Comparison of different approaches to simulation of heterogeneous reactions by DSMC method

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Abstract. The present work is devoted to simulation of hydrogen dissociation on the surface of a heated wire in a resting gas by the direct simulation Monte Carlo (DSMC) method. Two approaches to simulating heterogeneous reactions are investigated: with and without regard to the velocities of particles impinging on the surface. A numerical study was performed based on a two-step hydrogen dissociation-recombination model.

1. Introduction

The direct simulation Monte Carlo (DSMC) method is widely used to solve problems that require taking into account changes in the gas state at several mean free paths [1]. One of the promising areas of its application is the simulation of gas interaction with surfaces, both for their modification and gas activation with the use of catalytic properties of the surfaces.

Various approaches for modeling heterogeneous reactions within the framework of the DSMC method have been developed in recent years [2-5]. All of them are based on using a microscopic probability of a reaction, i.e. the probability that a particle impinging on the surface enters into a heterogeneous reaction. The microscopic probability is usually selected based on the reaction rate constant obtained from experimental and theoretical data. In this case, it is important to take into account the features of the interaction of particles with the surface [5]. Approaches of varying degrees of complexity are considered, namely, those taking into account the velocity of the impinging particle, the occupation degree of the active sites of the surface, and the possibility of heterogeneous reactions between particles on the surface. In these cases, errors of various nature arise, in particular, a bias in the value of the macroscopic reaction probability [5].

The present work is dedicated to the analysis of various approaches to simulate heterogeneous reactions by the DSMC method by the example a two-step model of hydrogen dissociation-recombination on a heated surface. Two approaches to simulating heterogeneous reactions are considered: one takes into account the velocities of particles impinging on the surface, and another one disregards it.

2. Statement of physical problem, method, and model description

The main approach to calculating the microscopic probabilities needed to simulate heterogeneous reactions by the DSMC method is to use reaction rate coefficients. In general terms, a change in the
surface number density $n_{HS}$ of adsorbed hydrogen atoms H under the influence of a heterogeneous reaction is determined by the equation:

$$\frac{dn_{HS}}{dt} = \pm Kn_{gas}n_{S},$$

(1)

where $K = AT^b \exp(-E/kT)$ is the reaction rate constant, $n_{gas}$ is the number density ($m^{-3}$) of gas particles that take part in this reaction, $n_S$ is the surface number density ($m^{-2}$) of adsorbed hydrogen atoms or the number density of free surface sites (depending on the reaction under consideration). The macroscopic probability of the reaction is determined by the equation: $P = \frac{\tilde{F}_g}{F_g}$, where $F_g$ is the flow of particles impinging on the surface, $	ilde{F}_g$ is the flow of particles impinging on the surface and participating in the heterogeneous reaction. The flow of particles impinging on the surface can be determined by the formula $F_g = \sqrt{2\pi m/kT_g}n_{gas}$. Here $k$ is the Boltzmann constant, $T_g$ is the gas temperature, $m$ is the mass of a gas particle. The flow of particles involved in chemical reactions can be determined by formula (1): $\tilde{F}_g = \left| \frac{dn_{HS}}{dt} \right| = Kn_{gas}n_{S}$. Then

$$P(T_{gas}) = \frac{\tilde{F}_g}{F_g} = \sqrt{2\pi m/kT_g} \cdot Kn_{S},$$

(2)

In [2, 4], microscopic reaction probability was derived from the known reaction rate constant based on the following considerations. It was assumed that the microscopic probability of the reaction $p$ depends on the particle velocity along the normal to the surface $v_n$. Then the macroscopic probability of the reaction, which depends on the gas temperature, is expressed as the mean of the microscopic probability by the formula:

$$P(T_{gas}) = \int_0^\infty p(v_n)v_nf(v_n,T_{gas})dv_n.$$

(3)

Here

$$f(v_n,T_{gas}) = \left(\frac{m}{2\pi kT_{gas}}\right)^\frac{3}{2} \exp\left(-\frac{mv_n^2}{2kT_{gas}}\right)$$

(4)

is the Maxwellian distribution function. In this case, the formula for the simulation of the microscopic probability has the following form [4]:

$$p(v_n) = 2K(T_n)n_{S}/v_n.$$

(5)

A simpler way is to use the macroscopic reaction probability itself as a microscopic probability:

$$p = P(T_{gas}).$$

(6)

In the present work, two approaches to simulating heterogeneous reactions are compared: one taking into account the velocity of particle impinging on the surface (5) and another one disregarding it (6).

Atomic hydrogen is widely used in many technological applications [6], in particular, in the deposition of diamond structures from the gas phase [7, 8]. One of the methods of producing it is the dissociation of molecular hydrogen on hot metal surfaces. To simulate the dissociation process, the rates of heterogeneous reactions (the probability for a particle impinging on a surface to enter a heterogeneous reaction) are needed. Mass spectrometric measurements, analysis of heat fluxes, optical spectroscopy methods, and molecular dynamics methods are used to obtain such data for hydrogen [9–15]. In [16], within the framework of the continuum approach, a numerical-experimental two-step model of hydrogen dissociation in contact with the heated tantalum surface was proposed. This model was developed using experimental data on the dissociation of hydrogen on a tantalum wire. Mass spectrometric measurements of the gas composition and the thermal model of the wire were used to evaluate the reaction rate
constants [16]. The model considers four gas-surface reactions (dissociation, recombination, desorption, and adsorption):

\[
S^* + H_2 = SH + H, \quad SH + H = S^* + H_2, \quad SH = S^* + H, \quad S^* + H = SH. \tag{7}
\]

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.

It is assumed that an infinite cylinder of radius \(R = 1.5\) mm heated to a temperature \(T_w\) is placed in a hydrogen gas atmosphere. At a 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 (figure 1).

![Figure 1. Computational domain.](image)

To simulate the interaction of hydrogen with the heated cylinder, a one-dimensional DSMC algorithm is developed [17]. The constants of the reaction rates are taken from [16]. 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. A numerical study was conducted for the following set of parameters: unperturbed gas pressure \(P_0 = 20\) Torr, surface temperature \(2200\) K \(\leq T_w \leq 2600\) K, \(L = 2\) mm, and accommodation coefficient \(\alpha = 0.414\). The calculation parameters were taken from [16]. In [16], the value of the accommodation coefficient taken from [18] was used for constructing a two-step model. In the course of the numerical study, the influence of approaches (5) and (6) under consideration on the power of the catalytic source of atomic hydrogen \(Q\) (the difference between the rates of birth and death of hydrogen atoms per 1 cm\(^2\) of the surface per second) and the degree of occupation of surface sites \(\Theta\) were studied.

3. Results and discussion

At the current moment, there is no established approach to assessing the effect of velocity of impinging particles on the rate of heterogeneous reactions. This is probably due to the large number of factors affecting the heterogeneous reaction. Various approaches have been developed. In particular, it is believed that a particle must have energy greater than the activation energy to enter the reaction [14]. The authors of [19] describe a nonlinear dependence of the probability of hydrogen dissociation with an increase in the energy of particles impinging the surface. In [15, 20], the molecular dynamics method was used to study the effect of the impinging particle energy on the probability of hydrogen recombination. In this paper, we analyze two approaches to simulating heterogeneous reactions in the framework of the DSMC method and assess their effect on the simulation results. Note that the use of formula (6) requires knowing the value of the gas temperature. In the numerical experiments we used temperature data obtained from preliminary calculations. When using the second approach, the probability \(p(v_n)\) calculated by formula (5) can be greater than one. In this case, the following expression is proposed to be used for simulating the microscopic reaction probability [4, 5]:
\[ \tilde{p}(v_n) = \begin{cases} p(v_n) & \text{if } p(v_n) < 1 \\ 1 & \text{otherwise}. \end{cases} \] \tag{8}

It is clear that using formula (8) leads to a bias in the obtained macroscopic probability. Let us estimate this bias:

\[ \Delta P = P(T_{gas}) - \int_0^\infty \tilde{p}(v_n)v_n f(v_n, T_{gas}) dv_n - \int_0^\infty v_n f(v_n, T_{gas}) dv_n. \] \tag{9}

Using formulas (2), (3), (4), (5), (8), (9), we obtain an analytical expression for the relative bias:

\[ \frac{\Delta P}{P(T_{gas})} = \text{erf}\left(\frac{P(T_{gas})}{\sqrt{\pi}}\right) - \frac{\left(1 - \exp\left(-P^2\left(T_{gas}/\pi\right)\right)\right)}{P(T_{gas})}. \] \tag{10}

The dependence of the relative bias on the value \( P \) is shown in figure 2a (line 1). As can be observed, the relative bias increases with increasing \( P \).

\[ \Delta P/P \]

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{The relative bias in the macroscopic reaction probability (a) and correction factor \( q \) (b). Lines correspond to analytical dependencies: 1 – formula (10), 2 – formula (13), 3 – formula (12). Symbols correspond to calculations by the DSMC method: 4 – using expression (8), 5 – using expression (11).}
\end{figure}

To reduce bias, the following way can be used. We introduce a correction factor \( q \) such that

\[ \left(\int_0^\infty v_n f(v_n, T_{gas}) dv_n + q\int_0^\infty p(v_n)v_n f(v_n, T_{gas}) dv_n\right)/C = P(T_{gas}). \]

Here \( C = \int_0^\infty v_n f(v_n, T_{gas}) dv_n, a = 2K(T_w)n_s \). Thus, to determine the microscopic reaction probability, the following expression can be used:

\[ \tilde{p}_1(v_n) = \begin{cases} q \cdot p(v_n) & \text{if } p(v_n) < 1 \\ 1 & \text{otherwise}. \end{cases} \] \tag{11}

In this case, the correction factor \( q \) is determined by the expression:

\[ q = 1 + \left(\text{erf}\left(\frac{P(T_{gas})}{\sqrt{\pi}}\right) - \frac{\left(1 - \exp\left(-P^2\left(T_{gas}/\pi\right)\right)\right)}{P(T_{gas})}\right)\left(1 - \text{erf}\left(\frac{P(T_{gas})}{\sqrt{\pi}}\right)\right). \] \tag{12}
The dependence \( q(P) \) is shown in figure 2b. Using formulas (3), (4), (11), and (12), we obtain an analytical expression for relative bias when using expression (11) to simulate the macroscopic reaction probability:

\[
\frac{\Delta P_i}{P(T_{gas})} = \text{erf}\left( q \cdot P(T_{gas}) \sqrt{\pi} \right) - \frac{1}{P(T_{gas})} \exp\left( - \frac{q^2 \cdot P^2(T_{gas})}{\pi} \right). \tag{13}
\]

The dependence of this value on the \( P \) is shown in figure 2a (line 2). The relative bias, in this case, is significantly less than the original one.

To analyze the effect of approaches (5) and (6) on the results of simulating heterogeneous reactions, several series of calculations by the DSMC method were performed. At the first stage, test calculations were conducted. These calculations were performed at a given value of the occupation degree, i.e. several adsorbed hydrogen atoms were generated on the surface at the beginning of each computation. The simulated gas mixture consisted of 10% atomic and 90% molecular hydrogen. The number of events was sampled after each time step, but the reactions themselves were not modeled, i.e. the mixture composition and the occupation degree did not change. The gas temperature was equal to the surface temperature to avoid possible inaccuracies when using the formula (2): \( T_{gas} = T_0 = T_w \). Figure 2a shows the relative bias obtained as a result of test calculations using formula (8) (symbols 4) and formula (11) (symbols 5). Note an agreement between the analytical and calculated data. Since \( P \) values are relatively small and the bias is only a few percent for the considered calculation options, formula (8) is used in the further numerical experiments.

**Figure 3.** The reaction probabilities (a) and the ratio \( W \) (b) obtained by the DSMC method using formula (5) (solid lines) and formula (6) (dashed lines) for different temperatures. Lines 1 and 4 correspond to the dissociation probability, lines 2 and 5 – to the recombination probability, and lines 3 and 6 – to the adsorption probability.

Figure 3a shows the macroscopic probabilities of heterogeneous reactions (dissociation, recombination, and adsorption) obtained as a result of test calculations using formula (5) and (6) for different temperatures. Figure 3b shows the corresponding ratios \( W \) of calculated probabilities to given ones. It can be observed that the calculated probabilities are quite close to the given ones. The reaction probabilities obtained using formula (5) are slightly smaller due to the bias.

At the second stage, DSMC calculations with a complete simulation of the reactions were performed. The gas temperature on the outer surface was \( T_0 = 1390 \) [16]. The inflow of molecular hydrogen from the outer surface and complete absorption of the particles hitting the outer surface was simulated. The gas temperature necessary for the implementation of approach (6) was taken from preliminary
calculations. Figure 4 shows the probabilities of the considered reactions, the surface occupation degree, and the catalytic source power of atomic hydrogen obtained by approaches (5) and (6). Both approaches give close results.

Conclusions
In the present work, we have analyzed two approaches to simulating heterogeneous reactions in the framework of the DSMC method: one, taking into account the velocity of a particle impinging on the surface, and another, not taking it into account. An analytical estimate of the bias of the first approach has been constructed. A technique for its reduction has been proposed. A numerical study using a two-step model of hydrogen dissociation-recombination by the example of a heated tantalum wire placed in a hydrogen atmosphere has been carried out. In the course of the study, the effect of the considered approaches on the power of the catalytic source of atomic hydrogen and the surface occupation degree has been studied. Both approaches under consideration are shown to give similar results.

![Figure 4. The reaction probabilities (a), the surface occupation degree Θ, and the catalytic source power of atomic hydrogen Q (cm²·s⁻¹) (b) obtained by the DSMC method using formula (5) (solid lines) and formula (6) (dashed lines). Lines 1 and 4 correspond to the dissociation probability, lines 2 and 5 – to the recombination probability, and lines 3 and 6 – to the adsorption probability. Lines 7 and 9 correspond to the surface occupation degree Θ, lines 8 and 10 – to the catalytic source power of atomic hydrogen Q.](image)

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