

Realistic model tips in simulations of nc-AFM

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Abstract

In this study we use first principle methods to study the interaction of three different tip models with a CaF₂(111) surface. The tip models are based on a ‘realistic’ approach to tip simulation and consist of a pure silicon tip, an oxygen terminated silicon tip and a water contaminated silica (SiO₂) tip. We find that each tip demonstrates characteristic features which should be observable in experiments and hence provide signatures which would aid in the identification of tip and surface species.

1. Introduction

The importance of the atomistic structure of the tip in understanding atomic resolution non-contact atomic force microscopy (nc-AFM) imaging has been emphasized in many previous studies [1]. Theoretical approaches to solve this problem usually involve simulating nc-AFM with several ‘idealistic’ tip models in the hope of finding a good match for experimental results. This method has proved successful in understanding contrast on the silicon(111) (7 × 7) [2] and CaF₂(111) surfaces [3]. In parallel to this theoretical development, there has been the introduction, initially via low temperature experiments, of experimental force curves over specific surface atoms [2, 4, 5]. This has provided even more opportunities, and challenges, for theoretical comparison [6]. The availability of a measured tip–surface interaction over a specific surface atom, means that simulations providing only qualitative agreement with experiment, although perhaps useful, are not extracting the maximum physics from the experimental data. Providing a quantitative match for experimental atomic force curves would give a very good idea of both the atom at the apex and directly under the tip.

However, even beginning to model ‘real’ tips is a very difficult process. Tips are fabricated from silicon, but are then exposed to the atmosphere, producing a native oxide layer, and then are probably contaminated by water. Finally, once the experiment starts, the tip can be changed due to contamination from surface species, or just due to tip atom rearrangements under the influence of the tip–surface interaction. In order to begin to develop a ‘reference database’ of tip properties, in this study we compare three different silicon-based tip models and try to highlight those characteristic features which may be seen

in experiments. As a reference surface we use the CaF₂(111) surface, since it represents perhaps the most studied insulating surface experimentally and theoretically in nc-AFM.

2. Methods

2.1. System setup

To model a pure silicon tip (Si tip) we use a ten-atom silicon cluster with a single dangling bond at the apex and its base is terminated by hydrogen (see figure 1(a)) [7, 8]. This tip is produced by taking three layers from the Si(111) surface and removing atoms to produce a sharp apex. It provides a fair model of the dangling bond characteristic of the most stable (7 × 7) reconstruction of the Si(111) surface. The small size, specific shape and hydrogen termination of the tip produce a surface electronic structure different from a standard silicon surface. However, this tip performs well when the short-range tip–surface interaction is determined by the onset of covalent bond formation between the dangling bond at the end of the tip and surface dangling bonds. This has been demonstrated by the good agreement of calculated and measured forces over a silicon surface [2].

In order to model a silicon tip contaminated by oxygen, a single oxygen atom was adsorbed onto the apex of the silicon tip (see figure 1(b)). This represents either contamination from ambient atoms, or even from the surface e.g. surface fluorine adsorbing to the tip. Previous studies using oxygen terminated tips on the CaF₂ surface [3, 9, 10] demonstrated that the contrast mechanism was dominated by the interaction between the negative potential from the tip apex and calcium ions in the surface. However, those studies used a very idealistic MgO

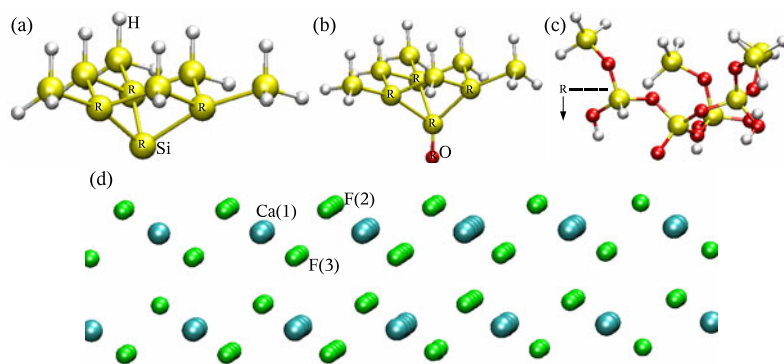


Figure 1. Atomic structures of the tips and surface considered in this study: (a) silicon tip, (b) oxygen contaminated silicon tip, (c) silica tip and (d) $\text{CaF}_2(111)$ surface. Relaxed tip atoms in (a) and (b) are labelled ‘R’, and all atoms below the line ‘R’ in (c) are relaxed.

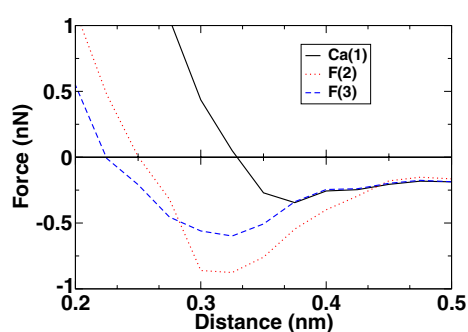


Figure 2. Calculated forces for the silicon tip over the CaF_2 surface.

cube tip, which is likely to be much more rigid and symmetric than experimental tips. The oxygen terminated silicon tip (SiO tip) offers a more realistic silicon-based model, which is softer and less symmetric.

Finally, to represent an originally oxidized tip exposed to the atmosphere ($\text{SiO}_2\text{-H}$ tip), we used extensive *ab initio* molecular dynamics (MD) calculations as a basis [11]. These calculations used simulated annealing to find the lowest energy structures of large quartz (SiO_2) clusters and found that the cluster surfaces were characterized by under-coordinated silicons bonded to two oxygens, and protruding oxygens bonded to a single silicon (as for the SiO tip). Upon introduction of water molecules to the system, the molecules dissociate, with OH adsorbing on surface silicons and H on surface oxygens. To represent this cluster in a computationally efficient form for AFM simulation, we have taken a smaller cluster of quartz and adsorbed hydrogen onto the base silicons (assuming the top of the tip is the ‘base’) and surface oxygens, and hydroxyl groups onto the surface silicons. The relaxed model of this tip is shown in figure 1(c). The lowest ‘probe’ atom is an oxygen atom bonded to a single silicon, but several OH groups are only slightly further from the surface (the closest is less than 0.01 nm).

The $\text{CaF}_2(111)$ surface itself is fluorine terminated, with the high fluorine atoms (F(2) in figure 1(d)) protruding by about 0.08 nm from the Ca(1) sublattice and the low fluorine atoms (F(3)) a similar distance below. In calculations, the surface is represented by a periodic cell of $(4 \times 4 \times 3)$ CaF_2 units.

2.2. Computational techniques

All calculations were performed using the linear combination of atomic orbitals (LCAO) basis SIESTA code [12, 13], which implements density functional theory (DFT) in a manner so as to achieve linear scaling in the construction of the Hamiltonian and overlap matrices. Solution of the self-consistent problem can also be performed with linear scaling for insulators, though here full diagonalization is employed so that the electronic structure of the surfaces can be studied in detail. The generalized gradient approximation (GGA) has been utilized in all calculations, based on the specific functional of Perdew, Burke and Ernzerhof (PBE) [14]. Core electrons are represented by norm-conserving pseudopotentials of the form proposed by Troullier–Martins [13], and we used the partial core correction scheme of Louie *et al* [15]. The pseudopotential for the silicon atom was generated in the electron configuration $[\text{Ne}] 3s^2 3p^2$, for calcium in $[\text{Ar}] 4s^2$, oxygen in $[1s^2] 2s^2 2p^4$, hydrogen $1s^1$ and that for fluorine in $[1s^2] 2s^2 2p^5$, where square brackets denote the core electron configurations.

Various basis set configurations were tested, and a good compromise between accuracy and efficiency was found with double ζ for F and triple ζ with double polarization for Ca. Double ζ with polarization was used for Si, O and H in the tip in all cases. All calculations were converged to the order of millielectronvolts in the total energy with respect to mesh cutoff and orbital cutoffs (i.e. energy shift [13]). An energy shift of 50 meV and a mesh cutoff of 255 Ryd were used—within these limits all the properties of the tips are well converged. Energy convergence with respect to k -point sampling was also tested on calculations of accurate surface geometries using smaller slabs, but for the large tip–surface systems only the gamma point was used. However, the surface structure did not change significantly between the small and large systems. During simulations, the top half of the tip and the bottom third of the surface were kept frozen, and all other ions were allowed to relax freely to less than 0.08 nN. We did not consider a full spin-polarized treatment of the problem since previous studies using similar [16] and identical methods [8] indicate that it does not make a qualitative difference to the results. The distance in all the following discussions is with reference to the relaxed equilibrium position of the Ca(1) sublattice in the surface. Note that the dynamic motion of the cantilever is not

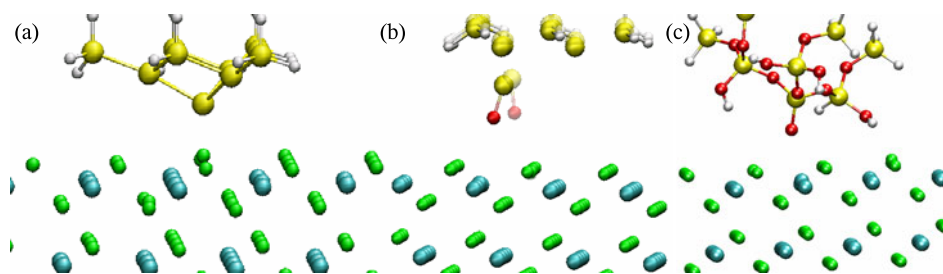


Figure 3. Simulation snapshots: (a) silicon tip at 0.300 nm over F(2), (b) oxygen terminated silicon tip at 0.350 and 0.325 nm (shaded) between F(2) and F(3), and (c) silica tip at 0.300 nm over Ca(1).

included in simulations and the tip is relaxed at a static position. However, the timescale of the cantilever oscillations is so much longer than the timescale of atomic motion (microseconds compared to femtoseconds) that a quasi-static approach is a good model.

3. Results

Figure 2 shows the calculated forces over the three CaF_2 sublattices using the Si tip. Since these results have been discussed to some degree before [10, 17], here we focus only on those details important for comparison to the other two tip models. Specifically we see that the force is dominated by interaction of the tip with the F(2) site, with the weakest interaction over the Ca(1) site. This is characteristic of silicon tips interacting with any insulating surface, as the force is mainly due to the formation of covalent bonds with the surface and this mechanism is strongest over anions in the surface [17]. Surface relaxation also plays a role in this interaction, with the F(2) displacing towards the tip by a maximum of 0.040 nm at 0.350 nm, before being pushed back in (see figure 3(a)). The other surface sites show negligible relaxation until electron–electron repulsion sets in at very close approach. Due to the softness of the tip (in comparison to, for example, MgO [10]) the apex tip atom also relaxes back into the body of the tip during approach, with a maximum of 0.025 nm retraction at 0.300 nm above F(2)—over Ca(1) this reduces to only 0.010 nm at the same height.

In contrast to the Si tip, for the SiO tip, figure 4 shows that the force is now largest over the Ca(1) sites in the surface, although the magnitude of the maximum force remains similar. This is as one would expect for the interaction of a negative oxygen ion at the end of the tip with a positive Ca^{2+} ion in the surface, as is the rapid onset of repulsion seen over the high negative F^- ions. This behaviour is qualitatively similar to that seen for the oxygen terminated MgO tip [10], although the reduced ionicity of the tip means the overall force is reduced by about a factor of two. Over the Ca(1) site, the Ca atom displaces out from the surface to a maximum of 0.017 nm at a distance of 0.310 nm, before being pushed back in. The Si–O bond at the tip apex is more rigid with respect to displacements than pure Si–Si bonds, and we see a reduction in displacements of the O apex atom in comparison to the Si apex atom from the silicon tip—only 0.010 nm at 0.310 nm. At a similar distance over the F(2) site, the F atom is pushed into the surface by 0.024 nm, with a corresponding retraction of the apex oxygen of 0.007 nm. There are no significant relaxations over F(3).

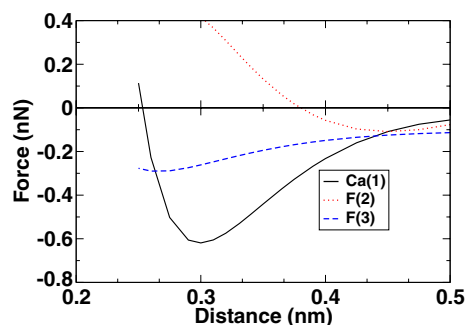


Figure 4. Calculated forces for the oxygen terminated silicon tip over the CaF_2 surface.

One significant difference between the SiO tip and Si and MgO tips that is not immediately apparent from the force curves, is the mobility of the apex oxygen. Although the Si–O bond is quite stiff in terms of displacements perpendicular to the bond, the fact that O has only one bond means it can move very easily in the x – y plane. This can be seen by looking at a force curve calculated with the tip i.e. the apex oxygen at a position halfway between F(2) and F(3). Intuitively one would expect to get a force in between the forces over F(2) and F(3)—in fact, the force is much larger. As you approach the surface, the apex oxygen switches so that it is much closer to the Ca(1) site (see figure 3(b)) producing a force curve qualitatively similar to that over Ca(1) with about two-thirds of the magnitude. This behaviour is also observed for the Ca(1)–F(2) and Ca(1)–F(3) midpoints. Over the F(3) site, the apex oxygen is actually 0.03 nm further from Ca(1) than at the F(2)–F(3) midpoint, so the switch does not occur. Simulated images calculated with this tip demonstrate bright contrast across most of the image, with only dark spots centred on the F(2) positions.

For the SiO_2 –H tip, figure 5 shows that calculations give a similar force hierarchy to the SiO tip, but that is where the similarity ends. Although the largest contribution to the force is the attraction between the apex oxygen and Ca in the surface, other atoms on the tip close to the surface also contribute. Figure 3(c) shows that both the Ca(1) under the apex oxygen and a F(2) under an OH group are significantly displaced towards the tip at a distance of 0.300 nm. This combination of attractive interactions means that the overall force is much larger than for the other two tips, and is similar to that for an MgO tip [10]. However, one important difference is that there is no long-range repulsive component in the forces. For the SiO tip, the strong electrostatic repulsion between the negative apex oxygen ion and the negative surface fluorine ion

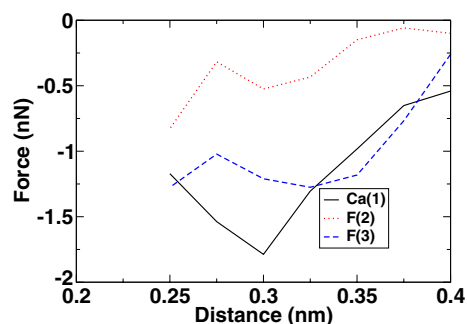


Figure 5. Calculated forces for the silica tip over the CaF_2 surface. (This figure is in colour only in the electronic version)

produces an overall repulsive interaction even at about 0.38 nm over F(2). For the $\text{SiO}_2\text{-H}$ tip the local repulsive interaction is compensated by other attractive interactions of the tip and overall repulsion will only be seen at very close approach when electron–electron repulsion dominates.

4. Discussion

In general the characteristic features of each of the tips can be summarized as follows.

- Silicon—the tip dangling bond forms strong covalent bonds with surface anions, but this is damped somewhat by significant displacement of the soft Si–Si bond at the apex. The nature of these bonds means that contrast is localized fairly well over atoms in the surface—interpretation should be more straightforward. There is no microscopic repulsive force over any sites.
- SiO—the negative oxygen ion at the tip apex interacts more strongly with cations in the surface, as for more ionic tips. However, the single bond between the O and the Si tip means it is very free to move in the x – y plane, and maximum contrast is quite non-localized over atomic sites, complicating interpretation. The interaction can be repulsive over anions in the surface.
- $\text{SiO}_2\text{-H}$ —the strong interaction between the surface and several probes on the surface results in a much larger interaction than would be expected for a single atomic probe–surface atom interaction. Different orientations of the tip could reduce the force, but net repulsion would be unlikely.

Although the principle of this work was to provide theoretical comparisons of different tips, so that their signature could be observed in future experiments, it is of course very interesting to compare them briefly with current experimental results to see if their characteristics have been observed. As mentioned previously, the contrast in images of $\text{CaF}_2(111)$ has been qualitatively understood using an idealistic MgO tip model [3, 9], where it was demonstrated that experiments corresponded with tips of both positive and negative electrostatic potential from the apex. If we move beyond the so-called ‘standard’, more reproducible images presented in that study, exactly the type of contrast predicted for the SiO tip has been observed (very rarely) in experimental images [18], suggesting that occasionally a stable, but mobile

atom is present at the tip apex. Furthermore, recent atomic force curves on CaF_2 [19] demonstrated very good quantitative agreement with theoretical predictions for the SiO tip over Ca(1) and F(3). However, they observed standard contrast patterns in images, i.e. not characteristic of a mobile apex atom, and did not see any repulsive force over F(2). This implies that their tip was terminated by an oxygen atom, but it was not mobile and other tip species contributed to the interaction over F(2), i.e. as for the $\text{SiO}_2\text{-H}$ tip.

Although in this study we have focused exclusively on the $\text{CaF}_2(111)$ surface, it is important to mention that many of the conclusions we make are generally applicable. For example, results for the Si tip are qualitatively similar for interactions on nearly all insulating and semiconducting surfaces [17]. Also, calculations for the SiO tip on the $\text{CeO}_2(111)$ surface, which has identical physical, but very different electronic structure to $\text{CaF}_2(111)$, show similar forces and tip mobility effects.

Providing an exact model of the tip used in an experiment is an impossible task, but by considering more seriously how a tip is created and the processes it undergoes during scanning, it is possible to establish some fundamental features of tips which can be seen in experiments. This can be developed into a database of characteristic tip–surface interactions, which will help greatly in bridging the gap between the wealth of unexplained experimental data and the idealistic theoretical picture.

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