

Tip-Dependent Corrugation of Graphite in Scanning Tunneling Microscopy

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We calculate scanning-tunneling-microscope images of graphite, for various one-atom tips. The results deviate from the s -wave tip model, in some cases severely, depending sensitively upon the tip atom. For relevant atoms, the corrugation of the image is less than 0.3 Å. The small size of the corrugation suggests that mechanical distortions, which enhance the apparent corrugation in experiments with graphite, are even more ubiquitous than has been recognized.

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Because it yields atomic-resolution images in air, graphite is the single most popular sample used in scanning tunneling microscopy¹ (STM). Yet despite extensive investigations,²⁻⁸ there are still major gaps in our understanding of STM of graphite. Experimentally, graphite images may be grossly distorted by mechanical interactions between tip and surface,^{6,7} which are not fully understood. Theoretically, studies to date^{2,4,5,9} have made use of the s -wave tip model of Tersoff and Hamann.¹⁰ While this model is generally quite accurate,^{11,12} graphite is precisely the case in which it is expected to err most.¹¹

Here we calculate STM images of graphite, using a realistic model for a single-atom tip. The images are found to be extremely sensitive to the choice of tip atom, indicating a breakdown of the s -wave tip model in this case. For atoms relevant to experiment, the intrinsic corrugation is much smaller than expected, < 0.3 Å. In fact, for a transition-metal atom, the calculated corrugation is only 0.1 Å. This is much smaller than seen in any experiment to date, suggesting that perhaps no graphite measurements have been free from distortion by mechanical interactions.

While graphite is the most popular sample for STM, it is, ironically, also the most pathological sample known, in at least three distinct ways. First, the peculiar electronic structure of graphite leads to enhanced resolution,¹³ and to anomalous corrugation in the local density of states (LDOS) at the Fermi level (E_F).^{4,5} (Within the s -wave tip model,¹⁰ the STM image corresponds simply to the surface LDOS.) Second, of all surfaces, graphite is expected to exhibit the largest deviations from the predictions of the s -wave tip approximation.¹¹

Third, mechanical interactions between tip and surface appear to play a major role in STM of graphite, enhancing the apparent corrugation in a way which is uncontrolled and poorly understood.^{6,7} As a result, the apparent corrugation of graphite in STM can be unphysically large, e.g., 10 Å. These interactions appear to be related to contamination.⁷ The only experiment reported to date in UHV found³ a more modest corrugation of about 1 Å.

Such a 1-Å corrugation seemed appropriate, since Selloni *et al.*² had previously calculated a similar corrugation for the LDOS of graphite, i.e., for the image expected within the s -wave tip model. However, there are two problems with this apparent agreement between theory and experiment.

Theoretically, because of the discrete sampling of the Brillouin zone, the calculation of Ref. 2 should be a lower bound on the corrugation of the LDOS at E_F (Ref. 4) (which would be infinite were it not for the finite lateral extent of the Fermi surface, as discussed below). The important point, though, is that Selloni *et al.*² assumed that the STM image corresponds to the LDOS, as it would for an s -wave tip.¹⁰ While this correspondence is rather accurate in most cases, as noted above, the s -wave tip model has been shown to break down under special circumstances,¹¹ of which graphite represents the most extreme example. Thus, calculations for graphite going beyond this approximation are essential for a meaningful comparison.

Experimentally, such a corrugation of 1 Å in the constant-current mode would imply that a measurement in the "fast-scan" mode, where the tip height remains essentially constant, should give a current varying by nearly 2 orders of magnitude¹⁴ with lateral tip position. However, actual measurements invariably give a much smaller variation. While a quantitative interpretation is difficult,¹⁵ this discrepancy could be understood if we assume that even the 1-Å corrugation includes a substantial enhancement from elastic distortions. In a more recent attempt to maintain scrupulously ideal conditions, Hamers¹⁶ was unable to obtain a corrugation greater than 0.3 Å.

Thus, we must conclude, based on the limitations of prior theory, and the apparent inconsistency among experiments, that it is not known what the STM image of graphite would look like ideally, in the absence of mechanical interactions. By calculating the image for a realistic tip, we offer a quantitative answer to this problem, while illustrating the dramatic corrections to the s -wave tip model which take place in this very special case.

The calculation of the tunneling current, within first-

order perturbation theory, only requires knowledge of the wave functions of the noninteracting surface and tip.¹⁰ Here, the tip wave functions are calculated exactly as in Ref. 17, for a single atom adsorbed on a planar jellium surface. The jellium density is taken as $r_s = 2a_0$, and the atom position is determined by minimizing the energy.

The graphite surface wave functions are represented by an accurate analytic model, similar to that in Ref. 4. We neglect the tiny lateral extent of the graphite Fermi surface, and treat it as two lines whose projections onto the surface Brillouin zone are two points at the inequivalent zone corners. Then, as discussed by Tománek *et al.*,⁵ at each of the two inequivalent corners of the surface Brillouin zone there are two degenerate states, localized on the inequivalent sublattices (see inset, Fig. 1).

In the vacuum region, the four distinct wave functions at E_F have the form

$$\psi = \sum_{n=1}^3 \exp[\pm i\mathbf{k}_n \cdot (\mathbf{x} - \boldsymbol{\tau})] \exp(-\kappa_k z). \quad (1)$$

Here, $\kappa_k^2 = \kappa^2 + k_n^2$, where $\hbar^2 \kappa^2 / 2m$ is the graphite work function; \mathbf{k}_n are three wave vectors of magnitude $4\pi/3a$, corresponding to three corners of the graphite surface Brillouin zone, 120° apart; $\boldsymbol{\tau}$ is one of two atomic sites in the unit cell; and the sign (\pm) distinguishes the two inequivalent corners of the Brillouin zone.

Because higher harmonics in the real wave function decay extremely rapidly, this simple model is essentially exact far from the surface, *except* for the neglect of the finite lateral size of the Fermi surface. Even this approximation will consistently overestimate the corrugation, so our calculations represent an upper bound on the actual corrugation. Since a central point here is the smallness of the corrugation, the approximation only strengthens our conclusion.

Each wave function has two nodes per cell, one on the

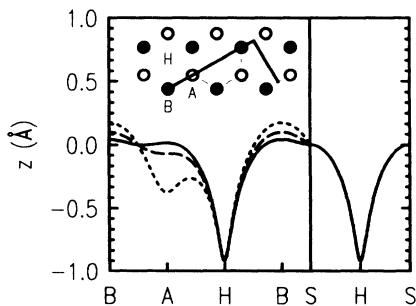


FIG. 1. Calculated STM scan for graphite, represented by Eq. (1), with a Na-atom tip. The three curves correspond to different assumed ratios of *A*-site to *B*-site densities of states: 0.9 (solid line), 0.5 (dashed line), and 0.1 (dotted line). Inset: Path along surface for line scan shown, corresponding to two straight segments: from *B* site (solid circle) through *A* (open circle) and hollow sites *H* to midbond site *S*, and then between two midbond sites across hollow.

hollow site in the graphite lattice, and one on the sublattice which does not include $\boldsymbol{\tau}$. As discussed by Tománek *et al.*,⁵ the two wave functions have very different dispersion with *perpendicular* wave vector, so their contributions to the current will be multiplied by different densities of states. The ratio of these contributions varies considerably with bias voltage,⁵ with the so-called *B* site (the site with no atom directly below) giving the larger current. This is consistent with the apparent asymmetry between *A* and *B* atoms seen experimentally,⁵ where the image may typically appear to show only one of the two atoms.

The calculated tip height versus lateral position, in constant-current mode, is shown in Fig. 1, for a Na tip atom. [Because of the electronic structure (1), the image is independent of tip height.⁴] The lateral path of the tip is indicated in the inset, and is chosen to sample a variety of symmetry points and lines. The three different curves represent three different assumptions about the site asymmetry, with the *A* atom contributing 90% as much current as the *B* atom, half as much, or 10% as much.

The intermediate case (dashed line) may be the most realistic, but all three are included for completeness, since according to Ref. 5 a range of behavior can be obtained by varying the voltage. Since the image along the path *SHS* is, by symmetry, independent of the (unknown) *A*:*B* ratio, we focus on that path in subsequent figures.

The most important result here is the comparison of different tip atoms, shown in Fig. 2. The results for a Na-atom tip corresponds fairly closely to those for the *s*-wave tip model, also shown in Fig. 2, except that the singularity is rounded out into a sharp dip, reaching a depth of 1 Å. A Ca atom gives a significant reduction in corrugation, to about 0.6 Å.

However, real tips are neither Na nor Ca, but rather transition metals, possibly contaminated with atoms from the surface (e.g., Si and C are common sample materials). For a Si-atom tip, the corrugation is reduced

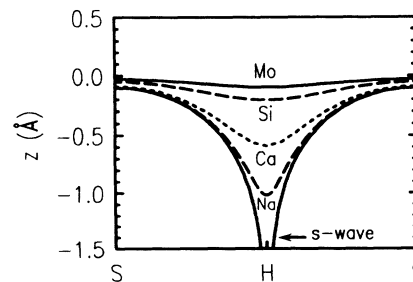


FIG. 2. Calculated STM scan along the *SHS* portion of the path shown in Fig. 1, for several different tip atoms. Curves correspond, from top to bottom (least to most corrugated), to tip of Mo (solid line), Si (dashed line), Ca (dotted line), and Na (dashed line), and to ideal *s*-wave tip (solid line).

drastically, to less than 0.3 \AA . The reduction is even more extreme for Mo, the only transition metal studied, with a corrugation slightly over 0.1 \AA .

The physical mechanism underlying these variations is quite simple. The wave functions (1) have a node at the hollow site in the graphite lattice. Thus, within the s -wave tip model, the current goes to zero when the tip is centered over this site. More generally, for any tip wave function with cylindrical symmetry (azimuthal quantum number $m=0$), the current vanishes by symmetry for the tip over the hollow site. This gives a singularity in the image (which in reality would be reduced to a sharp dip, both by the finite lateral extent of the Fermi surface and by the finite instrumental response⁴).

Any real tip, however, will have wave-function components with $m \neq 0$, leading to a significant tunneling current even over the hollow site. The greater these contributions, the smaller the corrugations. In order to quantify these contributions, we decompose the total current by m value. To avoid site dependence, this is done for a wave function of a smooth surface, consisting of a single one of the three terms in (1).

The results are shown in Table I. For Na, 97% of the current is associated with $m=0$, accounting for the close agreement with the s -wave model seen in Fig. 2. Since the isolated Na atom has an s^1 configuration, this is quite reasonable. For Ca, with an s^2 configuration for the free atom, adsorption can more easily mix in $m=1$ character, because the p resonance lies nearer E_F . The 9% contribution from $m=1$ from each plane wave in (1) results in a significant current even over the hollow site, and hence a large reduction in corrugation.

For Si, with an s^2p^2 atomic configuration, the $m=1$ contribution is almost as large as the $m=0$ (which includes both s and p_z). And for Mo, while the p contribution is reduced, this is more than compensated by the large contribution from states of d -like symmetry, which contributed negligibly in the other cases. Thus, the corrugation for Mo is quite small indeed.

The decomposition in Table I should not be viewed as typical for STM. The relative contributions of different m depend on the parallel wave vector, with higher m

becoming more important for larger wave vectors. Graphite has a uniquely large wave vector for states at the Fermi level, 1.7 \AA^{-1} . For a wave vector more typical in STM, 0.4 \AA^{-1} , the contributions for a Mo tip from $m=1$ and 2 are reduced to 22% and 1%, respectively, consistent with the small contribution of d states found in Ref. 18. Thus, it is the extremely small size of the unit cell, as well as the unique electronic structure, which makes graphite so sensitive to the identity of the tip atom.

It would be natural to include a carbon-atom tip in Fig. 2, since the tip might pick up an atom from the graphite. However, this case requires some discussion.

The calculated image for a C atom is shown in Fig. 3 (upper dotted line). While the corrugation magnitude is comparable to that for Si, the sign of the contrast is reversed, with a maximum current over the hollow site. This unexpected behavior results from the fact that the $m=1$ contribution dominates the current,¹⁹ as seen in Table I, apparently due to a cancellation between the contributions of the carbon s and p_z orbitals to the $m=0$ matrix element.

Such nearly complete cancellation represents an improbable coincidence, and can be easily spoiled. For example, a change of only 5% in the surface lattice constant (which affects the two terms in the matrix element differently) restores a more normal image, as seen in Fig. 3. (Note that both horizontal and lateral scales in Fig. 3 are dimensionless, and in ordinary length units would be different for each curve.) Similarly, for a C atom in a very different environment, e.g., bonded to a transition-metal tip or carbon cluster instead of to jellium, such a cancellation seems unlikely. Thus, this case, though interesting, should probably be viewed as merely academic.

We wish to stress that the severe deviations found here from the predictions of the s -wave tip model result only from the combination of two factors, the special elec-

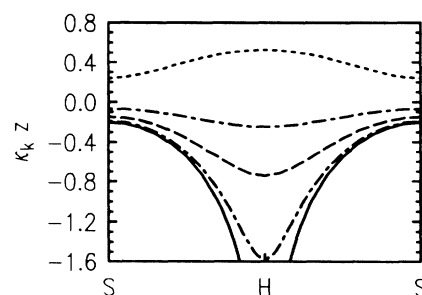


FIG. 3. Calculated STM scans as in Fig. 2, for C-atom tip. Note dimensionless x and z axes to facilitate comparison. The upper dotted line is actual result for graphite. For comparison, the calculation is repeated for a hypothetical surface with graphite electronic structure as described by Eq. (1), but with the lattice constant increased by about 5% (upper dot-dashed line), 100% (dashed line), and 300% (lower dot-dashed line). The lower solid line shows result for the s -wave tip.

TABLE I. Percent contribution to the current from $m=0$, 1, and 2, for different tip atoms, in the case of a plane-wave surface wave function with the same wave vector as graphite; and peak to trough corrugation Δ on graphite, in \AA , from Fig. 2. The $m=3$ contribution is negligible in every case. See discussion in text regarding C.

Atom	$m=0$	$m=1$	$m=2$	Δ
Na	97	2	1	0.9
Ca	88	9	3	0.5
Si	59	41	0	0.2
Mo	46	28	26	0.1
C	1	99	0	-0.2

tronic structure of graphite and its very small lattice constant. Based either on the analysis of Ref. 11 or on that of Chen,¹⁹ we anticipate that the identity of the tip atom will become relatively unimportant when the lattice constant is large compared with some characteristic "atomic size" (or, more precisely, when the surface wave vector is small compared with κ). This was alluded to in the discussion of Mo, where we noted that for smaller surface wave vector, the $m=0$ term dominated the current more than for higher wave vectors.

The expected behavior is confirmed in Fig. 3, for the case of C. As the lattice constant is increased, the image becomes more and more like that for an s -wave tip. A similar dependence on lattice constant occurs with any tip atom. Intuitively this seems natural; the s -wave tip is equivalent to a point tip,¹⁰ and the larger the lattice constant, the more the atom seems like a point on the relevant length scale.

In conclusion, graphite stands in stark contrast to other materials, in that its STM image is very sensitive to the identity of the tip atom. This sensitivity results both from the unusual electronic structure of graphite and from its extremely small lattice constant. In principle, even inversion of the contrast can occur, as was found for a C-atom tip. For all atoms studied which might reasonably occur on an STM tip, the corrugation amplitude is much smaller than has been believed.

We are grateful to R. J. Hamers for making results of Ref. 16 available prior to publication.

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¹⁴This would be only 1 order of magnitude for a metal with comparable corrugation amplitude; but graphite has an anomalously large value of κ_k in Eq. (1).

¹⁵While the normal "constant-current" mode is more susceptible to distortion from elastic interactions, the "constant-height" fast-scan mode suffers from the large dynamic range of the current. In either mode, the finite instrumental response time can reduce the apparent corrugation, especially since the maximum corrugation is determined by a narrow deep dip at the hollow site. Thus any quantitative analysis requires a careful treatment of the instrumental response.

¹⁶R. J. Hamers (to be published).

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¹⁹Chen has pointed out [C. J. Chen, *J. Vac. Sci. Technol. A* **6**, 319 (1988)] that peculiar effects could occur if the tip wave function had, e.g., purely p_x symmetry. However, this is certainly not the case for any real tip, and is quite different from the situation here for C.