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Heterogeneous activation of rarefied hydrogen in thin tubes

M. Yu. Plotnikov [a, *], E.V. Shkarupa [b]

[a] Institute of Thermophysics SB RAS, Novosibirsk, Russia
[b] Institute of Computational Mathematics and Mathematical Geophysics SB RAS, Novosibirsk, Russia

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ABSTRACT

The direct simulation Monte Carlo method was used to study the rarefied gas flow through a cylindrical channel, taking into account heterogeneous reactions of dissociation-recombination on the surface. The main emphasis was placed on the study of the influence of heterogeneous processes on the degree of dissociation of the flow, coming out of the channel. The study was conducted for different relations of the channel length to its radius, coefficients of dissociation and recombination, and in a wide range of gas rarefaction degrees: from free molecular to transitional regimes. The obtained results may be useful for optimization of gas-dynamic sources of activated gas, based on thin tubes.

1. Introduction

Currently the method of Hot-Wire Chemical Vapor Deposition (HWCVD) is widely used for thin film deposition. The main feature of the method is the deposition of films from a gas-precursor that has to be activated on metallic surfaces. For activation researchers use wires, placed in a virtually resting gas [1,2] or in high-speed flow [3], as well as cylindrical channels of different diameters and lengths (see, e.g. Ref. [4]). One of the ways of gas-precursor activation is its dissociation to active components on the surface of the activator. At that it is necessary to consider the possibility of the reverse reaction, i.e. recombination. The presented work is devoted to the numerical study of gas-dynamic aspects of the rarefied gas flow in a thin tube with consideration of dissociation and recombination on the surface. It should be noted that the gas flow in a cylindrical channel was studied in a considerable number of theoretical, numerical and experimental works (see, e.g. the review [5]). However, the vast majority of researchers considered gas flow regardless of possible influence of heterogeneous processes on the surface. The closest to the subject is work [6], where the flow of hydrogen in a high-temperature cylindrical tungsten channel is used to show the importance of considering the processes of dissociation and recombination in the analysis of gas dynamics of the flow in the tube. Following this work we consider the flow of hydrogen in a cylindrical channel. On the one hand, the choice of hydrogen is due to its wide use in many industrial chains (cleaning of surfaces, vacuum welding, deposition of diamond-like films, deposition of silicon films, development of sensors, etc.). On the other hand, it simplifies fundamental research due to the possibility to consider a mixture of two components.

In this study the direct simulation Monte Carlo method (DSMC) was used [7] to provide the greatest opportunities for numerical analysis of the rarefied gas flows. The main emphasis is on the study of the influence of heterogeneous processes of dissociation and recombination on the dissociation degree of gas, coming out of a cylindrical channel. The obtained results may be useful for optimization of gas-dynamic sources of activated gas, based on thin tubes.

2. Problem statement

Let the gas with preset flow rate is supplied on the left in a cylindrical channel of radius R and length L. The gas flows from the channel into vacuum. Let us introduce a Cartesian coordinate system XYZ for convenience in describing the problem (Fig. 1). Assume that the cylindrical channel axis coincides with the axis X. The left input to the channel is in the cross-section $x = 0$. The gas is supposed to flow into the channel from the unperturbed region with the density n_0 and the temperature T_0. If a particle returns to the plane of the channel input, it is specularly reflected. The surface temperature of the channel walls T_w is constant. On the right of the

* Corresponding author.
E-mail addresses: plotnikov@itp.nsc.ru (M.Yu. Plotnikov), sev@osmf.sscc.ru (E.V. Shkarupa).

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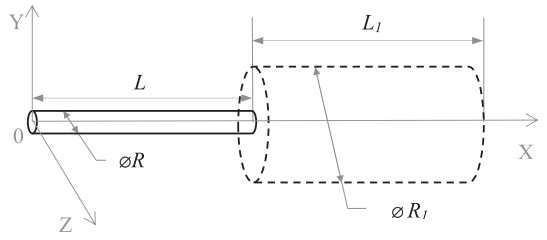

Fig. 1. Computational domain.

first channel there is a calculated area in the form of a second cylindrical channel. It ensures the correct simulation of gas outflow into vacuum. The radius of the second channel is $R_1 > R$, and its length is L_1. Particles move freely from one channel to another. If a particle hits the wall of the second channel, it is absorbed. In collision with the wall of the first channel a hydrogen molecule can dissociate into two atoms, and two hydrogen atoms can recombine into a molecule:

$H_2 \leftrightarrow 2H$.

To substantiate the boundary condition at the inlet we can present the following arguments. Particles "forget" its initial distribution function sufficiently rapidly because of collisions with the channel walls and with other particles [8]. Supply of a gas with preset flow rate directly into an activating tube is frequently used in experiments on thin film deposition.

To describe the process of particle interaction with the surface the model of specular-diffuse reflection [7] was used. This statistical model is widely used in calculations of rarefied flows and is well proven. It requires a number of parameters. The first one is the thermal accommodation coefficient α. It is determined [9] as the ratio

$$\alpha = \frac{E_i - E_r}{E_i - E_w},$$

where E_i and E_r are the energies of incident and reflected molecules, respectively, and E_w is the average energy of reflected molecules corresponding to the surface temperature. Thus a particle is reflected diffusely from the surface with complete accommodation of momentum and energy with the probability α, or it is reflected specularly with the probability $(1-\alpha)$.

To describe the dissociation (recombination) we use the coefficient α_d (α_r):

$$\alpha_d = \frac{J^-_{H_2} - J^+_{H_2}}{J^-_{H_2}},\ \alpha_r = \frac{J^-_H - J^+_H}{J^-_H},$$

where $J^-_{H_2}$ (J^-_H) and $J^+_{H_2}$ (J^+_H) are the particle fluxes of molecular hydrogen H_2 (atomic hydrogen H) impinging to and reflected from the surface, respectively. Thus a molecule of hydrogen with the probability α_d splits into two atoms or it remains a molecule with the probability $(1-\alpha_d)$. Similarly two atoms of hydrogen with the probability α_r recombine into a molecule or do not recombine with the probability $(1-\alpha_r)$.

Quite often such models use the coefficient of sticking α_s which describes the probability of a particle "sticking" to the surface (see, for example, [10]). Following the essence of the physical process, it is from the "sticky" particles that candidates for dissociation and recombination are chosen. In this formulation the sticking coefficient practically coincides with the coefficients of dissociation and recombination: a molecule with the probability α_d sticks to the surface and dissociates; atoms with the probability α_r stick to the surface and recombine. Therefore, the sticking coefficient is not used further in the article.

Since we consider the rarefied (relative to the channel radius) gas flow, the number of collisions with the walls exceeds the number of collisions in the gas phase. This allows neglecting the effect of gas-phase reactions. So dissociation and recombination in the gas phase was not considered.

Two values were used to evaluate the dissociation degree of hydrogen:

1) molar fraction of the dissociated particles:

$$K_d = \frac{\frac{1}{2}n_H}{n_{H_2} + \frac{1}{2}n_H}, \quad (1)$$

2) the particle flux ratio of the dissociated particles:

$$K_{d1} = \frac{\frac{1}{2}n_H V_H}{n_{H_2} V_{H_2} + \frac{1}{2}n_H V_H}. \quad (2)$$

Here n_H and n_{H_2} are densities of atomic and molecular hydrogen, and V_H and V_{H_2} are their velocity components along the axis X.

3. The numerical scheme

The core of the DSMC algorithm is the splitting of continuous motion of particles and their collisions into two successive stages:

- All particles move throughout a time interval Δt, according to their velocities. If particles cross the boundary surface certain actions are realized.
- Collisions between particles corresponding to the interval Δt are simulated. Velocities of particles before collision are replaced by the ones, acquired after collision.

Usually the simulated region of the physical space is divided into cells, and a certain number of particles is simulated in each cell. The time change is performed in discrete steps Δt that are small compared with the average time between collisions of particles. The information necessary for the calculation of the macroparameters of the gas flow is sampled at each time step.

Due to the problem geometry the plane $y = 0$ was believed to be mirror-like. Ring cells were used for simulation. To describe the interaction of particles the VSS model [7] with the parameters corresponding to hydrogen was used (see Table A1 in the Appendix). To characterize the degree of gas rarefaction the Knudsen number $Kn = \lambda/(2R)$ was used. The free path λ was determined by the density n_0 and the temperature T_0. To reduce the problem to dimensionless form the temperature T_0, the density n_0, the free path λ and the most probable thermal velocity of particles at the temperature T_0 were taken as characteristic values.

The interaction of particles with the channel walls was simulated in the following sequence:

1. At first particles were selected for the chemical reactions according to the given probability (α_d or α_r). The particles formed as a result of the chemical reactions were reflected from the wall surface with complete accommodation of momentum and energy.
2. Then the particles which did not react chemically were reflected diffusely from the surface with complete accommodation of