Numerical Analysis of Gas Flow in Porous Media with Surface Reaction

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Abstract. Gas flow with surface reaction in porous media appears in various regions of engineering. In porous media with holes as small as a molecular mean free path, Kn of gas flow in the narrow channel is on the order of unity. Therefore, the direct simulation Monte Carlo (DSMC) method is suitable to solve transport phenomena in such kind of porous media. We perform 2D DSMC simulations of such a flow. The shape of narrow channel in porous media is complicated. To reduce complexity, we propose the simplification for porous structures by cubes and polyhedra. Results for the simplification by polyhedra agree well with the result obtained in the case without simplification. Results for the simplification by cubes also show good agreement with the result without simplification when surface reaction probability is modified.

INTRODUCTION

Gas flow with surface reaction in porous media appears in various regions of engineering, e.g., catalytic converters and fuel cells. In order to improve performance of such devices, it is important to understand transport phenomena in porous media. In porous media with holes as small as a molecular mean free path, i. e., Knudsen number Kn of gas flow in the narrow channel is in the order of unity. Therefore, the direct simulation Monte Carlo (DSMC) method [1] is suitable to solve the transport phenomena in porous media. However, performing DSMC simulation of such a flow is difficult because of its complicated structure.

In this work, we develop a DSMC code for gas flow in porous media and perform 2D DSMC simulations of such a flow. Porous structures are produced by putting fine spherical particles randomly. Since we treat 2D simulation in the present work, we put cylinders with fine diameter. In general, the shape of narrow channel in porous media is complicated, and hence, the treatment of wall-molecule collisions requires large computational cost. In addition, we need to predict the shapes of these channels because actual measurement values are discrete. To decrease the cost and reduce the complexity, we propose the simplification for porous structures. Thanks to this simplification, it becomes easier to judge wall-molecule collisions and we can decrease computing time. We perform simulations for three kinds of solid boundary. In the first case, we treat boundaries without simplification as it is. In the second and the third case, we simplify solid bodies as aggregations of cubes and polyhedra, respectively. In the 2D simulation, we use squares and polygons for the simplification. We compare the results for three cases and investigate effects of the simplification.

NUMERICAL METHOD

In this work, we model porous structures as an aggregation of randomly placed spherical particles. Since the present simulation is 2D, it is modeled as an aggregation of cylinders. A radius of particles is set at 30nm. The gas is hydrogen with room temperature, T_g=293 K, and atmospheric pressure, P=101325 Pa. In this condition, the mean free path, λ, is about 119nm. If we use the particles radius, a, as representative length of the flow, the Knudsen

number $Kn(=\lambda/a)$ becomes larger than 0.1. It shows that we cannot treat this flow as a continuum. Such kind of nanoscale gas flow is in nonequilibrium due to lack of inter molecular collisions and is governed by the Boltzmann equation and not by the Navier-Stokes equations. Therefore, we use DSMC method, which is the stochastic solution of the Boltzmann equation.

The flow field is treated as two-dimensional, but molecular motions are treated as three-dimensional. Fig. 1 shows a schematic of the computational domain. The width and the length of the computational domain are 180 nm in the x-direction and 540 nm in the y-direction, respectively. It is divided into 60 cells in the x-direction and 180 cells in the y-direction respectively. The temperature of solid particles is also set at the room temperature, T_w=293K. The diameter of hydrogen molecule is set at 0.2745 nm. Although the mean free time of molecules is about 1.70 x 10^{-12} s, we use the much smaller time step, i.e. 1/40 to 1/200 of mean free time, to treat molecular collisions with solid wall with fine structure. The velocities of molecules reflected on solid wall are determined by using the diffuse reflection model with the wall temperature. The hard sphere model is used for intermolecular collision calculation. Intermolecular collisions are treated by using the maximum collision number method [2]. Intermolecular collisions in the same cell are calculated stochastically. We use a cyclic boundary condition in the y-direction. Upper and lower boundaries are treated as a free boundary. And we assume that the computational domain is surrounded by hydrogen gas with T_g=293 K, P=101325 Pa and velocity of 1 m/s in the y-direction. The motions and collisions of molecules are traced and hence, time evolution of the flow field is simulated.

As mentioned above, porous structure is given by an aggregation of randomly placed cylinders with the radius of 30nm. We simplify this porous structure with an aggregation of small squares which sides are 18 nm, 9 nm or 4.5 nm. We also simplify the porous structure with polygons. In the latter simplification, we put vertexes in condition that the center angles θ are smaller than θ_0. We set θ_0 at 30 degrees or 60 degrees. Schematics of these simplifications are shown in Fig. 2.

We assume that a hydrogen dissociation shown Eq. (1) can occur on the surface of only one specific particle.

$$H_2 \rightarrow 2H. \tag{1}$$

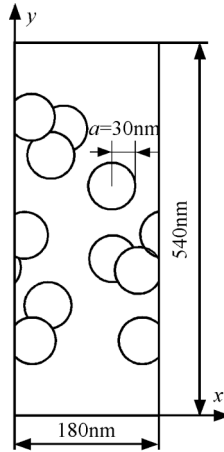The possibility of the reaction, P_r, is set at 0.2.

**FIGURE 1.** Schematic of the computational domain.

**FIGURE 2.** Approximated model of porous structures. (a) Cubes, (b) Polyhedrons.

RESULTS AND DISCUSSION

The number density distributions of H_2 molecules are shown in Fig. 3. Figure 3(a) is a result of the case using particles (cylinders) without simplification. The location of the particle with the surface reaction is also shown in Fig. 3(a). The number density of H_2 molecules out of the computational region is about 2.5×10^{25} /m^3. It decreases to 1.8×10^{25} /m^3 around the particle with surface reaction because H_2 molecules are dissociated into H atoms by the surface reaction. Figure 3(b) is a result of the case when the simplification by squares is used, 9 nm on a side. Compared with Fig. 3(a), it can be seen that the extent of decrease of the number density is larger in the case of squares. This is because the area with the surface reaction is enlarged by this simplification. Figure 3(c) is a result of the case when the simplification by polygons is used. The angle θ_0 is set at 30 degrees. The distribution of number density of H_2 molecules in Fig. 3(c) agrees well with that in Fig. 3(a).

Figure 4 shows the number density of H atoms. In the case of the simplification by squares in Fig. 4(b), more H atoms are produced than the case without simplification in Fig. 4(a). As well as H_2 molecules, the distribution of number density of H atoms in the case of the simplification by polygons in Fig. 4(c) agrees well with the result obtained without simplification in Fig. 4(a).
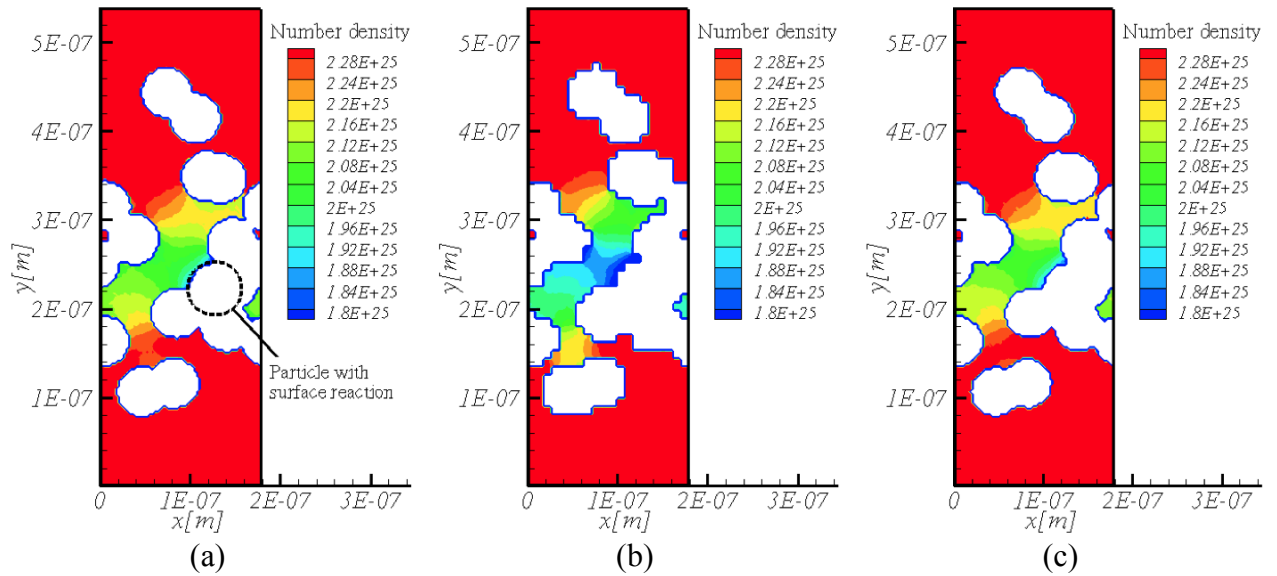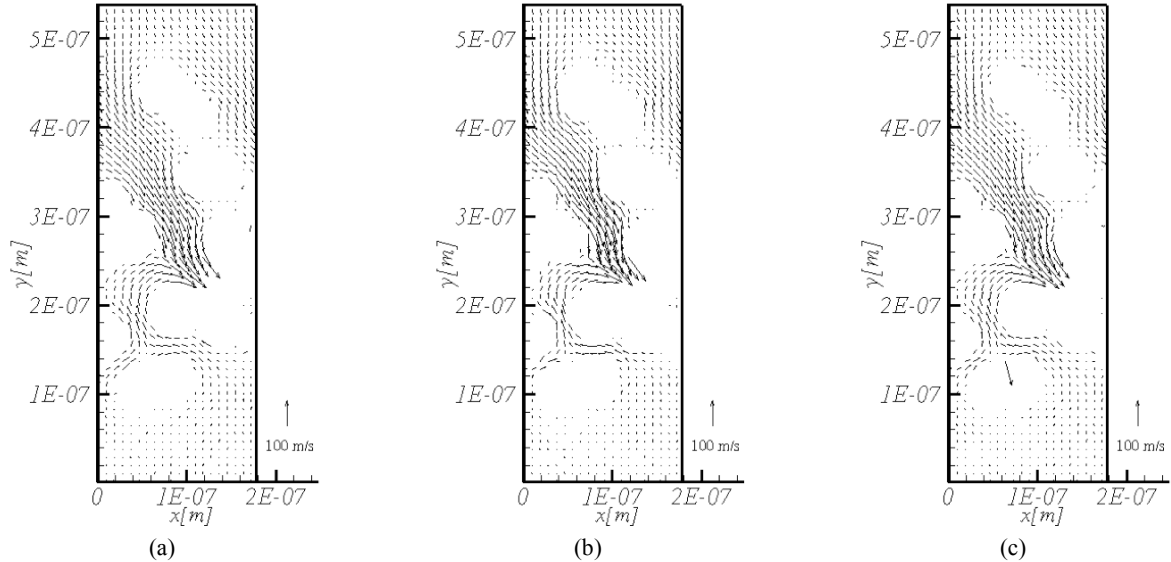

FIGURE 3. Number density distributions of H_2 molecules. (a) Cylinders, (b) Squares (d=9 nm), (c) Polygons (θ_0=30 degrees).
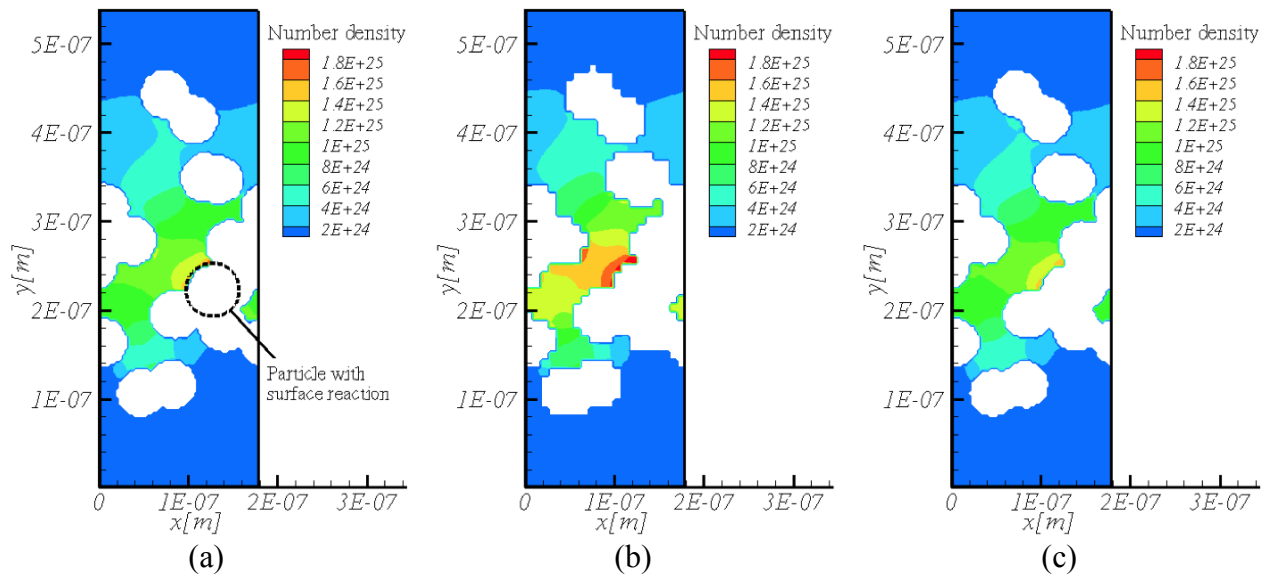
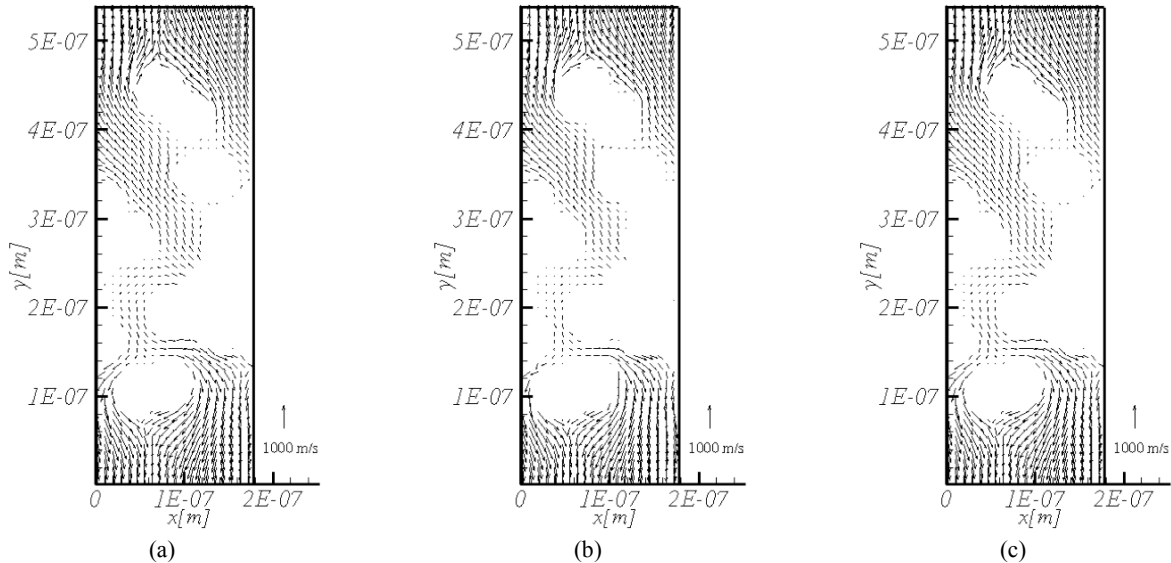
FIGURE 4. Number density distributions of H atoms. (a) Cylinders, (b) Squares (d=9 nm), (c) Polygons (θ_0=30 degrees).

Figure 5 and 6 show the velocity distributions of H_2 molecules and H atoms, respectively. H_2 molecules flow into the solid particle with the surface reaction and H atoms flow from the particle with the surface reaction out of the computational region in all cases. Although the configuration of flow channel is changed to some extent because of the simplification by squares as shown in Fig. 3(a) and (b), the velocity distribution of H_2 molecules shown in the case of simplification by squares in Fig. 5 (b) is still close to the result obtained without simplification in Fig. 5(a).

| (a) | (b) | (c) |

FIGURE 5. Velocity distributions of H_2 molecules. (a) Cylinders, (b) Squares(d=9 nm), (c) Polygons(θ_0=30 degrees).

| (a) | (b) | (c) |

FIGURE 6. Velocity distributions of H atoms. (a) Cylinders, (b) Squares(d=9 nm), (c) Polygons(θ_0=30 degrees).

To research an effect of the simplifications quantitatively, we compare number densities and flow velocities along a horizontal line. Figures 7 and 8 show number density distributions of H_2 molecules and H atoms at y=268.5 nm, respectively. Figures 9 and 10 show distributions of velocity components v_y of H_2 molecules and H atoms at y=493.5 nm, respectively. The distributions of number densities and velocities for the simplification by polygons of θ_0=30 degrees agree well with results of the case without simplification, i.e., the case of cylinders. Even if we use larger angle θ_0=60 degrees, its results show rather good agreement with the case of cylinders. As for the simplification by squares, the velocity distribution obtained in the case of smaller size of squares shows good agreement with the case of cylinders but the number density distributions differ from that of the case of cylinders.

Even if we use much smaller squares, the result will differ from the result for the case without simplification because the area with the surface reaction is enlarged by this simplification.

Using squares for simplification induces an error but it has the advantage that judgment of molecular-wall collisions is easy. To improve the accuracy of this simplification, we adjust the probability of the surface reaction, P_r. If a circle with the radius of a is simplified by smaller squares, its circumference is enlarged from $2\pi a$ to $8a$. We change the reaction probability P_r in inverse proportion to increasing rate of circumference. Therefore, we replace the reaction probability P_r with $(\pi P_r)/4$. Figures 11 and 12 show number density distributions of H_2 molecules and H atoms at $y=268.5$ nm line for the case of the simplification by squares and the case without simplification. When we use the revised probability, the results for small squares becomes close to the result of cylinder case. It shows the possibility of the simplification by squares.
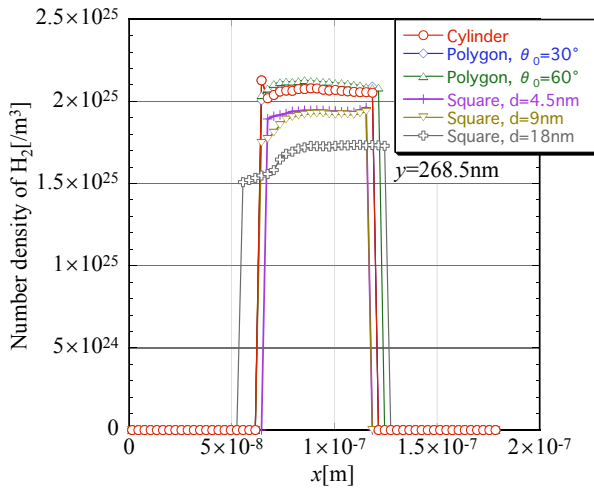

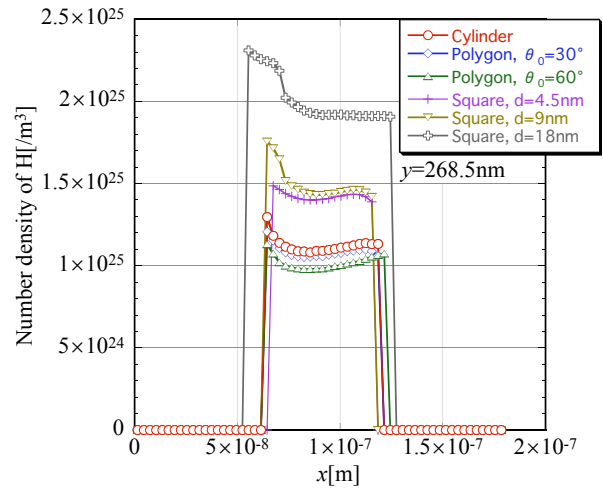**FIGURE 7.** Effect of simplification on the number densities of H_2 molecules.

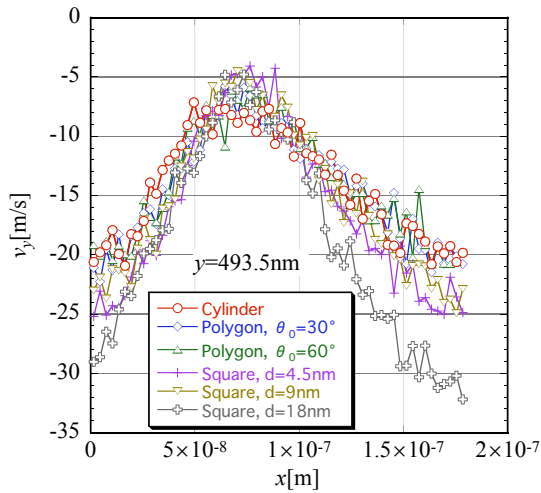**FIGURE 8.** Effect of simplification on the number densities of H atoms.

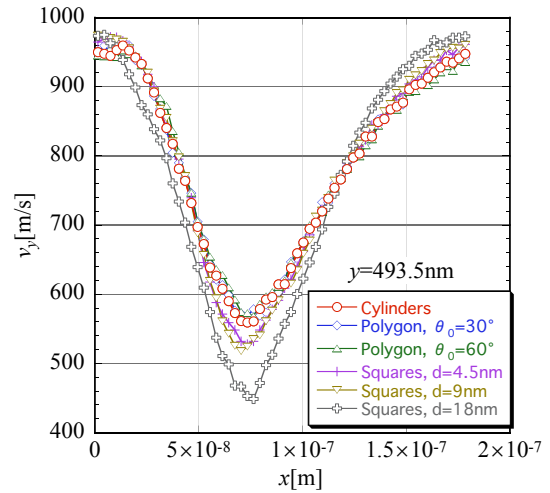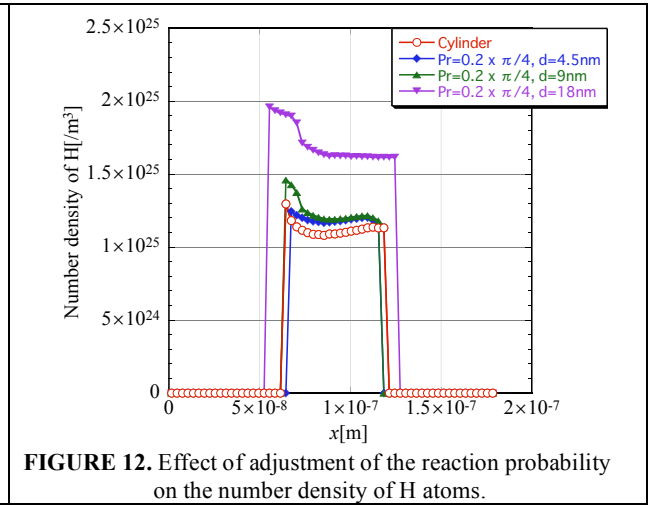**FIGURE 9.** Effect of simplification on the flow velocity v_y of H_2 molecules.

FIGURE 10. Effect of simplification on the flow velocity v_y of H atoms.

FIGURE 11. Effect of adjustment of the reaction probability on the number density of H_2 molecules.

FIGURE 12. Effect of adjustment of the reaction probability on the number density of H atoms.
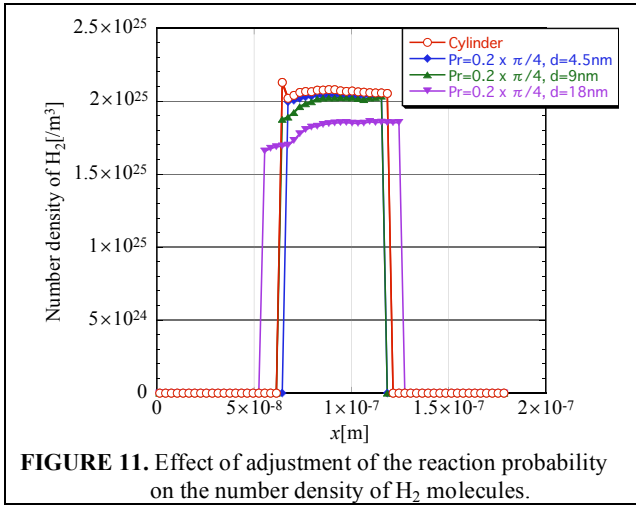
CONCLUSION

We have performed 2D DSMC simulations for a flow in a porous media with surface reaction. We conclude as follows.

(1) The number densities of H_2 molecules and H atoms in the case of the simplification by polygons agree well with the case of cylinder. On the other hand, the number densities in the case of the simplification by squares differ from the case of cylinder although it becomes closer to the case of cylinder to some extent when we use smaller squares.

(2) For the cases of the simplification by squares, the deviation of the number densities of H_2 molecules and H atoms from the case of cylinder can be largely improved by using the adjusted dissociation probability.

ACKNOWLEDGMENTS

REFERENCES

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2. K. Nanbu, *IEEE Transaction on Plasma Science* 28, 971, 2000