Limits of Resolution in Atomic Force Microscopy Images of Graphite.

W. ZHONG, G. OVERNEY(*) and D. TOMÁNEK

Department of Physics and Astronomy
Center for Fundamental Materials Research, Michigan State University
East Lansing, MI 48824-1116, USA

Abstract. – We calculate the limits of atomic resolution of an atomic force microscope (AFM) tip probing the elastic surface of graphite. Interaction energies between a «sharp» Pd tip with one apex atom and graphite are obtained from *ab initio* total energy calculations within the density functional formalism. The effect of long-range Van der Waals forces on the tip-substrate interaction is considered explicitly. We find that in the constant-force mode, atomic resolution is marginally possible for AFM loads (per atom) close to $5 \cdot 10^{-9}$ N. The optimum operating range is limited by unobservably small height corrugations for smaller lods and by irreversible substrate deformations for larger loads.

Atomic force microscopy (AFM) [1] is rapidly evolving into a powerful tool to examine the morphology and local rigidity of surfaces [2], especially those of insulators and semiconductors. Unlike the more established scanning tunneling microscope (STM) [3], which is sensitive to the electronic density of states near the Fermi energy [4], the AFM probes the force field between an «atomically sharp» tip and the substrate. This force is detected by the deflection of a soft cantilever which supports the tip. In the «constant force» mode, the vertical tip position z is recorded during a horizontal scan of the surface for a constant applied AFM load F_{ext}. Resolution of atomic-scale features in the substrate is possible if the equilibrium tip height z is sufficiently different at inequivalent (*e.g.*, on-top, hollow) surface sites. This is the case if the corresponding corrugation $\Delta z \gtrsim 0.05$ Å, the sensitivity of the AFM under ideal conditions.

The possibility of atomic resolution in the AFM is limited in two ways. First, if F_{ext} is very small and the tip is far from the surface, the corrugation Δz is too small to be observed.

(*) Permanent address: Institut für Physik, Universität Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland.

For «dull» tips with multiple apex atoms, the corrugation is further decreased due to the tip/substrate incommensurability. At large values of F_{ext}, where the tip is capable of probing the corrugation of the charge density, the tip-surface interaction is likely to destroy the substrate and/or the tip. So far, these limitations to possible atomic resolution have not been addressed in the literature. Present theoretical information is limited to calculations of the interaction between an infinite «periodic» carbon or aluminum tip and a rigid surface [5], and the interaction between a single AFM tip and an elastic surface represented by a semi-infinite continuum [2] or by a model system of finite thickness [6, 7].

In this letter, we discuss for the first time the theoretical limits of atomic resolution in AFM. We calculate the interaction between a «sharp» monoatomic Pd tip and the surface of graphite from first principles and predict corrugations for different loads F_{ext}. Our calculations also predict tip-induced elastic substrate deformations which limit the range of applicable loads F_{ext}.

As a first step towards understanding these tip-substrate interactions in AFM, we calculate the adsorption energy E_{ad} of Pd atoms in the on-top (T) site and the sixfold hollow (H) site on graphite as a function of the Pd-graphite separation z. The AFM probes the force on the «sharp» monoatomic tip, which is given by ([1])

$$f_{ext} = -\frac{\partial E_{ad}(z)}{\partial z}. \tag{1}$$

The main contribution to the tip-substrate interaction arises from chemical binding and has been determined with a high precision from first principles [8], using the local density approximation (LDA) [9]. We use the *ab initio* pseudopotential local orbital method which has been described elsewhere [10] and successfully applied to short-wavelength distortions of graphite [2]. In our calculation, we replace ionic potentials by norm-conserving ionic pseudopotentials of Hamann-Schlüter-Chiang type [11] and use the Hedin-Lundqvist [12] form of the exchange-correlation potential. The surface of hexagonal graphite is represented by a 4-layer slab and the adsorbate by a monolayer of Pd atoms in registry with the substrate. The basis consists of s, p and d orbitals with four radial Gaussian decays each on Pd sites and of s and p orbitals with three radial decays each on carbon sites, *i.e.* 40 independent basis functions for Pd and 12 basis functions for C. In order to obtain accurate energy differences between the «T» and «H» geometry, we introduce floating orbitals on sites not occupied by atoms and use the same extended basis [13] for both «T» and «H» calculations. To ensure full convergence and a high accuracy of total energies ($\delta E < 10^{-3}$ eV), we use an energy cut-off of 49 Ry in the Fourier expansion of the charge density and sample the 2-dimensional Brillouin zone with a mesh of 49 k-points, using a special-point scheme [14].

We also investigated the effect of the long-range Van der Waals forces on the tip-substrate interactions which are not described correctly by LDA especially at large tip-substrate distances. The Van der Waals force between an extended conical tip and a flat surface is estimated using the expression $F_{vdW}(z) = A_H \times tg^2 \alpha/(6z)$, where α is half the opening angle of the cone [15]. In this expression, A_H is the Hamaker constant and z is the distance between the cone tip and the surface. In our calculation, we consider $\alpha = 30°$ and $A_H = 3 \cdot 10^{-19}$ J, which is a typical value for metallic systems. For tip-substrate distances $z > 3$ Å, the Van der Waals forces are very small, typically $F_{vdW} < 10^{-10}$ N. At smaller distances, these forces can be neglected when compared to the closed-shell and internuclear repulsion which are described correctly within LDA. Since each of these regions is

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([1]) For large AFM tips, we distinguish the load per atom, f_{ext}, from the total load on the tip, F_{ext}.

dominated only by one type of interaction, we determine the total tip-substrate force F_{ext} as a superposition of the force described by LDA and the Van der Waals force. In fig. 1a), we present results for the total force $F = f_{ext}$ between a conical AFM tip with 1 Pd apex atom and a graphite substrate, together with a schematic top view of the geometry.
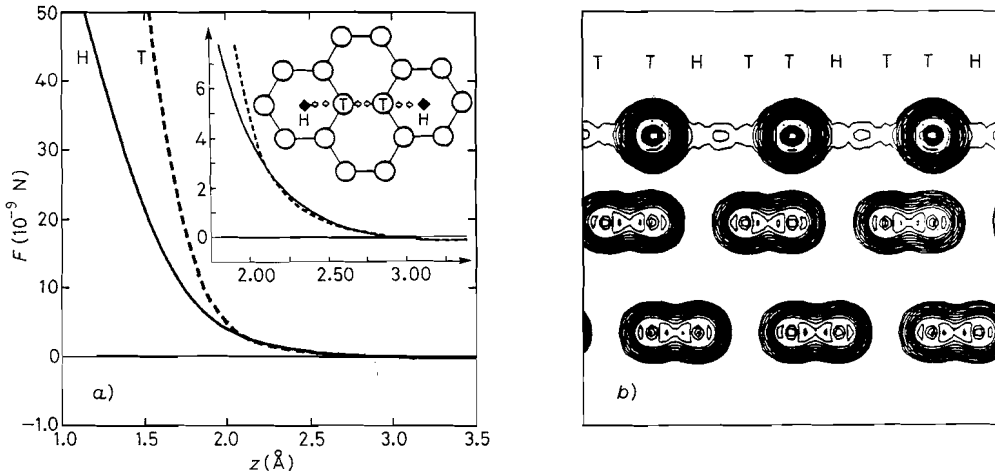

Fig. 1. – a) Calculated force F between a Pd AFM tip with one apex atom and the surface of hexagonal graphite, as a function of the Pd-graphite distance z. The solid and dashed lines correspond to the sixfold hollow (H) and the on-top (T) sites, respectively. An enlarged section of the graph near the equilibrium is shown in the inset. A second inset shows the adsorption geometry in top view. A possible trajectory of an AFM tip along x is shown by arrows. b) Valence charge density of the Pd/graphite system. The results of the LDA calculation are for the on-top adsorption site near the equilibrium adsorption distance z_{eq}, and are shown in the (x, z)-plane perpendicular to the surface. The ratio of two consecutive charge density contours $\rho(n+1)/\rho(n)$ is 1.2.

Our calculations yield nearly the same weak Pd-graphite interaction potential ($E_{ad} < 0.1$ eV) in the «H» and «T» sites beyond the equilibrium Pd-graphite bond length $z_{eq} \approx 3$ Å and consequently the same weak interaction force. This is plausible since E_{ad} is closely related to the total charge density ρ, shown in fig. 1b), which has only a very small site dependence in the attractive region of the potential at $z > z_{eq}$ due to Smoluchowski smoothening [16]. Consequently, the corrugation Δz in this region is too small to be detected by AFM. In the weakly repulsive region of the potential, for 2 Å $< z < 3$ Å, the on-top site is slightly favored with respect to the hollow site due to a weak chemisorption bond with substrate C $2p_z$ orbitals. For atom bond length $z < 2$ Å, the strongly repulsive Pd-graphite interaction is mainly determined by the closed-shell repulsion which energetically favors the hollow site. Hence, in the repulsive region of the potential, the Pd tip comes closest to the substrate near the «T» site for small loads. For large loads, the tip height is smallest near the «H» site.

Figure 2a) shows the expected AFM corrugation Δz during an xy scan of the graphite surface, for $f_{ext} = 10^{-8}$ N. We obtained the equilibrium bond length $z(f_{ext})$ at other than the calculated high-symmetry sites using a separate model calculation [17], which relates E_{ad} to the total charge density of the graphite host at the Pd adsorption site. This energy functional is assumed to be universal and reproduces E_{ad} in high-symmetry sites accurately. In this calculation, we assumed a perfectly rigid substrate and a monoatomic Pd tip. A top view of this tip at the graphite hollow site is shown schematically in the inset of fig. 2b).
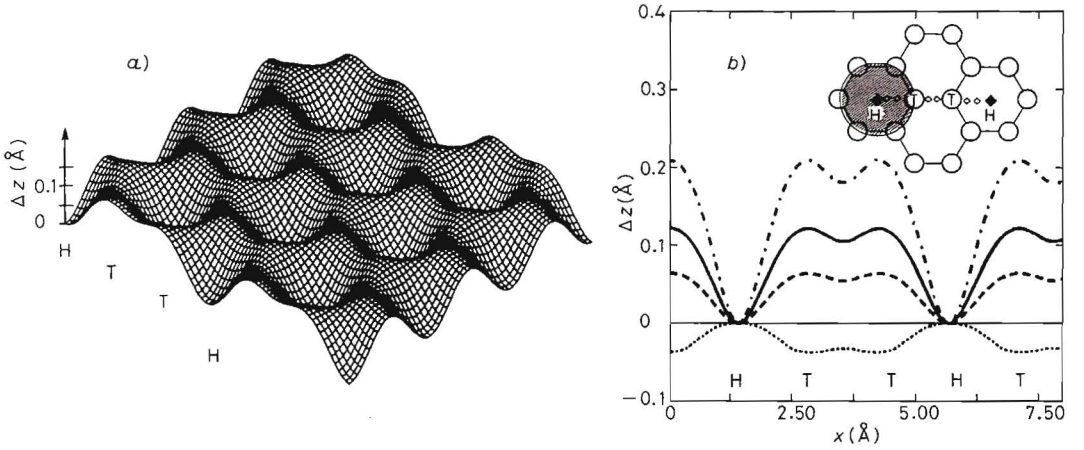
Fig. 2. – a) Surface corrugation Δz experienced by a monoatomic Pd AFM tip scanning the (x, y)-surface plane of rigid graphite under the applied AFM load (per atom) $f_{ext} = 10^{-8}$ N. b) Δz (with respect to the «H» site) along the surface x direction for a «sharp» 1-atom tip, for $f_{ext} = 10^{-9}$ N (dotted line), $5 \cdot 10^{-9}$ N (dashed line), 10^{-8} N (solid line), and $2 \cdot 10^{-8}$ N (dash-dotted line). The inset shows the geometry of the tip-graphite system in top view. The AFM tip is shown above the hollow site and the shaded area represents the Pd atom.

Figure 2b) shows the AFM corrugation $\Delta z(x)$ for different loads f_{ext}. The tip trajectory along the surface x-direction, shown by arrows in the inset of fig. 2b), contains the «T» and «H» sites and yields the largest corrugation. As discussed above, the favored surface site changes with changing load. For the sake of simple comparison, we set Δz (hollow site) = 0 in fig. 2b) and obtain a sign change of Δz near $f_{ext} = 2.5 \cdot 10^{-9}$ N. Our calculations show that atomic resolution in the constant force mode in the AFM, corresponding to $\Delta z \gtrsim 0.05$ Å, requires loads $f_{ext} \gtrsim 5 \cdot 10^{-9}$ N. Since the corrugation Δz along a trajectory connecting adjacent «T» sites is very small (see fig. 2b)), the observation of individual carbon atoms is unlikely, which has been confirmed by the experiment [18].

For an n-atom tip, which is commensurate with the substrate, the average load per AFM tip atom is $f_{ext} = F_{ext}/n$ and the equilibrium tip position z can be estimated from eq. (1). It should be noted that under certain conditions, such a «dull» multiatom tip can still produce atomic corrugation for f_{ext} similar to a monoatomic tip. This is the case for an ideally aligned tip with a close-packed (111) surface, since the unit cells of Pd and graphite are nearly identical in this case. Thus, for an incompressible substrate, the «sharpness» of the AFM tip does not play a decisive role in the resolution.

The range of applicable loads F_{ext} is limited by the condition that substrate distortions near the AFM tip should be small and remain in the harmonic region. Since full-scale LDA calculations of local AFM-induced distortions of a semi-infinite graphite surface are practically not feasible, we adopt the following approach. First, we use continuum elasticity theory [19], with elastic constants obtained from *ab initio* calculations [2], to determine the relaxation of carbon atoms at the graphite surface in response to the AFM load applied through an AFM tip. This continuum approach is applicable in the linear response regime and has been successfully used previously to calculate local rigidity, local distortions and the healing length of graphite near an AFM tip and near intercalant impurities [2, 19]. In a second step, the atomic structure in the total charge density of the Pd/graphite system is regained from a superposition of atomic charge densities given by LDA-atom calculations.

The semi-infinite system of graphite layers is characterized by the interlayer spacing d, the in-plane C—C bond length d_{C-C}, the flexural rigidity D, the transverse rigidity K (proportional to C_{44}) and c-axis compressibility G (proportional to C_{33}) [2, 19]. Our LDA calculations for undistorted graphite yield $d = 3.35$ Å and $d_{C-C} = 1.42$ Å, in excellent agreement with experiment [20]. In the continuum calculation, we further use $D = 7589$ K, $K = 932$ KÅ^{-2} and $G = 789$ KÅ^{-4} which have been obtained from calculated graphite vibration modes [2] and the experiment [20].

The total charge density of the graphite surface, distorted by a Pd AFM tip, is shown in fig. 3. A comparison of charge density contours with results of the self-consistent calculation in fig. 1*b*) proves *a posteriori* the applicability of the linear superposition of atomic-charge densities. Figure 3*a*) shows that the substrate distortion in response to a monoatomic AFM tip at a load $F_{ext} = f_{ext} = 10^{-9}$ N is moderate. According to fig. 2*b*), the corresponding corrugations during an AFM scan with this load are $\Delta z \approx 0.03$ Å and thus below the limit of detection. A larger load $F_{ext} = f_{ext} = 5.0 \cdot 10^{-9}$ N leads, according to fig. 2*b*), to marginally detectable corrugations $\Delta z \approx 0.06$ Å, but distorts graphite much more, as shown in fig. 3*b*).
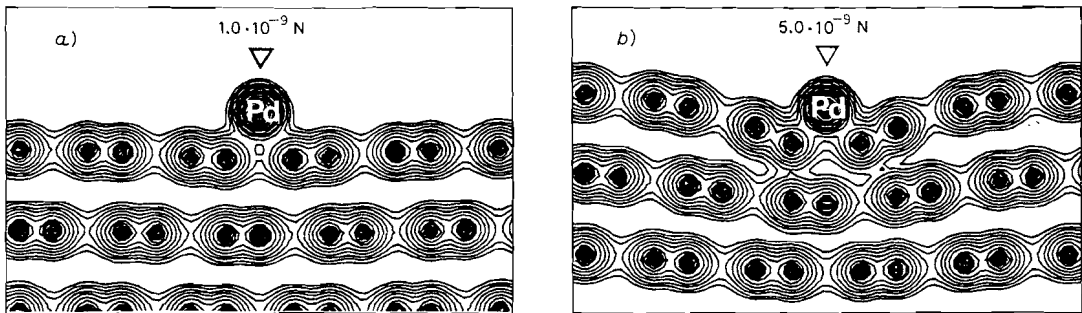

Fig. 3. – Total charge density ρ of the monoatomic Pd AFM tip interacting with the elastic surface of graphite near the hollow site. Contours of constant ρ are shown in the (x, z)-plane perpendicular to the surface, for *a)* $F_{ext} = f_{ext} = 1 \cdot 10^{-9}$ N and for *b)* $F_{ext} = f_{ext} = 5 \cdot 10^{-9}$ N. The ratio of two consecutive charge density contours $\rho(n + 1)/\rho(n)$ is 1.4. The location of the applied load acting on the Pd atom is indicated by a triangle.

For larger applied forces $F_{ext} = f_{ext} > 5.0 \cdot 10^{-9}$ N, which would lead to sizeable corrugations, the local distortions of graphite exceed the harmonic limit. A rough estimate of these distortions, based on continuum elasticity theory, indicates that for $f_{ext} \gtrsim 5 \cdot 10^{-9}$ N, the distance between graphite layers near the AFM tip approaches the value of intralayer C—C distances. This new diamondlike bonding geometry leads to a rehybridization of carbon orbitals and will necessarily result in an irreversible substrate deformation. An independent estimate of the critical AFM force for this plastic deformation can be obtained from an independent first-principles calculation [21] of the graphite-diamond transition as a function of external pressure. These results, corresponding to an «infinitely extended tip», indicate a critical force per surface atom of $f_{ext} = 10^{-9}$ N for this transition. Due to the large flexural rigidity of graphite, this force increases by half an order of magnitude for a one-atom tip, in agreement with our above result.

A realistic AFM tip is more complex than the model tip discussed above and could consist of a micro-tip of one or few atoms on top of a larger tip. A substantial portion of this larger tip could, through the «cushion» of a possible contamination layer, distribute the applied load more evenly across a large substrate area, reduce the large curvature near the tip (see fig. 3*b*)) and increase the minimum interlayer separation. This effect would increase the

upper limit of applicable loads f_{ext} compatible with elastic substrate deformations and would lead to atomic resolution [18].

In summary, we used *ab initio* calculations to determine corrugations observable in atomic force microscopy of graphite. We found that in the constant-force mode, atomic resolution is marginally possible for AFM loads (per atom) close to $5 \cdot 10^{-9}$ N. For smaller loads, the corrugation Δz is too small to be observed. For loads which are too large, graphite deformations exceed the elastic limit and subsequently result in the destruction of the substrate.

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