

## **Microscopic Analysis of Catalytic Recombination Process**

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### **ABSTRACT**

Heterogeneous catalytic recombination is responsible for additional heat transfer in hypersonic re-entry flows. Experimental studies in this field, using different approaches, have found a scatter in the recombination probability values. To better understand the catalytic recombination process from a microscopic perspective, a molecular dynamics (MD) study using ReaxFF with LAMMPS was conducted. The present work delivers preliminary results for oxygen atom recombination on a  $\beta$ -cristobalite surface at different wall temperature conditions. The incoming oxygen atoms are modeled based on the flux boundary condition for a given pressure of 10 atm. The incoming gas is assumed to be in thermal equilibrium with the wall. From the MD simulation, the measured recombination probability is observed to be larger than the one found from the measured data in the literature at low temperature. However, at high temperature, the MD simulation provides the similar recombination coefficients with the measured data.

### **1. INTRODUCTION**

Catalytic recombination process plays an important role in the heat transfer determination during the space vehicle flight. The recombined atoms release additional heat transfer, which can be accounted for 30% more for the Earth atmosphere and three times higher for the Mars atmosphere. The additional heat transfer may also affect the survivability of the space debris during the reentry process (Park and Park 2017).

The main objective in the catalytic study is to measure the recombination efficiency, which is defined as the ratio of the recombined flux with the incoming flux. Some theoretical formulation have been developed to study the relations between the recombination efficiency and stagnation heat transfer (Goulard 1958, Park 2013, Yang and Park, 2019a). Generally, there are two different approaches that have been applied to measure the efficiency: experimental and numerical approach (Herdrich et al. 2012). In the framework of the experimental approach, although some works have been applied to measure the catalytic properties (Cheung et al. 2016, Kim and Park 2019a,

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Kim and Park 2019b, Kim et al. 2019, Park 2012, Park 2013, Yang and Park 2019b), there still exists uncertainty in the catalytic measurement (Sanson et al. 2017). To solve the issue, the numerical approaches, which can be categorized as chemical kinetics or molecular dynamics (MD), are applied.

Within the scope of the chemical kinetics, some empirical formulation, based on some elementary surface reactions, are fitted into the results obtained from the ground measurements or flight. The fitting process is mainly applied for a SiO<sub>2</sub> material, which has found its many application as the coating material for thermal protection system (TPS). Despite many conducted studies, the empirical fitting formulation is not unique due to its dependency on some required fitting parameters.

Due to the limitation of the chemical kinetics formulation, some other numerical approach are developed by the means of molecular dynamics. In particular, the molecular dynamics method is used to determine energy parameters, potential energy surfaces, or estimate some other parameters by some statistical methods. When only classical mechanics are considered into the formulation, the method is named as classical molecular dynamics. On the other hand, when the surface lattice phonons are coupled with the atomic motion, the method is named as the semi-classical molecular dynamics.

Molecular dynamics for surface catalytic recombination also varies in terms of the considered surface material and the incoming gas types. Each study focuses in either an individual surface reaction or a whole recombination process. Valentini et al. (2010) mainly focused on the adsorption process of oxygen molecule on Pt (111) surface. Norman et al. (2010) measured the recombination efficiency on  $\beta$ -quartz at temperature between 500 K and 2000 K at different values of incoming pressure. Specifically, the incoming flux atom is modeled based on the incoming flux obeying the Maxwell-Boltzmann velocity distribution. Norman et al. (2011) also considered several surface chemical reactions whose reaction rate parameters were determined from the molecular dynamics (MD) analysis.

In this paper, following the initial work of Norman et al. (2010), a MD analysis for oxygen catalytic recombination on a  $\beta$ -cristobalite surface is performed. The recombination efficiency is counted based on the ratio between the incoming and outgoing flux on the surface. The operating pressure condition for the simulation is taken to be about 10 atm. The work specifically focuses on: the effects of the surface wall temperature varying from 300 K to 2000 K. In the analysis, a ReaxFF (reactive force field) potential function is used to define the interaction between the atoms. All simulations were done in LAMMPS (Aktulga et al. 2012, Plimpton 1995).

## 2. REAXFF MOLECULAR DYNAMICS

The reactive force field (ReaxFF) molecular dynamics is implemented to study the atomic interaction in the surface catalytic phenomena. Unlike the other force fields used in the MD simulation, the ReaxFF does not implement the fixed connectivity for chemical bonds between atoms. The connectivity is rather defined based on a bond order term, which is calculated based on the interatomic distances and updated at each time step computation. The bond-order between two particles in the MD simulation is shown in Eq. (1). The bond-order parameters  $BO_{ij}^{\sigma}$ ,  $BO_{ij}^{\pi}$ , and  $BO_{ij}^{\pi\pi}$  represent bond

orders of single bond ( $\sigma$  bond), double bond ( $\pi$  bond), and triple bond ( $\pi\pi$  bond). The required parameters to describe the atomic interactions between oxygen and silica surface is modeled based on a specialized ReaxFF developed for the gas-surface interaction (Norman et al. 2013).

$$\begin{aligned}
 BO'_{ij} &= BO'_{ij}{}^{\sigma} + BO'_{ij}{}^{\pi} + BO'_{ij}{}^{\pi\pi} \\
 &= \exp \left[ p_{bo,1} \left( \frac{r_{ij}}{r_0^{\pi}} \right)^{p_{bo,2}} \right] + \exp \left[ p_{bo,3} \left( \frac{r_{ij}}{r_0^{\pi}} \right)^{p_{bo,4}} \right] + \exp \left[ p_{bo,5} \left( \frac{r_{ij}}{r_0^{\pi}} \right)^{p_{bo,6}} \right]
 \end{aligned} \quad (1)$$

The energies between atoms in the formulation are all functions of bond order. The complete energy in the system also takes into account long range non-bonded terms such as Coulomb and Van der Waals interaction. Description of the energy and mode details about the reactive force field can be seen in the work of van Duin et al. (2003).

To confirm the capability for the potential function in modeling the surface atomic interaction, a neutron total scattering function, computed from the MD simulation, is compared with the experimental data. The experimental data for correlation function obtained for the amorphous silica is used for the comparison (Nakano et al. 1994). To model the amorphous silica, an annealing procedure is applied on  $\beta$ -cristobalite.  $\beta$ -cristobalite is chosen because it exhibits similar density with amorphous silica. A periodic crystalline of  $\beta$ -cristobalite is given initial temperature of 8000 K and propagated for 20 ps under NVT dynamics. The whole system is later cooled down at rate of 50 K/ps under NVT dynamics until it reached 300 K. Finally, the system is propagated for 40 ps under NPT dynamics at 300 K and 1 atm. During the propagation, some statistics of simulation is obtained during the last 20 ps.

### 3. SURFACE DEFINITION

For the present work, the considered surface of interest is a polymorph form for  $\text{SiO}_2$  material,  $\beta$ -cristobalite. The crystal structure for the atomic is obtained from the work of Wyckoff (1925). The surface recombination of oxygen atoms is specifically studied on the (001) plane of  $\beta$ -cristobalite shown in Fig. 1. The blue atoms represent the silicon atoms, whereas the red atoms represent the oxygen atoms.

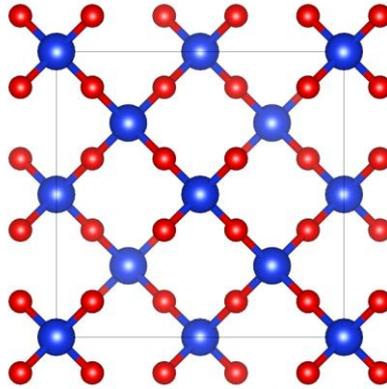


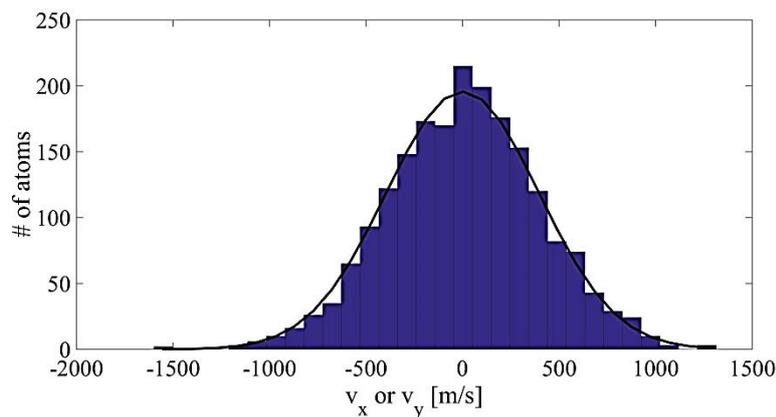
Fig. 1 Atomic configuration for (001) plane of  $\beta$ -cristobalite

#### 4. FLUX BOUNDARY CONDITION

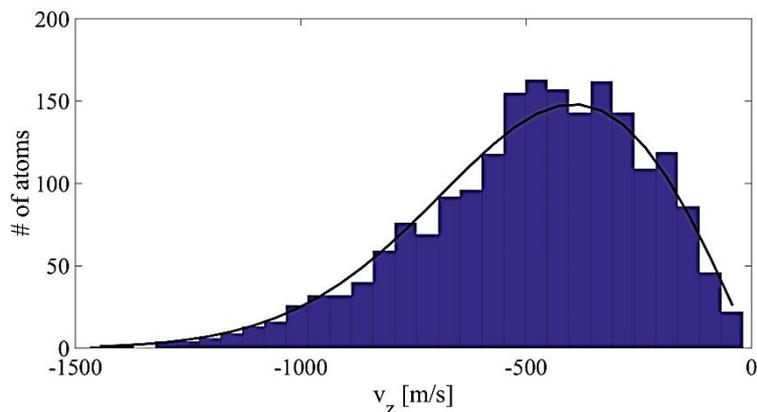
In the catalytic recombination process, the incoming molecules are assumed to obey the Maxwell–Boltzmann distribution function. To model the incoming velocity based on the Maxwell–Boltzmann distribution, a random number generator approach is applied (Garcia and Wagner 2006). The incoming velocity distribution are modeled based on the following equations.

$$v_x = \sqrt{\frac{k_B T}{m}} R_G \quad v_y = \sqrt{\frac{k_B T}{m}} R_G \quad v_z = -\sqrt{\frac{2k_B T}{m}} \sqrt{-\log R_U} \quad (2)$$

Fig. 2 shows the velocity distribution obtained following the random numbers generator method. In the figure, the comparison is made for the case where incoming temperature is approximately 300 K and the total number of incoming atoms is 2000.



(a) velocity distribution in x and y direction



(b) velocity distribution in z direction

Fig. 2 Maxwell–Boltzmann velocity distribution obtained from random number generators

The surface catalytic recombination is modeled based on the schematic shown in Fig. 3. The incoming atoms velocity is computed for a pressure of 10 atm and various temperature ranging between 500 K and 1500 K. For each temperature condition, the incoming atomic flux is calculated. From the flux calculation, the period insertion for a single atom into the simulation box, which area is  $2400 \text{ \AA}^2$  is computed. The simulation box is assumed to be periodic in x and y direction only. All simulations are performed for 2500 ps with time step of 0.5 fs.

To compute the recombination coefficient, the flux ratio between the incoming oxygen atom and outgoing oxygen molecules are computed. The flux is calculated by counting the number of atoms or molecules passing through a given plane in the simulation box. A post-processing code is developed to count the number of passing atoms or molecules based on the output data given from the MD simulation.

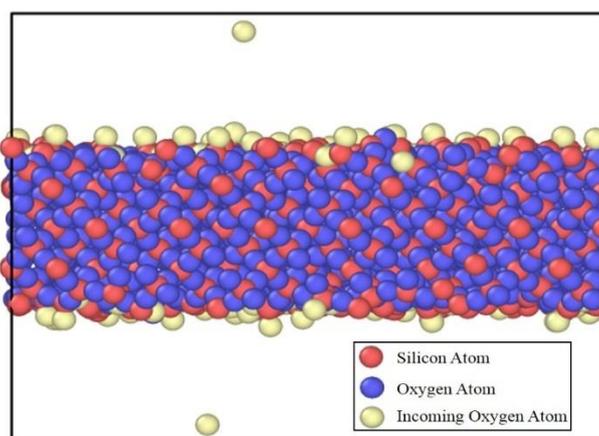


Fig. 3 Maxwell–Boltzmann velocity distribution obtained from random number generators

## 5. RESULTS AND DISCUSSION

To compute the recombination coefficient at different wall temperatures condition, a steady state adsorbed atoms condition is required. The adsorbed atom is counted as an atom which is bonded to the surface with bond distance is less than 1.2 Å. Fig. 4 shows the number of adsorbed oxygen atoms on the surface for a wall temperature of 500 K. For this case, it is assumed that the steady state is achieved after 1500 ps.

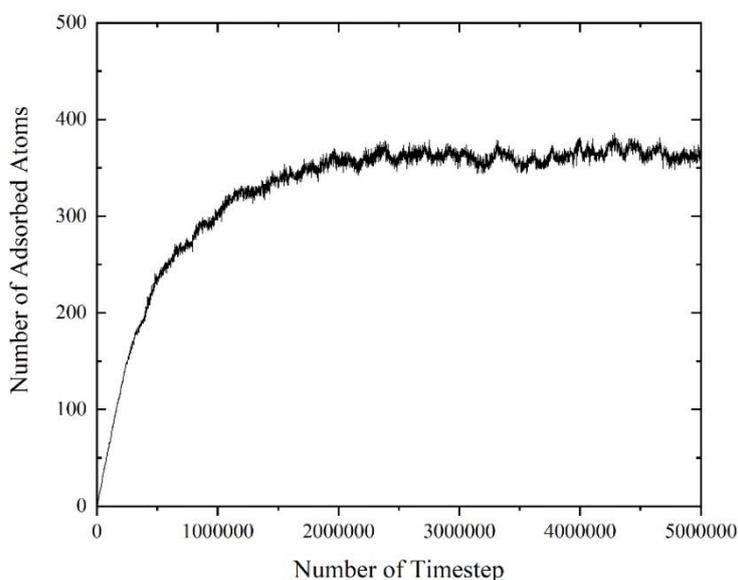


Fig. 4 Steady state adsorbed atom condition

Fig. 5 shows the obtained catalytic recombination coefficient based on the flux boundary method for various temperature conditions, ranging from 500 K and 1500 K. At low temperature ( $T = 500$  K), the measured coefficient value is higher than the measured value from Steward (1996). However, at high temperature, the recombination coefficient values obtained from MD simulation are quite matched with the one obtained experimentally.

To better understand the difference between the data obtained from the MD simulation and those obtained from the experimental work, two different types of recombination need to be considered. The first type, Langmuir–Hinshelwood recombination occurs between two adsorbed atoms. On the other hand, the second type of recombination named as Eley–Rideal recombination occurs between the incoming oxygen atoms and the adsorbed atoms.

Through the MD simulation, both types of recombination are considered in the estimation of the recombination coefficient. Due to this fact, at low wall temperature where is mostly dominated by the Langmuir–Hinshelwood recombination (Cacciatore et al, 1999), MD simulation over predicts the recombination values since the contribution

from the Eley–Rideal is also included. On the other hand, at high temperature the main contribution comes from the Eley–Rideal recombination type. The contribution from the Langmuir–Hinshelwood is usually negligible at this temperature region (Cacciatore et al., 1999). Consequently, the MD simulation gives a recombination value similar to the ones observed experimentally.

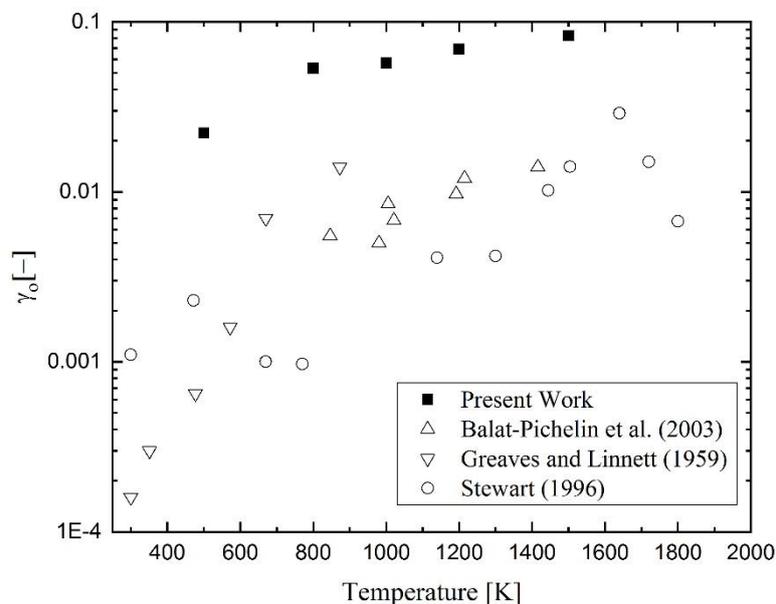


Fig. 5 Obtained catalytic recombination coefficient based on the flux boundary condition

## 6. CONCLUSIONS

In the present work, a molecular dynamics-based simulation to assess the oxygen catalytic recombination coefficient on  $\beta$ -cristobalite has been studied. The incoming gas pressure is fixed at 10 atm, whereas the temperature is varied between 500 K and 1500 K. The catalytic recombination process is modeled by counting the incoming and outgoing fluxes. The incoming flux obeys the Maxwell–Boltzmann velocity distribution. While comparing the efficiency value with the measured data, it is found that at high temperature, the molecular based simulation provides a similar value to those observed from the experimental. From the following study, it can be concluded that the application of the flux boundary condition is well suited to estimate the recombination coefficient at high temperature, where is mostly dictated by the Eley–Rideal recombination.

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## REFERENCES

- Aktulga, H.M., Fogarty, J. C., Pandit, A.S., and Grama, A.Y. (2012), "Parallel reactive molecular dynamics", *Parallel Comput.*, Vol. **38**(4-5), 245-259.
- Balat-Pichelin, M., Badie, J.M., Berjoan, R., and Bouber, P. (2003), "Recombination coefficient on ceramic materials under earth re-entry conditions by optical emission spectroscopy", *Chem. Phys.*, Vol. **291**(2), 181-194.
- Cacciatore, M., Rutigliano, M., and Billing, G.D. (1999), "Eley-Rideal and Langmuir-Hinshelwood recombination coefficients for oxygen on silica surfaces", *J. Thermophys. Heat Transfer*, Vol. **13**(2), 195-203.
- Cheung T.M., Schrijer, F.F.J., and Park, G. (2016), "Nitrogen catalytic recombination on copper oxide in tertiary gas mixtures", *J. Spacecraft Rockets*, Vol. **53**(4), 644-653.
- Goulard, R. (1958), "On catalytic recombination rates in hypersonic stagnation heat transfer", *J. Jet Propul.*, Vol. **28**(11), 737-745.
- Garcia, A.L. and Wagner, W. (2006), "Generation of the Maxwellian inflow distribution", *J. Comput. Phys.*, Vol. **217**(2), 693-708.
- Greaves, J.C and Linnett, J.W. (1959), "Recombination of atoms at surfaces: Part 6. Recombination of oxygen atoms on silica from 20°C to 600 °C", *Trans. Faraday Soc.*, Vol. **55**, 1355-1361.
- Herdrich, G., Fertig, M., Petkow, D., Steinbeck, A., and Fasoulas, S. (2012), "Experimental and numerical techniques to assess catalysis", *Prog. Aerosp. Sci.*, Vol. **(48-49)**, 27-41.
- Kim, I. and Park, G. (2019a), "Experimental study of oxygen catalytic recombination on a smooth surface in a shock tube", *Appl. Therm. Eng.*, Vol. **156**(25), 678-691.
- Kim, I. and Park, G. (2019b), "Surface heat transfer of tertiary gas mixtures with roughness controlled", in Sasoh, A., Aoki, T., and Katayama, M. (eds) 31<sup>st</sup> International Symposium on Shock Waves 1, ISSW 2017, Springer, Cham, 1099-1104.
- Kim, I., Park, G., and Na, J.J. (2019), "Experimental study of surface roughness effect on oxygen catalytic recombination", *Int. J. Heat Mass Trans.*, Vol. **138**, 916-922.
- Meana-Pañeda, R., Pauku, Y., Duanmu, K., Norman, P., Schwartzentruber, T.E., and Truhlar, D.G. (2015), "Atomic oxygen recombination at surface defects on reconstructed (0001)  $\alpha$ -quartz exposed to atomic and molecular oxygen", *J. Phys. Chem. C*, Vol. **119**(17), 9287-9301.
- Nakano, A., Kalia, R. K., and Vashishta, P. (1994), "First sharp diffraction peak and intermediate-range order in amorphous silica: finite-size effects in molecular dynamics simulations", *J. Non-Cryst. Solids*, Vol. **171**(2), 157-163.
- Nasuti, F., Barbato, M., and Bruno, C. (1996), "Material-dependent catalytic recombination modeling for hypersonic flows", *J. Thermophys. Heat Transfer*, Vol. **10**(1), 131-136.
- Norman, P., Schwartzentruber, T.E., and Cozmuta, I. (2010), "Modeling air-SiO<sub>2</sub> surface catalysis under hypersonic condition with ReaxFF molecular dynamics", *Proceedings of 10<sup>th</sup> AIAA/ASME Joint Thermophysics and Heat Transfer Conference*, Chicago, Illinois, AIAA Paper 2010-4320.
- Norman, P., Schwartzentruber, T.E., and Cozmuta, I. (2011), "A computational chemistry methodology for developing an oxygen-silica finite rate catalytic model for

- hypersonic flow”, *Proceedings of 42<sup>nd</sup> AIAA Thermophysics Conference*, Honolulu, Hawaii, AIAA Paper 2011-3644.
- Norman, P., Schwartzentruber, T.E., Leverentz, H., Luo, S., Meana-Pañeda, R., Paukku, Y., and Truhlar, D.G. (2013), “The structure of silica surfaces exposed to atomic oxygen”, *J. Phys. Chem. C*, Vol. **117**(18), 9311-9321.
- Park, G. (2013), “Oxygen catalytic recombination on copper oxide in tertiary gas mixtures”, *J. Spacecraft Rockets*, Vol. **50**(1), 540-555.
- Park, G. (2012), “Study of oxygen catalytic recombination”, *Proceedings of 43<sup>rd</sup> AIAA Thermophysics Conference*, New Orleans, Louisiana, AIAA Paper 2012-3098.
- Park, S.-H. and Park, G. (2017), “Reentry trajectory and survivability estimation of small space debris with catalytic recombination”, *Adv. Space Res.*, Vol. **60**(5), 893-906.
- Plimpton, S. (1995), “Fast parallel algorithms for short-range molecular dynamics”, *J. Comput. Phys.*, Vol. **117**(1), 1-19.
- Stewart, D. A. (1996), “Determination of surface catalytic efficiency for thermal protection materials-room temperature to their upper use limit”, *Proceedings of 31<sup>st</sup> AIAA Thermophysics Conference*, New Orleans, Louisiana, AIAA Paper 1996-1863.
- Sanson, F., Villedieu, N., Panerai, F., Chazot, O., Congedo, P.M., and Magin, T.E. (2017), “Quantification of uncertainty on the catalytic property of reusable thermal protection materials from high enthalpy experiments”, *Exp. Therm Fluid Sci.*, Vol. **82**, 414-423.
- Valentini, P., Schwartzentruber, T.E., and Cozmuta, I. (2010), “Molecular dynamics simulation of O<sub>2</sub> sticking on Pt (111) using the ab initio based ReaxFF reactive force field”, *J. Chem. Phys.*, Vol. **133**(8), 084703.
- van Duin, A.C.T., Strachan, A., Stewman, S., Zhang, Q., and Goddard, W.A. (2003), “ReaxFF<sub>SiO</sub> reactive force field for silicon and silicon oxide systems”, *J. Phys. Chem. A.*, Vol. **107**(19), 3803-3811.
- Wyckoff, R.W.G (1925), “Crystal structure of high temperature cristobalite”, *Am. J. Sci.*, Vol. **s5-9**(54), 448-459.
- Yang, Y. and Park, G. (2019a), “Analysis of catalytic heat transfer for a multi-species gas mixture,” *Int. J. Heat Mass Trans.*, **137**, 1088-1102.
- Yang, Y. and Park, G. (2019b), “Oxygen catalytic recombination on titanium surface”, in Sasoh, A., Aoki, T., and Katayama, M. (eds) 31<sup>st</sup> International Symposium on Shock Waves 1, ISSW 2017, Springer, Cham, 211-219.