

Molecular Dynamics modeling of O₂/Pt(111) gas-surface interaction using the ReaxFF potential

Paolo Valentini^{*}, Thomas E. Schwartzenruber^{*} and Ioana Cozmuta[†]

^{*}*Department of Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, Minnesota 55455*

[†]*Eloret Corporation, NASA Ames Research Center, Moffett Field, California 94035*

Abstract. We studied adsorption dynamics of O₂ on Pt(111) using Molecular Dynamics (MD) simulations with the *ab initio* based reactive force field ReaxFF. We found good quantitative agreement with the experimental data at low incident energies. Specifically, our simulations reproduce the characteristic minimum of the trapping probability at kinetic incident energies around 0.1 eV. This feature is determined by the presence of a physisorption well in the ReaxFF Potential Energy Surface (PES) and the progressive suppression of a steering mechanism as the translational kinetic energy (or the molecule's rotational energy) is increased. In the energy range between 0.1 eV and 0.4 eV, the sticking probability increases, similarly to molecular beam sticking data. For very energetic impacts (above 0.4 eV), ReaxFF predicts sticking probabilities lower than experimental sticking data by almost a factor of 3, due to an overall less attractive ReaxFF PES compared to experiments and DFT.

Keywords: Molecular Dynamics, reactive force field, heterogeneous catalysis, gas-surface interaction

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INTRODUCTION

The process of molecular adsorption on a surface has traditionally been the subject of intense investigation because of its fundamental importance in heterogeneous catalysis. Theoretical classical models, such as the hard-cube theory of gas-solid interaction, are often too simple to capture the rich physics of the molecular interactions with the surface. As such, they are often inapplicable for any but the simplest systems, for example adsorption of noble gases [1].

On the other hand, molecular beam experiments [2] have been routinely used for many decades to investigate adsorption dynamics. Sticking coefficients are measured as a function of, for example, incident energy, angle of incidence, surface coverage, or substrate temperature. Depending on how they vary with such factors, some information can be inferred on the mechanisms of adsorption. Various experimental techniques can also help in determining the type of adsorbates, and these include, among others, x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and thermal-desorption spectroscopy (TDS).

Atomic-level simulations represent a very desirable tool to study the adsorption process, as they allow one to precisely investigate the sticking dynamics under conditions much more controlled than conceivable in experiments. Typical force fields (FF) can be used to simulate rather massive systems (thousands to millions of atoms) without excessive computational resources, but their transferability is in many cases too restricted. Additionally, many FFs often assume a fixed connectivity, for example by prescribing harmonic bonds between atoms. As such, they are inapplicable for situations where the process of bond breaking/formation is important, e.g., in dissociative adsorption.

In this article, we use the Molecular Dynamics technique with the reactive force field ReaxFF [3] to investigate the sticking of O₂ on Pt(111). The interaction of molecular oxygen with Pt(111) is a model system in surface science, and it has been thoroughly investigated experimentally, mainly due to its technological importance in automotive catalytic exhausts. As such, it represents an ideal test case to judge the transferability of ReaxFF, and also its limitations. Because the O/Pt mass mismatch is less significant than for hydrogen, it is unsafe to neglect the surface motion. In fact, experiments have convincingly shown that sticking coefficients of oxygen on Pt(111) are strongly affected by the surface temperature [4]. And oxygen can adsorb both molecularly as well as dissociatively, as it has been well established empirically [5, 6, 7, 8, 9, 10, 11, 12, 13] and demonstrated theoretically [14, 15, 16, 17]. Therefore it is important to develop reliable and transferable FFs capable not only of describing chemical bonds, but also gas-phonon interactions, at a reasonable computational cost.

Here, we briefly summarize the main results of previous investigations. Molecular oxygen has been detected on the (111) platinum surface in three distinct states. On cold surfaces (below 40 K), a physisorbed species has been identified

using XPS [6], infrared reflection absorption spectroscopy (IRAS) [12], and near-edge x-ray-absorption fine-structure (NEXAFS) spectra [8]. At a surface temperature T_S up to about 120 K, oxygen is molecularly chemisorbed in two almost degenerate states, labeled peroxolike (O_2^-) and superoxolike (O_2^-) (e.g., [7]). This was also verified using *ab initio* electronic structure calculations [14, 15]. When T_S is between 150 K and 500 K, mostly adsorbed atomic oxygen is found on the surface, whereas subsurface oxidation is revealed at even higher substrate temperatures ($T_S > 1000$ K) [5].

The molecular beam experiments of Luntz and co-workers [4] have shown a strong non-monotonic behavior of the sticking probability S (in the limit of zero coverage) as a function of the incident kinetic energy E_i (Fig. 1). At low E_i , S quickly declines to reach a minimum at about $E_i = 0.1$ eV. For $0.1 \lesssim E_i \lesssim 0.5$ eV, $\partial S/\partial E_i > 0$, and S tends to a plateau of roughly 0.3 at high E_i , up to $\simeq 1.4$ eV. Such a behavior has traditionally been interpreted by invoking a precursor-mediated dissociation at low E_i and a direct dissociation at high E_i . The former is characterized by the presence of an intermediate state in which the molecule temporarily resides while equilibrating with the surface, before entering the dissociation channel. Because the molecule is only weakly bound to the surface due to van der Waals attraction, S is strongly influenced by T_S [4, 6]. But at high E_i , impinging molecules possess enough energy to overcome a dissociation barrier, and therefore directly dissociate. Under these circumstances, little to no surface temperature dependence is observed.

Recent Tight-Binding Molecular Dynamics (TBMD) simulations [18, 19] have challenged this traditional picture of O_2 adsorption by invoking a dynamic steering mechanism at low E_i [20] and only trapping into molecular chemisorbed states. The calculated sticking probabilities are large at low incident energies, when the repulsive tails of the PES are able to steer the slowly traveling molecules into a favorable configuration to enter an adsorption pathway. This beneficial effect is suppressed, however, by increasing either the collision speed or the rotational energy or both. Hence, Groß and co-workers [18] have shown that no physisorption state is needed to explain the strong decrease of S with E_i at low incident kinetic energies ($\lesssim 0.2$ eV). Yet their calculations have not reproduced the characteristic minimum of S at around 0.1 eV.

COMPUTATIONAL METHOD

The ReaxFF potential: overview and training

The ReaxFF formulation is based on a bond order/bond distance relation, similarly to the Tersoff potential originally developed for silicon [21]. Because no fixed connectivity is prescribed, the bond order $BO_{ij}(r_{ij})$ between any two atoms i and j is updated at every MD time step. Moreover, $BO_{ij}(r_{ij})$ is a smooth function of r_{ij} , and it goes to zero as $r_{ij} \rightarrow r_c$, where r_c is the potential cut-off radius. This is necessary to simulate the process of bond breaking and formation without introducing energy discontinuities at r_c . Then all energy terms are made dependent upon $BO_{ij}(r_{ij})$ and go smoothly to zero as the bond order vanishes (i.e., when the bond breaks). Similarly, energy continuity is guaranteed when a new bond forms. We refer the reader to the recent paper (and references therein) by Goddard and co-workers for a more complete overview of ReaxFF and its capabilities [22]. The complete and updated formulation of the functional form of each of the ReaxFF energy terms is contained in the supporting information of a recent article on hydrocarbon oxidation [23].

To derive the ReaxFF parameters for the Pt-O interactions, we used a training set which included:

- equations of state and heats of formation for PtO and PtO₂ (high- and low-temperature) condensed phases;
- binding energies of oxygen atoms to Pt(111) top, bridge, fcc and hcp sites (Ref. [24]);
- binding energies of the O₂ molecule to bridge, fcc, top and tilted (umgerade) fcc sites (Ref. [24]);
- dissociation barriers for O₂ on the bridge, fcc and tilted fcc sites (Ref. [24]);
- the Pt-Pt parameters were derived using the training set described in Ludwig et al. [25].

We found good agreement between ReaxFF and QM for all the above cases.

Simulation details

The surface consisted of 8×8 bulk cells in the $x - y$ plane, with total dimensions of $22.3 \text{ \AA} \times 38.7 \text{ \AA}$. Periodicity was used along the x and y directions. Six atomic layers were used in the z direction, giving a total of 768 Pt atoms.

The supercell dimension along the z axis was set such that the surface was exposed to vacuum. The fairly large surface minimizes the lateral interaction of the periodic images over the short time scale of the impact.

Similarly to Groß and co-workers [18, 19], the bottom Pt layer was frozen, and the next two thermalized using the Langevin thermostat to prevent the substrate from heating up due to the energy transfer upon the collision. Before each simulated O_2 impact, the substrate was first equilibrated to the desired T_S for at least 2 ps, and the in-plane dimensions were dynamically adjusted to release any stress using the Nosé/Hoover temperature thermostat and pressure barostat. Then, the cell dimensions were locked, and 4 ps of additional equilibration followed, using only the Langevin thermostat. The stochastic nature of the Langevin temperature control also provided a randomization of the coordinates and momenta of the Pt atoms for each molecular trajectory.

The MD simulations were performed with a time step Δt of 10^{-15} s (1 fs), which is approximately $\tau_{O_2}/20$, where τ_{O_2} is the vibrational period estimated using a harmonic approximation of the internuclear ReaxFF O_2 potential energy around the equilibrium value $d_0 = 1.2253$ Å. The symplectic velocity-Verlet scheme was used for the time integration.

The initial configuration of the O_2 molecule was also randomized, namely its in-plane location and its orientation with respect to the $x - y$ plane, whereas its initial height above the top Pt layer was set to 30 Å. No zero-point vibrational energy was included in the initial conditions. For all trajectories, the initial vibrational energy was set to zero. However, the vibrational state of the molecule could change due to its collision with the surface.

After the surface equilibration run, the molecule was given a translational velocity corresponding to the desired E_i and incident angle θ_i , and each oxygen atom velocity was adjusted to impose a prescribed E_r . Impacts at several incident angles were simulated. The molecule was considered trapped if it stayed on the surface for more than 3 ps for $E_i < 0.2$ eV and 2 ps for $E_i > 0.2$ eV, and within a distance of roughly 5 Å from the top Pt layer. During each MD run, a series of indicators were monitored and recorded to characterize the impact, including the O_2 translational, rotational, and total kinetic energy, its bond length, center-of-mass coordinates and momenta, and substrate temperature. A minimum of 420 trajectories were generated per each S . We estimated the uncertainty in our measurements of S with the Wald method [26], setting $\alpha = 0.05$ corresponding to a 95% confidence interval. We used the classical MD parallel simulation code LAMMPS [27, 28]. Each trajectory required four 1.15 GHz Quad-Core AMD Opteron™ CPUs for roughly up to 0.5 hrs.

RESULTS AND DISCUSSION

$T_S = 0$ K and $E_r = 0$ eV

The results for $T_S = 0$ K and non-rotating molecules are shown in Fig. 1 (a), and plotted with TBMD calculations [18, 19] and sticking data from several molecular beam experiments [4, 29].

The sticking probabilities calculated with ReaxFF agree very well with the molecular beam data for $E_i \leq 0.4$ eV. In the higher energy range ($E_i > 0.4$ eV), ReaxFF predicts lower values of S by roughly a factor of 3. Overall, the ReaxFF surface is less attractive than an experimental Pt(111) surface, more markedly so at high incident energies. Also, ReaxFF predicts a much more repulsive surface than TBMD over the whole energy range.

The ReaxFF parameters are determined with a fit of a rather extensive database of pre-computed DFT energies with an optimization procedure that minimizes the error between each DFT and ReaxFF energy in the training set. Therefore, slight discrepancies between DFT and ReaxFF are expected (less than 0.2 eV). For example, the chemisorption energy in the TBT state as predicted by ReaxFF is around -0.35 eV (Fig. 1(b)), whereas the corresponding B3LYP XC functional DFT energy is -0.49 eV [24].

Therefore, in the energy regime where trapping occurs in molecularly chemisorbed states ($E_i \leq 0.6$ eV, see later), the ReaxFF Pt surface is slightly more repulsive than an experimental Pt(111) surface, but significantly more repulsive than the TB one. Consequently, the trapping probability predicted by ReaxFF in Fig. 1(a) is generally lower.

In summary, for $E_i > 0.1$ eV, the O_2 adsorption occurs mainly in the molecular chemisorption well (-0.35 eV, Fig. 1(b)), and although dissociation events are common at $E_i = 1.1$ eV (around 70%), none are detected for incident energies below or at 0.6 eV.

Although our calculations predict that 30% of trapping events are associative at the highest incident energy considered in this work, EELS measurements [29, 30, 31] have clearly indicated that direct dissociation is a minor channel for E_i up to 1.4 eV ($T_S = 77$ K), contrary to the quasi-direct adsorption mechanism proposed by Luntz et al. [4]. Hence, our results differ from empirical evidence at very high E_i , thus indicating that further training of the potential is necessary, for example by including direct dissociation channels in the training set.

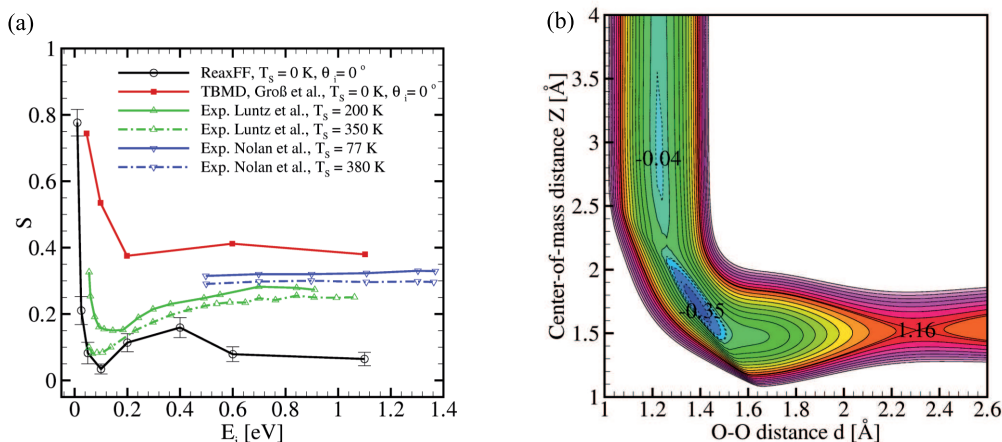


FIGURE 1. (a) Sticking probability for normal impacts ($E_r = 0$ eV). Comparison with TBMD [18, 19] and experiments [4, 29]. (b) PES of molecular adsorption of $O_2/Pt(111)$ determined by ReaxFF. Z denotes the distance of the molecule’s center of mass from the topmost Pt layer. The molecule is in the Top-Bridge-Top configuration. The energy zero is set to the free molecule, and values are in eV.

Lack of dissociative events at high E_i is also reported in the TBMD work of Groß and co-workers [18, 19], but over the whole energy range (i.e., up to $E_i = 1.1$ eV). Although they do not provide a value for the activation energy toward the dissociated state, they explain this phenomenon using steric arguments related to the marked “elbow” shape of the PES. It is reasonable to assume that the ReaxFF barrier for direct dissociation is too high for molecules with incident energies at or below 0.6 eV to overcome. In energy range $0.1 \text{ eV} < E_i < 0.6 \text{ eV}$, the dissociated state is hardly accessible, and trapping occurs in the molecular chemisorption state, whose adsorption energy is slightly underpredicted. This results in reduced sticking probabilities compared to molecular beam data for $E_i > 0.4$ eV.

$T_S = 0 \text{ K}$ and $E_r = 0.1 \text{ eV}$

The abrupt drop of S with E_i at low incident energies has been recently explained by Groß et al. [18, 19] by invoking a dynamic steering mechanism and considering only molecular chemisorption. Hence, we repeated the simulations at $T_S = 0 \text{ K}$ and set $E_r = 0.1 \text{ eV}$, a typical value of molecular beam experiments [32].

As Fig. 2(a) indicates, S is significantly reduced for rotating molecules. For $E_i = 0.01 \text{ eV}$ and $E_r = 0.1 \text{ eV}$, $S \simeq 0.3$, i.e., approximately 60% lower than the sticking probability obtained with $E_i = 0.01 \text{ eV}$ and $E_r = 0 \text{ eV}$. A similar reduction occurs for $E_i = 0.025 \text{ eV}$. Like in the TBMD simulations of Groß et al. [18, 19], we found that the additional rotational energy hinders the adsorption path.

Our analysis of the molecular trajectories clearly shows that trapping occurs as physisorption for $E_i < 0.1 \text{ eV}$. This mechanism is, however, progressively suppressed by increasing E_i due to steric hindrance, which is also revealed if $E_r \neq 0 \text{ eV}$. But when $E_i > 0.1 \text{ eV}$, molecules have enough incident kinetic energy to directly overcome a molecular adsorption barrier, and therefore S increases and oxygen is chemisorbed.

$T_S = 350 \text{ K}$ and $E_r = 0 \text{ eV}$

The role of the surface temperature was also investigated by determining the trapping probability as a function of E_i on a substrate equilibrated at $T_S = 350 \text{ K}$. All impacts were for non-rotating molecules, i.e., $E_r = 0 \text{ eV}$. As Fig. 2(b) shows, at $E_i = 0.01 \text{ eV}$, S is reduced by a factor of almost 2 compared to the result for a substrate at rest. Now Pt atoms have some thermal energy that they can transfer to the impinging molecules, practically kicking them out of the shallow physisorption basin. This results in a significant reduction of the trapping probability.

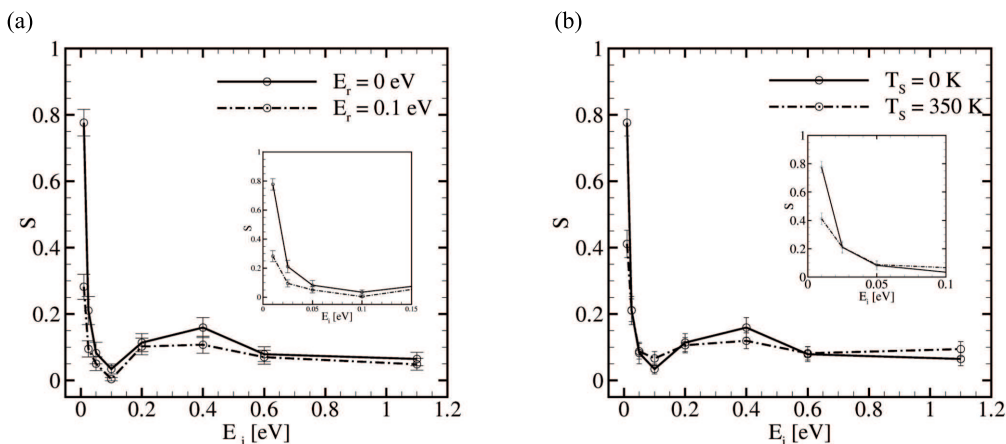


FIGURE 2. (a) ReaxFF sticking probability for normal impacts with $T_S = 0$ K and O_2 rotational energy $E_r = 0.1$ eV. (b) Trapping probabilities for a substrate equilibrated to $T_S = 350$ K. The inset shows S at low E_i for clarity.

At higher incident energies ($E_i \geq 0.05$ eV), however, S does not seem to be affected much by the heated substrate, as the error bars of each value of S from the two data sets largely overlap. The mean kinetic energy of the Pt atoms is roughly $(3/2)k_B T_S \simeq 0.045$ eV, where k_B is Boltzmann's constant. Hence, for intermediate incident energies, i.e., $0.05 \leq E_i \leq 0.1$ eV, the impacts are not energetic enough for the O_2 molecule to overcome the chemisorption barrier, but at the same time molecules possess enough energy to easily escape from the physisorption basin. This is demonstrated by the very low value of the trapping probability ($S < 0.1$). The thermal energy transfer from the surface atoms can be assumed to be $\mathcal{O}(0.01)$ eV, insufficient to provide the O_2 molecule with enough additional momentum to surmount the adsorption barrier toward the chemisorption state. At the same time, this extra energy may only slightly increase E_i , already largely sufficient to escape from the physisorption minimum. Finally, at $E_i > 0.1$ eV, when chemisorption occurs, the Pt thermal energy is at least an order of magnitude smaller than E_i , and thus it has a negligible effect on the impact dynamics, consistent with a direct adsorption mechanism.

Molecular beam experiments have found a very strong dependence of the sticking coefficients upon T_S over the whole range of incident energies, and this is shown in Fig. 1(a) which contains data from Luntz et al. [4] and Nolan and co-workers [29]. On the contrary, our calculations have shown a marked influence of T_S on the trapping probability only at very low E_i . Clearly, experiments access time scales $\mathcal{O}(s)$, which are many orders of magnitude larger than those reached by MD calculations, i.e., $\mathcal{O}(10^{-12}s)$. Hence, over the duration of typical molecular beam experiments, desorption events are likely to occur due to the finite substrate temperature, and thus the sticking coefficients may be generally lowered as T_S is increased (see Fig. 1(a)). This very weak dependence on T_S at high E_i was also observed by Grob et al. [18], who report a reduction of only 2% in S at $E_i = 1.1$ eV when $T_S = 300$ K compared to the sticking probability obtained on a 0 K substrate. But, for example, experimental data show a reduction of almost 30% when T_S is increased from 77 K [29] to 350 K [4] at the same E_i . We cannot exclude, however, that with a lower activation barrier to dissociate the O_2 molecule, the additional energy from the substrate atoms may be beneficial in promoting direct dissociation. If so, this could be a limitation in the transferability of the potential, and additional refining of the ReaxFF parameters may be necessary.

SUMMARY AND CONCLUSIONS

We have used ReaxFF Molecular Dynamics simulations to study the adsorption dynamics of O_2 on Pt(111). Our simulations have reproduced qualitatively well the data obtained with molecular beam experiments for a wide range of incident kinetic energies. Given the uncertainties in the experiments and time scale issues, the agreement is good.

For slow collisions ($E_i < 0.1$ eV), the adsorption is caused by long-range attractive forces, which determine a weakly-bound physisorption state. In this regime, the trapping dynamics is dominated by a steering mechanism coupled with a significant energy transfer to the substrate. This effect is suppressed due to steric hindrance by

increasing E_i or E_r or both, and consequently S is reduced. Up to $E_i = 0.1$ eV, trapping is caused by physisorption, and the simulations show that the thermal motion of the substrate atoms ($T_S < 350$ K) strongly affects the adsorption dynamics, as seen experimentally. At $0.1 < E_i < 0.4$ eV, the sticking probability increases, as observed in various molecular beam experiments, and trapping occurs in activated chemisorbed states. The strongly non-monotonic behavior of S as a function of E_i for kinetic energies lower than 0.4 eV is due to *both* the physisorption state and the progressive inhibition of the steering effect. At even higher kinetic energies ($E_i > 0.4$ eV), S levels off.

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