

Theories of scanning probe microscopes at the atomic scale: Origins, applications and limitations.

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Abstract

Significant progress has been made both in experimentation and in theoretical modelling of Scanning Probe Microscopy (SPM). The theoretical models used to analyse and interpret experimental SPM images and spectroscopic data now provide information not only about the surface, but also the probe tip and physical changes occurring during the scanning process. The aim of this review is to discuss and compare the present status of computational modelling of two of the most popular SPM methods - scanning tunnelling microscopy (STM) and scanning force microscopy (SFM) - in conjunction with their applications to studies of surface structure and properties with atomic resolution. In the context of these atomic-scale applications, for SFM we focus primarily on recent non-contact SFM (NC-SFM) results.

After a brief introduction into the experimental techniques and the main factors determining image formation, we focus on the theoretical models developed for STM and SFM. Both techniques are treated from the same general perspective of a sharp tip interacting with the surface - the only difference being that the control parameter in STM is tunnelling current and in SFM it is force. We describe the existing methods of calculation of STM and SFM images, and illustrate them using numerous examples, primarily from our own simulations, but also from the literature. We compare theoretical and practical aspects of the techniques applied in STM and SFM modelling. Finally, we discuss modelling related to SPM applications in studying surface properties, such as adsorption, point defects, spin manipulation and phonon excitation.

Contents

I. Introduction	6
II. SPM Definitions	8
A. SPM Setups	8
III. Main factors determining image formation	13
A. Controlling Interactions	13
B. Tunnelling Current	14
C. Bias voltage	16
D. Electrostatic Forces	17
1. Effect of electrostatic forces in STM	17
2. Macroscopic electrostatic forces in SFM	18
E. Chemical forces	20
F. Magnetic Forces	21
G. Summary	22
IV. Model Development	23
A. The Surface	24
B. The Tip	25
1. Idealized tips	27
2. Modelling of real tips	28
3. Combining Microscopic and Macroscopic Tip Models	31
C. Tip-Surface Interaction	32
1. Van der Waals Forces	33
2. Calculating Microscopic Forces	35
D. Modelling Currents	37
1. Tersoff-Hamann(TH) approach	38
2. Perturbation approach	38
3. Easy modelling: applying the Tersoff-Hamann model	39
4. Magnetic tunnelling junctions	42
5. Landauer-Bütticker approach	43

6. Keldysh-Greens function approach	44
E. Modelling Oscillations	45
F. Generating a Theoretical Surface Image	46
G. Summary	47
V. Studying the Surface	48
A. Metal Surfaces	49
B. Semiconductor Surfaces	55
1. Silicon Surfaces	55
2. Binary Semiconductor Surfaces	57
C. Insulating Surfaces	58
1. The Calcium Fluoride (111) Surface	60
Tip characterization with force curves	61
Simulating Scanning	63
Standard Images	64
Distance Dependence of Images	68
Ideal Silicon Tip	72
2. CaCO_3 ($10\bar{1}4$) Surface	74
D. Thin Insulating Films	79
1. NaCl-trilayer on Al(111) Surface	79
2. MgO thin films on Ag(001) Surface	80
3. NaCl Thin Films on Cu(111) Surface	81
VI. Studying Surface Properties	82
A. Adsorbates on Surfaces	83
1. $\text{C}_4\text{O}_3\text{H}_2$ on Si (100)-(2×1) surface	83
2. O on Fe (100) surface	85
B. Point defects	87
C. Surface Magnetism	88
1. Mn Surface	89
Image simulation	89
2. NiO Surface	91

D. Spin-manipulation	93
E. Phonon excitations	93
F. Electron dynamics	94
VII. Conclusion and Outlook	94
References	95

I. INTRODUCTION

Scanning Probe Methods (SPM) have developed into the most ubiquitous tools in surface science and the range of phenomena studied by these techniques is continuing to grow. These include surface topography, electronic and vibrational properties, film growth, measurements of adhesion and strength of individual chemical bonds, friction, studies of lubrication, dielectric and magnetic properties, contact charging, molecular manipulation and many other phenomena from the micrometer down to the sub-nanometer scale. The family of SPM techniques is very diverse with different methods specialising in different surface properties. In this review we will focus on the two most commonly used techniques - Scanning Tunnelling Microscopy (STM) and Scanning Force Microscopy (SFM). In both techniques a sharp tip is interacting with the surface and a topographic surface image is produced by scanning. However, parameters controlling the image formation are different. In an STM the control parameters of operation are tunnelling current and/or voltage, whereas in an SFM the control parameter is the force between tip and sample. In both cases the information about the system under research is encoded in a change of these parameters as the tip scans along the surface. The highly non-trivial relationship between these variables and the physical environment they reveal is the main topic of this review.

While early research in these fields often took experimental results at face value, many seemingly paradoxical results have now taught experimentalists a high degree of scepticism when they are confronted with an image. This is where theoretical modelling proved to be essential, and a driving force in any progress made. In addition, SPM methods increasingly employ other methods of analysis like external magnetic fields or electron/phonon excitations, so that ever more subtle changes of the current in an STM, or the force in an SFM need to be measured and accounted for. In itself this poses tremendous challenges to experimental methods, and thus drives the development of new tools to keep track of subtle changes. As the complexity of the experimental techniques continues to increase, experimental and theoretical groups have started to work together in an understanding that both sides of a problem need to be studied in order to arrive at sustainable models. The aim of theory is to provide an understanding of the basic principles of operation of SPM and the origins of image contrast, and to give interpretation of particular experimental images. In this paper we review the potentials and pitfalls of different approaches, and hope to give newcomers and

non-specialists some indication of how experimental results can be backed by sophisticated theoretical models. Also we discuss the real computational cost of these models, and where the current frontier lies in our abilities and our understanding of the physical processes. We compare theoretical modelling of two of the most popular SPM methods - STM and SFM from a common perspective and demonstrate many similarities of these two methods. However, when discussing applications of the methods we focus on those demonstrating true atomic resolution, and in particular for SFM, this has only been achieved using NC-SFM in ultra-high vacuum (UHV) conditions.

We shall limit our discussion to working methods, which is to say we do not consider in full detail the large amount of papers published which contain theoretical suggestions and propose new methods without yet any actual implementation. This seems necessary, because the actual value of a method lies in its reliability, and its versatility. In principle, it is the goal of theory to develop a reliable model of experiments, which can be used to interpret experimental images without resorting to direct simulation. However, this goal has not been achieved in either SPM technique. For STM, the various methods neglecting the effect of a tip on the tunnelling current and the obtained images have provided some insight into the imaging mechanism, and can be trusted in standard situations. Yet even so, ground-breaking experiments require complex simulation for their interpretation. For SFM, no simple model yet exists and all unambiguous assignment of chemical identities of image features is based on direct simulation.

Theoretical methods used in SPM are in many ways similar to those used in other branches of surface science. The main difference between SPM modelling and, for example, studies of adsorption, adhesion or cluster growth at surfaces, is that the SPM tip is a macroscopic object and is very rarely in force or thermal equilibrium with the surface. Image contrast represents the difference in the tip-surface interaction (SFM), or the tip-surface current (STM) at different surface sites, and all non-equivalent surface sites should be probed. Besides, many events observed experimentally are unique and are not subject to statistical averaging. Until recently, theory has been mainly concerned with qualitative predictions. However, continuous refinement of experimental and theoretical methods makes quantitative comparison increasingly possible. This requires determination of parameters for comparison, formulation of criteria of agreement, and common calibration for theory and experiment.

II. SPM DEFINITIONS

A. SPM Setups

The experimental setup of scanning probes such as STM and SFM (Binnig *et al.*, 1986; Binnig and Rohrer, 1982; Binnig *et al.*, 1982a,b; Bonnell, 2000; García and Pérez, 2002; Güntherodt *et al.*, 1995; Morita *et al.*, 2002) is determined mainly by the desired thermal and chemical environment. For traditional applications in surface science like the research of surface reconstructions, surface growth, surface dynamics, and surface chemistry, the instrument is mounted in a UHV chambers of less than 10^{-9} Torr. The UHV chamber and the analytical instruments themselves are mounted on rigid frames. This frame is externally damped by active (this is the latest trend) or passive damping elements, or mounted on rubber legs. Internally, vibrations of the UHV chamber and the analytical instruments are minimized by a combination of springs and eddy-current damping. The purpose of this elaborate scheme is to eliminate all vibrations from the environment, which would make the periodic motion of an SPM tip of less than 1 Å, invisible due to background noise. The best instruments today, which are mostly home-built, are capable of a vertical resolution better than 1pm, or one two-hundredth of an atomic diameter.

For biological applications, e.g. the research of DNA and single cells, as well as for electrochemical purposes, the SPM is operating under liquid conditions (see e.g. (Aoki *et al.*, 2001; Driscoll *et al.*, 1990; Engel and Müller, 2000; Güntherodt *et al.*, 1995; James *et al.*, 2001; Jandt, 2001; Ohnesorge and Binnig, 1993; Philippsen *et al.*, 2002)). From an experimental point of view these conditions substantially limit the obtainable information and spatial resolution at a given surface structure. It is, however, an important step towards a realistic environment. In biological applications a liquid is the environment of all living organisms, and is therefore in a sense indispensable. However, true atomic resolution has yet to be achieved under these conditions, hence we do not treat that aspect of SPM in this review.

The only experimental limitation for an STM is the requirement of conducting surfaces. Insulator interfaces for STM analysis are therefore grown to a few monolayers on a metal base (e.g. NaCl (Hebenstreit *et al.*, 2000), or MgO (Schintke *et al.*, 2001)). Provided the tunnelling current is still detectable, the insulator can be scanned in the same way as

conducting crystal interfaces. An SFM is generally free from these limitations and could be used to study any surface. However, for achieving atomic resolution it seems crucial that surfaces are smooth enough and that there are no strong long-range tip-surface forces, e. g. due to charging. In recent years, the emphasis in both STM and SFM studies is gradually shifting from the research of surface topography and surface reconstructions (Behm *et al.*, 1990; Chen, 1993) to surface chemistry (Fukui *et al.*, 1997b; Hahn and Ho, 2001a; Hla *et al.*, 2000; Sasahara *et al.*, 2001) and surface dynamics (Bennewitz *et al.*, 2000; Hoffmann *et al.*, 2001; Lauhon and Ho, 2000; Molinas-Mata *et al.*, 1998; Nishiguchi *et al.*, 1998; Schulz *et al.*, 2000).

Most STM experiments on semiconductors are done at room temperature, while high-resolution scans on metals rely, with but a few exceptions (Biedermann, 1991), on a low temperature environment of 4-16 K. Low-temperature SFM is still a less common practice. However, several home-built instruments have already demonstrated great improvement in resolution with respect to room temperature instruments (Allers *et al.*, 1998; Lantz *et al.*, 2000; Uozumi *et al.*, 2002) and there are commercial low- temperature SFMs on the market. In this case the sample and/or the whole SPM system are cooled by liquid helium. Thermal motion in this temperature range is greatly reduced, and high-resolution images of close-packed atomic structures can then be obtained much more routinely.

Figure 1 shows the setup of an STM. In most cases the STM is built into a UHV chamber. Its main components are a sample holder, on which the surface under study is mounted; a piezotube, which holds the STM tip; an electronic feedback loop; and a computer to monitor and record the operation.

SFM has quite similar components, as shown schematically in Figure 2. They can be effectively categorized into three areas: (i) tip - macroscopic size and shape, conductivity, microscopic chemical structure, charge; (ii) surface - macroscopic thickness, conductivity, microscopic chemical structure, charge; and (iii) experimental setup - type of control of cantilever motion, electric circuit and bias between tip and sample or sample holder. Thus, to really simulate the experimental process, one needs not only to know the tip-surface interaction and model the cantilever oscillations, but also take into account capacitance force, possible sample charging and other macroscopic effects.

Measuring very small forces and force variations over the surface places more emphasis on cantilever and tip. Most observations are made by monitoring normal and torsional

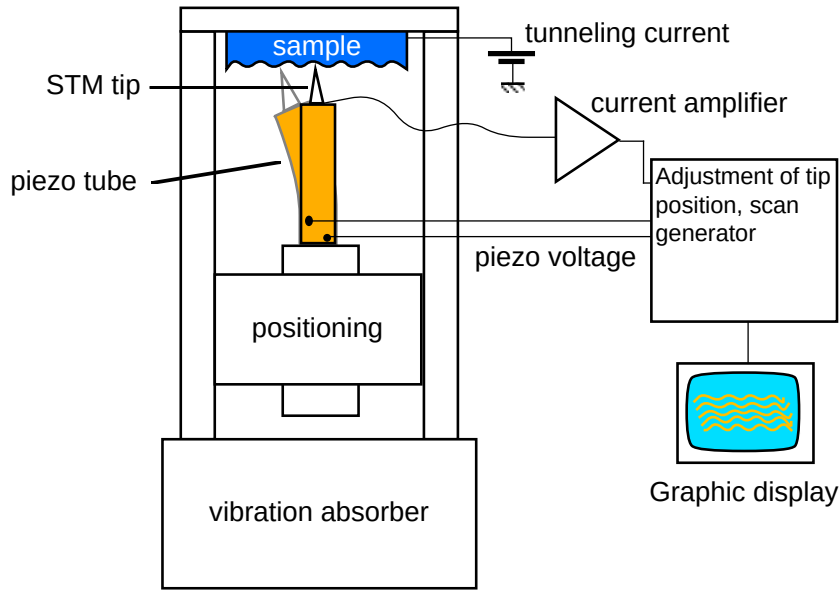


Figure 1 Setup of a scanning tunnelling microscope. The tip is mounted on a piezotube, which is deformed by applied electric fields. This deformation translates into lateral and vertical manipulation of the tip. Via an electronic feedback loop the position of the tip is adjusted according to the tunnelling current (constant current mode), and a two dimensional current contour recorded. This contour encodes all the information about the measurement. *Courtesy of M. Schmid* (Schmid, 1998).

cantilever deflections induced by the tip-surface interaction using various optical methods (Basel, 2000; Güntherodt *et al.*, 1995; Morita *et al.*, 2002). In initial SFM designs the tip was pressed to a surface either by the van der Waals force or by external elastic force of the cantilever and imaging was performed in the so called "contact mode". However, relatively recently it has been demonstrated that one can obtain much better sensitivity in measuring force variations on the atomic scale by employing dynamic force microscopy (García and Pérez, 2002; Morita *et al.*, 2002). In this case the cantilever is vibrated at certain frequency above the surface and the surface image is constructed by monitoring minute frequency changes due to the tip-surface interaction. Since in this case the tip is thought not to be in direct hard contact with the surface, this technique is often called Non-contact SFM (NC-SFM). It is currently the only reliable way of achieving true atomic resolution in SFM and in this review we will focus primarily on theoretical modelling underpinning this method. In later discussion, if a section of the review applies to SFM in general then it will be specifically stated, otherwise it is written in the context of NC-SFM. Several reviews of contact mode

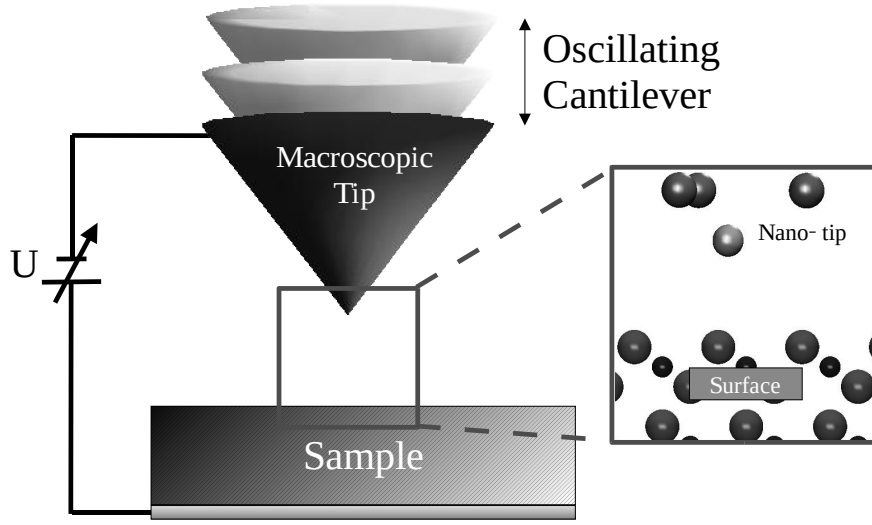


Figure 2 Idealized schematic of the setup needed to model an NC-SFM experiment on an insulating surface. The tip approaches the surface with frequency f_0 and U is a bias voltage between the conducting tip and the conductive sample support.

SFM can be found in refs. (Bonnell, 2000; Giessibl, 1994; Güntherodt *et al.*, 1995; Shluger *et al.*, 1999).

Not every surface can be imaged in STM or SFM with high resolution. To achieve atomic resolution, the surface in most cases needs extensive preparation. Sputtering (bombardment with ions, mostly Ar^+), and annealing (heating to the point where the surface defects are smoothed out) over weeks and even months in controlled cycles is not uncommon, e.g. on metal surfaces (Bischoff *et al.*, 2001). Surface preparation in itself is a sophisticated art, and one of the keys to successful imaging (Briggs and Fisher, 1999b; Chen, 1993; Himpsel *et al.*, 1998). Contrary to k -space methods like ion scattering or electron diffraction, to be imaged by SPM a surface need not be ordered. In fact single impurities and step edges on a surface are often used by experimentalists to check the quality of their images. Such an impurity is only imaged as a single structure, assuming no distorting effects like double-tips are present.

The tip is the crucial part in imaging in all SPM methods. STM tips are often made from a pure metal (tungsten, iridium (Chen, 1993)), a metal alloy (PtIr (Braun and Rieder, 2002)), or a metal base coated with 10-20 layers of a different material (e.g. Gd or Fe on poly-crystalline tungsten (Wiesendanger and Bode, 2001)), often produced in the lab from metal wire. In some cases heavily doped Si tips are also used for STM imaging. Although similar tips could also be used for SFM measurements, this is very rare. This is due to the

fact that a cantilever holding a tip plays a very important role in monitoring force changes in SFM: i) in many SFM realisations cantilever deflections are measured by detecting light reflected from the back of the cantilever; ii) cantilever spring constant, tip shape and tip sharpness both play crucial roles in image formation. Therefore standard cantilevers are required. In most cases these are produced from silicon by micro-fabrication in very much the same way as semiconductor chips.

In some cases the tip is modified by controlled adsorption of molecules (Capella and Dietler, 1999; Hahn and Ho, 2001b; Nishino *et al.*, 2001; Wertz *et al.*, 1997). In STM it has been shown that this affects the apparent height of molecules on a surface (Hahn and Ho, 2001b; Nishino *et al.*, 2001). The exact geometry of the tip is commonly unknown except for some outstanding STM measurements, where the tip structure was determined before and after a scan by field-ion microscopy (Cross *et al.*, 1998b). To complicate matters further, the tip geometry is decisive for reproducible scanning tunnelling spectroscopy (STS) measurements (Crommie *et al.*, 1993), unfortunately the tip most suitable for STS is also shown to be unsuited for topographic measurements, because it does not yield a high enough resolution (Feenstra *et al.*, 1987). Currently the most widely held opinion is that SPM tips consist of a base with rather low curvature, and an atomic tip cluster with a single atom at the foremost position.

In STM, all the current in the tunnelling junction is transported via this "apex" atom, the area of conductance is consequently rather small and in the range of a few $\text{\AA}^2$ (Chen, 1993) (see Fig. 3). This is the origin of STM precision, because it makes the current very sensitive to the electronic environment of a very small area of the surface. Variations in the interaction of the last several atoms of the sharp tip apex with the surface atoms determine the image contrast also in SFM images. However, this sensitivity to atomic structure is also the origin of the features which make the interpretation of STM and SFM images so difficult because the actual geometry and chemistry of the tip apex, which influences the conductance in the vacuum barrier between surface and tip and tip-surface forces, cannot usually be determined. Even for simple metal surfaces like Cu(100) and NaCl(100) this leads to different experimental results for different scans (Bennewitz *et al.*, 2000; Clarke *et al.*, 1996b).

As the determining factors in SPM experiments are not fully known, their relevance needs to be inferred from simulations. Simulations need to be done in a systematic manner, e.g. by

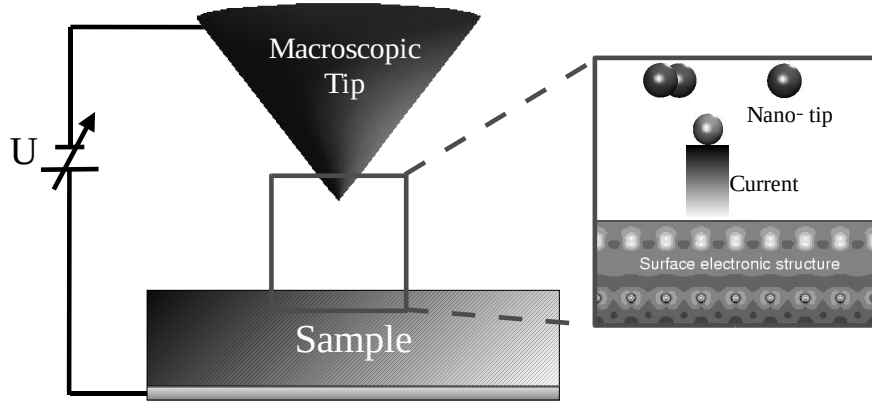


Figure 3 Tunnelling current in a scanning tunnelling microscope. The surface of the tip is generally not smooth. A microtip of a few atoms will bear the bulk of the tunnelling current, due to this spatial limitation of current flow the electronic properties of a scanned surface can be extremely well resolved (resolution laterally better than $1 \text{ \AA}$).

studying the effect of adsorbates on the electronic structure of model tips (Hofer *et al.*, 2001c, 1999), and by modelling the effect of these adsorbates on STM scans (Hofer and Redinger, 2000). Experimentally, the difficulty is circumvented, at least in careful measurements, by recording a series of scans and presenting decisive measures like the surface corrugation as a statistical average.

III. MAIN FACTORS DETERMINING IMAGE FORMATION

A. Controlling Interactions

The control parameter in an STM, the current in the tunnelling junction, is always due to the same physical process. An electron in one lead of the junction has a non-vanishing probability to pass the potential barrier between the two sides, and to tunnel into the other lead. However, this process is highly influenced by (i) the distance between the leads, (ii) the chemical composition of surface and tip, (iii) the electronic structure of both systems, (iv) the chemical interactions between surface and tip atoms, (v) the electrostatic interactions of sample and tip. The main problem, from a theoretical point of view, is that the order of importance of all these effects depends generally on the distance and therefore on the tunnelling conditions.

In contrast to STM, force controls SFM imaging, and it is not always due to just one

physical process. Although it is impossible to discuss every possible interaction that may occur during an experiment, it is clear that for a technique to be reliable a consistent set of significant forces must exist. If the interactions varied wildly between experiments then no useful comparisons or conclusions could be made. In this Section the interactions significant to standard imaging are discussed, with specific reference to those forces important to the applications discussed later. Several other interactions, e.g. image forces, capacitance forces, forces due to discrete charges, can be important for specific tip-surface setups and environments (Burnham *et al.*, 1993; Capella and Dietler, 1999; Morita *et al.*, 2002). These components of long-range electrostatic interaction between tip and surface can normally be minimized by applying a compensating bias during scanning (Bennewitz *et al.*, 1999c).

B. Tunnelling Current

The tunnelling current is the control parameter in most STM experiments. It is set to a fixed value, and the position of the STM tip relative to the scanned surface is varied via the distortions of a piezocrystal, so that the current remains constant. The tip in this case describes a constant current contour. The extreme sensitivity of the tunnelling current with respect to the tip-sample distance is the basis of vertical resolution in STM. Qualitatively, it can be described in the following way.

The potential barrier in the vacuum range of the two subsystems determines the decay of surface wave-functions in the same range. For a square potential barrier the current decays exponentially with a constant exponent, which is proportional to $\sqrt{\phi}$, where ϕ is the work-function of the two surfaces:

$$I(z) \propto e^{-k\sqrt{2\phi}z} \quad (1)$$

Here k a constant, and z is traditionally the distance between the two surfaces - to be precise, it is the distance from the nucleus of surface atoms to the nucleus of the tip apex.

In practice, this relation is only a good approximation. The work-functions of sample and tip are in general not equal; the decay of electron states is not constant, but depends on their location in the surface Brillouin zone; and the density of states above the surface is typically varied.

It has been noted by experimentalists that the decay constant, or the apparent barrier

height, remains remarkably stable even for low distances (Binnig *et al.*, 1984; Payne and Inkson, 1985; Schuster *et al.*, 1992). This seems at odds with the expectation that the mutual penetration of surface and tip electron charge, as well as the existence of image charges should lower the potential barrier in the low distance regime. In fact, the contrary has been observed: the decay constant increases as the two surfaces approach each other (Binnig *et al.*, 1984). This behaviour is due to interactions: as the distance between the atoms of surface and tip becomes small enough, chemical forces change the atomic positions. This shift of positions increases the tunnelling current faster, during an approach, than expected from the electronic structure alone (Hofer *et al.*, 2001b). It more than compensates the saturation of current, and thus the decrease of the apparent barrier height, as the two systems come into contact. Experiments reveal substantial oscillations of the tunnelling current immediately before the two surfaces jump into contact (Gimzewski and Moeller, 1987). Also this is an indication of the low stability of STM operation in this range.

The tip-sample distance can be experimentally estimated by a two-step procedure: (i) the decay constant is determined from the current decay at a suitably large distance and consequently low currents; and (ii) given a constant decay the point, where the conductivity equals $2e^2/h$, one conductance quantum is determined: this is seen as the point where the two surfaces are in contact. The procedure is wrought with problems, because current decay at large distances is no indication of its behavior at small distances, and the movement of atoms due to chemical forces is neglected. Therefore experimentalists usually describe the distance in terms of their piezo-voltage, or the voltage applied to the z -coordinate of the STM positioning device. A difference in this voltage corresponds to a difference in the z -coordinate of the STM tip, the scale is usually calibrated by comparisons with the (known) step-height on sample surfaces. This is without doubt an objective measure, but it has the drawback that it describes the distance only correctly for suitably large separation, and it fails in the range where high resolution measurements are usually performed. For this reason the empirical estimates of tip-surface separations have mostly been over-estimated by 1-2 Å. It took detailed simulations of coupled surface-tip systems to establish the actual distance range in high resolution scans (Hofer and Redinger, 2000; Hofer *et al.*, 2000b, 2001b).

C. Bias voltage

Yet another parameter important in both STM and SFM experiments is the bias voltage. The relation between tunnelling current and bias voltage is directly measured in STS experiments. In these experiments the current feedback loop is disengaged and the STM tip positioned at one point above the surface, usually described by its lateral position and the tunnelling conditions, e.g. bias potential and tunnelling current. A spectrum can be produced in two ways: (i) either by sweeping the bias voltage from a defined lower to a defined upper limit. The resulting $I - V$ is then recorded and numerically differentiated; (ii) or by extracting the differential directly from an experiment, where the bias voltage is oscillating with low frequency (in the range of kHz). The differential $I - V$ curve is then compared with simulations of the electronic surface structure. Tunnelling spectra are very sensitive to surface states (Biedermann *et al.*, 1996; Hofer *et al.*, 2000b; Stroscio *et al.*, 1995) and states in the bulk bandgap of semiconductors (Briggs *et al.*, 1992).

In general the change of bias voltage has two effects: (i) it shifts the Fermi level of one lead (sample or tip) relative to the other lead; and (ii) it compensates for this effect by the creation of a surface dipole. Both of these effects are understood in principle, even though no detailed simulations actually exist. The reason is that a simulation requires treating the coupled system of two leads and the interaction range in a non-equilibrium situation. Even though the theoretical framework for such a treatment in the STM context, the non-equilibrium Green functions formalism of Keldysh has been known for some forty years (Keldysh, 1965), its numerical implementation became only recently possible (Taylor *et al.*, 2001). Provided the electronic density of states (DOS) of the surface and tip structure are fairly smooth, then the current increases approximately linearly with the applied bias voltage. This is due to an increase of the energy difference between the Fermi level of sample and tip, which increases the number of electron states provided by one lead, the number of empty states provided by the other, and to the condition of resonant tunnelling.

Application of voltage in SFM setup is usually used to compensate for the macroscopic electrostatic forces described below. Again, although the effect is well known on the empirical level, calculations of real systems are still quite rare (see, e.g. refs. (Gomez-Moñivas *et al.*, 2001; Jacobs and Stemmer, 1999)). This is mainly due to the complexity of the tip shape, and difficulty in describing surface charging and work-function anisotropies.

D. Electrostatic Forces

The differences in Fermi level due to bias voltage, combined with the general differences between the Fermi level of a sample and the tip, introduces electrostatic effects into the interfaces. Although of the same origin, these effects have different consequences in STM and SFM measurements.

1. *Effect of electrostatic forces in STM*

These effects have been analyzed by theoretical models of STM in various instances: (i) the effect of the tip potential on semiconductor surfaces with an adsorbed organic molecule like acetylene (Ness and Fisher, 1997; Stokbro *et al.*, 1998), (ii) the effect of the tip potential on the electronic structure of metal surfaces (Hofer *et al.*, 2000b), and (iii) the effect of electrostatic fields on the structure of sample and tip in a continuum model (Hansen *et al.*, 1998). In the first case the effect leads to a change of the tip-sample distances in the range of 0.1 Å, and for distances less than 6 Å. This effect depends on the distance. In actual measurements under normal experimental conditions (- 2V and 50pA lead to a median distance of about 6 Å on Si(100) (Hofer *et al.*, 2001a)), the effect is present, but not substantial enough to alter the image in a decisive way. In case (ii) and (iii) the applied field had to be very high. On a Fe(100) surface, for example, decisive changes of the electronic structure, even though it is known to be very volatile, are limited to fields of more than 1 V/Å. Even in high resolution scans this value is beyond the limit of topographic imaging. It seems therefore safe to conclude that electrostatic fields of the STM tip do not substantially alter the electronic surface structure. In case (iii), the continuum model of tip and sample deformations due to fields, the minimum bias potential for observable changes on a metal surface was about 2 V. Since STM images on metals are usually recorded with a bias potential of less than 0.1 V, even a difference of the Fermi levels of about 1 eV would not have a substantial effect, hence we may conclude that field effects on metal or semiconductor surfaces can safely be neglected.

The effect of static fields due to non-conducting overlayers on metals or semiconductors has so far not been analyzed in STM theory. There is some indication from SFM theory that these fields via their forces may lead to a distortion of the system. However, since these

measurements are still comparatively rare and in most cases satisfactory explained by an analysis of the surface electronic structure (Hebenstreit *et al.*, 2000; Kliewer and Berndt, 2002; Schintke *et al.*, 2001), it seems implausible that they may lead to significant effects. To sum up, even though electrostatic effects are known to exist for acetylene on silicon and under the condition of very high bias voltages on metal surfaces, these effects are either confined to very low distances between tip and sample (Hofer *et al.*, 2001b) or depend on very specific configurations.

2. Macroscopic electrostatic forces in SFM

Macroscopic forces are those which generally do not depend on the atom directly under the tip, and can be approximated by some sort of continuum or analytical expression. These forces are generally important in SFM in any conditions, but obviously also play a role in NC-SFM. In this section we will focus on those macroscopic forces most relevant to applications we discuss later, and more detailed general information can be found in Refs. (Burnham *et al.*, 1993; Capella and Dietler, 1999).

The *van der Waals force* represents the electromagnetic interaction of fluctuating dipoles in the atoms of the tip and surface. On the atomic level, it is one of the weakest interactions, responsible, for example, for bonding in rare gas crystals. However, this force is nearly always attractive, and therefore small interactions between individual atoms of macroscopic tip and sample sum up into a resulting force of the order of several nano-Newton (nN). Although this force is small by macroscopic standards, it exceeds the chemical forces discussed below and in many cases dominates the tip-surface interaction. It is present regardless of the tip/surface setup used or the environmental conditions of the experiment (excepting SFM experiments in liquids (Israelachvili, 1991)).

The *image force* is the interaction due to the polarization of the conducting electrodes (i.e. of the conducting tip and the substrate) by the charged atoms of the sample. This is important for any tip-surface (or just surface) setup containing conducting materials e.g. interaction of a conducting tip with an insulating surface or studying the properties of an insulating thin film on top of a metal substrate. As discussed in Ref. (Kantorovich *et al.*, 2000a) the image force can be strongly affected by applied voltage (V) between tip and substrate. The image force is in principle a microscopic force (and is calculated as such

(Kantorovich *et al.*, 2000a)), but it depends on the charge of the atoms in the surface rather than their chemical identity.

If there is a direct electrical connection between the tip and sample (in the case of SFM, the tip and sample/substrate connected directly by a wire) then electrons are allowed to flow between two different conducting materials. This results in a *capacitance force* due to the potential difference between the tip and surface. The potential difference is due to two components: (i) there will be a contact potential U between the tip and surface, as the electrons must pay energy to travel from the material with the smaller work function to the material with the higher one, and (ii) the applied voltage, V , across the system. Kelvin probe microscopy allows one to measure the local contact potential difference across the surface by measuring the applied bias voltage required to compensate the capacitance force due to contact potential (Jacobs and Stemmer, 1999). The capacitance force can be easily calculated analytically as a function of the tip/sample geometry and U (Hudlet *et al.*, 1995; Jean *et al.*, 1999). Note that although in principle electrons can transfer between the end of tip and the surface, at the scanning ranges used in NC-SFM this effect is negligible.

The discussion of capacitance force above makes an assumption about surfaces that is not always valid. By calculating the capacitance force as a function of z alone, it is assumed that the work function is uniform across the surface. On real surfaces, inequivalencies in the work function across the surface can arise due to surface preparation, adsorbates, crystallographic orientation and variations in local geometry (Burnham *et al.*, 1992, 1993). Real surfaces of any material are not perfectly smooth, as is suggested by the very small scale NC-SFM images usually seen. This is especially relevant for the electrostatic minimization procedure used in experiments (see section V.C.1), as this minimizes at a single point on the surface before scanning. Variations in the work function over the region scanned could render the minimization process invalid, or at least approximate. Other studies (Burnham *et al.*, 1993) have already suggested that *work function anisotropies* are the most likely source of the long-range interactions observed in force microscopy of graphite with diamond tips. The contribution of work function anisotropies to the tip-surface interaction cannot be calculated explicitly, however they can be represented by increased surface charge density or increased/decreased applied bias when calculating the image force contribution (Burnham *et al.*, 1993).

Many processes in NC-SFM imaging can introduce charge into the tip and surface. Sur-

face preparation by cleavage is known to induce very large charges on insulating surfaces (Engelhardt *et al.*, 2000; Harris and Fiasson, 1985; Luna *et al.*, 1998; Wintle, 1997), although these can be reduced by annealing. These charges are usually localised on edges of cleavage tips and around dislocations. Tip and surface sputtering can also cause charging, as can ion exchange between tip and surface during scanning (tribo-charging). On the microscopic scale, these charge defects can appear as strange artefacts in images or as unexpected interactions close to the surface. On the macroscopic scale, *tip and surface charging* can dominate the interactions, and in some cases even prevent stable imaging.

E. Chemical forces

Although the chemical forces are not the strongest between tip and surface, they are the most important interaction both in STM and NC-SFM. In SFM they can really distinguish atomic identities and are therefore responsible for atomic resolution in images (see further discussion in Section IV.C). They also define the atomic structure of the tip and surface, and are responsible for atomic displacements when the tip is close to the surface. Although other forces, such as the van der Waals and image forces, result from atomic interactions, in most cases they can be accurately approximated by a macroscopic interaction.

In the context of STM these issues are even less trivial and encourage the study of the formation of chemical bonds between tip and surface, and the range at which a chemical bond can be considered to exist. If a chemical bond forms, then the energetic level of the bond may end up below the energy level of the conductance band of the leads. In this case no tunnelling current will be observed, even though the bond formation results in attractive forces between atoms of the surface, and atoms of the STM tip. However, the relaxation of atoms due to these forces will reduce the distance between the two surfaces and thus, via a secondary effect, enhance the tunnelling current. If the energy level of the combined electrons lies within the conductance band of the leads, then the electrons oscillating between the two atomic centers will freely propagate through the drain side of the junction: no chemical bond will form. From this qualitative model it is clear that chemical forces will only affect the observed tunnelling currents from a certain onset. The main question then is, where this onset actually lies in terms of tip-sample separation. This question has been discussed without conclusive results for more than twenty years (Cho and Joannopoulos, 1993; Clarke

et al., 1996a; Pethica and Sutton, 1988a; Sacks, 2000; Sacks and Noguera, 1988; Ventra and Pantelides, 1999).

Due to the advent of first principles methods and powerful computers it could finally be resolved by a calculation of the combined tip-sample system (Hofer *et al.*, 2001b). The point of onset for chemical bonding was found to be at a distance of 4.6 - 4.7 Å. As the tip approaches the surface, chemical forces rapidly become large enough to destroy the stability of a tip-sample system in STM due to ions jumping to/from the tip from/to the surface. The point of destruction is about 4.0 - 4.1 Å. From the onset of chemical forces to the limit of mechanical stability the two main effects are: (i) An increase of the tunnelling current beyond exponential growth; and (ii) an increase of surface corrugation by a factor of 2 - 3. Both effects are observed in experiments (Gimzewski and Moeller, 1987; Hallmark *et al.*, 1987). They show, unambiguously, that high-resolution STM operates within the range of chemical forces, and that the main effect, omitted in any straightforward perturbation model, is the relaxation of surface atoms due to chemical interactions. It is perhaps not surprising that theoretical modelling predicts the onset of contrast formation in NC-SFM on semi-conductors and insulators at approximately the same distance range (Barth *et al.*, 2001; Lantz *et al.*, 2000; Livshits *et al.*, 1999). Quantitative comparison between theory and experiment, discussed in Section V.C.1, demonstrates that the distance range of 3.5 - 4.5 Å is where the best contrast can be achieved in stable NC-SFM imaging of insulator surfaces.

F. Magnetic Forces

Magnetic forces are really only important when both the tip and sample demonstrate magnetic behaviour e.g. both are ferromagnets. This situation is not encountered in normal NC-SFM, but modifications of the standard setup have been performed so that the magnetic properties of materials can be probed on the nano-scale. These Magnetic Force Microscopes (MFM) (Martin *et al.*, 1987) have proved successful in imaging magnetic domains at very small scales, and offer a great deal of potential for nano-scale magnetic recording.

The force sensitivity of the NC-SFM technique on the atomic scale has encouraged studies of the atomic scale magnetic properties of surfaces. In particular, interest in the possibility of directly measuring differences of the exchange interaction with different surface sites has been motivated by the early suggestions from spin-polarized Scanning Tunnelling Microscopy

(STM) (Wiesendanger *et al.*, 1990), that the magnetic force between tip and sample at small distances (2 - 5 Å) could be measured. The recent introduction of low temperature ($T < 15$ K) NC-SFM (Allers *et al.*, 1998) and the associated reduction in thermal noise has made this possibility even more feasible, and now several experimental NC-SFM groups are actively pursuing the measurement of atomic scale spin structure with magnetised metallic tips. In spite of several attempts (see, for example Refs. (Allers *et al.*, 2001; Hosoi *et al.*, 2000)) experimental measurement of exchange forces proves extremely challenging and no conclusive results have been obtained so far. A theoretical analysis of the possibility of NC-SFM measuring exchange forces has been presented in Refs. (Foster and Shluger, 2001; Nakamura *et al.*, 1999), and is discussed later.

On the contrary, magnetic surfaces are one of the main areas of STM research on metals. The reason for this burgeoning interest is due to their technical importance, e.g. for storage, their potential for nanotechnology, e.g. magneto-electronics ("spintronics"), and their wealth of intricate effects. The full potential of an STM to record and differentiate electrons of different spin-orientation has only recently been exploited (Heinze *et al.*, 2000; Piezsch *et al.*, 2001; Wiesendanger and Bode, 2001). It entails essentially coating of the tip by magnetic material. The main experimental applications today are in tunnelling spectroscopy (Wiesendanger and Bode, 2001), and topography with magnetic contrast (Heinze *et al.*, 2000).

Theoretically, the influence of magnetism on the tunnelling current comes from two origins: (i) The magnetic moment and electronic structure of different spins; (ii) The orientation of the magnetic axes. Again, the electronic structure and the magnetic moment can be determined from DFT calculations. The orientation of the magnetic axis is in principle obtainable from DFT methods including spin-orbit coupling. In practice it is often constrained by experimental conditions for one or the other subsystem. The tunnelling current then depends on the angle ϕ between the magnetization vector of the sample and the magnetization vector of the tip (Hofer and Fisher, 2002a).

G. Summary

As described in this section, an SPM is a local atomic probe, which utilizes the fact that charge flow and forces between atoms are very sensitive to the physical environment.

This makes it possible, with such an instrument, to probe the environment directly by carefully recording the local changes. It depends not least on the ability to measure and to react to minute changes in the control parameters within very short intervals (less than one millisecond). The ability to control the tip-sample distance on the picometre scale via piezoelectric elements was really the technological breakthrough which moved SPM from the meso to the nanoscale.

IV. MODEL DEVELOPMENT

Modelling the SPM involves several stages, which differ in detail for STM and SFM. The task can be broken down in five discrete steps: (i) Establishing a realistic model of the surface from experiment and theory; (ii) establishing a realistic model of a SPM tip using properties known experimentally and inferred from theory; (iii) explicitly modelling the interactions between the tip and surface; (iv) calculating the current (STM) or the oscillations of the cantilever (NC-SFM) under the influence of these interactions and constructing a theoretical image; and (v) comparing with experimental images.

The main differences between STM and SFM concern step (ii) and (iii). For a realistic model of an SFM tip the macroscopic form of the tip plays an essential role, because this macroscopic form has a decisive influence on long-range interactions. For an STM tip, this is generally irrelevant, since the main effects observed in experimental conditions are due to the microscopic structure of the tip and the electronic states as well as the atomic positions at the apex of such a tip. While the focus in SFM simulations is on a precise rendering of the macroscopic (long-range forces) as well as the microscopic (chemical and short range forces) tip structure, the focus in STM simulations is only on the microscopic structure.

The difference between STM and SFM in step (iii) is due to the measured variable itself. In STM images the current is *altered* by interactions, compared to the non-interacting cases; in NC-SFM the change of frequency is *determined* by the very same forces. It is therefore generally sufficient in STM simulations to estimate the influence of interactions in a given experimental situation, and this influence can be determined by model calculations of specific systems. The interactions themselves, in this case, need not be treated in every situation (see also section III.A).

The additional complication in STM simulations is the demand that the electronic states

on the tip surface must be precisely simulated, because these states determine the obtainable contrast and thus the simulated STM image. For this reason STM tip simulations generally have to rely on first principles methods solely, although we shall see that first principles methods are also used as a fundamental reference for simulations of SFM.

The level of complexity needed to calculate the atomistic interactions in NC-SFM depends on the properties of the system being studied. First, it is important to establish the criteria for choosing a method. For the interactions of ionic systems, where the electron charge density is localized on the atomic cores and there is no significant charge transfer, it is sufficient to use Atomistic Simulation methods (AS) (Catlow and Mackrodt, 1982) based on classical inter-atomic potential treatment and the Shell Model (SM) (Dick and Overhauser, 1958) for ionic polarisation. Atomistic simulation techniques are very computationally effective and systems of several hundred atoms can be calculated on a PC. However, the interactions in AS calculations must be parametrized for each pair of atoms and this leads to problems in overall accuracy - although very high accuracy can be achieved for specific physical properties. It should be noted that the parameters for the AS interactions are always checked by comparison to experiment or quantum mechanical calculations. Examples of this can be seen in Sections V.C.1 and V.C.2.

For semi-conducting and metallic systems it is important to represent the delocalized electron density correctly and to consider covalent bonds between tip and surface. Therefore a more rigorous Quantum Mechanical (QM) treatment, such as *ab initio* Hartree Fock Theory (HF) or Density Functional Theory (DFT) (Ohno *et al.*, 1999) should be used throughout (see, for example, Refs. (Ke *et al.*, 1999; Pérez *et al.*, 1997; Shluger *et al.*, 1997; Tóvik *et al.*, 1999)).

A. The Surface

The first stage of the modelling process is establishing a good representation of the surface being studied. The wealth of experimental methods of surface preparation is to a certain extent responsible for the wealth of surface effects which are studied by atomic probe instruments. In the simplest cases, and if a clear consensus on the surface structure has been established previously then this can be used directly, e.g. the examples in Sections V.A and V.C.2. If there is no clear consensus, then an accurate structure in some cases can be found

from a combination of other experimental techniques and theoretical methods. The most difficult situation is when establishing the unknown surface structure is the sole purpose of SPM experiments. Notwithstanding the famous example of the Si(111) surface, where SPM revealed the (7×7) reconstruction (Binnig *et al.*, 1983), this is not a trivial task. In view of the ambiguities of the experimental results, alternative surface models should be used and checked, before an agreement is sought from a broad set of experimental data.

Preliminary models of the surface topography, for example, can be determined by atomic-probe methods, ion-scattering, electron diffraction, or Auger spectroscopy. The chemical bonds of adsorbates can be estimated from infrared spectroscopy. The surface electronic structure is accessible by photoelectron emission techniques. Experimental techniques in surface science have developed in parallel with advances in surface preparation. Today, surfaces can nearly be tailored to individual needs by physical and chemical methods (Himpsel *et al.*, 1998; Shen and Kirschner, 2002; Wolkow, 1999).

In case the surface structure is known, its electronic structure has to be computed with sophisticated methods, existing codes more and more rely on first principles density functional theory (DFT) (Kresse and Furthmüller, 1996; Kresse and Hafner, 1993; Wimmer *et al.*, 1985), or, in case of tight-binding models (Turchi *et al.*, 1998), they obtain their parameters from a fit to DFT data (Cerdeña and Soria, 2000). The fit is not without ambiguities, since it is unknown whether the density of states used for the fit is really unique.

B. The Tip

It is well known that contact between the bottom of the tip and the sample surface will not be between two smooth, regular surfaces. In particular, the bottom of the tip may contain many asperities and one of these asperities will serve as the probe. To accurately model an SPM tip, one should know its shape and a Hamaker constant of its van der Waals interaction with the surface (SFM), as well as the chemical nature and crystallographic orientation of its apex (SFM, STM). Unfortunately there is very little information on the properties of (SPM) tips, effectively only the most basic qualities are known.

In STM experiments the most common tip is made from a tungsten poly-crystalline wire, other tip materials are commonly transition metals (platinum, iridium, alloys) (Chen, 1993). These tips are electrochemically etched in NaOH. The obtained curvature of the tip depends

on the duration of etching, it ranges from 20 - 100 nm (Chen, 1993). This tip is further altered *in situ* by frequent voltage pulses of 10-20 V. It is generally agreed today that only a very sharp tip with a single atom at its pinnacle is suitable to obtain atomic resolution on close-packed surfaces. But such a tip is highly unstable. Therefore, the fabrication and characterization of defined tips, e.g. by field ion microscopy, has not been achieved, nor can it be expected for the near future. Other experimental preparations include tip sputtering with Ar^+ ions, or tip coating with additional layers (Wiesendanger and Bode, 2001). Only a limited number of experimental images obtained with these tips are actually recorded and made public. Among the non-recorded images are usually the ones obtained with multiple-tips, or tips which render images of poor quality. In case of STS experiments, the reproducibility of spectral data requires fabrication of a very blunt tip (Feenstra *et al.*, 1987), which is unsuitable for high resolution scans of metal surfaces.

SFM tips are micro-fabricated from silicon in much the same way as computer chips and, as-produced, have a pyramidal shape. However, this only gives their structure on the micrometre scale, and there is no direct method for imaging the very end of the tip - the ‘nano-tip’. Therefore additional information is needed to reconstruct tip structures. In particular, it is known that the tips are oxidized due to exposure to the atmosphere and, although the oxide layer can be removed by argon ion sputtering, they can be contaminated by residual water always present in UHV chamber. Some recent atomically resolved images use untreated tips covered by an oxide layer (Fukui *et al.*, 1997a) and specially prepared silicon tips cut from silicon wafers (Giessibl *et al.*, 2000). Metallic (Erlandsson *et al.*, 1996) and silicon tips covered by metal (Allers *et al.*, 2001; Hosoi *et al.*, 2000) have also been used in NC-SFM experiments.

In many SPM experiments atomically resolved images are obtained after tips were in contact with the surface and are most likely covered by the surface material. Tip crashes often happen spontaneously due to the strong tip-surface interaction, presence of debris on the surface, and due to other artefacts. However, in many cases ‘gentle’ contact is arranged intentionally, as it has been noted that this increases chances of obtaining good atomic resolution. Tip contamination by the surface material has been explored in Refs. (Livshits and Shluger, 1997a,b) using classical molecular dynamics. A MgO cube tip was indented into the LiF surface and then retracted back from the surface. In another set of calculations the surface scanning has been simulated after indentation. In both cases stable clusters of

the surface material were formed on the tip.

Still, this information gives only a very preliminary idea about the possible tip's chemical composition, and nothing about the geometric structure, stoichiometry and charge of the nano-tip. One solution to this difficult problem is to use idealized nano-tips. This method has been used in recent *ab initio* studies of SFM on semiconductor surfaces (Ke *et al.*, 1999; Pérez *et al.*, 1998) and in atomistic simulations on ionic systems (Shluger *et al.*, 1999; Shluger and Rohl, 1996). It is a good basis for beginning the tip modelling process. Another direction of modelling would be to try and find the most realistic tip model for a particular set of experiments. This approach has been applied in some SPM simulations (Foster *et al.*, 2001b). Below we briefly outline the main features of both these approaches.

1. Idealized tips

The approaches using idealized tips are based on two main considerations. Firstly, they assume that the tip structure is too complex to be treated explicitly and is likely to change during experiments. Therefore one should try and reproduce only general qualitative features which can be responsible for image contrast inspite of all the complex issues discussed above. Secondly, to keep calculations practical, nano-tips cannot be large and should include 20-30 atoms.

The prevailing perception of STM modelling has been, since the work of Tersoff and Hamann (Tersoff and Hamann, 1985a,b), that a single tip orbital is responsible for the image contrast. In simulations this orbital was thought to be an electron state of the tip metal. The question, as to whether the symmetry of this orbital is *s*-like (radial symmetry), or rather *d*-like (elongation in one or two directions) (Chen, 1990a,b) has led to heated discussions. It was only solved by detailed simulations of the tip apex, which showed that the tip orbitals are *d*-like (electron states of transition metal atoms), even though the convolution of all states near the Fermi level frequently shows radial symmetry (Hofer *et al.*, 2001c).

In STM simulations based on single tip orbitals, this is due to the existence of free parameters in the evaluation (decay κ and radius R in both the Tersoff-Hamann model and Chen's modification), which are fitted to experimental data. This procedure removes the possibility to compare simulations to the experimental tunnelling currents. In fact, it reduces the accuracy of the comparison quite substantially, because the only measure left

for comparison is the protrusion of single atoms (this is called the *corrugation* or *corrugation height* of surface atoms). This is problematic for two reasons: (i) The corrugation height is in most cases not unique, whether a surface is corrugated (atoms stick out) or anticorrugated (atoms are seen as holes) cannot be determined from experimental images. (ii) The simulated corrugations are usually fitted to the experimental data, which leads to an estimate for the tip-sample separation. Nearly without exceptions, these estimates are too low when compared to detailed simulations (Hofer *et al.*, 2001b).

In SFM simulations, the most common perception in modelling on Si and other semiconductor surfaces has been that the main component of the tip-surface interaction responsible for image contrast on these surfaces is due to the interaction of a dangling Si bond at the end of the tip with the surface atoms. This dangling bond can be well described using relatively small 4 or 10 atom Si clusters saturated by H atoms (Pérez *et al.*, 1998). Another approach has been used to model tips for simulating SFM images of ionic surfaces. Here it has been assumed from the start that the electrostatic forces between the tip and surface will be most important and mainly ionic tips have been considered (Shluger *et al.*, 1999; Shluger and Rohl, 1996).

2. Modelling of real tips

The tip models described above have been successful in developing the qualitative understanding of the origins of image contrast in SPM on metals, semiconductors and insulators. However, they fail in most cases to reproduce the quantitative results of experiments. The solution to these problems is to compare images to simulations with a number of different tip-models.

The most suitable STM-tip model on semiconductor surfaces is a tungsten pyramid, on metal surfaces a tungsten film with either a tungsten apex atom or an atom of the sample surface. On metal alloy surfaces, for example, it is likely that the apex of the STM tip is composed either of atoms of the tip material (e.g. tungsten), or of single atoms of the scanned surface, because it comes frequently in very close contact with the surface. Since most metal surfaces of technical importance are transition metals, it suffices to model tips with transition metal adsorbates, to be able to study a large proportion of all STM experiments on metals. In principle, it would be necessary to vary also the surface orientation of the STM tip, but

in practice it turns out that the chemical composition is the dominant influence for the electronic structure.

The effect of single STM tips can be studied qualitatively by analyzing their surface electronic structure. If it is composed to a high degree of single electron states (Kohn-Sham states), which protrude far into the vacuum within a small area, then the electron tunnelling from the sample to the tip will be far more localized: the tip, in this case, resolves the surface electronic structure very well. The opposite is true, if the wave-functions are very delocalized: then the conductance for one state will cover a large area and sample the surface electronic structure in a statistic manner. The detailed information about the surface in this case is lost.

The curvature of the wave-functions at the Fermi level and thus the obtained corrugation on a surface depend on the chemical (and magnetic) nature of the apex atom. To illustrate this point we show the local density of states (LDOS) of various magnetic and non-magnetic transition metal atoms adsorbed on W(100) surface (see Fig. 4). The two panels show the electronic structure of magnetic (Cr, Mn, Fe, Co) and non-magnetic adsorbates (Mo, Rh, Pd, Ag) on tungsten films. The contour plots depict the LDOS in a plane perpendicular to the tip surface of all states near the Fermi level ($E_F \pm 0.1$ eV), two single contours are emphasized, and the distance from the STM tip surface is marked. The graphs below show the DOS integrated over the volume of the apex atom (black) or the vacuum region (grey), we have differentiated between the spin-up and spin-down states of magnetic atoms.

These and similar STM tip models have been used in simulations of STM experiments on metal alloys. From a comparison of simulations and experiments on different metal surfaces in a statistical manner, it is evident that the best agreement is achieved if the apex atom of the STM tip is an atom of the sample surface (Hofer and Redinger, 2000). This, in turn, tallies nicely with the experimental practise of increasing surface contrast by controlled crashes of the tip into the surface.

To obtain realistic tip models DFT calculations of the electronic structure of fully relaxed tungsten films with one or two surface layers of either tungsten atoms or adsorbates have proven to be the most suitable choice (Hofer *et al.*, 2001c, 1999). The adsorbates so far considered include most transition metals. In single cases, where the STM tip was covered by 10-20 layers of Fe, the tip has been modelled by a Fe(100) film covered by one atom or a layer plus one atom of sample surface atoms (Hofer and Fisher, 2002a).

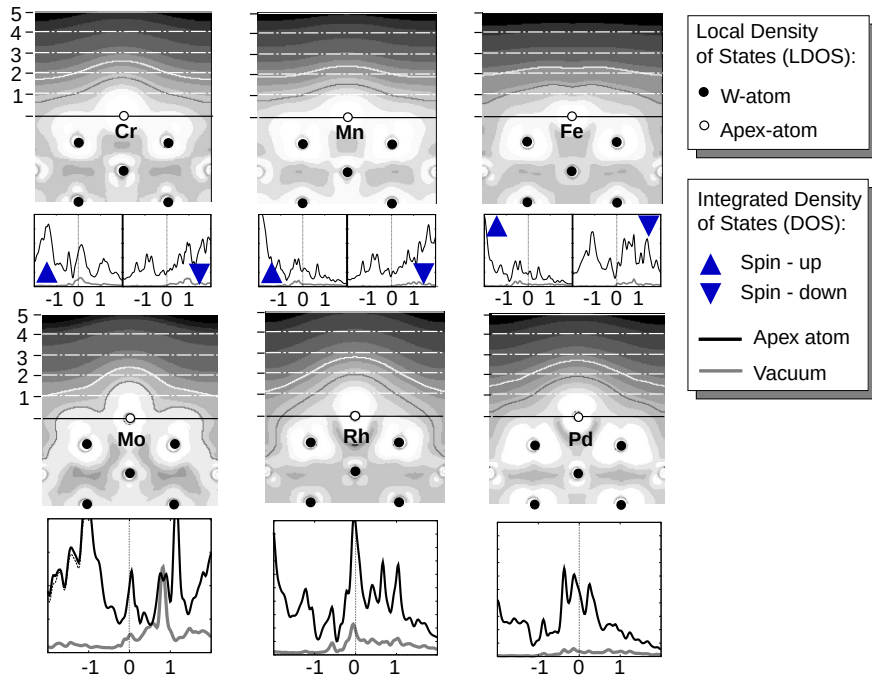


Figure 4 Local density of states (LDOS) and integrated density of states (DOS) of selected magnetic and non-magnetic STM tip models. The tip is mimicked by a W(100) surface with single 3d and 4d impurities. *Reprinted with permission* (Hofer *et al.*, 2001c).

For SFM a study of different possible nano-tip models was performed to try and determine which most closely matches experimental behaviour, e.g. on NaCl surfaces (Bennewitz *et al.*, 2000). Firstly, it was found that if the bottom of the tip was flat i.e. no nano-tip, then the interaction with the surface was averaged over several tip ions and no contrast was produced. When a nano-tip is included, it must extend significantly beyond the main part of the tip to reproduce the interaction observed in experiment. Specifically a nano-tip of only a few atoms would not atomically resolve lower terraces of stepped surfaces, which contradicts experiments on the NaCl surface (see Fig. 25(a)).

Silicon tips are likely to be contaminated by residual oxide, adsorbed hydrogen and water (Zaibi *et al.*, 1997), or even the surface material. To investigate the electrostatic properties of clean and contaminated silicon tips, the electrostatic potentials of Si_{10} clusters with adsorbed contaminant species were calculated using DFT and the VASP code in Ref. (Sushko *et al.*, 1999). The results clearly showed that the adsorbed hydrogen has no effect on the potential from the uncontaminated silicon cluster. However, the adsorbed oxygen and hydroxyl group causes a significant change in the potential gradient from the Si adatom. Both potentials

decay over a much longer range than the uncontaminated cluster, and their stronger gradients suggest they would interact much more strongly with the surface. Interestingly, the potential gradient from the MgO cube corner is very similar to that of the oxygen contaminated silicon cluster, a strong negative potential. The cube can also be orientated with an Mg ion down, providing a strong positive potential. For many SFM experiments on insulators, the purely ionic MgO tip model proved to provide excellent qualitative and quantitative agreement for the reproducible contrast patterns observed. However, recent increases in experimental sensitivity have reduced the possibility of large scale tip contamination by ionic material, and it has also become important to use conducting tip models when studying insulating surfaces. Now simulations calculate the relative influence of pure Coulomb interactions, polarization and charge transfer by using different tips on the same surface. This builds a more complete picture of the tip-surface interaction, and allows a much wider spectra of SFM experiments to be understood. An example of this approach to simulations can be seen in the study of CaF_2 in Sec. V.C.1.

3. *Combining Microscopic and Macroscopic Tip Models*

So far we have considered the nano-tip models. However, the tip-surface interaction is determined by the properties of the whole tip. The fact that the whole tip model is separated into two components, the microscopic and macroscopic, means that the properties of a silicon tip missing in an e.g. MgO microscopic model can be introduced in the macroscopic model of the tip. This can be done via the Hamaker constant and also via including the image and capacitance forces pertaining to conductive tips. Whether these forces are important and should be included at all is impossible to know *a priori*. Nevertheless some information regarding the possible tip shape, conductivity and charging can be found from analysing the experimental dependence of the NC-SFM cantilever frequency change vs. tip-surface separation measured before and just after imaging (Foster *et al.*, 2000a; Guggisberg *et al.*, 2000). Success in extracting the main components of the tip-surface interaction on different substrates (Guggisberg *et al.*, 2000; Loppacher *et al.*, 2000; Sounilhac *et al.*, 1999) suggests two main approaches to tip characterization. Both of them exploit different behaviour of van der Waals and electrostatic forces as a function of the tip-surface separation. One approach is based on using a well-characterized, e.g. metallic surface as a reference before or after

scanning the surface of interest. A more direct method is to analyze frequency change vs. tip-surface separation curves measured on the same surface just after imaging. An example of this latter approach will be given in Section V.C.1.

C. Tip-Surface Interaction

The force can be split into two general components: (i) the *microscopic* chemical force between atoms in the tip and surface, and (ii) the *macroscopic* force between the tip and surface, which always includes the van der Waals and various other (electrostatic) interactions depending on the specific tip/surface combination studied. Extensive SPM modelling suggests that only the short-range chemical forces are responsible for atomic resolution (Foster *et al.*, 2001a; Hofer *et al.*, 2001b; Livshits and Shluger, 1997b), whereas the macroscopic forces can be treated as a *background attractive force*. This background force is important to reproduce experimentally observed frequency changes in SFM, but is independent of the identity of the atom under the tip and does not play a role in atomic displacements. Therefore it is generally irrelevant for STM experiments.

In terms of STM modelling, this means that only microscopic forces have to be considered in specific situation (high resolution scans), in general (low resolution, semiconductors) even these forces can be neglected and the theoretical model can be reduced to perturbation theory. In SFM simulations the chemical and macroscopic components of the interaction can be calculated separately and just combined for the final stages of modelling to give the total force.

Certainly not all known types of interactions can be included in the theoretical modelling on an equal footing. Thus, a strategy focusing on the most important determinants of the actual characteristics measured must be implemented. In discussing the forces relevant to NC-SFM, we will focus on experiments performed in UHV, and certain forces, for example capillary forces, which are relevant for SFM in air will not be discussed. Excellent reviews of the forces which are relevant to SFM in general can be found in Refs. (Burnham *et al.*, 1993; Capella and Dietler, 1999).

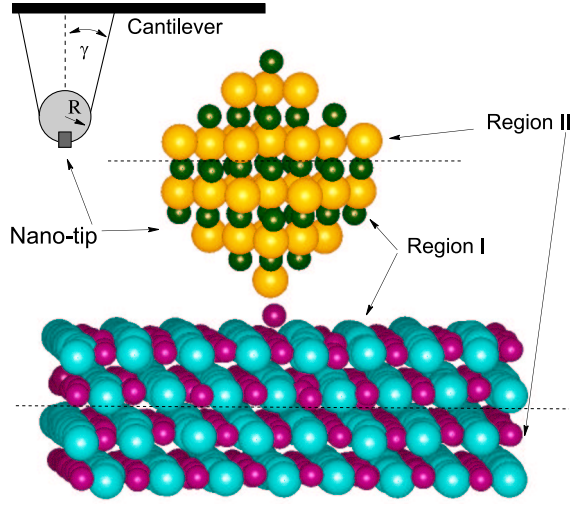


Figure 5 Schematic of integration of macroscopic and microscopic tips.

1. Van der Waals Forces

The van der Waals interaction is non-additive as atoms polarize each other. Nevertheless an additive approximation is used in many practical applications, including AS calculations of SFM. In particular the van der Waals interaction between the atoms at the end of the tip and in the surface is taken into account explicitly by summing the interaction of all pairs of atoms. However, the full tip contains billions of atoms and it is impossible to sum all the interactions, therefore an approximation must be made based on the material and structure of the tip. The van der Waals interaction potential is:

$$V(r) = -\frac{C_6}{r^6} \quad (2)$$

where C_6 is the interaction constant as defined by London (London, 1937) and is specific to the identity of the interacting atoms. Hamaker (Hamaker, 1937) performed the integration of the interaction potential to calculate the total interaction between two macroscopic bodies using the following approximations:

- additivity - the total interaction can be obtained by the pairwise summation of the individual contributions.
- continuous medium - the summation can be replaced by an integration over the volumes of the interacting bodies assuming that each atom occupies a volume dV with a

number density ρ .

- uniform material properties - ρ and C_6 are uniform over the volume of the bodies.

This then allows the total force between two arbitrarily shaped bodies to be given by:

$$F_{vdw} = \rho_1 \rho_2 \int_{v_2} \int_{v_1} f(r) dV_1 dV_2 \quad (3)$$

where ρ_1 and ρ_2 are the number densities, $f(r)$ is equal to $-\nabla V(r)$ and V_1 and V_2 are the volumes of bodies 1 and 2 respectively. The Hamaker constant for the interaction is then:

$$H = \pi^2 C_6 \rho_1 \rho_2 \quad (4)$$

Useful expressions for the van der Waals interaction between bodies of different shape are discussed in Ref. (Israelachvili, 1991). Argento and French (Argento and French, 1996) derived expressions for the total van der Waals force between a conical tip of angle γ with a sphere of radius R at the end (see Fig. 5) and a plane:

$$F_{vdw} = \frac{H R^2 (1 - \sin \gamma) (R \sin \gamma - z_0 \sin \gamma - R - z_0)}{6 z_0^2 (R + z_0 - R \sin \gamma)^2} \quad (5)$$

$$- \frac{H \tan \gamma (z_0 \sin \gamma + R \sin \gamma + R \cos (2\gamma))}{6 \cos \gamma (z_0 + R - R \sin \gamma)^2} \quad (6)$$

where z_0 is the tip-surface separation. The expressions for pyramidal and more complex tips are given in Refs. (Suresh and Walz, 1996; Touhari *et al.*, 1998; Zanette *et al.*, 2000). Calculation of the van der Waals contribution to the total tip-surface force requires only knowledge of γ , R and H . γ and R depend only on the tip-shape, and this can be estimated from experimental studies of NC-SFM tip properties (see Section V.C.1). The Hamaker constant, H , depends on the geometry and materials of the tip and surface. However, if the NC-SFM system is well represented by a conical or pyramidal tip and a planar surface, then H effectively depends only on the material of the tip and surface. The experimentally determined values for Hamaker constants for different pairs of materials are given in Refs. (Argento and French, 1996; French *et al.*, 1995).

The STM simulations presented here rely on a two-step procedure. First, the electronic structure of the relaxed system is calculated. The coupled sample-tip system is represented by a 3-dim repeat unit comprising the surface (e.g. a five layer Au(111) film), the tip (a five layer Au(111) film with a tungsten tetrahedron mounted on the reverse), and a variable vacuum range between surface and tip. For a given distance, induced from the outset by a variation of the vertical dimension of the repeat unit, the electronic structure is calculated via a pseudopotential DFT method (VASP (Kresse and Furthmüller, 1996; Kresse and Hafner, 1993)). This code uses a residual minimization technique for faster convergence to the groundstate solution. From the electronic groundstate solution the Hellman-Feynman forces on ions are calculated analytically. A Newton algorithm is used to find the most likely ionic positions, and the system is again converged to its electronic groundstate in the new configuration. Such a self-consistency cycle, involving the ionic positions and the electronic groundstate, is repeated until the forces on single ions are less than a preset threshold value, usually around $0.01\text{eV}/\text{\AA}$. Separating the system into two components, the surface and the tip, and calculating the electronic groundstate of the frozen half-systems, the forces on surface and tip ions are directly determined (since the attractive force due to the presence of the other half-system is now missing, the calculation yields a force on the surface ions of exactly the same magnitude, but opposite direction) The setup of the calculation is shown in Fig. 6.

Nearly all the SFM simulations presented in this review were performed using atomistic simulation (AS) techniques as implemented in the MARVIN computer code (Gay and Rohl, 1995; Shluger and Rohl, 1996; Shluger *et al.*, 1994). MARVIN treats surfaces in 2D periodic model by repeating a unit cell of atoms in 2 dimensions by specified lattice vectors. For tip-surface calculations this unit cell includes the whole tip and a large block of the surface (see Fig. 5), but for surface-only calculations the unit cell may contain only a few atoms. Only the full interactions for this unit cell are calculated explicitly and an Ewald summation is used to calculate the long-range electrostatic contribution of the infinite system to the total energy. MARVIN uses the Conjugate Gradient algorithm and a hybrid Newton algorithm to minimize the total energy with respect to the geometry of the unit cell.

Figure 5 shows how the tip and surface are represented within the atomistic simulation.

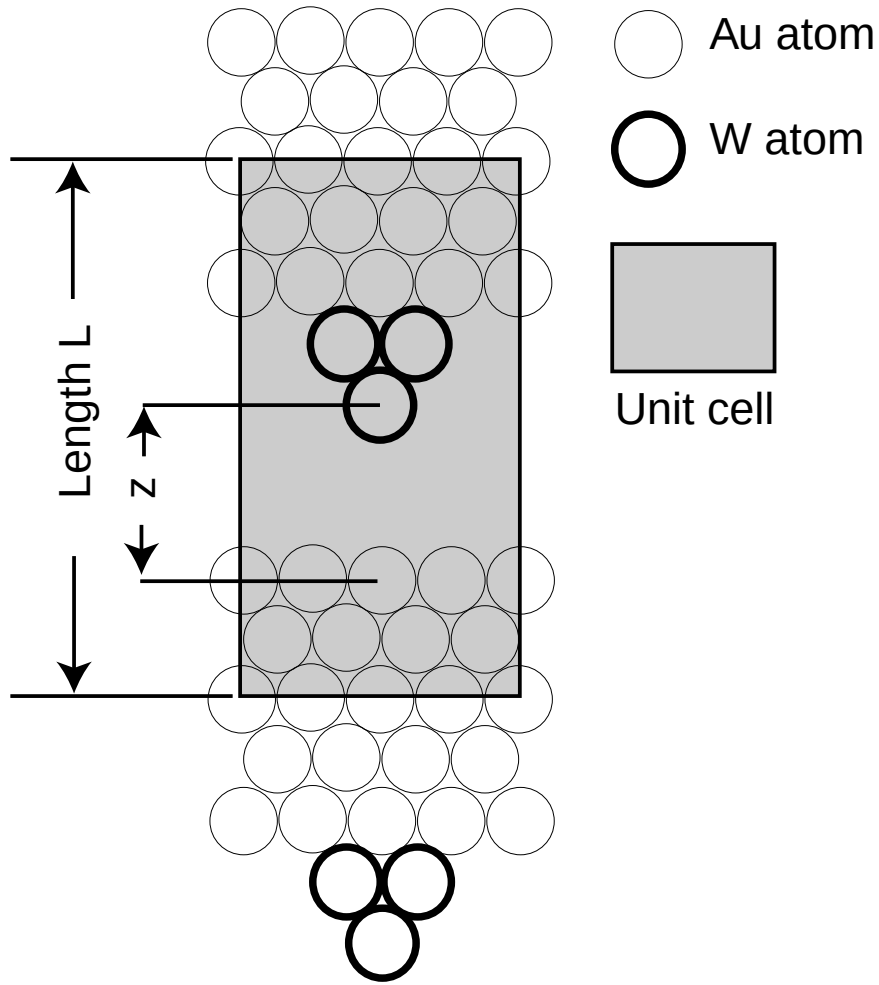


Figure 6 Setup for the calculation of forces between an Au(111) surface and a W(111) tip. The tip is mounted on the reverse of a five layer Au(111) film, by varying the vertical length L of the unit cell an approach of the STM tip is simulated. The distance z between the surface and the tip (which is called the *piezoscale* distance, if all atoms are in their groundstate positions) is changed due to relaxations of sample and tip atoms.

The nano-tip and the upper surface layers are divided into two regions, I and II. The region I ions are relaxed explicitly, whilst the region II ions are kept fixed to reproduce the potential of the bulk lattice and the remaining tip ions on the relaxed ions. The calculation is periodic so that the infinite surface is represented, however this means large surface unit cells must be used to avoid interactions between tip images in different cells. This is not a problem as AS calculations are very cheap and large systems do not represent a significant problem. It should be noted that the accuracy of this type of simulation depends critically on the quality of the parameters used to represent the interactions. The parameters for the interactions

of the tip ions are well tested and are fully described in Ref. (Grimes *et al.*, 1989; Shluger *et al.*, 1994). The parameters for the surfaces studied will be discussed in the appropriate Sections.

The total force acting on the tip takes into account the relaxation of the tip and surface atoms induced by the tip-surface interaction. It is calculated at a range of tip-surface separations, producing curves as a function of tip-surface separation for both energy and force. The shell-model contribution to the force is completely converged with respect to the size of the periodically translated simulation cell. By calculating these curves over many surface positions, a map of the microscopic tip-surface interaction is generated. This can then be combined with the surface position independent macroscopic force to give the total tip-surface force as a function of tip-surface relative position, $F(x, y, z)$. Note here that a slight 'double-counting' occurs when the microscopic and macroscopic forces are combined. The frozen atoms of the nano-tip are in effect already part of the macroscopic tip and their van der Waals contribution to the force is effectively counted twice. However, this effect is very small and it is more important to include a large enough tip so that a significant number of atoms at the apex can be relaxed and also that the nano-tip is kept neutral.

D. Modelling Currents

A complete survey of all methods to calculate the tunneling current, developed over the last few decades, is given in (Briggs and Fisher, 1999a). In increasing order of theoretical difficulty, the four main approaches are: (i) the Tersoff-Hamann approach (Tersoff and Hamann, 1985a,b), where constant current contours are modelled from the electronic structure of the surface alone; (ii) the transfer Hamiltonian or the Bardeen approach (Bardeen, 1961), where the tip electronic structure is explicitly included in the calculation; (iii) the scattering or Landauer-Bütticker approach (Bütticker *et al.*, 1985), which includes multiple pathways of tunnelling electrons from their initial to their final crystal states; and (iv) the Keldysh or non-equilibrium Greens function approach (Meir and Wingreen, 1992), which also considers inelastic effects like electron-electron or electron-phonon scattering.

1. Tersoff-Hamann (TH) approach

This method is today incorporated in nearly every state-of-the-art DFT code. Despite an extension of existing simulation methods, especially with respect to quantitative comparisons between experiments and theory, it continues to be the "workhorse" (Lucas, 1990) of STM theory. In this method the tunnelling current is proportional to the local density of states at the position of the STM tip (Tersoff and Hamann, 1985a,b):

$$I(\mathbf{R}) \propto \sum_{\substack{E_n < E_F \\ E_n > E_F - eV_{bias}}} |\psi(\mathbf{R}, E_n)|^2 =: n(\mathbf{R}, V_{bias}) \quad (7)$$

Here, I is the tunnelling current, E_n the eigenstates of the crystal electrons, E_F the Fermi level, V_{bias} the bias voltage, and n the electron density. In many standard situations, e.g. in the research of molecular adsorption or surface reconstructions, the model provides a reliable qualitative picture of the surface topography, even though it does not generally reproduce the observed corrugation values.

2. Perturbation approach

Within a transfer Hamiltonian approach the two subsystems of sample and tip are treated as separate entities. This approach is also known as the Bardeen approach (Bardeen, 1961). The tunnelling current is then described by the equation:

$$I = \frac{4\pi e}{\hbar} \sum_{\mu, \nu} \left| \int_S (\chi_\nu^* \nabla \psi_\mu - \psi_\mu \nabla \chi_\nu^*) \right|^2 \delta(E_\nu - E_\mu - eV_{bias}) \quad (8)$$

Here, χ_ν are the eigenstates with energy E_ν of the STM tip, ψ_μ the eigenstates of the surface with energy E_μ . The integral extends over the separation surface S between sample and tip, the summation includes all eigenstates within a given interval from the Fermi level. This interval is determined by experimental conditions, e.g. the temperature within the STM. The scheme of the method is shown in Fig. 7.

It is clear from this expression that the quality of the wavefunctions in the vacuum range above the surfaces is decisive for good agreement between experiments and simulations. In fact, the most suitable expansion is a 2-dimensional Fourier expansion in the lateral direction. Linear combinations of atomic orbitals (LCAO) in this respect have the disadvantage that

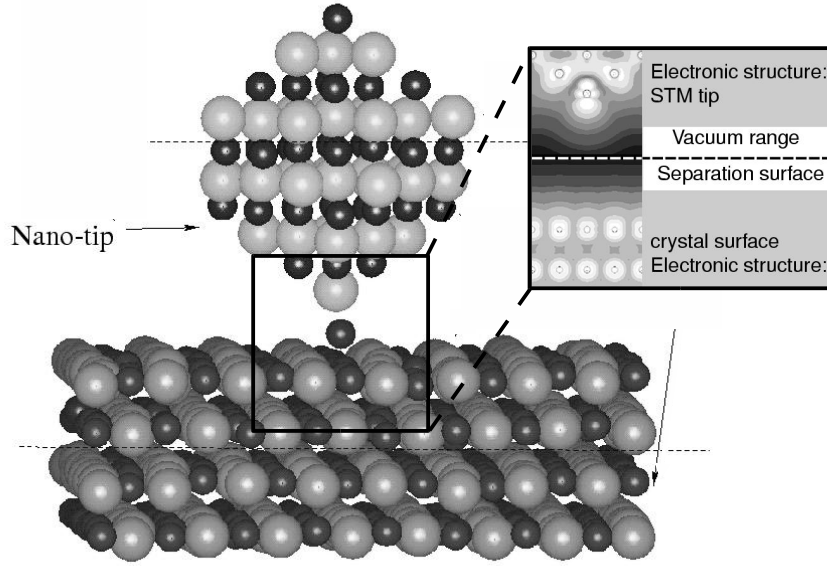


Figure 7 Theoretical modelling of the STM current within a perturbation approach. The surface and the tip are treated as separate systems, their electronic structure is determined by first principles DFT calculations. The current through the separation surface is determined by numerical integration at the plane of the surface.

they decay too rapidly into the vacuum, which in turn renders the currents and corrugations at a given distance unreliable.

3. Easy modelling: applying the Tersoff-Hamann model

Numerical methods to compute the tunnelling currents from first principles by the Bardeen method, used to elucidate even subtle features of experimental images, are already well advanced (see the following sections). However, from a practical point of view it is frequently desirable to gain an understanding of experiments without highly demanding and thus very time-consuming model calculations. In principle, the TH model, which is based on the electronic structure of the analyzed surface alone, provides just such an easy method. In particular, since advanced codes in DFT generally come with an interface to compute constant density contours in a straightforward manner. In this spirit, one seeks to determine the limits within which the method is reliable, and to estimate the density con-

tour value which roughly corresponds to a given tunnelling current. Both of these objectives are attainable if the Bardeen method of calculating the currents is simplified by suitable approximations, which we shall demonstrate presently. Concerning the reliability of the TH model, the following criteria seem sufficient:

- No substantial chemical interactions between surface and tip.

This condition is not trivial to quantify, since the experimental measure of tip-sample separation, the tunnelling resistance R , which is given by the ratio of applied bias voltage and tunnelling current, $R = V_{bias}/I$, differs strongly for different systems and experimental conditions. On metal surfaces, the distance has to be larger than 5-6 Å. This corresponds, for an ambient environment and very low bias voltages (less than 80 meV) to a tunnelling resistance R of 10-100 MΩ. Temperature enters this estimate, because a thermal environment of transiting electrons allows them to reach a substantial higher number of final states even under the condition of elastic tunnelling: under ambient conditions the energy difference between initial and final state can differ by about 80 meV. For this reason the experimental tunnelling resistance (e.g. for a bias voltage of -1 mV and a current of 1 nA), and thus the estimate of the distance, can be quite misleading. Comparing with the actual values obtained from explicit calculations of all possible transitions the estimate under these conditions is too low by one or two orders of magnitude. Thermal excitations, in short, have a similar effect as increased bias voltages.

On semiconductors, the corresponding problem is the exact location of the Fermi level with respect to the upper band edge of the valence band. In this case the same condition (100 MΩ tunnelling resistance) can lead to very small distances, if the chosen bias voltage includes only very few states of the semiconductor surface. However, if the bias voltage is high enough (above 2V, say), then this condition is usually sufficient.

- A feature size of surface structures which is well above the typical lengthscale of electron states of the STM tip.

This condition is far easier to quantify, since the typical lengthscale of a tip state is about half the interatomic distance of the tip metal, it is therefore between one and two Å. For feature sizes well above this value, the exact geometry of tip states will not enter the shape of the current contour in a decisive way. It is evident that this condition is in general not

fulfilled in high resolution scans, i.e. scans with atomic resolution. In all other cases it is quite safe to omit the explicit structure of the STM tip in a simulation.

Under these conditions the constant current contour can be related to the charge density contour of the surface in a unique way. This can be done in the following way:

Most DFT codes contain a feature to sum up the charge density within a given energy interval. For a bias voltage of $-V_{bias}$ one starts by computing the density for the interval $E_F - V_{bias}$ to E_F . The appropriate contour for a given current value can then be estimated with the following approximations:

1. The bulk of the tunnelling current passes through a small cross-section of about 2 Å radius.
2. the decay length of surface states (and tip states) is equal to the decay length of an electron state at the Fermi level of a metal surface with a workfunction $\Phi \approx 4$ eV. The wavefunction of the state is thus (in atomic units):

$$\psi(z) = \psi_0 e^{-kz} \quad k = \sqrt{2\Phi} \quad (9)$$

3. The convolution of surface and tip states in the Bardeen integral is simplified by setting $\psi_{sample} \approx \chi_{tip}$ and by assuming that the first term in the integral is of the same order of magnitude as the difference:

$$\begin{aligned} I &= C \cdot \left| \int_S dS \left(\chi_{tip}^* \frac{\partial \psi_{tip}}{\partial z} - \psi_{sample} \frac{\partial \chi_{tip}^*}{\partial z} \right) \right|^2 \approx \\ &\approx C \cdot \Delta S^2 k^2 n^2(sample) \end{aligned} \quad (10)$$

Here, C denotes a constant, ΔS the area of wavefunction overlap, and n the electron density (see also Fig. 7). Since all the constants are known (Hofer and Redinger, 2000), the estimate is straightforward and yields:

$$n(I) \quad [^{-3}] \approx 2 \cdot 10^{-4} \quad \sqrt{I} \quad [nA] \quad (11)$$

For a current value of 1 nA, e.g. on a metal surface, the appropriate charge density contour will thus be at $2 \cdot 10^{-4-3}$.

In a magnetic tunnelling junction the rotational symmetry of electron spins of sample and tip surfaces is broken due to magnetic anisotropy. The spin states in this case are projected onto the crystal's magnetic axis. Depending on the orientation of the magnetic axes two limiting cases have to be distinguished. The magnetic axis of sample and tip are either parallel (ferromagnetic ordering) or antiparallel (antiferromagnetic ordering). Ferromagnetic ordering is described by:

$$\mathbf{M}_S \uparrow \quad \left\{ \begin{array}{cc} n_S^\uparrow & \longrightarrow n_T^\uparrow \\ n_S^\downarrow & \longrightarrow n_T^\downarrow \end{array} \right\} \quad \uparrow \mathbf{M}_T \quad (12)$$

In this diagram $\mathbf{M}_S$ and $\mathbf{M}_T$ describe the magnetic axes of sample and tip, n_S and n_T the spin density, and the arrows $\uparrow$ and $\downarrow$ spin-up and spin-down states, respectively. We denote the tunnelling current due to ferromagnetic ordering by I_F . Antiferromagnetic ordering is described by:

$$\mathbf{M}_S \uparrow \quad \left\{ \begin{array}{cc} n_S^\uparrow & \longrightarrow n_T^\downarrow \\ n_S^\downarrow & \longrightarrow n_T^\uparrow \end{array} \right\} \quad \downarrow \mathbf{M}_T \quad (13)$$

Within DFT the tunnelling current is commonly described in terms of ϕ_M , the angle between the two magnetic axes, and $P_{S(T)}$, the polarization of the sample (tip) surface:

$$I(\phi_M) = I_0(1 + P_S P_T \cos \phi_M) \quad (14)$$

$$\cos \phi_M = \frac{\mathbf{M}_S \cdot \mathbf{M}_T}{|\mathbf{M}_S| |\mathbf{M}_T|} \quad (15)$$

For constant tunnelling matrix elements and within a perturbation approach the current I_0 and polarizations $P_{S(T)}$ are given by:

$$I_0 \propto \frac{1}{2} \left(n_S^\uparrow + n_S^\downarrow \right) \left(n_T^\uparrow + n_T^\downarrow \right) \quad (16)$$

$$P_{S(T)} = \frac{n_{S(T)}^\uparrow - n_{S(T)}^\downarrow}{n_{S(T)}^\uparrow + n_{S(T)}^\downarrow} \quad (17)$$

I_0 and $P_S P_T$ can be written in terms of the ferromagnetic and antiferromagnetic currents:

$$I_0 = \frac{1}{2}(I_F + I_A) \quad P_S P_T = \frac{I_F - I_A}{I_F + I_A} \quad (18)$$

If the tunnelling matrix element is not constant, the current has to be calculated numerically from the Bardeen integral over the separation surface (Bardeen, 1961; Hofer and Redinger, 2000). In this case the current contributions have to account for the spin orientation of a given eigenstate. In DFT the energetic minimum for magnetic crystals is reached by optimizing the distribution of spin-up density $n^\uparrow$ and spin-down density $n^\downarrow$. The currents for ferromagnetic and antiferromagnetic coupling are computed by calculating the transition matrix elements for the spin polarized Kohn-Sham states of sample and tip:

$$I_F = I(n_S^\uparrow \longrightarrow n_T^\uparrow) + I(n_S^\downarrow \longrightarrow n_T^\downarrow) \quad (19)$$

$$I_A = I(n_S^\uparrow \longrightarrow n_T^\downarrow) + I(n_S^\downarrow \longrightarrow n_T^\uparrow) \quad (20)$$

The main advantage of the approach is its flexibility and robustness, while including the main physical effects under tunneling conditions. More involved approaches usually require the development of a program, which delivers DFT calculations *and* tunneling current simulations in a combined step. This usually leads to maintenance difficulties, as DFT codes become faster and more sophisticated. By contrast, the perturbation approach can be tailored to every DFT program, which provides the single Kohn-Sham orbitals of a surface. It can thus be used in combination with the DFT method most suitable for a precise description of the electronic surface properties.

The main disadvantage, from the viewpoint of scattering theory, is its unclear limit of application. Since it is based on perturbation theory, it relies on electronically decoupled surface and tip systems. The exact limits of the approach are difficult to estimate, in fact these limits were determined by model calculations in conditions where the perturbation approach breaks down.

5. Landauer-Bütticker approach

Within a scattering approach the transition matrix is usually calculated based on the Landauer-Bütticker formula (Bütticker *et al.*, 1985). In this formulation the conductance

G across a tunneling junction is given by the ratio of transmission probability to reflection probability. And since reflection probability R is close to unity, one obtains:

$$G = \frac{I}{V_{bias}} = \frac{e^2}{\pi\hbar} \frac{T}{R} \approx \frac{2e^2}{h} \cdot T \quad (21)$$

The tunneling current in this approach is usually written:

$$I(V_{bias}) = \frac{2e}{h} \int_0^{eV_{bias}} T(E) dE \quad (22)$$

The transition probability matrix T , for multiple channels of the tunneling current, could in principle be evaluated in any basis set. However, the actual implementation of the formula is uniquely done within a tight-binding approach and based on atomic orbitals (Cerdeira *et al.*, 1997). The reason for this limitation is that the lateral position of the STM tip needs to be varied to obtain individual scan-lines and thus the constant current contours, which can be compared to experiments. Within a DFT treatment of the problem, such a lateral variation is difficult for a reasonable system size because of periodic boundary conditions in z direction.

The main advantage of the approach is its mathematical rigor and its inclusion of the different boundary conditions of the STM leads. In principle it should thus yield a more accurate description of the tunneling condition. In addition, the treatment includes interference effects between separate conductance channels. The main disadvantage today is its limitation to tight-binding models of surface and tip electronic structures, even if the parameters in these models are taken from first principles simulations. Within a tight-binding model the localized basis set usually disagrees with the decay characteristics of current and corrugation found in the experiments.

6. Keldysh-Greens function approach

During the last years theoretical treatments of the tunneling process on the basis of a non-equilibrium Green's function formalism (Keldysh, 1965) have become increasingly popular (Reuter *et al.*, 2001; Taylor *et al.*, 2001). The most complete treatment of the problem considers the Hamiltonian of a system comprising two leads and a barrier region (Feuchtwang, 1974, 1975, 1976; Meir and Wingreen, 1992):

$$H = \sum_{k,\alpha \in L,R} \epsilon_{k\alpha} c_{k\alpha}^+ + H_{int}(\{d_n^+\}, \{d_n\}) + \sum_{k,\alpha \in L,R} (V_{k\alpha,n} c_{k\alpha}^+ d_n + H.c.) \quad (23)$$

Here, the first term comprises the electron energy in the leads (L, R), the second term the orthogonal system of eigenstates in the barrier, and the third term the interactions between electrons in the leads and in the barrier. The tunneling current in this case is given by the following expression:

$$J = -\frac{2e}{\hbar} \int dE [f_L(E) - f_R(E)] \Im \left[Tr \left(\frac{\Gamma^L \Gamma^R}{\Gamma^L + \Gamma^R} G^R \right) \right] \quad (24)$$

In this formulation it is assumed that the coupling to the leads, given by the Γ_L and Γ_R differs only by a constant factor. The full Greens function G_R of the Keldysh approach includes all inelastic processes, spin-flips, and multiple scattering events. If we analyze the time scales involved in tunneling processes, then we get for normal tunneling conditions ($I \approx 1$ nA) an interval between single electron processes of about 10^{-10} s. Considering, that this interval is one hundred to one thousand times longer than the typical timescale of lattice excitations, it seems safe to neglect interactions of electrons in the barrier. In this case Eq. 24 reduces essentially to the Landauer-Bütticker formula:

$$I = \frac{e}{\hbar} \int dE [f_L(E) - f_R(E)] Tr [t^+(E)t(E)] \quad (25)$$

In principle this approach could also be used to compute the tunnelling current. However, since the interaction of electrons *within the vacuum barrier* is negligible, tunnelling currents are not usually calculated within this theoretical framework. Due to the wide range of interactions included in the formalism, Keldysh's method is the most accurate today. It's main problem is the computational cost, which either has to be made up for by approximations in the description of the solid state systems, or by limiting the number of atoms in the interaction range.

E. Modelling Oscillations

Although for SFM in general the controlling interaction is the force between tip and surface, for NC-SFM we must also contend with the fact that the real experiment uses an oscillating cantilever. The link between the tip-surface interaction and a NC-SFM simulated

image is a model of the oscillations of the cantilever under the influence of the tip-surface interaction. A detailed analysis of the tip oscillations and ways to model them are given in Refs. (Aimé *et al.*, 1999; Dürig, 2000; García and Pérez, 2002; Giessibl, 1995, 1997; Giessibl *et al.*, 1999; Morita *et al.*, 2002; Sasaki and Tsukada, 1999; Schwarz *et al.*, 2000b). However, a simple model can be derived under some basic assumptions. For a tip oscillating with large constant amplitude above the surface, and the tip deflection measured at constant frequency change, the oscillations of a cantilever over a surface point (x, y) driven by an external force, F_{ext} , in a force field $F(z)$ can be described by the equation of motion:

$$\ddot{z} + \frac{\omega_0^2}{k}\alpha\dot{z} + \omega_0^2 z - \frac{\omega_0^2}{k}F(z+h) = \frac{\omega_0^2}{k}F_{ext} \quad (26)$$

where ω_0 is the oscillating frequency of the cantilever in the absence of any interaction with the surface, k is the spring constant of the cantilever, α is the damping coefficient and h is the equilibrium height of the cantilever above the surface in the absence of interaction. At constant amplitude and frequency change we can assume that any damping is completely cancelled by the external force and that $F(z)$ does not depend on time. This simplifies equation (26) to the following:

$$\ddot{z} + \omega_0^2 z - \frac{\omega_0^2}{k}F(z+h) = 0 \quad (27)$$

Following the derivation in Ref. (Livshits *et al.*, 1999) we finally obtain the frequency of cantilever oscillations in the presence of the interaction, ω , as

$$\left(\frac{\omega}{\omega_0}\right)^2 = 1 - \frac{1}{\pi k A_1} \int_0^{2\pi} F(z+h) \cos(\tau) d\tau \quad (28)$$

Note that there are some subtle differences in the oscillation behaviour between the externally driven cantilever discussed here, and a self-driven cantilever (Hölscher *et al.*, 2001) used in some experiments. However, these differences do not significantly affect any of the following discussion.

F. Generating a Theoretical Surface Image

Shifting the position of the SPM tip laterally and vertically produces, by the above procedure, a map of tunnelling currents (STM) or changes in frequency of the oscillations

of the cantilever due to the influence of the tip-surface interaction (SFM).

The current maps are used to extract the contours of constant current (STM), or the change of current with a change of the applied bias voltage (STS). In a further step the maxima and minima of the current contours for a specific current value are determined: this corrugation amplitude is then directly compared to images. It is clear from the procedure that specific tunnelling conditions (bias voltage and tunnelling current) uniquely determine a constant current contour and a corrugation amplitude. In this sense the calculation does not involve any parameter or fit to experimental data. Therefore, it can be said to be fully *ab initio*.

In SFM simulations the map is interpolated to find the cantilever deflections to keep the cantilever oscillating at a constant frequency change (or constant modified frequency). The deflections can then be plotted as a function of surface position (x, y) to give the theoretical image. At this point, the theoretical image and data can be compared with the experimental equivalents. It should be noted that the theoretical image is generated using experimental values for all known parameters such as frequency ω_0 , amplitude A_1 , elastic constant k and frequency change $(\omega - \omega_0)$. All parameters which are not known from experiment, such as tip radius, are taken from the best experimental or theoretical estimate as appropriate. The specific parameters used for each system studied will be discussed in later Sections.

G. Summary

Although we have outlined consistent methods to simulate the fundamental aspects of SPM experiments, no model can reproduce all features of a physical environment. In this sense every model depends crucially on basic assumptions, and for the applications we discuss here these are, for SPM in general:

- The groundstate properties of a system are equal to the properties at finite temperatures (e.g. in an ambient environment)
- there is a hierarchy of interactions, which allows separation of different effects in the theoretical models (no inclusion of e.g. cumulative or time-dependent interactions)

for STM specifically:

- macroscopic interactions do not affect the tunnelling current

- the resistance in the STM-circuit is only due to the tunnel-barrier
- the current cross-section is centered at the apex atom of the tip
- current flow does not change the properties of a system.

The last point has recently been analyzed by Todorov *et al.* (Todorov *et al.*, 2000), and it was found that the current flow slightly changes the position of the surface atoms. The assumptions for SFM specifically are:

- charge transfer between tip and surface is not a significant component of the interactions for an insulating surface
- that the effects of the system electronics, such as apparent dissipation (García and Pérez, 2002; Gauthier and Tsukada, 1999; Morita *et al.*, 2002), do not affect the physics of the tip-surface interaction

Note that the effect of charge transfer on the interactions of a pure silicon tip are discussed to some extent in Section V.C.1.

V. STUDYING THE SURFACE

In this section we review the applications of SPM methods to some characteristic classes of materials, and the extra information which theory provides over experiment alone.

For STM, we mainly study applications of the transfer Hamiltonian method (Bardeen, 1961) to plain and contaminated metal/semiconducting surfaces. The emphasis in this section will be on demonstrating how simulations extend the experimental method. Only by simulating STM scans do the physical origins of measured effects become accessible. In particular we shall focus our demonstration on model calculations to solve the following, widely discussed, problem of the relaxation of tip/surface atoms and their effect on the tunnelling current on the gold surface. Simulations also demonstrate the exact limitations of the perturbation approach.

For SFM, we focus on studies of several classes of insulating surfaces, each demonstrating specific features important to understanding imaging: (i) clear image interpretation from the complex CaF_2 (111) surface, and (ii) imaging of covalent structures in an insulating surface from the molecular solid surface, calcite ($10\bar{1}4$).

Finally, we look at thin insulating films, where both STM and SFM can contribute. Here we see the influence of low-coordinated sites in imaging, especially the increased contrast at kink and corner sites for SFM imaging of NaCl thin films.

A. Metal Surfaces

Metal surfaces have been widely studied by STM and other methods. There have been only very few NC-SFM studies of these surface (see e.g. (Loppacher *et al.*, 2000)) as most of the SFM effort is focused on semiconductor and insulating surfaces. The main results include: (i) *reconstructions*, or surfaces with a different arrangement of surface atoms than in the bulk; (ii) *relaxations*, or the trend for surface layers to possess a different interlayer spacing than bulk crystals; and (iii) *surface states*, or electron states trapped in the surface region due to the potential boundary (Inglesfield, 1982; Wille and Durham, 1985).

The surface chemical composition plays an important role in STM imaging of metal surfaces. It is a well-known fact in STM experiments, that oxygen or carbon atoms on a surface change the image locally in a decisive way (Bischoff *et al.*, 2001; Hofer *et al.*, 2001b). Both atoms usually appear in STM images as distinct depressions, even though their actual position is sometimes well above the surface plane. Hence, one of the main problems in STM experiments on metals is the contamination of the bulk with carbon. On the other hand, oxygen on a surface can lead to stable reconstruction of the entire surface, and this effect may be used to render imaging actually easier than on a clean metal surface. These are very drastic examples of chemical effects changing the tunnelling current on surfaces. Similar effects, even though not as drastic, change the apparent image of single atoms on a surface depending on the chemistry of their neighbours (Hofer *et al.*, 1998).

It took about ten years, from the invention of the STM (Binnig and Rohrer, 1982; Binnig *et al.*, 1982a,b), until the instruments were precise enough to be able to discriminate not only between substrate atoms and adsorbates, or different adsorbates, but even between different substrate e.g. metal atoms (Schmid *et al.*, 1993). The experiments marked an important point, because they made the concept of a chemical atom visible for the first time. An atom, henceforth, could be seen as a small sphere in some shade of grey (see Fig. 8).

But if the chemical nature of a substrate atom can change the observed STM image, then also the chemical nature of the tip apex can have a decisive role. This effect changed the

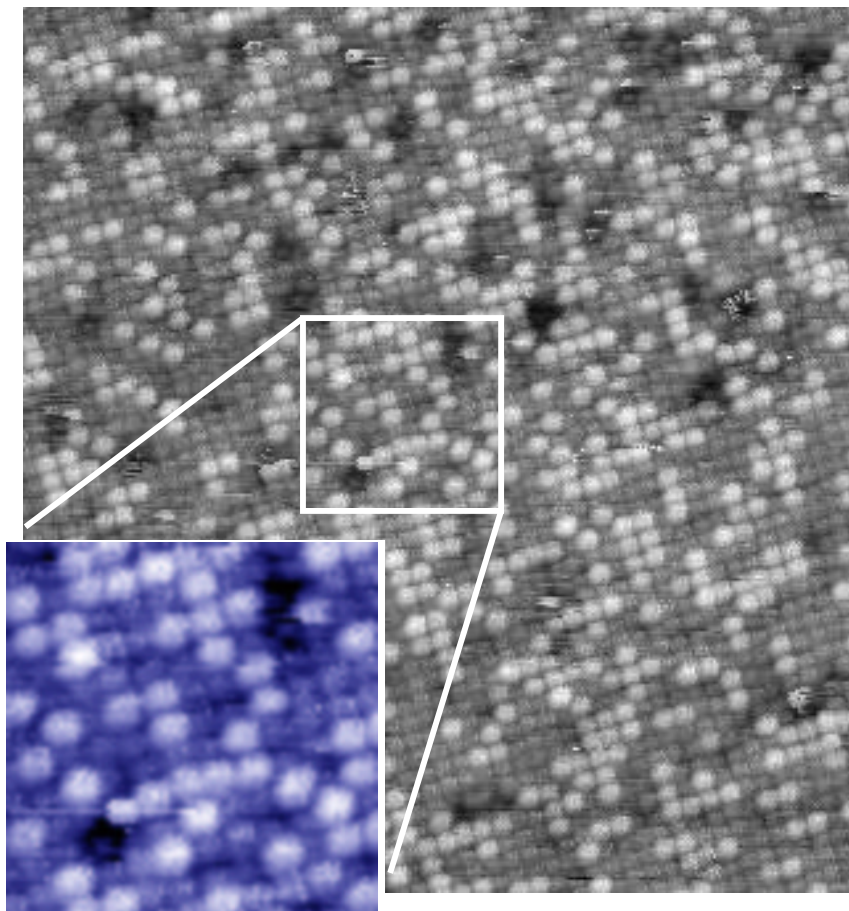


Figure 8 STM scan of a binary PtRh(100) surface. Rh atoms possess a different electronic structure due to alloying with adjacent Pt atoms, they are therefore clearly discriminated by their greater apparent height (see detail). Measurements of this type are the first real-space visualizations of chemical atoms. *Reprinted with permission* (Wouda *et al.*, 1996).

focus in STM theory somewhat from the discussion about single tip-orbitals (most theoretical work previously assumed that the representation of a tip by one orbital would be sufficient), to the chemistry of the STM tip. This is still a very lively topic today, not least because subtle effects are more and more dominating in experimental practice. All these effects can be substantially influenced by the chemical composition of the STM tip (Hofer and Redinger, 2000).

Another issue acknowledged in STM research nearly from the beginning is that chemical forces must play an important role in the imaging process (Cho and Joannopoulos, 1993; Clarke *et al.*, 1996a; Pethica and Sutton, 1988a; Sacks, 2000; Sacks and Noguera, 1988; Ventra and Pantelides, 1999) on metal surfaces. The strong adhesion interaction between

an atomically defined W(111) tip and an Au(111) sample has been studied recently using NC-SFM (Cross *et al.*, 1998a). However, the exact mechanism, and, more importantly, the quantitative effect of the tip-surface chemical interaction in STM images could not be conclusively determined. It was, for example, unclear whether these forces would lead to a contrast reduction, an enhancement only in the low distance regime, or no effect at all for scanning on close packed metal surfaces. Especially the so-called "giant corrugation" on Au(111) or Al(111) remained a puzzle for over fifteen years.

To study the problem of chemical forces on a model surface, a combined tip-sample system consisting of an Au(111) surface and a W(111) tip was simulated (Hofer *et al.*, 2001b). By reducing the unit cell in the z -direction the approach of an STM tip to a sample surface can be described. To obtain the real corrugation height on the surface the simulation of the coupled system was performed for two separate tip positions: the on-top position, and the threefold hollow between Au atoms (see Fig. 6). The main problem in such a simulation is the scale of numerical calculations. To be sufficiently precise the unit cell has to be reduced in steps of about 0.01 nm in the range, where chemical forces are noticeable. Given two separate configurations and a vertical distance scale of about 0.2 nm, this amounts to several weeks of computation time on a massively parallel computing unit. From an initial tip-sample separation of 1 nm the distance was gradually reduced, initially in steps of 0.05 nm. At every step the system was fully relaxed. The onset of significant mechanical interactions between tip and sample occurs at about 0.5 nm. Surface wavefunctions were computed for the fully relaxed sample and tip systems at every distance and for two tip positions. In this part of the calculation the initial system was separated into two subsystems, a surface system and a tip system. The wavefunctions of the separate systems provided the input for the current calculation within the Bardeen approach (see previous sections). The procedure leads to separate constant current contours of the surface, depending on the position of the tip.

The calculations establish an early onset of relaxations, which depend strongly on the position of the tip. For the on-top position of the STM tip we observe an onset of forces and relaxations at about 0.47 nm. The surface atom reaches its furthest distance from the surface at a tip-sample separation of 0.45 nm; it is then 0.13 nm above its position on the isolated surface. This point marks the beginning of atomic instability, which in case of atomic transfers is observed as a hysteresis of forces in single approach/retraction cycles

(Cross *et al.*, 1998a). If the tip is in the threefold hollow, the onset of forces and relaxations is substantially retarded and occurs at 0.43 nm. The maximum outward relaxation of the three gold atoms is somewhat lower and about 0.1 nm (reached when the tip-sample separation is 0.41 nm). The tungsten tetrahedron of the STM tip relaxes about the same amount in both positions: the apex atom approaches the sample by about 0.05 nm at the point of closest approach. The change is due to an increase of the interlayer distance of the tungsten atoms by about 0.01 to 0.02 nm, and a buckling of the layers underneath, which extends about two layers into the lead. The forces on the tungsten tip are shown in Fig. 9. The values for tip-sample relaxations are given in Fig. 10 (a). Owing to the strong interactions between tip and sample at close range, the core-core distance between tip and sample is decreased. The net effect of relaxations is a decrease of the distance between tip and sample. A deviation of about 0.2 nm between the distance inferred from simulations, and the distance inferred from measurements of the current decay in the high distance range, has actually been observed (Hofer *et al.*, 2000b). In the critical range of 0.46 to 0.41 nm the actual distance changes by about 0.2 nm. This points to an effect frequently observed in experiments with atomic resolution: it is difficult to obtain atomically-resolved images, because sizable corrugations in most cases require a distance below 0.5 nm, but in this mechanically highly unstable situation the tip easily jumps into contact with the surface. This, in turn, destroys the microstructure of the atomic arrangement at the tip apex and leads to a sudden change of the observed image.

The curves in Fig. 10 show the current for the hollow position. We obtained the change due to surface and tip relaxations by calculating the current in frozen atomic configurations of sample and tip. These configurations are different for every piezoscale distance, as are the logarithmic graphs of the tunnelling current. The z -labels on individual graphs give the tip-sample separation before relaxation (= piezoscale). It is interesting to note that the logarithmic current curves are more or less straight lines down to 4.1 Å tip sample separation. At this point the atom at the apex of the tungsten tip is so far apart from the adjacent atoms that the wavefunctions in the vacuum above the tip change from crystal wavefunctions to atomic orbitals. This feature accounts for the highly non-linear behavior of the tunnelling current, since it is now composed of components which comply with the exponential decay of the crystal wavefunctions above the tungsten subsurface atoms and components which results from the overlap with the atomic wavefunctions of the separated

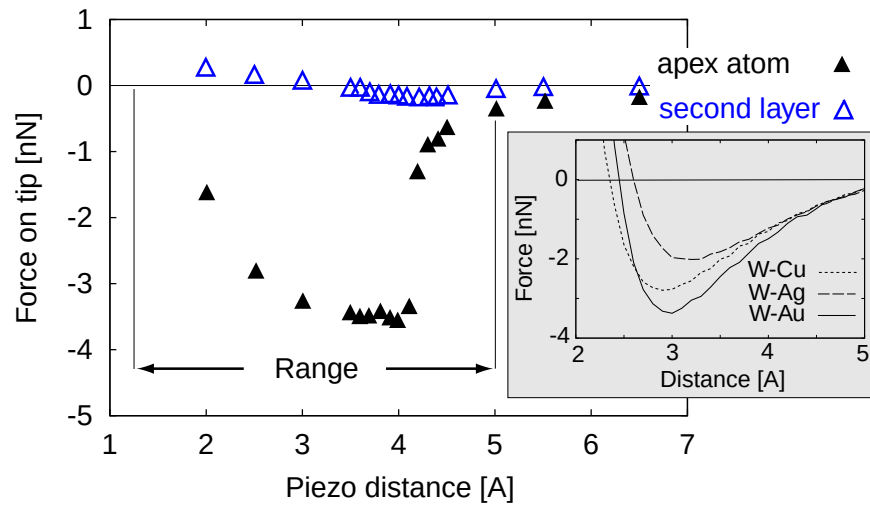


Figure 9 Distant dependent forces on the apex atom (full triangles) and the subsurface atoms (empty triangles) of the tungsten tip above the hollow position of the surface. The forces show a steep onset at about 4.6 Å, the range of forces is approximately 4 Å. Forces are generally limited to the apex atom. For comparison we show the forces between diatomic dimers. In this case it is seen that the force characteristics above 4 Å do not depend on the chemical nature of the surface atom. *Reprinted with permission* (Hofer *et al.*, 2001b).

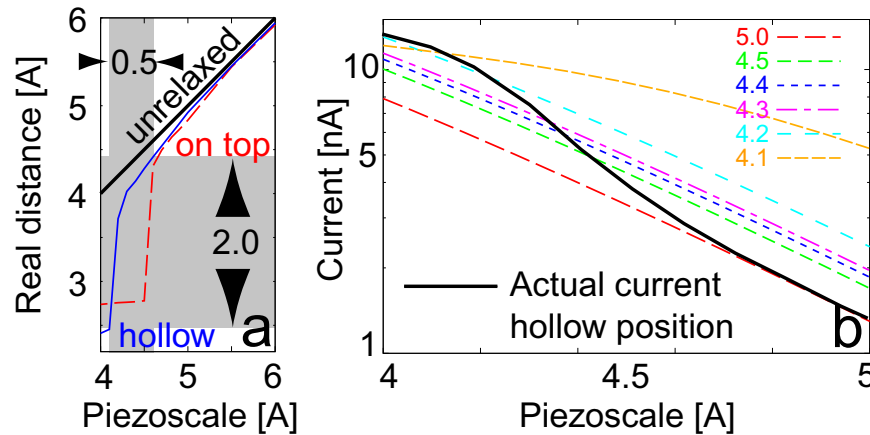


Figure 10 Distance dependent tip-sample separation versus the theoretical distance (a), and current curves for frozen atomic positions during an approach (b). The tip-sample separation changes by about 2 Å within 0.5 Å of the theoretical (piezo) scale. Due to atomic relaxations the actual current does not follow an exponential characteristic, but shows an excess of about 100 % over one Å distance. *Reprinted with permission* (Hofer *et al.*, 2001b).

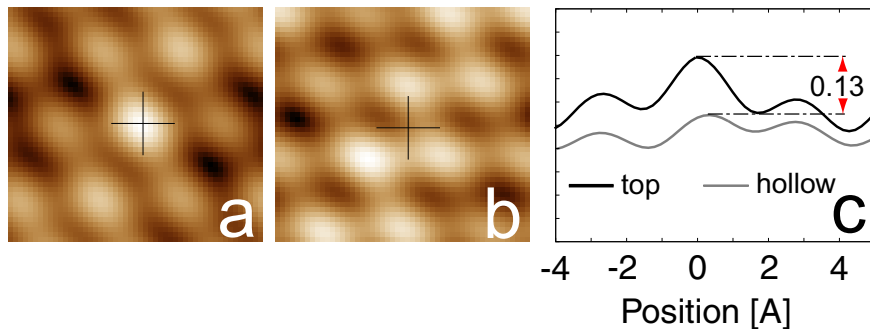


Figure 11 Current contour plots using the relaxed configurations of sample and tip for a distance of $4.7 \text{ \AA}$ (tip on top of an Au atom, frame (a)), and $4.5 \text{ \AA}$ (tip in the threefold hollow position, frame (b)). Simulated linescan from left-to-right across a single atom (c), for the setup in the on-top position and for the setup in the hollow position. All scans correspond to a current of 5.1 nA . An actual scan would have enhanced corrugation due to relaxation effects (see dash dotted lines in frame (c)). *Reprinted with permission* (Hofer *et al.*, 2001b).

apex atom.

The true increase of the current is determined by taking only a single point of each graph. In practice we interpolated between the computed points to obtain the smooth black curve shown in the figure, giving an enhanced increase in the current. For an experimentalist who estimates the potential barrier between tip and sample from the exponential decay of the current, the apparent barrier height increases in this range. Note that the current was calculated for a sample bias of -0.1 V .

To determine the true surface corrugation, the tunnel currents in the simulations were assumed to be 5.1 nA in both configurations (tip on-top of a Au atom, and tip in the hollow between Au atoms), but owing to the site-dependent relaxation of the systems the two constant-current contours differ. The piezoscale would give a distance of 0.47 nm on top of a gold atom and 0.45 nm in the fcc hollow site. These distances are at the lowest limit of stability for the tip-sample system. The difference of 0.02 nm describes the experimental corrugation of the Au(111) surface, when measured with a tungsten terminated tip (Hallmark *et al.*, 1987). The simulated scans with the tips and surfaces frozen in the two configurations are shown in Fig. 11(a) and (b). Fig. 11(c) shows two simulated linescans across a single atom. The two separate curves describe the linescan for the two setups used (on-top, and hollow). It can be seen that the relaxation leads in effect to an enhancement of

the corrugation by about 0.13 nm. Only with this relaxation included is agreement between experiments and simulations obtained (Hallmark *et al.*, 1987). The problem of "giant corrugations" on close packed metal surfaces can therefore be assigned to chemical forces between tip and surface.

B. Semiconductor Surfaces

Semiconductor surfaces have an enormous range of technical applications and have therefore generated an impressive body of experimental and theoretical research. The principal surfaces under investigation are Si(100) and GaAs(100). The Si(111) surface, even though widely imaged by SPM, is substantially less important technologically. In fact, it is today mostly imaged to calibrate the instrument and to study adsorption of various species.

1. Silicon Surfaces

The surface of Si(100) reconstructs in dimer rows along the (011) direction, the Si-Si dimer bond is 2.2 Å long, adjacent dimers are 3.8 Å apart (Hofer *et al.*, 2001a). The dimer reconstruction was subject of intense dispute around 1990, since photoemission spectra suggested a buckled dimer (Bringans *et al.*, 1986), while STM images clearly revealed a flat dimer structure (Hamers *et al.*, 1986). The riddle has been solved by a combination of experimental and theoretical techniques. Experimentally, it was realized, that a tilted dimer in fast flip-flop motion would appear flat in STM images due to the low time-resolution of the STM. At temperatures below 90K the motion of dimers is frozen, individual dimers under these conditions appear tilted, as Wolkow showed in 1992 (Wolkow, 1992). The same feature is observed if the buckling is pinned down by surface defects.

Comprehensive electronic structure calculations based on DFT established that the groundstate surface structure is a (2×1) reconstruction, where adjacent dimers are tilted in opposite directions (Dabrowski and Scheffler, 1992; Payne *et al.*, 1989). The energy difference of 80 meV between a flat and a tilted dimer agrees well with the thermal conditions at room temperature, where this activation barrier is easily overcome by thermal fluctuations. It is currently established opinion that this dynamic buckling is the reason, that the dimers appear flat in STM images (Hata *et al.*, 1999). Dynamical buckling was modelled

by calculations of the electronic surface structure in various positions of the dimer, and by averaging the ensuing STM images over full cycles of dimer motion (Hofer *et al.*, 2001a). As the simulations reveal, this statistical average is virtually indistinguishable from the image based on flat Si-dimers. Given the high distance between the STM tip and the sample surface of 6 Å in typical conditions (-2V, 50 pA), the assumptions of current induced buckling (Badziag *et al.*, 1991), or buckling due to tip-surface interactions (Clarke *et al.*, 1996a) seem to lack experimental and theoretical confirmation.

Recent tight-binding simulations of NC-SFM imaging of the Si(001) surface with a silicon tip (Tagami and Tsukada, 2000) demonstrated a very strong effect of the tip-surface interaction on the image contrast. In particular, it was found that as the tip approaches the down dimer atom to about 3.5 Å this atom suddenly adheres to the tip. This in turn results in the discontinuous increase of the attractive force on the tip. In a similar way, when the tip is retracted from the surface, the buckling angle of the dimer changes drastically at a certain tip height where the force again shows a discontinuous jump. The buckling orientation is reversed after one cycle of cantilever dynamics. If the tip does not get that close to the surface, the described atomic instability does not occur. However, simulations with the Si tip predict only the upper dimer atom to be visible. By their thermal average, the images at room temperature are predicted to have (2×1) periodicity, as observed experimentally both in NC-SFM (Uchihashi *et al.*, 1999) and STM (Wolkow, 1992). The described tip-induced instability of the surface (or tip) atoms is characteristic for any surface and has first been observed in SFM modelling of tip interaction with a metallic surface (Pethica and Sutton, 1988b). A qualitatively similar behaviour involving an up dimer atom has been observed in the simulations of the interaction of the Si(001) surface with a carbon nanotube tip modelled by C_{60} (Tagami *et al.*, 2000).

In SFM studies of semiconductors, the Si(111) - 7×7 surface has attracted much more theoretical simulation. Greatest success was achieved in a full *ab initio* theoretical study (Pérez *et al.*, 1997) of the forces and contrast mechanism for that system. This study demonstrated that the force between a model silicon tip and surface would be dominated by the onset of covalent bonding between a localized dangling bond at the apex of the tip and dangling bonds on the surface adatoms. More importantly, the tip-surface force over the adatoms was calculated directly, giving a direct measure for comparison with experiment. In an extended study (Pérez *et al.*, 1998), the force calculations were also performed over

the rest atoms in the silicon surface, demonstrating the possibility of imaging both sites in an experiment. This 'force spectroscopy' over the surface unit cell is the most quantitative tool for comparison between experiment and theory, yet it remains a significant challenge experimentally. Only low temperature NC-SFM experiments on the silicon (111) - 7×7 surface (Lantz *et al.*, 2000) obtained the sensitivity to really measure the forces over specific atomic sites. A direct comparison of the magnitude of these forces with the theoretical results gave good agreement, supporting the theoretical assumption that the tip apex is basically silicon, and that the silicon surface adatoms would be imaged as bright. However, theory seemed to underestimate the softness of the tip and a much wider force minimum was observed in experimental force curves. Increasing the size of the tip and allowing more tip ions to relax reduced the discrepancy between theory and experiment, but could not eliminate it. Nevertheless, the agreement in magnitude of forces between experiment and theory gives strong support to the dangling bond interaction as the mechanism of contrast for high quality images of the silicon (111) 7×7 surface.

2. Binary Semiconductor Surfaces

In SFM studies of more complex semiconductor systems, theoretical modelling has not been so successful in resolving image interpretation problems. Experiments have been performed on complex binary semi-conductors such as InP (Sugawara *et al.*, 1995) and InAs (Schwarz *et al.*, 2000a), but interpretation of images is difficult. On the InAs(110) - 1×1 surface with low temperature NC-SFM, Schwarz *et al* (Schwarz *et al.*, 2000a) observed direct experimental evidence for tip-induced relaxation of the two neighboring As-atoms around an individual In-vacancy. *Ab initio* calculations of InP (Tóbiš *et al.*, 1999, 2001) and GaAs (Ke *et al.*, 1999, 2001) demonstrated that in general for III-V semiconductors the anion is imaged as bright with a silicon tip, agreeing with experimental results on InAs. However, both simulation and theory saw a strong dependence of contrast on the tip atomic structure and it was not possible to make a universal unique interpretation of images. Tips with adsorbed surface species produced very different interactions compared to pure silicon tips.

C. Insulating Surfaces

In this Section we briefly review some of the applications of the simulation methods discussed above to insulators. Due to the requirement of a conducting surface for STM imaging, this section focuses almost exclusively on SFM.

Difficulties in preparing clean, flat insulating and semi-insulating surfaces has so far limited successful atomic resolution to only a few surfaces, such as NaCl (Bammerlin *et al.*, 1997) and several other alkali halides (Bammerlin *et al.*, 1998), TiO₂ (Fukui *et al.*, 1997a), CaF₂ (Reichling and Barth, 1999), NiO (001) (Hosoi *et al.*, 2000), KBr (001) (Hoffmann *et al.*, 2002) and Al₂O₃ (0001) (Barth and Reichling, 2001). However, only in the case of TiO₂ experimental studies (Fukui *et al.*, 1997b) of the adsorption of formate ions on the (110) - 1×1 surface has chemical identification been established fairly conclusively: the bridging oxygen ions on the surface were imaged as protrusions in NC-SFM. This result was achieved by combining STM and NC-SFM, and using the theoretical interpretation of the STM images as an aid in interpreting NC-SFM images of the same surface. Recent combined theoretical modelling of STM and NC-SFM (Ke *et al.*, 2002) has confirmed the original experimental interpretation. Although this double technique is very useful for extracting more information than is available from only one type of experiment, it is, by the nature of STM, limited to surfaces which can be made to conduct. Although the stoichiometric TiO₂ surface is insulating, real surfaces are always non-stoichiometric and the oxygen vacancies introduce surface states which significantly reduce the band gap.

Although not strictly within the insulating surface class (at least not graphite), interpretational success in atomically resolved NC-SFM was achieved on the van der Waals surfaces graphite (0001) (Hölscher *et al.*, 2000) and xenon (111) (Allers *et al.*, 1999). For xenon, theory and experiment gave excellent agreement on Xe as the bright centres. However, for graphite the interpretation was more complex, with the hollow sites in-between six carbon atoms responsible for the strongest interaction, and bright contrast in images.

In spite of extensive theoretical modelling (Foster *et al.*, 2001b; Shluger *et al.*, 1999; Shluger and Rohl, 1996), interpretation of NC-SFM images of wide-gap insulators, such as alkali halides, proved to be much less conclusive. This is mainly due to the structural equivalence of anion and cation sites, and ambiguity in the nano-tip structure discussed below. Nevertheless modelling of NC-SFM on these materials allowed us to establish some

general features of the tip-surface interaction responsible for the image contrast.

In particular, it has been demonstrated that, for realistic macroscopic tip parameters, the interaction of ionic nano-tips (such as the MgO cube nano-tip) with these ionic surfaces predicts image contrast in broad agreement with experiments (Livshits *et al.*, 1999). This is an indication that all relevant forces are accounted for in the simulation. The image contrast (the variations of the frequency change over different surface sites) was shown to be determined primarily by the electrostatic interaction between the nano-tip and the surface. We should stress that this interaction is caused by the whole surface and whole nano-tip rather than individual surface and tip ions. The balance of forces acting e.g. on the tip ion closest to the surface is determined by the full surface electrostatic potential, which decreases exponentially with the distance from a neutral, ideal and rigid surface, and the full tip electrostatic potential. Any surface or tip defects, such as surface steps, vacancies, adsorbed ions and even strong displacements of regular ions from their sites cause much more long-range Coulomb and dipole contributions to the interaction. This has two main consequences. First, the displacements of the surface and tip ions from their regular sites caused by the tip-surface interaction strongly enhance the image contrast with respect to rigid tip and surface (Livshits *et al.*, 1999). Secondly, charged surface defects, such as impurities, vacancies and adsorbed ions should give strong image contrast (Kantorovich *et al.*, 2000a; Livshits *et al.*, 1999). As we will show later, even neutral step edges enhance image contrast with respect to regular surface sites (Bennewitz *et al.*, 2000).

Yet another important consequence of the electrostatic interaction is that the sign of the surface electrostatic potential alternates and is opposite, e.g. above Na^+ and Cl^- surface sites. For an atomically sharp tip, such as the one shown in Fig. 5, the repulsion and attraction above different surface sites will depend on the sign of the electrostatic potential at the end of the tip. For example, the O-terminated MgO cube nano-tip shown in Fig. 5 has a negative electrostatic potential and will be attracted to Na^+ sites in the NaCl (001) surface and repelled from Cl^- sites. The Mg-terminated MgO cube nano-tip, on the other hand, will be attracted to the Cl^- sites. Of course, this interaction will be much less clear-cut for more complex tip and surface structures. However, this simple model illustrates the main problem of interpretation of NC-SFM images of high symmetry surfaces, such as NaCl: unless the sign of the tip potential is known, alternative interpretations of the chemical identity of the surface ions are equally possible. The same is true even for less symmetric surfaces of TiO_2 .

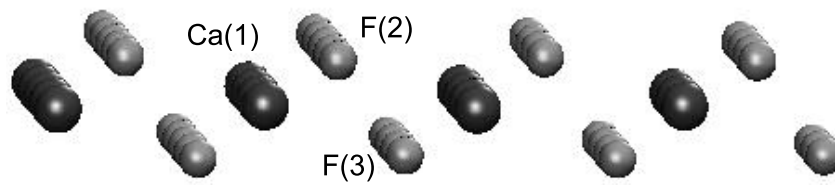


Figure 12 Fluorine terminated CaF_2 (111) surface. The calcium layer is labelled 1, the outermost fluorine layer is labelled 2 and the lower fluorine layer is labelled 3. The layers are separated by 0.08 nm.

The method of identifying the chemical identity of the surface species applied on this surface sets an important principle: one can 'mark' certain surface sites by adsorbing some atoms or molecules which will stick only to these sites (Fukui *et al.*, 1997b).

Another possible method for reliable interpretation of images is to exploit the dependence of contrast on the tip structure and properties. This can be done when imaging a lower symmetry surface, where tips with different sign of electrostatic potential give qualitatively different contrast patterns. This was achieved for the bulk wide gap insulator CaF_2 , where collaboration between theory and experiment played a crucial role in establishing the chemical identity of image features. Therefore, we will use this system as an example for illustration and critical analysis of the theoretical method discussed above.

1. The Calcium Fluoride (111) Surface

The CaF_2 (111) surface has been demonstrated to be fluorine terminated (Reichling and Barth, 1999) and, as can be seen from Fig. 12, the outermost fluorine layer protrudes out from surface. For convenience, in further discussion we will call the fluorine ions in the upper surface layer (labelled F(2) in Fig. 12) - 'high' F^- ions and these in the third surface layer (labelled F(3) in Fig. 12) - 'low' F^- ions. It is interesting to note that high F^- ions stick out of the surface in a similar manner to the bridging oxygens seen on the TiO_2 surface or As atoms in the InAs surface. A common previous assumption in dynamic SFM imaging is that protruding atomic layers are imaged as bright, and it is important to establish whether this 'intuition' holds theoretically.

For reliable modelling of atomic contrast, one principally needs knowledge on the atomic configuration at the tip end as well as information on the material, shape and curvature of the tip. These latter parameters can be estimated by the analysis of experimental frequency detuning curves as a function of the tip-surface distance. As has been shown in Refs. (Foster *et al.*, 2000a; Guggisberg *et al.*, 2000), such analysis can help to determine inter-relations between the main mesoscopic forces (such as van der Waals, capacitance and electrostatic force due to tip and/or surface charging), which contribute to the background force. The background force determines the average frequency detuning during scanning, whereas the relation between different constituent forces contains information about tip shape, composition and charge (Foster *et al.*, 2000a). This information can then be used as input for theoretical simulations of SFM images.

The experimental procedure employed to measure frequency detuning vs. distance curves and characterise the tips used in CaF_2 surface imaging is thoroughly described in Ref. (Barth *et al.*, 2001). The main idea is to make this *in situ* immediately after taking the last image. We should note that lateral thermal drift of the sample, which is unavoidable at room temperature, does not allow precise tip positioning over a specific ionic site. Therefore, these data represent an average over a spread of lateral positions. However, as the force curves are analysed only with respect to long range forces, this uncertainty does not affect the conclusions presented below.

In NC-SFM imaging it is common practice to minimize long-range electrostatic interactions by applying a bias voltage, a procedure similar to that described in reference (Bennewitz *et al.*, 1997) and this was also done for measurements shown in Fig. 13. The measured frequency detuning curves strongly depend on tip preparation. The curve in Fig. 13 was prepared by bringing the tip into contact with the surface to produce a much blunter tip.

Using the SFM model described above, the theoretical curves were fitted to experimental data obtained at both oscillation amplitudes. The macroscopic van der Waals force between the tip and surface is proportional to the tip radius and the Hamaker constant. The value of the Hamaker constant was fixed at 1 eV corresponding to a characteristic value for the interaction between silicon and a wide-gap insulator (French *et al.*, 1995). Therefore free parameters of the fit were only the tip radius and the bias voltage. The bias voltage applied

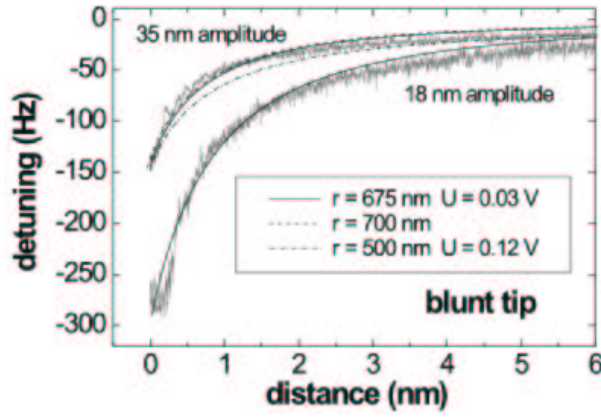


Figure 13 Comparison of experimental and theoretical force-distance curves.

in the theoretical model affects long-range electrostatic forces due to uncompensated tip and surface charge, and image interaction (Foster *et al.*, 2000a).

Best fit results are shown as dashed lines in the graphs of Fig. 13. The tip parameters for the fit are the same at both amplitudes, confirming that theory gives a consistent agreement. Distances given in the graphs of Fig. 13 have been obtained by shifting experimental data to align with theoretical curves assuming that closest approach of the tip to the surface occurs at 0.4 nm. We should stress that this is clearly a crude estimate. It is based on previous intuitions regarding closest approaches in experiments, and we will show later that modelling predicts much closer approaches. However, errors of the order of 0.1 nm in background force distances does not strongly influence the results, since contrast is determined by the microscopic forces where distance is clearly defined.

The theoretical best fit was found for a tip radius of 675 nm and 0.03 V bias voltage. It should be noted that, within the assumptions discussed above, these parameters are unique and a similar fit could not be found with an increased bias and reduced radius. This is due to the very different behaviour of van der Waals and electrostatic forces as a function of distance (Foster *et al.*, 2000b). In both cases, the macroscopic van der Waals force dominates the interaction and the long-range electrostatic force due to bias is insignificant. The latter is consistent with the fact that fitting was made to curves obtained under conditions where electrostatic forces have been minimized by the applied bias voltage. In real experiments, it is very unlikely that an originally sharp tip (about 10 nm) could be blunted so severely that the radius increases by a factor of fifty. This probably indicates that the macroscopic

model is not sophisticated enough, but in so much as it incorporates the experimental force vs. distance behaviour it is satisfactory for the simulation.

Simulating Scanning

A large number of high quality atomically resolved experimental images were produced with the blunt tip and some of them are reported in Refs. (Barth *et al.*, 2001; Foster *et al.*, 2001a). Therefore, theoretical images have also been calculated using a macroscopic tip of radius 675 nm and an applied bias of 0.03 V. Real tips were unsputtered, covered by oxide and were also likely to be contaminated by surface material. Since the force curves do not exhibit long-range electrostatic interaction, the tip and the surface in the image area are most probably neutral. Therefore the MgO cube could be a good model to represent the tip electrostatic potential. Another advantage of using this nano-tip is that its interaction with the ionic CaF_2 (111) surface can be well described within the AS model.

The setup of the calculations is the same as in Fig. 5, with the cubic surface replaced by the CaF_2 (111) surface unit cell (shown in Fig. 12). The microscopic force is calculated using a periodic static atomistic simulation technique and the MARVIN2 code. The parameters for the surface interactions were generated to match experimental bulk structural, elastic and dielectric constants, and gave good agreement with *ab initio* surface relaxations (Barth *et al.*, 2001). Parameters for the interactions between the MgO tip and the CaF_2 surface are taken from Binks (Binks, 1994) and Bush *et al* (Bush *et al.*, 1994). MgO tip parameters are as discussed in Section IV.C.2. The bottom 2/3 of the nano- tip and the top of the CaF_2 surface are relaxed explicitly. In terms of notations shown in Fig. 5, region I consists of the bottom of the MgO nano-tip and the top three layers of the CaF_2 surface, and region II the remaining layers.

Since we do not know in advance the nature of the electrostatic potential of the tip in a given experiment, scanning was simulated using the MgO tip orientated with an oxygen and a magnesium at the lower apex, producing a net negative and net positive electrostatic potential respectively. In both cases, a full surface map of the force field over the CaF_2 surface unit cell was calculated, beginning at a tip-surface height of 2 nm and approaching to almost 0 nm with respect to the position of the Ca sublattice. In the final stage, the oscillations of the cantilever were modelled, as described in Section IV.E, after introducing

the macroscopic background forces to the total force. Note that to match the experimental method, simulated images were calculated in 'constant height' mode such that an image is a plot of the change in frequency across the surface at a constant height. Experimental parameters were used in the simulation where possible: a cantilever amplitude of 23 nm, a eigenfrequency of 84 kHz, a spring constant of 6 N/m, and a mean frequency change of -155 Hz.

Standard Images

Many of the experimentally observed images of the CaF_2 (111) surface exhibit disk-like and triangular contrast patterns. The interpretation of these two characteristic patterns is discussed in this Section. They have been seen in several separate experiments using different tips and thus can be considered as 'standard' images. The other contrast patterns seen on this surface are associated with more short-range scanning and tip-changes, and are discussed, and explained, in the next Section. This distance will be referred to as tip height in further discussion. We will first discuss the properties of simulated images at a single constant height and compare them directly with experiment. Note, however, that the interaction ranges strongly depend on the true microscopic tip in an experiment, and any references to distance can only be considered as rough estimates. The images discussed in this Section were produced for a setup where the shortest distance between the oscillating tip and the surface was 0.35 nm. At this height the average simulated contrast matches the experimental average contrast which is a good measure of comparable interaction strength.

Figure 14(a) shows a simulated image and scanline produced with a negative electrostatic potential tip at 0.35 nm. The image demonstrates a clear circular or 'disk-like' contrast with strongest brightness centred on the position of the Ca ions in the surface. The scanline shows that contrast is dominated by a large peak over the Ca ion, with a much smaller peak in between the high and low fluorine ions. The smaller peak is due to a minimum in repulsion between the tip and F^- ions, however this peak is so small in comparison to the main peak over Ca that it has no affect on the contrast pattern.

The domination of Ca in the negative potential tip contrast pattern has two components: (i) the positive surface potential over the Ca^{2+} sites has a strong attractive interaction with the negative potential from the tip. Fig. 15(a) shows clearly the domination of the

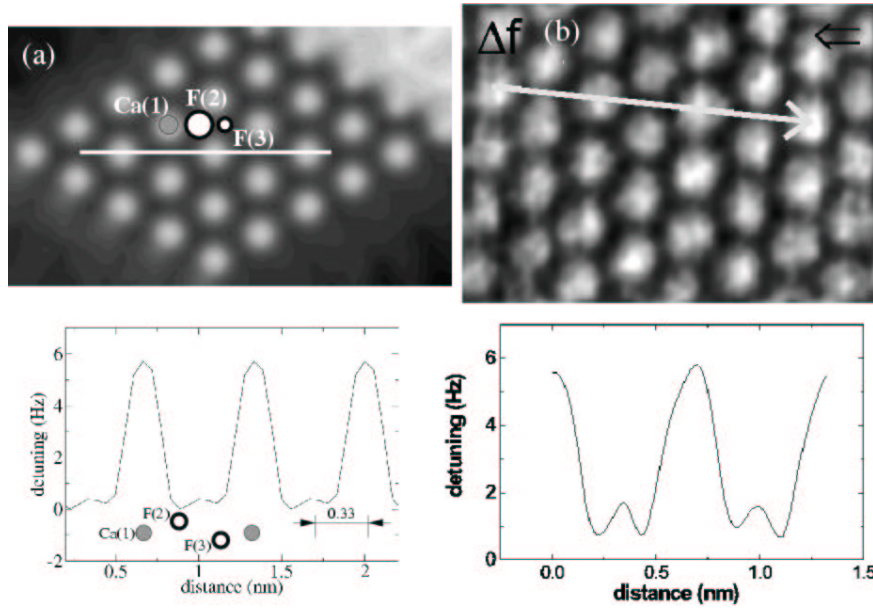


Figure 14 (a) Simulated image and scanline produced using a tip with a negative electrostatic potential scanning at 0.35 nm. Atomic labels refer to similar conventions used in Fig. 12. (b) Example experimental image and scanline demonstrating 'disk-like' contrast. The white lines in the images are along the $[211]$ direction and indicate the position of the scanlines. *Reprinted with permission* (Foster *et al.*, 2002).

attractive interaction over the Ca^{2+} ions; and (ii) as the tip approaches the surface, the Ca^{2+} ions displace towards it and the F^- ions are pushed into the surface. Fig. 15(b) shows that, at 0.350 nm over the Ca(1) site, the Ca^{2+} ion displaces by 0.118 nm outwards, also forcing the high F^- ion outwards. However, as the tip moves towards the the F(2) site, the Ca^{2+} ion drops back to the surface and the high F^- ion is actually pushed in by 0.027 nm. The low F^- ions (F(3)) are not displaced significantly from their equilibrium positions at this scanning height. Displacement of ions from the surface greatly increases the range of the local surface electrostatic potential (Livshits *et al.*, 1999) and increases tip-surface interaction.

If we now compare simulated results with experimental results in Fig. 14(b), we immediately see a clear qualitative agreement. The experimental image shows disk-like contrast, and the scanline has a very similar form to that in the simulation. However, we can extend the comparison to a quantitative level - the simulation predicts (based on surface geometry) that the smaller peak should appear at 0.33 nm from the main peak over the Ca sublattice. If we take over 70 experimental scanlines from images which show disk-like contrast, we find that the average position of the small peak is 0.32 ± 0.05 nm, in excellent agreement with

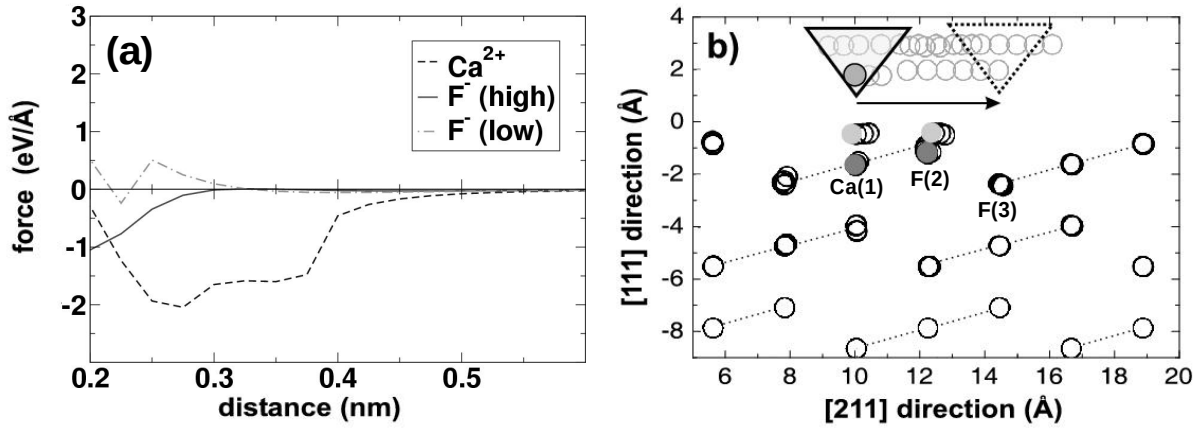


Figure 15 Theoretical data from simulations with a negative electrostatic potential tip: (a) chemical force curves over the Ca, high and low F atomic sites; (b) full trajectories of atoms in a plane as the tip follows the $[\bar{2}11]$ scanline at a height of 0.350 nm . Labels Ca(1), F(2) and F(3) are as in Fig. 14. The atoms shaded light grey in the surface indicate initial positions of the most relevant atoms when the tip is over Ca(1) (leftmost tip position in figure), whereas atoms shaded dark grey are final positions when the tip is over F(3) (rightmost position). Note that trajectories of only the bottom four atoms (1 O^{2-} and 3 Mg^{2+} ions) of the tip have been included. *Reprinted with permission* (Foster *et al.*, 2002).

theory.

Figure 16(a) gives a simulated image and scanline when using a tip with a net positive electrostatic potential from the apex. The contrast pattern is now clearly triangular, with the centre of brightness over the high F^- ions, but also with an extension of the contrast towards the position of the low F ions in three equivalent directions forming the triangle. The simulated scanline shows a large peak over the high F^- position dominating the contrast, but also we see a shoulder to this main peak over the position of the low F^- ion. Since this shoulder is a significant fraction of the height of the main peak, it can be seen in images and is responsible for the triangular contrast pattern. The triangular contrast pattern has three components: (i) the negative surface potential over F^- sites gives a strong attractive interaction with the positive potential tip (see Fig. 17(a)). This interaction is comparable to the interaction of the negative tip over the Ca^{2+} ions, since although the F^- ions have half the charge of the Ca^{2+} , the high fluorine protrudes 0.08 nm further from the surface (see Fig. 17(b)); (ii) the ions in both the F^- layers displace towards the tip as it approaches, and the Ca^{2+} ion is pushed inwards; and (iii) when the tip is over the low F^- ion, there is also

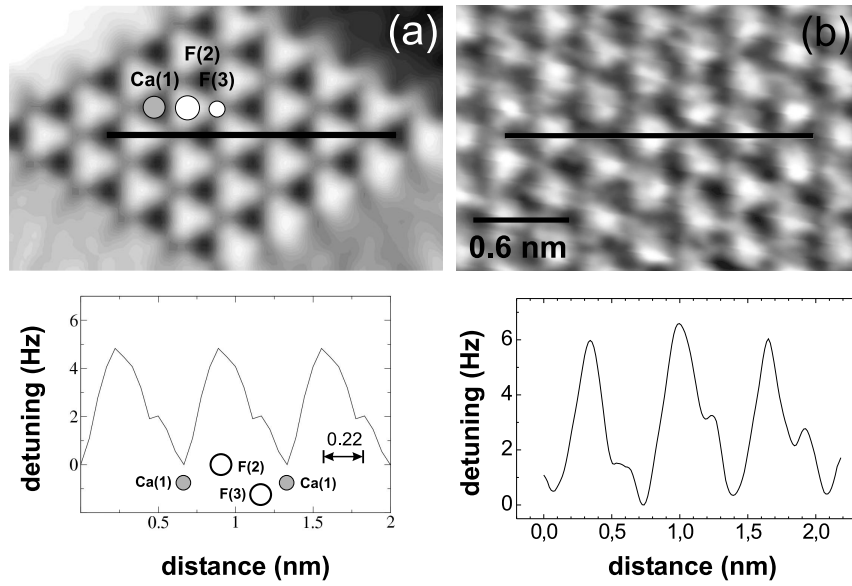


Figure 16 (a) Simulated image and scanline produced using a tip with a positive electrostatic potential scanning at 0.35 nm. Atomic labels refer to similar conventions used in Fig. 12. (b) Example experimental image and scanline demonstrating triangular contrast. The white lines in the images are along the $[\bar{2}11]$ direction and indicate the position of the scanlines. *Reprinted with permission* (Foster *et al.*, 2002).

some interaction of the tip with the next row of high F^- ions (see Fig. 17(d)). Hence the shoulder has some component from this interaction, as well as the direct interaction with the low F^- sublattice. The role of displacements is discussed in detail in the next section.

Comparing with the experimental results in Fig. 16(b), once more we see that there is a good qualitative agreement between experiment and theory. The experimental image shows triangular contrast, and the scanline shows large peaks with shoulders. Quantitatively we find that the average position of the shoulder with respect to the main peak in over 75 scanlines is 0.24 ± 0.04 nm, which compares very well with the theoretical prediction of 0.22 nm.

The described semi-quantitative agreement of the theoretical images obtained with model tips with the experimental images supports the model of ionic tip, which may have two signs of the electrostatic potential probing the surface. Although the MgO tip is clearly an idealised model it seems to capture correctly both the possibility of different types of tip contamination by the surface and ambient ions and the strength of the short-range chemical interaction.

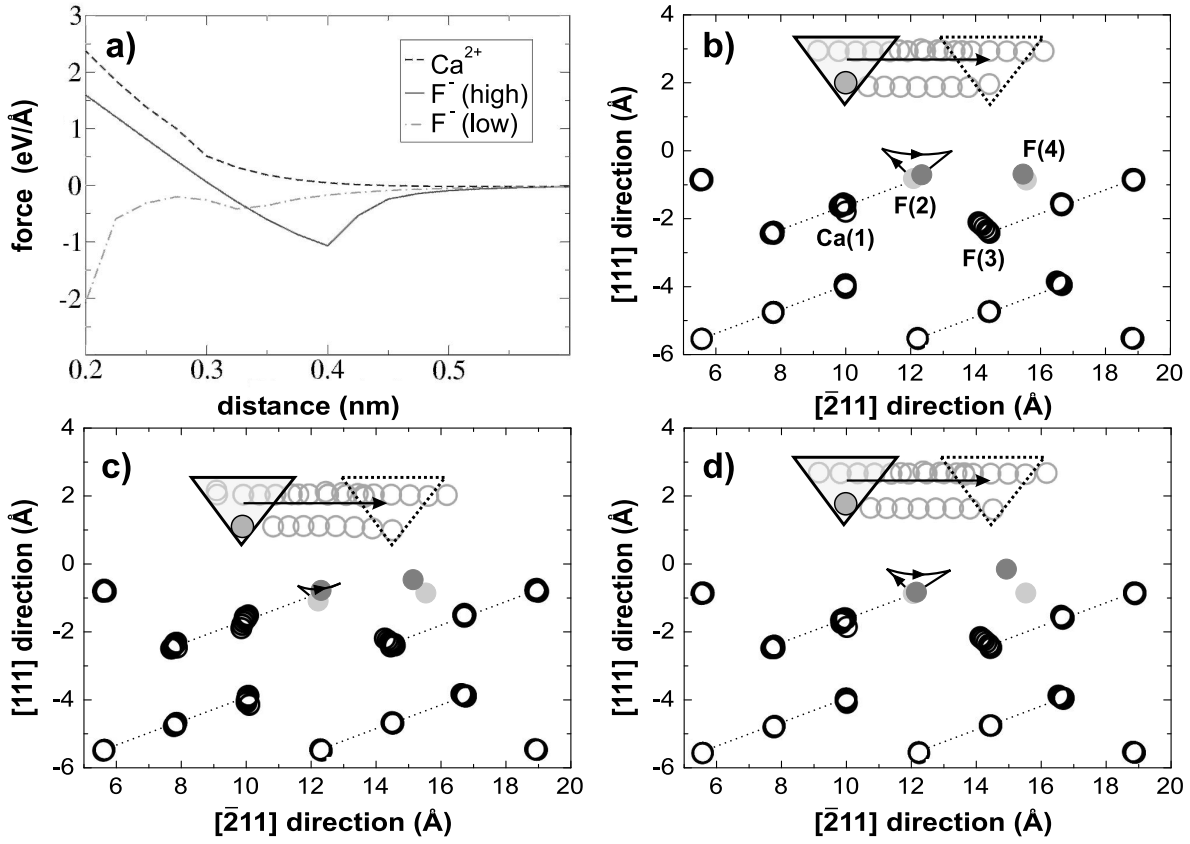


Figure 17 Theoretical data from simulations with a positive electrostatic potential tip: (a) chemical force curves over the Ca, high and low F atomic sites; full trajectories of atoms in a plane as the tip follows the $[2\bar{1}1]$ scanline. Tip-surface distance is (b) 0.350 nm ; (c) 0.250 nm ; (d) 0.325 nm . Labels Ca(1), F(2) and F(3) are as in Fig. 14. The atoms shaded light grey indicate initial positions of the most relevant atoms when the tip is over Ca(1) (leftmost tip position in figure), whereas atoms shaded dark grey are final positions when the tip is over F(3) (rightmost position). F(4) is a high fluorine atom out of the plane, but its trajectory has been projected on to the same plane as the other atoms for clarity. Note that trajectories of only the bottom four atoms (1 Mg^{2+} and 3 O^{2-} ions) of the tip have been included. *Reprinted with permission* (Foster *et al.*, 2002).

Distance Dependence of Images

Since we have demonstrated both qualitative and quantitative agreement between experiment and theory at a certain height, it is interesting to see whether the comparison is still favourable when a range of heights is considered. Figs. 18(a-c) show experimental images at increasing average frequency change i.e. reduced tip-surface separation. Figures 18(a,

b) clearly show the triangular contrast discussed above. Persistence of this pattern in experimental images obtained under different conditions shows that the triangular contrast pattern is not a unique feature seen only at a specific height, but is rather a distinct pattern related to the potential of the tip. However, in the image at closest approach we see that the contrast pattern has changed considerably. Figure 18(c) shows a 'honey-comb' pattern, with the F sites now completely linked in bright contrast.

To understand whether this very distinct change in contrast could be explained within the same model as discussed in the previous Section, further extensive modelling was performed. Figs. 18(d-g) show the development of contrast in simulated images as the scanning height (i.e. the closest distance between the turning point of tip oscillations and the surface) is reduced. Fig. 18(d) demonstrates that even at very large distances the triangular contrast pattern is consistent, even if it is unlikely that experiments could measure such small chemical forces. As the tip approaches (Figs. 18(e,f)), theory predicts that the triangular pattern becomes even more vivid, as seen in the experimental images. Finally, at 0.275 and 0.25 nm separations in Fig. 18(g,h), the simulated images develop the honey-comb contrast pattern seen clearly in experimental image Fig. 18(c).

Further agreement can be seen by comparing the change in experimental and theoretical scanlines. Figures 19(a,b) show that at long range both experiment and theory demonstrate the large peak/small shoulder scanlines characteristic for the triangular contrast pattern. However, as the tip approaches closer the magnitude of the shoulder increases until for scanlines from the honey-comb images it is clear that the shoulder is at least equal to the original main peak.

A more thorough understanding of this agreement in contrast development requires studying in detail the changes in forces and atomic displacements as the tip approaches the surface. Figure 17(a) gives the chemical force over the relevant sites in the CaF_2 surface as a function of distance for a tip with positive termination. For distances larger than 0.400 nm, the curves are as one would expect them, i.e. we find repulsion over the positive Ca^{2+} ion and attraction above the F^- ions. From the ionic interaction, we find some attraction over the low F^- ion and stronger attraction over the high F^- ion. Moving closer than 0.400 nm, we observe that the attraction over the high F^- ions reduces and it increases over the low F^- site, until around 0.320 nm the greatest attraction is now over the low F^- site. This behaviour can be understood by looking at atomic displacements as the tip approaches. At 0.350 nm there is

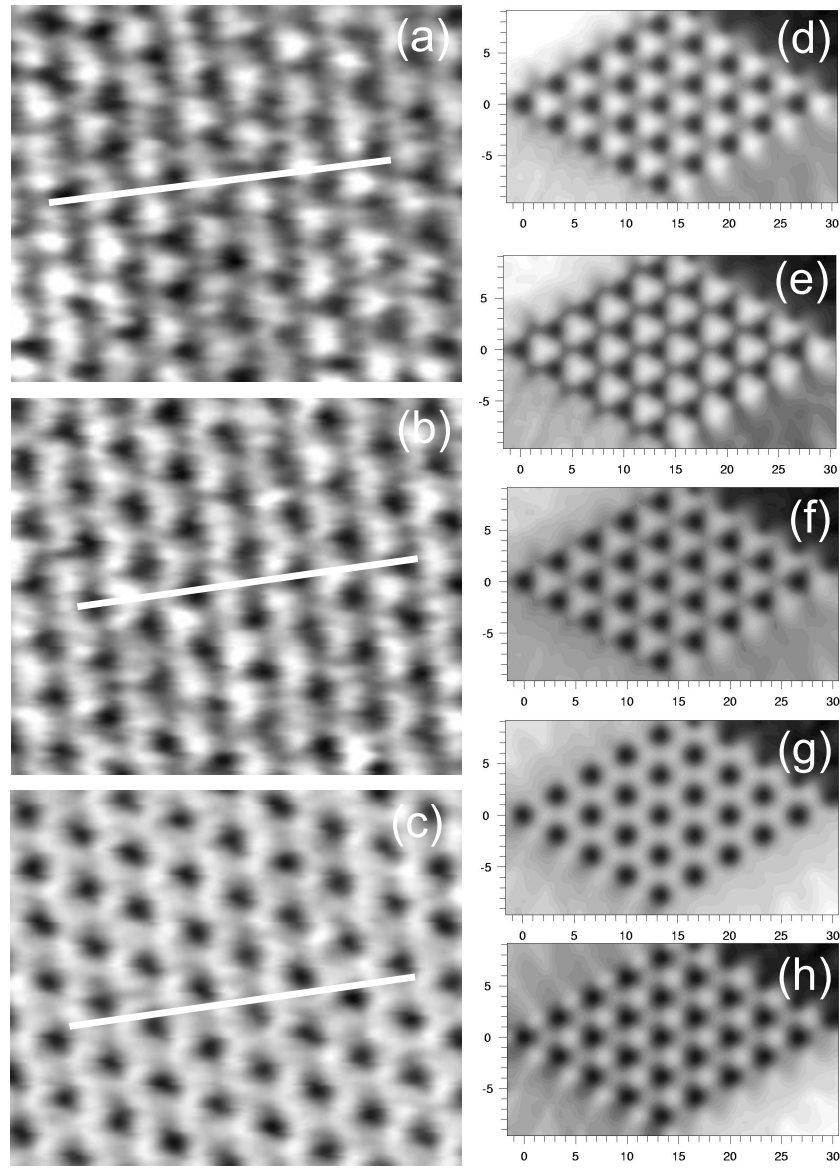


Figure 18 (a-c) Experimental images taken as the tip approaches the surface (Barth *et al.*, 2001). (d-g) Simulated images at 0.500, 0.375, 0.325, 0.275 and 0.250 nm using a positive potential tip. *Reprinted with permission* (Foster *et al.*, 2002).

strong displacement of the high F^- ion ($F(2)$) towards the tip (see Fig. 17(b)) producing a very strong attractive interaction, however as the tip moves closer, this F^- ion is driven back into the surface and the force is reduced. Frame (c), shows that the high F^- ion has been pushed effectively back into its original lattice position at a tip-surface separation of 0.250 nm. However, when the tip is over the low $F(3)$ site, we see very little movement of the closest high F^- ion, but in fact, aided by the proximity of the Ca^{2+} ion, there is a much

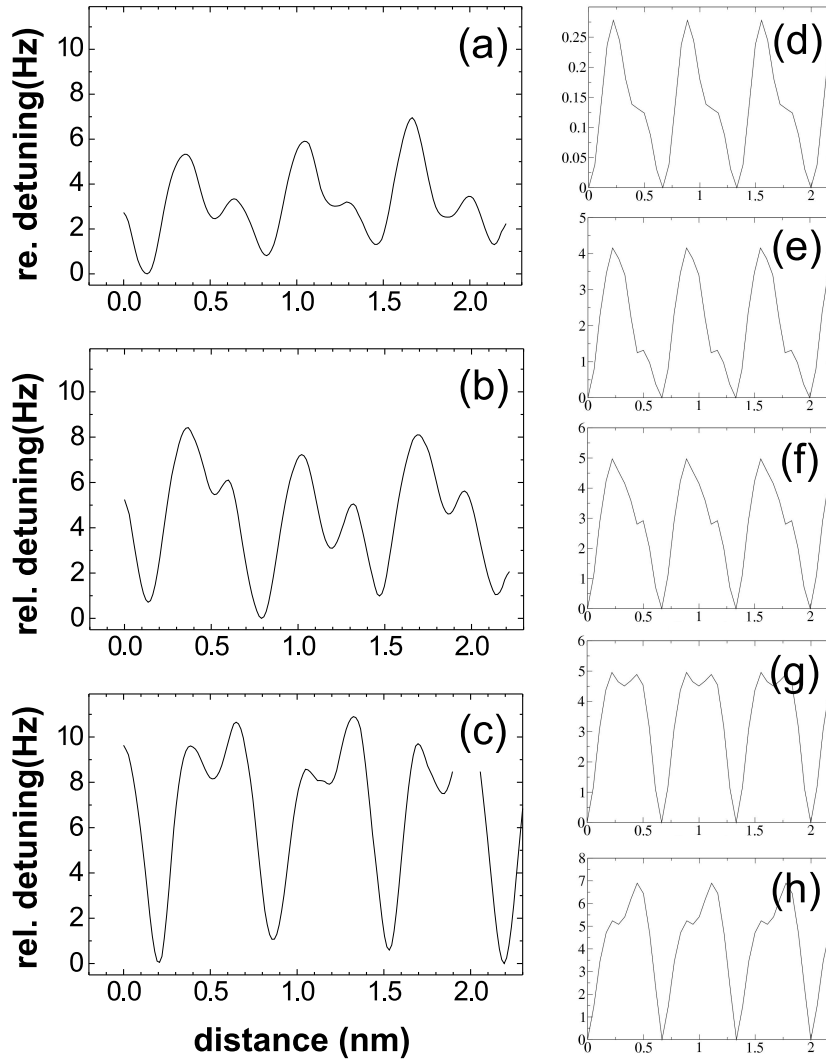


Figure 19 Comparison of (a-c) characteristic experimental and (d-h) simulated scanlines taken from the images in Fig. 18 as the tip approaches the surface. *Reprinted with permission* (Foster *et al.*, 2002).

smaller barrier for displacement of the high F^- ion from next nearest row (F(4)). Frame (d) shows how the next nearest high F^- ion displaces very strongly to the tip at 0.325 nm when it is over the F(3) site.

In summary, at a distance of 0.5 nm the interaction with the high F^- atom dominates, and we see only relatively small shoulders in scanlines over the low F^- sites. As the tip approaches, the nearest high F^- ion is pushed into the surface reducing its dominance, and the interaction with low F^- and the next nearest high F^- ion increases the relative size of the shoulder. This corresponds to increasing vividness of the triangular contrast pattern in

images. Finally, the contribution from the high F^- is balanced by the contribution from the low F^- /next high F^- ion, and the main peaks and shoulders are equivalent in scanlines, and it is this equivalence which produces the characteristic honeycomb contrast pattern.

These results alter the previous perception (Barth *et al.*, 2001; Livshits *et al.*, 1999) that, due to adhesion of the surface ions to the tip, SFM tips should be prone to rapid changes during short-range scanning. It was expected that large displacements of the surface and tip ions may lead to instabilities of the SFM operation and to tip crashes. Although this effect certainly has been observed in many experiments (as discussed in more detail in the following Section) it does not necessarily always result from large displacements and instabilities of the surface ions. As these results demonstrate, such effects can be reversible and may not disrupt imaging. The remarkable agreement between theory and experiment serves as an indirect, but powerful indication that the displacements of the tip and surface ions (which cannot be imaged directly) play an extremely important role in contrast formation.

Ideal Silicon Tip

In this Section, we extend the discussion to a non-ionic tip, which is modelled by a pure silicon tip. On more reactive, semi-conducting surfaces, it has been shown that for a pure silicon tip, contrast is dominated by the onset of bonding between dangling bonds in the tip and surface (Lantz *et al.*, 2000; Pérez *et al.*, 1997), and these forces have recently been explored in detail experimentally (Lantz *et al.*, 2001). However, for insulating surfaces, clean silicon tips are normally not used in experiments published so far, although several attempts have been made (Allers *et al.*, 2001, 1999; Ashino *et al.*, 2001). Nevertheless, it is useful to explicitly calculate the interactions of a clean silicon tip with the CaF_2 surface.

To represent a pure silicon tip, we use a ten atom silicon cluster, with its base terminated by hydrogen. This has been shown previously (Lantz *et al.*, 2000; Pérez *et al.*, 1998) to provide a good model of a clean silicon tip with a single dangling bond at the apex. The smaller size of the silicon cluster compared to the MgO cube allows us to use a correspondingly smaller surface size, and the crystal is here simulated by a cluster of $(4 \times 4 \times 3)$ CaF_2 units. The bottom two layers of the tip and the top two layers of the surface are allowed to relax with respect to atomic forces, as in the previous simulations.

Figure 20 shows calculated tip-surface forces as the silicon tip approaches the Ca^{2+} , high

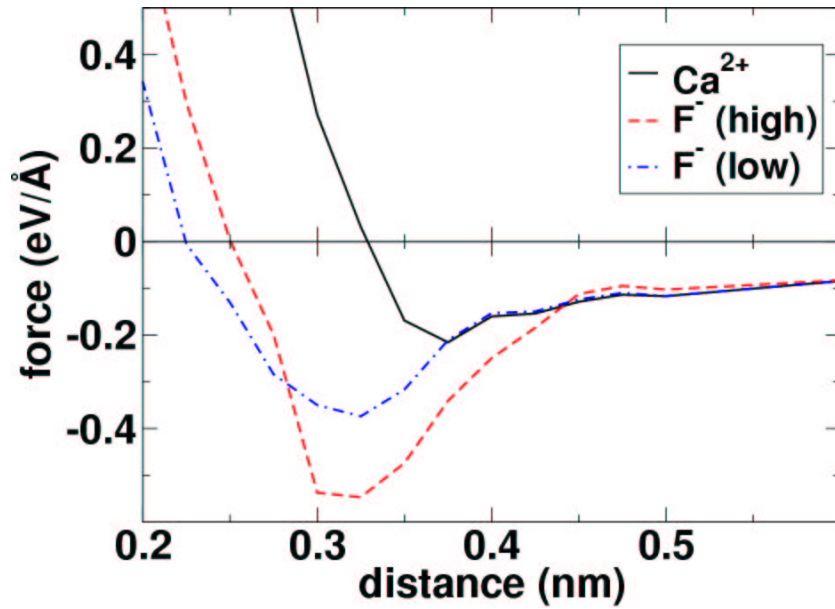


Figure 20 Simulated force curves taken over the Ca, high and low F sites in the CaF_2 (111) surface with a pure silicon tip. *Reprinted with permission* (Foster *et al.*, 2002).

F^- and low F^- sublattices in the CaF_2 surface. It is clear that contrast in images with a silicon tip would be dominated by interaction with the high F^- sublattice, and to a lesser extent the low F^- sublattice. The interaction with Ca^{2+} is much weaker, and enters repulsion at larger tip height (about 0.33 nm) than over the F^- sites (about 0.25 nm). The interaction between the tip and the F^- ions is due to the onset of covalent bonding between Si and F^- , involving charge transfer from the F^- ions into bonding states. At 0.3 nm tip height, charge transfer is 0.18 e for the high F^- , but only 0.02 e for the low F^- (based on Mulliken population analysis (Mulliken, 1949)). Over Ca, there is no charge transfer until small heights (about 0.3 nm), where charge is actually transferred from the neighbouring high F^- site to the tip. However, at this point the tip has already entered the repulsive interaction region and the effect is negligible.

If we now compare the silicon tip force curves with those in Fig. 17(a) we see qualitatively the same behaviour in the range between 0.300 nm and 0.500 nm: very weak interaction beyond 0.450 nm; largest interaction over high F^- ; weakest interaction over Ca^{2+} ; and low F^- somewhere between. Note that the onset of repulsion over the Ca^{2+} site even occurs at qualitatively the same position as in Fig. 17(a), at the maximum in attraction over the high F^- site. This agreement implies that a pure silicon tip could only produce a triangular contrast pattern, as for the positive potential ionic tip at medium to long range. At smaller

ranges, the differences in force for the ionic tip are due to the strong displacements induced by tip approach, in agreement with experiment (see previous section). Note, that for the silicon tip, interaction forces are considerably smaller than for the ionic tip and, therefore, displacements for a pure silicon tip are much smaller. Over the Ca^{2+} ions, there is almost no surface ion displacement until very small tip-surface separations when the Ca^{2+} directly underneath the tip is pushed in. Over the high F^- , at 0.350 nm the F^- ion under the tip is at a maximum displacement of 0.040 nm towards the tip, before being pushed back in. There is no significant displacement of the low F^- , or any atoms not directly underneath the tip. Due to the softness of the silicon tip in comparison to the ionic MgO tip, tip atom relaxations play a more significant role in the interaction. Over the high F^- there is no significant displacement of the apex Si atom towards the surface, but at 0.300 nm tip height it is displaced by 0.025 nm into the tip due to strong repulsion from the proximity of the F^- . Over the Ca^{2+} ion a similar process occurs, but the tip apex displacement at the same height is only 0.010 nm. These tip atom relaxations slightly reduce the overall tip-surface interaction, but would have no significant influence on images due to their short-range and small magnitude. However, it is possible that for other, even softer, tips, this contribution could be significant in contrast patterns.

Comparing the magnitude of force curves for the two different tips, we see immediately that the force between a pure silicon tip and the CaF_2 surface is much less than for positive potential ionic tip. On first sight, one might expect that there is a strong interaction between Si and F, as F is known as a very reactive species. However, in this case we are effectively dealing with F^- ions with a full outer shell, not atoms, and there is no possibility of the large charge transfer characteristic of Si and F interacting in atomic form. If we calculate the maximum possible contrast for a pure silicon tip imaging CaF_2 , it is about 2 Hz - several times smaller than that seen for simulations with an ionic tip, and, more significantly, in experiments. This is a consequence of both the weaker attraction to the F^- ions, and the lack of medium-range repulsion over Ca^{2+} ions, reducing the overall contrast.

2. CaCO_3 ($10\bar{1}4$) Surface

Calcite (CaCO_3) is an ionic compound with relevance in nature and technology. It is well known for its strong birefringence, which has been exploited in a variety of optical applica-

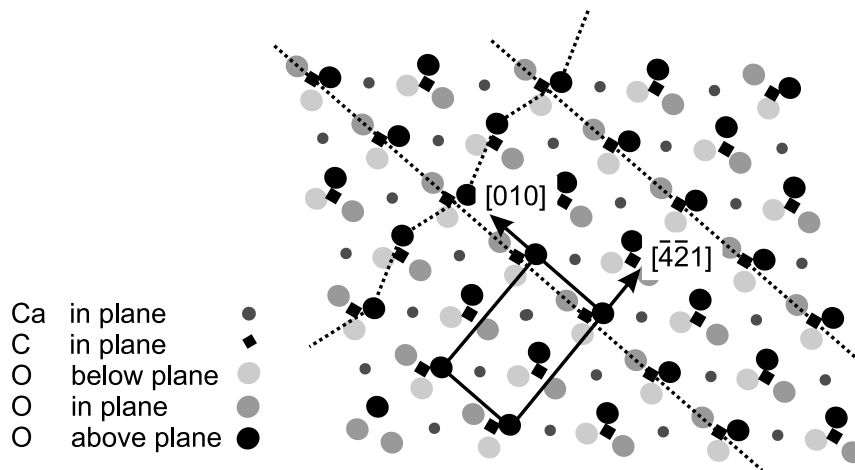


Figure 21 Schematic representation of the $\text{CaCO}_3(10\bar{4}1)$ surface.

tions, but it is also a mineral found in nature in great abundance, and a most interesting substrate for biomimetic materials chemistry (Heywood, 1996). The $\text{CaCO}_3(10\bar{4}1)$ surface is the most stable cleavage face (de Leeuw and Parker, 1997) and has been subject of a variety of theoretical (Skinner *et al.*, 1994) and experimental (Stipp, 1999a; Stipp and Jr, 1991) studies, including contact force microscopy (Hillner *et al.*, 1992; Liang *et al.*, 1996; Ohnesorge and Binnig, 1993; Stipp *et al.*, 1994). In these studies it has been claimed that atomic resolution can be obtained by performing the measurement in an aqueous environment where a snap into contact is avoided by compensating attractive van der Waals forces by capillary forces acting on the tip apex, however, interpretation of images under such conditions is difficult and to date there is no theory that could confirm this in detail. In the context of understanding contrast formation in dynamic force microscopy, this surface is most interesting since it is a very low symmetry ionic system, where one ionic species is a covalently bound group, namely CO_3^{2-} . The main features of the $(10\bar{4}1)$ surface are depicted in Fig. 21. The surface unit cell is composed of two Ca^{2+} ions and two CO_3^{2-} groups where the calcium ions define a surface parallel plane that also contains carbon atoms. Only one oxygen atom of each CO_3^{2-} group shares this plane while the others are located about 0.06 nm above and below. The CO_3^{2-} groups appear in two different orientations with respect to a rotation around an axis perpendicular to the surface plane, therefore neighbouring rows of groups along the $[010]$ direction are not equivalent while the most protruding oxygen atoms form a zig-zag structure oriented along the $[\bar{4}21]$ direction.

Intuitively, one would expect that all these surface features should be represented in atomically resolved force images. In fact, a major issue of this study was establishing which sub-lattice would dominate image contrast and hence, whether force microscopy would be able to resolve individual oxygen atoms within the covalent group or whether this group would appear as a single feature. Previous attempts to image this and other similar minerals did not resolve all chemical species (Ohnesorge and Binnig, 1993; Shindo and Nozoye, 1992; Stipp, 1999b).

Simulations on calcite were performed in the same way as described in Section V.C.1 for CaF_2 . The setup is the same as in Fig. 5, but now the surface is a $4 \times 4 \times 3$ extension of the side Section shown in Fig. 22(a). The top two layers of the surface and the bottom of the nano-tip are allowed to relax in the simulations. Interaction parameters for the tip are the same as previously, and calcite parameters are taken from Ref. (Pavese *et al.*, 1996). The oscillations of the cantilever are simulated with an amplitude of 67 nm and a frequency of 77 kHz, as in experiments. The tip radius of 30 nm is fitted to experimental force vs. distance curves over calcite.

The complex displacements of atoms in the calcite surface play an important role in contrast formation and strongly affect tip-surface interaction. Scanning with a negative potential tip at 0.425 nm produces a combination of rotation/displacement of the carbonate group and displacement of the Ca^{2+} ion as shown in Fig. 22(a). The Ca^{2+} has a simple displacement out of the surface as the tip passes, but the carbonate group also rotates as it is pushed into the surface. This combination reduces the influence of the orientation of the carbonate group on images, and the position of the Ca^{2+} ion dominates contrast in images produced with a negative potential tip. For a positive tip (see Fig. 22(b)) the Ca^{2+} ion is pushed into the surface, and the whole carbonate group is strongly displaced out with a slight rotation. The very large displacement of the highest oxygen of the carbonate (0.045 nm) causes a very strong interaction with the tip, and its position dominates contrast in images with a positive potential tip. Figure 23(a) shows a simulated image produced using a tip with a net positive potential, with the protruding oxygen sites connected by lines. The clear zig-zag contrast pattern can be characterized by an angle of 13° from the vertical and possibly used as a basis for interpretation of experimental images. Figure 22(c) shows the displacements of the calcite surface when scanning with a positive potential tip at 0.4 nm. At this closer separation, the whole carbonate group at first displaces out from the surface

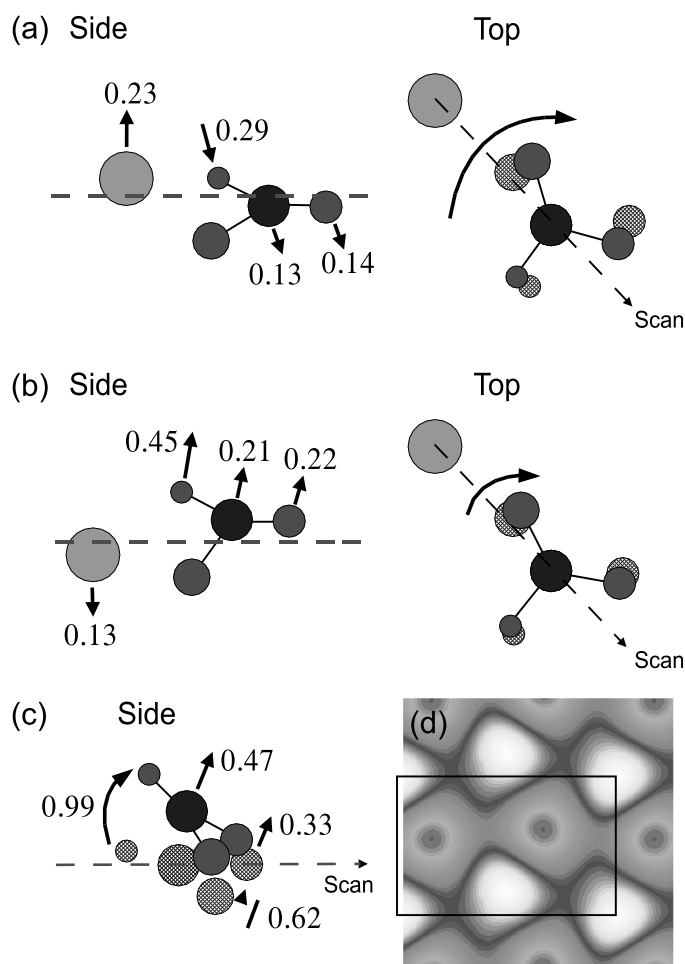


Figure 22 Schematic diagrams of atomic displacements of the calcite (10 $\bar{1}$ 4) surface as the tip scans across at 0.425 nm (a and b). The numbers are in Å, and show the displacements when the tip is directly over that atom. C atoms are dark grey, Ca atoms are light grey and O atoms are medium grey. (a), and the size of the oxygen atoms in the carbonate group is in perspective i.e. the larger the atom the further 'out' of the page it lies. The cross hatched atoms in some drawings show the undisplaced position of the atoms when the tip is not in proximity, and the arrows give an indication of the displacement direction as the tip approaches. (a) Scanning with a negative potential tip. (b) Scanning with a positive potential tip. (c) Scanning at 0.4 nm from the surface with a positive potential tip causes the whole carbonate group to flip up from the surface. (d) DFT calculated electrostatic potential at 0.250 nm above the calcite surface in a plane parallel to C, Ca and middle O atoms in the surface. The black rectangle is the unit cell of the (10 $\bar{1}$ 4) calcite surface.

considerably, and then actually flips up, pivoting on the middle oxygen atom. This kind of displacement causes extreme changes in the force, and is likely to strongly influence the contrast pattern.

Thus modelling of the image contrast with the atomically sharp MgO cube tip clearly suggests that, although the image contrast is caused predominantly by electrostatic forces, the carbonate groups should be imaged as a whole in NC-SFM. To understand further the nature of contrast on calcite, Fig. 22(d) shows the electrostatic potential calculated in a plane parallel to a plane through C, Ca and middle O atoms of the surface, and at a height of 0.250 nm from the surface. This corresponds to an effectively infinitely sharp tip. One can see that, even from this very close view, the individual oxygen ions of the CO_3^{2-} group cannot be clearly distinguished in the electrostatic potential probed. This suggests that the nature of chemical bonding rather than the tip size plays the decisive role in determining whether individual atoms can be resolved inside the molecular group such as carbonate.

Figure 23(b) shows one of the experimental images of the $\text{CaCO}_3(10\bar{4}1)$ surface. All ionic rows are present and one can see the expected zig-zag pattern, which we regard as a piece of evidence that the surface features imaged are CO_3^{2-} groups and not calcium ions. The carbon and oxygen atoms are not resolved as predicted by the theory. It is intuitively clear that on the low symmetry $\text{CaCO}_3(10\bar{4}1)$ surface, the details of nuclear movement depend on the orientation of the nano-tip with respect to carbonate groups in a non-trivial way. This is illustrated in Fig. 24 (b) showing the projection of the last oxygen and three magnesium ions of the tip on the carbonate group of the surface. The MgO cube is orientated by its (111) axis perpendicular to the surface (see Fig. 5) as in all previous calculations. Rotation of the tip by 20° degrees with respect to this axis changes the projection as shown in Fig. 24 (b). This relatively small rotation of the tip leads to a distinct difference of the interaction with the surface as evident in Fig. 24 (a) where the corresponding interaction curves are labelled as twisted. These considerations suggest that the effect can be much stronger for more complex tip structures. It is most pronounced at relatively short distances of 0.3 nm and closer to the surface. We did not attempt to simulate the surface scanning with the rotated tip, but it is clear from the previous discussion that the surface deformation will be also different for different tip orientations. The image should be most significantly influenced at closest tip-surface separation. It demonstrates the complexity of processes involved in dynamic mode force scanning in the presence of strong surface relaxation.

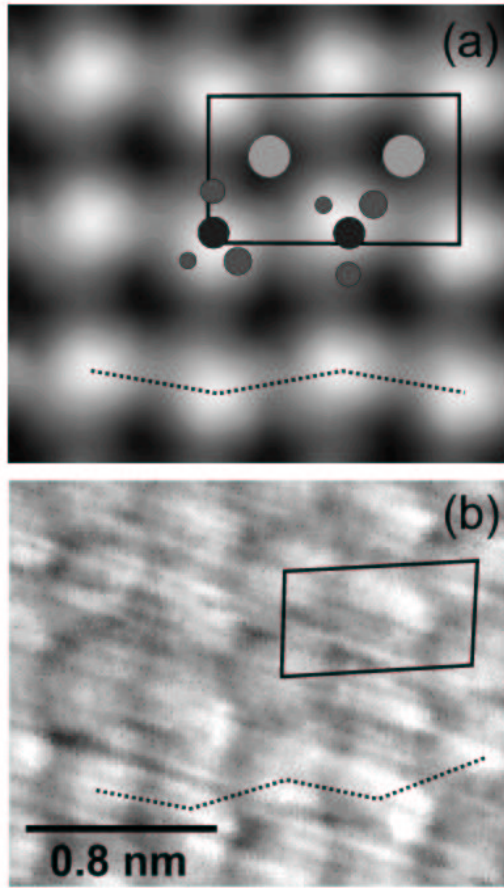


Figure 23 (a) Simulated image of calcite produced using a tip with a positive net electrostatic potential. Atomic colour scheme is the same as in Fig. 22 (b) Experimental image of calcite. .

D. Thin Insulating Films

1. *NaCl-trilayer on Al(111) Surface*

Only a very few facets of the ionic NaCl crystal are stable, in particular the (001) face. This is due to the arrangement of Na^+ and Cl^- ions, which makes such a facet electrically neutral. A (111) facet of the same crystal consists of only one sort of ions, such a polar surface is unstable due to its high surface energy: this facet does not occur in nature. It came therefore as a surprise, when NaCl(111) trilayers on Al(111) were detected in STM images. The atomically resolved images left no doubt that the triangular-shaped islands exhibit a lattice with sixfold symmetry, and a lattice constant corresponding to bulk NaCl (Hebenstreit *et al.*, 1999). The puzzle was resolved by first principles calculation of the electronic structure, which revealed that the Fermi level of the NaCl trilayer is situated in

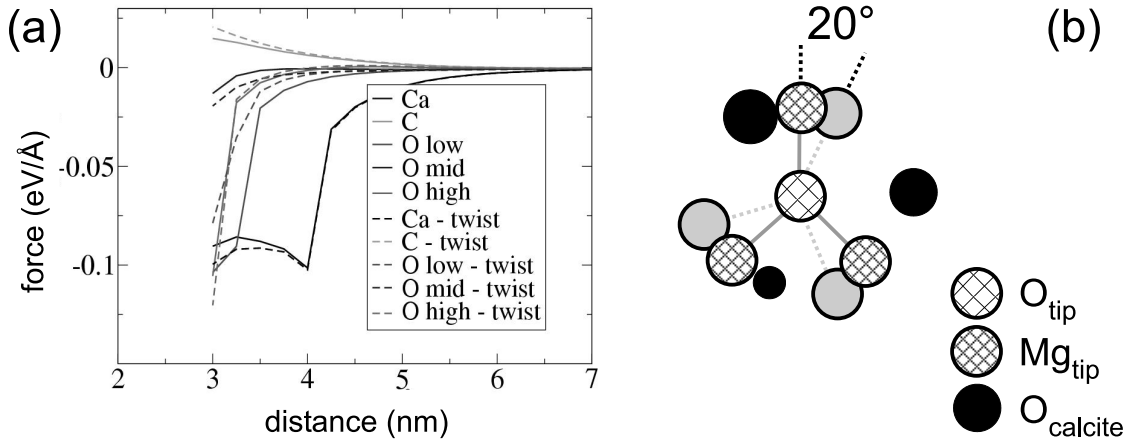


Figure 24 (a) Comparison of the force as a function of tip-surface separation between a normal tip and a tip rotated by 20° around the z-axis. The curves are taken over the various sublattices in the calcite surface, curves labelled 'twist' in the legend are produced with a rotated tip. (b) Schematic showing how the orientation of the projection of the end of the MgO tip on the carbonate group changes when rotated.

the middle of the Na 3s band. Therefore both Na-atoms of the Na-Cl-Na compound possess 0.5e effective charge. In this case the NaCl(111) trilayer is neutral and therefore stable.

2. MgO thin films on Ag(001) Surface

It is technologically important to know the thickness limit for insulating films to remain as insulators. This property is essentially given by the bandgap of the insulator's electronic structure. A system of 1-3 monolayers of MgO on Ag(001) was studied by STM and STS. The images of MgO islands of a single monolayer revealed the underlying atomic structure of the Ag surface (Schintke *et al.*, 2001) (at 30 mV and 2 pA). This feature indicates that one monolayer of MgO is not sufficient to sustain the insulating properties of the crystal. However, the very low current indicates that the transport of electrons from the tip into the sample is already substantially impeded by the MgO layer. The transition from a single monolayer to a bilayer and a trilayer cannot be analyzed by STM, because the conductance in the low voltage regime becomes too low for images with atomic resolution.

Therefore it was analyzed by a combination of STS and electronic structure calculations, in particular the study of the local density of states with increasing surface coverage. As it turned out, three layers of MgO on the Ag surface are sufficient to completely screen the

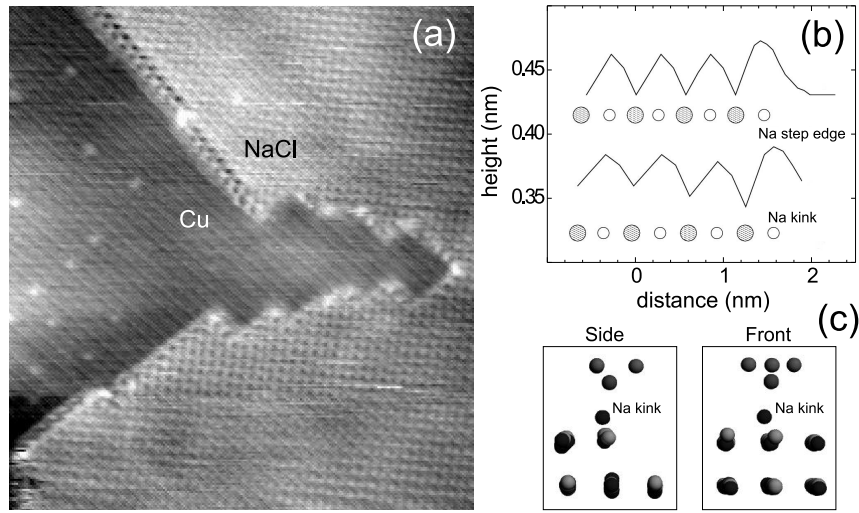


Figure 25 (a) Experimental image of NaCl thin film on Cu demonstrating increased contrast at step-edge and kink sites. (b) Simulated scanlines over Na and Cl kink sites in a NaCl thin film. (c) Atomic snapshots from the simulation as the tip passes the kink site. *Reprinted with permission* (Bennewitz *et al.*, 2000).

electronic structure of the metal. The electronic structure at the surface of the trilayer in this case is already equal to the electronic structure at the surface of an MgO crystal.

3. NaCl Thin Films on Cu(111) Surface

Recent scanning tunnelling microscopy studies of thin insulating films grown on conducting substrates (Fölsch *et al.*, 2000; Glöckler *et al.*, 1996; Hebenstreit *et al.*, 1999) have motivated NC-SFM studies of similar surfaces. Specifically, high quality atomic resolution was achieved on NaCl (001) films on copper substrates (Bennewitz *et al.*, 1999a, 2000). Growth modes, orientation and lattice constants of ultra-thin films were revealed (Bennewitz *et al.*, 1999b) and atomic resolution at step edges was demonstrated (Bennewitz *et al.*, 1999a). Also, the prevalence of low-coordinated sites, such as steps, corners and kinks on these thin films makes them of special interest for catalytic studies and NC-SFM offers the possibility of imaging these features in atomic resolution.

Figure 25(a) clearly demonstrates atomic resolution on the terrace and increased contrast at edges and kink sites of the NaCl island grown on the copper (111) surface (Bennewitz *et al.*, 1999a, 2000). The nature of the enhanced contrast at edges and kink sites has been

explained using an atomistic simulation in Ref. (Bennewitz *et al.*, 2000). For the edge, the enhanced contrast is much more localized directly over the edge ion, whereas a change from standard terrace contrast can be seen several rows from the kink site. This effect is due to the low-coordination of the edge and kink ions, which has two effects: (i) the electrostatic potential over the low coordinated sites extends much farther than over the ideal terrace (Livshits *et al.*, 1999) and, (ii) the low coordination of the ions increases their displacements due to the interaction with the tip. For a tip scanning the surface at 0.45 nm over the terrace, Na ions displaced by 0.014 nm, but this increases to 0.024 nm for Na ions at the step-edge and 0.025 nm at the kink. However, the extremely low-coordination at the kink site means that even the nearest Na neighbour to the kink ion is also displaced by 0.018 nm, producing a stronger and more extended increase in contrast.

These results directly confirmed the importance of the electrostatic interaction and ionic displacements for contrast formation on ionic surfaces. They suggest that even stronger contrast could be observed for charged defects, such as impurities, adsorbed ions and vacancies. However, the low concentration and high mobility of vacancies and some adsorbed species prevent their observation by NC-SFM. Stable aggregates of several di-vacancies have recently been observed on the KBr surface (Bennewitz *et al.*, 2001). Atom-size impurities have been observed on the CaF₂ (111) surface after surface chemical reactions (Reichling and Barth, 1999). However, to image and establish the identity of *individual* surface defects and study their properties has proved extremely challenging.

VI. STUDYING SURFACE PROPERTIES

Some of the most captivating research emerging in the last years deals with fundamental physical processes, and how they can be influenced by the tip-surface interaction. This concerns e.g. phonon-excitations of substrates and adsorbates by injection of electrons, surface magnetism, targeted excitations of spin-rotations, or electron interactions during ballistic transport in solids.

A. Adsorbates on Surfaces

Adsorption on surfaces has been studied with different methods well before the invention of SPMs (Zangwill, 1988). However, due to the real space image of SPMs and their potential to study the processes in real-time, analytical methods become more and more focused on this instrument. In this context it is interesting to determine what an SPM can tell us about the changes electron orbitals undergo during adsorption processes.

1. $C_4O_3H_2$ on Si (100)-(2×1) surface

The question as to whether the STM can in fact resolve single electron states or even the lateral extension of single electron wavefunctions is an intriguing puzzle and, until very recently, the answer seemed to be no. Experimentally, the resolution of electron wavefunctions by STM has already been demonstrated (Lemay *et al.*, 2001). Here, we review a case where only the conjunction of experiment and theory leads to the same conclusion.

The model system consists of maleic anhydride ($C_4O_3H_2$) molecules on a Si(100) surface (Hofer *et al.*, 2002). The Si(100) surface reconstructs in a characteristic (2×1) row of silicon dimers (Hofer *et al.*, 2001b), which is very well researched due to its relevance for the fabrication of microchips (Wolkow, 1999). Therefore the STM images of the adsorbed molecules (Bitzer *et al.*, 2001), depicting the adsorption site between adjacent dimer rows, contain no ambiguity. Experimentally, the main results were: (i) a groundstate adsorption between dimer rows, and (ii) an apparent height of the molecule 0.7 Å (bias voltage - 1.8V), and 1.2 Å (bias voltage - 2.7V).

The surface was initially mimicked by a Si(100)-(2×2) eight layer film. During the surface simulations it became clear that the size of the system was too small - adjacent molecules on the surface exert a very high strain on the lattice, which leads to the rupture of a Si-dimer bond. Energetically this process is very unfavorable. Consequently, simulations were repeated with a (4×2) unit cell, in this case the molecule occupies only every second inter-dimer position and the strain on the lattice and the Si-dimer bonds is substantially reduced. It was found that for a coverage of 1/8 (molecule per dimer) the inter-dimer site is energetically favored, contrary to a chemist's intuition and many examples, where molecules on this surface react via a [2+2] cyclo-addition (Hofer *et al.*, 2002), in other words, they

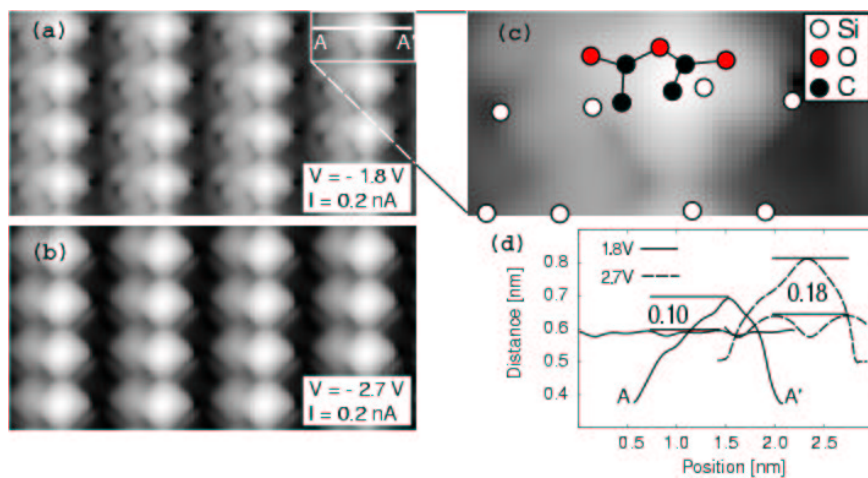


Figure 26 Simulated STM images and linescans of maleic anhydride on Si(100) for two different bias voltages, -1.8 and -2.7 V, respectively. (a) Simulation of the current contour for 1.8 V and 0.2 nA, the molecule is seen as a distinct protrusion. Due to the size of the molecule simulated current contours on adjacent cells overlap. (b) Simulation of the current contour for 2.7 V and 0.2 nA, the qualitative features of the image remain unchanged. (c) Enlarged unit cell with the position of the molecule. (d) Simulated linescan across the molecule. The apparent height changes by $0.8 \text{ \AA}$, if the bias voltage is increased from -1.8 to -2.7 V. *Reprinted with permission* (Hofer *et al.*, 2002).

adsorb on top of a silicon dimer. The STM images, recorded with a tunnelling current of 0.5 nA, were simulated by assuming that the structure of the microtip in the apex was akin to a tungsten pyramid in (100) orientation. The simulated STM images and linescans are displayed in Fig. 26. Clearly, if the bias potential is increased by 0.9 V, the apparent height of the molecule on the surface changes by about $0.8 \text{ \AA}$. The simulated results agree well with the experimental ones, since the difference in experiments is $0.5 \text{ \AA}$. To understand the difference, it was necessary to analyze the electronic structure of the molecule and the silicon surface. The density of states (DOS) of the surface-adsorbate system shows three distinct peaks at -0.6 (1), -1.8 (2), and -2.4 eV (3). Plotting the charge density of these states, it was found that only two of them, (1) and (3), protrude into the vacuum above the molecule. Since the tunnelling probability depends on the overlap of wavefunctions between sample and tip, a high local density of states in the vacuum above the molecular position indicates a high contribution to the tunnelling current from this state. It turned out that the most significant contribution to the increase of the apparent height due to the increased bias potential is due to only one state (3) of the molecule. The increase of the bias potential

from 1.8 to 2.7 V is therefore in effect a tuning in on the energy range of a single molecular orbital.

2. O on Fe (100) surface

The question as to how the electric field of the STM tip affects the vacuum barrier of the surface electronic structure, and thus the decay length of the tunnelling current has been a widely discussed topic since the invention of the STM (see previous sections). In particular the role of image forces, which should lead to a lowering of the potential barrier, remained unclear (Binnig *et al.*, 1984; Lang, 1988). Related to this problem is the question of when a perturbation approach to tunnelling becomes insufficient. In general, the regime of field interactions is not accessible to STM experiments, as will be seen. However, by measuring a 3-dimensional map of currents on a Fe(100) surface in such a way that the tip-position is adjusted manually by a change of the piezo-voltage, the transition from the tunnelling regime to point contact can be studied experimentally (Hofer *et al.*, 2000b). From the 3D current map the corrugations can be extracted in a straightforward manner. In addition, the apparent height of atoms can be determined by adsorbing e.g. oxygen on a surface. Since the position of the adsorbant is known (e.g. for oxygen on Fe(100) the preferred site is the fourfold hollow site), its position with respect to the maxima and minima of the constant current contour can be determined. The measurements revealed the following behavior: (i) the positions of the Fe atoms on the surface are imaged as protrusions for $z \geq 0.4$ nm, (ii) these positions are imaged as depressions if $z \leq 0.4$ nm, (see Fig. 27) (iii) the corrugation height is in all cases very small and below 0.002 nm, and (iv) the 3D current maps were generally obtained with a stable tip and in one single sweep. The absolute distance in the experiments was determined by extrapolating the currents from two separate point measurement to the point of contact, defined by a conductance of $2e^2/h$, the conductance quantum.

The measurement with a stable tip suggested that the tip was not contaminated. For this reason the STM tip chosen in the simulations was a clean tungsten tip. Since the surface orientation at the apex of the polycrystal is *a priori* unknown, simulations were performed with all three low index surfaces, (100), (110), and (111). The surface electronic structure of sample and tip were calculated with a full potential DFT code (Hofer *et al.*, 2000a), with

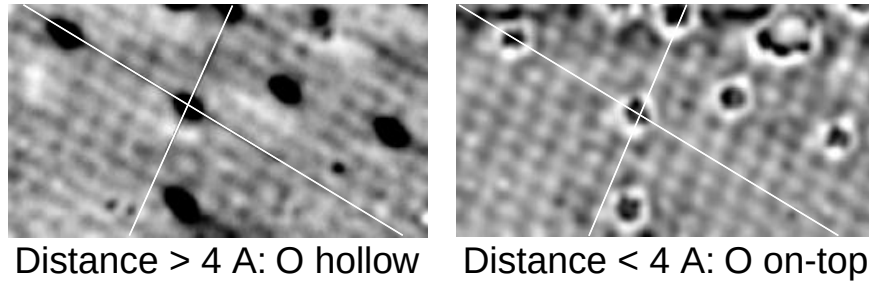


Figure 27 STM images of Fe(100) with an adsorbed oxygen atom. Oxygen appears to be adsorbed at the hollow site of the surface for distances above 4 Å (correct), but it appears to be at the on-top site for distances below 4 Å (incorrect). The conclusion from the experiments is a reversal of surface corrugation in the low distance regime. *Reprinted with permission.* (Hofer *et al.*, 2000a)

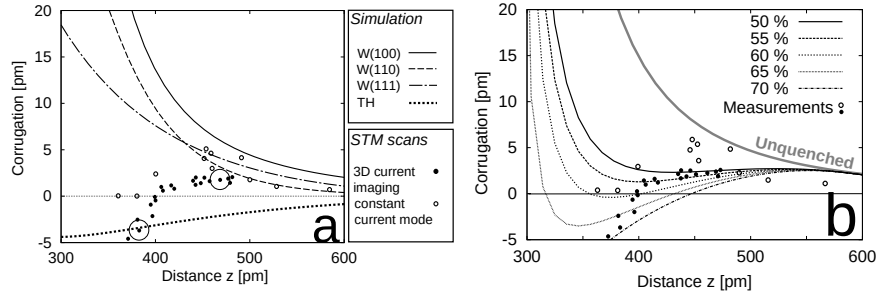


Figure 28 Simulated corrugation of Fe(100) surface with three different tungsten tips, as well as a model tip of radial symmetry (Tersoff-Hamann model (TH)) (a), and simulation of scans of the same surface if the surface states are quenched due to the STM tip potentials (b). The quenching of surface states due to the tip in the very close distance regime leads to a corrugation reversal, which is actually observed in the experiments. *Reprinted with permission* (Hofer *et al.*, 2000a).

the surfaces represented by free standing films in a vacuum. The results were also checked with a Fe terminated tungsten tip, but in this case agreement was not obtained between experiments and simulations, therefore this tip model was ultimately excluded.

The current was calculated for nine positions of the STM tip on the Fe(100) surface: the top site, the bridge sites, and the hollow sites. From the distance dependent current curves the corrugation amplitudes were extracted. The results of the calculations are shown in Fig. 28(a). The first conclusion to be drawn from the simulations is therefore that the tip most likely used in the experiments was a clean tungsten tip. The positive corrugation on an anticorrugated surface in this case arises from the high contribution of d_{xz} and d_{yz} states in the electronic structure of the tip. This, in itself, is one more confirmation that

the electronic structure of tungsten tips is not accurately described by a single orbital of d_{z^2} symmetry (Chen, 1990a,b).

While the simulation agrees well with the experimental results in the distance range above 0.4 nm, it does not agree at all in the distance regime below 0.4 nm. Experimentally, the positions of the Fe atoms are imaged as depressions, in simulations they appear as protrusions. The reason for this obvious disagreement can only be that the tip interacts with the surface. Neglecting the effects of chemical forces, since they generally lead to a corrugation enhancement and thus would further increase positive corrugation, the only possibility is that the field of the tip influences the surface electronic structure. This effect can be simulated by an applied bias potential on the Fe(100) surface. On Fe(100) a substantial contribution to the tunnelling current originates in a surface state near the $\bar{\Gamma}$ -point of the Brillouin zone (Stroscio *et al.*, 1995). Surface states are generally an expression of the boundary conditions at the vacuum boundary of a crystal. Their existence thus depends on the existence of this boundary. If a tip approaches the surface then the tip-potential will gradually lower the vacuum potential barrier. The surface layer gradually loses its surface characteristics, this leads to the loss of surface states. In principle, such a behavior can be simulated by a distance dependent quenching of the surface state density. Since surface states on Fe(100) are states in the minority spin band, we have simulated the quenching by reducing the contributions from the minority band during an approach. Numerically, this was done by a polynomial of second order. The results are shown in Fig. 28(b). The percentage describes what part of the minority states density was quenched in the simulation for a distance of 0.3 nm. Comparing experiments with simulations we see that a quenching of about 50%-70% is sufficient to reproduce the measurements.

B. Point defects

As discussed previously, identifying surface defects is a difficult, but very desirable objective. Topographic SFM images help if there is a reliable theoretical 'portrait' of each defect for comparison. For example, a theoretical image of an Mg^{2+} ion - cation vacancy pair on the surface of LiF has been calculated in Ref. (Livshits *et al.*, 1999). However, unambiguous identification needs more information. Moreover, for typical concentrations and typical scanning areas ($50 \times 50 \text{ \AA}$), one is unlikely to encounter more than one defect

of each kind. Measuring optical absorption usually only confirms the presence of a certain defect within the sample. To identify a *particular* defect, one must correlate topographic and spectroscopic signals, e.g. by perturbing defect excited states by the SFM tip. Specifically, the SFM probe can alter the balance between radiative and non-radiative defect processes. Scanning nearfield optical microscopy aperture probes fabricated using conventional optically transparent SFM tips allow one to obtain topographic images and *simultaneously* excite surface nano-scale species and collect luminescence in near-field (Nishikawa and Isu, 1999). Very small specially shaped apertures already in use (20 nm, across which is several times smaller than a typical distance for most impurities) should allow one to get an optical signal from isolated defects.

First theoretical calculations which correlating a topographic and luminescence images of the same impurity defect have been performed in Refs. (Kantorovich *et al.*, 2000b, 2001). They predict a characteristic topographic image of the Cr^{3+} impurity centre at the MgO surface in NC-SFM and a pronounced effect of the SFM tip on its optical properties. The two effects can be correlated, e.g. through observation of an enhanced luminescence signal and energy shift when the tip is probing the defect centre. The predicted effect would be even stronger for excited defect states which are less localised than those of the Cr ion considered in Refs. (Kantorovich *et al.*, 2000b, 2001). In systems with excited state lifetimes exceeding the tip oscillation period, changes in the topographic image with electronic state could be observed.

C. Surface Magnetism

It is quite fashionable to explain the interest in magnetism, especially on the atomic scale, with the giant investments taken in the computer industry to produce reliable and small scale storage devices (Shen and Kirschner, 2002). Quite apart from this application viewpoint, there is also a scientific interest in the way magnetic properties change with a change of the physical environment. So far, experimental research in this area has been hampered by the low resolution of existing methods (in the range of about 50 nm (Stöhr *et al.*, 1999)). The combination of experiments with a spin-polarized STM or SFM, and refined theoretical models greatly enhance the possibility and quality of data at this extreme limit of resolution.

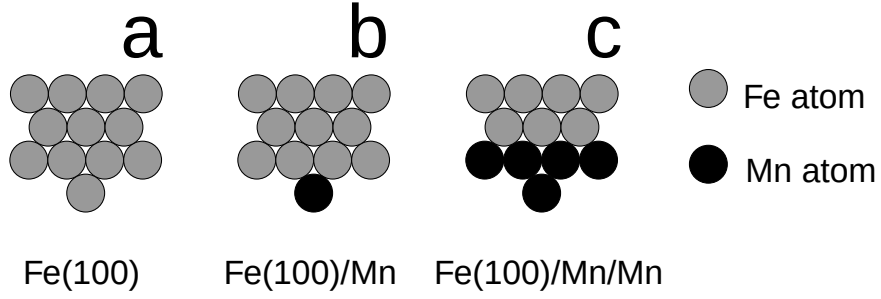


Figure 29 STM tip models for spin-resolved measurements. The tip model consists of a five layer Fe(100) film with (a) a single Fe apex atom, (b) a single Mn apex atom, or (c) a Mn layer and a single Mn apex atom. These models mimic a clean ferromagnetic tip or a tip contaminated by surface atoms.

1. Mn Surface

The STM tip in the experiments consisted of a tungsten polycrystal (paramagnetic tip) coated with ten to twenty layers of iron (ferromagnetic tip). In addition, contamination of the tip by atoms of the sample surface (manganese) cannot be excluded, especially in view of the high tunnelling currents of about 40 nA at very low bias voltages of 3 mV (Heinze *et al.*, 2000). For this reason a number of separate tips have to be included in the analysis (Hofer and Fisher, 2002b). The most important ones are: a clean Fe tip, mimicking the polycrystal W wire coated with Fe; a Fe tip contaminated by a single Mn atom (low contamination of the tip); a Fe tip contaminated with a surface layer and a single Mn atom (high contamination of the tip). On the technical side we note that the free standing film consisted of five layers with (100) ordering and two additional layers for the apex. The STM tip models are displayed in Fig. 29.

Image simulation

The angle ϕ_M (30) in the experiments is in general unknown. Therefore images for all possible angles have to be simulated for a comparison with experimental images. But this also means that a unique map from angles ϕ_M to corrugation amplitudes can be used to determine the actual angle from the apparent height of the atoms on the surface. We omit displaying the simulated image for the paramagnetic tip model, it is published in (Hofer and Fisher, 2002a).

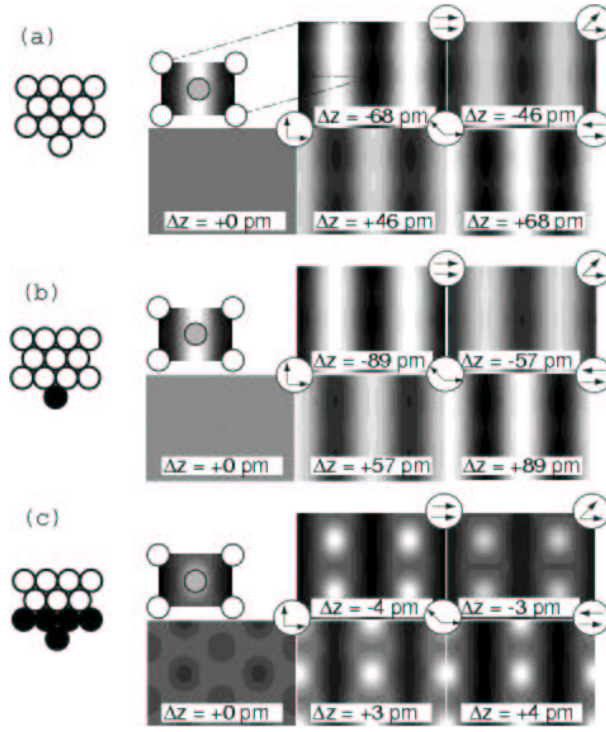


Figure 30 Simulated STM images of W(110)Mn for three different STM tip models and a range of angles ϕ_M between the magnetic axis of sample and tip. The simulations with a clean tip (a) and a slightly contaminated tip (b) reveal a surface corrugation well in excess of experimental values, while the highly contaminated tip provides the best agreement with experiments (c). *Reprinted with permission* (Hofer and Fisher, 2002a).

In practice two separate simulations were performed for every single tip model and the antiferromagnetic Mn overlayer: one simulation for ferromagnetic ordering in the tunnelling transitions ($I_F(x, y, z)$), and one for antiferromagnetic ordering ($I_A(x, y, z)$). The two separate current maps were then compiled into a single image by defining an angle ϕ_M from the outset. In Fig. 30 we show the images with three different tips at a median distance of 0.45 nm (lower limit of stability).

The most remarkable result is the strong dependence of the apparent height of single atoms on the contamination of the STM tip. This is most obvious for the transition from a tip with low contamination (one Mn atom on a Fe(100) surface) to a tip with high contamination (one Mn atom and a surface layer on the surface). The position of individual atoms is only resolved in the simulated images with a highly contaminated surface. The decrease of the apparent height between the atoms has also been observed in the experiments. This is not the case for the clean Fe-tip and the tip with low Mn-contamination. In those cases the

relative variation of the constant current contour is too low to be observable. The results prove once again, that tip contamination plays a crucial role in the quantitative results obtained in STM experiments. The second point of interest, especially for experimentalists, is the high magnetic contrast of the surface. Considering that close packed metal surfaces like Mn or Fe are notoriously difficult to image, a coating of the tip by magnetic layers may improve the contrast by more than one order of magnitude. It is also evident that the magnetic contrast vanishes, if the magnetic axes of the two surfaces are perpendicular. This entails a strong dependency of the magnetic contrast on ϕ_M , which in turn can be used to study the effect of impurities on the atomic scale and in real space.

2. NiO Surface

Due to the well-defined magnetic surface structure and the ease of preparation of an atomically clean surface (Henrich and Cox, 1996), most atomic scale magnetic studies in SFM have focused on the anti-ferromagnetic nickel oxide (001). The magnetic properties of NiO are well known and various techniques have established the antiferromagnetic AF₂ structure as the most stable with each Ni ion having 2 unpaired electrons (Terakura *et al.*, 1984).

As yet, no difference in contrast over opposite spin Ni ions has been observed in NC-SFM (Hosoi *et al.*, 2000) with magnetic tips. This directly motivates a theoretical study to investigate whether it should be feasible to measure the difference in the exchange force over NiO in an experiment and also to establish the criteria for success. Several previous theoretical studies have focused on calculating the magnitude of the exchange force over simpler, metallic magnetic surfaces, such as Fe (Nakamura *et al.*, 1997), Cr and Ni (Ness and Gautier, 1995), and it is therefore difficult to compare them directly with imaging of NiO.

The most spectacular way of experimental demonstration of the effect with NC-SFM would be to measure a difference in contrast along parallel rows of Ni ions with anti-parallel spins. However, since the surface sub-lattice seen as bright in images is unknown *a priori*, this cannot be the only way. A possibly more promising approach could be to measure force vs. distance curves above different surface sites. This is within the reach of low-temperature NC-SFM (Lantz *et al.*, 2000), but requires very high sensitivity, low signal to noise ratio and

good statistics. The latter implies repeating these measurements many times over different sites with the same tip. The short-range of the exchange interaction means that to reliably measure the difference one may need to advance a tip very close to the surface. This may lead to instability in SFM operation caused by too strong tip-surface interaction and by large displacements of the surface/tip atoms and their adhesion to the tip/surface (Livshits *et al.*, 1999). This in turn may lead to tip crashes and prevent reproducible measurements with the same tip.

Combined atomistic simulations and *ab initio* Unrestricted Hartree Fock (UHF) calculations (Foster and Shluger, 2001) of the interaction of various model magnetic tips with the NiO surface demonstrated that it should be feasible to measure the difference in exchange force over opposite spin Ni ions. The calculations predicted an maximum range of 0.375 nm for detecting the difference with resolution appropriate to a modern low temperature NC-SFM. However, they also suggested that much greater success would be achieved with tips that weakly chemically interact with surface, thereby greatly reducing scanning disruption due to ion jumps. Current experiments favour iron coated silicon tips, but iron is well know to strongly interact with oxide surfaces (Henrich and Cox, 1996).

The study also highlighted the fact that the extreme sensitivity of the low temperature NC-SFM means that it can atomically resolve the surface via microscopic forces at distances much farther than normal NC-SFM. The atomic contrast in frequency change predicted by modelling of the CaF₂ surface (Foster *et al.*, 2001a) was still about 0.2 Hz at 5.0 Å, so a low temperature NC-SFM could potentially measure atomic contrast at tip-surface separations in this range. This is too far for the difference in exchange force over spin up and spin down Ni ions to be measured, and in real low temperature NC-SFM experiments atomic resolution of the difference in microscopic force over O and Ni ions will be achieved before it is possible to measure the difference in exchange force over Ni ions. Successful imaging of the exchange force will require first achieving atomic resolution on the surface of NiO, at distances where opposite spin Ni ions appear identical in images. Then the frequency change should be gradually increased to reduce further the shortest tip-surface separation until the exchange force can be measured. This procedure is extremely difficult, but has already been achieved with room-temperature NC-SFM techniques on the CaF₂ surface (Barth *et al.*, 2001) and most recently on the NiO (001) surface itself (Schwarz *et al.*, 2002). However, the absence of exchange contrast suggests that either surface ion instabilities are occuring too early in the

tip’s approach or the magnetic properties of the tip are not yet fully controlled.

D. Spin-manipulation

The most frequently employed STM-tips consist of paramagnetic metals (tungsten, platinum or iridium), where the tunnelling current possesses no spin-selectivity. This can be changed in two separate ways: (i) Either the signal from a specific spin state is periodically modified by external magnetic fields, or (ii) the tip is coated by ferromagnetic or antiferromagnetic metal layers. In case of (i), the periodic component of the tunnel current is filtered out by lock-in amplifiers, and the spin-signal is directly detected with atomic-scale resolution. A demonstration of this method has recently been given by Durkan and Welland (Durkan and Welland, 2002). In the experiments the spin-states of free radicals in an organic molecule were made to precess around the axis of a low-intensity magnetic field with the Larmor frequency. This signal was subsequently isolated in the periodic tunnelling current. As images show, the spin-states of the molecule can be resolved with about 1 nm resolution. Coated tips are used in either spectroscopic or topographic images of magnetic surfaces, in particular ultrathin magnetic films of one or two layers thickness. The potential of the method has been demonstrated for single and double layers of 3d ferromagnetic metals (Fe,Mn) on flat or vicinal W(110) surfaces (Pratzer *et al.*, 2001; Wiesendanger and Bode, 2001). Theoretically, these experiments cannot yet be described by fully quantitative models. Given the importance of magneto-electronics for industrial applications, this situation is not expected to prevail for too long.

E. Phonon excitations

One aim of surface chemistry is to determine how adsorbates bond to a surface. This can be done by comparing STM topographies and simulations, and by studying the shape of a molecule in both images (Sautet, 1997). But this method is quite frequently not precise enough to unambiguously identify an adsorption site. As surfaces are more and more tailored for particular purposes this ambiguity needs to be overcome. One method to this end is vibrational spectroscopy, which more and more STM groups are routinely employing. Here, the bias voltage modulation at the resonance energy of a rotational or vibrational mode of

either the molecule or the chemical bond between molecule and surface produces a distinct current spectrum, which can be directly related to the position and the bonding geometry of a molecule (Lauhon and Ho, 1999; Stipe *et al.*, 1999). The theoretical simulations of the method so far are based on the electronic structure of the surface and molecule alone, and no first principles simulation of the current and spectrum exists to date (Lorente and Persson, 2000a,b).

F. Electron dynamics

The dynamics of electrons at surfaces and interfaces are studied within many-body theory. Of particular interest are studies of interference effects on surfaces due to scattering at step edges or atoms of a "quantum-corral" (Braun and Rieder, 2002; Bürgi *et al.*, 2000; Heller *et al.*, 1994). The decay of the interference pattern, e.g. with increasing distance from a step-edge, is an indication of electron-electron and electron-phonon interactions, which reduce the phase memory of the electron. In the context of Fermi-liquid theory this measure is related to the lifetime of a quasi-particle (Bürgi *et al.*, 2000).

Electronic and transport properties of interfaces, buried beneath the surface of a crystal, are often studied by a modified STM based on the principle of ballistic transport (de Andres *et al.*, 2001; Bell and Kaiser, 1996). Initially invented to study the Schottky barrier (Zangwill, 1988) of a metal-semiconductor interface (Bell and Kaiser, 1988) it is currently employed to gain a systematic understanding of electron-electron interactions in solids. The most advanced theoretical models in this field are based on the non-equilibrium Greens function formalism of Keldysh (de Andres *et al.*, 2001; Keldysh, 1965).

VII. CONCLUSION AND OUTLOOK

Quantitative methods developed for analysis of SPM images reflect the change of the field from the earliest experiments on Si(111) surfaces until today. The cutting edge in theory is now an exact description of currents, forces, and inelastic effects. The most striking results are achieved where experiment and theory can combine to really reveal the atomic processes being imaged. However, this requires immense sophistication from both sides and has so far rarely been achieved. Further progress in this field should eventually allow us to study

not only surface topography, but also surface dynamics, excitations, and chemical processes. An essential ingredient to the successful characterisation of any surface process remains the development of methods for a quantitative comparison between theory and experiment.

Although the theoretical methods used to simulate SPM can vary widely, the most important simplifications include the inability to treat truly the real structure of the tip. Even though theoretical analysis has proved to be very useful in determining the tip sample separation in STM and SFM experiments, it still remains problematic in both techniques. As yet no reliable error estimation of simulation methods exists. Tip and surface atomic relaxation have proved to be so crucial to imaging that they are increasingly included. Only in this way can the distance dependent contrast observed in both STM and SFM be accounted for.

Finally, we note that parallel analysis of STM and SFM the presented in this work clearly demonstrates many similar features. With the development of combined STM/SFM machines both techniques will come even closer together and, with a little cross-fertilisation by theoretical insight, will serve as increasingly powerful tools in surface and nano-science.

Acknowledgements: ASF and ALS would like to thank C. Barth and M. Reichling for their extensive collaboration and advice. We would like to thank W. Allers, T. Arai, A. Baratoff, R. Bennewitz, A. Biedermann, T. Bitzer, M. Bode, J. Cerda, A. Fisher, J. D. Gale, F. Giessibl, H. Guo, H. Hölscher, H. Hug, R. Hoffmann, L. N. Kantorovich, G. Kresse, E. Meyer, H. Ness, C. Pang, R. Perez, R. Podloucky, J. Pethica, J. Polanyi, R. Raval, J. Redinger, N. Richardson, A. L. Rohl, N. Sasaki, M. Schmid, U. D. Schwarz, R. Stadler, G. Thornton, M. Tsukada, P. Varga, R. Wiesendanger and R. Wolkow for useful discussions during the course of this work. We are grateful to S. Fain, P. Gruetter, A. Schwarz, K. Stokbro and A. M. Stoneham for helpful comments on the manuscript. ASF has been supported by the Academy of Finland through its Centres of Excellence Program (2000 - 2005). We are grateful to EPSRC and the British Council for financial support.

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