2. Molecular Dynamics Simulations

In contrast to previous computational chemistry work in this area where isolated single-event collisions are studied on graphene sheets (one atomic layer), we simulate sequential gas-surface collisions on multi-layer graphene representing HOPG with large surface area. We do this to simulate the evolution of oxidized HOPG as observed on graphene sheets (one atomic layer), we simulate sequential gas-surface collisions on multi-layered graphene. Molecular Dynamics Simulations are performed with the LAMMPS molecular dynamics program, using the ReaxFF potential.

2.1 ReaxFF Potential

ReaxFF is a bond order dependent potential that uses a relationship between bond distance and bond order along with bond order and bond energy to describe bond dissociation propensity. This allows natural creation and destruction of bonds which is critical to our simulations. The complete energy of a system is given by a number of terms, including long range non-bonded terms such as Coulomb and Van der Waals interactions:

\[ E_{\text{total}} = E_{\text{bond}} + E_{\text{corr}} + E_{\text{bond}} + E_{\text{E}} + E_{\text{E}} + E_{\text{E}} + E_{\text{E}} + E_{\text{E}} + E_{\text{E}} \]

The force field parameters used in the present simulations have already been optimized by Chenoweth et al. [1] and it has been demonstrated that graphene-oxygen interactions are accurately modeled with this potential.

2.2 Surface Preparation

The collision of a 5 eV O atom with the atomistic-scale HOPG surface in each MD simulation results in a significant increase in the temperature of the simulated 'slab' of HOPG. Under low pressure experimental conditions, any transfer of energy to the surface would be conducted into the bulk material long before the next O atom collision. In our simulations we thermostated the bottom layer of the HOPG slab to maintain a constant surface temperature. However, in addition, we also had to wait roughly 12.5 ps before the increased temperature of the top layer cooled back to the thermostated surface temperature as shown in Figure 2. Figure 6 shows the gas-phase O atom being injected into the vacuum between two graphene sheets. Collisions of O at 1 ps intervals without temperature control results in very high surface temperatures which cause the HOPG to expand much faster than it would in the experiment. However, simulating the system for 12.5 ps between collisions is computationally expensive and there are no reactions over this time scale. In fact, most reactions were observed to occur at short timescales (<1 ps).

Thus, we simulate the collisions with a NVE ensemble for 1 ps, which is sufficient to determine the outcome of the collision (reflection, adsorption, oxidation, etc.). After the reaction is over (after 1 ps), we then thermostat the entire system for 0.75 ps to restore the surface temperature to its proper value. This added complexity, compared to previous studies involving single isolated collisions, is essential for both physical accuracy and computational efficiency.

2.3 Surface Coverage

It is well known that pristine HOPG does not undergo oxidation due to O atom collisions even with high energy O atoms (5eV). However, the HOPG surface also becomes populated with adsorbed O atoms either in epoxide form (COO) or O-C-O term, and possibly other intraplanar surface defects. Thus it is reasonable to begin our MD simulations with HOPG and this surface coverage. If we initialize our MD simulation with a complete epoxide coverage on the HOPG surface (at \( t = 0 \)) and then integrate the system, we find that the top atomic layer of the HOPG surface buckles as shown in Figure 6(a). This buckling then accelerates the oxidation of the HOPG slab in our simulations. However, we have confirmed that this buckling is an artifact of the simulation. Instead, we start with a pristine HOPG surface, thermostated it to the desired temperature, and then place oxygen atoms in the epoxide positions (at the equilibrium bond distance) with velocities sampled from a Gaussian distribution at the surface temperature. The entire system is then integrated in NVE ensemble and a certain number of the oxygen atoms remain bonded to the surface in the epoxide configuration. The non bonded oxygen atoms are removed from the system and the process is repeated for a few times. If this procedure is followed, which is physically more realistic in that full oxygen coverage would not occur instantaneously, an HOPG surface with oxygen coverage is obtained without buckling. This then, is how we prepare our HOPG surfaces prior to gas-phase oxygen impacts.

2.4 Continuous Collisions

Oxygen atoms at 5 eV are continuously injected towards the HOPG surface. A total of 1000 continuous collisions are performed. The simulations predict the pit growth in the interplanar direction to be much more rapid than the intraplanar direction (reflection, adsorption, oxidation, etc.). After the reaction is over (after 1 ps), we then thermostat the system for 12.5 ps between collisions. Our continuous collision results are compared with the experimental data. We could then run simulations at high surface temperatures and a variety of crystal orientations to investigate the oxidation reactions present under hypersonic conditions for more realistic carbon-based surface ablator materials.

Figure 6 indicates the number of carbon atoms removed as a function of the number of collisions. On close observation of Figure 6, it is clear that the number of carbon atoms removed after 1000 collisions is less than that predicted by our model. This result suggests that the oxidation would increase with higher flux of incoming O atom which is also observed in experiments.

2.5 Effect of surface temperature

The work in Ref. [1] also shows that the rate of oxidation increases with an increase in surface temperature. The experiments were done in the temperature range of 298 - 573 K. In Molecular Dynamics simulations, the variation in this narrow range of temperature would be difficult to capture, as a large number of ensemble averages (many simulations) may be required to reduce scatter in the results. We simulated the collisions over a much larger temperature range of 300K, 600K, 1000K, and 1500K. The results are tabulated in Table 1. As shown in Table 1, the oxidation rates do indeed increase with higher temperature increases compared to experimental observations. Specifically, this trend with temperature should reveal the activation energies of the specific reactions that lead to oxidation. If determined, these mechanisms and activation energies could be useful for finite-rate models used in CFD simulations.

Table 1: Surface Temperatures vs Number of Carbon atoms removed

<table>
<thead>
<tr>
<th>Temperature(K)</th>
<th>Number of Carbon atoms removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>112</td>
</tr>
<tr>
<td>600</td>
<td>154</td>
</tr>
<tr>
<td>1000</td>
<td>224</td>
</tr>
<tr>
<td>1500</td>
<td>360</td>
</tr>
</tbody>
</table>

3 Conclusions and Future Work

In this work, we have studied the oxidation of HOPG by hyperthermal O atoms. To avoid long wait times between successive collisions, we thermostated the system to the desired target temperature. It was also observed that the pristine HOPG sheet does not oxidize even at the highest temperature of 1500K. However, a surface covered with oxygen groups and small intrinsic defects lead to oxidation of the surface. We created a surface coverage of O atoms on the surface by allowing the O atoms to bond naturally to the surface instead of placing them in epoxide form which resulted in a layer of the surface. Our continuous collision results are compared with the trends observed in molecular beam experiments. We observed that oxidation in the interplanar direction is faster than in the intraplanar direction as observed in experiments, and also that the oxidation rate increases with surface temperature. Finally, our simulations predicted higher production of CO2 compared to CO and in relative amounts that were in agreement with experimental observations. These preliminary results are promising for the validation for our simulation techniques including the interatomic potentials and modeling assumptions.

In future work, we wish to characterize the rates quantitatively of all species formed on the surface and to run larger length scale and time scale MD simulations to validate our results as close as possible to available experimental data. We could then run simulations at high surface temperatures and a variety of crystal orientations to investigate the oxidation reactions present under hypersonic conditions for more realistic carbon-based surface ablator materials.

4 References