

# Theory of elastic tip-surface interactions in atomic force microscopy

Gregor Overney,<sup>a)</sup> Weiqing Zhong, and David Tománek  
*Department of Physics and Astronomy and Center for Fundamental Materials Research,  
Michigan State University, East Lansing, Michigan 48824-1116*

(Received 24 July 1990; accepted 30 October 1990)

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  $\approx 10^{-8}$  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 Binnig *et al.* in 1987,<sup>1,2</sup> this new field of research has made rapid progress. Several groups have achieved atomic resolution on highly oriented pyrolytic graphite (HOPG).<sup>3,4</sup> 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 microscope (STM),<sup>5</sup> 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<sup>6</sup> or a single tip interacting with a model system of finite thickness.<sup>7</sup> More recently, tip-substrate interactions and atomic-scale friction have been studied by molecular dynamics techniques.<sup>8</sup> In this paper we determine the interaction between a tip and a deformable surface of a semi-infinite system from first principles. Since *ab 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.<sup>9</sup> 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 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 initio* Density Functional formalism and Continuum Elasticity theory.<sup>10</sup>

We determine the elastic constants of graphite from a first-principles total energy calculation within the local density approximation (LDA).<sup>11</sup> The electron-ion interaction is described by *ab initio* pseudopotentials generated by the scheme of Hamann, Schlüter, and Chiang,<sup>12</sup> and the exchange-correlation energy is evaluated using the functional form of Hedin and Lundqvist.<sup>13</sup> 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  $d_{\text{C-C}} = 1.42$  Å and the interlayer spacing  $d = 3.35$  Å, which are in very good agreement with experimental results. Furthermore, we calculate the vibration frequency of the in-plane mode  $\omega(E_{2g})$  and the out-of-plane mode  $\omega(A_{2u})$ . Also for these frequency modes, we get a very good agreement with the experimental result. From the vibration frequency of the out-of-plane mode  $\omega(A_{2u})$ , we determine the flexural rigidity to be  $D = 7589$  K, which compares very favorably with the experimental value<sup>14</sup>  $D = 7076 \pm 420$  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 allows 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 the AFM tip. We will show that intercalant-induced deformations can be observed by the AFM and that such images contain valuable information about *local* surface rigidity.

Graphite is described in the framework of the Continuum

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.<sup>15</sup> The force distribution due to the AFM tip, as well as an intercalant impurity, is modeled by a distribution of  $\delta$ -function-like (or point-like forces).<sup>10</sup> 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  $C_{33}$ ), and the interlayer spacing  $d$ . For a given distribution of forces (due to the AFM tip or an intercalant impurity), the vertical distortion  $w_n(\mathbf{r})$  of the  $n$ th layer is obtained by solving the following set of coupled differential equations:

$$\begin{aligned} (D\nabla_r^4 - K\nabla_r^2)w_1 + G(w_1 - w_2) &= F_1(\mathbf{r}), \\ (D\nabla_r^4 - K\nabla_r^2)w_n + G(-w_{n-1} + 2w_n - w_{n+1}) &= F_n(\mathbf{r}), \quad n \geq 2. \end{aligned}$$

In our continuum calculation, we use LDA values for the equilibrium structure and the flexural rigidity  $D$ , and experimental values<sup>16</sup> for the  $c$ -axis compressibility  $G = 789 \text{ K } \text{\AA}^{-4}$  and the transverse rigidity  $K = 932 \text{ K } \text{\AA}^{-2}$ .

The profile of the graphite surface near a structural impurity can be obtained by AFM. In Fig. 1 we show the calculated vertical tip position  $z_t$  as a function of the horizontal tip distance  $r_t$  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  $2.75 \text{ \AA}$ . 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 decreases for a larger AFM tip radius. In general, local changes in the elastic constants of graphite are expected near intercalant impurities in intercalation compounds (in analogy to observed changes<sup>17,18</sup> in  $d_{c-c}$ ), mainly due to the large

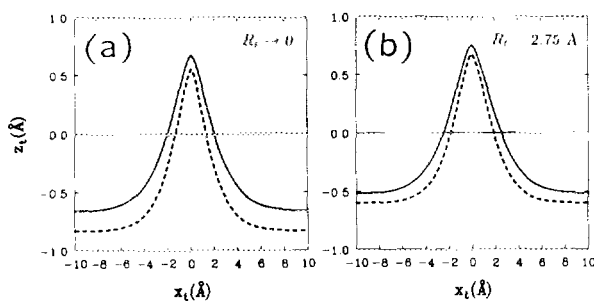


FIG. 1. Vertical position  $z_t$  of the AFM tip as a function of its horizontal distance  $r_t$  from the intercalant with a diameter  $d_t = 5.3 \text{ \AA}$ . (a) Results for a  $\delta$ -function-like tip force  $F_{\text{ext}} = 10^{-9} \text{ N}$  based on the calculated value of the graphite flexural rigidity constant  $D = 7589 \text{ K}$  (—) are compared to distortions for a reduced  $D = 3795 \text{ K}$  (- - -). (b) Corresponding results for a force distribution in the form of a full cylinder with a radius of  $2.75 \text{ \AA}$ . In both cases, the force distribution of the intercalant is modeled by a pair of  $\delta$  functions.

J. Vac. Sci. Technol. B, Vol. 9, No. 2, Mar/Apr 1991

charge transfer which modifies the type of bonding. We expect 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,<sup>20</sup> by calculating the adsorption energy  $E_{\text{ad}}$  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 inequivalent surface sites (hollow and top). From our calculations, we obtain nearly the same weak Pd-graphite interaction potential for these two sites ( $E_{\text{ad}} < 0.1 \text{ eV}$ ) for the Pd-graphite bond length  $z_{\text{eq}} \geq 3 \text{ \AA}$ . At a bond length  $z < 2 \text{ \AA}$ , the strongly repulsive Pd-graphite interaction is mainly determined 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  $f_{\text{ext}} = F_{\text{ext}}/N$ , where  $F_{\text{ext}}$  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  $f_{\text{ext}}$ . 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 comparison, we set  $\Delta z(\text{hollow site}) = 0$  in Fig. 3. Our calculations show that in order to achieve observable corrugations  $\Delta z \geq 0.1 \text{ \AA}$  leading to atomic resolution in AFM, the load on the tip should be in the range  $f_{\text{ext}} \geq 10^{-8} \text{ N}$ . Since the corru-

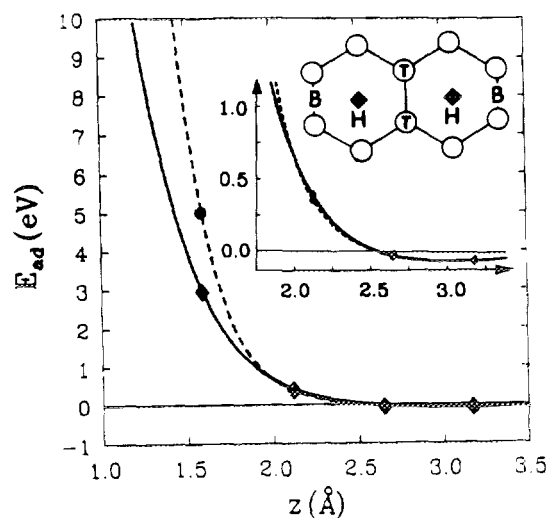


FIG. 2. Adsorption energy  $E_{\text{ad}}$  of a Pd atom as a function of the adsorption height  $z$  above the surface of hexagonal graphite. (—) and (- - -) correspond to the sixfold hollow ( $H$ ) and the on-top ( $T$ ) sites, respectively. An enlarged section of the graph near equilibrium adsorption is shown as an inset. A second inset shows the adsorption geometry in top view (from Ref. 18, ©American Physical Society).

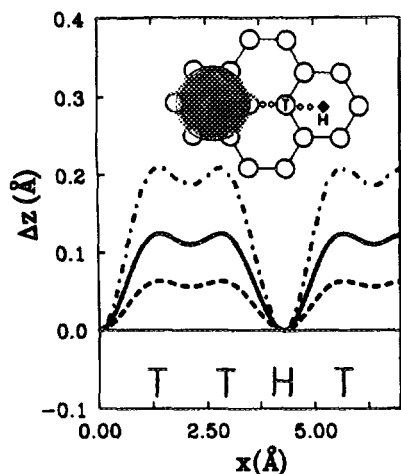


FIG. 3.  $\Delta z$  (with respect to the  $H$  site) along the surface  $x$  direction for a 1-atom tip, for  $f_{\text{ext}} = 5 \times 10^{-9}$  N (---),  $10^{-8}$  N (—), and  $2 \times 10^{-8}$  N (-.-). The inset shows the geometry of the tip-graphite system in top view. The AFM tip is shown above the hollow site and the shaded area represents the Pd atom.

gation  $\Delta z$  along a trajectory connecting adjacent  $T$  sites is very small (see Fig. 3), the observation of individual carbon atoms is unlikely, which has been confirmed by the experiment.<sup>3</sup>

In the next step, we describe the surface deformation due to the AFM tip by the Continuum Elasticity theory (presented in Sec. II). The upper limit of applicable loads  $F_{\text{ext}}$  is given by the condition that substrate distortions near the AFM tip should be small and remain in the elastic region. We show that the substrate distortion in response to a monatomic AFM tip of a load  $F_{\text{ext}} = f_{\text{ext}} = 5.0 \times 10^{-9}$  N is moderate. According to Fig. 3, the corresponding corrugations during an AFM scan with this load are  $\Delta z \approx 0.05$  Å and thus barely at the limit of detection. A larger load  $F_{\text{ext}} = f_{\text{ext}} = 1.0 \times 10^{-8}$  N leads, according to Fig. 3, to observable corrugations  $\Delta z > 0.1$  Å. The value of  $\Delta z$  is expected to decrease for a multiatom tip. As we have shown in an independent calculation,<sup>19</sup> the effect for  $F_{\text{ext}} > 10^{-8}$  N is to reduce locally the interlayer spacing for graphite by  $> 50\%$ . At this point, the similar value of inter- and intralayer C-C distances would lead to orbital rehybridization and consequently to a destructive plastic deformation of the substrate. Hence our results show that in the constant-force mode, atomic resolution is marginally possible in a very small load range, which is limited by too small height corrugations for loads below  $10^{-8}$  N (per Pd tip atom) and by irreversible substrate deformations for loads beyond  $10^{-8}$  N.

#### IV. ATOMIC-SCALE FRICTION

We describe friction on the atomic scale between a Pd AFM tip and ideal graphite substrate<sup>20</sup> 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<sup>21,22</sup> and the use of the AFM have made the observation of atom-

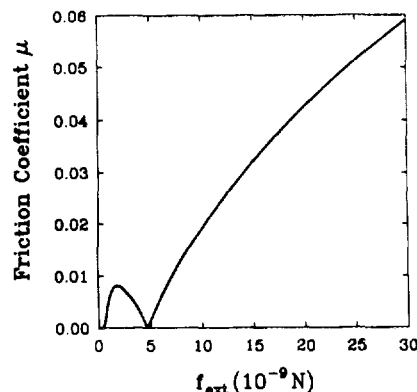


FIG. 4. The microscopic friction coefficient  $\mu$  as a function of the external force per atom  $f_{\text{ext}}$  (from Ref. 18, ©American Physical Society).

ic-scale friction force under near-ideal conditions possible.<sup>22</sup> 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  $\Delta V_{\text{max}}(F_{\text{ext}})$  which results from variations of the adsorption bond energy and the work against  $F_{\text{ext}}$ . Hence the energy investment for this process is  $\Delta V_{\text{max}}(F_{\text{ext}})$ , which in general increases with increasing external force  $F_{\text{ext}}$ . If we assume a very slow horizontal motion of the tip, the subsequent energy gain  $-\Delta V_{\text{max}}(F_{\text{max}})$  will be dissipated into heat (occurring as phonons or electron-hole pair excitations).<sup>23</sup> The average friction force is related to this dissipated energy and is given by  $\langle F_f \rangle \leq \Delta V_{\text{max}}(F_{\text{ext}})/\Delta x$ . Due to the small dependence of the Pd-graphite interaction on the tip position  $x$  for loads  $F_{\text{ext}} \approx 10^{-8}$  N per tip atom, we find  $\langle F_f \rangle$  to be very small. In Fig. 4, we show the friction coefficient (defined as  $\mu = \langle F_f \rangle / F_{\text{ext}}$ ) which turns out to be  $\mu \approx 10^{-2}$  in this load range. The dependence of  $\mu$  on the load  $f_{\text{ext}}$ , shown in Fig. 4, has been discussed elsewhere.<sup>20</sup> In general, we find that  $\mu$  increases with increasing load, in agreement with a recent AFM experiment.<sup>22</sup>

#### 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  $f_{\text{ext}} \approx 10^{-8}$  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.

## ACKNOWLEDGMENTS

We thank Professors H.-J. Güntherodt, S. G. Louie, S. D. Mahanti, H. Miyazaki, as well as Z. Sun, Y. Wang, and the AFM/STM group of the University of Basel for stimulating discussions. This work has been supported by the Office of Naval Research under Contract No. N00014-90-J-1396 and, in its initial stage, by the Director, Office of Energy Research, Office of Basic Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. CRAY computer time at the National Magnetic Fusion Energy Computer Center and the National Center for Supercomputing Applications and CONVEX computer time have been provided by a grant from the U.S. Department of Energy, the National Science Foundation and Michigan State University, respectively. G. O. acknowledges partial financial support from the Swiss National Science Foundation and Kommission zur Förderung der wissenschaftlichen Forschung.

<sup>\*)</sup> Permanent address: Institut für Physik, Universität Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland.

<sup>1</sup>G. Binnig, C. F. Quate, and Ch. Gerber, *Phys. Rev. Lett.* **56**, 930 (1986).

<sup>2</sup>G. Binnig, Ch. Gerber, E. Stoll, T. R. Albrecht, and C. F. Quate, *Europhys. Lett.* **3**, 1281 (1987).

<sup>3</sup>E. Meyer, H. Heinzelmann, P. Grütter, Th. Jung, Th. Weisskopf, H. R. Hidber, R. Lapka, H. Rudin, and H.-J. Güntherodt, *J. Microsc.* **152**, 269 (1988).

<sup>4</sup>T. R. Albrecht and C. F. Quate, *J. Appl. Phys.* **62**, 2599 (1987).

<sup>5</sup>G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, *Phys. Rev. Lett.* **49**, 57

(1982).

<sup>6</sup>I. P. Batra and S. Ciraci, *J. Vac. Sci. Technol. A* **6**, 313 (1988).

<sup>7</sup>F. F. Abraham and I. P. Batra, *Surf. Sci.* **209**, L125 (1989).

<sup>8</sup>U. Landman, W. D. Luedtke, and M. W. Ribarsky, *J. Vac. Sci. Technol. A* **7**, 2829 (1989); *Mater. Res. Soc. Symp. Proc.* **140**, 101 (1989); U. Landman, W. D. Luedtke, N. A. Burnham, and R. J. Colton, *Science* **248**, 454 (1990).

<sup>9</sup>S. Lee, H. Miyazaki, S. D. Mahanti, and S. A. Solin, *Phys. Rev. Lett.* **62**, 3066 (1989).

<sup>10</sup>D. Tománek, G. Overney, H. Miyazaki, S. D. Mahanti, and H.-J. Güntherodt, *Phys. Rev. Lett.* **63**, 876 (1989); *ibid.* **63**, 1896 (E) (1989).

<sup>11</sup>W. Kohn and L. J. Sham, *Phys. Rev. A* **140**, 1133 (1965).

<sup>12</sup>D. R. Hamann, M. Schlüter, and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979).

<sup>13</sup>L. Hedin and B. J. Lundqvist, *J. Phys. C* **4**, 2064 (1971).

<sup>14</sup> $D$  is proportional to the bending modulus  $B$ .  $D = \rho B$ , with  $\rho = 2M_c / (3\sqrt{3}a^2/2)$  is the area mass density ( $M_c$  = mass of carbon atom,  $a = 1.42 \text{ \AA}$ ). The experimental value for  $B = (2.55 \pm 0.15) \times 10^{-5} \text{ cm}^4/\text{s}^2$  is listed in Ref. 16.

<sup>15</sup>K. Komatsu, *J. Phys. Soc. Jpn.* **6**, 438 (1951).

<sup>16</sup>H. Zabel, in *Graphite Intercalation Compounds I*, Springer Series in Materials Science 14, edited by H. Zabel and S. A. Solin (Springer, New York, 1990).

<sup>17</sup>C. T. Chan, K. M. Ho, and W. A. Kamitakahara, *Phys. Rev. B* **36**, 3499 (1987).

<sup>18</sup>C. T. Chan, W. A. Kamitakahara, K. M. Ho, and P. C. Eklund, *Phys. Rev. Lett.* **58**, 1528 (1987).

<sup>19</sup>W. Zhong, G. Overney, and D. Tománek, *Europhys. Lett.* (1991).

<sup>20</sup>W. Zhong and D. Tománek, *Phys. Rev. Lett.* **64**, 3054 (1990).

<sup>21</sup>J. Skinner, N. Gane, and D. Tabor, *Nat. Phys. Sci.* **232**, 195 (1971).

<sup>22</sup>C. M. Mate, G. M. McClelland, R. Erlandsson, and S. Chiang, *Phys. Rev. Lett.* **59**, 1942 (1987).

<sup>23</sup>J. E. Sacco, J. B. Sokoloff, and A. Widom, *Phys. Rev. B* **20**, 5071 (1979).