Simple theory for the atomic-force microscope with a comparison of theoretical and experimental images of graphite

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(Received 11 October 1988)

In this theory the atom-atom interactions within the sample are modeled with use of a force-constant matrix that is valid in the harmonic approximation. The tip-atom-sample interactions are modeled by a Lennard-Jones potential. Images for single-atom tips that are calculated from this theory, in which the atoms are allowed to relax, are similar to previous theoretical images that were calculated from a rigid-sample model. The asymmetric images produced by experiment could be reproduced theoretically with double-atom tips. All calculations were performed using a commercially available desk-top computer.

With the invention of the scanning tunneling microscope[1] (STM) and the atomic force microscope[2] (AFM), there is new interest in understanding the interaction between a single atom and a surface. Highly oriented pyrolytic graphite (HOPG) has been the focus of numerous STM experiments because of HOPG's well-known physical properties.[3] These experiments have shown that a wide range of images are possible with the STM;[4-8] consequently a number of theories explaining the content of the images have been developed.[9-12] Unfortunately, the AFM is not yet as reliable an instrument as the STM so both experimental images[13-15] and theoretical images[16,17] have been less abundant. Our group has successfully imaged graphite during the process of developing better AFM's.[15] This paper is a report on our efforts to understand the information contained in these images.

Our goal was to reproduce experimental images[13-15] using a simple theory of the interaction between the AFM tip and the graphite surface. In our theory the atoms in the surface were allowed to relax. It turned out, however, that for applied forces in the range of 10^{-11}–10^{-8} N our single-atom-tip images were nearly indistinguishable from those produced by a rigid-sample model[16] (one in which the atoms are not allowed to relax). The key to reproducing experimental images turned out to be going beyond single-atom-tip images and simulating asymmetric tips. Fortunately, just going to the simplest asymmetric tip, one with two atoms, was sufficient to reproduce experimental images.

Figure 1 is the first experimental image we tried to reproduce. It was processed from a previously published[18] image by unit-cell averaging. Corrugation distances measured were 0.02 nm between the hole and the highest site (designated as A) and 0.002 nm between A and the second type of site (designated as B). The force applied by the tip could not be accurately determined.[15]

We first apply a single-atom-tip theory in an attempt to reproduce the image. To begin with, we assume the system is always close to equilibrium. This assumption is appropriate since the force constants in graphite yield relaxation times which are much shorter than the time required to move the AFM an appreciable distance.[3] Our problem then becomes one of determining the many-body potential $U(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$, where $\mathbf{r}$ is the tip position and $\mathbf{r}_1,\ldots,\mathbf{r}_N$ are the positions of the graphite atoms, and of solving the $3N+1$ equations:

$$\frac{\partial U}{\partial \mathbf{r}_i}=0, \quad i=1,\ldots,N ,$$

$$-\frac{\partial U}{\partial z}=F_z ,$$

where z is the component of $\mathbf{r}$ perpendicular to the surface. Here F_z is fixed by the experiment, $\mathbf{R}$, the components of $\mathbf{r}$ parallel to the surface, are given and we plot $z=z(\mathbf{R},F_z)$. This is known experimentally as constant-

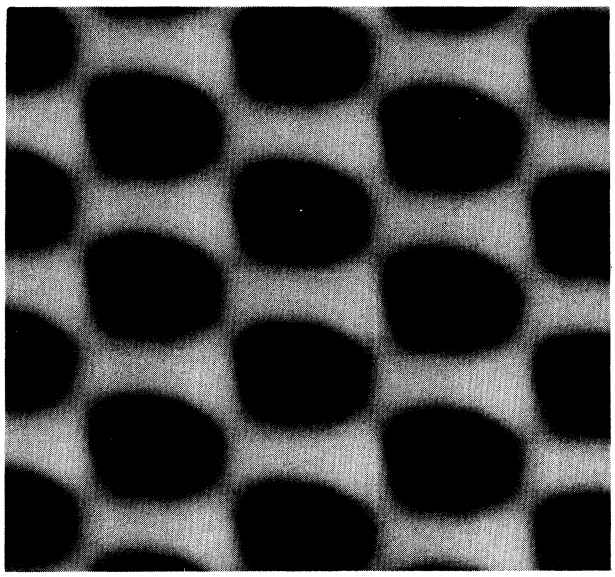

FIG. 1. Atomic-force microscope image of graphite. This image was filtered using a low pass filter and then unit-cell averaged. Note the apparent presence of two types of atoms: three bright and three dim in each ring, differing in height by approximately 10%.

force mode. The surface corrugation, $\bar{z}$, given by the difference of the maximum and minimum z values, is one quantity measured by the AFM that the theory must reproduce.

We make the simplifying assumption that the tip atom interacts with any graphite atom only through a pair potential and that this potential is the same for all graphite atoms, i.e.,

$$U(\mathbf{r},\mathbf{r}_1,\ldots,\mathbf{r}_N)=\sum_i V(\mathbf{r}-\mathbf{r}_i)+\bar{V}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\ .$$

Here $\bar{V}(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ is the many-body graphite potential in the absence of the tip (see Fig. 2). This approximation has the advantage of producing a theory which is easily solved, although it would be more appropriate for an ionic material, such as an alkali halide crystal. We point out that this view is, in a sense, the opposite extreme to that of Batra and Ciraci,[16] who considered the tip interaction with the electrons in the surface, but allowed no relaxation; subsequently our conclusions complement theirs.

For small displacements from equilibrium, the harmonic approximation is valid

$$\bar{V}(\mathbf{r}_1,\ldots,\mathbf{r}_N)=\tfrac{1}{2}\sum_{i,j,\mu,\nu} u_\mu^{(i)} D_{\mu\nu}^{(i,j)} u_\nu^{(j)}\ ,$$

where $u_\mu^{(i)}$ is the μth Cartesian component of the displacement from equilibrium of the ith atom, and $D_{\mu\nu}^{(i,j)}$ is the matrix of force constants for the solid. For HOPG, Nicklow *et al.*[3] calculated the force constants by fitting them to phonon dispersion curves, found from neutron scattering. We used their values, assuming an ideal surface,[19] where the surface layers are identical to the bulk layers.

Finally, on physical grounds we choose a simple Lennard-Jones potential for V:

$$V(|\mathbf{r}_{\rm tip}-\mathbf{r}_{\rm atom}|)=V_0[\tfrac{1}{2}(r_0/r)^{12}-(r_0/r)^6]\ .$$

The values for the constants V_0 and r_0 are not well known. Calculations for the values using noble gas-surface models have not been verified experimentally.[20] In our calculations, we fit them with two criteria: (1) the tip to sample distance at which the force on the tip changes from repulsive to attractive should be in good agreement with Soler's and Batra's calculations,[11,16] and (2) the experimental corrugation should be reproduced. The values, $V_0=2.8\times10^{-21}$ J, $r_0=0.28$ nm, meet these criteria. We would like to emphasize that these values for V_0 and r_0 are not necessarily unique.

Once the potentials were determined, the tip was placed above the surface and the surface relaxed. A standard numerical technique (Fletcher-Reeves method of steepest descent) was employed to determine the configuration of minimum energy,[21] and calculations were performed on an Intel-80386 based computer equipped with an Intel-80387 math coprocessor.[22] To calculate an image took from 4 to 20 h depending on the required resolution and the force applied. Increasing either the resolution or force increased the time required to produce an image.

Repeated computations showed that a surface of six to eight atoms across and two to three layers deep with the other atoms fixed was sufficient for producing images. Adding more atoms did not significantly affect the force measured by the tip. Images of tip height for constant forces as well as images of force for constant tip height were produced. A typical constant force image is shown in Fig. 3. Since the harmonic approximation restricted us to small atomic displacements, the largest repulsive force we could apply was 10^{-8} N.

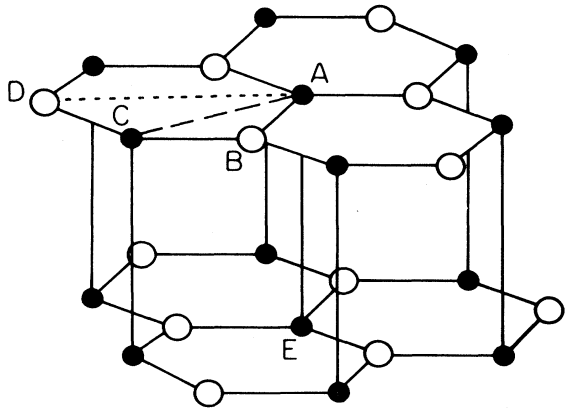

FIG. 2. Schematic of graphite showing that there is an atom directly beneath only half the surface atoms. In our model, there is an interaction between any carbon atom and its four nearest neighbors.

The results of our computations indicated that the corrugation, $\bar{z}$, which for graphite is the difference in heights of site A and the hole, could be reproduced by the reasonable values for V_0 and r_0 given above. We further found that the corrugation increases with applied force, and that, for forces up to approximately 10^{-8} N the difference between the corrugation predicted by our mod-

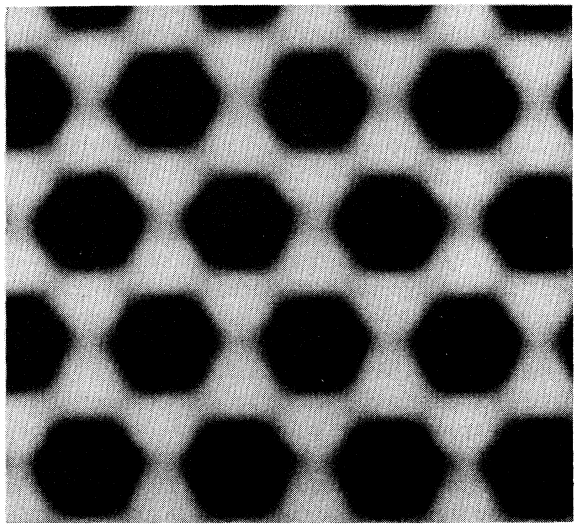

FIG. 3. Typical image of graphite created with the model using a single-atom tip. The difference in heights between the two types of sites was approximately 1%, much smaller than Fig. 1. Adding more force did not increase the percentage difference.

el and that predicted by a rigid-sample model was negligible. This was due to the atomic relaxation being small for these forces.

Another quantity the experiment determined was z_{AB}, the difference in height between A and B sites, which was found to be about 10% of $\bar{z}$. Our model could not reproduce this result; the largest value we found was approximately 1% of $\bar{z}$. This can be understood from the force constants: the force constants between atoms in different planes are roughly 1% of the force constants between atoms within the same plane.

Since the experimental asymmetry between A and B sites could not be explained with a single-atom tip, we next tried double-atom tips. Other authors have previously shown that multiple-atom tips can reproduce STM images of graphite[23] and both STM (Ref. 24) and AFM (Ref. 25) images of silicon.

Figure 4 shows six theoretical AFM images of graphite for various double-atom tips. For example, Figure 4(a) is a result of one atom on the tip being approximately one graphite bond (0.142 nm) away and slightly higher than the other atom on the tip (0.02 nm). It reproduces Fig. 1 quite well. The image shows two distinct sites, with corrugation values similar to what was measured by the AFM. In fact, the agreement is close enough that even detailed contour plots agree (Fig. 5) very well. We have also compared our theoretical images with other published experimental images. Figures 4(a), 4(d), and 4(e) are similar to Figs. 4(c), 4(d), and 4(b), respectively, of Albrecht and Quate,[14] while Fig. 4(b) is similar to Binnig, Gerber, and Stoll's Figs. 2(d) and 2(e).[13]

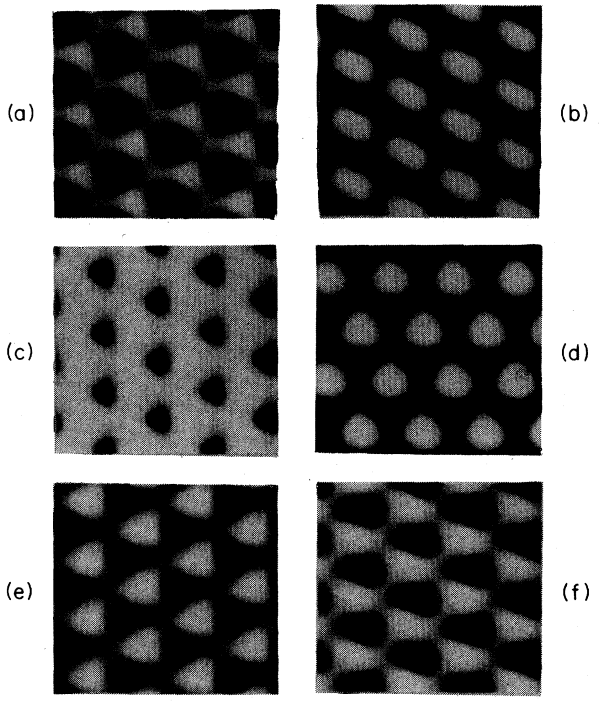

FIG. 4. Theoretical images of graphite created with different double-atom tips. (a) reproduces the experimental image in Fig. 1.

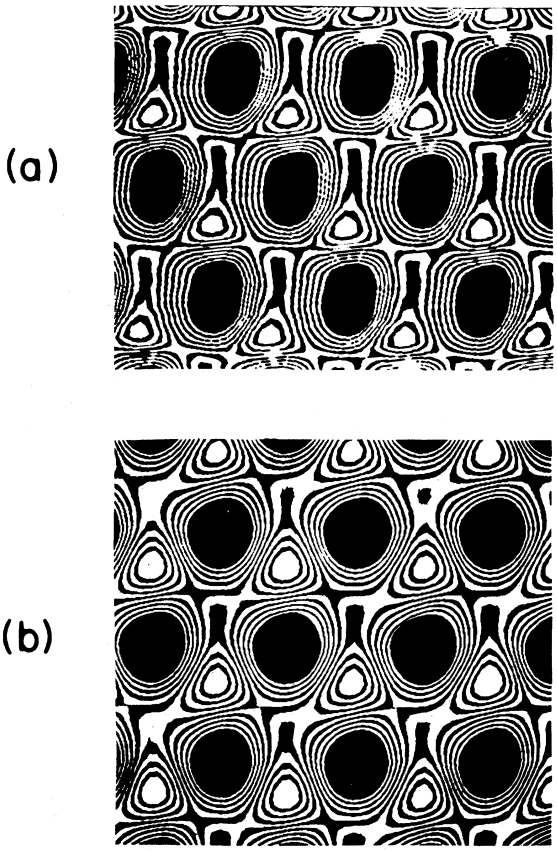

FIG. 5. These contour images of experimental data (A) and our theoretical model with a specific double tip (B) allow closer comparison than Figs. 1 and 4(a). Note that neither image shows the threefold rotational symmetry that would be present if the difference in heights was due to either electronic charge distribution or second-layer effects.

In summary we have used a simple theory to reproduce nearly all published experimental AFM images of graphite. In this theory, each tip atom interacts with each atom in the sample through a Lennard-Jones 6-12 potential. Each atom in the sample relaxes and interacts with the other atoms in the sample via a matrix of force constants that can be measured by neutron scattering. We find that for small forces ($< 10^{-8}$ N), local deformations are small enough to justify the assumption[16] of a rigid surface in an electronic model. The key to reproducing experimental images is modeling the asymmetric tips that are used in experiments with double-atom tips in the theory.

We would like to thank H. Metiu and J. Jenson for their suggestions. This work was supported by the National Science Foundation—Solid State Physics—Grant No. DMR 8613486 (S.A.C.G, P.K.H) and by the Office of Naval Research Grant No. N00014-84-K-0548 (K.B.).

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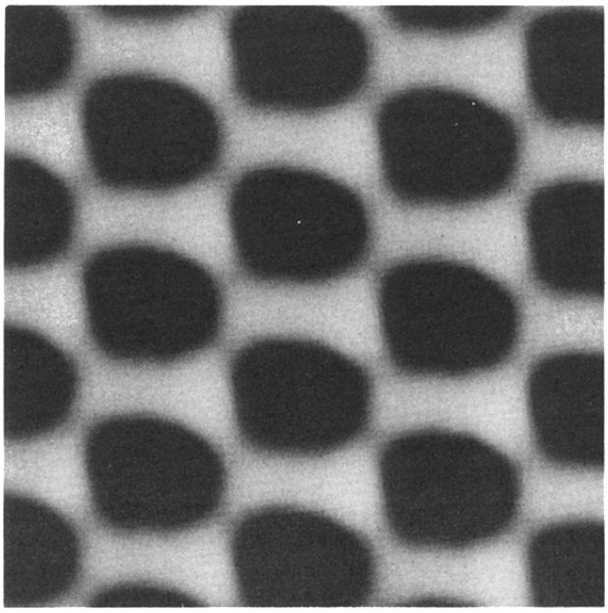

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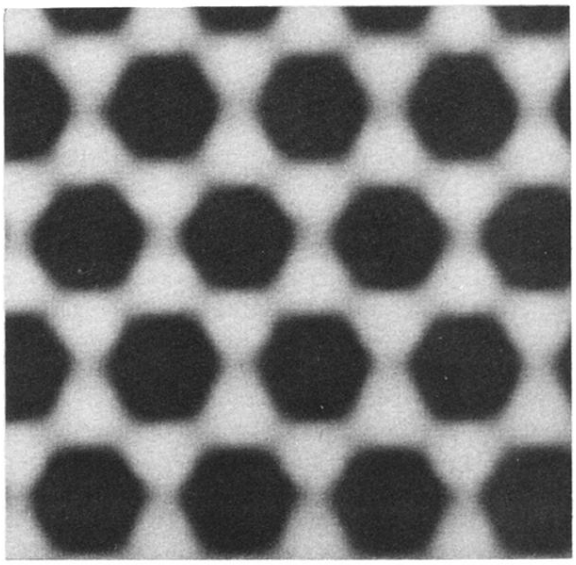

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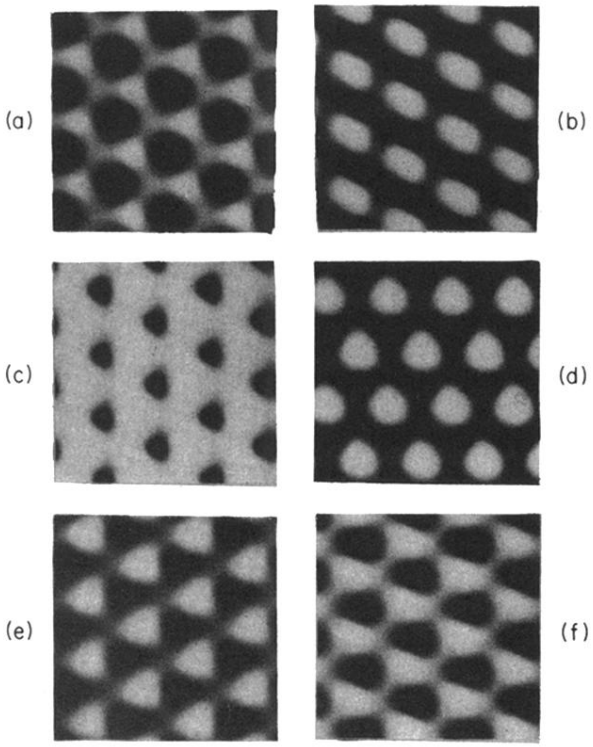

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