Can Atomic Force Microscopy Achieve Atomic Resolution in Contact Mode?

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Atomic force microscopy operating in the contact mode is studied using total-energy pseudopotential calculations. It is shown that, in the case of a diamond tip and a diamond surface, it is possible for a tip terminated by a single atom to sustain forces in excess of 30 nN. It is also shown that imaging at atomic resolution may be limited by blunting of the tip during lateral scanning.

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The atomic force microscope (AFM) [1] was developed as a tool capable of resolving surface structures by probing the spatial variation of the interatomic forces between a tip and a surface. The total tip-surface force is the sum of both long range van der Waals (vdW) and short range chemical interactions. For distances below 2 Å, the chemical interaction is dominated by the Pauli repulsion and starts to balance the attractive vdW force. AFM images taken at small tip-surface distances, where the total tip-surface force is repulsive (the vdW interaction is smaller than the short range atomic repulsion), are said to be formed during contact mode (CM).

Experimental evidence questions whether CM-AFM can display genuine atomic resolution. Atomic resolution images of layered materials such as graphite and boron nitride have been reported in the literature [2,3], but the images rarely show individual surface defects, which are routinely observed with the STM. Furthermore, these images persist at large forces (100 nN) where the contact area is predicted to be of the order of 100 $Å^2$. These results suggest that both tip and sample are deformed by the repulsive interaction and that they are far from the single atom tip scenario needed for real atomic resolution [4]. Apparent atomic resolution could be related to the very easy shear along the basal plane of these layered materials, with lateral tip movement being accommodated by sliding of planes just beneath the tip [5]. Atomic resolution images have also been observed on ionic surfaces such as NaCl. Livshits and Shluger [6] have proposed a self-lubrication mechanism by which atomic resolution imaging may be obtained on ionic surfaces. This mechanism is complex and damages the surface and is unlikely to provide a general and reliable basis for CM-AFM.

The development of dynamic mode force microscopy, where the oscillation of the cantilever overcomes the "jump-to-contact" instability, has resulted in significant progress in the attainable resolution. Of particular note are the "tapping" or intermittent contact mode and the noncontact frequency modulation technique, where low-temperature UHV images of quality comparable to STM—showing both the adatoms and rest atoms of the Si(111)-7 × 7—have been recently obtained [7].

The basic question underlying the possibility of atomic resolution in CM-AFM is whether or not the repulsive interactions can balance the vdW force without a significant distortion of the tip and the sample. The vdW force between the tip and the surface depends on the shape of both tip and surface and the chemical composition of the two. Given this information the vdW force may be estimated without detailed consideration of the quantum mechanics. In contrast the short range repulsive interaction between the tip and the surface is intrinsically quantum mechanical and is expected to relate to the strength of the material. Thus a hard material like diamond, commonly used for AFM tips, seems to be the appropriate choice to answer this question. This requires determination of the mechanical response of tip and surface at distances close to contact. This information is not only relevant to CM-AFM. The interpretation of both "tapping" mode and the amplitude modulation experiments in noncontact AFM—where the tip is probing the repulsive part of the interaction during part of its oscillation cycle— will benefit from this study. Moreover, friction properties are related to these close contact interactions.

In this Letter we describe the results of *ab initio* quantum-mechanical simulations designed to investigate whether it is possible for the repulsive force exerted by the surface on a diamond tip terminated by a single atom to balance the vdW force. The results of our simulations for a diamond tip impinging on a diamond surface indicate that such a tip can indeed balance the vdW force, and forces in excess of 30 nN can be sustained. Approach curves were studied at two different surface sites and also using a tip terminated by a different chemical species, boron, that modifies the reactivity of the tip apex. The magnitude of the force was found to be insensitive to these changes because of extensive tip relaxations. A simulation will also be presented in which the tip is moved laterally from an estimate of the equilibrium vertical position. This simulation suggests that at high loads the apex atom does not move with the tip and, therefore, imaging will degrade.

Although a number of groups have modeled CM-AFM and indentation [8–10], few of them have focused on diamond tips and diamond or graphite samples. Among these

last studies one can find analytic work based on elasticity theory [11] applied to graphite surfaces, and empirical potential molecular dynamics [12], but no *ab initio* simulations. The work of Harrison *et al.* [12] is the most closely related to that presented in this Letter, but differs in important respects. They followed a different methodology using empirical potentials to model the indentation of a diamond tip into a diamond (111) surface. As their primary goal was the interpretation of indentation experiments in ambient conditions, the tip used in their calculations departs significantly from the single atom tip geometry and has all the dangling bonds saturated with hydrogen atoms.

In order to estimate the maximum force sustainable by a tip terminated by a single atom we simulated a diamond tip impinging on a (111)-(2 × 1) Pandey reconstructed diamond surface [13]. The (111)-(2 × 1) surface was chosen because this surface is particularly hard and the (2 × 1) Pandey reconstruction is stable and clean. The surface should therefore be potentially favorable for imaging. The tip was designed to be stable and strong and was bound by three (111) planes which intersect at the tip apex. Hydrogens were used to saturate the dangling bonds in the base plane of the tip. They were oriented towards the locations which would have been occupied by the next layer of carbons in the tip. This saturation simulates the bulk continuation of the tip and provides the correct sp^3 hybridization to the tip atoms.

The simulations for both the approach curves and the lateral scans are performed by moving the tip in a quasistatic manner in increments of 0.2 Å. After each advance of the tip a full atomic relaxation was performed [14].

We have employed a standard total-energy pseudopotential method [15] with the generalized gradient approximation [16] to describe exchange and correlation. The electronic states were expanded at the Γ point of the Brillouin zone using a plane-wave basis set truncated at 44 Ry. Optimized nonlocal pseudopotentials [17], applied in the Kleinman-Bylander form [18], were used to describe scattering from the 1*s* cores of the carbon and the boron atoms. A Coulomb potential was used for hydrogen.

First, the results of two approach curves will be presented. In the first of these, the apex atom of the tip was initially positioned directly above one of the carbon atoms in the surface Pandey chain (top site, approach curve 1). In the second, the apex atom was initially located above the center of one of the open rings in the surface (hollow site, approach curve 2). Figure 1 shows the initial atomic configuration [19].

One of the striking features of the calculations was the large forces, up to 30 nN, which the single atom tip was able to sustain during the approach. These repulsive forces are significantly in excess of those which would be required to balance the vdW force between the tip and the surface for various tip shapes [20]. Figure 2 shows the vertical force on the tip as a function of tip height. Tip height is measured by the vertical distance between the rigid hydrogens at the base of the surface and the rigid hydrogens

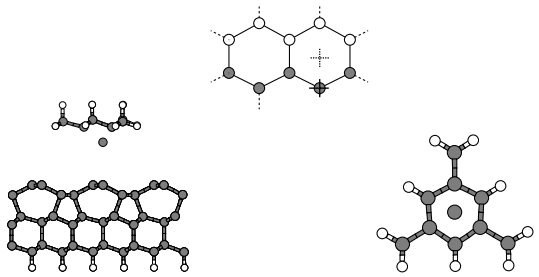

FIG. 1. (left) Relaxed initial atomic positions at the start of approach curve 1. The hydrogen atoms at the base of the surface and in the upper layer of the tip were held rigid during the simulations. The unit cell contained 154 carbon atoms and 39 hydrogen atoms. (right) The tip viewed from below. The tip contained 10 carbon atoms and 15 hydrogen atoms. (center) The (111)-(2 × 1) surface viewed from above. The solid and dotted crosses indicate the initial position of the apex atom for approach curve 1 (top site) and approach curve 2 (hollow site), respectively.

in the base plane of the tip. To make the distance readily interpretable, a constant has been subtracted so that, at the start of approach curve 1, the tip height is equal to the distance between the tip apex atom and the carbon atom beneath it. Thus at tip height 0.0 Å the apex atom would be at the same height as the Pandey chain, if no deformation due to repulsion had taken place. An estimate of the force due to the vdW interaction is also shown. This force is sensitive to the unknown tip geometry and has been estimated for the geometry of a 0.1 μm shaft terminated by a spherical cap [21]. As contact is likely to take place at a nanoasperity, the cap is assumed to terminate 5 Å above the apex. This choice of geometry is conservative to illustrate that even in this case the single atom tips can sustain the vertical force. It is expected that lower vdW forces of 1–2 nN are achievable experimentally.

Consider first the vertical force during approach curve 1. The apex carbon has a dangling bond which initially bonds

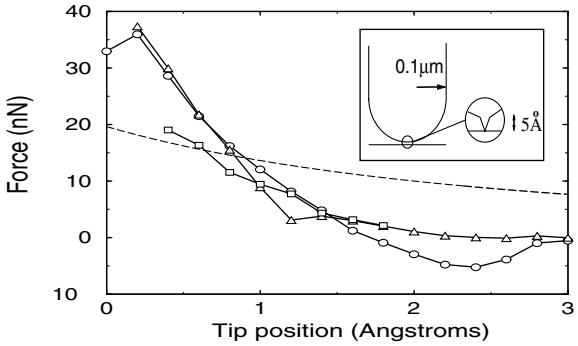

FIG. 2. Vertical repulsive force on the tip during indentation. (left) Circles indicate approach curve 1 (top site). Triangles indicate approach curve 2 (hollow site). Squares correspond to a simulation such as approach curve 2 in which the carbon atom at the tip apex is replaced by a boron atom. The dashed line indicates a conservative estimate of the vdW force estimated using the geometry shown (inset).

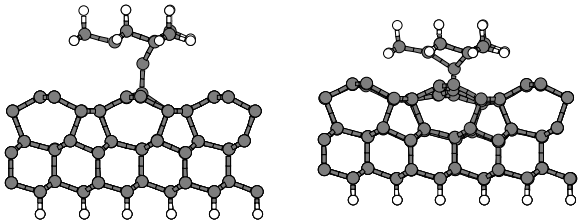

FIG. 3. Atomic configurations for tip heights 1.6 Å (left) and 0.2 Å (right) during approach curve 1.

to the surface leading to the attractive force at large separations. As the tip is lowered this attractive force becomes repulsive and forces of up to 30 nN are sustained before a yield point is reached. Between tip heights 2.2 and 0.2 Å although the base of the tip has advanced by 2 Å the separation between the apex and the atom immediately beneath it has changed by only 0.35 Å. The tip apex distance during this interval is very close to the bond length in bulk diamond. The drop in force at 0.0 Å is accompanied by a reconstruction in which the tip apex is absorbed into the surface thereby creating two seven membered carbon rings. Figure 3 shows the atomic configurations at the onset of the repulsive force (tip height 1.6 Å), and immediately prior to yielding of the Pandey chain (tip height 0.2 Å).

Quite unexpectedly, the normal forces arising at small separations during the tip approach on top of a hollow site (approach curve 2) are similar to those arising on the approach curve where the apex was originally on top of one of the atoms in the Pandey chain. This surprising behavior is due to the relaxation of the tip induced by the interaction with the surface; the apex carbon atom has broken several bonds with the tip and moved above the Pandey chain. This relocation occurs at a tip height of 1.6 Å, where the vertical force is still small (between 2–3 nN). The relocation leaves those carbons in the tip, to which the apex was formerly bonded, in a reactive state. As a consequence of this, together with the favorable geometry, bonds form between the second layer of the tip and the surface Pandey chains at close separations. Different atomic configurations from approach curve 2 are shown in Fig. 4.

The above results suggest that large vertical forces may be sustained by a single atom tip. However, in approach curve 2 the strength may arise because the carbon at the tip apex has relocated to a position above the Pandey chain. This relocation is driven by an attractive interaction between the dangling bond on the apex carbon atom and the π-bonded carbon chain. To investigate whether the sustainable force is reduced when the chemical environment is altered we repeated a segment of approach curve 2 but substituting the carbon atom at the tip apex by a boron atom, with only 3 valence electrons that saturate the 3 bonds with the rest of the tip. Relevant atomic configurations are shown in Fig. 5.

The repulsive force developed as the boron tip is advanced is comparable to that developed by the carbon tip (see Fig. 2). However, the mechanism by which this force

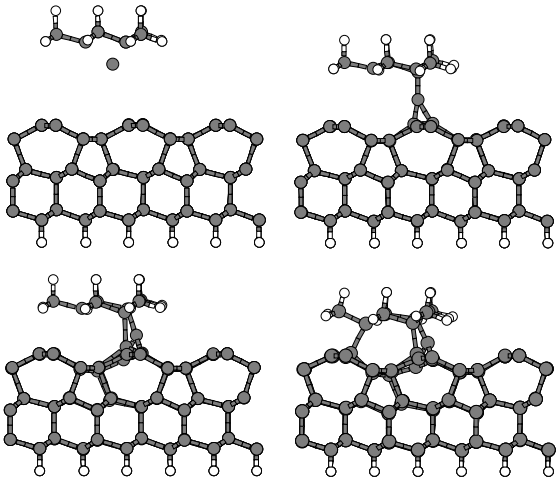

FIG. 4. Atomic configurations for tip heights 3.0 Å (top left), 1.6 Å (top right), 1.0 Å (bottom left) and 0.4 Å (bottom right) during approach curve 2.

is generated differs in some respects. Initially the boron atom at the tip apex remains approximately in its central position. At tip height 1.4 Å the boron moves towards the Pandey chain and forms a bond. This bond is weaker than in the case of carbon, and as the tip continues to advance the boron atom returns to a more central position where it forms bonds with carbon atoms in the surface. Additionally, the second layer carbon atoms in the tip form strong bonds with the surface.

Taken together, these results provide strong evidence that, at least for extremely hard materials, it is possible for a tip terminated by a single atom to balance the attractive vdW interaction. This is a prerequisite for atomic resolution CM-AFM. However, sustaining the vertical force does not imply that imaging is possible. In addition the tip apex atom must move with the tip when the tip is displaced laterally under load. To investigate this question we performed a simulation in which we started from vertical position 0.8 Å in approach curve 2 and moved the tip horizontally, through a distance of 1.6 Å. In the course of this interval the apex carbon atom did not change its bonding configuration and moved a horizontal distance of only 0.4 Å. This indicates that the carbon is highly likely to be lost as the tip advances further, and is certainly not moving smoothly over the surface. Between the start and

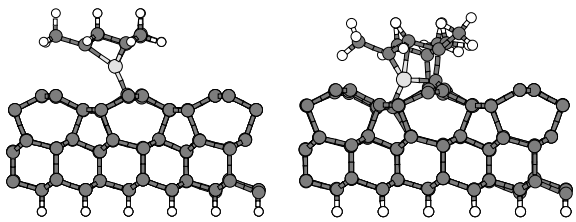

FIG. 5. Atomic configurations for tip heights 1.4 Å (left) and 0.4 Å (right) during the simulation (analogous to approach curve 2) in which the carbon at the tip apex was substituted by a boron atom.

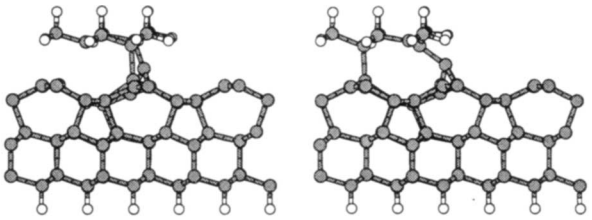

FIG. 6. Atomic configurations for the start of the lateral scan. This is equivalent to tip height 0.8 Å in approach curve 2 (left) and the end of the lateral scan when the tip has been advanced through a horizontal distance of 1.6 Å (right).

end of this simulation the vertical force on the tip dropped from 15.5 to 6.8 nN. Figure 6 illustrates the extensive deformation the tip undergoes during the lateral scan. It is clear that many of the atoms in the tip are involved in the reconstruction and, given the limited size of the tip, it is necessary to verify that the essential features of the deformation are insensitive to the tip size. To test this, new relaxed atomic configurations were calculated for certain tip positions using a larger tip. There were no qualitative differences in configuration between the larger tip and the smaller. The main difference between the simulations was that, with the larger tip, the shear forces in the upper layer of the tip lead to additional lateral relaxation. This has the result that, with the larger tip, one has to move through a greater horizontal distance in order to achieve the same degree of deformation.

Because of computational expense, a lateral scan was not performed using the tip terminated with boron. In this case it is not clear whether the surface will retain the apex atom, but lateral movement will be difficult as there are several strong covalent bonds which need to be broken. Also at small tip-sample separations the bonds between the boron and the surface are shorter than the bonds between boron and the tip indicating that is it more strongly bonded to the surface than the tip and hence likely to be retained by the surface during lateral movement. Taking bond distances as a guide, we can estimate a value of 2.4 nN as the largest possible repulsive force for safe operation with atomic resolution. This actually means experimental operation at net loads which are less than this by the magnitude of the vdW force, and constrains the possible tip geometries.

In summary, we have presented calculations which show that it is possible for covalent tips terminated by a single atom to sustain vertical forces in excess of that required to balance the vdW force. These forces are related to extensive tip relaxations, which are rather insensitive to the chemical reactivity of the apex. Similar tip apex relaxations have been found in the interaction of Si tips with III-V (110) surfaces [22,23], where large lateral forces due to the interaction with the neighboring anions appear even for distances where the repulsive force is still not larger than 1 nN. We have demonstrated that, at least in the case of high load, atomic resolution imaging may be degraded by a blunting mechanism in which the tip apex is lost to the surface. These calculations provide evidence that even in the favorable case of a single atom diamond tip imaging a diamond (111) surface true atomic resolution CM-AFM images may not be possible.

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