

Theory for the Atomic Force Microscopy of Deformable Surfaces

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We present a theory for the atomic force microscopy (AFM) of deformable surfaces and apply it to graphite with and without intercalated atoms. Using continuum elasticity theory for graphite layers, with parameters obtained from *ab initio* calculations, we determine quantitatively local distortions in the vicinity of a sharp AFM tip as a function of the applied force. Our calculations show that AFM should be a unique tool to determine *local* surface rigidity and to measure the healing length of graphite in the vicinity of intercalated impurities or steps.

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The recently developed¹ atomic force microscope (AFM) is finding increasing recognition as a new powerful tool for the determination of surface structures, very much as the similarly working scanning tunneling microscope² (STM) did several years ago. The power of these real-space (i.e., nondiffractive) techniques lies in the ability to resolve isolated atomic defect structures such as steps or impurity atoms. Like the more established STM, the AFM uses an "atomically" sharp tip which scans across the sample surface at a sample-to-tip separation of few angstroms. The AFM probes the structure of the sample by measuring the tip height z which leads to a constant preset force F between the surface and the tip as it scans the surface horizontally. This force is obtained from the deflection of a soft spring which supports the tip (see inset in Fig. 1). In contrast to this technique, the STM observes the tunneling current due to a small bias voltage which is applied between the (conducting) sample and the tip.

It has been shown³ that under idealized conditions, (STM) images reflect local density of states near the Fermi level. A commonly used interpretation of STM images in terms of atomic structure can be very misleading in special cases such as graphite where band-structure effects make every other atom "disappear."⁴ AFM images should be much simpler to interpret since atomic forces reflect the total charge density. Present theories of AFM have so far calculated the repulsive force between a semi-infinite "periodic" tip with a rigid surface⁵ or a single tip interacting with a model system of finite thickness.⁶

In this Letter, we investigate the interaction between an isolated tip and a deformable surface of a semi-infinite system. Since *ab initio* calculations of distortions near an isolated impurity in an extended system are prohibitively time consuming and apply only to special cases, we adopt a novel approach here. We calculate

bulk elastic constants from first principles and then determine equilibrium deformations near structural impurities exactly using a continuum elastic theory.⁷ 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., the dilute limit). Since we are working with a system of differential equations, several analytic and universal results have been obtained. A direct comparison with AFM results showing atomic resolution is possible if one identifies the envelope function associated with the atomic displacements at the surface as given by the above elastic continuum theory. The atomic resolution

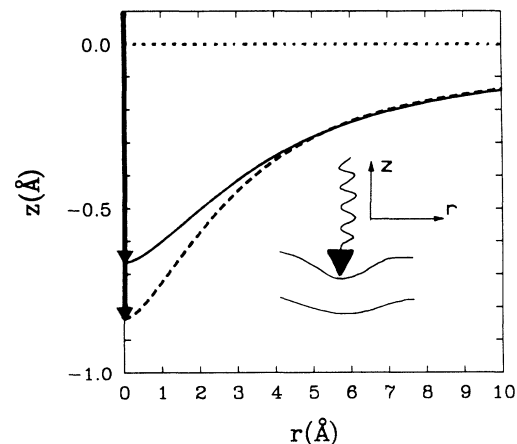


FIG. 1. Vertical position z of the topmost graphite layer as a function of the radial distance r from the AFM tip. Results for a tip force $F = 10^{-9}$ N based on the calculated value of the graphite flexural rigidity constant $D = 7589$ K (solid line) are compared to expected distortions for a reduced $D = 3795$ K (dashed line). Layer positions for zero applied force are shown by the dotted line. Inset: actual geometry.

sacrificed in the continuum approach can be regained by placing discrete atoms on their distorted positions and superposing their charge densities.

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 the healing length and *local* surface rigidity. The semi-infinite system of graphite layers is characterized by flexural rigidity D , transverse rigidity K (proportional to C_{44}), c -axis compressibility G (proportional to C_{33}), and interlayer spacing d . The vertical distortion $w_n(\mathbf{r})$ of the surface layers due to a general external force $F_1(\mathbf{r})$ acting on the topmost layer is given by

$$(D\nabla^4 - K\nabla^2)w_1 + G(w_1 - w_2) = F_1(\mathbf{r}). \quad (1a)$$

The corresponding expression for deeper layers is

$$(D\nabla^4 - K\nabla^2)w_n + G(-w_{n-1} + 2w_n - w_{n+1}) = F_n(\mathbf{r}), \quad n \geq 2. \quad (1b)$$

The absolute vertical position of atoms in the n th layer (with respect to the undistorted topmost layer) is then given by

$$z_n(\mathbf{r}) = -nd + w_n(\mathbf{r}). \quad (2)$$

We assume that the AFM tip is atomically sharp, as implied by the name of the technique, and approximate the external AFM force by a δ function. Similarly, we model the effect of a single intercalant impurity in the first gallery by δ -function forces which will be discussed below. To obtain the graphite layer distortions in response to these forces, it is convenient to perform a Fourier transformation of Eq. (1), which yields the recursive relation

$$\frac{w_n(\mathbf{q})}{w_{n-1}(\mathbf{q})} = \frac{1}{X(\mathbf{q}) - w_{n+1}(\mathbf{q})/w_n(\mathbf{q})} = L(\mathbf{q}), \quad n \geq 3, \quad (3)$$

where

$$L(\mathbf{q}) = \frac{1}{2} \{X(\mathbf{q}) - [X^2(\mathbf{q}) - 4]\}^{1/2} \quad (4)$$

and

$$X(\mathbf{q}) = q^4 + 2\delta q^2 + 2. \quad (5)$$

In Eq. (3), $w_n(\mathbf{q})$ is the Fourier transform of $w_n(\mathbf{r}/l_0)$, where $l_0 = (D/G)^{1/4}$ is the characteristic length of the system and $\mathbf{q} = l_0\mathbf{k}$ is a dimensionless quantity. δ is defined by $\delta = K/[2(DG)^{1/2}]$. The distortion of the n th graphite layer is related to $w_2(\mathbf{q})$ as

$$w_n(\mathbf{q}) = \{L(\mathbf{q})\}^{n-2} w_2(\mathbf{q}), \quad n \geq 3. \quad (6)$$

This equation, together with the Fourier transform of Eq. (1), allows us to determine the distortion w_n of each individual layer. In the case of the AFM tip only, we ob-

tain

$$w_n(\mathbf{q}) = -f_t \frac{L(\mathbf{q})^{n-1}}{q^4 + 2\delta q^2 + 2 - L(\mathbf{q})}, \quad (7)$$

where f_t is the scaled tip force

$$f_t = F_t/(DG)^{1/2}. \quad (8)$$

In our calculation, an isolated intercalant impurity is modeled by a pair of equal δ -function-like forces acting in opposite direction on the first and second layer. Their strength is chosen in such a way that the interlayer distance at the intercalant site is the same as the diameter d_i of the (incompressible) intercalant. In linear-response theory, all distortions w_n are proportional to the applied force. Moreover, the total layer distortion in the presence of an AFM tip *and* an intercalant is given by the linear superposition of the distortions due to each of them separately. In the limiting case of an isolated impurity, the distortions of the n th layer, w_n , should be zero in a rigid system (flexural rigidity $D \rightarrow \infty$). As can be seen, this is indeed the case since $f_t = 0$ in Eq. (8) and hence $w_n = 0$ in Eq. (7).

We determined the elastic constants of graphite from a first-principles total-energy calculation within the local-density approximation (LDA).⁸ We used the *ab initio* pseudopotential local orbital method which has been described elsewhere⁹ and successfully applied to short-wavelength distortions of graphite. In our calculation, we replace ionic potentials by norm-conserving ionic pseudopotentials of Hamann-Schlüter-Chiang type.¹⁰ We use the Hedin-Lundqvist¹¹ form of the exchange-correlation potential. The LDA calculations are carried out using a basis of Gaussian orbitals which are localized on atomic sites. At each C site, we consider s and p orbitals with three radial Gaussian decays each, i.e., twelve independent basis functions. 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 LDA charge density and potentials have been obtained by sampling the Brillouin zone with a fine mesh of 245 \mathbf{k} points, using a special-point scheme.¹²

The accuracy of our LDA calculations has been first checked by determining the in-plane C-C bond length $d_{C-C} = 1.42 \text{ \AA}$, the vibration frequency of the in-plane mode $\omega(E_{2g_2}) = 1541 \text{ cm}^{-1}$, and the out-of-plane mode $\omega(A_{2u}) = 809 \text{ cm}^{-1}$. These values are in very good agreement with experimental values¹³ $d_{C-C} = 1.42 \text{ \AA}$, $\omega(E_{2g_2}) = 1582 \text{ cm}^{-1}$, and $\omega(A_{2u}) = 868 \text{ cm}^{-1}$ and previously calculated values^{14,15} $d_{C-C} = 1.42 \text{ \AA}$, $\omega(E_{2g}) = 1598 \text{ cm}^{-1}$, and $\omega(A_{2u}) = 839 \text{ cm}^{-1}$. In our calculation, we assumed *AA* layer stacking which is appropriate for intercalated graphite. This explains the small differences between our results and previous experimental and theoretical data which have been obtained for *ABAB* stacked (hexagonal) graphite.

In a second step, we used the LDA formalism to determine the value of the flexural rigidity constant and find it to be $D=7589$ K, which also compares very favorably with the experimental value¹⁶ $D=7076 \pm 420$ K. In the following continuum calculation, we use this value and experimental values¹³ for the c -axis compressibility $G=789$ K \AA^{-4} , transverse rigidity $K=932$ K \AA^{-2} , and the interlayer spacing $d=3.35$ \AA .

In Fig. 1 we compare calculated vertical positions z of carbon atoms in the topmost layer in the vicinity of an AFM tip pushing against the surface (solid and dashed lines) to their position in the absence of external forces (dotted line). In linear-response theory, surface distortions w_1 ($=z$ for the topmost layer) should be proportional to the applied force F , but the healing length λ_p of pristine graphite, corresponding to the distance at which the layer distortion decreases to half its maximum value, should be independent of F . On the other hand, we expect both λ_p and z to depend on the surface flexural rigidity D . Our results for $F_t=10^{-9}$ N shows that λ_p decreases from 4.2 to 3.2 \AA and the maximum layer distortion

z_t at the tip position $r=0$ \AA increases from 0.67 to 0.84 \AA when the graphite flexural rigidity constant $D=7589$ K is reduced to half its value. Since changes of the vertical tip position due to force changes $\delta z_t = z_t(F_t) - z_t(F_t=0)$ depend sensitively on D , the AFM measurement of δz_t as a function of F_t should provide a unique experimental access to local elastic constants at the surface. While it is difficult to determine precisely the tip position z_t for $F=0$, it is useful to note that δz_t can be measured using $\delta z_t \approx z_t(F_t + F'_t) - z_t(F'_t)$ if linear response is assumed.

Since within our continuum model, the vertical position z_t of an AFM tip scanning the surface of perfect pristine graphite is constant for a constant force, such a scan does not provide easy access to the healing length λ_p discussed above. On the other hand, the healing length in the vicinity of a structural defect, such as a step or an intercalant in the first gallery, can be easily probed by the AFM experiment. The model intercalant which we consider in Fig. 2 is a K atom with a diameter $d_i=5.3$ \AA (larger than the graphite interlayer spacing $d=3.35$ \AA). The AFM tip, which is 5 \AA away from the intercalant, exerts a force $F=10^{-9}$ N onto the graphite substrate. In Fig. 2(a) we show the vertical positions z of carbon atoms in the three topmost graphite layers, in a plane which contains the intercalant and the tip and which is perpendicular to the layers. A 3D view of the topmost layer topography in the presence of a single intercalant impurity and the AFM tip is shown in Fig. 2(b). Our results in Fig. 2(a) show that graphite distortions die out after the fourth graphite layer which would justify the use of finite-thickness slabs for future first-principles calculations of a discrete graphite lattice.

The profile of the graphite surface near a structural impurity is accessible to the AFM experiment. In Fig. 3 we show the calculated vertical tip position z_t as a function of the horizontal tip distance r_t from the intercalant, for a vanishing AFM force [Fig. 3(a)] and for $F=10^{-9}$

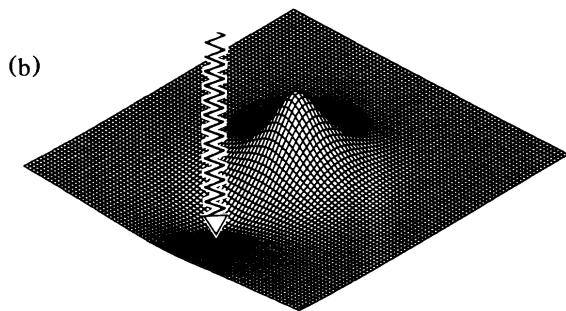
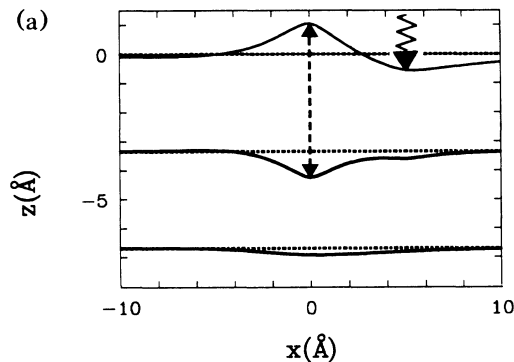


FIG. 2. Structure of graphite interacting with an AFM tip, in case of a single intercalant impurity. (a) Positions z of three topmost graphite layers, shown in a plane perpendicular to the graphite layers. The intercalant and the tip lie along the horizontal x axis. (b) 3D view of the topmost layer topography. The intercalant with a diameter $d_i=5.3$ \AA models a K atom between the topmost and the second layer. The AFM tip, which is 5 \AA away from the intercalant, exerts a force $F=10^{-9}$ N onto the graphite substrate.

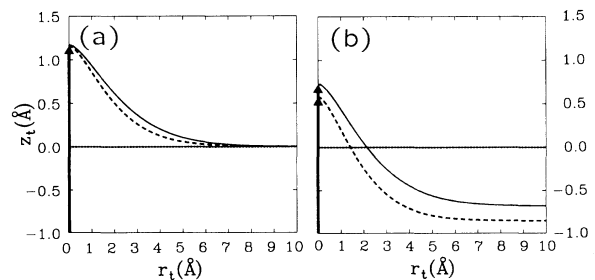


FIG. 3. Vertical position z_t of the AFM tip as a function of its radial distance r_t from an intercalant with a diameter $d_i=5.3$ \AA . (a) Results for zero tip force based on the calculated value of the graphite flexural rigidity constant $D=7589$ K (solid line) are compared to expected distortions for a reduced $D=3795$ K (dashed line). (b) Corresponding results for a tip force $F=10^{-9}$ N.

N [Fig. 3(b)]. Results in Fig. 3(a) describe, in an alternative interpretation, the dependence of the topmost layer topography on the flexural rigidity constant D and show that the healing length λ_i near the intercalant decreases from 2.1 to 1.8 Å as D decreases from 7589 K (solid line) to 3795 K (dashed line). The most important effect of a nonzero AFM force [Fig. 3(b)] is a compression of the graphite substrate along the c axis. From the comparison of results for different values of D , we find that the *apparent* size of the intercalant [given by $z_i(r_i=0) - z_i(r_i \rightarrow \infty)$] increases by 0.14 Å as D decreases from 7589 to 3795 K, but the values of the healing length λ_i lie close to the values for $F=0$. Local changes in the layer rigidity D graphite are expected to occur due to charge transfer near intercalant sites in intercalation compounds (in analogy to similar observed changes^{14,15} in d_{C-C}) and are presently being investigated.¹⁷

In conclusion, we developed a theory for the atomic force microscopy (AFM) of deformable surfaces, based on a combination of *ab initio* density functional formalism and continuum elasticity theory. We applied this theory to graphite with and without intercalated atoms and determined quantitatively local distortions in the vicinity of a sharp AFM tip as a function of the applied force. We believe that AFM should be a unique tool to determine *local* surface rigidity and to measure the healing length of graphite in the vicinity of intercalated impurities or steps.

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¹G. Binnig, C. F. Quate, and Ch. Gerber, Phys. Rev. Lett. **56**, 930 (1986); Appl. Phys. Lett. **40**, 178 (1982).

²G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, Phys. Rev. Lett. **49**, 57 (1982).

³J. Tersoff and D. R. Hamann, Phys. Rev. Lett. **50**, 1998 (1983); Phys. Rev. B **31**, 805 (1985).

⁴D. Tománek, S. G. Louie, H. J. Mamin, D. W. Abraham, R. E. Thomson, E. Ganz, and J. Clarke, Phys. Rev. B **35**, 7790 (1987); D. Tománek and S. G. Louie, Phys. Rev. B **37**, 8327 (1988).

⁵I. P. Batra and S. Ciraci, J. Vac. Sci. Technol. A **6**, 313 (1988).

⁶F. F. Abraham and I. P. Batra, Surf. Sci. **209**, L125 (1989).

⁷S. Lee, H. Miyazaki, S. D. Mahanti, and S. A. Solin, Phys. Rev. Lett. **62**, 3066 (1989).

⁸W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

⁹C. T. Chan, D. Vanderbilt, and S. G. Louie, Phys. Rev. B **33**, 2455 (1986); C. T. Chan, D. Vanderbilt, S. G. Louie, and J. R. Chelikowsky, Phys. Rev. B **33**, 7941 (1986).

¹⁰D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

¹¹L. Hedin and B. J. Lundqvist, J. Phys. C **4**, 2064 (1971).

¹²D. J. Chadi and M. L. Cohen, Phys. Rev. B **8**, 5747 (1973).

¹³H. Zabel, in *Graphite Intercalation Compounds*, edited by H. Zabel and S. A. Solin, Topics in Current Physics (Springer-Verlag, New York, 1989).

¹⁴C. T. Chan, K. M. Ho, and W. A. Kamitakahara, Phys. Rev. B **36**, 3499 (1987).

¹⁵C. T. Chan, W. A. Kamitakahara, K. M. Ho, and P. C. Ekland, Phys. Rev. Lett. **58**, 1528 (1987).

¹⁶ D is proportional to the bending modulus $B = (2.55 \pm 0.15) \times 10^{-5} \text{ cm}^4/\text{sec}^2$ which is listed in Ref. 13.

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