Employing one-dimensional approach to calculate mixture composition evolution caused by gas-phase reactions for the gas flowing through a cylindrical channel

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Abstract. Two approaches to evaluate the mixture composition with a small reactive admixture for the gas flowing through a cylindrical channel are compared. Both are based on solving the Navier-Stokes equations. In the first one, the Navier-Stokes equations are solved for the reacting gas mixture. In the second one, they are solved for non-reacting mixtures and gas-phase reactions are taken into account by solving the one-dimensional (along the flow axis) chemical kinetics equations. Comparison of the obtained results for CH₄+H₂ mixture have shown the possibility of using of one-dimensional approach for correct description of the mixture composition evolution caused by gas-phase reactions.

1. Introduction

Studies of the rarefied gas flow through the channels of different configurations have more than a century-long history [1, 2]. Usually when modeling these processes, gas-phase and heterogeneous reactions are not considered, while heated channels are widely used for activation of passing gases for different applications [3]. The direct simulation Monte Carlo (DSMC) method [4] provides wide opportunities for detailed analysis of the flow through channels with inlets into the low-pressure zone. The DSMC method consists in simulation of the motion and collision of certain particles; therefore, it naturally allows taking into account gas-phase and surface chemical reactions [4]. The disadvantages of the method are its infeasible computational cost, in particular, for the correct description of gas mixtures with great difference in component concentrations (of several orders of magnitude).

An example of the DSMC method employment is its use for simulation of the processes within the gas-jet method of diamond structures synthesis from the hydrogen/methane mixture flow (with small ~1 % methane admixture), developed in recent years [5, 6]. It is based on thermal activation of the gas passing through the channel with heated walls. A distinctive feature of this approach consists in using the heterogeneous dissociation of hydrogen during its multiple collisions with a hot surface [7, 8]. For
optimizing the deposition processes, information on concentration of carbon-containing molecules and radicals formed during the gas-phase decomposition of methane is required. In paper [9], the DSMC method with surface chemical reactions on the channel walls and substrate was used for studying the gas-jet synthesis. For estimating the methane decomposition degree via gas-phase reactions a one-dimensional approach was used [9]. It is based on solving 1D chemical kinetics equations (equilibrium rate coefficients, no diffusion) with molecular and atomic hydrogen concentrations and methane concentration, as well as temperature and mixture velocity taken from the DSMC simulations. In [10], macroparameters of the gas-jet flow obtained while solving the Navier-Stokes equation and in the DSMC calculations are compared. Analysis performed in [10] shows, that, despite the relatively rarefied flow regime, the existence of zones with essential translational non-equilibrium, the difference in computational domains and computational algorithms, as well as results for macroparameters and deposition rate obtained within both methods are close to each other.

The main goal of our paper is to test the one-dimensional approach for estimating the evolution of the gas mixture composition caused by chemical reactions when the gas flows through the cylindrical channel. For that, simulations of the gas mixture evolution are performed using 1D chemical kinetic equations with the reaction set from [11] and macroparameters taken from the Navier-Stokes equations solution for the non-reacting mixture. The results are compared with the corresponding data obtained by solving the Navier-Stokes equations for reacting mixture with the same set of reactions and the same rate coefficients. One-dimensional approach is described in detail in [9].

2. Physical problem statement and method and model description

Computational problem statement is chosen to be close to an experimental setup for gas-jet deposition [5, 6]. A molecular hydrogen/methane mixture is fed into the cylindrical channel (figure 1). The channel consists of two parts: input (cold) section and output (hot) section. The length of the input section \( L = 0.01 \) m in all computations, whereas the length of the output section \( L \) is varied from 0.011 m to 0.033 m. Wall temperature of the input section is 300 K, and of the output section is 2400 K. A substrate is at the distance \( l_{\text{sub}} = 0.01 \) m from the channel exit. Substrate temperature is 1200 K. The diameters of the channel and substrate are 0.003 m and 0.016 m, respectively. Molecule hydrogen flow rate is 1500 sccm, and methane flow rate is 15 sccm. The mixture expands from the channel into the vacuum chamber. Background gas pressure in the vacuum chamber is set at 20 Torr. The hydrogen is assumed to dissociate and recombine on the channel walls and on the substrate. More details can be found in [10].

For simulation of the decomposition of the initial mixture, thirteen pairs of chemical reactions (forward and reverse) are taken into account [9, 11]. An 11-component mixture: \( \text{H}_2, \text{H}, \text{CH}_4, \text{CH}_3, \text{CH}_2, \text{CH}_2(\text{s}), \text{CH}, \text{C, C}_2\text{H}_2, \text{C}_3, \text{C}_2\text{H} \) is considered.

At the first stage no gas-phase reactions are taken into account. Spatial distributions of the number density of atomic hydrogen and of the mixture temperature obtained by solving the Navier-Stokes equations for non-reacting mixture are presented in figure 1. Simulation is done for channel length \( L = 0.022 \) m. Note that significant non-uniformity along the channel radius is observed at the entrance to the hot zone of the channel. However, the parameters are uniformly distributed along the channel radius downstream, which is important for correct application of the one-dimensional approach. Results for \( L = 0.011 \) mm and 0.033 mm show the similar pictures. At the second stage, the obtained macroparameters are used for calculating the evolution of the mixture composition within the 1D approach.

For verification of the 1D approach, similar simulations are performed by solving the 2D Navier-Stokes equations for the reacting mixture with the same set of reactions and rate coefficients [11]. Thermodynamic characteristics are calculated via the JANNAF coefficients. For more details see [10].
3. Results and discussion

For the correct use of the one-dimensional approach, the effect of gas-phase chemical reactions on the temperature and the velocity component $V_x$ (directed along the channel axis) has to be small. The distributions of these macroparameters along the channel axis for similar conditions are presented in [10]. There, the results are obtained on the basis of the Navier-Stokes equations with and without gas-phase reactions. It is clearly seen that the reactions make a minimal contribution to the change of flow velocity and temperature. Pressure variation is also insignificant, since variation of concentrations of both molecular and atomic hydrogen is small, while methane in the initial mixture is only 1%.

![Figure 1](image1.png)

**Figure 1.** Fields of atomic hydrogen molar fraction (top) and the temperature (bottom, in K) in the case without gas-phase reactions with $L = 0.022$ m.

![Figure 2](image2.png)

**Figure 2.** The number density ($m^{-3}$) of mixture species averaged over the channel radius obtained by the one-dimensional approach (lines without marks) and by solving the Navier-Stokes equations for the reacting mixture (lines with marks), $X$ in m.
Figure 2 presents the axial distributions of the number density of mixture species averaged over the channel radius for channel length $L = 0.022$ m. It can be seen that the evolution of the mixture composition along the axis, obtained by both approaches, is quite close, no matter that the difference in concentrations of the mixture components is of several orders. Maximum of the difference is observed in the area where reactions are initiated, and the difference decreases downstream.

For a clear representation of the results the relative deviation of the number density, calculated according the formula $N_0 = |n_{NS} - n_{1D}| / n_{NS}$ will be shown below. Here $n_{NS}$ and $n_{1D}$ are the number densities obtained by solving the Navier-Stokes equations with gas-phase reactions and within the one-dimensional approach. Relative deviations of the number densities at the exit from the channel and at the substrate are presented in figure 3.

![Figure 3. Relative deviation $N_0$ of number densities as a function of the channel length $L$ at the channel outlet (a) and near the substrate (b).](image)

The one-dimensional approach is seen to provide quite accurate data for the species concentrations at the exit of the channel. This can be primarily explained by the considered geometry: directional movement of the gas mixture along the tube, uniform heating along the radius and rather smooth change in the flow macroparameters along the axis (figure 1). The direction of gas movement is kept at a certain distance after leaving the channel. All that, as well as slowdown of the chemical reactions after the exit from the channel, guarantees the possibility of estimation of the evolution of the mixture composition in the domain between the channel outlet and the substrate within the one-dimensional approach.

It is generally accepted that H and CH$_3$ radicals play the main role in diamond deposition [12, 13]. Atomic hydrogen can form active sites on growing surface, passivate them or etch CH$_3$-groups. CH$_3$ radicals are the main bricks of carbon skeleton that preserve the memory about sp$^3$-hybridization. Still, as shown in [11] in some sets of chemical surface reactions such radicals as C$_3$ can play an important role in carbon deposition process due to direct insertion into the diamond structure. In a number of studies [12, 13], a possible contribution of C$_2$H$_2$ molecules to diamond synthesis is discussed.

Relative deviation $N_0$ of number density for the mixture components at the midpoint of the channel, at the channel outlet, at the middle point between the channel outlet and the substrate, and near the substrate are presented in histograms in figure 4. The relative deviation of the atomic hydrogen density varies from 0.005 to 0.05, depending on the points under consideration and the channel length (figure 4a). Relative deviation of CH$_3$ density is about 0.1 (figure 4a). This accuracy is sufficient for evaluation of diamond deposition rate in different conditions. The relative deviation for components with a lower number density, C$_2$H$_2$ and C$_3$, varies from 0.01 to 0.6 and from 0.05 to 1, respectively.
Thus, the error in estimating the deposition rate within the 1D approach is not significant if only those radicals are considered in the diamond formation concentrations of which are directly determined by the concentrations of the background gases (H$_2$, CH$_4$ and H, the last one can be considered as a background one since it is produced in surface reactions, which are taken into account in all simulations), such as CH$_3$. If the species that are produced during further steps of the reaction chain, such as C$_3$ or C$_2$H$_2$, significantly contribute to the deposition, the approach may be less accurate.

Figure 4. Relative deviation $N_0$ of the mixture components at the midpoint of the channel ($M = 1$), at the channel outlet ($M = 2$), at the middle point between the channel outlet and the substrate ($M = 3$) and near the substrate ($M = 4$). □ — $L = 0.011$ m, Δ — $L = 0.022$ m, ○ — $L = 0.033$ m.

Note that the channel length and the proximity of the substrate strongly influence the relative deviation. This fact should be taken into account when using a one-dimensional approach.

To estimate the contribution of the gas-phase reactions under consideration to gas heating, the enthalpy is calculated. It shows that gas-phase reactions slightly increase enthalpy. Thus, their contribution against the background of the general gas heating by channel walls cannot significantly influence the flow macroparameters.

Conclusions
One-dimensional approach for estimating the mixture composition evolution by solving the 1D chemical kinetic equations has been tested. Comparison with the exact Navier-Stokes equations solution shows that this approach can be applied to estimate the species concentration for flows, when the depositing species are obtained in one step reactions.

The obtained results allow employing this approach to optimize the process of gas-jet deposition of diamond structures, as well as to estimate the evolution of mixture composition along the reacting flow in the cylinder for a number of other similar applications.

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