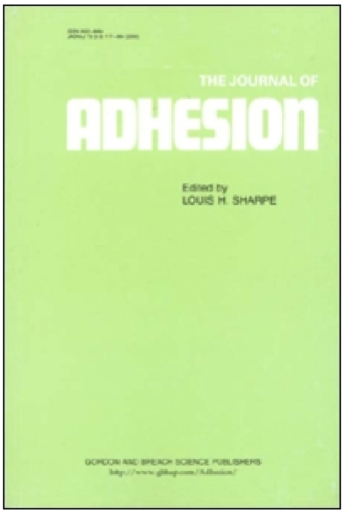

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First Principles Study of Polymer-Metal—Metal-Oxide Adhesion

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First Principles Study of Polymer-Metal–Metal-Oxide Adhesion

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Ab initio, local orbital quantum molecular dynamics is used to study the binding of molecules and polymers to an aluminum and amorphous alumina surface. Specific examples are methane, ethylene, polyethylene and a poly(methyl-methacrylate) (PMMA) monomer on Al and PMMA on alumina. The hydrocarbons exhibit very little binding to Al, while we find that a clean Al surface strips the carbonyl oxygen from PMMA. For PMMA on alumina, a strong chemical bond is formed between the carbonyl group of PMMA and surface Al atoms for the alumina surface.

KEY WORDS PMMA; polyethylene; chemisorption; physisorption; aluminum; alumina; theory; local orbital quantum molecular dynamics; surface.

INTRODUCTION

The study of the bonding between molecules or polymers and a metal or metal-oxide surface is of fundamental interest, both for learning the nature of adhesion at an atomistic level and for a wide variety of applied problems concerning metallic coatings, the quest for better adhesives, and connections with the packaging and fabrication of microelectronics.

Because there are several different length scales in such a problem, it is necessary to study adhesion with methods appropriate to the different scales. At the atomistic level, it is possible to consider the bonding between a segment or functional group of a polymer and a metal surface *via* a complete treatment of the system's electronic structure. A full treatment of adhesion would also include a discussion of the bulk rheology of the polymer and how this affects the adhesion. It is the purpose of this article to provide a detailed treatment of the first part of this problem for some illustrative systems. We have used *ab initio*, density functional total energy/molecular dynamics (MD) techniques to model the surface-polymer segment interaction and discuss the atomistic nature of the bonding of molecules and a poly(methylmethacrylate) monomer (PMMA) to an Al surface and PMMA on a model amorphous alumina (a-Al_2O_3) surface. This is the first application of *ab initio* MD to this important problem of the theory of materials.

Polymer-metal interfaces can be formed by depositing metal atoms on polymers, yielding diffuse interfaces, or depositing polymers on metals, producing a sharp interface. Earlier theoretical work along these lines has involved studies of the bonding of segments of PMMA to Al atoms.[2] Such work is closely related to experiments in which Al atoms are deposited on PMMA. In agreement with others[2] we find this to be a very different phenomenon from polymers interacting with a *metal surface*. This distinction is obvious, since the polymer interacts with metallic atomic orbitals for the early stages of depositing metals on a polymer, *versus* extended metallic surface states. In the present study, we have found that internal reorientation/relaxation of the polymer segments can be *essential* to a proper description of bonding for these metal-molecule or metal-oxide–molecule systems. The availability of reliable (transferable) atomic forces (to relax the adsorbate-surface system) afforded by *ab initio* MD is clearly crucial to such a study.

METHODOLOGY

We employ the *ab initio* local orbital density functional MD scheme of Sankey,[3] as generalized by Drabold to nonelemental systems. The method is well documented in the solid state physics literature. The techniques have been used in studies of Si and C in cluster, crystalline and amorphous form, semiconductor and Al surfaces and systems involving Si and H.[4] For completeness, we describe the elements of the theory here. The essential approximations are: (1) Only the valence electrons of the surface and adsorbate are active in the binding. To implement this approximation, we use non local, norm conserving pseudopotentials, evaluated exactly (without local approximations). (2) A minimal basis set is used, consisting of a set of four local orbitals per site with the confinement boundary condition.[3] The four atomic species present in this problem are H, C, O and Al. We employed confinement radii of 3.5, 5, 5 and 6 Bohr radii, respectively. The reason for using compact orbitals is twofold: First, there is good theoretical evidence that there is a contraction of the charge density (compared with the free space pseudoatom) which may be mimicked by the confining of the orbitals.[13] Secondly, because interactions between sites have a finite range of overlap, the number of interacting neighbors is reduced and the calculation is, therefore, much more efficient. (3) The method uses the Harris functional implementation of the local density approximation (LDA).[5] The Harris functional is a non-self-consistent version of density functional theory that has been employed in a wide variety of studies. For covalent bonding there is abundant evidence that the Harris functional is highly reliable. Its limitations are (1) very ionic bonds are less well described (but see the work of Polatoglou and Methfessel on NaCl)[12] and, (2) systems consisting of two spatially separated parts are not necessarily correctly represented because of the non-self-consistency. Because of (2) we do not discuss desorption events, since these obviously (eventually) yield the case of separated systems. Despite these caveats, we stress that this method is vastly better than any empirical scheme attempting to describe the interaction between surfaces and molecules or polymers. This is because the underlying complexity of the interaction potential between a surface and a complex system like PMMA is due to the many body nature of the electronic interactions. Only a theory that "bites the bullet" and offers a good approximate solution of the electronic structure problem can hope to describe surface-adsorbate interactions properly.

A final point about this approach is that it is a *real space* method (meaning that electronic wavefunctions, charge densities etc. are all directly computed in real space, not in Fourier (reciprocal) space). This is very convenient for the present study, since no artificial periodicity is required by our approach, unlike the plane-wave *ab initio* methods.[6] Furthermore, because the oxygen pseudopotential is very strong, these systems would be very difficult to treat with reciprocal space methods (because a very large number of plane waves would be necessary to describe the spatially localized O orbitals).

In this paper we report the interactions of molecular or polymer systems with a 32-atom slab cell (periodic in two dimensions and 4 layers deep) of Al forming a (100) surface. In all cases we used two distinct Monkhorst-Pack[7] special points for Brillouin zone (BZ) sampling (to verify the adequacy of this approximation, we also tried 10 special points and found very small differences from the 2-point calculations). It is important in this work to perform a reasonable sampling of the BZ, since the Al slab is metallic (and, hence, possesses a Fermi surface).[8] The Al(100) surface was obtained from a MD relaxation of the free surface truncated from the bulk: there was a very small contraction of the surface layer (there seems to be no precise experimental data available on this point, though it is established that the relaxation is very small).[11] In a similar way, we considered the interaction of a PMMA monomer with a model amorphous alumina surface.

Energy relaxations were performed by a "simulated quenching" method. This is essentially a steepest descent quench from the initial imposed configuration to the final conformation. In a "real" system, a larger part of phase space may be sampled by the adsorbate-surface system because of thermal vibrations. By looking at a variety of initial orientations (at least for the relatively simple systems described in this paper) we have seen that there is, in fact, little dependence upon the initial conditions. For a true polymer, and more complicated surfaces (for example, surfaces which are already partly covered by the adsorbate), it is clear that initial conditions will be important. Such effects are beyond the scope of this paper.

RESULTS AND DISCUSSIONS

As a preliminary test of the method we examined CH_4 and C_2H_4 interacting with the surface and found an interaction of less than 0.01 eV/carbon atom. This was found to be true for a rigid molecule interacting with the surface or if we allowed for a MD relaxation near the surface. This is in agreement with experiment.[9] A more interesting study involved rigid polyethylene (C_6H_{12} repeated indefinitely with periodic boundary conditions) oriented along the [110] direction of the (100) surface. In Figure 1 we illustrate the interaction energy as a function of height above the surface. We find a weak, attractive interaction (with a depth of about 0.041

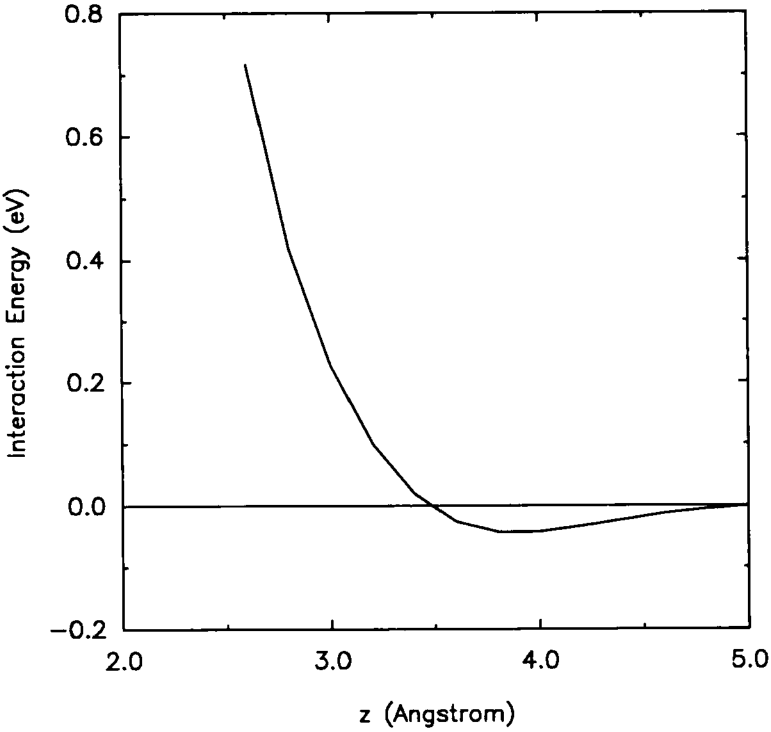

FIGURE 1 Interaction energy of rigid polyethylene chain (using periodic boundary conditions) as a function of distance of carbon atoms from Al surface.

eV/carbon atom), and a MD relaxation produces little additional binding. It is, therefore, seen that the completely passivated C atoms are almost entirely inactive in bonding with the Al surface.

As an example of a system believed to interact strongly with both metal and metal-oxide surface, we studied PMMA in the form of a relaxed 17-atom monomer segment given in Refs. 1 and 2 (a representation of the relaxed monomer is provided in Fig. 2). This monomer is just the usual PMMA 1-mer with the chain continuations passivated with H atoms. Throughout this paper we should stress that the results pertain directly to a hydrogenated monomer unit of PMMA, not an actual polymer. We call the molecule "PMMA" (instead of methyl isobutyrate) because the results are salient to the "real" polymer system, particularly in connection with what functional groups are reactive, etc. We relaxed the proposed monomer coordinates with our MD code and observed a minor variation in bondlengths from the original result (maximum shift of about 0.15 Å), and no change in topology. Rearrangements of this order are to be expected from the use of our minimal basis set. This equilibrium geometry is close to that produced by quantum chemistry Gaussian 90 calculations.[1]

To study the surface-molecular bonding, we start with the molecule well above the surface and perform an *ab initio* energy minimization to find the bonded conformation. We performed a calculation in which the PMMA was started with the carbonyl oxygen closest (2 Å) to the Al surface and the system's energy was minimized with *ab initio* MD. This orientation was chosen out of the expectation that

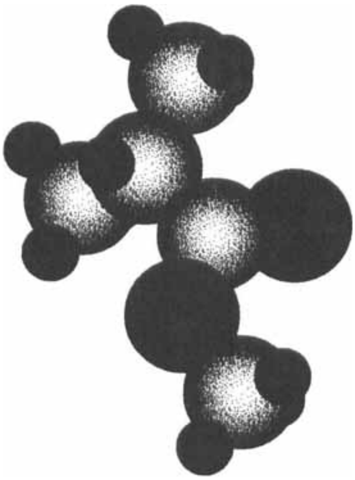

FIGURE 2 Relaxed 17-atom PMMA monomer used in these studies. Large light atoms are C, large dark atoms are O, small dark atoms are H. No special significance is attached to the atomic radii.

the C=O group would be predominantly responsible for metallic bonding. We found that the system relaxed by *breaking* the carbonyl bond, with the carbonyl oxygen then bonding to the Al surface. The breaking of the carbonyl bond was seen to be independent of the starting configuration of the monomer, provided, of course, that the monomer was within interaction range of the surface.

There is a very substantial orientation dependence in the PMMA-surface interaction. For example, if the carbonyl O was initially directed away from the surface, there was only a weak interaction between the surface and monomer. However, it is clear that, in thermodynamic equilibrium, the monomer would eventually reorient itself into a very energetically-favored orientation (*e.g.* with the carbonyl O interacting strongly with the Al) that would result in the dissociation of the molecule as described above.

It has recently been found that the COOH group of aliphatic acids decomposes on Al at room temperature[16] in agreement with our simulation on the somewhat analogous PMMA system. Once again, this is easily understood as a consequence of the aluminum surface—carbonyl O interaction being sufficiently strong to fragment the molecule.

Other calculations[1] suggest that PMMA chemisorbs to clean Al with a binding energy of a few volts. The present calculations are much more reliable; a far more complete treatment of the electronic structure is provided by the present genuine density-functional method.

A problem of more technological interest involves the binding of polymers to alumina. It is a difficult task to obtain a clean Al surface because of its extremely high reactivity. Most often, bulk Al is encountered with an amorphous Al_2O_3 layer about 30–40 Å deep; therefore, we have constructed a model of an a-Al_2O_3 surface, and have studied the adhesion of PMMA to it. To construct this surface, we started with a periodic (space filling) 60-atom model of Kieffer *et al.*[14] and relaxed it with *ab initio* MD with the omission of periodic boundary conditions in one direction. After a substantial rearrangement, a structure was found having a local minimum in

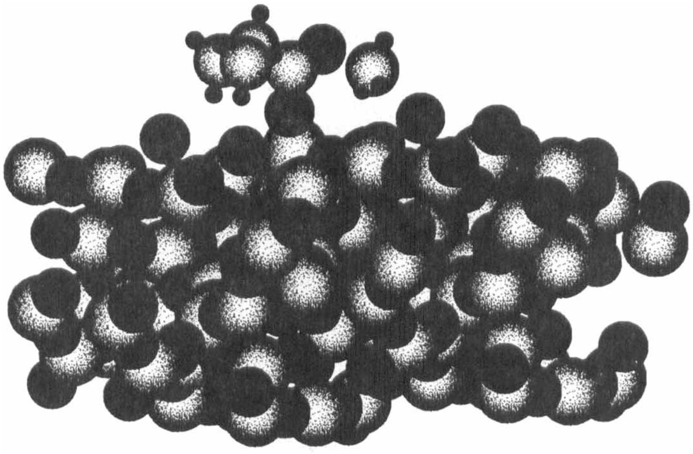

FIGURE 3 Geometry of PMMA monomer adsorbed on alumina from MD relaxation. Large light atoms are Al, small dark atoms are H, medium dark atoms are O, medium light atoms above Al are C. The roughness at the cell boundary is due to missing atoms from adjacent cells.

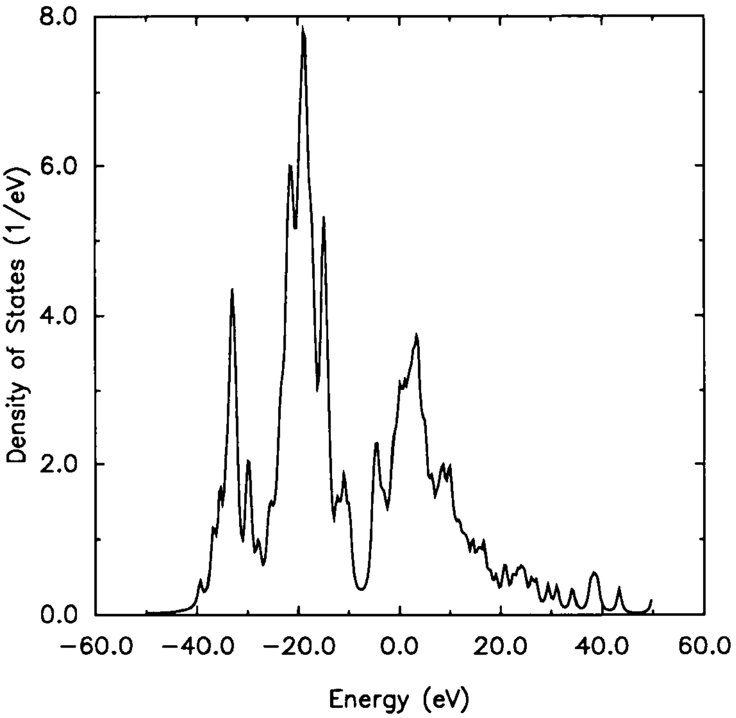

FIGURE 4 LDA Lorentz broadened electronic density of states of PMMA on alumina. The Fermi level is near -9.2 eV.

the configurational energy. We found that the Al atoms had three oxygen (nearest) neighbors and O had two (just what one would expect from the "8-N" rule).[17] The Al—O bond was found to be very ionic, in agreement with simple electronegativity arguments. A large LDA optical gap of 8.26 eV was found for the bulk structure.[15] The experimental gap is 9.5 eV for $\alpha - Al_2O_3$ (sapphire).[10] We will discuss the a-Al_2O_3 in more detail in future publications. Its primary role in this paper is to provide a plausible aluminum oxide layer from which we study adhesion. With a model of bulk a-Al_2O_3 in hand, we then suppressed periodicity in one dimension and relaxed the resulting surface. A rough surface was obtained and we then studied carbonyl bonding to this surface. We found that the carbonyl O strongly binds to surface *aluminum* atoms, but was repelled by surface O atoms (because of the strongly ionic bonding of the substrate). A typical bonding conformation is given in Figure 3 (with a binding energy of 6.0 eV). We have computed the electronic density of states from the LDA-Harris functional eigenvalues (Fig. 4). We note that the usual care must be given in interpreting LDA eigenvalues as quasiparticle energies for comparisons with experiment. Unfortunately, it is difficult to draw simple conclusions from this plot (by contrast, bonding to a simple metal surface usually may be understood at least to some extent with a resonant level picture). We also reproduce the vibrational spectrum in Figure 5.

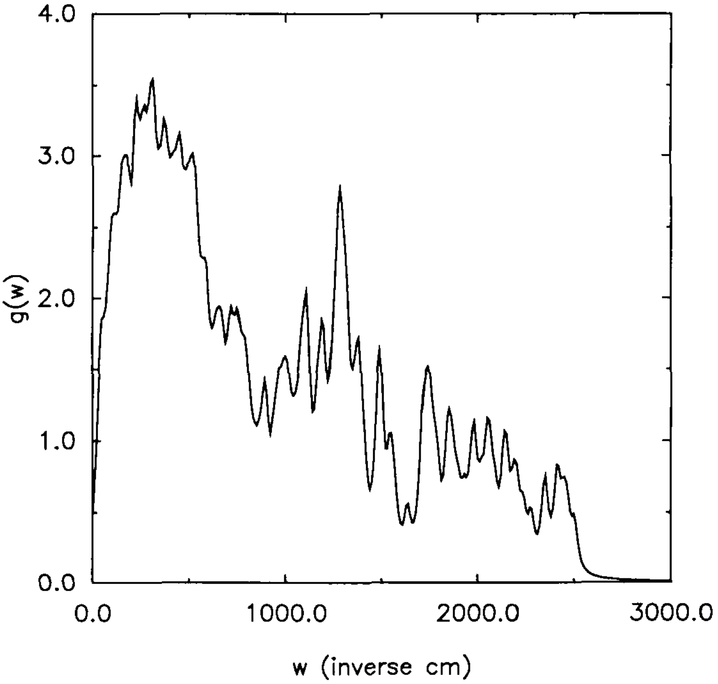

FIGURE 5 Vibrational spectrum of PMMA on alumina. In Ref. 13, CCO stretched modes are reported at 1245 and 1275 cm^{-1}, CH_3 bending modes at 1389 and 1483 cm^{-1} for bulk PMMA. Several vibrational modes strongly localized on the PMMA are calculated to occur in bands between 1266–1279 cm^{-1} and 1298–1319 cm^{-1}.

In order to examine the range of application of these results, we also looked at the bonding of the simplest-imaginable carbonyl-bearing molecule possible, formaldehyde (CH_2O). We find that bonding of formaldehyde to the same Al surface site on the a-Al_2O_3 surface produces a binding energy of 5.9 eV, fairly close to the 6.0 eV obtained for PMMA. This suggests that the details of the adsorbate structure are less important than the functionality active in binding, at least where the carbonyl group is concerned.

CONCLUSION

In conclusion, we have performed the first *ab initio,* quantum mechanical calculation of polymer-surface adhesion with realistic models for both the surface and the adsorbate. We have predicted a detailed conformation of PMMA on a-Al_2O_3, the energetics of the chemisorption and have drawn some general conclusions about the nature of the surface-adsorbate bond. We have shown that a clean aluminum surface strips O from PMMA.

Acknowledgements

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