Activated O$_2$ dissociation and formation of oxide islands on the Be(0001) surface: 
Another atomistic model for metal oxidation

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By simulating the dissociation of O$_2$ molecules on the Be(0001) surface using the first-principles molecular dynamics approach, we propose a new atomistic model for the surface oxidation of sp metals. In our model, only the dissociation of the first oxygen molecule needs to overcome an energy barrier, while the subsequent oxygen molecules dissociate barrierlessly around the adsorption area. Consequently, oxide islands form on the metal surface, and grow up in a lateral way. We also discover that the firstly dissociated oxygen atoms are not so mobile on the Be(0001) surface, as on the Al(111) surface. Our atomistic model enlarges the knowledge on metal surface oxidations by perfectly explaining the initial stage during the surface oxidation of Be, and might be applicable to some other sp metal surfaces.

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Most metal surfaces are thermodynamically allowed to react with oxygen molecules in the atmosphere, to form thin oxide films. This phenomenon is very important for many technological applications, because they are directly relevant to surface corrosion and the formed metal oxide films have been widely used as catalysts, sensors, dielectrics, and corrosion inhibitors. In addition, studying the oxidation reactions from the atomic view is also of great scientific importance. However, the detailed atomistic models for the surface oxidation of metals are not yet mature. A “Hot-Atom” O$_2$ dissociation and oxide nucleation model was recently proposed for the oxidation of the Al(111) surface, in which the dissociative adsorption of O$_2$ molecules occurs via a “Hot-Atom” mechanism and O atoms are spontaneously incorporated underneath the topmost Al surface layer, initiating the nucleation of the oxide far below the saturation coverage of one O adlayer. However, the applicability of this model has not been checked for other metals, for example, whether the dissociated O atoms on other metal surfaces are “hot” is still beyond the present knowledge. Besides, there is a contradiction with experimental observations in the atomistic model. The initial sticking probability of thermal O$_2$ molecules at Al(111) is measured to be low by many independent experiments, suggesting a sizeable energy barrier for the O$_2$ dissociation, which however is not included in the “Hot-Atom” mechanism. The lack of an energy barrier is contributed to the fact that in the adiabatic first-principles calculations the lowest unoccupied electronic state of oxygen is aligned with the Fermi level at any distance between the molecule and the surface, allowing a partial filling of the empty molecular orbital, which finally drives the dissociation.

Based on this background, in this paper we have carried out first-principles molecular dynamics (FPMD) simulations for the O$_2$ dissociation on the Be(0001) surface. Chемically, Be is even simpler than Al because it has only two valence electrons, so it is also an ideal model system to study the initial stages of metal oxide formation. Besides this basic point of interest, our present study is also motivated by the fact that Be has vast technological applications due to its high melting point and low weight. During these applications, surface oxidation as the main kind of corrosion always needs to be prevented. Experimentally, the surface oxidation of Be is reported to begin by forming separate oxide islands, and saturate after the islands grow laterally together forming an oxide layer. Theoretically, we have calculated the adsorption properties of O$_2$ molecules on the Be(0001) surface, and identified both the physisorbed and chemisorbed molecular precursor states. Remarkably, we have revealed that unlike the Al(111) surface, the alignment of the lowest unoccupied electronic state of oxygen with the Fermi level does not happen when it is in close with the Be(0001) surface. Therefore, the Be(0001) surface is in some way a better model system for studying the metal oxidation using adiabatic first-principles methods.

Our calculations are performed using the spin-polarized version of the Vienna ab-initio simulation package. The PW91 generalized gradient approximation and the projector-augmented wave potential are employed to describe the exchange-correlation energy and the electron-ion interaction, respectively. The cutoff energy for the plane wave expansion is set to 400 eV. The molecular dynamics (MD) simulations are performed using the Verlet algorithm with a time step of 1 fs within the micro canonical ensemble. In our present study, the Be(0001) surface is modeled by a periodically repeated slab of five Be layers separated by a vacuum region correspondent to six metal layers. We consider a (4x4) surface unit cell, which includes 16 Be atoms in each atomic layer. The surface Brillouin zone is sampled...
by a $3 \times 3$ $k$-point distribution using the Monkhorst-Pack scheme \cite{11}. The calculated lattice constant of bulk Be and the bondlength of isolated O$_2$ are 5.03 Å and 1.24 Å, respectively, in good agreement with the experimental values of 4.95 Å \cite{12} and 1.21 Å \cite{13}. The O$_2$ is placed on one side of the slab, namely on the top surface, whereas the bottom two layers are fixed. All other Be layers as well as the oxygen atoms are free to move during the MD simulations.

We start our simulations with different orientations of an O$_2$ molecule placed over different surface sites (one representative case is illustrated in Fig. 1(a)). In all initial configurations, the mass center of the O$_2$ molecule is initially set to be 4 Å away from the metal surface. In the cases of Al(111) and Mg(0001), the failure of adiabatic FPMD simulations in producing an activated-type dissociation process has been ascribed to the unphysical output that charge transfer occurs at any molecule-metal distance, which has led to speculations that nonadiabatic effects may play an important role in the oxygen dissociation process at these metal surfaces with simple sp electrons \cite{2,14}. However, this requirement is not always needed. In our calculations, we find that at enough molecule-metal distance, the unphysical large-distance charge-transfer effect does not happen between O$_2$ and the Be(0001) surface. The calculated spin-split electronic states of O$_2$ in close to the Be(0001) surface shows no change with respect to the free molecule. The lowest unoccupied molecular orbital remains empty and the charge-density difference is zero everywhere. Subsequently, the molecular bond length and spin of O$_2$ are not influenced at all by the presence of the Be(0001) surface \cite{5}. Thus we are confident in carrying out our present first-principles molecular dynamics simulations.

For the adsorption of the first O$_2$ molecule, the substrate atoms are initially at rest. Since we have known from our static calculations that an energy barrier is needed for the dissociation of O$_2$ molecule on the clean Be(0001) surface \cite{5}, we set two different initial kinetic energies for the O$_2$ molecule, respectively 0.06 eV and 0.6 eV. From the MD simulations, we find that the O$_2$ molecule with the initial kinetic energy of 0.06 eV does not dissociate at all on the Be(0001) surface after 3 ps, but the one with the initial kinetic energy of 0.6 eV easily dissociate in 200 fs. These results clearly prove that an energy barrier exists during the O$_2$ dissociation on the Be(0001) surface, with the value between 0.06 and 0.6 eV. The structural evolution for the O$_2$ dissociation with the initial kinetic energy of 0.6 eV is depicted in Fig. 1. We can see that the surface Be atoms have no motions until $t=116$ fs, when only electronic interactions happen. From the time $t=116$ fs to 163 fs, one surface Be atom is pulled out a little during the departure of the two oxygen atoms. After $t=116$ fs, the two oxygen atoms steadily adsorb at the two hcp hollow sites, and the adsorption system begins to vibrate in its intrinsic frequencies.

The FPMD simulations for the O$_2$ dissociation are subtle. We find in our testing calculations that using inappropriate mixing parameters might lead to unphysical change of O$_2$ from the triplet to singlet state, and resulting wrong trajectories. With the appropriate mixing parameters, we get the true dissociation process as shown in Fig. 1 and the natural spin evolution as shown in Fig. 2(a). It is clearly shown that the total spin of the system gradually decrease into zero as the O$_2$ molecule gets closer to the Be surface and dissociates. We can also see

![Figure 1](image1.png)

**FIG. 1:** (color online). Snapshots from a FPMD simulation of the dissociative chemisorption of an O$_2$ molecule on the Be(0001) surface. Only the four outermost Be layers are shown. Red and yellow balls respectively represent oxygen and Be atoms. (a) Initial geometry (simulation time $t=0$ fs) with the molecule parallel to the surface. The distance between the center of mass of the molecule and the topmost surface layer is 4.00 Å. (b)-(e) The atomic geometry of the adsorption system at $t=91, 116, 163,$ and 182 fs. (f) Final configuration in equilibrium after relaxation ($t=202$ fs). The final O-O distance is 2.33 Å.

![Figure 2](image2.png)

**FIG. 2:** (a) The total spin magnetization of the system in a FPMD simulation of the dissociative chemisorption of an O$_2$ molecule on the Be(0001) surface. (b) and (c) The total free energy and kinetic energy of the system in the same FPMD simulation. The inset in (b) is zoomed out to show the 0.16 eV energy barrier during the O$_2$ dissociation.
that the dissociation process and the electronic evolution go on at the same time.

At the beginning of the adsorption process, the total free energy of the adsorption system is \(-232.49\) eV. When the \(\text{O}_2\) molecule gets to be 2.36 Å from the Be surface, the free energy is enlarged by 0.16 eV [as shown in the inset of Fig. 2(b)], which corresponds to the energy barrier for the \(\text{O}_2\) dissociation on the clean Be surface. The value differences with our static potential energy surface results \[1\] come from that we have chosen a much larger \(4 \times 4\) supercell, and the motions of surface Be atoms are considered here. Accompanying with the enlargement of the total energy, the kinetic energy decreases by 0.16 eV, as shown in Fig. 2(c). After that, the kinetic energy begins to fluctuate, and reach the equilibrium value of 4.52 eV at \(t=202\) fs. At the same time, the total free energy of the adsorption system becomes \(-236.41\) eV, which is 3.92 eV below the initial value of the adsorption process.

Although the adsorption energy is large, we see no movement of the dissociated oxygen atoms during simulation process. Instead, the oxygen atoms steadily adsorb at two neighboring hcp hollow sites and vibrate. Comparing with the hot oxygen atoms on the \(\text{Al}(111)\) surface, which move away very fast after dissociation \[2\], the dissociated oxygen atoms on the \(\text{Be}(0001)\) surface are not so hot, without any fast movements. Thus, our finding for the dissociation mechanism of \(\text{O}_2\) is very different from the “Hot-Atom” picture, which was theoretically understood mostly through simulating the \(\text{O}_2/\text{Al}(111)\) prototype \[2\]. The different dissociation mechanisms may come from different surface electronic structures of \(\text{Al}\) and \(\text{Be}\). In particular, our result that the dissociated oxygen atoms have low mobility is very consistent with the experimental observations that the surface oxidation of \(\text{Be}\) begins by forming separate nucleation islands.

The evolution of the spin configurations during the adsorption and dissociation of \(\text{O}_2\) molecules on metal surfaces is of great theoretical importance \[7, 14\]. Since the adiabatic calculations are suitable enough for the \(\text{O}_2/\text{Be}(0001)\) system, we would like to take a look at the evolutions in spin configurations of \(\text{O}_2\) during the dissociative adsorption process. Figure 3 shows the spin-resolved densities of states for the two oxygen atoms at different times. We can see that at the very beginning, the \(\text{O}_2\) molecule is in the triplet state, with the spin splittings of about 2 eV for both bonding and antibonding orbitals. Until \(t=66\) fs, no big changes happen in the electronic structures of \(\text{O}_2\), except that the spin splitting decreases about 0.2 eV for all orbitals. After that, the total spin starts to distribute both around oxygen and around the neighboring Be atoms. Then at the transition state \((t=91\) fs\), the spin splitting decreases to be negligible around each oxygen atom. We can see that the spin quenching effect from electronic hybridizations between \(\text{O}_2\) and the \(\text{Be}(0001)\) surface happens really fast. After crossing the transition state, the total free energy quickly goes down since the two oxygen atoms are separated and begin to bond with surface Be atoms. At the meantime, the energy difference between bonding and antibonding orbitals of \(\text{O}_2\) reduces and finally to be zero at \(t=182\) fs. In total, there are two stages during the \(\text{O}_2\) dissociation. At the first stage (i.e. before the transition state), the electronic interaction results in spin quenching and makes the two oxygen atoms to separate from each other. At the second stage, the two oxygen atoms begin to bond with Be atoms, blurring the distinction in bonding and antibonding orbitals.

It has been experimentally reported that the surface oxidation of \(\text{Be}\) begins by forming separate oxide islands. There might be two different mechanisms responsible for this observation: i) The dissociated oxygen atoms are very mobile and tend to cluster with each other; ii) The subsequent \(\text{O}_2\) molecules are easier to dissociate around the oxygen-adsorbed \(\text{Be}\) surfaces. The first mechanism
has been proposed to explain the oxide nucleation on the Al(111) surface [2]. Since we have revealed that the dissociated oxygen atoms are not so mobile on the Be(0001) surface as on the Al(111) surface, the formation of oxide islands on the Be(0001) surface should have a different mechanism (mechanism ii). We then simulate the adsorption of a second O$_2$ molecule on the Be(0001) surface.

For the adsorption of the second O$_2$ molecule, the substrate Be and O atoms are no longer at rest. Their initial velocities are taken from the equilibrium state of the MD simulation for the first O$_2$ molecule [12]. At the same time, the second O$_2$ molecule is initially set at rest, i.e., with zero initial kinetic energy. After the dissociation of the first O$_2$ molecule, the temperature within the 4 × 4 surface area raises by about 700 K. If the second O$_2$ molecule approaches the same surface area, it will be activated from the triplet groundstate to the singlet state under such a high temperature. From our FPMD simulation, we see that the second O$_2$ molecule dissociates easily in 600 fs, and the total free energy decrease about 4.76 eV, as shown in Fig. 4. Therefore, we can see that the dissociation of the second O$_2$ molecule can be motivated by the adsorption energy of the first dissociated O$_2$ molecule. Since the adsorption energy of the second O$_2$ molecule will further enlarge the temperature of the same surface area, we can foretell that a subsequent third O$_2$ molecule will also dissociate barrierlessly. At last, the O$_2$ molecules always dissociate easier around the oxygen covered Be surfaces to form separate oxide islands. And if more oxygen molecules are introduced, the separate oxide islands will grow larger, until finally meet each other laterally. One can see that our atomistic model that the oxide islands grow laterally to be autocatalytic [17], in accordance with our atomistic model that the oxide islands grow laterally to be oxide films. All these similarities make us believe that our atomistic model might be also applicable to some other sp metals.

In summary, we have systematically investigated the adsorption and dissociation of O$_2$ molecules on the Be(0001) surface within spin-polarized first-principles molecular dynamics simulations. We find that the previous “Hot-Atom” mechanism are not suitable for the O$_2$/Be(0001) system. The O$_2$ dissociation is found to be an activated process on the Be(0001) surface, and the dissociated oxygen atoms are not very mobile. Based on our calculational results, we propose a new atomistic model for the surface oxidation of sp metals, in which the dissociation of the first O$_2$ molecule needs to overcome an energy barrier, while the subsequent O$_2$ molecules dissociate barrierlessly at the same surface area. In this way, separate oxide islands form on the metal surface, and grow up together in a lateral way as more oxygen molecules are introduced.

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FIG. 4: The total free energy of the adsorption system in the FPMD simulation for the dissociative adsorption of the second O$_2$ molecule.

\[ E_0 - 252 \]

\[ E_0 - 250 \]

\[ E_0 - 246 \]

\[ E_0 - 244 \]

\[ 0 \quad 500 \quad 1000 \quad 1500 \quad 2000 \quad 2500 \quad 3000 \]

Time (fs)

\[ 0 \]

\[ -244 \]

\[ -252 \]

\[ -250 \]

\[ -246 \]

\[ -244 \]

\[ 0 \quad 500 \quad 1000 \quad 1500 \quad 2000 \quad 2500 \quad 3000 \]

\[ 0 \]

\[ -244 \]

\[ -252 \]

\[ -250 \]

\[ -246 \]

\[ -244 \]
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