Imaging problems on insulators: What can be learnt from NC-AFM modelling on CaF$_2$?

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Abstract. By combining theoretical modelling with experimental data on CaF$_2$, we studied the interactions responsible for atomic resolution in this system; we discuss the general significance of these results for imaging other insulators. Theoretical modelling was used to calculate the tip–surface interactions in noncontact atomic force microscopy (NC-AFM) imaging of a charged and neutral CaF$_2$ (111) surface. The modelling predicts that both the Ca and F sublattices can be imaged depending on the nature of potential from the tip. However, the theoretical scanlines of the surface are characteristic for each sublattice, and a method for determining the sublattice imaged in future experiments is suggested. It was found that atomic resolution was independent of the nature of the background force, and imaging problems with other insulators are likely to be due to surface roughness.

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Difficulties in noncontact atomic force microscopy (NC-AFM) imaging have so far prevented atomic resolution from being achieved on surfaces of many insulators, most notably MgO and alumina. These difficulties are usually associated with blunt tips, surface charging or surface roughness after cleavage. However, the mechanism behind the imaging instabilities is not well understood, and it is not clear how these factors interfere with stable AFM operation. Recent experiments [1] have successfully demonstrated atomic resolution on the (111) surface of CaF$_2$, and, as a wide gap insulator, bulk CaF$_2$ represents a good example for comparison with other, as yet, unimaged insulating surfaces. The normalized frequency change [2] of 38.6 for those experiments also implies that a large macroscopic van der Waals force due to a blunt tip or significant electrostatic forces due to tip and surface charging are present. Both explanations are feasible, since AFM studies [3] of CaF$_2$ have already demonstrated that charging due to cleavage could be significant and tip

charging and bluntness due to sputtering is a common preparation problem [4]. By studying theoretically the effects of a blunt tip and charging on NC-AFM imaging of the CaF$_2$ (111) surface, some general conclusions about the importance of these effects in imaging of other insulators can be made.

Several other factors also make CaF$_2$ an attractive system to study theoretically. Structurally, the CaF$_2$ (111) surface offers more interesting physical features than other flat insulators, such as NaCl. The surface has been demonstrated to be fluorine terminated [1], and, as can be seen from Fig. 1, the outermost fluorine layer protrudes out from 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 NC-AFM imaging has been that protruding atomic layers are imaged as bright, and it is important to establish whether this "intuition" holds theoretically.

The experimental study itself demonstrated a general problem in NC-AFM imaging, in that the defect and the sublattice seen as bright in images were unable to be chemically identified. It also suffered from a technical problem which exaggerated the apparent contrast measured on the surface. This combination of instrumental problems and lack of information obtained from experimental images motivates the use of theoretical modelling to try and extract more information about the surface and tip–surface interaction and to aid in interpreting experimental images.
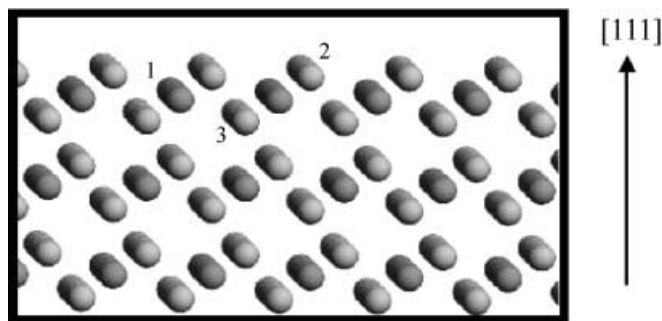

Fig. 1. Fluorine-terminated CaF$_2$ (111) surface. 1: calcium layer; 2: outermost fluorine layer; 3: lower fluorine layer. The layers are separated by about 0.08 nm

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1 Method

The model used in this study is the same as that described in [5,6], so this section will focus on those aspects of modelling that are specific to the study of CaF$_2$.

A schematic of the tip and surface setup used in the calculations is shown in Fig. 2. The doped Si tip has a conical shape at the macroscopic scale with a sphere of effective radius R at the end. It is very likely to be contaminated by exposure to air and to be coated by an oxide layer of unknown thickness, however at the macroscopic scale we assume the tip is conducting. As in our previous studies, we use a 64-atom MgO cube embedded into the macroscopic tip to represent a generic oxide "nano-tip". The cube is oriented so that it is symmetric about the z-axis with either a single oxygen or magnesium ion at the lowest point of the tip.

The tip–surface interaction can be split into three general components depending on the specific tip–surface combination studied: (a) the microscopic chemical force between atoms in the tip and surface, which includes the van der Waals force between ions; (b) the macroscopic van der Waals force between the tip and surface; and (c) the electrostatic force due to bias in the system, charging and polarization of conducting materials [6]. To integrate macroscopic and microscopic interactions in the same model we used the approach described in [5,6]. For a locally neutral system the macroscopic van der Waals and image force act as a background attractive force, which is important in terms of reproducing experimentally observed frequency changes, but is independent of the identity of the atom under the tip. This means that the interactions can be calculated separately and combined only for the final stages of modelling. In the scanlines shown in the next section, the macroscopic force is included by calculating the image force and macroscopic van der Waals force, and then adding them to the microscopic force as a function of tip–surface distance to give the total force. The distance dependence of the van der Waals force is calculated using a Hamaker constant of 1 eV and the method described in [7].
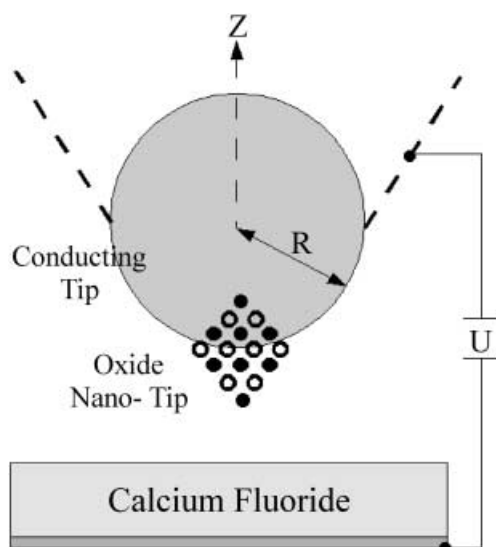

Fig. 2. Schematic of the model used here to simulate the interaction between the tip and the sample. R is the effective radius of the macroscopic tip and U is the bias applied between conducting tip and conducting substrate. The nano-tip is a schematic representation of the 64-atom MgO cube used

The microscopic force is calculated using a periodic static atomistic simulation technique and the MARVIN2 code [8]. The bottom of the nano-tip and the top of the CaF$_2$ surface are relaxed explicitly in the same way as in previous studies [5,6]. The empirical parameters used for the CaF$_2$ surface interactions were optimized from an original set by Binks [9] and checked by comparison with ab initio Density Functional Theory (DFT) calculations of the bulk and surface of CaF$_2$. Parameters for the interactions between the MgO tip and the CaF$_2$ surface are taken from Binks [9] and Bush et al. [10]. The parameters for the tip remain as in previous studies [5].

We simulate the oscillations of the cantilever under the influence of the total tip–surface interaction and calculate the change in oscillation frequency at a given tip–surface separation [5]. A simulated DFM scanline is then produced by calculating the effective cantilever deflection for a given frequency change. All scanlines were produced with a cantilever amplitude of 23 nm, an eigenfrequency of 84 kHz, a spring constant of 6 N/m, and a frequency change of 155 Hz, as in experimental images [1].

2 Results

Although the general setup shown in Fig. 2 is consistent throughout this study, two different interaction schemes were used, each representing an extreme model where the entire background force is dominated by one source. Firstly, to model a system with no surface charge where the macroscopic van der Waals interaction dominates the background force, a very blunt tip of radius 400 nm was used. Secondly, to model the interaction of a charged tip with a charged surface, a sharp tip of radius of 3.33 nm was used. The tip held a discrete electric charge of $+4\,e$, and the surface a charge of $0.6\,e/nm^2$. These charges produce a long-range electrostatic force, which dominates the background force. Note that the surface charge is unrealistically large and represents an extreme limit. For bulk CaF$_2$ the sample is so thick (3–5 mm) that the distance between the tip and the conducting substrate makes the image force (and bias effects) negligible for neutral systems. However, when the surface is charged there is a strong interaction between the surface charges and their images in the conducting tip, and the image force makes a significant contribution to the background force.

2.1 Anion-terminated tip

The first simulations were performed with the nano-tip oriented so that a negative O^{2-} ion is closest to the surface. This represents the situation where the original silicon tip is oxidized or contaminated by ambient oxygen. The electrostatic potential gradient from an oxygen-terminated MgO nano-tip has been shown [11] to be similar to that of an oxygen-contaminated silicon tip.

Figure 3 shows simulated scanlines produced over the CaF$_2$ surface with an O-terminated tip. The overall qualitative behaviour for the sharp and blunt tip scanlines is the same, with contrast dominated by the strong short-range electrostatic interaction between the negative potential from the tip and the positive Ca ions in the surface. Surface relaxation also plays a role in the interaction, with the Ca ions displacing
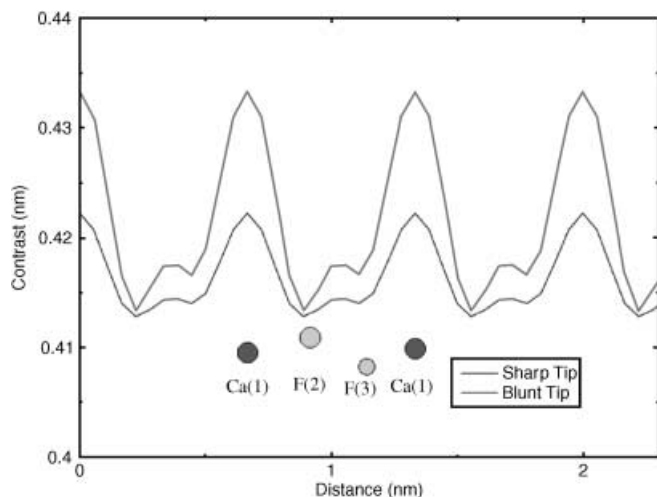
Fig. 3. Simulated scanlines of the CaF$_2$ (111) surface with an oxygen-terminated nano-tip. Tip–surface separation is calculated with respect to the Ca layer. The numbers below the schematic atoms refer to the labels in Fig. 1. The blunt tip scanline is from the simulation with a large radius tip and a background force consisting of only van der Waals. The sharp tip scanline uses a small radius tip, and the background force is composed of a van der Waals force and an electrostatic interaction due to surface charging

Fig. 4. Simulated scanlines of the CaF$_2$ (111) surface with an magnesium terminated nano-tip

towards the tip by about 0.01 nm during scanning and actually jumping to the tip at tip–surface separations of less than 0.38 nm. The magnitude of contrast is about 0.020 nm for the sharp tip and 0.010 nm for the blunt tip. This contrast is much smaller than the 0.1 nm observed in the original experiments. This is consistent with the assertion made in [1] that electronics exaggerates the experimentally observed contrast. The difference in contrast between the two curves is a direct result of the significant difference between the long-range tip–surface interactions for the two systems [12]. Although the interactions are similar at close range, the van der Waals dominated blunt tip interaction decays much more quickly than the electrostatic dominated sharp tip interaction. This means that the sharp tip must move slightly further from the surface than the blunt tip to feel the same frequency change. In both curves a second maximum can be observed at a distance of 0.33 nm from the main peaks. This is due to a minimum of repulsion from the two fluorine ions when the tip is equidistant between them, producing an increase in the overall attraction.

2.2 Cation-terminated tip

Simulations were also performed using a nano-tip terminated by a positive Mg^{2+} ion. This reproduces the situation where the original tip is contaminated by a positive ion from the surface or from the environment, and also the case where the original uncontaminated tip is terminated by a cation, a situation which cannot be ruled out by experimental data at present.

Figure 4 shows simulated scanlines over the CaF$_2$ surface with a magnesium-terminated tip. Again the overall qualitative behaviour of the blunt and sharp tip scanlines is the same. For the Mg-terminated tip, the contrast is dominated by the strong short-range electrostatic attraction between the positive potential from the tip and the negative F ions in the
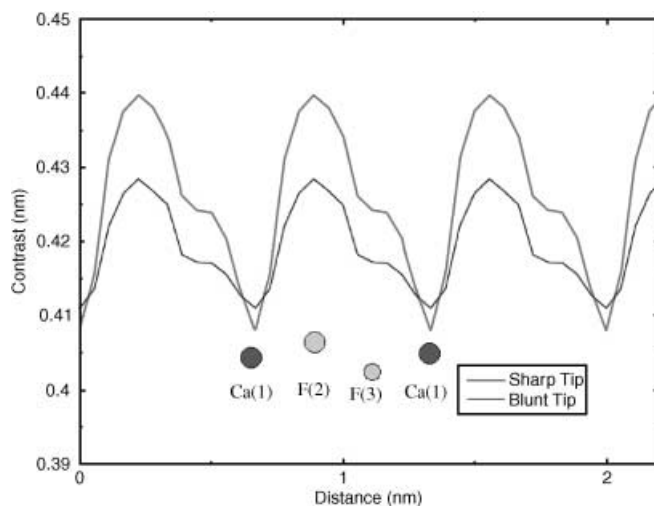
surface. The F ions displace by about 0.02 nm towards the tip while scanning and jump to the tip at tip–surface separations of less than 0.40 nm. Note that, as mentioned in Fig. 3, tip–surface separation is calculated with respect to the Ca layer and the tip is in fact about 0.07 nm closer to the F layer. The magnitude of contrast is about 0.032 nm for the sharp tip and 0.017 nm for the blunt tip. The difference in contrast between the sharp and blunt tips is consistent with that seen for the O-terminated scanlines and is due to same source. However, instead of a second maximum, as seen in Fig. 3, the scanlines in Fig. 4 have a shoulder at 0.22 nm to the right of the main peaks. This is due to the attraction of the tip to the fluorine ions in the third layer of the surface; effectively both types of fluorine site are imaged with the Mg-terminated tip.

3 Discussion

The simulated scanlines with an O-terminated tip demonstrate that it is not necessarily the most protruding surface feature which is imaged as bright in NC-AFM. Even though the Ca ions are in the second surface layer and are shielded by the outer F layer, they are still responsible for contrast with a negative potential tip. In combination with the fact that the second contrast maximum in the O-terminated scanlines is due to the minimum in repulsion between two F ions, this demonstrates that NC-AFM does not image atoms directly, but images the attraction between the tip and surface electrostatic potential. In general the surface potential will be strongest over atomic positions, but the contrast mechanism also depends crucially on the nature of the tip's electrostatic potential.

The contrast predicted in all theoretical scanlines is much smaller than that found in the original experiments. This is consistent with the technical problems in the experiment, and also with more recent experiments with improved electronics, which observe smaller contrast (about 0.04–0.05 nm) [13]. By the magnitude of contrast alone there is no way of distinguishing whether the Ca or F sublattice is observed experimentally, as the scanlines with cation- and anion-terminated tips show similar contrast. However, the secondary features

in the theoretical scanlines do offer the possibility of identifying the sublattice imaged. Three-dimensional plots of the theoretical image demonstrate that the secondary features are not just artifacts of the scanlines chosen. The difference of 0.11 nm in the position of the secondary features means that if any secondary features are seen in experiments the sign of the tip potential and the sublattice can be identified by a careful analysis of their position.

This study has shown that the exact nature of the background force does not have a large effect on the contrast mechanism in NC-AFM imaging. The much slower decay of the electrostatic force [12] does not seem to be a significant factor in resolution, and scanlines produced using a van der Waals dominated background force were qualitatively similar to those produced with a background force dominated by long-range electrostatic forces due to tip and surface charging. The balance between van der Waals and electrostatic forces in a real experiment can only be established by comparing directly theoretical force versus distance curves with experimental curves achieved after atomic resolution. More recent experimental images on CaF_2 [13] have demonstrated the onset of ion jumps as the tip approaches the surface. This data can be combined with the theoretical predictions for ion jumps so that a distance reference can be readily established in the experimental force versus distance curves, greatly aiding in interpretation.

More generally, the theoretical results show that blunt tips and homogeneous surface charging are not an obstacle to atomic resolution on insulating surfaces. The large forces introduced by these factors can be compensated by the appropriate experimental setup, as was shown in [1]. This implies that it is the roughness of some insulating surfaces after cleavage which causes imaging instabilities. AFM studies on MgO [14] and alumina [15] demonstrate that these surfaces have a very high density of steps and "nano-debris" compared with the large flat terraces which can be seen in images of NC-AFM atomically resolved systems such as CaF_2 and NaCl [16]. The inhomogeneity of the force field over a rough surface increases tip instability and makes stable imaging much more difficult. In conclusion, this study predicts that there should be no greater difficulty in imaging insulators such as MgO and alumina in atomic resolution if surfaces of sufficient smoothness can be produced.

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