Interatomic Forces in Scanning Tunneling Microscopy: Giant Corrugations of the Graphite Surface

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We show that scanning tunneling microscopy (STM) images can be dominated by elastic deformations induced by atomic forces between tip and surface. New STM experiments on graphite (0001) showing a strong variation of the giant corrugation amplitudes with varying current at constant voltage are direct evidence of this atomic-force concept. Corrugations up to 8 Å on a lateral scale of 2.4 Å are associated with forces up to 10^{-8} N for compression and 2×10^{-10} N for expansion.

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In this Letter, we demonstrate that scanning tunneling microscopy (STM)[1,2] images can be completely dominated by elastic deformations induced by the interatomic forces between tip and surface. This provides a natural explanation for the giant corrugation amplitudes observed in graphite[3,4] and laminar compounds,[5] and offers a novel approach to the imaging of atomic forces with the STM. We elucidate this atomic-force concept for the case of graphite, and corroborate it with new STM measurements of the dependence of the giant corrugation amplitudes on tunnel current at constant voltage. Similarities to and differences from the atomic force microscopy (AFM)[6] recently introduced will become evident as we proceed.

In the constant-current mode of STM,[2] the tunnel tip traces contours of constant density of states.[7-9] On clean metal surfaces, in general, such an STM image is representative of the surface topography; on semiconductor surfaces, the varying local density of states (LDOS) mixes features of purely electronic origin into the STM images.[2,10] In graphite[3] and laminar compounds,[5] the STM image was ascribed to LDOS features alone.[11,12] We show here that the giant corrugation amplitudes observed in these materials are due to a huge enhancement of the electronically based corrugations by local elastic deformations.

Flatness and inertness make the cleavage (0001) plane of graphite an ideal substrate in surface-science and STM applications.[13] In a recent preport, Selloni *et al.*[11] showed that the contours of constant LDOS at the Fermi level exhibit a corrugation of about 0.8 Å in contrast to the 0.2 Å of that of the total charge density. This should lead to a purely electronically derived corrugation in an STM image which would flatten out with increasing voltage, to the remaining total charge corrugation, as was observed experimentally.

In the preceding Letter, Tersoff[12] attributes the huge corrugation observed in laminar compounds and occasionally in graphite to an anomalous corrugation of the contours of constant LDOS at the Fermi level due to the special electronic structure of these materials. He further shows that the contours are equally spaced and independent of distance from the surface, and concludes that the STM image is likewise independent of distance, read current, at constant voltage. However, new experiments do show that the corrugations of the STM image increase strongly with tunnel current, at constant voltage, as shown in Fig. 1. If we consider the small density of states at the Fermi level, and the short decay length of the charge density outside the surface,[11,12] the tunnel tip has to be extremely close to the surface at the imaging conditions of $I\approx1$ nA and $V\approx1$ mV. Tip displacements of a few angstroms then imply "physical" contact of tip with surface, at least at the closest approach. It is then clear that the actual tip displacement cannot be solely a matter of the electronically induced corrugation.

In Fig. 2(a), we sketch one of the possible paths of the tip with respect to the surface while tracing a contour of constant LDOS. At point A, the force between tip and surface is repulsive, zero at B, and attractive at C [see Fig. 2(b)]. Figures 2(c) and 2(d) illustrate the situations at points A and C of Fig. 2(a). The tip-surface distance, d (tip jellium edge to top-layer carbon position), is determined by the tunneling parameters, and the local elastic deformation u by the tip-surface potential and the elastic constants of graphite.

To calculate the deformation u, we used standard elastic theory.[15] We assume a rigid, paraboidal tip with a radius of curvature at the apex of $R=2$ Å. For a perpendicular force $f(\mathbf{r})$ per unit area, with cylindrical symmetry with respect to the tip axis, we find that

$$u = C\int_0^\infty f(r)\,dr, \tag{1}$$

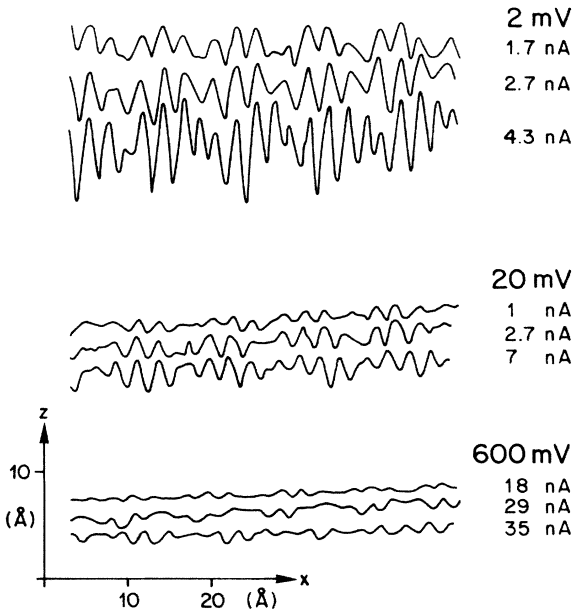

FIG. 1. Graphite STM traces obtained at ambient-air pressure and room temperature with a "pocket-size" STM (Ref. 14) with scanning speeds between 1 and 5 sec per scan. The varying corrugation within a scan is due to the mismatch between crystallographic and scanning directions (Ref. 3); plateaus in the traces indicate the saddle points in the LDOS (Refs. 3 and 11).

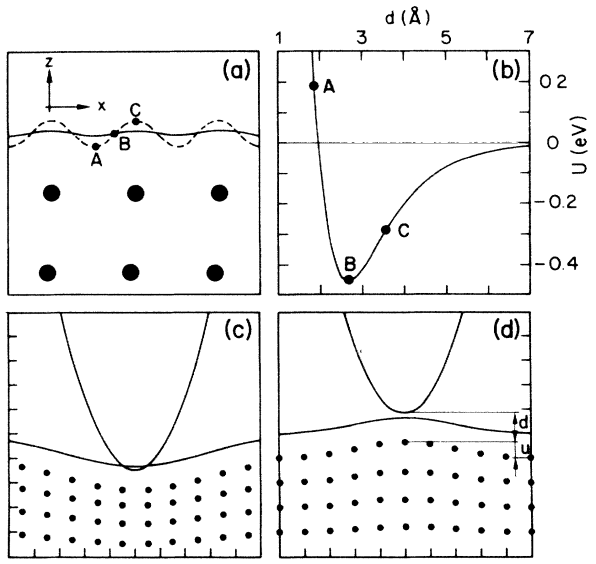

FIG. 2. (a) Contour of constant local density of states (dashed line), and contour of total charge density (solid line). Filled circles indicate the positions of carbon atoms of the top two layers. (b) Potential used for the interaction of tip and surface. Schematic (c) compression and (d) expansion of graphite for the tip at points A and C, respectively, of (a).

where r is the distance parallel to the surface from the tip center, and C is a constant which depends only on the elastic properties of the sample. For a very anisotropic medium like graphite, it may be calculated by performance of a Fourier analysis and summation of the elastic deformations over all possible wave vectors. We find that the only important elastic constants are the compressibility perpendicular to the surface and the shear between different basal planes. The constants given by Nicklow, Wakabayashi, and Smith[16] give $C=8\times10^{-11}$ m^2/N. We approximate $f(z)$ by a Morse potential,

$$f(z)=2bV_0(e^{-2b(z-z_0)}-e^{-b(z-z_0)}), \quad (2)$$

with parameters appropriate for the force between graphite planes,[17] i.e., $V_0=0.28$ J/m^2, $b=0.97$ Å^{-1}, and $z_0=3.35$ Å. This is expected to be a good approximation for a carbon atom or carbon cluster at the apex of the tip.[3] Inserting (2) into (1) with $z(r)=d+r^2/2R$, and neglecting the small, total charge corrugation, we obtain the simple relation

$$u(d)=-1.2(e^{-2b(d-d_0)}-e^{-b(d-d_0)}), \quad (3)$$

where $d_0=3.0$ Å, and u and d are both in angstroms. In Fig. 3, we have represented the enhanced vertical displacement of the tip, $d+u$, as a function of the distance d between tip and sample. It is clear that, in the repulsive region, the amplification of a corrugation Δd is enormous.

The average tip-sample distance d as a function of applied voltage V_a and tunnel current I was calculated with use of the density of states of Selloni *et al.*[11] and the tunneling-current formalism of Tersoff and Hamann,[7] as modified by Garcia and Flores.[8] Note that the "effective tunnel barrier" is $\phi_{\text{eff}}=\phi+ak_{\parallel}^2 \approx 4.7+7.3=12$ eV, since only states at the K point of the surface Brillouin zone contribute to the tunnel current at low voltages[11,12,18]; ϕ is the average of the work function of graphite and tip. Electron transport then still occurs via tunneling, even if ϕ is completely quenched by correlation and image-potential effects[19] at the touching condition. Once d has been obtained, we calculate the total corrugation amplitude $\Delta d+\Delta u$, as sketched in Fig. 3, using a constant $\Delta d^*=\Delta d-\Delta C=0.6$ Å, which is the difference between the corrugation amplitudes of the contours of constant LDOS, $\Delta d=0.8$ Å, and those of constant force, $\Delta C=0.2$ Å.[11] The results for $\Delta d+\Delta u$ are shown in Fig. 4, together with the experimental corrugations. The salient feature of the atomic-force model as applied to graphite is the dependence of the corrugation amplitudes on the tip-surface distance, d, only, with their dramatic increase at small d. Since in the voltage range considered $I\propto V$, as experimentally confirmed,[20] d and thus the corrugation amplitude are functions of I/V. This behavior, which is independent of the various assumptions made (e.g., choice of a par-

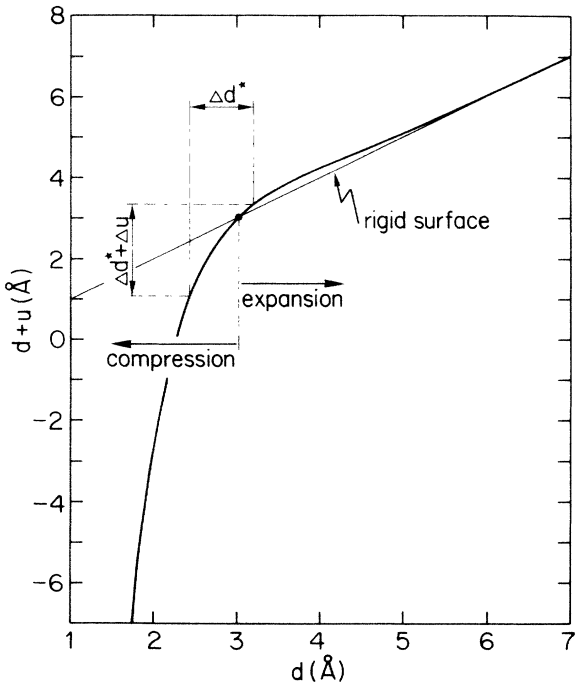

FIG. 3. Deformation of graphite by the tunnel tip. The heavy solid line gives the total tip displacement $d+u$ vs tip-surface distance d. A tip motion Δd^* with respect to the surface results in an enhanced tip displacement $\Delta d^*+\Delta u$. A deformation by $u=1$ Å corresponds to a force of 6×10^{-10} N for repulsion and 9×10^{-10} N for attraction, respectively.

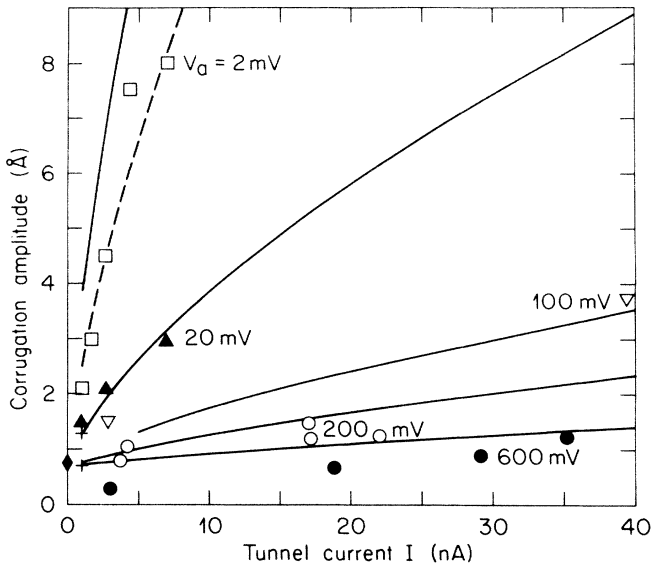

FIG. 4. Measured (symbols) and calculated (solid lines) corrugations as a function of tunneling current and voltage. The dashed line was obtained with $d^*=0.4$ Å. The two crosses at 1 nA correspond to the measured corrugations at 50 and 400 mV, respectively, of Ref. 3; the diamond at zero current indicates the corrugation of the LDOS at the Fermi level (Ref. 11).

ticular tip-surface interaction), is convincingly verified by the experiment. Calculations and experimental data have not been collapsed to a single curve in Fig. 4 in order to better illustrate the ever stronger increase of corrugation amplitude with current at decreasing applied voltage. (The quantitative agreement of calculations with experiment in the medium voltage range is a matter of fortuitous choice of parameters, and should not be overrated.) The strongly nonlinear amplification is also evident in the rapidly changing minima-maxima asymmetry in the traces of Fig. 1. At small currents, i.e., low amplification, the maxima—with respect to the flat saddle-point parts—are more pronounced; at large currents, the minima become the strong features of the traces.

In the above analysis we have used a constant Δd. This is in the spirit of Tersoff's model, for varying current at fixed voltage. For varying voltages, on the other hand, the corrugation amplitude of the state density contributing to the tunnel current was predicted[11] to decrease with increasing voltage as apparently confirmed experimentally in the voltage range 50 mV to 1 V (see Fig. 3 of Ref. 3). In the light of the present model, however, we should view those experiments—in the voltage range 400 to 50 mV—rather as an increase of the corrugation from a bare electronic value of 0.75 Å at 400 mV to a deformation-enhanced value of 1.3 Å at 50 mV, and only at higher voltages does the decrease of electronic corrugation become noticeable. The small experimental corrugations measured at 600 mV are attributed to such a reduction of Δd. The experimental values taken at 2 mV are likewise considerably smaller than predicted by our model. We believe that this is due to the close proximity of tip and graphite surface layer enhancing the density of states at the Fermi level. This enhancement is expected to decrease Δd, analogously to the effect of increased voltage. It further increases the tip-surface separation d and thus decreases the amplification factor.

The measured corrugations can vary from experiment to experiment. We attribute this to changed tip conditions and thus to a change in d for a given current and voltage. However, the general dependence of the corrugation on current and voltage remains unchanged within an experiment.

The corrugation amplification by elastic deformation rests on the conditions that (a) the tip traces a corrugation with respect to the surface which is different from that of the tip-surface interaction potential, (b) the tip-surface separation is very small, and (c) the material under investigation is sufficiently soft. With this in mind, we reinspect the pronounced difference in the corrugation observed in the charge-density-wave laminar compounds $1T$-TaS_2 and $2H$-$TaSe_2$.[5] Both com-

pounds have elastic constants similar to that of graphite. But whereas $2H$-$TaSe_2$ possesses a metallic density of states, $1T$-TaS_2 is a semimetal with a low density of states similar to that of graphite. This implies a very small tip-surface separation at the tunneling conditions of the experiment, and thus a large deformation enhancement of whatever LDOS corrugation is present.

The fact that STM images can be dominated by elastic deformations can of course be exploited to study the very same deformations and thus interatomic potentials and local elastic constants. Separation of deformation- and tunnel-current-induced contributions to the total tip displacement can be done by performing experiments at different distances, i.e., tunnel currents. The analogy to the separation of electronic and structural features in STM via tunneling spectroscopy is evident. The role of voltage is played by the current-controlled distance; the quantities of interest are interatomic potentials and local elastic constants instead of electronic properties. This type of atomic-force spectroscopy and imaging is not restricted to compact materials of the kind described above; it will be likewise important in the study and imaging of any "soft" object ranging from simple adsorbates to biological material.

In summary, we have shown the important role that interatomic forces between tunneling tip and surface can have in STM imaging. Their effect is to amplify or attenuate the tunnel-current-driven motion of tunnel tip with respect to the surface via elastic deformations. Tunnel-tip displacements, therefore, can become very large on a lateral scale of atomic dimensions, dictated solely by the resolution power of the tunnel-current filament. The giant corrugations formed in graphite are direct experimental evidence for these interatomic forces. A new type of tunneling spectroscopy for interatomic forces and local elastic properties is proposed. An alternative approach to the experimental verification of interatomic forces in STM, which does not require intrinsic softness of the sample, will be presented by Dürig *et al.*[21]

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