, the stiffness of the lever, and on the characteristic range of the tip-to-surface interaction. In general the smaller, i.e., sharper the tip is, the smaller is the surface area sampled (interaction volume) and hence, the better is the lateral resolution. For long-range interactions the resolution is less dependent on tip shape.

Generally, an optical detection method is used in SFM for measuring deflection of the probe (lever and tip). As the tip is rastered across a surface by a piezoelectric positional stage in the x - and y - directions, the bending, buckling and twisting motion of the lever deflects a laser beam which is aimed at, and reflected from, the free end of the cantilever (with the tip attached directly below the point of reflection). The reflected laser beam is focused onto a position sensitive photo detector (PSPD), where changes in on-axis and off-axis angles generate differential photo-currents on the four quadrants (A, B, C & D on the PSPD). Figure 3 shows a schematic of the principal elements of the SFM. The varying signal changes are monitored via the feedback system, with the output displayed on a computer, for example as topographical or frictional images, and quantitative data (e.g., f -d curves and friction loops).

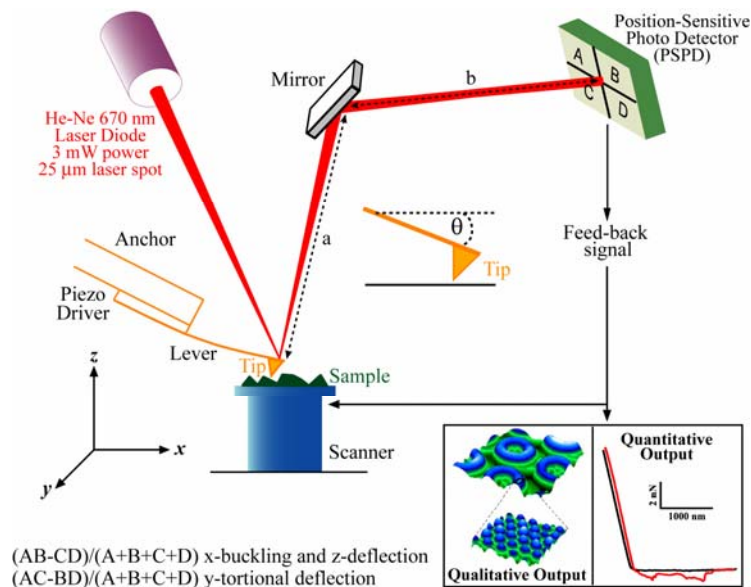


Figure 3 – A schematic showing the principal elements of the Scanning Probe Microscope.

4. The SPM Attributes

Some of the attributes and features of the SPM are summarized in Table 1 below. The most remarkable features are the spatial resolution figures. The interaction volume can be defined as being the region in space from which averaged information is obtained and it is approximately the product of lateral resolution by the practical range of the interaction.

Table 1 – Current SPM Techniques: Features and Attributes [6].

Mode	Interaction	z -Resolution (nm) xy -Resolution (nm) Interaction Vol. (m^3)	Probe/Tip	Information Attributes
STM/STS	Electron tunneling	0.005 0.05 < 10^{-30}	Sharp Tip	Topography, Electron spectroscopy, 'work' function
AFM Contact	Interatomic forces (repulsive)	0.02 0.15 < 10^{-28}	Cantilever + Tip	Topography, Molecular structure
AFM Noncontact	Interatomic forces (attractive)	0.2 1 < 10^{-26}	Cantilever + Tip	Topography
AFM Contact	Interatomic forces (lateral)	n.a. 0.3 < 10^{-28}	Cantilever + Tip	Tribology, Friction
AFM spectroscopy	-	0.2 1 < 10^{-26}	Cantilever + Tip	F-d analysis
MFM noncontact	Magnetic Force	1 5-50 < 10^{-25}	Cantilever + magnetized tip	Magnetic topography, Domains/walls, magnetic spectroscopy
EFM/SCM noncontact	Electrostatic or capacitive force	5 100 < 10^{-23}	Cantilever + insulating tip	Topography, Patch charge, Capacitance
ECM contact	Electrical conductivity	0.05 50 < 10^{-25}	Cantilever + conducting tip	Topography, Electrical conductivity, breakdown voltage I-V spectroscopy
SThM noncontact	Heat loss	1 100 < 10^{-21}	Thermocouple tip	Topography, thermal conductivity, emissivity

The AFM is the most common technique used to study surfaces. Due to its versatility, the AFM can be used in all fields of science. Some of its applications, in both qualitative as well as quantitative terms, are listed in Table 2 below. Although initially used as a tool for imaging, AFM has also proven a useful technique for analyzing a wide variety of physical, chemical and biological systems. Examples of a

biological, chemical, physical and lithographic application are shown in figure 4 (a), (b), (c) and (d) respectively. One of the more important biological advantages of the AFM over traditional high resolution imaging techniques, most notably the EM (electron microscope), is its ability to study *living* biological structures at high spatial resolution in a bio-compatible liquid environment.

Table 2 – Examples of Surface Analysis using the AFM

BIOLOGY	CHEMISTRY	PHYSICS
Cell observation/manipulation in situ [7-9]	Characterization of composite materials [18, 19]	Surface Deformations of Metals, plastics etc [29, 30]
Identification and morphology of intracellular structures [7, 8]	Reaction Kinetics at interfaces [20]	Quantification of surface forces in 3 dimensions [31, 32]
Identification and morphology of surface structures [9-12]	Functional group identification [21-23]	Atomic scale imaging of materials [33]
DNA protein imaging and structure analysis [13, 14]	In situ observation of chemical reactions at interfaces [24]	Frictional, Adhesive etc. forces at the micro and atomic scales [32, 34, 35]
Elasticity of Cells/Structures [7, 8]	Visualization and analysis of granular nanostructure in crystalline polymers [25, 26]	Surface Stiffness measurements [36, 37]
Study of insect and plant nanostructures for survival [15-17]	Nanomanipulation of polymeric surfaces [27, 28]	Nano-writing/machining [38-40]

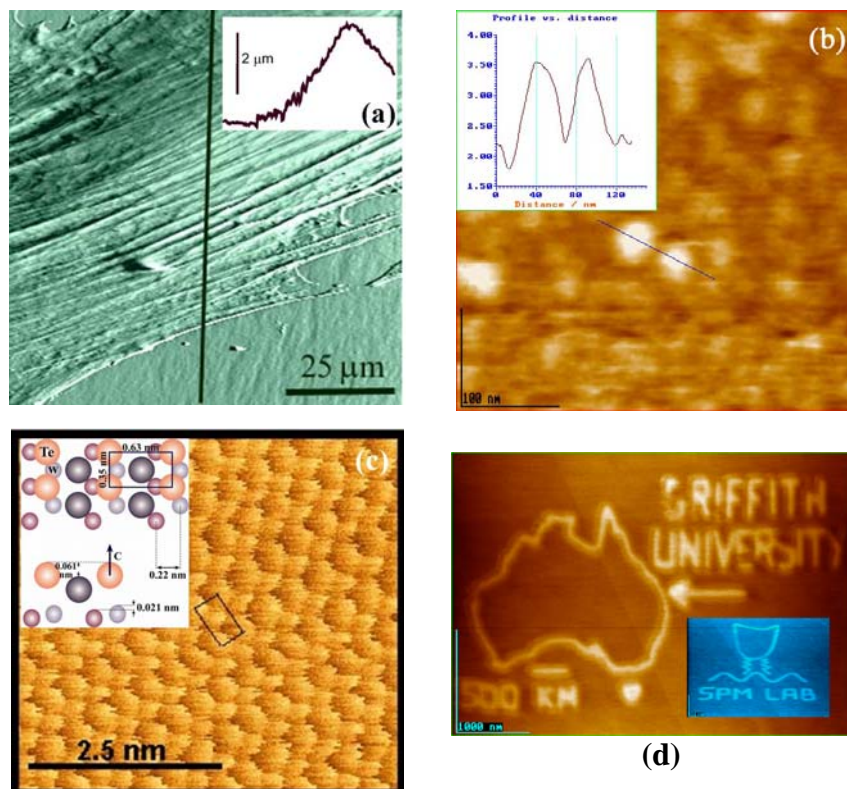


Figure 4 – Topographical images of; (a) living human fibroblast and corresponding line profile, and (b) dendrimer clusters attached to a functionalised silicon surface. (c) Lateral force image of the atomic structure of a transition metal dichalcogenide (WTe_2) with the inset showing a schematic drawing of the surface Te and sub-surface W layers in WTe_2 . (d) Topographical image of a previously manipulated diamond-like-carbon (DLC) surface (average line width of tens of nanometers), with the inset showing the GU SPM lab logo.

5. The F-d Mode

The AFM force-vs-distance mode involves the approaching/retracting tip, at a fixed location in the x - y plane, while sensing interactions at the interface in various environments (liquid, gas or vacuum). The tip is driven towards the surface at a rate which is slow in comparison with the mechanical response of the system, but fast in comparison with thermal drift. The net force (deflection of the lever) is sensed during the approach, contact and retract parts of the cycle. This interaction between tip and sample can be described by force-distance curve analysis. The curves' sensitivity to the tip-to-sample forces is dependent on the cantilever spring constant making the f-d curve a result of the interactions and the spring constant.

Analysis in the f-d mode is now routinely deployed across a wide range of scientific disciplines in order to measure the local z component of the force between a tip and a surface. The resolution reaches the low pN range, as described by Smith, [41], van der Vegte and Hadziioannou, [21], and Zlatanova *et al.*, [42]. Studies by Engel and Müller, [43], and Fisher *et al.*, [13] have also shown that the binding of single molecular bonds can be characterized.

Figure 5 shows a representative f-d curve on a ‘hard’ surface, where compression at the point of contact can be neglected, obtained in air. The horizontal axis of the f-d curve represents the position of the sample/scanner-stage along the z -direction. The vertical axis represents the force exerted on the tip along the z -direction. The f-d curve can be broken up into a number of points (A-G) reflecting the tip-sample distance and interaction along the z -direction, with the approach curve shown in red and retract curve shown in blue. The hysteresis created between the approaching and retracting probe is a consequence of frictional forces acting between the tip and surface, scanner hysteresis and the irreversibility of the meniscus interaction.

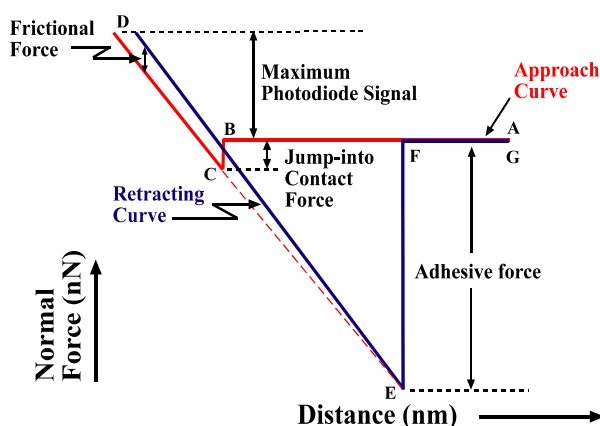


Figure 5 – Representative calibration curve on a hard surface (e.g., mica) in air. The red curve represents the approach cycle and the blue represents the retract cycle, defined below.

Point A-B and F-G; sample and probe not in contact but approaching/retracting with no forces acting. B-C; the tip senses attractive forces which cause the lever to bend downward, the attractive force gradient exceeds the spring constant of the lever, and this instability causes the tip to snap into contact with the surface. C-D; the response of the sensor which measures cantilever displacement. The cantilever continues to bend, being the only compliant element, so that extent of lever bending is precisely equal to stage travel. D-E; the tip begins to retract from the surface. Adhesion between the tip and sample maintains the contact. E-F; the jump of the cantilever away from surface, when the cantilever force becomes greater than the adhesive forces. The vertical excursions BC and EF are usually taken to represent the range of the attractive force plus the thickness of any adsorbed layer(s), and the adhesion, respectively.

6. Summary

Since the first introduction of SPM's in the mid 1980's they have become a part of a large number of laboratories working in the field of surface and/or interface characterisation of materials. The popularity of SPM methods is based on their extremely high resolution in real space and time (down to the pN range), the relatively low costs compared with e.g., electron microscopes, and the easy implementation of most of the SPM methods. Their extreme sensitivity to forces and chemical changes, particularly with the force-vs-distance mode in atomic force microscopy, provide quantitative details about the strength of surface forces at the interface, for example, friction, adhesion, van der Waals and electrostatic forces, as well as providing useful information about micromechanical properties and compliance of surfaces in different environments, including multi-layered systems. Over and above that, the SPM methods can be used for atomic and molecular engineering, i.e., the purposeful creation, manipulation and (bio)chemical sensing of structures on a sub-nanometer scale.

Due to the adjustable/tunable tip radius of curvature and varied spring constants and geometry of the tip and lever, the resolution of the SPM can be varied according to the specific needs of the experimentalist.

With well defined methods for coating SPM probes, it has become possible to identify or distinguish the chemical functional groups on the surface of interest. With the application of quantitative models for tip/surface interactions one can, for example, produce information about single chemical bond strengths from the distribution of adhesive force measurements. Data acquisition in the force-distance mode is in the range of 0.1 to 2 seconds enabling the study of fast changing systems. The SPM family's use, therefore, is not limited to a single branch of science, rather it is truly a multi-disciplinary tool capable of revealing the mysteries in the micro- and nano-world.

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