First-Principles Theory of Atomic-Scale Friction

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We determine the atomic-scale friction associated with a layer of Pd atoms moving across a graphite substrate from *ab initio* total-energy calculations. We evaluate the friction energy caused by variations of the chemical bond strength and work against an external force (load) due to variations of the bond length along the trajectory. We find only a very small dependence of the Pd-graphite interaction on the adsorption site which gives rise to a very small friction coefficient $\mu \approx 10^{-2}$ for loads near 10^{-8} N. We also find μ to increase with load in agreement with recent experiments.

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Friction forces are observed in nature when two bodies in contact are in relative motion.[1] They occur in addition to the reaction forces of classical mechanics and are related to the external force (load) F_{ext} applied between these bodies as

$$F_f = \mu F_{\text{ext}} . \tag{1}$$

The coefficient of friction μ ranges typically between 10^{-2} for smooth surfaces and 1 for rough surfaces. Friction forces have dissipative character: They couple macroscopic mechanical degrees of freedom of two objects in contact to microscopic degrees of freedom which occur as heat or plastic deformations. Moreover, friction forces depend sensitively on the interface structure which makes their prediction an extremely difficult undertaking. This second problem has experienced much progress recently due to increasing sophistication in the characterization of the interface, from the use of rather rough interfaces[2,3] to atomically flat contact areas.[4] The recent application of the atomic-force microscope[5] (AFM) to this problem has led to the observation of a friction force resolved on the atomic scale.[6]

In this Letter, we present the first predictive theory of atomic-scale friction. We use *ab initio* techniques to calculate the interaction of a perfect layer of atoms with the substrate as a function of their relative position and use this information to determine the friction coefficient μ. Our results include quantitative predictions of μ as a function of the external force, a qualitative understanding of the increase of μ with increasing surface roughness, and a qualitative understanding of the decrease of μ with increasing relative velocity of the objects in contact (gliding friction).

Graphite is an ideal substrate for the study of friction since the binding energy of atoms and its variations along the surface are negligibly small near equilibrium adsorption (Fig. 1). In our calculation, we determine the adsorption energy of Pd atoms in the on-top (T) and the sixfold-hollow (H) sites as a function of the Pd-graphite separation. Total energies are calculated from first principles using the local-density approximation.[7] We use the *ab initio* pseudopotential local-orbital method which has been described elsewhere[8] and successfully applied to short-wavelength distortions of graphite.[9] In our calculation, we replace ionic potentials by norm-conserving ionic pseudopotentials of Hamann-Schlüter-Chiang type[10] and use the Hedin-Lundqvist[11] form of the exchange-correlation potential. The surface of hexagonal graphite is represented by a four-layer slab and the adsorbate by a monolayer of Pd atoms in registry with the substrate (one Pd atom per surface Wigner-Seitz cell of graphite). 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 geometries, we introduce floating orbitals on sites not occupied by atoms and

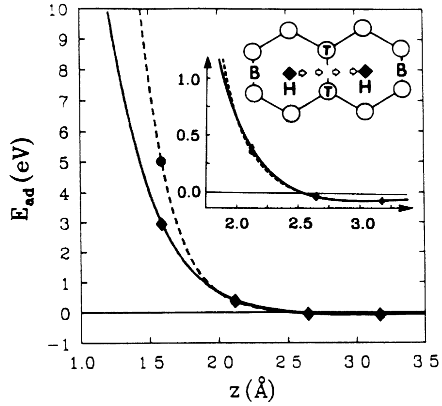

FIG. 1. Pd adsorption energy E_{ad} as a function of the adsorption height z above the surface of hexagonal graphite. The solid and dashed lines correspond to the sixfold-hollow (H) and the on-top (T) sites, respectively. Lower inset: An enlarged section of the graph near equilibrium adsorption. Upper inset: The adsorption geometry in top view; a possible trajectory of the Pd layer along x is shown by arrows.

use the same extended basis[12] for both T and H calculations. To insure high accuracy and complete convergence of total energies, we use an energy cutoff of 49 Ry in the Fourier expansion of the charge density and sample the two-dimensional Brillouin zone with a mesh of 49 **k** points, using a special-point scheme.[13]

In Fig. 1 we show the adsorption energy E_{ad} of a Pd atom (representing the Pd monolayer), defined by

$$E_{\mathrm{ad}} = E_{\mathrm{total}}(\text{Pd-graphite}) - E_{\mathrm{total}}(\text{Pd}) - E_{\mathrm{total}}(\text{graphite}) ,$$

for the on-top- and hollow-site registry. We obtain a very weak adsorption bond strength ≤ 0.1 eV at an equilibrium adsorption height $z \approx 3$ Å. At this distance from the substrate, the corrugation of the graphite charge density is negligibly small due to Smoluchowski smoothening and the position dependence of the adsorption bond strength is $\ll 0.1$ eV.[14] Our calculations show that at bond lengths $z \leq 2$ Å, the hollow site is favored with respect to the on-top site. At $z \approx 2$ Å, the adsorption energies are nearly the same, and at larger distances, it is the on-top site which is slightly favored by < 0.05 eV. This is consistent with the dominant interaction changing from closed-shell repulsion (which strongly favors the hollow site at very small adsorption bond lengths) to a weak chemisorption bond[15] (which is stabilized by the hybridization with p_z orbitals in the on-top site).

For a microscopic understanding of the friction process, we first consider the motion of an atomic layer along the surface. This layer is in registry with the substrate and experiences an external force per atom[16] f_{ext} normal to the surface. At each site, the equilibrium adsorption length z is given by the condition

$$f_{\mathrm{ext}} = -\partial E_{\mathrm{ad}}(z)/\partial z . \tag{2}$$

We consider a straight trajectory along the x direction in the surface connecting nearest-neighbor hollow sites which are separated by Δx [see the inset in Fig. 2(a)]. The position-dependent part of the potential energy V of the system has two main components. These are variations of the adsorption bond energy and work against the external force f_{ext} applied to the adsorbate due to variations of the adsorption length. Hence,

$$\begin{aligned} V(x,f_{\mathrm{ext}}) = {} & E_{\mathrm{ad}}(x,z(x,f_{\mathrm{ext}})) \\ & + f_{\mathrm{ext}} z(x,f_{\mathrm{ext}}) - V_0(f_{\mathrm{ext}}) , \end{aligned} \tag{3}$$

where we arbitrarily set the potential energy to zero at the hollow site by defining

$$V_0(f_{\mathrm{ext}}) = E_{\mathrm{ad}}(x_H, z(f_{\mathrm{ext}})) + f_{\mathrm{ext}} z(x_H, f_{\mathrm{ext}}) . \tag{4}$$

In Fig. 2(a) we show $V(x)$ for different external forces.[17] We find that the mechanical component dominates and is only partly compensated by adsorption-energy differences. As a result of variations of V along x, there is a position-dependent force f_x along the x direction, shown in Fig. 2(b), which is given by

$$f_x(x,f_{\mathrm{ext}}) = \partial V(x,f_{\mathrm{ext}})/\partial x . \tag{5}$$

The maximum value of f_x describes the static friction governing the onset of stick-slip motion. The gliding friction, on the other hand, must be obtained as a weighted average over this force from the energy dissipated in friction along x. We first consider a conservative part of this process corresponding to a potential-energy increase $\Delta V_{\max}(f_{\mathrm{ext}}) = V_{\max}(f_{\mathrm{ext}}) - V_{\min}(f_{\mathrm{ext}})$ along Δx which yields a positive value of f_x. The nonconservative part corresponds to a decrease of $V(x)$ along x and a negative value of f_x. Friction losses ΔE_f along Δx must not exceed the maximum increase in the potential energy; hence,

$$\Delta E_f \leq \Delta V_{\max} . \tag{6}$$

For very slow tracking velocities, any gain in potential energy during the nonconservative part of the friction process is efficiently transferred into surface phonons and electron-hole pairs.[18] Then, we can consider both sides of Eq. (6) to be equal which corresponds to $f_f = |f_x|$, shown in Fig. 2(b). This is the first quantitative predic-

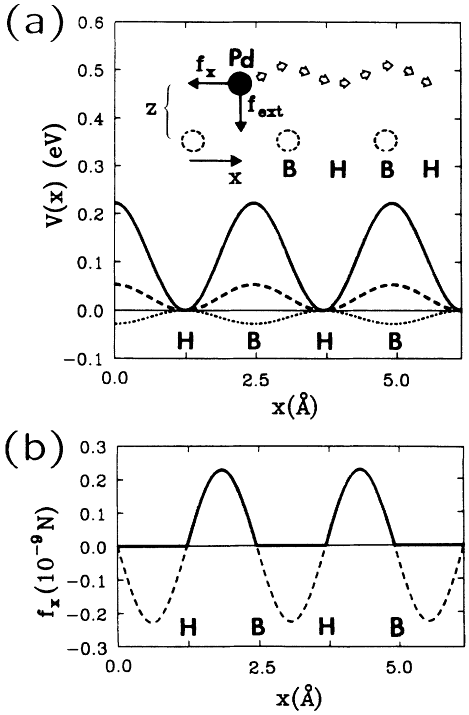

FIG. 2. (a) Potential energy $V(x)$ of the Pd-graphite system as a function of the position of the Pd layer along the surface x direction, for external forces $f_{\mathrm{ext}} = 3\times10^{-9}$ (dotted line), 6×10^{-9} (dashed line), and 9×10^{-9} N (solid line). Inset: The adsorption geometry and trajectory of the Pd layer in side view. (b) Atomic-scale structure of the force along the surface f_x (dashed line) and the friction force $f_f = |f_x|$ (solid line) for $f_{\mathrm{ext}} = 9\times10^{-9}$ N.

tion of atomic-scale structure in the friction force which has been observed recently.[6]

The energy dissipated in friction along Δx can also be related to the average friction force $<f_f>$ along the trajectory as

$$\Delta E_f = <f_f> \Delta x\,. \tag{7}$$

Using Eq. (6) for ΔE_f, we obtain[19]

$$<f_f> = (1/\Delta x)\Delta V_{\max}\,. \tag{8}$$

Applying the definition of the friction coefficient μ in Eq. (1), we find

$$\mu = \frac{<f_f>}{f_{\text{ext}}} = \frac{\Delta V_{\max}}{f_{\text{ext}}\Delta x}\,. \tag{9}$$

In Fig. 3 we show μ as a function of f_{ext}. We find a general increase of μ with increasing external force. The minimum in $\mu(f_{\text{ext}})$ near $f_{\text{ext}} = 5\times10^{-9}$ N is caused by the switching of the minima in $V(x)$ from H to B, shown in Fig. 2(a).[20] From our former calculations[9] we conclude that if the external force (per atom) exceeds 10^{-8} N, the graphite surface is very strongly deformed[21] and likely to be ruptured.[4] Since no plastic deformations have been observed in the AFM studies,[6] the applied forces were probably in the region $f_{\text{ext}} < 10^{-8}$ N. For these values of f_{ext}, our calculated friction coefficient of the order $\mu \approx 10^{-2}$ agrees with the experiment.[4,6]

In order to obtain a meaningful comparison with observable friction forces, we have to make further assumptions about the macroscopic interface and the elastic response of the substrate to external forces. In the simplest case, we consider an atomically flat interface, where N atoms are in contact with the substrate, and neglect elastic deformations. Then, the external force per atom f_{ext} is related to the total external force F_{ext} by

$$f_{\text{ext}} = (1/N)F_{\text{ext}}\,. \tag{10}$$

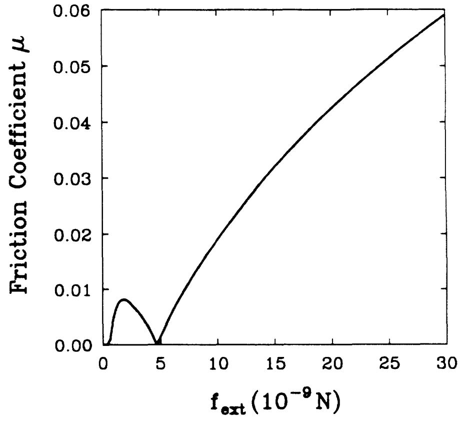

FIG. 3. Microscopic friction coefficient μ as a function of the external force per atom f_{ext}.

In Fig. 4 we use the calculated $\mu(f_{\text{ext}})$ to plot the total friction force F_f for such a perfectly flat interface consisting of 1500 Pd atoms. Since μ increases with increasing value of f_{ext}, the F_f vs F_{ext} relationship is nonlinear, which has also been observed in the AFM experiment.[6]

In the case of large external forces and an elastic substrate such as graphite, elastic theory predicts[22] the substrate deformations to be proportional to $F_{\text{ext}}^{1/3}$. In the case of a spherical tip,[6] the tip-substrate interface area and the corresponding number of atoms in contact is proportional to $F_{\text{ext}}^{2/3}$. Then, the force per atom f_{ext} is proportional to $F_{\text{ext}}^{1/3}$. Hence, for increasing external forces, variations of the effective force per atom and of μ are strongly reduced due to the increasing interface area. This is illustrated by the dashed line in Fig. 4, where we used $N=1500$ atoms for $F_{\text{ext}} = 10^{-6}$ N. These results are in good agreement with the AFM results for a large unspecified tungsten tip with a radius $R = 1500$–3000 Å on graphite,[6] but show a slightly larger increase of the friction force than observed for the range of external forces investigated.

Our theory can also be used to explain the dependence of μ on the roughness of the interface and on the relative velocities of the two objects in contact. At a rough surface, the number of atoms N in contact with the substrate is smaller than at a flat surface which leads to an increase of f_{ext} and hence of μ. Also, with increasing relative velocity, the coupling between macroscopic and internal microscopic degrees of freedom (phonons, electron-hole pairs) gets less efficient. Then, $\Delta E_f < \Delta V_{\max}$ in Eq. (6) which causes a decrease of $<f_f>$ and μ.

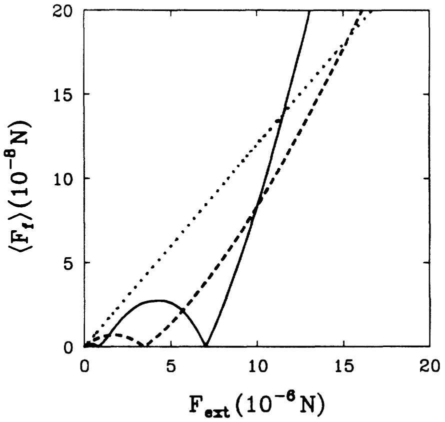

FIG. 4. Macroscopic friction force F_f as a function of the external force F_{ext} for a large object. The solid line corresponds to a "flat" object, the surface of which consists of 1500 atoms in contact with a rigid substrate. The dashed line corresponds to the friction of a large spherical tip and also considers the effect of elastic substrate deformations on the effective contact area. The dotted line corresponds to a constant friction coefficient $\mu = 0.012$.

In summary, we have determined the atomic-scale friction associated with a layer of Pd atoms moving across a graphite substrate from *ab initio* total-energy calculations. We evaluated the friction energy caused by variations of the chemical bond strength and work against an external force. The calculated value of the friction coefficient is very small, of the order $\mu \approx 10^{-2}$ for loads near 10^{-8} N, which could be explained by the Pd-graphite interaction being only weakly dependent on the adsorption site. We also found μ to increase with load in agreement with recent atomic-force-microscopy experiments.

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[14] This effect is also responsible for the large value of the surface diffusion constant and apparently small sensitivity of surface friction to adsorbed films as discussed in Ref. 4.

[15] The magnitude and site dependence of van der Waals interactions between the AFM tip and the surface is negligible in the weakly repulsive region of the Pd-graphite potential considered here.

[16] We denote microscopic forces per atom by f and macroscopic forces applied to large objects by F.

[17] We obtain the periodic potential $V(x)$ at other than the calculated high-symmetry sites from a Fourier expansion over the reciprocal lattice. We keep the lowest seven components of this expansion and determine the expansion coefficients from the calculated values for the T and H sites. The interpolated potential agrees well with an independent model calculation which determines V from a universal embedding energy of Pd atoms in the charge density of the graphite host.

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[19] The fact that the friction force depends only on the *extrema* of the interaction potential offers *a posteriori* another justification for the interpolation scheme used for $V(x)$.

[20] Near $f_{\mathrm{ext}} = 5\times10^{-9}$ N, the lowest-order Fourier components of the potential V vanish. According to our interpolation scheme discussed in Ref. 17, this leads to $\mu = 0$ (shown in Fig. 3). In reality, a small nonzero value of μ is expected due to higher-order Fourier components of V (which are usually much smaller than those considered).

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