

# Investigation of heterogeneous atoms recombination by molecular dynamics method

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**Abstract.** “MD Trajectory” software complex was developed earlier for investigation of the elementary gas phase chemical reactions (dissociation, exchange reaction, process of vibrational relaxation) by quasi-classical trajectory (QCT) method. “MD Trajectory” functionality was extended for study of heterogeneous atoms recombination by molecular dynamics method. “MD Trajectory” permits to investigate both Eley-Rideal and Langmuir-Hinshelwood mechanisms of heterogeneous recombination. Preliminary calculations of heterogeneous recombination of O atoms on the Si-based surface were conducted and satisfactory fit with other authors’ results was obtained.

**Keywords:** heterogeneous atoms recombination, molecular dynamics method, Eley-Rideal, Langmuir-Hinshelwood,  $\beta$ -cristobalite, oxygen

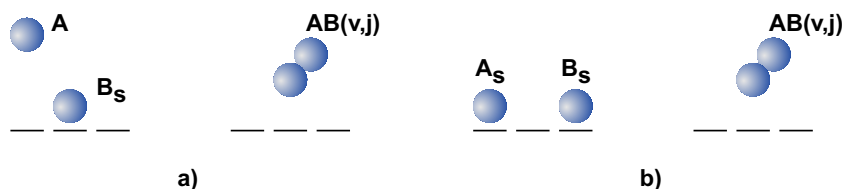
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## INTRODUCTION

Creation of reusable space vehicles such as russian “Buran”, american “Shuttle” was directly connected with design and development of reliable thermal protection system (TPS). New interest splash to this problem is initiated by development of international space station, project of scientific expedition to Mars and also creation of aeroassisted orbital transfer vehicles (AOTV). Therefore the one of important problem is investigation of interaction of gas mixtures with catalytic surfaces at the hypersonic airflow.

The strong shock waves are created at the entry of space vehicle into the atmospheres of Earth, Mars and other planets. Behind the shock wave front translational gas temperature can reach tens thousand degrees and physical and chemical processes are proceeding at the thermal nonequilibrium conditions (absence of equilibrium between translational, vibrational and rotational freedom degrees of reagent molecules). As the result of these processes, molecular components of gas mixtures mainly dissociate into atoms which interact with surface of thermal protection system.

Simulation of gas phase chemical reactions taking into account nonequilibrium effects gives modification of heat flow in comparison with equilibrium approach approximately 20-25%. On the other hand, the heat flow can be changed in several times at the using of different models of heterogeneous chemical reactions. Therefore it’s very important correctly to take into account the influence of heterogeneous atoms recombination on the surface of thermal protection covering of space vehicles.



**FIGURE 1.** Two types of atoms recombination processes: a) Eley-Rideal and b) Langmuir-Hinshelwood

There are two main types of heterogeneous recombination processes which can lead to surface heating (see Fig.1). First of them is Eley-Rideal mechanism describing interaction between adsorbed atom  $B_s$  on the surface and incident gas atom A. Second one (Langmuir-Hinshelwood mechanism) implies interaction between two adsorbed atoms  $A_s$  and  $B_s$  on the surface. Reactions through both mechanisms lead to the same products  $AB(v, j)$  molecule in  $v$ -th vibrational

state and  $j$ -th rotational one and surface, heated by part of energy released during recombination. There are two main characteristics describing heterogeneous recombination process: coefficient of heterogeneous recombination  $\gamma$  is the reaction probability and coefficient of chemical energy accomodation  $\beta$  is the energy part released through reaction and going to surface heating.

## CLASSICAL MOLECULAR DYNAMICS

“MD Trajectory” software complex was developed earlier for investigation of the elementary gas phase chemical reactions (dissociation, exchange reaction, process of vibrational relaxation) by quasi-classical trajectory (QCT) method. “MD Trajectory” functionality was extended for study of heterogeneous atoms recombination by molecular dynamics method. “MD Trajectory” permits to investigate both Eley-Rideal and Langmuir-Hinshelwood mechanisms of heterogeneous recombination. The main purpose of these calculations is determination of coefficients of recombination  $\gamma$  and chemical energy accommodation  $\beta$ .

Classical treatment was realized in the “MD Trajectory” for simulation heterogeneous recombination. In the framework of this approach atoms are divided in two groups:

1.  $i = 1, \dots, n$  – gas-phase atoms
2.  $k = 1, \dots, N$  – lattice atoms

Total hamiltonian is

$$H = \sum_{i=1}^n \sum_{\gamma=x,y,z} \frac{1}{M_i} P_{i\gamma}^2 + \sum_{k=1}^N \sum_{\gamma=x,y,z} \frac{1}{M_k} P_{k\gamma}^2 + \sum_{i<j} V_{11}(R_{ij}) + \sum_{k<l} V_{22}(R_{kl}) + \sum_{ik} V_{12}(R_{ik}) \quad (1)$$

where the first two terms are the kinetic energy of the gas-phase and surface atoms and last three terms are potential energy of interaction between gas-phase atoms –  $V_{11}$ , between lattice atoms –  $V_{22}$  and between gas-phase and surface atoms –  $V_{12}$ .  $R_{ij}$  – is interatomic distance between  $i$ -th and  $j$ -th atoms,  $P_{i\gamma}$  – is  $\gamma$ -component (in Cartesian coordinates  $\gamma = x, y$  or  $z$ ) of the impulse of  $i$ -th atom.

Motion equations in Hamilton form are written for both gas phase and lattice atoms:

$$\begin{aligned} \dot{\gamma}_i &= \frac{P_{i\gamma}}{M_i} \\ \dot{\gamma}_k &= \frac{P_{k\gamma}}{M_k} \\ \dot{P}_{i\gamma} &= -\frac{\partial H}{\partial \gamma_i} = -\sum_{j \neq i} \frac{\partial V_{11}}{\partial R_{ij}} \frac{\partial R_{ij}}{\partial \gamma_i} - \sum_k \frac{\partial V_{12}}{\partial R_{ik}} \frac{\partial R_{ik}}{\partial \gamma_i} \\ \dot{P}_{k\gamma} &= -\frac{\partial H}{\partial \gamma_k} = -\sum_{l \neq k} \frac{\partial V_{22}}{\partial R_{kl}} \frac{\partial R_{kl}}{\partial \gamma_k} - \sum_i \frac{\partial V_{12}}{\partial R_{ik}} \frac{\partial R_{ik}}{\partial \gamma_k} \end{aligned} \quad (2)$$

where

$$R_{ij} = |R_i - R_j| = \sqrt{(X_i - X_j)^2 + (Y_i - Y_j)^2 + (Z_i - Z_j)^2} \quad (3)$$

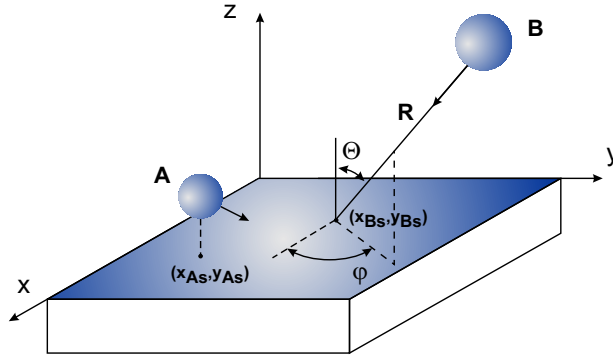
and

$$\frac{\partial R_{ij}}{\partial \gamma_i} = -\frac{\partial R_{ij}}{\partial \gamma_j} = \frac{\gamma_i - \gamma_j}{R_{ij}} \quad (4)$$

MD simulation is reduced to solving of motion equations at the various initial conditions which realize real collisions. On the Fig.2 the collision scheme for Eley-Rideal recombination process between adsorbed atom  $A_s$  and gas phase atom B is represented. For this process initial conditions can be written as:

- For incident gas atom B

$$\begin{aligned} X_B &= R_B \sin \theta_B \cos \varphi_B + X_{B_s} \\ Y_B &= R_B \sin \theta_B \sin \varphi_B + Y_{B_s} \\ Z_B &= R_B \cos \theta_B \end{aligned}$$



**FIGURE 2.** Collision scheme of Eley-Rideal recombination process

$$\begin{aligned} P_{X_B} &= -P_{R_B} \cos \theta_B \cos \varphi_B \\ P_{Y_B} &= -P_{R_B} \sin \theta_B \sin \varphi_B \\ P_{Z_B} &= -P_{R_B} \cos \varphi_B \end{aligned}$$

and

$$\begin{aligned} \theta_B &= \arccos(1 - 2 \cdot \xi_1) \in [0, \pi] \\ \varphi_B &= 2\pi \cdot \xi_2 \in [0, 2\pi] \\ X_{B_s} &= X_{max} \cdot \xi_3 \in [0, X_{max}] \\ Y_{B_s} &= Y_{max} \cdot \xi_4 \in [0, Y_{max}] \\ P_{R_B} &= \sqrt{2M_B E_{coll}} \end{aligned}$$

where  $\xi_i$  – random numbers uniformly distributed in the interval (0,1),  $M_B$  – mass of atom B,  $R_B$  is fixed and is taken so large as the initial interaction between atom B and lattice can be neglected,  $E_{coll}$  – relative collisional energy between atom B and lattice.

- For adsorbed gas atom A

$$\begin{aligned} X_A = X_{A_s} &= X_{max} \cdot \xi_5 \in [0, X_{max}] \\ Y_A = Y_{A_s} &= Y_{max} \cdot \xi_6 \in [0, Y_{max}] \\ P_{X_A} &= -P_{R_A} \cos \theta_A \cos \varphi_A \\ P_{Y_A} &= -P_{R_A} \sin \theta_A \sin \varphi_A \\ P_{Z_A} &= -P_{R_A} \cos \varphi_A \end{aligned}$$

and

$$\begin{aligned} P_{R_A} &= \sqrt{2M_A k T_s} \\ \theta_A &= \arccos(1 - 2 \cdot \xi_7) \in [0, \pi] \\ \varphi_A &= 2\pi \cdot \xi_8 \in [0, 2\pi] \end{aligned}$$

where  $M_A$  – mass of atom A,  $k$  – Boltzmann constant,  $T_s$  – surface temperature,  $Z_A$  is fixed and is taken so small that potential energy of interaction between atom A and lattice is higher than kinetic energy of atom A and it cannot leave the surface.

- For lattice atoms

$$\begin{aligned} R_{k\gamma} &= R_{k\gamma}^0 + \sqrt{2kT_s/F_k} \cos(\varphi_{k\gamma}^0) \\ P_{k\gamma} &= \sqrt{2M_k k T_s} \sin(\varphi_{k\gamma}^0) \end{aligned}$$

where  $R_{k\gamma}^0$  – equilibrium position,  $F_k$  – force constant for k-th atom,  $\phi_{k\gamma}^0$  – phase angle, randomly distributed in  $[0, 2\pi]$  (depending on random numbers  $\xi$ ),  $M_k$  – mass of k-th atom.

The each trajectory calculation is stopped when the distance criterion is realized. It's easy for check during numerical integration and can be formulated as:

- $Z_A + Z_B > R_{max}$  - at least one atom leaves surface
- $Z_A + Z_B < R_{min}$  during  $\tau_{calc} > \tau_{max}$  - both atoms during the long calculation period  $\tau_{calc}$  are near the surface.

where  $R_{min}, R_{max}, \tau_{max}$  - fixed values.

If both atoms leave surface, atomic pair AB has to be checked for bound, quasi-bound or dissociative state. If the molecule AB is in the bound or quasi-bound state, vibrational  $v$  and rotational  $j$  numbers can be determined using special iteration procedure, more details can be given in [1, 2].

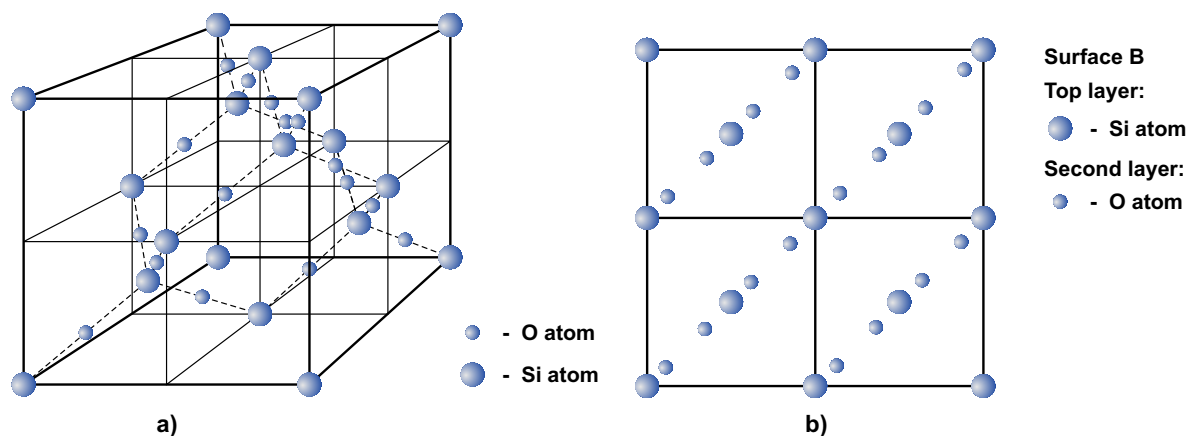
Simulation is performed at the fixed parameters  $T_s$  and  $E_{coll}$  and varied other parameters, randomly distributed in the corresponding intervals. Averaging results over varied parameters the key characteristics of heterogeneous recombination  $\gamma(T_s, E_{coll})$  and  $\beta(T_s, E_{coll})$  can be obtain as functions of surface temperature  $T_s$  and collision energy  $E_{coll}$ . The appropriate results with good accuracy can be obtained only if huge number of trajectories will be calculated.

Therefore MD calculations require a lot of computational resources. The modern supercomputer clusters achieved now a huge measure of productivity. To use cluster systems the MD code was parallelized on the basis of Message Passing Interface (MPI) technology. “MD Trajectory” was tested on supercomputer clusters of Moscow State University and Russian Academy of Sciences and very high efficiency was achieved. Thus, software complex “MD Trajectory” is rather powerful tool for investigation of chemical reaction by MD method especially for conditions hardly realized in experiment.

## ELEY-RIDEAL OXYGEN RECOMBINATION $O + O_s \rightarrow O_2$ ON THE $\beta$ -CRISTOBALITE

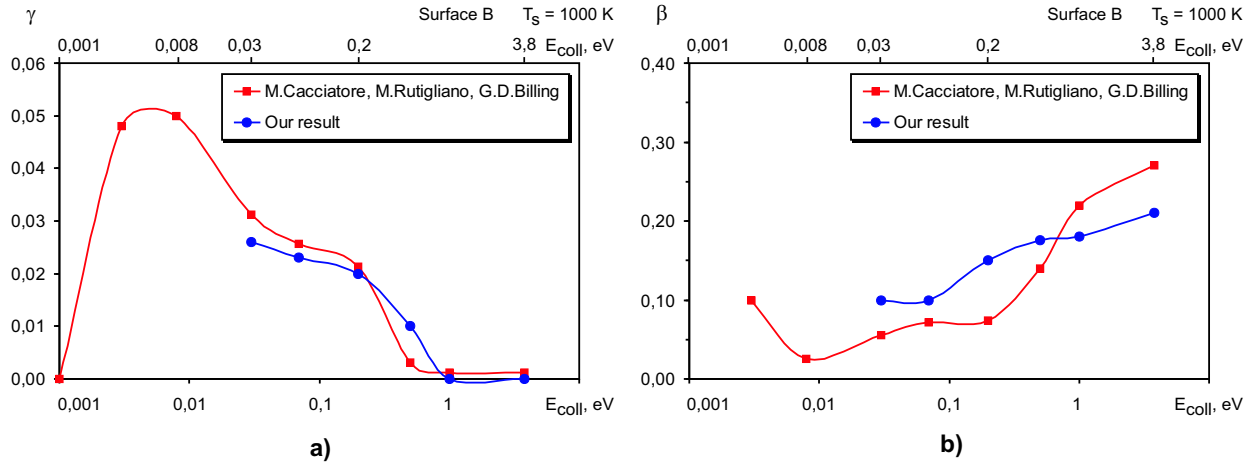
At the reentry space vehicles into the Earth atmosphere the key reactions on the surface of thermal protection systems (TPS) are heterogeneous recombination of oxygen and nitrogen atoms. There are many experimental works for investigation of this processes on the different types of silicon-based TPS (silicon carbide, silicone dioxide and etc.) on plasmatron setups. During these experiments the effective integral characteristic  $\gamma \cdot \beta$  of investigated processes was measured [3, 4]. Another experimental work on the MESOX setup [5] permits to split these characteristics and to obtain pure coefficient of heterogeneous recombination  $\gamma$ .

There are very few theoretical works simulated heterogeneous recombination by MD method. In the article [8] the semiclassical MD approach, developed by G. D. Billing, was applied for study of heterogeneous recombination of oxygen atoms on the  $\beta$ -cristobalite. Both Eley-Rideal and Langmuir-Hinshelwood mechanisms were examined, and both coefficients  $\gamma$  and  $\beta$  were calculated.



**FIGURE 3.** a) Unit cell of  $\beta$ -cristobalite lattice; b) Top layer structure of the surface

We selected the same investigated system for verification of our software complex “MD Trajectory”. Unit cell of  $\beta$ -cristobalite (see Fig.3.a) has complex structure and includes nine layers [7]. In our calculations we considered



**FIGURE 4.** Eley-Rideal process  $O + O_s \rightarrow O_2$ . a) Coefficient of heterogeneous atoms recombination and b) Chemical energy accomodation coefficient

surface with Si atoms on the top layer (see Fig.3.b, surface B from paper [8]) and modelled Eley-Rideal recombination mechanism. Surface had dimensions  $2 \times 2$  unit cells, with boundary layer conditions for simulation of infinite surface. Surface temperature  $T_s$  was taken 1000K.

Potential energy surface (PES) for investigated system was taken from [8]. It's necessary to pointed out that PES for  $\beta$ -cristobalite [6] has not only pair potentials but also three-particle terms and have enough complicated form:

$$V(r_1, r_2, r_3, \dots, r_N) = \sum_i V_1(r_i) + \sum_{i < j} V_2(r_i, r_j) + \sum_{i < j < k} V_3(r_i, r_j, r_k)$$

Modified form of the Born-Mayer-Huggins (BMH) potential:

$$\begin{aligned} V_2(r_i, r_j) &= V_2(r_{ij}) = A_{ij} \exp(-r_{ij}/\rho) + (Z_i Z_j e^2 / r_{ij}) \operatorname{erfc}(r_{ij}/\beta_{ij}) \\ A_{ij} &= (1 + Z_i/n_i + Z_j/n_j) \cdot b \cdot \exp((\sigma_i + \sigma_j)/\rho) \end{aligned}$$

where  $r_{ij}$  – separation distance,  $Z_i$  – formal ionic charge,  $b$  – constant,  $\rho, \beta_{ij}$  – adjustable parameters,  $n_i$  – number of valence shell electrons,

$$V_3(r_i, r_j, r_k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{jk}, r_{ji}, \theta_{kji}) + h(r_{ki}, r_{kj}, \theta_{ikj})$$

where

$$\begin{aligned} h(r_{ij}, r_{ik}, \theta_{jik}) &= \lambda_i \exp[\gamma_i / (r_{ij} - r_i^c) + \gamma_i / (r_{ik} - r_i^c)] \left( \cos \theta_{jik} - \cos \theta_{jik}^c \right)^2 \quad \text{for } (r_{ij} < r_i^c \text{ and } r_{ik} < r_i^c); \\ h(r_{ij}, r_{ik}, \theta_{jik}) &= 0 \quad \text{in other case} \end{aligned}$$

where  $\lambda_i, \gamma_i, r_i^c, \cos \theta_{jik}^c$  – constants,  $\theta_{jik}$  – angle subtended by  $r_{ij}$  and  $r_{ik}$ .

**TABLE 1.** Parameters of the modified BMH two-body potential

| index X-Y | $A_{X-Y}$ , eV | $\beta_{X-Y}$ , Å |
|-----------|----------------|-------------------|
| Si-O      | 1847           | 2.6               |
| O-O       | 449            | 2.55              |
| Si-Si     | 1173           | 2.53              |

Detailed calculations on the supercomputer cluster were conducted. More than 100000 trajectories for each point of  $E_{coll}$  at the fixed surface temperature  $T_s = 1000$  K were calculated. Recombination coefficient and accomodation coefficient of chemical energy were determined for the wide range of collisional energy  $E_{coll}$ . Good agreement between our results and results of Cacciatore et al. was obtained (see Fig.4).

**TABLE 2.** Parameters of the three-body potential

| index X | $\lambda_X$ , eV | $\gamma_X$ , Å | $r_X^c$ , Å | $\cos \theta_X^c$ |
|---------|------------------|----------------|-------------|-------------------|
| Si      | 112              | 2.6            | 3.0         |                   |
| O       | 2                | 2.0            | 2.6         |                   |
| O-Si-O  |                  |                |             | -1/3              |
| Si-O-Si |                  |                |             | -1/3              |

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## REFERENCES

1. A. I. Voronin, V. I. Osherov, *Molecular Reaction Dynamics*, Nauka, Moscow, 1990 (in Russian).
2. Gert D. Billing, *Dynamics of Molecular Surface Interactions*, John Wiley&Sons, New York, 2000.
3. V. L. Kovalev, A. F. Kolesnikov, *Fluid Dynamics*, **40** (2005)
4. S. P. Pidan, M. Auweter-Kurtz, G. Herdrich and M. Fertig, *Journal of Thermophysics and Heat Transfer*, **19**, pp. 566–577 (2005).
5. M. Balat-Pichelin, J. M. Badie, R. Berjoan and P. Boubert, *Chemical Physics* **291**, pp. 181–194 (2003).
6. B. P. Feuston and S. H. Garofalini, *Journal of Chemical Physics* **89**, pp. 5818–5824 (1988).
7. Ralph W. G. Wyckoff, *American Journal of Science, Ser.5* **9**, pp. 448–459 (1925).
8. M. Cacciatore, M. Rutigliano and G. D. Billing, *Journal of Thermophysics and Heat Transfer*, **13**, pp. 195–203 (1999).