DSMC simulation of hydrogen dissociation on wire surface in resting gas

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Abstract. In the present work, the specific features of the simulation of hydrogen dissociation on the surface of a heated wire in a resting gas by the direct simulation Monte Carlo (DSMC) method were studied. The influence of the boundary conditions on the processes occurring near the wire, in particular, on the rate of atomic hydrogen production, was studied. The obtained data were compared with the experimental data.

1. Introduction

Atomic hydrogen is widely used in many technological applications [1], in particular, in the deposition of diamond structures from the gas phase [2, 3]. One of the ways to obtain it is the dissociation of molecular hydrogen on heated metal surfaces. Studies related to the dissociation of hydrogen on heated metal surfaces have more than a century of history, starting with the work of Langmuir and Mackay [4]. One of the characteristics of hydrogen dissociation is its experimental dependence on pressure which consists in stopping the increase in the rate of formation of atomic hydrogen on a heated surface with gas pressure increasing above 20 Torr (see for example [5]).

Now the development of science is difficult to imagine without numerical modeling. Numerical methods can significantly complement the process information obtained during the experiments. The direct simulation Monte Carlo method (DSMC) is currently the most popular numerical method for simulation of the rarefied gas flows [6]. Originally developed for solving problems associated with high-altitude aerodynamics, it has found application in a wide range of problems where it is important to take into account changes in the state of a gas over several mean free paths. One of the promising areas of its application is the simulation of the interaction of gas with surfaces, both in order to modify them and to use the catalytic properties of surfaces to activate the gas. This raises the problem of modeling the heterogeneous reactions in the framework of the DSMC method.

The probabilistic approach to simulation of heterogeneous reactions naturally incorporates into the DSMC method [7]. Its implementation requires data on the rates of heterogeneous reactions. One of the common approaches to estimating the rates of hydrogen dissociation-recombination reactions is related to the analysis of experimental measurements of the energy balance of hot wire loss to radiation, gas heating (thermal conductivity) and heterogeneous reactions [4,5,8,9]. For example, note the work [8], where a numerical-experimental two-step model of dissociation-recombination of hydrogen when interacting with the heated tantalum surface is proposed within the framework of the
continuum approach. This model allows taking into account the dependence of hydrogen dissociation on pressure.

The present work is devoted to the specific features of the DSMC simulation of hydrogen dissociation on the heated wire surface in a resting gas. Special attention is paid to the influence of boundary conditions on the simulation results.

2. Statement of physical problem, method and model description

It is assumed that an infinite cylinder of diameter $D = 0.003$ m heated to temperature $T_w$ is placed in a hydrogen gas atmosphere. At distance $L$ from the cylinder surface there is an outer imaginary cylindrical surface, on which the unperturbed state of the gas with pressure $P_0$ and temperature $T_0$ is simulated (Fig. 1). To simulate the interaction of hydrogen with the heated cylinder, a one-dimensional DSMC algorithm is developed. The algorithm includes simulation of heterogeneous reactions based on a two-step model of hydrogen dissociation-recombination [8]. The constants of the reaction rates are taken from [8]. To simulate the two-step model under consideration, an approach to the simulation of catalytic reactions by the DSMC method from the work [7] is used.

The VSS model with parameters corresponding to molecular and atomic hydrogen [10] was used to describe the interaction of gas particles in the DSMC simulation. The interaction of particles with the surface is the main point of interest in this problem. When gas particles collide with the surface, it is necessary to simulate the exchange of momentum and energy, the adsorption and desorption of atoms, the dissociation of molecular hydrogen and the recombination of atomic hydrogen. The process of gas particles exchanging momentum and energy with the surface was described using the model of specular-diffuse reflection [6], determined by the accommodation coefficient $\alpha$. The other processes are part of the two-step model.

In [8], a numerical-experimental two-step model of hydrogen dissociation-recombination when interacting with the surface of heated tantalum is proposed. Two reversible gas-surface reactions are considered:

$$S^* + H_2 = SH + H \quad SH = H + S^*$$

Figure 1. Computational domain.

Here, $S^*$ denotes the free surface site on the surface of a solid, $H_2$ and $H$ are the hydrogen molecule and atom in the gas phase, $SH$ is the hydrogen atom attached to the surface site. A distinguishing feature of this model is a decrease in the probability of hydrogen dissociation with increasing pressure due to an increase in the occupation degree of surface activation sites. The two-step model was developed using experimental data on the hydrogen dissociation on a tantalum wire. In this case, mass spectrometry measurements of the gas composition and the thermal model of the wire were used to estimate the reaction rate constants. The developed model includes the dependence on the surface...
temperature and is applicable to a wide range of pressures (from 5 Torr to 100 Torr). Thus, it compares favorably with existing data on the probability of dissociation obtained for specific temperatures and usually for low-pressure conditions [10–12].

The densities $n_{H_2}$ and $n_H$ of molecular and atomic hydrogen, their temperature, occupation degree of surface sites $\Theta$ (ratio of the number of occupied sites to their total number), probability of dissociation $P_d$, recombination $P_r$, catalytic source power $Q$ (differences in the rates of birth and death of atoms H per 1 cm$^2$ surface per second), the degree of hydrogen dissociation $K_d=n_H/(2n_{H_2}+n_H)$ were calculated in the course of the DSMC calculations.

3. Results and discussion

A numerical study was conducted for the following set of parameters: unperturbed gas pressure $P_0 = 20$ Torr, surface temperature $2200 \leq T_w \leq 2600$ K, $0.002 \leq L \leq 0.01$ m. For numerical simulation of the problem by the DSMC method, the accommodation coefficients on the surface, the distance $L$, and the gas temperature and composition on the outer surface must be specified. Note that complete absorption of the particles hitting the outer surface was simulated, but to ensure the specified temperature and pressure, the influx of particles from the outer surface was simulated. In doing so, different variants of the influx of molecular hydrogen or a mixture of molecular and atomic hydrogen were considered. In what follows, the influence of different parameters on the simulation results is considered.

![Figure 2](image_url)

**Figure 2.** a) The spatial distribution of the translational temperatures of molecular (solid lines) and atomic (dashed lines) hydrogen for four values of the accommodation coefficient ($\alpha=0, 0.25, 0.5, 1.0$). b) Occupation degree $\Theta$, catalytic source power $Q$, probability of dissociation $P_d$ and recombination $P_r$, depending on the accommodation coefficient $\alpha$.

Note that the accommodation coefficient determines the heat flux from the wire surface to the gas and thus affects the temperature of the gas near the surface. In addition, the number of collisions of gas particles with the surface area $S$ per unit of time can be estimated by the formula

$$N = n u_T S / 4 = n S (T / 2 k \pi m)^{1/2}, \quad (2)$$

where $n$ and $T$ are the density and the temperature of gas near the surface, $u_T$ is the average thermal velocity of particles, $k$ is the Boltzmann constant. So the accommodation coefficient also affects the number of collisions. The value of accommodation coefficient $\alpha = 0.414$ taken from [14] was used for construction of two-step model in [8, 13].
Figure 2 shows the simulation results for different values of the accommodation coefficient. The parameters of the problem are $T_w = 2440$ K, $T_0 = 1390$, $L = 0.002$ m. Only the inflow of molecular hydrogen from the outer surface was simulated. Note that the difference in the temperatures of molecular and atomic hydrogen is observed only near the surface of the wire and the outer surface. Moreover, the difference increases with a decrease in the accommodation coefficient. The occupation degree and the probability of recombination slightly increase with a decrease in the accommodation coefficient, while the probability of dissociation practically does not change. All this leads to a decrease in the source power with a decrease in the accommodation coefficient.

Figure 3a shows the simulation results for different values of the flux of atomic hydrogen from the outer surface. The parameters of the problem are $T_w = 2440$ K, $T_0 = 1390$, $L = 0.002$ m. To change the flux of atomic hydrogen, we used the coefficient $q$, which determines the proportion of the incoming flux. When $q = 1$, the flux corresponded to the total value of the flux determined from the data of [13]. It turned out that the flux of atomic hydrogen from the outer surface practically does not affect the temperature distribution due to its small value. As expected, it practically did not affect the probabilities of dissociation and recombination. There is a slight increase in occupation degree with increasing flux. Nevertheless, a considerable decrease in the catalytic source power is observed with an increase in the flux of atomic hydrogen. This is due to an increase in the number of atomic hydrogen in the computational domain, which leads to an increase in the number of recombination.

Figure 3b shows the simulation results for different values of distance $L$ between the wire surface and the outer surface. The wire surface temperature is $T_w = 2360$ K. At first, a reference calculation with maximum value $L = 0.01$ m and value $T_0 = 840$ K was executed. Then, calculations were carried out at smaller values of distance $L$, using the values of the temperature $T_0$ withdrawn from the corresponding data of the reference calculation. In this case, two approaches to simulate the flux of atomic hydrogen from the outer surface were considered: the zero flux and the flux according to the atomic hydrogen density withdrawn from the data of the reference calculation (lines with marks at the Fig. 3b). The spatial distributions of temperature of molecular hydrogen coincided well for all calculations. With a decrease in the computational domain, the outer boundary conditions begin to
influence the calculated parameters (Fig. 3b). When using the first approach (zero flow of atomic hydrogen), a decrease in distance $L$ leads to a decrease in the occupation degree, an increase in the dissociation probability, a decrease in the recombination probability, and, accordingly, a significant increase in the catalytic source power compared to the reference results. The use of the second approach made it possible to improve the situation, as the occupation degree, catalytic source power and the probability of dissociation and recombination became close to the reference results. Figure 4 shows the spatial distribution of the hydrogen dissociation degree for these calculations. The use of a zero flux leads to a decrease in the hydrogen dissociation degree as the distance $L$ decreases. The use of the atomic hydrogen flux from the data of the reference calculation made it possible to obtain a dissociation degree close to the reference results.

Figure 4. Spatial distribution of the dissociation degree for different values of the distance $L$. The lines without marks relate to the zero flux of atomic hydrogen from the outer surface. The lines with marks relate to the flux according to the atomic hydrogen density withdrawn from the data of the reference calculation.

Figure 5. The spatial distribution of the translational temperature of molecular hydrogen.

In [9], experimental values of the hydrogen temperature depending on the distance to the tantalum wire surface were obtained. Note that a coiled wire was used in this experiment. Based on these data, the calculation was carried out for the following set of parameters: $T_w = 2360$ K, $T_0 = 840$, $L = 0.01$ m. Figure 5 shows the experimental data from [9] and our numerical data for two variants of the accommodation coefficient: 1) $\alpha = 0.414$ and 2) values of the accommodation coefficient for molecular $\alpha_{H_2} = 0.026$ and atomic hydrogen $\alpha_{H} = 0.013$ calculated by the Baule formula. The Baule formula [15] $\alpha = 2.4^* (m/M)/(1 + m/M)^2$ was proposed for estimating the accommodation coefficient for the gas particle reacting with a clean surface. Here $m$ is the mass of gas particle and $M$ is the mass of surface atom. In [16], it was suggested to use this formula to estimate accommodation coefficients for the temperature range under consideration. A fairly good agreement between the numerical data at accommodation coefficients estimated by the Baule formula and experimental data on temperature [9] can be observed.

Conclusions
In the present work, the specific features of the DSMC simulation of hydrogen dissociation on the surface of a heated tantalum wire in a resting gas were studied. It is shown that the accommodation
coefficients significantly affect the gas temperature. When the accommodation coefficient decreases, the occupation degree and the recombination probability slightly increase, and the catalytic source power decreases.

The calculations for different values of the atomic hydrogen flux from the outer surface showed that it has little effect on the dissociation and recombination probability and the occupation degree. Nevertheless, a rather significant decrease in the catalytic source power with an increase in the atomic hydrogen flux is observed. In addition, a significant dependence of the hydrogen dissociation degree on the atomic hydrogen flux from the outer surface can be noted. The performed numerical study showed that the use of zero flux of atomic hydrogen from the outer surface is reasonable only if the outer surface is sufficiently far from the wire surface. The correct assignment of the atomic hydrogen flux improves the situation, as the occupation degree, the catalytic source power, the probability of dissociation and recombination, and the degree of hydrogen dissociation become close to the reference data. A good agreement between the numerical and experimental data on temperature was obtained when using accommodation coefficients estimated by the Baule formula.

The study allows us to estimate the degree of influence of different boundary conditions on the temperature and composition of the gas mixture, the probabilities of dissociation and recombination, and the occupation degree of the surface sites. The obtained results can be useful for correction of the parameters of the two-stage model of hydrogen dissociation-recombination using the DSMC method and new experimental data.

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