Palladium-graphite interaction potentials based on first-principles calculations

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We use *ab initio* total-energy calculations to derive an interaction potential between Pd and graphite. A parametrized form of the potential, inspired by density-functional theory, is presented for use in molecular-dynamics simulations and the interpretation of atomic-force-microscopy images of graphite.

Due to the relative ease of surface preparation, graphite is one of the most commonly used systems in atomic-force-microscopy[1] (AFM) and scanning-tunneling-microscopy[2] studies of surface morphology.[3] The inert nature of graphite layers is responsible for easy cleavage and makes it an ideal substrate for studies of adsorbates, and the small interlayer coupling is responsible for its favorable lubricating properties. Considerable progress has been achieved recently in molecular-dynamics simulations of the tip-substrate interaction in atomic force microscopy.[4]

In order to address questions relevant to materials science, such as friction between the AFM tip and the substrate, molecular-dynamics calculations determine and monitor the detailed atomic motion in very large systems over relatively long time periods.[4,5] The computational effort involved requires the use of very simple parametrized interaction potentials which have been used for a variety of materials.[6,7] Model potentials for interactions with graphite, the material of interest in this study, are typically obtained by averaging interactions with a "generic" carbon solid.[7] These model potentials clearly cannot distinguish the surface reactivity of diamond with an sp^3 configuration from that of graphite with sp^2 bonding.

In this Brief Report, we present a simple expression for the metal-graphite interaction potential which is based on a first-principles total-energy calculation of Pd on graphite.[8] While derived specifically for the Pd-graphite system, the form of the interaction potential is more general and is a good prototype for the interaction of any metal adsorbate on graphite. Our expression for the metal-graphite interaction, inspired by the local-density approximation[9] (LDA), provides a basically correct picture of many-body interactions in the adsorption system. The simple parametrization is a major advantage which will allow this potential to be used in computationally intensive molecular dynamics simulations.

The first-principles calculation of Pd-graphite has been performed using the local-density approximation[9] and the *ab initio* pseudopotential local orbital method.[10] 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 results of this calculation as well as the computational details have been published elsewhere.[8] Our results for the adsorption energy E_{ad} of a Pd atom on graphite, which is defined by $E_{ad} = E_{tot}(\text{Pd/graphite}) - E_{tot}(\text{Pd}) - E_{tot}(\text{graphite})$, are shown by the data points in Fig. 1 for the "hollow" (H) and the "on-top" (T) site.

We find that the LDA results for E_{ad} can be well approximated by a local function which depends only on the total charge density of the graphite host at the Pd adsorption site,

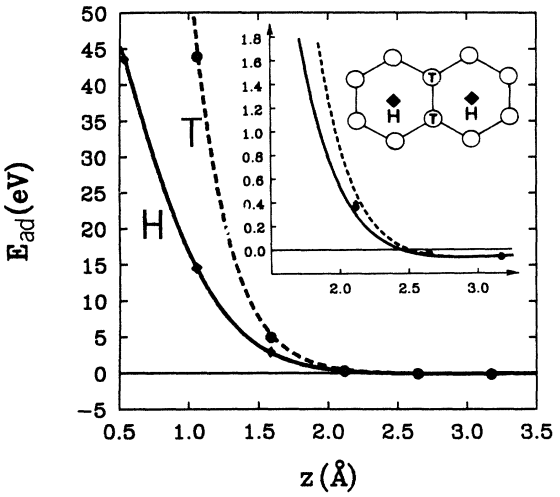

FIG. 1. Adsorption energy E_{ad} of Pd on graphite as a function of the height z of Pd atoms above the graphite surface. Previously published (Ref. 8) first-principles results are given by ◇ and • for the hollow and the on-top site, respectively. These data are compared to the present results, obtained using Eqs. (2)–(4) and given by the solid and the dashed line for the hollow and the on-top site, respectively. Upper inset: Schematic top view of the adsorption geometry. Lower inset: An enlarged section of the graph near equilibrium adsorption.

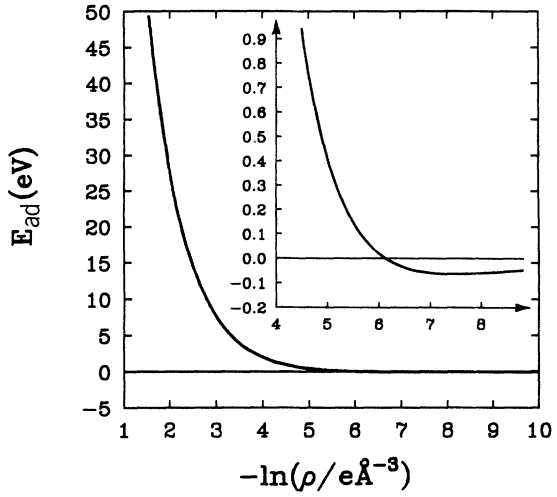

FIG. 2. Relation between the Pd adsorption energy $E_{ad}(\mathbf{r})$ and the total charge density of graphite $\rho(\mathbf{r})$ at the adsorption site $\mathbf{r}$, given by Eq. (2). An enlarged section of the graph near equilibrium adsorption is given in the inset.

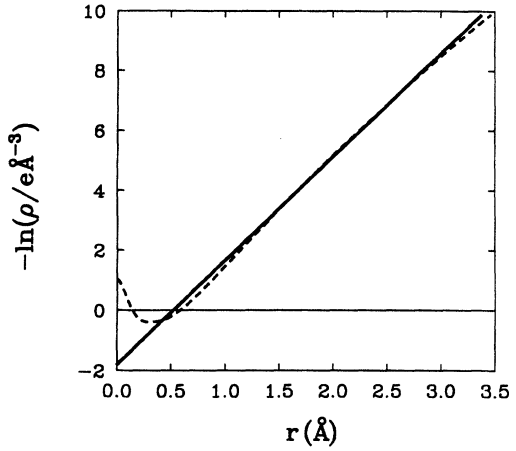

FIG. 3. Radial plot of the charge density of a carbon atom $\rho_{at}(\mathbf{r})$, based on an LDA calculation (dashed line). The solid line shows the parametrized form of the charge density, given by Eq. (4).

$$E_{ad}(\mathbf{r}) = E_{ad}(\rho(\mathbf{r})) \ . \tag{1}$$

This form of the interaction potential is inspired by the the density functional formalism[9] and the embedded atom method.[11] We find that $E_{ad}(\rho(\mathbf{r}))$ can be conveniently parametrized as

$$E_{ad}(\rho(\mathbf{r})) = \epsilon_1 \ (\rho/\rho_0)^{\alpha_1} - \epsilon_2 \ (\rho/\rho_0)^{\alpha_2} \ . \tag{2}$$

In the case of Pd on graphite, ϵ_1=343.076 eV, ϵ_2=2.1554 eV, α_1=1.245, α_2=0.418 06, and ρ_0=1.0 e/Å^3. The dependence of E_{ad} on ρ, obtained using the parametrized form in Eq. (2), is shown in Fig. 2. Adsorption energies of Pd on a flat graphite surface, based on the expression in Eq. (2), are compared to LDA results in Fig. 1.

From an independent LDA calculation of graphite surfaces, we find that the total charge density can be well approximated by a superposition of atomic charge densities,

$$\rho(\mathbf{r}) = \sum_n \rho_{at}(\mathbf{r} - \mathbf{R}_n) \ . \tag{3}$$

This parametrization is especially convenient in case of deformed surfaces where an LDA calculation is difficult due to reduced symmetry. On flat surfaces, the maximum difference between the LDA charge density and the superposition of atomic charge densities is only few percent.

Finally, it is useful to parametrize the charge density of carbon atoms. We find that ρ_{at}, as obtained from an atomic LDA calculation, can be conveniently expressed as

$$\rho_{at}(r) = \rho_C e^{-\beta r} \ , \tag{4}$$

where ρ_C=6.0735 e/Å^3 and β=3.459 Å^{-1}. As shown in Fig. 3, this expression is a very good approximation to the LDA results especially in the physically interesting range 1.4< r <3.0 Å.

One of the primary uses of the above potential is to describe the interaction between a metal AFM tip and graphite. In the case of a large tip, we expect a contribution to the interaction potential from van der Waals forces, which are not described correctly by LDA especially at large tip-substrate distances. As we discussed elsewhere,[12] these forces are not very important since they are very small (typically < 10^{-10} N) at tip-substrate separations $\gtrsim$3 Å. At smaller separations, they are dominated by the substrate-tip repulsion which is described correctly within LDA. These dispersive forces are also not very important for the interpretation of experimental results, since they do not show atomic resolution[13] and are easily compensated in the experiment by adjusting the force on the cantilever which supports the tip.

In summary, we used *ab initio* total-energy calculations to derive an interaction potential between Pd and graphite. A parametrized form of the potential, given in Eqs. (2)–(4), allows for a very fast and efficient evaluation on a computer[14] and is ideally suited for molecular-dynamics calculations.

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[14]The FORTRAN program GRMET can be obtained by contacting the first author at BITNET%"TOMANEK@MSUPA."