Theory of elastic tip–surface interactions in atomic force microscopy

Gregor Overney, Weiqing Zhong, and David Tománek
Department of Physics and Astronomy and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824-1116

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We present a first-principles study of elastic surface deformations, limits of atomic resolution, and of atomic-scale friction in atomic force microscopy (AFM). In the case of a Pd AFM tip interacting with a graphite surface, we find that atomic resolution can be achieved in a narrow load range near $10^{-8}$ N (per Pd tip atom). For these loads, we determine the microscopic friction coefficient to be $\mu \approx 10^{-2}$.

I. INTRODUCTION

Since the first presentation of the atomic force microscope (AFM) by Binning et al. in 1987,1 this new field of research has made rapid progress. Several groups have achieved atomic resolution on highly oriented pyrolytic graphite (HOPG).2–4 The power of AFM measurements lies in the ability to resolve isolated atomic defect structures such as steps or impurity atoms. Like the more established scanning tunneling microscopy (STM),6 the AFM uses an "atomically" sharp tip which scans across the sample surface at a sample-to-tip separation $z$ of a few angstroms. The AFM probes the structure of the sample by measuring $z$ for a constant external force (load) $F_{\text{ext}}$ applied to the tip during a horizontal scan. The load is detected from the deflection of a soft spring which supports the tip.

Present theories of AFM have so far calculated the repulsive force between a semi-infinite "periodic" tip with a rigid surface or a single tip interacting with a model system of finite thickness.5 More recently, tip–substrate interactions and atomic-scale friction have been studied by molecular dynamics techniques.6 In this paper we determine the interaction between a tip and a deformable surface of a semi-infinite system from first principles. Since $ab\text{ initio}$ calculations of distortions near an isolated impurity in extended system are very time consuming and apply only to special cases, we treat this problem using a novel approach. We calculate bulk elastic constants from first principles and then determine equilibrium deformations near structural impurities exactly using a Continuum Elasticity theory.6 This procedure allows for a fairly simple adaptation to a variety of geometries which are computationally beyond the scope of a first principles calculation (e.g., large-scale deformations near an AFM tip).

This paper is organized as follows: In Sec. II we present a first-principles formalism for the study of elastic surface deformation, based on a combination of $ab\text{ initio}$ Density Functional and Continuum Elasticity theory. In Sec. III we describe the interaction between a Pd AFM tip and the surface of pristine graphite. In Sec. IV we determine the atomic-scale friction at a Pd–graphite interface. Finally, in Sec. V we summarize our results.

II. ELASTIC DEFORMATIONS IN LAYERED MATERIALS

In order to describe large-scale deformations of an elastic surface, which are induced by localized forces due to the AFM tip or intercalant atoms, we develop a novel formalism which combines $ab\text{ initio}$ Density Functional formalism and Continuum Elasticity theory.6

We determine the elastic constants of graphite from a first-principles total energy calculation within the local density approximation (LDA).11 The electron–ion interaction is described by $ab\text{ initio}$ pseudopotentials generated by the scheme of Hamann, Schlüter, and Chiang.12 The exchange-correlation energy is evaluated using the functional form of Hedin and Lundqvist.13 We use an energy cutoff of 49 Ry in the Fourier expansion of the charge density in order to ensure complete convergence of the LDA spectrum and total energies. The accuracy of our LDA calculation has been first checked by determining the in-plane C–C bond length $d_{\text{CC}} = 1.42$ Å and the interlayer spacing $d = 3.35$ Å, which are in very good agreement with experimental results. Furthermore, we calculate the vibrational frequency of the in-plane mode $\omega(E_{\text{v}})$ and the out-of-plane mode $\omega(A_{\text{v}})$. Also for these frequency modes, we get a very good agreement with the experimental results. From the vibrational frequency of the out-of-plane mode $\omega(A_{\text{v}})$, we determine the flexural rigidity to be $D = 7589$ K, which compares very favorably with the experimental value14 $D = 7076 \pm 420$ K.

In the next step, these elastic constants are used in the framework of the Continuum Elasticity theory. In this formalism, the elastic response of the substrate is described by a set of coupled differential equations which allow us to obtain several analytic and universal results. Our results can be directly compared to AFM images with atomic resolution if we associate an envelope function with the equilibrium positions of substrate atoms after distortion. We apply our formalism to graphite and determine the deformations due to intercalants and/or AFM tip and will show that intercalant-induced deformations can be observed by the AFM and that such images contain valuable information about local surface rigidity.

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Elasticity theory by a semi-infinite system of layers. Each
graphite layer is considered as a two-dimensional elastic
continuous medium, or a thin elastic plate. The force
distribution due to the AFM tip, as well as an intercalant impu-
rity, is modeled by a distribution of $\delta$-function-like (or
point-like forces). In the case of an intercalant in the first
gallery, these forces are acting on the first and second layer.
The semi-infinite system of graphite layers is characterized by
the flexural rigidity $D$, the transverse rigidity $K$ (proportional
to $C_{44}$), the $c$-axis compressibility $G$ (proportional to $C_{11}$),
and the interlayer spacing $d$. For a given distribution of
forces (due to the AFM tip or an intercalant impurity), the
vertical distortion $w_t(x)$ of the nth layer is obtained by solv-
ing the following set of coupled differential equations:

$$
(D^2 - KV_t^2)w_t + G(w_t - w_{t+1}) = F_t(x),
$$

$$
(D^2 - KV_t^2)w_{t+1} + G(w_t - w_{t+1} + 2w_{t+2} - w_{t+1})
- F_t(x) = 0.
$$

In our continuum calculation, we use LDA values for the
equilibrium structure and the flexural rigidity $D$, and experi-
mental values$^{15}$ for the $c$-axis compressibility $G = 789$
K$\text{Å}^{-1}$ and the transverse rigidity $K = 932$ K$\text{Å}^{-1}$.

The profile of the graphite surface near a structural impu-
rities can be obtained by AFM. In Fig. 1 we show the calculat-
ed vertical tip position $z$, as a function of the horizontal tip
distance $x$, from a potassium intercalant atom in the first
gallery, assuming two different tip shapes and considering a
"rigid" and a "soft" graphite surface. In Fig. 1(a) we use a $\delta$
-function-like force distribution for the AFM tip and in Fig.
1(b) we use a distribution of $\delta$-function-like forces within a
cylinder with a radius of 2.75 Å. The force distribution of the
intercalant is modeled in both cases by a pair of $\delta$ functions
acting on the first and second graphite layer. The difference
in the AFM image between the rigid and soft surface de-
creases for a larger AFM tip radius. In general, local changes
in the elastic constants of graphite are expected near interca-
lant impurities in intercalation compounds (in analogy to
observed changes$^{15}$ in $d_{100}$, mainly due to the large
charge transfer which modifies the type of bonding. We ex-
pect the observed AFM corrugation to lie between the
curves obtained for the soft and the rigid graphite surface.

III. LIMITS OF ATOMIC RESOLUTION IN AFM

We apply the theory of Sec. II to describe the interaction
between a Pd AFM tip and the surface of pristine graphite.
First we determine the Pd–graphite interaction using LDA,$^{20}$
calculating the adsorption energy $E_{ad}$ of a Pd atom in the on-top ($T$) site and the sixfold hollow ($H$) site
on graphite as a function of the Pd–graphite separation $z$.

The results and a schematic top view of the geometry are
given in Fig. 2. The calculated Pd–graphite interaction is used
to determine the equilibrium tip height $z$ at two inequi-
valent surface sites (hollow and top). From our calcula-
tions, we obtain nearly the same weak Pd–graphite interac-
tion potential for these two sites ($E_{ad} < 0.1$ eV) for the Pd–
graphite bond length $z_{eq} \approx 3$ Å. At a bond length $z < 2$ Å, the
strongly repulsive Pd–graphite interaction is mainly deter-
mined by closed-shell repulsion which energetically favors
the hollow site. Hence, in the strongly repulsive region of the
potential, the Pd tip comes closest to the substrate near the
"H" site for large loads.

We define a load per tip atom $F_{ad} = F_{ad}/N$, where $F_{ad}$ is the
total load on the tip and $N$ is the number of tip atoms in
contact with the graphite surface. Figure 3 shows the AFM
corrugation $\Delta z(x)$ for different loads $F_{ad}$. The tip trajectory
along the surface $x$ direction, shown schematically in top
view by arrows in Fig. 3, contains the "T" and "H" sites and
yields the largest corrugation. For the sake of simple com-
parison, we set $\Delta z$ (hollow site) = 0 in Fig. 3. Our calcula-
tions show that in order to achieve observable corrugations
$\Delta z > 0.1$ Å leading to atomic resolution in AFM, the load on
the tip should be in the range $F_{ad} > 10^{-4}$ N. Since the cor-

The microscopic friction coefficient $\mu$ as a function of the external force per atom $f_{ext}$ (from Ref. 18. © American Physical Society).

In order to determine the energy dissipated in friction, we first consider moving the AFM tip between two neighboring equivalent sites (e.g., hollow sites) which are separated by $\Delta x$. During this scan process, the system has to cross a potential energy barrier $\Delta V_{\text{max}}(F_{ext})$ which results from variations of the adsorption bond energy and the work against $F_{ext}$. Hence the energy investment for this process is $\Delta E_{\text{max}}(F_{ext})$, which in general increases with increasing external force $F_{ext}$. If we assume a very slow horizontal motion of the tip, the subsequent energy gain $-\Delta V_{\text{max}}(F_{max})$ will be dissipated into heat (occurring as phonons or electron-hole pair excitations). The average friction force is related to this dissipated energy and is given by $\langle F_j \rangle < \Delta V_{\text{max}}(F_{\text{max}})/\Delta x$. Due to the small dependence of the $F_{ext}$-graphite interaction on the tip position $x$ for loads $F_{ext} \approx 10^{-6}$ N per tip atom, we find $\langle F_j \rangle$ to be very small. In Fig. 4, we show the friction coefficient (defined as $\mu = \langle F_j \rangle / F_{ext}$) which turns out to be $\mu \approx 10^{-2}$ in this load range. The dependence of $\mu$ on the load $F_{ext}$, shown in Fig. 4, has been discussed elsewhere. In general, we find that $\mu$ increases with increasing load, in agreement with a recent AFM experiment.

IV. ATOMIC-SCALE FRICTION

We describe friction on the atomic scale between a Pd AFM tip and ideal graphite substrate in analogy to a "surface diffusion" of the AFM tip under an external force (load), along a straight trajectory in the surface $x$ direction. The Pd-graphite interaction has been discussed in Sec. III and is shown in Fig. 2. Progress in surface preparation and the use of the AFM have made the observation of atomic-scale friction force under near-ideal conditions possible. In order to determine the energy dissipated in friction, we first consider moving the AFM tip between two neighboring equivalent sites (e.g., hollow sites) which are separated by $\Delta x$. During this scan process, the system has to cross a potential energy barrier $\Delta V_{\text{max}}(F_{ext})$ which results from variations of the adsorption bond energy and the work against $F_{ext}$. Hence the energy investment for this process is $\Delta E_{\text{max}}(F_{ext})$, which in general increases with increasing external force $F_{ext}$. If we assume a very slow horizontal motion of the tip, the subsequent energy gain $-\Delta V_{\text{max}}(F_{max})$ will be dissipated into heat (occurring as phonons or electron-hole pair excitations). The average friction force is related to this dissipated energy and is given by $\langle F_j \rangle < \Delta V_{\text{max}}(F_{\text{max}})/\Delta x$. Due to the small dependence of the $F_{ext}$-graphite interaction on the tip position $x$ for loads $F_{ext} \approx 10^{-6}$ N per tip atom, we find $\langle F_j \rangle$ to be very small. In Fig. 4, we show the friction coefficient (defined as $\mu = \langle F_j \rangle / F_{ext}$) which turns out to be $\mu \approx 10^{-2}$ in this load range. The dependence of $\mu$ on the load $F_{ext}$, shown in Fig. 4, has been discussed elsewhere. In general, we find that $\mu$ increases with increasing load, in agreement with a recent AFM experiment.

V. CONCLUSIONS

We developed a theory for the AFM of deformable surfaces, based on a combination of ab initio Density Functional formalism and Continuum Elasticity theory. Using this theory, we calculated local distortions in the vicinity of a "sharp" AFM tip as a function of the applied force. Our results show that AFM should be a unique tool to determine local changes of the surface rigidity which occur near intercalant impurities. Furthermore, we found that in the constant-force mode, the AFM can marginally achieve atomic resolution for loads per tip atom near $F_{ext} \approx 10^{-6}$ N. This load range is limited by a too low corrugation $\Delta z$ on the lower end and by too large substrate distortions on the upper end. Finally, we determined the friction coefficient for a Pd AFM tip on graphite and found it to be very small ($\mu \approx 10^{-2}$). We also found that $\mu$ increases with increasing applied load.

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19Permanent address: Institut für Physik, Universität Basel, Klingelbergstrasse 162, CH-4056 Basel, Switzerland.


33D is proportional to the bending modulus $B$. $B = \rho R$, with $\rho = 2M/(3\epsilon_0/2)$ is the area mass density ($M = $ mass of carbon atom, $\epsilon_0 = 1.42 \AA$). The experimental value for $B = (2.55 \pm 0.15) \times 10^{-4} \text{cm}^2/\text{m}^2$ is listed in Ref. 16.


