

Molecular Dynamics Modeling of Hypersonic Gas-Phase and Gas-Surface Reactions

T. E. Schwartzenruber, P. Norman, and P. Valentini

*Department of Aerospace Engineering and Mechanics,
University of Minnesota, Minneapolis, MN 55455*

Abstract. Efforts to use molecular dynamics (MD) to develop both non-equilibrium dissociation models required in the shock layer as well as gas-surface interaction models specifically for surface catalysis will be summarized. First, an accelerated MD algorithm for dilute gases is presented, called the Event-Driven/Time-Driven (ED/TD) MD method. The method detects and moves molecules directly to their impending collision while still integrating each collision, including multi-body collisions, using conventional Time-Driven (TD) MD with an arbitrary inter-atomic potential. The simulation thus proceeds at time steps approaching the mean-collision-time. Preliminary nonequilibrium relaxation and normal shock wave simulations are in excellent agreement with direct simulation Monte Carlo (DSMC) results with large speedups over conventional TD MD, especially at low densities. Second, an MD simulation technique to study surface catalysis employing the ReaxFF inter-atomic potential is detailed. SiO₂ surfaces are equilibrated with a dissociated gas mixture at various temperatures and pressures, establishing surface coverage. Rates of dominant reaction mechanisms, including adsorption, desorption, and E-R/L-H recombination, are then determined by counting individual events. The experimentally measured exponential dependence of recombination coefficient on temperature is well predicted by the MD simulations.

Keywords: Molecular Dynamics, reactive force field, heterogeneous catalysis, gas-surface interaction

PACS: 34.35.+a, 34.20.-b, 82.65.+r

INTRODUCTION AND MOTIVATION

As computer resources continue their rapid growth, advancements in computational chemistry have the potential to accurately predict detailed rate data for use in high-fidelity thermochemical models; data that is difficult to measure experimentally. High temperatures within the shock layer of a hypersonic flow lead to the dissociation of gas molecules. These dissociated species diffuse through the boundary layer and may recombine on the thermal protection system in an exothermic, surface catalyzed reaction. Studies have shown that heterogeneous catalysis contributes up to 30% of the total heat flux on a thermal protection system during planetary re-entry [1] and that the stagnation point heat flux for Mars entry varies by almost a factor of 3 between weakly and highly catalytic wall assumptions [2]. It is important to understand that the gas-phase thermochemical model provides the boundary conditions for the gas-surface interaction model, and thus both gas-phase and gas-surface models must be accurate.

High-fidelity state-to-state dissociation models require a large number of rate constants that are currently inaccessible to experimental measurements. As a result, researchers are beginning to use quantum chemistry calculations to determine collision cross-sections for the large number of possible internal energy and reaction transitions [3]. Typically such cross-sections are determined by integrating over a large number of individual collision simulations. However, this article describes an accelerated Molecular Dynamics algorithm for dilute gases called the Event-Driven/Time-Driven (ED/TD) MD method [4]. The method detects and moves molecules directly to their impending collision while still integrating each collision, including multi-body collisions, using conventional Time-Driven (TD) MD with an arbitrary inter-atomic potential. The simulation thus proceeds at time steps approaching the mean-collision-time and thus enables pure MD simulation of flow features such as shock waves. Essentially, the ED/TD-MD method computes millions of individual gas-phase collisions within an actual flow simulation, thereby not only producing collision cross-section data, but also a high-fidelity solution to certain flow features of interest.

High-fidelity gas-surface interaction models [5] also require a large number of surface reaction rates that are largely unknown and difficult to measure experimentally. This article also describes an MD simulation technique aimed at identifying the dominant mechanisms and associated rates for surface catalysis on silica materials. SiO₂ surfaces are equilibrated with a dissociated gas mixture at various temperatures and pressures, establishing surface coverage. Oxygen recombination rates are then computed by counting individual mechanism events and are compared to available experimental data.

GAS-PHASE INTERACTIONS

Event Driven/Time Driven Molecular Dynamics Methodology

Rigid particles interact only through instantaneous asynchronous collisions. Provided no external force field is present (e.g., gravity), they move along straight lines at constant velocity between two successive interactions. For such systems, Event-Driven (ED) algorithms just compute the times when collisions occur, and therefore they do not integrate the trajectories using small time slices like Time-Driven (TD) MD. For rigid spheres, the future collision time of any two pair is easily calculated. If all particles have the same diameter r_c , then at the instant when they collide the distance between their centers will be equal to r_c :

$$\left\| \mathbf{r}_i(\theta_{i,j} + t_0) - \mathbf{r}_j(\theta_{i,j} + t_0) \right\| = r_c, \quad (1)$$

where $\theta_{i,j}$ is the time elapsed from t_0 . Because between collisions each sphere moves at constant velocity, given its position at t_0 , it follows that at a later time $t_0 + \theta$,

$$\mathbf{r}_i(\theta + t_0) = \mathbf{r}_i(t_0) + \theta \mathbf{v}_i(t_0). \quad (2)$$

Combining Eq. (1) with Eq. (2) leads to the well-known quadratic equation for $\theta_{i,j}$ [6], whose solution is

$$\theta_{i,j} = \frac{(-\mathbf{v}_{i,j} \cdot \mathbf{r}_{i,j}) \pm \sqrt{(\mathbf{v}_{i,j} \cdot \mathbf{r}_{i,j})^2 - \mathbf{v}_{i,j} \cdot \mathbf{v}_{i,j} (\mathbf{r}_{i,j} \cdot \mathbf{r}_{i,j} - r_c^2)}}{(\mathbf{v}_{i,j} \cdot \mathbf{v}_{i,j})}, \quad (3)$$

where $\mathbf{v}_{i,j} = \mathbf{v}_i - \mathbf{v}_j$, and $\mathbf{r}_{i,j} = \mathbf{r}_i - \mathbf{r}_j$. Depending on the discriminant in Eq. (3), $\theta_{i,j}$ is determined. By simply checking all pairs, the calculation of each $\theta_{i,j}$ is easy, but inefficient. Therefore, a standard linked-list cell method [7] is implemented. Finally, $\theta = \min(\theta_{i,j})$ represents the time of the next impending collision. For an elastic re-bounce, the post-collision velocities can be determined analytically, and with them the algorithm can once again search for the next θ . Within machine accuracy, this procedure is exact for a Hard-Sphere (HS) gas.

For soft particles, i.e., material points interacting through a continuous potential energy function, the standard EDMD algorithm can not be used, because (i) collisions are now ill-defined, (ii) post-collision states are not the result of simple elastic re-bouncing, and (iii) at higher densities, many particles may interact at once, thus violating the assumption of binary interactions. Moreover, if unphysical overlaps occur, they are likely to cause the simulation to crash by causing extremely large forces. In a rarefied gas, the mean free path $\lambda \sim \lambda_p$ becomes much larger than the potential cut-off distance r_c . For instance, if $\rho \sim 10^{-4}$ kg/m³ then $\lambda \sim 1.15$ mm. For typical soft-sphere potentials not including the Coulombic interaction, r_c is usually set between 2 or 3 times the molecular diameter ($\sim 10^{-10}$ m) [7]. Therefore, if the standard TDMD approach is used, Newton's equations are repeatedly integrated for many thousands of time steps for all particles, irrespective of whether the resultant force is zero or not. This is very inefficient. The proposed combined Event-Driven/Time-Driven approach is intended to speed up MD simulation when the gas is rarefied. This is accomplished by taking advantage of the limited range of the interactions and the dilute conditions, which allow the correct detection of the impending interaction, similarly to the Event-Driven

approach. Therefore, the trajectory is not integrated for all particles. At the same time, each interaction is correctly described using the necessarily small time step typical of Time-Driven finite-difference integration schemes ($\sim 10^{-15}$ s). Furthermore, many-body interactions, although rare, are detected and simulated, with a small approximation as described below.

Specifically, if $\theta \neq 0$, all particle positions are advanced to $t_0 + \theta$, using Eq. (2). At this time, a pair of molecules, denoted with α and β , will be separated by a distance $r_c - \varepsilon$, and thus, they will interact. Because the density is low, α and β are likely to evolve independently of the rest of the system, and for a short duration compared to the mean-collision-time, τ . Therefore, the sub-system $\Gamma\{\alpha, \beta\}$ is evolved in time, while the rest of the particles are kept still. It is intuitive that at low densities, the likelihood that α and β start interacting with a third body is small, but it can not be excluded *a priori*. Hence, while the trajectory of α and β is being integrated, if a frozen particle ϕ gets within $r_c - \varepsilon$ of either α and/or β , it is added as $\Gamma\{\alpha, \beta, \phi\}$. From that point on, ϕ is evolved in time too. When all particles contained in Γ are separated by a distance larger than r_c , the algorithm moves on to determine the next θ , and the procedure is repeated. The efficient determination of whether a third (or more) body must be added to Γ is not trivial and further details can be found in Ref. [4].

Molecular Dynamics Simulations of Normal Shock Waves

The EDTD-MD method is used to simulate a Mach 9 argon shock wave at low free-stream density ($\rho = 10^{-3}$ kg/m³, $T = 300$ K). Such conditions are similar to those of typical experiments [8]. The total number of simulated MD argon atoms was roughly 18,000. The interatomic potential used is the Lennard-Jones potential which models argon well:

$$\psi(r_{i,j}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{i,j}} \right)^{12} - \left(\frac{\sigma}{r_{i,j}} \right)^6 \right], \quad (4)$$

where $\varepsilon/k = 119.18$ K, $\sigma = 3.42$ Angstroms [9], and here $r_{i,j} = \|\mathbf{r}_{i,j}\|$. Although this gas dynamics problem is essentially one-dimensional, MD simulations are three-dimensional. The simulation box extended for roughly $12\lambda_\infty$ upstream and $12\lambda_\infty$ downstream of the shock. The other two dimensions were set to 200 by 100 Angstroms. Because of the non-periodic nature of the problem, the correct far field boundary conditions must be imposed in the flow direction, while periodicity can be prescribed along the other two dimensions. To this purpose, atoms whose $x < \lambda_\infty$ and $x > 23\lambda_\infty$ were periodically removed and regenerated using the far field primitive variables resulting from the perfect gas inviscid one-dimensional Rankine-Hugoniot jump conditions. Each atom velocity was then drawn from a Maxwell-Boltzmann distribution at the corresponding bulk velocity and temperature. Because these boundary atoms were placed at random spatial locations, overlaps might occur. Therefore, a Steepest Descent routine minimized their potential energy while keeping the rest of the particles frozen.

The computational domain was subdivided into 100 bins in the x direction. In addition to density, bulk velocity, and temperature profiles, the perpendicular velocity distribution functions were extracted at various locations throughout the nonequilibrium region of the shock (shown in Fig. 1). The velocities were rescaled using $c = \sqrt{2kT/m}$ (with $m = 6.624 \times 10^{-26}$ kg for argon). Each vdf was sampled using a bin size $\Delta v_x / c = 0.2$. As seen in Fig. 1, the vdfs obtained with the ED/TD-MD method agree very well with those obtained with direct simulation Monte Carlo (DSMC). For the DSMC simulations, the Variable Hard-Sphere (VHS) model was used with $\omega = 0.7$ which is known to be highly accurate for the conditions considered [10]. The essential features are very well captured, both qualitatively and quantitatively, namely their strongly bimodal shape, and the location and value of the local maxima and minimum. In these simulations, $\langle \theta \rangle / \Delta t_{MD} = 300$ and the ED/TD algorithm drastically accelerates such simulations enabling the calculations shown in this article to be obtained using a single processor.

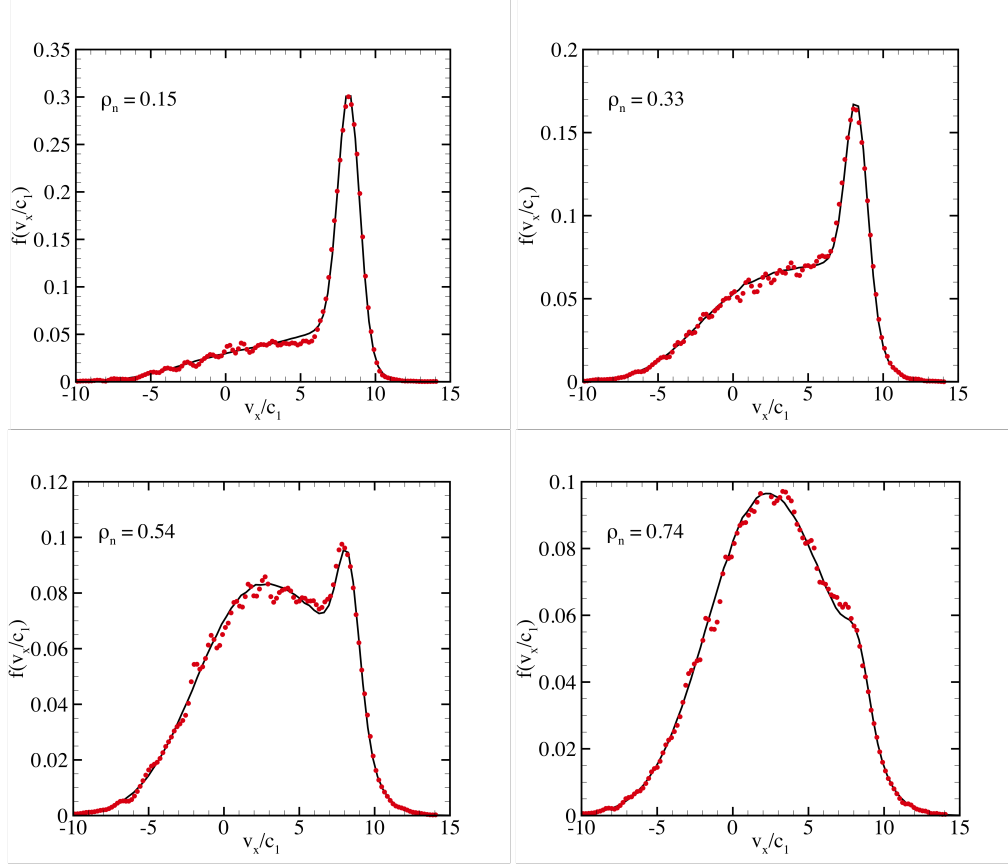


FIGURE 1. Velocity distribution functions computed by the ED/TD-MD method (dots) compared to those computed by DSMC (lines) at various locations within a Mach 9 shock wave in low-density argon gas.

GAS-SURFACE INTERACTIONS: CATALYSIS

ReaxFF Interatomic Potential and Validation

ReaxFF_{SiO} is a classical potential parameterized from quantum chemical (QC) calculations that was developed by van Duin and coworkers [11] to provide a consistent description of silicon and silicon oxide bonding over a wide range of crystal structures. One fundamental difference between ReaxFF and other force fields is that ReaxFF does not use fixed connectivity for chemical bonds. Rather, a bond order term is calculated from interatomic distances, which are updated at every MD time step. The bond order is a smooth function which goes to zero as the interatomic distance approaches the cutoff radius. Bonding energies (E_{bond}), as well as energies associated with bond angles (E_{val}) and torsion angles (E_{tor}) are all functions of bond order, ensuring that all terms vanish properly when a bond is broken. 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:

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{ip}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{vdWalls}} + E_{\text{Coulomb}} \quad (5)$$

For a full description of the ReaxFF force field and its parameterization, we refer the reader to the original work [11]. ReaxFF_{SiO} was validated for a range of silica polymorphs, including α -cristobalite, coesite, stishovite, trydimite, and α -quartz. Here we investigate the performance of the ReaxFF potential for β -quartz. To find the crystal structure predicted by the ReaxFF potential, equation of state calculations are performed by scaling one unit cell of the crystal and performing a minimization. All minimizations are performed with the conjugate gradient minimization method in the LAMMPS molecular dynamics package [12]. Equation of state curves can be compared

to DFT results and at the minimum of these curves we find the crystal geometry, which can be compared to experimental measurements. Quartz is a polymorph of SiO_2 that can occur in two phases: α -quartz and β -quartz. The computed equation of state for both α -quartz and β -quartz are shown in Fig. 2, which demonstrates that ReaxFF predicts similar behavior under compression and expansion to DFT. The crystal structure and cohesive energy of β -quartz were taken at the minimum, and are in reasonable agreement with DFT and experimental measurements. The largest deviation from the experimental crystal structure is the Si-O-Si angle, which has a difference of 6.44° or 4.2%. Such agreement with experiment and DFT lends confidence to the ability of ReaxFF_{SiO} to model β -quartz.

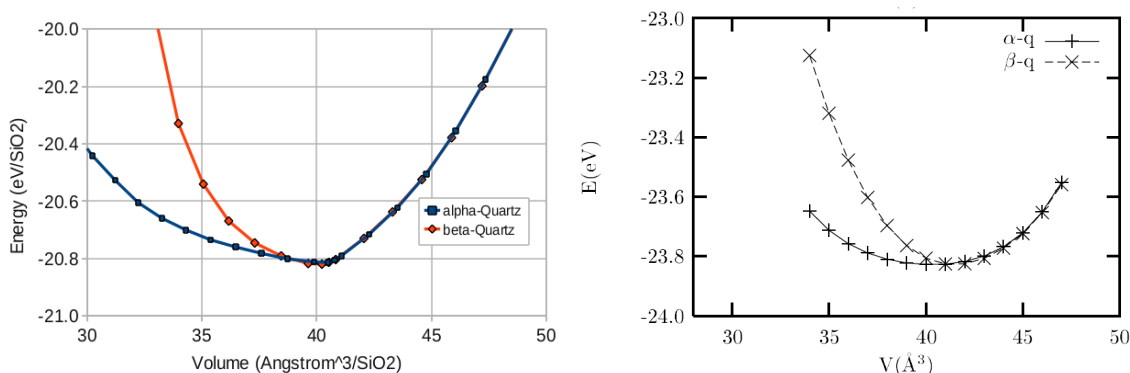


FIGURE 2. Equation of state computed by ReaxFF (left) and by DFT (right) for α -quartz and β -quartz.

Validation should also be performed via Potential Energy Surfaces (PES) relevant to gas phase interactions with a surface, such as energy and location of oxygen adsorption minima. To determine the PES for oxygen adsorption, an oxygen atom is moved normally above a given site on the frozen β -quartz surface cut along the (001) plane. The surface is 10 atomic layers thick and terminated with Si atoms. This thickness was verified to be adequate, as thicker surfaces did not change the PES. The PES for oxygen adsorption on the T1 site is shown in Fig. 3. To our knowledge, there are no QC results for oxygen adsorption on β -quartz, however there are results for oxygen adsorption on β -cristobalite. As shown in Fig. 3, the ReaxFF potential predicts that the PES for oxygen adsorption on a top site of a (001) β -cristobalite surface is similar to the PES for oxygen adsorption on β -quartz. Given the similarity of these two potential energy surfaces, we compare the ReaxFF results on β -quartz to DFT results on β -cristobalite. A comparison of PES in Fig. 3 shows that ReaxFF predicts a stronger adsorption minimum, closer to the surface than DFT and hybrid methods. We can see that the long-range terms in ReaxFF (Van der Waals and Coulomb) act to attract the atom towards the surface at longer distances. An elevated energy of adsorption could affect the overall catalytic of the surface. The flexibility of the ReaxFF potential lies in the fact that, if desired, the oxygen adsorption energies from DFT could be added to the original ReaxFF_{SiO} training set, thereby improving the performance of the potential for this problem.

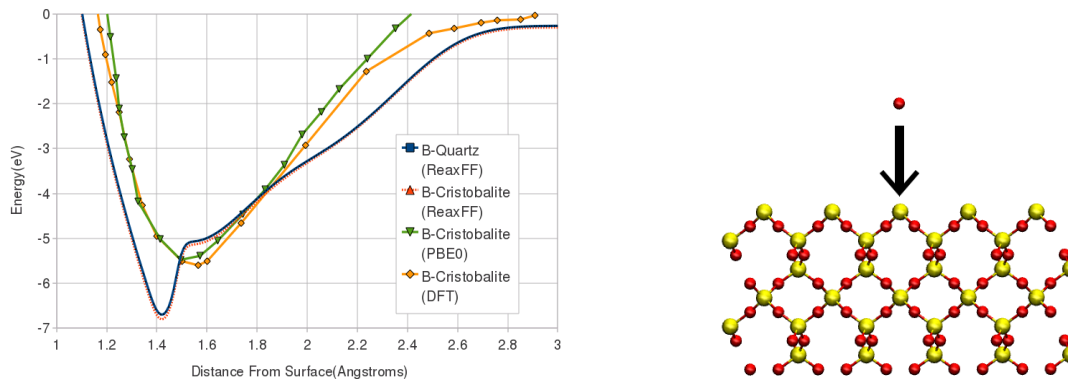


FIGURE 3. 1D PES computed by ReaxFF corresponding to an oxygen atom approaching the T1 site of β -quartz (image right) compared with PES from ReaxFF, DFT, and hybrid PBE0 functional for β -cristobalite (image left).

Surface Catalysis Simulation Methodology

To simulate the gas surface interface between an oxygen gas and silica surface, we implement a flux boundary condition, where gas phase atoms enter and leave the domain over the course of the simulation. This approach assumes that the surface is interacting with a uniform, non-changing volume of ideal gas, essentially eliminating gas-phase collisions from the simulation. The number of atoms colliding with the surface (per unit area per unit time) is given by the flux of an ideal gas through a plane, $F = n\bar{C}/4$, where n is the number density and \bar{C} is the average molecular speed. Molecular additions are distributed randomly over the course of the simulation by sampling from a Poisson distribution based on the expected flux through the plane above the surface for each time step. Molecules are placed randomly on a plane at 10 Angstroms above the surface, which is beyond the interatomic force cutoff used in our calculations. Any species more than 15 Angstroms from the surface is deleted from the simulation. The translational velocity of impinging molecules is sampled from the Maxwell-Boltzmann distribution as described by Garcia and Wagner [13]. In cases where diatomic molecules are added to the simulation, their rotational energy is sampled from the rotational energy distribution for the rigid rotor approximation of a diatomic molecule. Initial vibrational energy of injected molecules is neglected, however, this could be added by sampling from the vibrational energy distribution of a harmonic oscillator. The harmonic coefficient predicted by ReaxFF_{SiO} for O₂ was found to be 1268 N/m, which is in reasonable agreement with the experimentally measured value of 1142 N/m [14]. In order to maintain a constant gas-surface temperature, the middle atomic layer is held fixed, the surrounding two layers are thermalized using the Langevin thermostat, and the remaining layers (exposed to the gas) are not restricted in any manner. This prevents the small surface from heating up due to collisions/reactions and essentially simulates the conduction of heat into the bulk material.

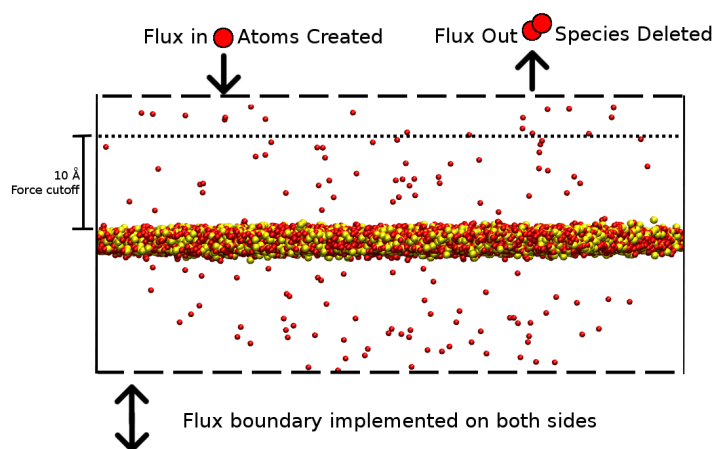


FIGURE 4. Snapshot of a ReaxFF MD simulation of atomic oxygen interacting with a β -quartz surface using a flux boundary condition.

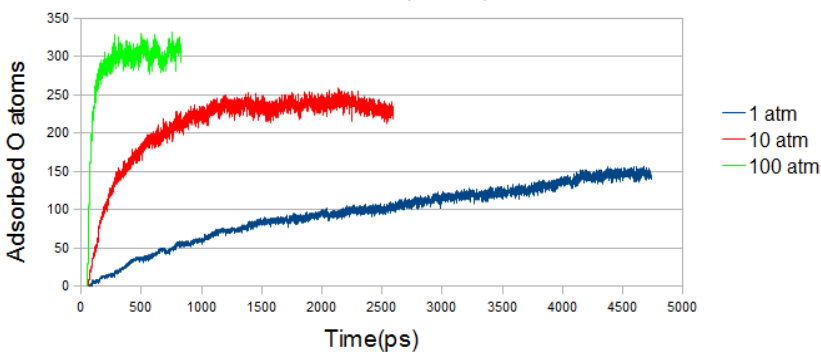


FIGURE 5. Surface population (adsorption of atomic oxygen) at various pressures.

order to avoid the assumption of a specific surface coverage, we use the flux boundary condition to expose the initially vacant surface to a gas at a given temperature and pressure. Gas atoms adsorb on the surface, which eventually reaches a steady-state composition, as shown in Fig. 5. At very high pressures, the formation of O₂ molecules on the surface results in a higher surface coverage. After a steady-state coverage has been reached, recombination coefficients can be computed based on the continued flux towards and away of the surface. Due to the relatively long timescale (in MD terms) required for surface population, this is the most computationally expensive step. As shown in Fig. 5, surface population takes longer at lower pressures. Using LAMMPS [12] in its

Since exposing a vacant surface to a gas is quite unphysical, before recombination coefficients can be computed, the initially vacant β -quartz surface must first be allowed to reach a steady-state with the gas phase. At the macro-scale this would happen virtually instantaneously and of interest is the continued catalytic reactions occurring for a given surface coverage corresponding to certain (T, p) conditions. In

parallel capacity, a 250 ps simulation for a surface of ~ 2000 requires 12 hours on 16 processors. To obtain results in a reasonable amount of time, this sets the lower pressure limit of our method at about 1 atm. However, given enough computer resources, lower pressure simulations are technically possible. For the simulation results presented in this paper, all surfaces had reached a steady-state population. It is interesting to note that recombination coefficients measured during population did not change significantly as long as the number of atoms on the surface was not rapidly changing with time.

Recombination Coefficients

Using the above methodology, simulations were performed to calculate recombination coefficients (γ) for a variety of conditions. Recombination coefficients (collected over the course of 1.5 ns) were computed for a range of gas-surface temperatures for a pure atomic oxygen gas at 10 atm, as shown in Fig. 6. The computed recombination coefficients increase with temperature, which is in agreement with experimental results. Furthermore, Fig. 6 shows that recombination coefficients follow an exponential trend, which is also seen experimentally. The exponential factors that result from Arrhenius curve-fits are tabulated in Table 1 for comparison. Since activation energies extracted from curve-fits essentially combine the activation energies of all catalytic mechanisms under the specific experimental conditions, it is not clear that different experimental techniques or these initial MD results should produce the same value.

Most experimental results for the magnitude of the recombination coefficients are closer to those measured by Kim *et al.* [15] and Balat-Pichelin *et al.* [16] (shown in Fig. 6). Thus the ReaxFF computed values ($0.01 < \gamma < 0.35$) are higher than most experimental results for oxygen recombination of quartz. However, it may be somewhat misleading to compare directly to experimental recombination coefficients because of the significant difference between computational and experimental conditions. The experimental results by Kim *et al.* and Balat-Pichelin *et al.* were carried out at pressures much lower than the lowest pressure used in our simulations. Additionally, the gas in the experiments was air, as opposed to the pure oxygen used in our calculations. Under experimental conditions, the surface also has inherent roughness, which has been shown to effect recombination coefficients [15]. Whereas the surface used in the molecular dynamics simulations is atomistically flat. These factors could significantly affect the catalytic of the surface, and are as of yet not accounted for in molecular dynamics simulations.

TABLE 1. Activation energies resulting from Arrhenius curve-fits to the trends of γ vs. Temperature.

Source	Exponent Factor
10 atm ReaxFF simulation, O	0.26 eV
Carleton <i>et al.</i> (RCG) [18]	0.14 eV
Balat-Pichelin <i>et al.</i> (Quartz) [16]	0.19 eV

There have been numerous experimental studies to measure recombination coefficients on silica, and the measured values for γ have ranged over several orders of magnitude [17]. For example, the highest (to our knowledge) recombination coefficients for oxygen on silica were those measured in an atomic beam experiment performed by Carleton and Marinelli [18]. In this experiment, a sample of Reaction Cured Glass (RCG) was effectively cleaned under ultra high vacuum conditions (1×10^{-9} Torr) by an atomic beam of 50/50 oxygen/argon. Under these conditions, recombination coefficients were measured to range between 0.4 at 1000 K to 0.08 at 700 K, as shown in Fig 6 above. RCG contains 3-7% B_2O_3 , however it has been shown by Jumper and Seward that it has a similar catalytic properties to pure silicon dioxide [19]. Because the surface is effectively cleaned under ultra-high vacuum conditions, it may be that this surface more closely resembles the ideal surface used in our simulations. Moreover, the recombination coefficients measured in this experiment were significantly higher than any other values we found in the literature, but they were measured under different conditions with a different experimental technique. Future work will focus on identifying precisely how such MD simulations should be scaled to specific experimental and flight conditions.

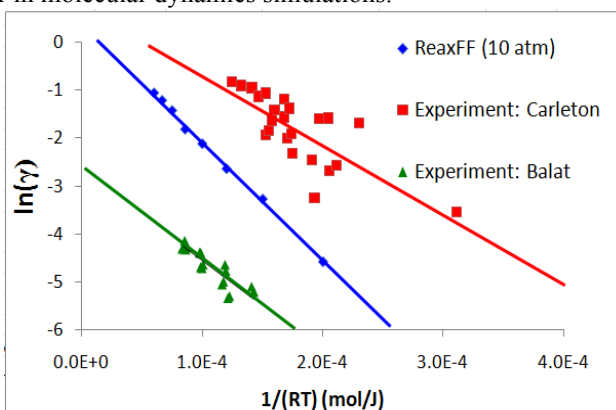


FIGURE 6. Variation of recombination coefficient (γ) with temperature computed by ReaxFF MD simulation and compared with experimental data.

CONCLUSIONS

In this work, an algorithm to speed-up the simulation of rarefied gases using spherically symmetric soft potentials is presented. In particular, the proposed algorithm correctly identifies the time of the next interaction, fast-forwards the system to that time, and processes each interaction using Time-Driven MD with the sufficiently small time step to correctly resolve the atomic motion. Many-body interactions are also detected and simulated, with a small approximation. The method is tested for a Mach 9 shock wave in a rarefied argon flow. The results we obtained are remarkably accurate, both in terms of bulk quantity profiles, i.e., temperature and density, and in terms of molecular velocity distributions throughout the nonequilibrium region of the shock front. Using this approach, the total number of steps per free-stream mean collision time is reduced by roughly 300 times, thus making such simulations using a realistic soft potential feasible even on a single CPU.

Second, a numerical method is described for modeling surface catalysis on a silica. This method provides sufficient statistics for calculating recombination coefficients for pressures >1 atm in a reasonable amount of time. The method is implemented with the publicly available LAMMPS molecular dynamics program [12]. The ReaxFF_{SiO} potential accurately reproduces the structure of β -quartz. However, the adsorption energy for oxygen on β -quartz is higher than predicted by DFT on a similar system. It is possible that this affects the computed recombination coefficients, however future work will involve adding relevant DFT energies to improve the ReaxFF_{SiO} potential for surface catalysis. The calculated recombination coefficients increased exponentially with temperature, as seen experimentally, with $0.01 < \gamma < 0.35$. These recombination coefficients are higher than the majority of experimental values for quartz and are slightly lower than those measured by molecular beam experiments on RCG. With the current assumptions made in the MD simulations, it is unclear whether the magnitude of computed recombination coefficients should agree with any particular experimental result. Future work using an improved potential, and adding dissociated gas mixtures at much lower pressures will help understand the (T, p, concentration) dependence and dominant catalytic mechanisms. Ultimately, such MD simulations may help inform high-fidelity gas-surface interaction models applicable to flight conditions.

ACKNOWLEDGMENTS

This work was supported by AFSOR grant #FA9550-09-1-0157. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of the AFOSR or the U.S. Government. The authors would like to thank Dr. A.C.T. van Duin for his support with ReaxFF force field development.

REFERENCES

1. M. Barbato, S. Reggiani, C. Bruno, and J. Muylaert, *J. of Thermophysics and Heat Transfer*, **14**, No. 3, 412-420 (2000).
2. D. Bose, M. J. Wright, and G. E. Palmer, *J. of Thermophysics and Heat Transfer*, **20** (4), 652-662 (2006).
3. T. Magin, M. Panesi, M. Bourdon, R. Jaffe, and D. Schwenke, *AIAA 2009-3837* (2009).
4. P. Valentini and T. E. Schwartzentruber, *J. of Comp. Phys.*, **228**, 8766-8778 (2009).
5. P. Valentini, T. E. Schwartzentruber, and I. Cozmuta, *AIAA 2009-3935* (2009).
6. J. M. Haile, in *Molecular Dynamics Simulation – Elementary Methods*, Wiley, 1997.
7. M. P. Allen, D. J. Tildesley, in *Computer Simulation of Liquids*, Oxford, 1987.
8. H. Alsmeyer, *J. Fluid Mech.*, **74** (2), 497–513 (1976).
9. J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, in *Molecular Theory of Gases and Liquids*, John Wiley and Sons, 1954.
10. P. Valentini and T. E. Schwartzentruber, *Phys. of Fluids*, **21**, 066101 (2009).
11. A. C. T. van Duin, A. Strachan, S. Stewman, Q. Zhang, and W. A. Goddard III, *J. of Phys. Chem.*, **107**, 2802-2811 (2003).
12. S. Plimpton, *J. Comp. Phys.*, **117** (1995): lamps.sandia.gov.
13. A. Garcia and W. Wagner, *J. of Comp. Phys.*, **217**, 693-708 (2006).
14. D. McQuarrie and J. D. Simon, in *Physical Chemistry: A Molecular Approach*, University Science Books, 1997.
15. Y. C. Kim and M. Boudart, *Langmuir*, **7** (1991).
16. M. Balat-Pichelin, J. Badie, R. Berjoan, and P. Boubert, *Chem. Phys.*, **291**, 181-194 (2003).
17. L. Bedra and M. Balat-Pichelin, *Aerospace Science and Technology*, **9**, 318-328 (2005).
18. K. Carleton and W. Marinelli, *J. of Thermophysics and Heat Transfer*, **6**, 650-655 (1992).
19. J. E. Jumper and W. A. Seward, *J. of Thermophysics and Heat Transfer*, **8**, 460-465 (1994).