Quantitative modelling in scanning probe microscopy

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Abstract

Significant progress has been made in the theoretical modelling of scanning probe microscopy. The models available now are sufficiently refined to provide information not only about the surface, but also the probe tip, and the physical changes occurring during the scanning process. This has significantly improved the quantitative analysis of experimental and theoretical results. Scanning probe microscopes can now be reliably used to analyse events on the level of single atoms and single electrons. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Scanning probe methods (SPM) have developed into one of 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. Sophisticated theoretical approaches proved to be an essential ingredient in any progress made. The aim of this paper is to review and compare theoretical modelling of two of the most popular SPM methods — scanning tunneling microscopy (STM) and scanning force microscopy (SFM) — in conjunction with their applications to studies of surface properties with atomic resolution. The research done today in this field can broadly be divided into three areas:

1. the chemistry of surfaces, including relaxations, reconstructions, and ordering;
2. the chemistry of adsorbates, including bonding sites, reaction pathways, and chemical reactions/dissociation;
3. the physics of surface electrons, plasmons, vibration, and bond formation.

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 Tersoff–Hamann approach [1] has provided some insight into the imaging mechanism, yet even so, most experiments still rely on direct simulation for their interpretation. For SFM, no simple model yet exists and all interpretation is based on direct simulation. It is by now fairly common that experimental results are routinely simulated by advanced theoretical methods. This contradicts the original theoretical ideal of a simple theory for image interpretation and perhaps reflects the extreme complexity of the experimental techniques. Once it became clear that SPM techniques were not limited to gaining information on topography, theoretical simulations have rapidly evolved to keep up with the aspects of physics being probed, and have moved away from presenting an overall model which includes all possible imaging interactions. This feature, in turn, has shaped the field in the last years. Moreover, 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.

In light of this, it is important to review the quantitative level that has been reached in modelling of these techniques, and establish the quantity and quality of physics

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that can be extracted from images by combining experiment and theory.

2. Experiment and theory

Information about surface properties is obtained in STM and SFM by monitoring different types of interaction between a tip attached to a cantilever and the surface under study. The main differences between SPM modelling and, for example, studies of adsorption, adhesion or cluster growth at surfaces is that: (i) the SPM tip is a macroscopic object and is very rarely in force or thermal equilibrium with the surface; (ii) the measured physical parameters are the tunnelling current and the force of the tip–surface interaction at different tip–surface separations; (iii) the system coordinate space for calculating an image is much larger than that for adsorption at particular sites; and (iv) many events observed experimentally are unique and are not subject to statistical averaging.

In STM, the variations of tunnelling current are mapped as the tip scans the surface. In SFM, an image is detected by measuring cantilever deflections due to the tip–surface forces. To study the local surface electronic properties one can use tunnelling spectroscopy, i.e., to measure the tunnelling current as a function of applied voltage at fixed tip lateral positions [2]. To study adhesion between tip and surface, one can measure the dependence of the force on the distance between the SFM tip and surface at fixed lateral tip positions, which is called force spectroscopy [3]. To image the surface topography one monitors normal cantilever deflections as the tip scans the surface continuously along some trajectory. This information is processed and presented in the form of three-dimensional topographic maps, which are interpreted as a surface image. The experimental set-up in SPM experiments commonly depends on the research field. For the chemistry of surfaces most groups use a room temperature STM or SFM, however, low- and high-temperature equipment is also available. The microscope in these measurements is in an UHV chamber, an additional vacuum chamber is used for surface preparation: sputtering, annealing, doping, or crystal growth.

The aim of theoretical modelling is 2-fold: (i) to provide an understanding of the basic principles of operation of both techniques; (ii) to give interpretation of particular experimental images. Although the first of these aims has been largely achieved, quantitative comparisons between theory and experiment are hampered by the fact that many vital experimental details are unknown or cannot be reliably established. These include:

- the atomic structure of the tip apex;
- the effect of the bias potential on the electron states of sample and tip, provided the tip structure is known;
- the actual distance between tip and sample which is not directly measurable;
- the rearrangement of atoms and the changing of bonding configurations due to the interactions between tip and sample;
- in STM, the effects of confinement of the electrons in the tunnelling process to the very small region between tip apex and sample surface;
- in STM, the inelastic electronic effects related to dynamic changes during a high resolution scan.

In reality, not even all the known effects can be included in the theoretical treatment on an equal footing. This motivated a strategy focusing on the most important determinants of the actual characteristics measured. Another issue concerns quantitative comparison between theory and experiment. 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. The latter can be based on the tip–surface distance because this is the main parameter determining the absolute values of the tunnelling current and of the tip–surface interaction. However, the tip–surface distance is poorly defined experimentally. Therefore direct comparison between theory and experiment still entails many difficulties.

2.1. Scanning tunnelling microscopy

In STM modelling, the calculated parameters are the corrugation of a surface in an image, the tunnelling current at a given bias potential, and, in very recent experiments, also vibrational spectra. The tunnelling current and the force between tip and sample are rarely measured and calculated simultaneously. There is evidence today that under normal tunnelling conditions fairly good quantitative agreement can be obtained by concentrating theoretical efforts on the surface regions of sample and tip, and by neglecting atomic rearrangement, inelastic effects and the changes of electron states due to the bias potential.

Most of the theoretical methods used in STM modelling differ in the way they balance the accuracy of treating the surface and tip electronic structures, and electron tunnelling. Generally speaking, the theoretical techniques can be characterised by their treatment of (a) the scattering of electrons, and (b) the electronic structure of the leads. No technique available today treats both of these aspects of a tunnelling junction with theoretical rigour. The reason is that scattering approaches commonly rely on a Green's function formalism, which requires the Hamiltonian of a system. If both sides of the junction are treated on an equal footing, then the Hamiltonian of the coupled system must be known. And given the limitation of density functional

theory, it is either constructed by semi-empirical methods (extended Hückel molecular orbitals, as in Ref. [4]), or the exact treatment is limited to only one side of the junction, while the other side is treated as a single orbital [5]. The approaches focusing on the electronic structure of the leads [6], or of the sample surface alone [7] employ a perturbation approach to describe the tunnelling electrons.

One of the primary roles of STM is to study relaxation, reconstruction and ordering of surfaces with high resolution. However, most of these phenomena are long ranged. In particular, surface reconstructions can lead to very large unit cells, and segregation effects play a major role in the formation and ordering of single layers. In consequence, theoretical models of these processes are still beyond the reach of ab initio methods. While the literature about experiments abounds in this field, simulations are nearly always limited to semi-empirical methods. A first principles simulation of island growth, for example, has only recently been undertaken using DFT and Monte Carlo methods [8]. Alloying, as far as it concerns interactions between nearest neighbours, can be treated with advanced theoretical means. Studies showing the effect of PtRh(100) alloys on STM imaging have recently been published [6,9], but in this case the results were obtained with very expensive full potential calculations. The quantitative agreement between observed and simulated corrugations is in the range of 20%. For the wider field, treating reconstructions and segregation in conjunction with STM imaging, the perspective is less favourable. Given the limitations of DFT, we do not expect significant changes in the near future.

The chemistry of adsorbates, and related topics, is the field with the greatest overlap of experimental and theoretical work. The main reason is the short range of effects, which mostly concern only nearest neighbours. Experimentally, reactions on metal surfaces are usually studied with low-temperature STM, operating in a range below 10 K [10,11]. There exists a wide range of experimental work on this topic, because catalytic reactions are of crucial importance in industrial applications.

The first quantitative theoretical methods used in this field were developed by Sautet and Joachim [12]. They are treating the vacuum barrier between the metal/adsorbate and the STM tip as an impurity in an infinite system. Initially, their method was limited to identical crystals on both sides of the junction, but this limit was removed by Cerda et al. [4]. Due to the use of atomic wave-functions in the vacuum range, the method encounters some problems in the exponential decay of the vacuum tails. The prediction of distances between the STM tip and the sample is therefore not all too reliable. In essence, one either reproduces the current or the corrugation of an experiment, but not both. On the other hand, the method involves a theoretically advanced treatment of the tunnelling process via surface Green's functions and a scattering matrix approach. In principle it should therefore be applic-

able to all distances and currents. Sautet [13] and his co-worker have simulated a number of atomic adsorbates on Pt(111) surfaces and analysed their appearance in STM images. Further research was devoted to CO on Pt(111) [14], and the dissociation of O_2 molecules on Pt(111). They also studied imaging of benzene on Pt(111) [13]. Given the results it seems that the method is precise enough to resolve the adsorption site of molecules on surfaces. However, the error margin is hard to quantify. Because distances are uncertain, it contains an arbitrary parameter in the choice of the distance of evaluation. Since the actual distance in STM experiments is not precisely known, one has to resort to other methods to clarify this point.

In their recent review Briggs and Fisher gave an exhaustive overview of theoretical and experimental methods [15]. They compared experimental results of small molecules adsorbed on Si(001) and GaAs(001) with a theoretical model based on a Green's function approach developed by Ness and Fisher [5]. In particular they could show the polarisation of electronic surface states by the electric field in the tunnel junction. However, due to the approximate coupling of electron states to the reservoirs, the method cannot provide absolute values for the conductance and thus the tunnelling current.

Hirose and Tsukada [16] have developed a more advanced non-perturbative and self-consistent method for STM modelling. Its setup consists of a few atomic surface layers on both sides of the vacuum barrier. The leads of the tunnel junction are simulated with a jellium model. In their model they obtained a distance of 5 Å, for the point where the potential barrier between an STM tip and a sample surface breaks down. It is unclear whether the same distance would apply to other atoms, specifically to the 5d tungsten atoms, of which the tip is usually composed.

The chemical nature of the apex atom is a decisive influence in the quantitative results of STM scans, as has been shown by Hofer and Redinger [6]. The authors used a perturbation approach to tunnelling based on first principles methods for calculating the one-electron wave-functions of sample and tip. In this model the two crystals of the junction can be treated more accurately using plane wave density functional based methods, while the probability of tunnelling is described by the overlap between the wave-functions on either side of the junction. The authors obtain quantitative agreement with experiments provided the distance between tip and sample is large enough. From model calculations of Fe(100) they give as the closest range of approach the distance of 4–4.5 Å [17]. Only below this range is the change of the electronic structure due to interactions sufficiently high to effectively quench the surface states of the sample. Their results suggest, furthermore, that STM experiments on metals are usually performed with a tip contaminated by an atom of the sample [6]. This assumption is so far based only on comparisons between experimental and theoretical results.

Whether it is a general feature of STM scans on metals can only be decided on the basis of scans, where the chemical nature and the geometry of tip and sample in the experiments are known.

One of the main problems of theoretical analysis is that many experiments themselves do not provide unbiased statistics of the events on a physical level. This point becomes more critical the less data for analysis there is. The problem is rapidly becoming a real issue in vibrational spectroscopy, where single excitations occur on a time-scale of seconds and even hours. Research of these subtle effects has traditionally been theory-biased, because quantitative results in experiments seemed beyond obtainable precisions. With the improvement of low temperature STM, especially concerning the stability against thermal drift, the situation has changed in the last years. It is now possible to measure single-mode excitations at atomically defined locations. Among these effects, tip-induced dissociation and desorption are certainly the most striking examples of an STM's ability to manipulate and change surfaces on a single atom basis [18,19] (see Fig. 1). In these experiments the bond of single atoms is directly affected, either by inelastic electron tunneling [18] or by inelastic scattering of holes [19].

A theoretical model of general applicability has recently been introduced by Lorente and Persson [7,20]. They focused on quantitative methods to describe inelastic tunneling processes. The method is based on a resonance model for electronic structure of surface and adsorbate, and non-adiabatic electron-vibration coupling. While the technique of vibrational spectroscopy is experimentally very demanding, it could ultimately, in connection with theoretical models, provide a more detailed picture of chemical
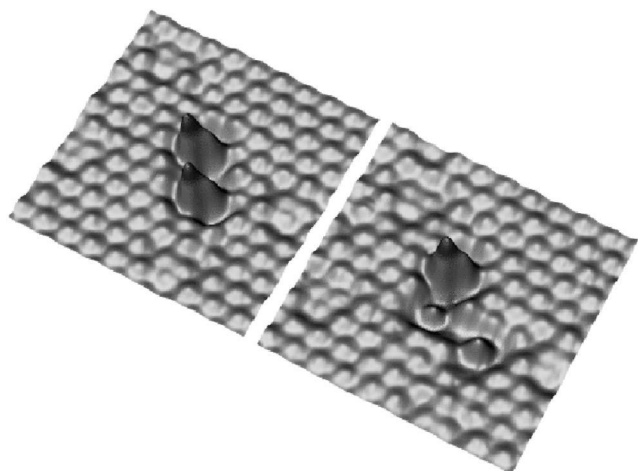

Fig. 1. STM images of tip-induced dissociation of an oxygen molecule. Two oxygen molecules are adsorbed on a Cu(110) surface (left image). The STM tip is positioned above one molecule, and a single pulse of 0.3 V lasting a few milliseconds is sufficient to break the bond of the molecule. The molecule is dissociated into two oxygen atoms (right image). Courtesy of W. Ho.

processes. The authors could show that inelastic tunnelling is highly localised and due to changes of the tunneling amplitude in the vicinity of vibrational states of the molecule. In detail it was shown that agreement between experiments and theoretical results can be obtained for CO on Cu(100) [7,21] and C_2H_2 on Cu(100) [20,22]. Since the treatment couples a perturbation approach (transition of electrons from the tip to the molecule), with a resonance model (transition from excited to ground state) it is hard to give an estimate of numerical precision. But judging from the agreement it seems that two essential features of the processes are well reproduced: (i) the frequency of excitations (even though it involves an assumption about the active vibrational mode); (ii) the local confinement of the tunneling electrons. The second feature makes it possible to pin down the location to single atomic sites. In this sense the atom of experiments and theoretical calculations is a real single object.

2.2. Non-contact scanning force microscopy

While the STM experimental technique has remained largely unchanged since development, the original contact mode of SFM operation is currently used mainly for large-scale topography studies. It is unreliable for atomic resolution due to the high probability of tip contamination by surface ions. Now all experiments aiming at atomic resolution make use of a non-contact (NC-SFM) mode of operation, in which the cantilever is oscillated above the surface. This technique proved much more successful in getting reliable atomic resolution of surfaces, such as the silicon (111)–7×7 surface [23], as well as various metallic, semi-conducting and insulating surfaces [24,25]. However, only in a very few cases has it been possible to really establish the identity of the atoms resolved in an image, or even establish whether atoms are resolved at all. The lack of even qualitative understanding in many experiments has generally prevented attempts to compare theory and experiment quantitatively, although this remains a crucial step for development of the technique.

Modelling of NC-SFM has also made rapid progress over the last few years [26–30]. It includes two main components: (i) modelling of cantilever oscillations using known tip–surface forces; (ii) calculation of the tip–surface forces. The first problem has been considered in detail in [30–32]. However, the main challenge of SFM modelling remains the calculation of the tip–surface forces. Some of the long range forces [33] between tips and surfaces include the van der Waals attraction, a capillary force due to the presence of fluid films at the surface when imaging in liquid or air, and an electrostatic force due to patch charges and the surface charging after cleavage. In intimate contact, the repulsive and attractive short-range forces between a smaller number of tip and sample atoms in the contact area play a decisive role in regulating the

force equilibrium. In order to have a convenient terminology, we will refer to these latter forces as comprising the chemical interaction force between the tip and sample.

Construction of the surface image in contact or non-contact mode requires extensive calculations of three-dimensional chemical force-fields. These calculations are made using fairly standard static and molecular dynamics techniques. Calculations of metal–insulator interfaces require a careful account of the image forces [34]. Simplified tip models made of insulating materials (diamond, SiO_2 and MgO) are used in most SFM simulations on ionic surfaces, and metallic tips on metal surfaces, respectively. Although some of the calculations of the chemical interaction are done using high quality quantum mechanical methods [27,29], these methods are still too expensive for routine image modelling. Therefore classical atomistic simulation and molecular dynamics techniques are used much more often. However, here one encounters the problem of validation of the inter-atomic potentials [35]. One of the main advantages of using classical techniques is that they allow one to consider relatively complex tip structures, and to include full tip and lattice relaxation when modelling contact formation and surface scanning.

The initial successful experiments on the silicon (111)–7×7 surface encouraged an ab initio theoretical study [36] 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 [37], 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 [3] 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 surface. A similar experimental and theoretical study was performed

on the graphite surface [38,39]. In this case, the very weak forces over the graphite surface made it much easier to measure the force spectrum, even with a room temperature NC-AFM. A comparison of theoretical and experimental forces demonstrated that contrast in images was due to the interaction of the tip with the hollows between carbon atoms and not the carbon atoms themselves.

In both these cases, the interpretation of experimental results was greatly aided by the simplicity of the systems and the tip–surface interaction, but this limits the generality of the conclusions made. For example, on insulating surfaces, where no dangling bonds are present, the interpretation from studies of silicon cannot hold. Even moving to more complex semiconductor systems introduces interpretation problems that cannot be immediately addressed. Experiments have been performed on more complex binary semi-conductors such as InP [40] and InAs [41], but interpretation of images is difficult. On the InAs(110)–1×1 surface with low temperature NC-SFM, Schwarz et al. [41] observed strong dependence of contrast on the tip atomic structure and it was not possible to make a unique interpretation of images. Ab initio calculations of InP [27] and GaAs [28] have focused only on the imaging mechanism for a neutral silicon tip, as in previous studies of silicon, limiting the possibilities of interpreting some of the tip-dependent results seen in experiments.

NC-SFM experiments [42] and simulations [29] of silver on the silicon(111) surface also emphasised the importance of the tip atomic structure in imaging. The fact that the experimental images remained similar at different tip–surface separations suggested that the short-range dangling bond interaction predicted for imaging of silicon alone could not be responsible for contrast in this case. The experimentalists speculated that there was a silver atom at the end of the tip, which drastically changed the imaging mechanism. The theoretical study produced similar images, but without any statistical analysis of images or force spectroscopy to compare with directly, the final interpretation remained inconclusive.

Interpretation problems are even greater for insulators, the systems SFM was actually designed for. Difficulties in preparing clean, flat, insulating surfaces has limited successful atomic resolution to only a few surfaces, such as NaCl [43], TiO_2 [44] and CaF_2 [45]. On TiO_2, experimental studies [46] of the adsorption of formate ions on the (110)–1×1 surface established fairly conclusively that the bridging oxygen ions on the surface were imaged as protrusions in NC-AFM. 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. 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 TiO_2 surface is insulating, real surfaces are always non-stoichiometric and

the oxygen vacancies introduce surface states which significantly reduce the band gap.

As a possible solution to the problems of preparing bulk insulator surfaces, some experiments have been performed on insulating thin films grown on metal substrates. A combined experimental and theoretical study [47] was performed on NaCl thin films on a copper substrate. The experimental images showed atomically resolved islands of NaCl on the copper (see Fig. 2), with increased contrast at island edges and corners. Static atomistic simulations using inter-atomic potentials reproduced all the contrast features well, but were again limited by lack of knowledge about the tip. Due to the symmetry of the NaCl lattice, it was impossible to identify the sub-lattice (Na or Cl) seen as bright in images without knowing the sign of the electrostatic potential from the tip. The latter is determined by the unknown chemical composition of the tip apex.

One possible method for more reliable interpretation of images is to exploit the clear dependence of contrast on the tip structure and properties. This can be done when imaging a low symmetry surface, where different tips give different contrast patterns, which can be characterized quantitatively. This was done for the bulk wide gap insulator, CaF_2. Several different experiments performed on the $CaF_2(111)$–1×1 surface with different tips demonstrated [48,49] a very clear triangular contrast pattern at all tip–surface separations. An extensive statistical analysis of the images allowed, for the first time, a quantitative comparison with theory. By calculating an average scan-line from over 30 'real' scan-lines from images, it was
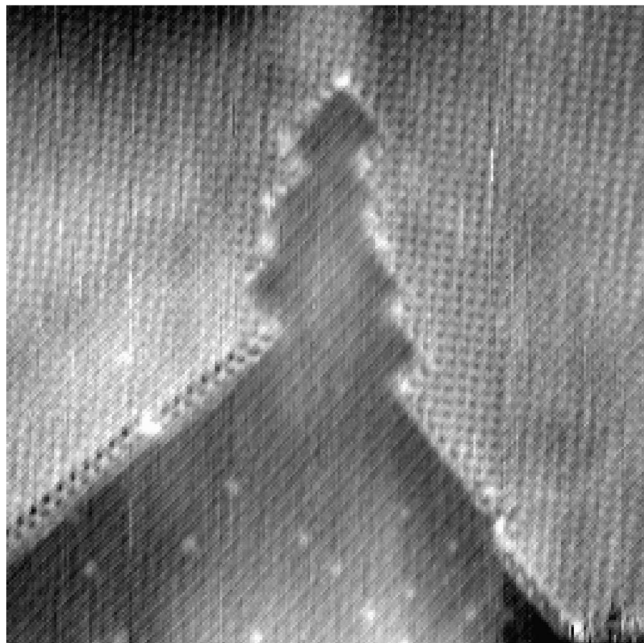

Fig. 2. NC-AFM 'Christmas Tree' image of a NaCl thin film on a copper substrate. The terrace, step-edges and kinks of the film are all atomically resolved, and atomic sized defects can be seen on the copper substrate in the lower part of the figure. Courtesy of R. Bennewitz.

demonstrated that the triangular contrast was due to shoulders on the main scanline peaks which elongates the contrast in the [221] and equivalent directions. Atomistic modelling [48,49] of the system predicted that this triangular pattern is due to a tip with a positive electrostatic potential interacting with both fluorine sub-lattices in the surface, and that the shoulders should appear at 0.22 nm from the main peaks. The experimental average position was 0.247 ± 0.05 nm, in excellent agreement with theory. The interpretation was also supported by agreement of primary features in the power spectra of experimental and theoretical images obtained by a two-dimensional Fourier transformation. This, for the first time in NC-SFM of insulators, allowed unambiguous image interpretation.

As the tip of an oscillating cantilever interacts with the sample, part of the cantilever energy is lost due to dissipation. Existing NC-SFM methods, which are able to measure these losses with high accuracy, demonstrate that they are different above different surface sites and correlate with topographic images [47]. This effect is called 'damping' and can be related to surface vibrational properties. Therefore it recently attracted significant theoretical efforts [50–52]. In the case of insulators, it has been demonstrated that the stochastic nature of the tip–surface interaction leads to two competing damping mechanisms. One component of a friction force acting on the tip is determined by the response of the phonons associated with the surface atoms [50]. On the other hand, it has been shown that the surface atoms may experience instabilities at the close approach by the tip [32]. This may lead to formation of local soft vibrational modes at the surface, which should interact strongly with the tip resulting in an adhesion hysteresis phenomenon. Strong theoretical efforts are now been made to calculate relative contributions of both effects for comparison with experiment.

3. Discussion

Although the theoretical methods used to simulate SPM techniques can vary widely, the most important simplifications bear on the inability to treat the real structure of the tip and to determine an accurate value for the tip–surface separation. Therefore to date no reliable error estimation of simulation methods exists. On the other hand, it is a common experience in SPM experiments that scans are not always reproducible. Experimentally, a well-defined problem consists of a series of scans, all showing, within statistical bandwidth, an identical feature. Only in this case, it appears, can theoretical modelling be more than just an educated guess.

In STM, for example, theorists have only recently begun to calculate the effects of chemical changes of the tip and surface relaxations on the obtained tunnel current [10]. In this sense the only reliable measure of errors originates from quantitative comparisons of experimental and theoret-

ical values [6]. There it seems that corrugations are less prone to error than currents. While state-of-the-art simulations can reproduce corrugations within a margin of 20–30%, currents are quite frequently off by more than 100%. This pertains mainly to the low distance regime, below a core–core distance of sample and tip of about 5 Å. In this case the main effect seems to be that atoms near but not directly at the tip of the STM also provide channels for tunnelling electrons. And since in most models current is calculated via a single apex atom of the tip, these contributions remain unconsidered.

In NC-SFM, chemical changes and atomic relaxation have proved so crucial to imaging that they are now routinely included [47]. However, most studies do not account for charge transfer processes and represent interactions at the empirical level. These assumptions are reasonable for most insulating surfaces, and are much less significant compared to the assumptions involved in representing the chemical structure of tip. In current models, the tip is represented by a very simple silicon or oxide cluster, and image interpretation is very dependent on the choice of tip model. Only recently have attempts [29,47,48] been made to quantify the effects of the tip model in imaging and highlight the need for greater control over tip preparation. The lack of knowledge of the tip structure also prevents a good estimate of the closest approach of the tip to the surface, further limiting the quantitative comparison between theory and experiment.

Existing quantitative methods reflect the change of the field from the earliest images of the Si(111)–(7×7) [23,53] surface until today. The cutting edge in theory is now the exact description of forces (and thus relaxations) and inelastic effects. But even though theoretical models are still far from a complete treatment of the coupled systems, this limitation is, in fact, no longer decisive. Under most circumstances the experimental conditions determine the importance of single influences. Theoretical modelling then only has to aim at describing the main physical processes correctly. Such a relaxed approach to theoretical rigour is one of the key ingredients of all successful schemes existing today.

Generally, the interplay between experimental and theoretical methods is the main driving force for new developments in the field. This makes a critical assessment of experimental results — not only theoretical — currently a necessity. There is evidence that the apex atom of the tip is important and that changes in the identity of this atom can drastically affect imaging. But these effects usually lead to images, which cannot be interpreted unambiguously, for this reason they are often discarded by experimenters. And since they do not provide any data, they cannot be modelled. From the experimental side, several groups have explored the potential of combining SPM with a field ion microscope [54], which should in principle allow scans with atomically defined tips. Also a combination of STM and NC-SFM allows, via sophisticated multiplexing, pro-

duction of STM and NC-SFM images at the same time [44], greatly increasing the amount of available information.

To summarise, the most striking results are achieved where experiment and theory can combine to really prove that atomic processes are being imaged. However, this requires immense sophistication from both sides and has so far been rarely achieved, especially for the more immature field of NC-SFM. Further progress in this field should eventually allow us to study chemical processes at surfaces in 'slow motion', considering, for example, every reaction step from an initial configuration of single atoms to the final configuration of a molecule.

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