A Gas-Surface Interaction Model based on Molecular Dynamics for Hypersonics

T. E. Schwartzentruber --- FA9550-09-1-0157 --- U of Minnesota

Determining mechanism rates for gas-surface interactions through *reactive* Molecular Dynamics simulations

STATUS QUO

Super-catalytic / Non-catalytic

- Either all/no atoms recombine on surface
- Unphysical assumptions giving upper/lower bounds for heating rates (large variation)

Recombination coefficient: $0 < \gamma < 1$

- Limited data available for parameterization
- Physical mechanisms ignored, therefore difficult to accurately/generally parameterize
- Large uncertainties $\gamma(T, p, \text{material}, ?)$

NEW INSIGHTS

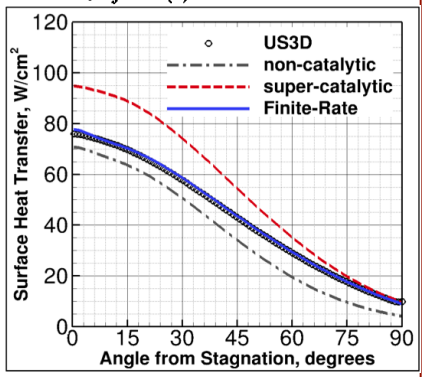
Finite-Rate Catalytic Surface Eqns.

- Replace CFD boundary condition with set of catalytic mechanisms with associated rates

$$\begin{aligned}
A_i + (s) &\rightarrow A_i(s) && \text{Adsorption}\\
A_iA_j + 2(s) &\rightarrow A_iA_j(s)_2 &&\\
A_iA_j + 2(s) &\rightarrow A_i(s) + A_j(s) &&\\
A_i(s) &\rightarrow A_i + (s) && \text{Desorption}\\
A_iA_j(s)_2 &\rightarrow A_iA_j + 2(s) &&\\
A_i + A_j(s) &\rightarrow A_iA_j + (s) &&\\
A_i(s) + A_j(s) &\rightarrow A_iA_j + 2(s) && \text{Recombination}
\end{aligned}$$

NASA-DPLR and UMN-US3D in excellent agreement

However, rates remain uncertain

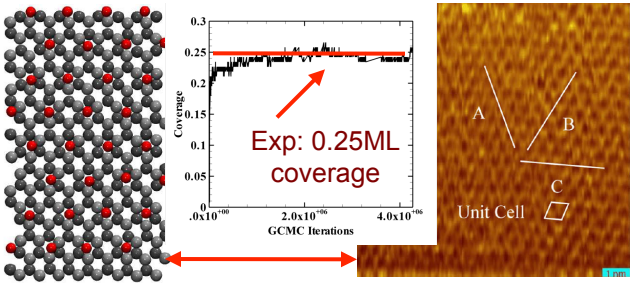


MAIN ACHIEVEMENTS:

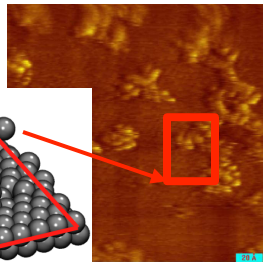
- A new method for predicting the **in-situ** (high T, low p) **surface state** during exposure to dissociated oxygen
- Successful *validation* for oxygen coverage on platinum
- Published: *J. Chem. Phys. 2010* and *Surface Science 2011*

HOW IT WORKS: Grand Canonical Monte Carlo

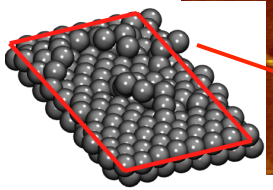
- Molecules are randomly inserted/displaced/removed with appropriate probability, acceptance probability is a function of the change in energy of the system vs. the overall chemical potential of the system

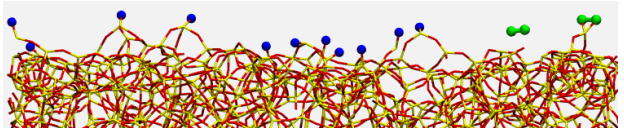


- Oxygen coverage on Pt(111) including Pt reconstructions



- Catalytic defects (active sites) and oxygen coverage on amorphous SiO_2 (below)





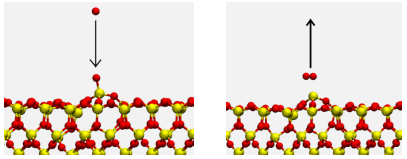
ASSUMPTIONS AND LIMITATIONS:

- Currently predicts equilibrium surface state
- Types of active sites predicted, but concentration of sites is not (scaling factor req'd)

QUANTITATIVE IMPACT

Current Impact

- With **in-situ surface state**, Molecular Dynamics can be used to determine catalytic processes with gas molecules, including actual mechanisms and associated rates



- *A preliminary model for oxygen-silica interactions has been developed with rates:*

Mechanism	Name	
$O + \equiv Si\cdot \rightarrow \equiv Si\text{-}O\cdot$	Atomic Adsorption	(1)
$O + \equiv Si\text{-}O\cdot \rightarrow \equiv Si\text{-}O_2$	O_2 Formation	(2)
$O + \equiv Si\text{-}O\cdot \rightarrow O_2 + \equiv Si\cdot$	ER Recombination	(3)
$O + \equiv Si\text{-}O_2 \rightarrow O_2 + \equiv Si\text{-}O\cdot$	ER Recombination II/ O_2 Replacement	(4)
$\equiv Si\text{-}O_2 \rightarrow O_2 + \equiv Si\cdot$	O_2 Desorption	(5)

Planned Impact

- Must understand large variations in experimental data and relate to simulations
- Planning to compute mechanism rates for dissociated air molecules in function of surface temperature at low pressures

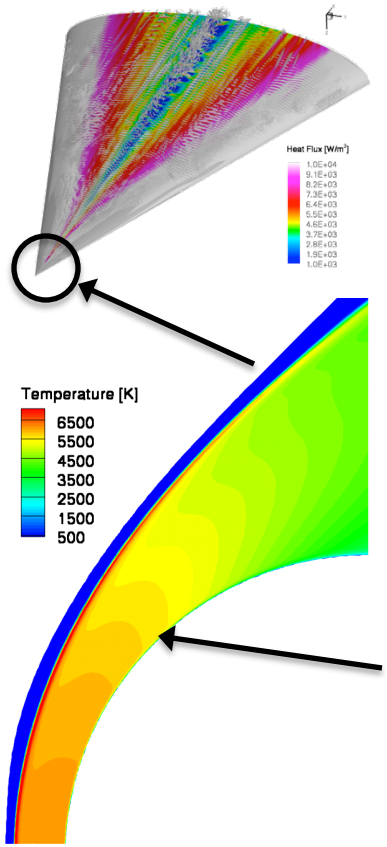
END-OF-PHASE GOAL

Research Goals

- Greatly reduce the uncertainty in gas-surface mechanism rates via MD simulation
- Incorporate rates into CFD boundary conditions to reduce uncertainty in surface heating rates due to catalytic effects

A Finite-Rate Gas-Surface Chemistry Model

Surface reactions now modeled similar to gas-phase

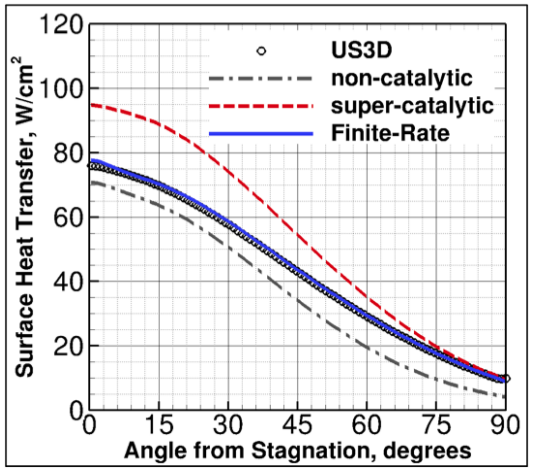


- Prediction of surface heat flux vital for **weight savings** and **survivability** of TPS for hypersonic vehicles
- **Heat flux** may depend on local **catalytic gas-surface reactions** (dissociated atoms recombining on the surface)

Model now directly linked to fundamental surface chemistry

$$
\begin{aligned}
&(1)\quad O + [s] \rightarrow O_s \\
&(2)\quad N + [s] \rightarrow N_s \\
&(3)\quad O + O_s \rightarrow O_2 + [s] \\
&(4)\quad N + N_s \rightarrow N_2 + [s] \\
&(5)\quad O + N_s \rightarrow NO + [s] \\
&(6)\quad N + O_s \rightarrow NO + [s] \\
&(7)\quad O_{s,m} + O_s \rightarrow O_2 + 2[s] \\
&(8)\quad N_{s,m} + N_s \rightarrow N_2 + 2[s] \\
&(9)\quad O_{s,m} + N_s \rightarrow NO + 2[s] \\
&(10)\quad N_{s,m} + O_s \rightarrow NO + 2[s] \\
&(11)\quad O_s \rightarrow O + [s] \\
&(12)\quad N_s \rightarrow N + [s]
\end{aligned}
$$

- Can we move away from the super-catalytic assumption for TPS design?



Dr. Schwartzentruber

Assistant Professor

- 2011 Visiting Professor, *von Karman Institute*
- AFOSR *Young Investigator Award* (2009)
- 2007 AIAA *Orville and Wilbur Wright Award*

Advances in computational chemistry enable investigation of *realistic amorphous surfaces.*

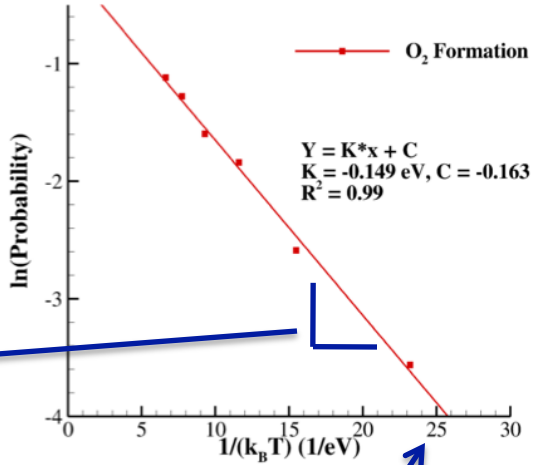
- A finite-rate model is being developed for oxygen-silica interactions
- SiO_2 is a main component in many re-useable and ablative TPS
- SiO_2 oxide layers form on SiC and UHTCs when exposed to dissociated air

(1) $O + [s] \rightarrow O_s$
(2) $N + [s] \rightarrow N_s$
(3) $O + O_s \rightarrow O_2 + [s]$
(4) $N + N_s \rightarrow N_2 + [s]$
(5) $O + N_s \rightarrow NO + [s]$
(6) $N + O_s \rightarrow NO + [s]$
(7) $O_{s,m} + O_s \rightarrow O_2 + 2[s]$
(8) $N_{s,m} + N_s \rightarrow N_2 + 2[s]$
(9) $O_{s,m} + N_s \rightarrow NO + 2[s]$
(10) $N_{s,m} + O_s \rightarrow NO + 2[s]$
(11) $O_s \rightarrow O + [s]$
(12) $N_s \rightarrow N + [s]$

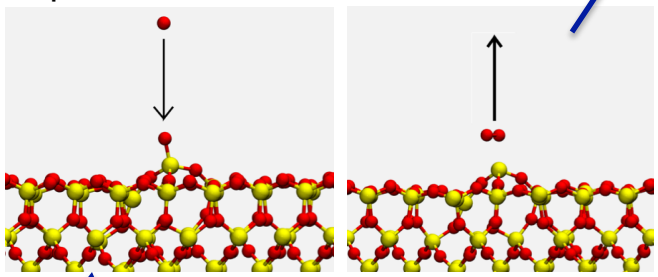
- Parameterize the Finite-Rate model

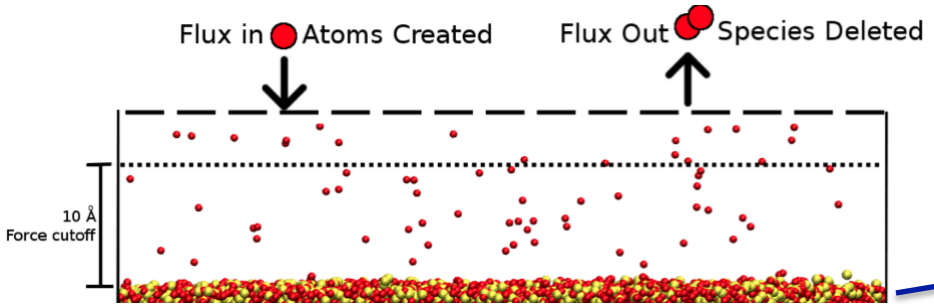
$$k_f = \vec{F}_{kin} \Phi_o A e^{-E_a/(RT)}$$

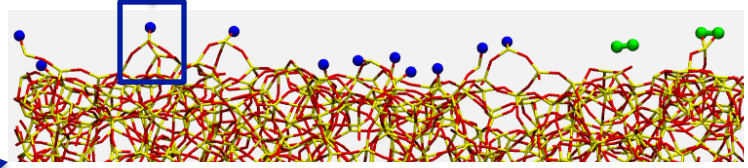
$$E_a = 0.15 \text{ eV}$$



- Compute activation energies for specific reactions on active sites







- Predict in-situ surface structure
- Identify catalytic defects (active sites)