NO production on the reentry spacecraft thermal protection system surface in the direct simulation Monte Carlo method

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Abstract. This work is aimed at development of an approach for modeling surface chemistry with multiple reaction channels in the direct simulation Monte Carlo method. In particular, production of NO on spacecraft thermal protections system surface is considered in detail. The approach is based on the previous works of the authors where a surface chemistry molecular model based on macroscopic detailed reaction sets was developed. The new approach has been implemented in SMILE++ code and verified by comparison with theoretical values of the surface population of atomic species in thermal equilibrium. Excellent agreement between computational results and theoretical prediction has been demonstrated.

1. Introduction
Surface chemical reactions have significant impact on the heat transfer to the thermal protection system (TPS) of the descent vehicle entering the Earth atmosphere. Since these reactions are exothermic, ignoring these processes in an aerothermodynamic computational model may lead to a significant underprediction of the heat flux to the surface of the descent vehicle [1, 2]. Thus, a correctly developed surface catalytic model allows to increase the accuracy of prediction of heat flux in aerothermodynamics computations. For example, accurate prediction of heat flux to the surface reduces the weight of the heat shield and hence increases the payload.

When modeling the aerothermodynamics of descent vehicles at high altitudes (more than 80 km), one cannot rely on continuum gas models due to the significant flow nonequilibrium. The main tool for the numerical analysis of such flows is the direct simulation Monte Carlo (DSMC) method [3]. To simulate surface processes in the DSMC method, macroscopic chemical data is not enough and information on probabilities and times of processes for specific molecular species is required. In [4-6], Molchanova et al. proposed an approach for obtaining such microscopic information based on detailed macroscopic kinetic mechanisms of surface processes. One of the limitations of the proposed approach is its inability to take into account recombination reactions leading to the formation of nitric monoxide. As noted in [7, 8], such reactions can play a significant role in the kinetics of surface processes. In this work, we generalize the approach [6] to the kinetics of surface processes, including the formation of nitric monoxide. The generalized approach is implemented in the SMILE++ code [9, 10]. The approach has been applied to the Kurotaki macroscopic kinetic mechanism for SiO$_2$-based thermal protection system [11] that includes reactions producing NO. Verification of the approach is performed by comparing equilibrium surface fraction of the adsorbed species obtained in DSMC computations with the theoretical values.
2. Modification of the model of Molchanova et al

Processes involved in a surface chemical mechanism are typically divided into impact (such as Eley-Rideal, ER, recombination) and surface (such as Langmuir-Hinshelwood, LH, recombination) processes. NO molecules can be produced on the surface by both of the recombination processes. These reactions cannot be simulated within the model [6] because it was constructed in such a manner that only one ER and one LH process can be considered for each reagent. For example, if \( N + N_s \rightarrow N_2 \) recombination is modeled (which is one of the primary processes) than \( N + O_s \rightarrow NO \) cannot be taken into account. Index \( s \) denotes here particles adsorbed at the surface. So, the modification of the approach [6] performed in the present work is primarily related to the modeling multiple ER and LH recombination channels. The modified algorithms are presented below separately for impact and surface processes. Below we focus only on the differences of the present modified approach from the approach of Molchanova et al., all the common details of the original and modified algorithms can be found in [6].

2.1. Impact processes

The schematic of the present modified algorithm of the impact processes is shown in figure 1. Let us consider a particle A (atom or molecule) impinging onto the panel (an elementary element) of the surface. When the particle A collides with the surface, the following events are possible: reflection, adsorption (with the probability \( P_{ad} \)), Eley-Rideal recombination between particles A and A\(_s\) (with the probability \( P_{ER1} \)), Eley-Rideal recombination between particles A and B\(_s\) (with the probability \( P_{ER2} \)), etc. All these events are incompatible and form a complete group of events. The probability of a reaction in the interaction with the surface is \( P_{mult} = P_{ad} + P_{ER1} + P_{ER2} \). Comparing \( P_{mult} \) with \( Rn \) (a random variable uniformly distributed on the interval \([0,1]\)) shows whether the particle will reflect from the surface or participate in one of the surface processes. To understand which process is realized, we need to compare the position of \( Rn \) value on the interval \([0, 1]\) with the position of interval visualizing the probabilities of all surface processes.

![Figure 1. Modified impact mechanism algorithm.](image-url)
2.2. Surface processes

Although Molchanova et al. have already implemented the algorithm for simulating Langmuir-Hinshelwood recombination, it was shown in [12] that when this algorithm is extended in the straightforward manner to multiple reaction channels, a bias towards some of the processes arises and rates of the processes are modeled incorrectly. This behavior is due to the fact that in Molchanova et al. algorithm surface processes are modeled one by one which does not reflect the real physical situation where the reactions occur simultaneously. Such an approach works properly only for LH recombination with a single reaction channel (e.g., \( N_s + N_s \rightarrow N_2 \)). If one includes another possible channel (e.g., \( N_s + O_s \rightarrow NO \)) then the rate of the reaction which is modeled first is artificially increased, and for the subsequent reactions is, on the contrary, reduced. This is due to the fact that the average time between reactions is inversely proportional to the number of reagents. Consequently, less and less of them are available to subsequent reactions, which ultimately creates the mentioned bias. A modified LH algorithm taking into account multiple reaction channels should reflect the simultaneous nature of surface reactions as accurately as possible and maintain optimal performance.

The modified LH algorithm diagram can be seen in figure 2. At the beginning of each computational iteration, all available Langmuir-Hinshelwood recombination reactions are initialized, after which their list is randomly mixed so they are modeled in the random order. For each reaction, the time equal to the computation time step \( \Delta t \) is allocated during which it can occur. One starts with the first reaction in the randomly shuffled reaction lists. The following steps are performed consequently:

- **If** there are available reagents **AND** the allocated time is greater than zero than the time to the next reaction \( t_{\text{react}} \) is modeled in the manner similar to presented in [6], the reaction is simulated, and \( t_{\text{react}} \) is subtracted from the allocated time (**Else** the reaction is not modeled),

- move to the next reaction in the list.

These steps are performed until there are reagents and positive allocated time for any of the reactions. The modified algorithms have been implemented into the SMILE++ software system. The results of verification are presented in the next section.

3. Numerical results

A detailed macroscopic mechanism of Kurotaki, employed in the present work includes surface reactions of adsorption, desorption, Eley-Rideal recombination, and Langmuir-Hinshelwood recombination for N and O atoms (formation of \( N_2 \), \( O_2 \) and \( NO \)).
The calculation was carried out for a stationary gas, under conditions of thermal equilibrium between the gas and the wall for different wall temperatures. The gas density was set to be $9 \times 10^{-6}$ kg/m$^3$. Gas-phase reactions were neglected.

Sampling of surface macroparameters was performed after achieving steady state in terms of surface fraction of the adsorbed atomic species N and O. This state corresponds to zero mass flux through the surface and can be calculated by solving the system of kinetic equations from the Kurotaki catalytic model. Comparison of the DSMC results with this theoretical solution was performed in order to verify implementation of the model.

The results of the calculation that was carried out for the case of adsorption and desorption reactions are shown in figure 3a. The obtained dependence is in excellent agreement with the theoretical model for all considered temperature range.

Figure 3b presents the equilibrium surface population for the case of adsorption, desorption, Eley-Rideal recombination, which also coincides well with the theoretical curve. In comparison with the adsorption-desorption case, the proportion of oxygen on the surface decreases for temperature close to 1000 K. The obtained dependence is in good agreement with the theoretical prediction too.

Figure 4 shows the distribution of the fraction of nitrogen and oxygen on the surface for the case of adsorption, desorption and Langmuir-Hinshelwood recombination taken into account. It can be seen that the Langmuir-Hinshelwood recombination has a high rate, significantly reducing the concentration of both oxygen and nitrogen that their total fraction on the surface becomes less than unity at relatively low temperatures (there are some vacant sites). The obtained dependence is also in good agreement with the theoretical curve.

All numerical results demonstrate that the present DSMC model predict correct rates in thermal equilibrium for complex chemical mechanism with multiple channels including nitrogen monoxide production.
4. Conclusion

In the present work, an approach has been developed that allows including surface chemistry with multiple reaction channels in the direct simulation Monte Carlo computations. The approach is easily generalized to any number of surface reactions and can be applied for chemical mechanism with NO production on the surface.

Modified surface chemistry algorithms have been implemented into SMILE++ code. The DSMC computations have shown excellent agreement with theoretical predictions under conditions of thermal equilibrium. The future work should address the effect of the surface reactions with NO production on high-altitude aerothermodynamics of re-entry spacecraft.

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Figure 4. Comparing equilibrium surface fraction of the adsorbed species obtained in DSMC computations with the theoretical values for adsorption, desorption and Langmuir-Hinshelwood recombination.
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