Atomic-force-microscopy Images of Graphite due to van der Waals Interactions

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The theoretical investigation of atomic-force-microscopy (AFM) images of graphite, in the case where van der Waals interactions play a major role, is presented. It is shown that the images display a centered hexagon formed by the center of the atomic hexagon on the top layer when the AFM is operated at distances at which forces between the tip and the surface become attractive. At closer distances at which forces change from attractive to repulsive, all atomic sites on the top surface of graphite become visible. Effects of multiple atoms lying on the top of the tip are examined. It is shown that, if the atomic arrangement on the top of the tip does not meet with the threefold symmetry of the graphite surface, the AFM images are significantly deformed.

I. INTRODUCTION

Atomic force microscopy (AFM) (Refs. 1 and 2) has recently been developed as a new technique for extending the high-resolution capabilities of scanning tunneling microscopy (STM).[3,4] Since AFM profiles a surface by measuring interatomic forces between the tip and the surface of interest, it can be applied to imaging nonconducting as well as conducting surfaces.

In order to investigate how the images obtained by AFM (Refs. 5 and 6) are different from those obtained by STM,[7,8] it would be most appropriate to take graphite as the substrate. In fact, graphite is an ideal substrate for studying with both STM and AFM in the sense that it is easily cleaved to give a flat and well-ordered surface. In response to experimental observations on graphite using STM, there have been a number of theoretical publications.[9-13] On the other hand, there have been few theoretical works[14,15] published for AFM images of graphite.

It has been resolved clearly by STM that the (0001) surface of graphite has two inequivalent atoms, which are called A- and B-type atoms, respectively. The A-type atoms have atoms directly below in the adjacent planes, whereas the B-type atoms do not have atoms below. A theoretical interpretation of the STM images is mostly due to the work of Batra *et al.*[11] Performing self-consistent charge-density calculations for three layers of graphite representing the (0001) surface, they have shown that there is a slightly higher charge in the vacuum region coming out of the B sites as compared to the A sites. In accordance with this tendency of inequivalence between A and B sites, it has been argued[13] that the local density of states at the Fermi level, by which the tunneling current is completely determined,[10] involves only B-type atoms. Therefore, it has been concluded that STM of graphite images only B-type atoms.

On the other hand, AFM images surface topography by mapping interatomic forces between the AFM tip and the surface of the sample. The interatomic force is given by differentiating the total energy of the system, consisting of the tip and the surface, with respect to the tip-to-surface distance. Within a good approximation, the total energy of the system at a fixed tip-to-surface distance can be expressed in terms of the total valence charge density. Therefore, the interatomic forces involve total valence charge density,[15,16] even though they are not related directly to the valence charge density. Usually, it can be considered that the interatomic force has two components: one originates from interactions between ion cores and the other is associated with valence electrons. This is in contrast to the case of STM, in which local density of states at the Fermi energy E_F plays the major role. Consequently, it is conceivable that AFM and STM might be sensitive to different types of sites on the graphite surface.

In general, the AFM operating at close proximity to the surface of graphite, interatomic interactions are considered to induce not only relaxation of electronic charge distribution but also atomic displacements leading to elastic deformation of the surface. The first theoretical calculation of interatomic forces between the tip and the surface of graphite was performed by Ciraci and Batra,[14] by using a self-consistent-field (SCF) pseudopotential method allowing for a full relaxation of the electronic charge distribution. Although the effect of atomic displacements induced by the tip has been neglected, it has been shown that the images of AFM operating at 1.4–2.5 Å above the surface are not necessarily identical to those obtained by STM and depend on tip-to-surface distances. Recently, Ciraci, Baratoff, and Batra[15] have presented a more extensive analysis of tip-sample interaction effects, based on a similar SCF pseudopotential calculation of electronic charge densities, total energy, and atomic forces for a graphite monolayer and larger arrays of single-atom and multiple-atom aluminum tips. Their results reveal that the ion-ion repulsion plays a dominant role in determining the corrugation at small tip-sample

separations, where most measurements have been made to date. Effects of electronic charge rearrangements are also drastic at sufficiently small separations, producing localized states and even chemical bondings. In their calculations, effects of lattice deformations have not been considered. On the other hand, the local distortions of a deformable surface of graphite in the vicinity of the AFM tip have been investigated by Tomànek et al.[17] on the basis of elastic continuum theory.

In this paper, we investigate the ideal case where the AFM tip operates at a distance not sufficiently close to the surface of graphite, so that the effect of the atomic displacements can be neglected. Such a tip-sample distance in the case of a carbon tip would be in the range $\gtrsim 3.35$ Å, which is comparable to or larger than the interlayer distance of graphite. In fact, Ciraci and Batra[14] have demonstrated that the magnitude of the repulsive force between the carbon tip and the surface of graphite is drastically reduced for a tip-sample distance beyond 3 Å or more. We simulate the tip with carbon atoms for simplicity of argument. In the present paper, therefore, we are primarily concerned with a tip-to-surface distance of about 3.35 Å or more. At this distance, the effect of a rearrangement of the electronic charge distribution can be considered to become not so significant because of a small overlap between the tip and sample wave functions. Therefore, we assume that the interactions between the tip and the surface in this range can be approximated by van der Waals interactions. It is shown in this system that the AFM images clearly display different patterns, which are not necessarily identical to patterns of STM images, depending on the tip-to-surface distance. Effects of multiple atoms lying on the top of the tip are examined. It is demonstrated that if the atomic arrangement on the top of the tip does not meet with the symmetry of the graphite surface, the AFM images are significantly deformed.

II. van der WAALS INTERACTIONS

For simplicity of calculation, we simulate the tip with a single carbon atom. Since we confine ourselves to the case where the AFM tip operates at distances not so close to the surface of graphite, say, around 3.35 Å or more, we assume that the effects of atomic displacements of the surface and rearrangement of the electronic charge distribution can be neglected and that van der Waals interactions between the tip and the surface play a major role. Taking van der Waals interactions with a Lennard-Jones-type potential[18] between carbon atoms, we can describe the atomic force $f(\mathbf{r})$ between the tip (atom) and the (0001) surface of graphite as follows:

$$f(\mathbf{r}) = \frac{-\partial U(\mathbf{r})}{\partial z} \, ,$$

$$U(\mathbf{r}) = \sum_{l,k} u(|\mathbf{r} - \mathbf{R}_{l,k}|) \, ,$$

$$\mathbf{R}_{l,k} = l_1 \tau_1 + l_2 \tau_2 + l_3 \tau_3 + \kappa_k \, ,$$

$$\kappa_1 = (0,0,0), \quad \kappa_2 = (a/2, -a/2\sqrt{3}, 0) \, ,$$

$$u(\rho) = 4\epsilon[(\sigma/\rho)^{12} - (\sigma/\rho)^6] \, ,$$

where z is the tip-to-surface distance, $\mathbf{r}$ is the position vector of the carbon atom on the tip, and $\mathbf{R}_{l,k}$ describes the position of carbon atoms of graphite. Parameters of the Lennard-Jones potential[18] are taken to be $\sigma = 3.44$ Å and $\epsilon = 1000$ K. The numerical calculation is performed by utilizing the crystalline symmetry of graphite.

Figure 1 shows the result calculated for a tip-to-surface distance z of 3.48 Å. The contour map represents the strength of atomic forces between the tip and the surface of graphite. For a reference, the atomic hexagon on the top layer is indicated by dotted lines. It is noticed that the atomic forces between the tip and the surface are attractive everywhere. Since the attractive force for the tip lying above the H site, which is the center of the hexagon in the top layer, is stronger than others, one may observe by AFM the centered hexagon formed by H sites. However, we should note that the atomic force is of the order of 10^{-10} N, and does not seem experimentally accessible to date. At present, therefore, we aim to illustrate qualitatively how the variation of the AFM pattern depends on tip-sample separation z. If the tip comes closer to the surface, then the contribution of the repulsive part of van der Waals interactions to the resultant atomic forces increases. In fact, at about $z = 3.42$ Å, forces on A and B sites turn out to be weakly repulsive, while forces on H sites are weakly attractive. At $z = 3.35$ Å, which is comparable to the interlayer distance of graphite, we obtain an equicontour map similar to Fig. 1, but the forces become repulsive everywhere. Since the forces on A and B sites are about 6×10^{-10} N and stronger than those on H sites, one may observe in the AFM both A and B sites. There is no distinction between A and B sites, because van der Waals forces due to atoms in the second layer are still too small at this distance. This pattern of repulsive forces appears to be emphasized as the tip comes closer to the surface. However, at such a close proximity to the surface, the present model of van der Waals interactions is no longer valid.
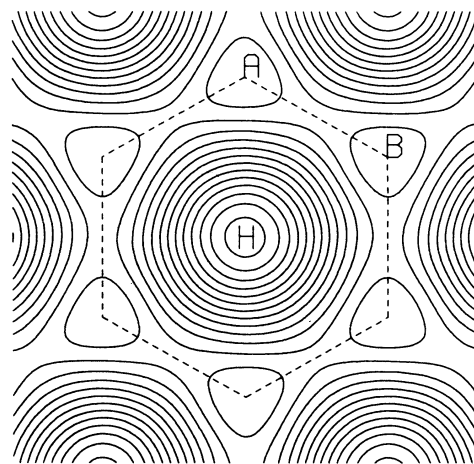

FIG. 1. Contour plots of atomic forces between the tip and the surface for $z = 3.48$ Å. Dotted lines indicate the atomic hexagon on the top layer of graphite. The most attractive forces are on the H sites. The contour lines closest to the H and A (or B) sites are -0.65×10^{-9} and -0.3×10^{-9} N, respectively.

III. MULTIPLE-ATOMIC TIP

In this section we examine the effect of multiple atoms lying on the top of the tip. For simplicity of argument we take diamond as the tip. The force on the center of mass of the tip is obtained by summing forces over all the tip atoms, since we assume no surface relaxation. The distance between the center of mass of the tip atoms and the surface of graphite is denoted by z. We are still interested in the range of z for which van der Waals interactions are considered to play an important role. Since the effect of symmetry of atomic arrangement on the top of the tip relative to the surface of graphite is found to be most important, we will show results only for $z = 3.42$ Å.

First we consider the case where the tip has only two carbon atoms protruding towards the surface of graphite. The interatomic distance between the two atoms is 1.80 Å. It is assumed that in the AFM operating at a distance of $z = 3.42$ Å only these two atoms play an important role, since other neighboring atoms, which are more distant from the surface of graphite, are found to yield qualitatively no significant alteration on the final results. The important results are summarized as follows.

(i) If the tip is scanned over the graphite surface by keeping the axis of these two atoms parallel to the H-H direction on the surface of graphite, then the equicontour of forces on the center of mass of two atoms is obtained as shown in Fig. 2. For a reference, the hexagon on the top layer of graphite is superimposed by dotted lines. In this case, one may observe that the AFM images show a centered hexagon formed by ellipses representing the most attractive forces, and a zigzag row of small ellipses representing the most repulsive forces. However, it is remarkable that the positions for the maximum or minimum forces do not correspond to A, B, or H sites.

(ii) If the axis of the two atoms on the top of the tip is inclined by 30° with respect to the H-H direction of graphite, then the equicontour map of forces is significantly deformed, as is shown in Fig. 3. In this case, the AFM images will show a centered hexagon formed by ellipses representing the most repulsive forces. The ellipses are elongated along the direction perpendicular to the axis of the two atoms. It is again noticed, however, that the positions representing the most repulsive forces do not correspond to A, B, or H sites.

Those anisotropically deformed images obtained in (i) and (ii) clearly originate from the fact that the orientation of two atoms on the tip relative to the surface of graphite does not meet with the threefold symmetry of the surface.[19,20]

Next we consider the case where only three atoms among tetrahedrally bonded carbon atoms on the top of the tip protrude toward the surface of graphite and equally play a major role in the AFM. The equicontour maps of forces on the center of mass of the three atoms are shown in Fig. 4. The images obtained look symmetric but evidently differ depending on the orientation of the triangle of three atoms relative to the symmetry axis of the surface of graphite. We denote the angle between the baseline of the triangle and the H-H direction on the surface of graphite by θ. For θ less than about 10°, the positions for strongest repulsive forces are on A (or B) sites, while those for strongest attractive forces are on B (or A) sites, even though we cannot identify which are the A or B sites. The typical pattern is shown in Fig. 4(a) for $\theta = 10°$. For an angle θ beyond about 20°, the repulsive force on the H site starts to exceed the repulsive (or attractive) force on the A (or B) site, and for $\theta = 30°$ the H site turns out to become the position for the strongest repulsive force, as shown in Fig. 4(b). We can conclude, therefore, in the case of the three-atom tip that one may
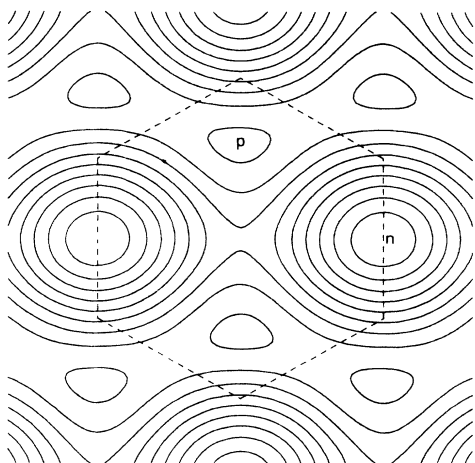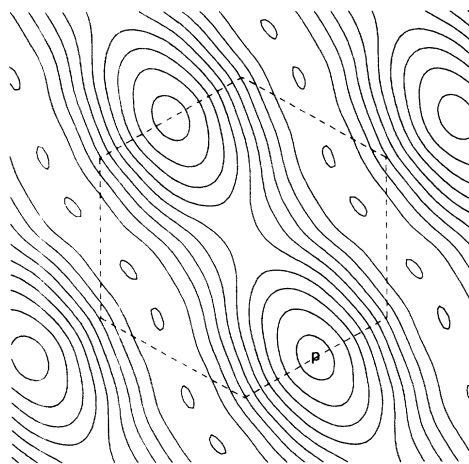

FIG. 2. Contour plots of forces on the center of mass of the two-atom tip for $z = 3.42$ Å. This is the case where the axis of the two atoms is kept parallel to the H-H direction on the surface of graphite. The atomic hexagon on the top layer is indicated by dotted lines for a reference. Positions for the most attractive or repulsive forces are indicated by n or p, respectively. The contour lines closest to the points n and p are -0.4×10^{-9} and $+0.4 \times 10^{-9}$ N, respectively.

FIG. 3. Contour plots of forces on the two-atom tip for $z = 3.42$ Å, provided that the axis of the two atoms is inclined by 30° with respect to the H-H direction. The atomic hexagon on the top layer is indicated by dotted lines for reference. The most repulsive positions are indicated by p. The contour line closest to the point p is $+0.4 \times 10^{-9}$ N. The contour spacing is 0.05×10^{-9} N.
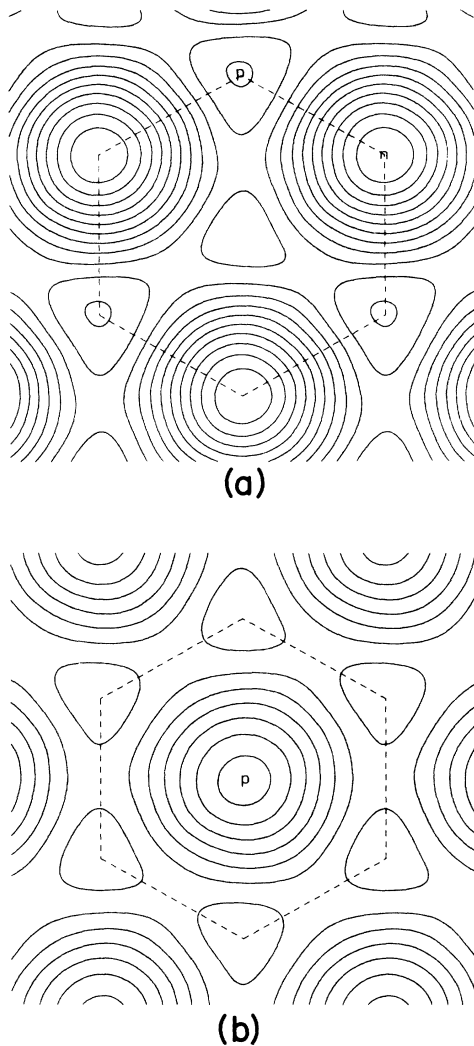
(a)

(b)

FIG. 4. Contour plots of forces on the center of mass of the three-atom tip for $z=3.42$ Å. The atomic hexagon on the top layer is indicated by dotted lines for reference. (a) The case for $\theta=10°$. The positions for most attractive or repulsive forces are indicated by n or p, respectively. The contour lines closest to the points n and p are -0.45×10^{-9} and $+0.45\times10^{-9}$ N, respectively. (b) The case for $\theta=30°$. The forces are repulsive everywhere. The most repulsive forces are on H sites. The contour line closest to the H site is $+0.4\times10^{-9}$ N. The contour spacing is 0.05×10^{-9} N.

obtain AFM images which show a centered hexagon formed by A, B, or H sites, even though they cannot be identified. Although we have considered the ideal case where the plane of the triangle of three atoms is parallel to the (0001) plane of graphite, we can easily imagine that the AFM images would be deformed, as in the case of a two-atom tip, if the triangular plane is inclined to the surface of graphite.

From the results obtained in the cases of two-atom and three-atom tips, we can understand how anomalous images arise and that they are not a property of the surface of graphite. It should be noted that if we take into account atoms other than the outermost ones on the top of

the diamond tip, we would find that the transition from attractive to repulsive regimes takes place at smaller separations, owing to the attractive forces due to the remote atoms.

IV. CONCLUSION

Assuming that van der Waals interactions between the diamond tip and the surface of graphite play a major role in the AFM operating at tip-to-surface distances of 3.35–3.48 Å, we have calculated the atomic forces between the tip and the rigid surface. Since the minimum of the van der Waals potential drops within those ranges of distance, the resultant atomic forces between the tip and the surface, which are given by a superposition of attractive and/or repulsive forces over all atoms, become attractive or repulsive depending on the tip-to-surface distance z. This has been demonstrated in the simplest case where the tip is simulated by a single carbon atom. In accordance with this variation of forces the AFM images will show various patterns depending on z. In the AFM operating at ~ 3.48 Å above the surface one may observe a centered hexagon formed by H sites, although the attractive forces are weak and of the order of 10^{-10} N. On the other hand, in AFM operating at ~ 3.35 Å one may observe both A and B sites instead of H sites, because the repulsive forces on A and B sites are much stronger than those on H sites. There is no distinction between A and B sites. If the tip comes much closer to the surface, we have to take into account the effect of electronic and atomic relaxations,[21] which is beyond the scope of the present model.

Since the atomic forces become attractive or repulsive, as described above, depending on the tip-to-surface distance in the range of 3.35–3.48 Å, it is important to examine the effect of the multiple-atom tip. We have examined two simple cases of multiple-atom tips, taking diamond as the tip. The results obtained for $z=3.42$ Å are summarized as follows.

(i) In the case where the tip has only two carbon atoms protruding toward the surface of graphite, the pattern of AFM images is deformed anisotropically depending on the orientation of the two-atom axis relative to the symmetry axis of the surface. The anisotropic deformation of AFM images originates from the fact that the orientation of two atoms on the tip relative to the surface of graphite does not meet with the threefold symmetry of the surface. The important result in the case of the two-atom tip is that the positions for the maximum (or minimum) forces do not correspond to A, B, or H sites.

(ii) In the case where only three atoms among tetrahedrally bonded carbon atoms on the tip protrude toward the surface of graphite, we obtain the equicontour maps of forces which differ depending on the orientation of the triangle of three atoms relative to the symmetry axis of the surface of graphite. There are two kinds of characteristic patterns: (a) repulsive forces are strongest on A (or B) sites, while attractive forces are strongest on B (or A) sites, or (b) H sites become the positions for strongest repulsive forces. Thus, in the AFM imaging repulsive or attractive forces, one may observe a centered

hexagon formed by A, B, or H sites, but they cannot be identified.

These results described above in the cases of two- and three-atom tips are useful in understanding how anomalous images arise and that they are not a property of the surface of graphite. It should be noted that the identification of A, B, or H sites is not necessarily possible in AFM images taken using a multiple-atom tip. Obviously, a more realistic model for the tip deserves future investigations. Finally, it should be noted that in spite of small atomic forces, the AFM operating at such large tip-sample distances as studied in this paper will provide us with fruitful information, because the effects of atomic relaxation on the surface of graphite can be neglected.

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