1 Introduction

The flow over hypersonic vehicles is characterized by extreme conditions with shock layer temperatures reaching 10000 K and heat fluxes as high as 5 kW/cm\(^2\). Thermal protection systems (TPS) consisting of carbon-based surface-ablation materials are effective structures that enable much of the heat flux to be carried away from the vehicle by the ablating material.

At these high temperatures, dissociated oxygen atoms (O) strike the TPS surface leading to several possible gas-surface chemical reactions. Specifically, the oxygen atom can chemically bond to the surface, it could recomcombine with another adsorbed oxygen and leave the surface as a molecule (O\(_2\)), or the impinging atom could "unodate" the carbon surface resulting in products such as CO and CO\(_2\) leaving the surface and being injected into the boundary layer. Such oxidation reactions result in the recession of the surface (surface ablation). Currently, much uncertainty exists in both the dominant reactions themselves as well as the rates of these reactions. The mechanisms and rates are required as input into state-of-the-art CFD simulations of hypersonic flows. Experimental determination of the chemical mechanisms themselves under extreme hypersonic conditions is difficult and often they must be inferred from macroscopic observations such as heat flux and surface recession measurements. However, as the field of computational chemistry continues to evolve in step with advances in computational power, fundamental chemical studies may be able to provide insight into the chemical mechanisms and associated rates for such surface ablation processes.

The goal of this work is to develop finite rate models through large scale Molecular Dynamics (MD) simulations using the ReaxFF force field. Our current effort is to validate our ReaxFF simulations with existing data available from molecular beam experiments. In this work, we simulate the collision of hypersonic (5 eV) O atoms with Highly Oriented Pyrolitic Graphite (HOPG) and compare our results to the molecular beam experiments performed by Moton and co-workers.

2 Molecular Dynamics Simulations

In contrast to previous computational chemistry work in this area where isolated single-collision events are studied on graphene sheets (one atomic layer), we simulate sequential gas-surface collisions on multi-layered graphene (representing HOPG) with large surface area. We do this to simulate the evolution of oxidized HOPG. All calculations are performed using fully atomistic MD simulations including the net removal of surface carbon atoms, the product species created, and the geometry of the etch pits. 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 long range non-bonded terms such as Coulomb and Van der Waals interactions:

\[
E_{\text{bond}} = E_{\text{bond}}^{\text{pen}} + E_{\text{bond}}^{\text{perp}} + E_{\text{rep}} + E_{\text{vdW}} + E_{\text{elec}} + E_{\text{vdW}}^{\text{disp}} + E_{\text{vdW}}^{\text{disp}}
\]

The force field parameters used in the present simulations have all 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 such MD simulations results in a significant increase in the temperature of the simulated "slab" of HOPG. Under low pressure experimental conditions\([1]\), any transfer of energy to the surface would be conducted into the bulk material long before the O atom comes off. In our simulations we thermostat 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 thermostat temperature as shown in Figure 3. We see the first gas-phase atom is injected prior to this, it hits a surface at high speed, leading to the observation. Colliding atoms at 1 ps intervals without temperature control results in very high surface temperatures which causes the HOPG to sublimate 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 collision 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.

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 thermally equilibrated the system to the desired target temperature. It was also observed that the pristine HOPG surface does not oxidize even by the collision of hyperthermal O atoms. However, a surface covered with oxygen groups and small intrinsic defects lead to oxidation of the surface. We created a surface coating of O atoms on the surface by allowing the O atoms to bond naturally to the surface instead of placing them in epitaxial form which results in removal of the surface. Our simulations predict a higher production of CO\(_2\) compared to CO and in reasonable agreement with experimental observations. These preliminary results are promising for the validation of 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 large 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 assess the effects of crystal orientations on ablation-reaction processes present under hypersonic conditions for more realistic carbon-based surface ablation materials.

4 References