Theory of Atomic Force Microscopy on Elastic Surfaces

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We combine *ab initio* Density Functional and Continuum Elasticity theory to determine elastic surface deformations, limits of atomic resolution, and atomic-scale friction in Atomic Force Microscopy (AFM). We apply this formalism to the interaction of a Pd AFM tip with graphite. Our results show that, in the constant-force mode, atomic resolution is marginally possible in a narrow 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. For loads near 10^{-8} N, we determine the microscopic friction coefficient to be $\mu \approx 10^{-2}$.

After being introduced by Binnig, Quate and Gerber in 1986, Atomic Force Microscopy (AFM) has become a very powerful tool in detecting surface structures, especially those of semiconductors and insulators.[1,2] The AFM consists of a very sharp tip suspended on a soft spring. In the constant-force mode, tip deflection due to the interaction with the surface is recorded during the surface scan for a given applied load. Atomic resolution is achieved when the observed surface corrugation is sufficiently large, typically ≥ 0.1 Å.

Calculation of the interaction between an AFM tip and a solid is possible to a high precision within the Density Functional formalism, using the Local Density Approximation (LDA).[3] The predictive strength of these parameter-free *ab initio* calculations is, however, counterbalanced by the practical limitation of applicability to periodic structures with less than $10 - 10^2$ atoms per unit cell. In order to describe large-scale elastic deformations occurring in AFM interacting with elastic surfaces, we develop a new formalism by combining LDA with Continuum Elasticity theory. We apply this theory to describe the interaction between a Pd AFM tip and graphite.

In a first step, we use LDA to determine the Pd-graphite interaction and elastic constants of graphite.[4] In Fig. 1 we show the force acting between graphite and a Pd atom in the on-top and hollow site. We use *ab initio* pseudopotentials of Hamann-Schlüter-Chiang type,[5] a local Gaussian basis, a large energy cutoff of 49 Ry in the Fourier expansion of the charge density ρ, and a fine 47 $\vec{k}$-point mesh sampling the 2-dimensional Brillouin zone. The graphite surface is approximated by a rigid 4 layer slab; the unit cell contains 8 carbon atoms and 2 Pd atoms.[4] The equilibrium structure and elastic constants of the graphite substrate have been obtained from a similar calculation for bulk graphite. The calculated in-plane C-C bond length $a = 1.42$ Å and inter-plane spacing $c = 3.35$ Å agree very well with the experiment. The forces between Pd and graphite shown in Fig. 1 have been obtained from a polynomial fit of the LDA total energies.

In the next step, we describe the deformation of graphite due to localized forces by Continuum Elasticity Theory. The elastic response of graphite due to external forces

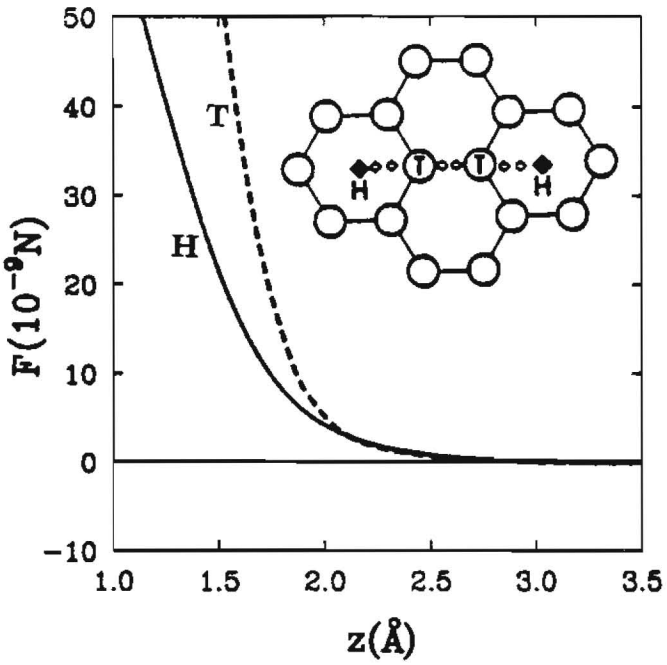

FIG. 1. Force F between a 1-atom Pd AFM tip and graphite, as a function of the tip height z above the surface of hexagonal graphite. The solid and dashed lines correspond to the sixfold hollow (H) and the on-top (T) sites, respectively. The inset shows the adsorption geometry in top view.

(which can be due to the AFM tip or intercalant atoms) are determined by solving a set of coupled differential equations.[6] The distortion of graphite layers, which are approximated by homogeneous plates in this step, is described by elastic constants determined from LDA. Consequently, surface deformations observed by AFM can be used to determine local variations of the elastic constants such as the flexural rigidity which can occur near intercalant impurities or steps.[6]

Once the new equilibrium positions of carbon atoms in the distorted layers have been obtained, the total charge density of the system ρ can be well approximated by a superposition of atomic charge densities obtained from LDA. The resulting charge density of the deformed surface is shown in Fig. 2.

In order to estimate the limits of atomic resolution in AFM, we use the calculated Pd–graphite interaction to determine the equilibrium tip height z at inequivalent surface sites as a function of applied load. We define a load per tip atom $f_{ext} = F_{ext}/N$, where F_{ext} is the total load on the tip and N is the number of tip atoms in contact with the graphite surface. For loads $f_{ext} > 2.0 \times 10^{-9}$N, we find $\Delta z \equiv z_{on-top} - z_{hollow} > 0$. Atomic resolution can be achieved experimentally when Δz is sufficiently large to be detected, i.e. typically $\Delta z \geq 0.1$ Å, which corresponds to $f_{ext} > 10^{-8}$N. On the other hand, our

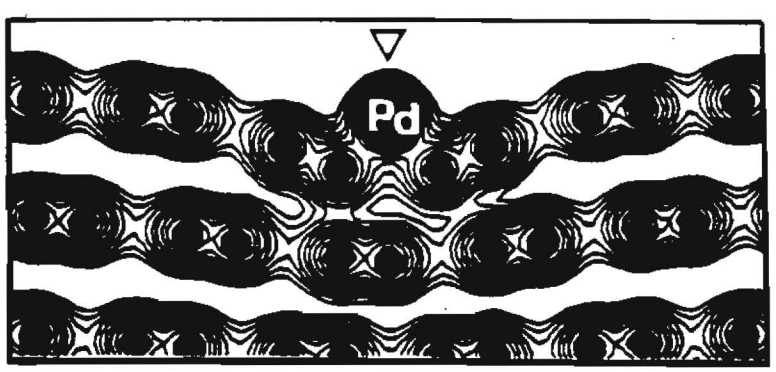

FIG. 2. Total charge density ρ of a 1-atom Pd AFM tip interacting with the elastic surface of graphite near the hollow site, for a load of 5×10^{-9} N. Contours of constant ρ are shown in the xz plane perpendicular to the surface. The position of the AFM tip is indicated by $\triangledown$.

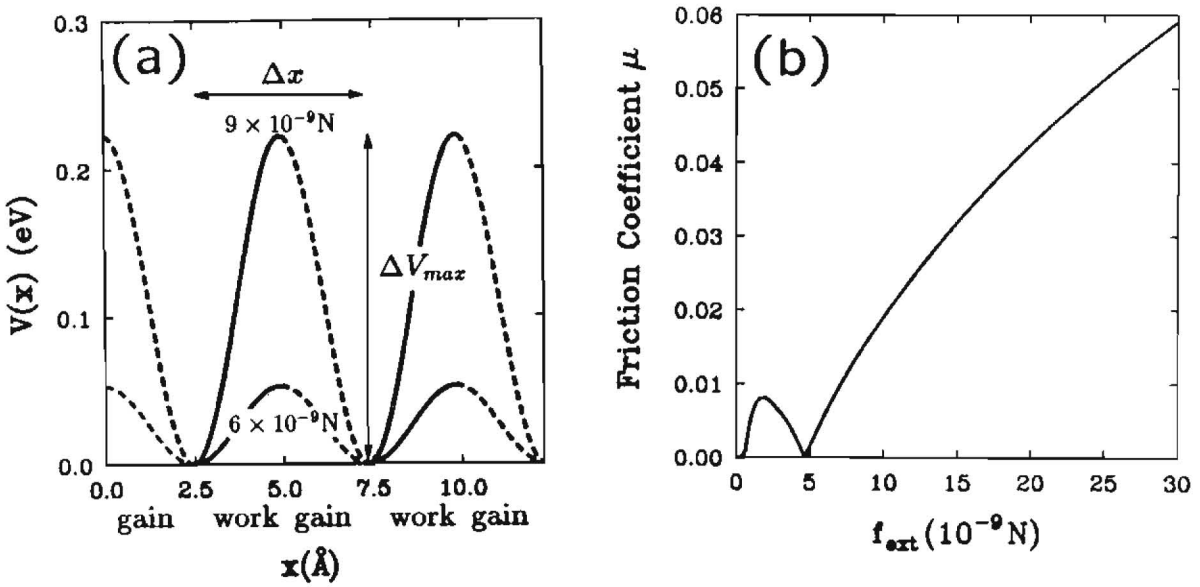

FIG. 3. (a) Potential energy $V(x)$ of the Pd–graphite system as a function of the Pd tip position along the surface x–direction, for external forces $f_{ext} = 6 \times 10^{-9}$ N and 9×10^{-9} N. (b) Microscopic friction coefficient μ as a function of the external force per atom f_{ext} (from Ref. 7). (© American Physical Society)

calculation of elastic graphite deformations for $f_{ext} \geq 10^{-8}$N indicates that such large local forces can rupture the graphite surface, in agreement with experiment.[7]

The present results for the Pd–graphite interaction can also be used to describe atomic–scale friction on an ideal substrate.[4] Friction is a dissipative process which is generally dominated by plastic deformations at the interface and dislocation motion within the two bodies in contact. This complexity makes a predictive description of friction a very difficult undertaking. However, progress in surface preparation[7,8] and use of the AFM have made the observation of atomic–scale friction force under near–ideal conditions possible.[8]

We describe the friction process between an AFM tip and graphite by considering a "surface diffusion" of the AFM tip under external load, along a straight trajectory in the surface x direction. The position–dependent part of the potential energy $V(x)$ of the system is shown in Fig. 3(a). The two main components of $V(x)$ are variations of the adsorption bond energy and work against the external force f_{ext} in case of nonzero corrugations Δz. We first consider the energy involved in moving the AFM tip between two neighboring equivalent sites which are separated by Δx. During this process, the system has to cross a potential energy barrier $\Delta V_{max}(F_{ext})$ (shown by a solid line in Fig. 3(a)). Assuming a very slow horizontal motion of the tip, the subsequent energy gain $-\Delta V_{max}(F_{ext})$ (shown by a dashed line in Fig. 3(a)) will be dissipated into heat (occurring as phonons or electron–hole pair excitations).[9] The average friction force is related to this dissipated energy and is given by

$$< F_f > \leq \frac{\Delta V_{max}(F_{ext})}{\Delta x}. \tag{1}$$

The friction coefficient is defined by the ratio of the friction force and the applied load,

$\mu = F_f/F_{ext}$. In our calculation, we find the dependence of the Pd–graphite interaction on the tip position x to be very small for loads $f_{ext} \approx 10^{-8}$ N per tip atom. Consequently, the friction coefficient in this load range is very small, $\mu \approx 10^{-2}$. We expect this value to be a realistic estimate of μ for the ideal conditions discussed above. As shown in Fig. 3(b), μ increases with increasing load, in agreement with a recent AFM experiment.[8]

In summary, 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 and determined quantitatively local distortions in the vicinity of a sharp AFM tip as a function of the applied force. We conclude that AFM should be a unique tool to determine *local* changes of the surface rigidity which can occur near intercalant impurities or steps. Using our formalism, we found that in the constant–force mode, the AFM can marginally achieve atomic resolution for loads (per tip atom) near $f_{ext} \approx 10^{-8}$ N. The load range is limited by a too low corrugation Δz on the lower end and by too large substrate distortions leading to surface rupture on the upper end. We also estimated the friction coefficient between a Pd AFM tip and graphite by considering the energy dissipated along the tip trajectory. We found the friction coefficient to be very small, in the order $\mu \approx 10^{-2}$ for loads near 10^{-8} N, and found μ to increase with increasing applied load.

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