

Hydrogen-Oxygen Detonation Study by the DSMC Method

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Abstract. The DSMC method was applied to perform a numerical study of detonation in an H_2/O_2 mixture with detailed chemical kinetics at the molecular level. Collision chemistry models were modified to correctly reproduce the chemical equilibrium in mixtures of polyatomic molecules. The DSMC results on homogeneous constant-volume adiabatic autoignition of the stoichiometric H_2/O_2 mixture are in good agreement with the numerical solution of equations of chemical kinetics. The results of the DSMC modeling of a nonstationary detonation wave for different values of pressure yield the velocity of detonation that coincides with the Chapman-Jouguet velocity. The structure of the detonation wave obtained in the DSMC simulation is in qualitative agreement with the Zeldovich – von Neumann – Doering theory.

Keywords: Direct Simulation Monte Carlo method, detonation, combustion

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INTRODUCTION

When studying numerically the propagation of detonation waves at small scales, the kinetic approach should be employed to take into account the effects associated with rarefaction and thermal non-equilibrium. The molecular kinetic description of the gas based on the solution of the Boltzmann kinetic equation is usually used for flows of a rather dilute gas, in particular, in problems of high-altitude aerothermodynamics of space vehicles, though it is also applicable for values of pressure typical for detonation processes (close to ground-level atmospheric pressure). The most effective numerical method for solving the Boltzmann equation is currently the Direct Simulation Monte Carlo (DSMC) method [1].

The problem of the internal shock-wave structure is the classical problem of the kinetic theory. During the last decades, many numerical solutions were presented for different kinetic gas models (see, e.g., [2-4]). It is even more challenging to apply the molecular kinetic description in investigating the detonation-wave structure. The main objective of the present work is the numerical modeling of the structure of a detonation wave in a hydrogen-oxygen mixture at the molecular kinetic level with the use of the DSMC method.

The previous DSMC detonation studies are based on chemical kinetics [5-8] with one or two irreversible reactions for unstructured particles. Though such reduced chemical mechanisms are widely used in the continuum CFD, they yield only qualitative estimates of detonation processes in the framework of the DSMC method. In contrast to the continuum approach, where realistic thermodynamic data can be used in the reduced chemical mechanism, the above-mentioned model of unstructured particles in the DSMC method corresponds to a monatomic gas with the ratio of specific heats $\gamma=5/3$, which is far from thermodynamic properties of real detonating mixtures.

Another approach of DSMC modeling of gas detonation implies using detailed chemical mechanisms and molecular models that correctly describe physical properties of molecules, in particular, take into account their rotational and vibrational energies. Such studies were started in [9] and continued in papers [10,11]. A detailed H_2/O_2 chemical kinetic mechanism for a six-species mixture of molecules with rotational and vibrational energies was implemented in the DSMC simulations taking into account

- rotation-translation (RT) and vibration-translation (VT) energy transfer processes;
- dissociation, exchange, and recombination reactions.

The DSMC modeling [10,11] of the non-stationary detonation generated by breakdown of the diaphragm between the channels of low and high pressure yielded the detonation wave propagating in a stoichiometric H₂/O₂ mixture with the Chapman-Jouguet velocity. The internal structure of this detonation wave obtained in the DSMC simulations agreed qualitatively with the steady detonation-wave structure calculated on the basis of the Zeldovich – von Neumann – Doering (ZND) theory. A considerable quantitative difference should be noted; in particular, the flow parameters in the chemically equilibrium state behind the detonation-wave front differed from theoretical predictions within 10%.

The use of the kinetic approach for describing detonation in an H₂/O₂ mixture is further validated in the present paper. In particular, the existing chemical models are modified to obtain a correct description of the state of chemical equilibrium. The results of DSMC simulations performed by the SMILE software system are compared with the solution of the chemical kinetics equations for the problem of self-ignition of the mixture at constant volume and with the results of the ZND theory for the problem of detonation-wave propagation.

COLLISION MODELS

Previous investigations [10,11] were performed with simple and widely used molecular collision models: Variable Soft Sphere (VSS) [12] model for elastic collisions, Larsen-Borgnakke [13] model for RT and VT energy transfer with temperature-dependent collision numbers, Total Collision Energy [1] model for the dissociation and exchange reactions, and its modification [4] for recombination reactions. The rotational and vibrational energies of molecules were assumed to be continuous, and anharmonicity of vibrations was not taken into account. An important fact here is that the implemented models were not completely consistent in terms of detailed balance, which probably was the reason for the above-mentioned differences from the ZND theory.

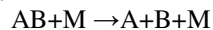
Collisions without chemical transformation. The VSS collision model was also used in the present study. The main difference in the description of internal energy of molecules from [10,11] was as follows. Continuous rotational and discrete vibrational energies were assumed. An anharmonic oscillator model was used for vibrations of diatomic molecules. Simple harmonic oscillators truncated at a dissociation energy E_d were used for each vibrational mode of the polyatomic molecule (H₂O), with each mode having its own relaxation number Z_v . A selection methodology with prohibited multiple relaxation events was implemented [14], which ensures exact agreement with specified rates of relaxation processes at the macroscopic level. Details of modeling chemical reactions are given below.

Chemical collisions. As far as the authors are aware, there are no complete data on cross sections of chemical reactions for the mechanism of combustion in the H₂/O₂ mixture in publications. One reason is the complexity of elementary chemical processes in this mechanism (in particular, reactions that involve polyatomic molecules, such as H₂O). For this reason, a conventional approach of the DSMC method with the use of cross sections obtained on the basis of macroscopic reaction rates is used here. The rate constants from H₂/O₂ ONERA chemical kinetic scheme for 6 species: H, O, H₂, O₂, OH, and H₂O were used. This kinetic scheme includes the following reactions:

- H₂O+M↔H+OH+M
- H₂+M↔2H+M
- H₂+O₂↔2OH
- H+O₂↔OH+O
- H₂+OH↔H₂O+H
- H₂+O↔OH+H
- 2OH↔H₂O+O

where M stands for any species. The rate constants can be found in [15]. The modeling of chemical collision processes contains two stages: determining the reaction probability (or the total reaction cross section) and determining the rule of post-collisional velocity/energy distribution. These stages are considered below.

Reaction probability: dissociation and exchange. Let us consider a dissociation reaction (for instance, the second reaction in the list in the forward direction, where M is an atom for simplicity):



The change in the concentration of the species AB as a result of this reaction is described by the differential equation

$$\frac{dn_{AB}}{dt} = -k_d n_{AB} n_M,$$

where k_d is the reaction rate constant. On the other hand, the change in the concentration of the species AB can be written as

$$\frac{dn_{AB}}{dt} = -N_{col}^{AB,M} \bar{P}_d,$$

where $N_{col}^{AB,M}$ is the frequency of binary collisions of particles of the species AB and M, and P_d is the probability of dissociation. Assuming thermal equilibrium and that the reaction probability is a function of the vibrational level m and the sum of translational and rotational energies E_{tr} , one can write the rate constant in the form

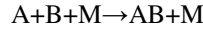
$$k_d(T) = \frac{\overline{\sigma(g)g}}{\Gamma(\xi_{tr}/2)Q_v(T)} \sum_{m=0}^{N_{max}} \exp\left(-\frac{E_m}{kT}\right) \int_{E_d-E_m}^{\infty} P_d(m, E_{tr}) \left(\frac{E_{tr}}{kT}\right)^{\frac{\xi_{tr}}{2}-1} \exp\left(-\frac{E_{tr}}{kT}\right) \frac{dE_{tr}}{kT} \quad (1)$$

Taking into account that dependence of the reaction rate constant at equilibrium temperature is given by the Arrhenius equation

$$k_d(T) = AT^B \exp\left(-\frac{E_a}{kT}\right),$$

one can determine P_d as a solution of the integral equation (1).

Reaction probability: recombination. The simple model [4] is used in the present study for recombination reactions. The change in the concentration of the species AB as a result of the reaction (e.g., the second reaction in the ONERA kinetic scheme in the reverse direction)



is described by the differential equation

$$\frac{dn_{AB}}{dt} = k_r n_A n_B n_M,$$

where k_r is the recombination rate constant. On the other hand,

$$\frac{dn_{AB}}{dt} = N_{col}^{A,B} \bar{P}_r,$$

where $N_{col}^{A,B}$ is the frequency of binary collisions of particles of the species A and B, and P_r is the probability of an event where the particles A and B interact with a third particle M during their interaction and an AB molecule is formed as a result of this collision. Assuming that this probability given by

$$P_r = \beta E_c^\chi n_M$$

and taking into account that the temperature dependence of the recombination rate constant usually has the form

$$k_r = aT^b,$$

one obtains the relation

$$aT^b = \beta \frac{\overline{\sigma(g)g}}{\Gamma(\xi/2)} \int_0^\infty E_c^\chi \left(\frac{E_c}{kT}\right)^{\frac{\xi}{2}-1} \exp\left(-\frac{E_c}{kT}\right) \frac{dE_c}{kT}.$$

This relation, after integration, yields the constants β and χ and, hence, P_r whose form is uniquely determined by the reaction coefficients a and b , and also by the properties of the colliding molecules.

Post-reaction energy redistribution. In DSMC detonation studies, it is especially important to provide the correct state of the mixture in chemical equilibrium. Hence, the chemical models (and, in particular, the energy redistribution rules) of forward and reverse reactions must be consistent in terms of the detailed balance. Owing to fast translation-rotation relaxation and relatively slow vibrational relaxation under the conditions of interest, it seems to be especially important to satisfy the detailed balance in forward/reverse reactions in terms of vibrational states. The rule of sampling the post-reaction vibrational state (and, hence, vibrational energy) is discussed below. The remaining collision energy is redistributed between the translational and rotational modes of the reaction products with the Larsen-Borgnakke model, and the post-collisional velocity direction distribution in the center of mass frame of reference is assumed to be isotropic.

Let us consider the dissociation-recombination reaction



with the rate constants of forward and reverse reaction k_d and k_r , respectively. Then, in chemical equilibrium, we have

$$k_d n_{AB} = k_r n_A n_B.$$

The DSMC chemical models should satisfy the following relation in thermal and chemical equilibrium:

$$k_d(m) n_{AB}(m) = k_r(m) n_A n_B,$$

where m is the vibrational level of molecule AB, and $k_d(m)$, $k_r(m)$ are state-specific constants of the process

$$\text{AB}(m)+\text{M} \leftrightarrow \text{A}+\text{B}+\text{M}.$$

In terms of probabilities, this relation can be written in the form

$$F(m \mid d)=F(r \mid m),$$

where $F(m \mid d)$ is the mean probability of molecule AB selected for dissociation to be in state m (determined by the form of the dissociation probability P_d) and $F(r \mid m)$ is the mean probability of the recombination product AB to appear in state m (determined by the recombination energy redistribution rule).

This means that the probability $F(m \mid d)$ determined by the dissociation model should be used to obtain the vibrational level m of the recombination product AB(m). The dissociation VDF model [16] with the parameter $\varphi=0$ was implemented in the present study for dissociation of diatomic molecules, which has the probability of dissociation of the form

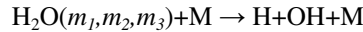
$$P_d(m, E_r) = \beta \frac{(E_r + E_m - E_d)^\nu}{E_r^{\xi'}}$$

and provides a given macroscopic dissociation rate. This model has the simplest form of the function

$$F(m \mid d) = 1/(N_{max}+1) = const,$$

which is easy to use for the recombination modeling.

The model can be generalized to polyatomic molecules, e.g., to the reaction



$$P_d(m_1, m_2, m_3, E_r) = \beta \frac{(E_r + E_{m_1} + E_{m_2} + E_{m_3} - E_d)^\nu}{E_r^{\xi'}}$$

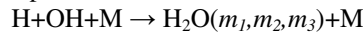
and

$$F(m_1, m_2, m_3 \mid d) = 1/(N_{1max} + N_{2max} + N_{3max} + 3) = const.$$

Under current assumptions, however, any vibrational mode of polyatomic molecules can possess an energy up to E_d ; hence, there are such vibrational states m_1, m_2, m_3 for which $E_{m_1}+E_{m_2}+E_{m_3} > E_d$. Recombination to these states is not always possible because the required energy is higher than the recombination energy release, which equals E_d . This fact leads to violation of the detailed balance in terms of state-to-state rates. To overcome this difficulty, the dissociation from (and recombination to) the vibrational states for which $E_{m_1}+E_{m_2}+E_{m_3} > E_d$ is prohibited, i.e., the dissociation probability is multiplied by the characteristic function

$$I_{E_d} = \begin{cases} C & \text{if } E_{m_1} + E_{m_2} + E_{m_3} < E_d \\ 0 & \text{otherwise} \end{cases}$$

where C is a constant. Then, modeling of the post-collisional vibrational states in recombination reaction



is performed with the following probability function:

$$F(r \mid m_1, m_2, m_3) = F(m_1, m_2, m_3 \mid d) = I_{E_d} / (N_{1max} + N_{2max} + N_{3max} + 3),$$

and C is determined from the normalization condition $\sum F(r \mid m_1, m_2, m_3) = 1$. The dissociation/recombination models modified in such a manner allow correct reproduction of the chemical equilibrium in complex mixtures of polyatomic gases, in particular, the H_2/O_2 mixture.

A similar analysis was applied in the present work to forward and reverse exchange reactions.

COMPUTATIONAL RESULTS

For this realization of the ONERA chemical kinetic mechanism, spatially uniform DSMC computations were performed for a stoichiometric hydrogen-oxygen mixture with autoignition under adiabatic constant-volume conditions at an initial pressure $P_0=240$ kPa and a temperature $T_0=1903.6$ K. The results are compared with the numerical solution of chemical kinetic equations in Fig.1. The temperatures of translational, rotational, and vibrational modes are shown in Fig.1a. At the instant of ignition, the temperatures of all modes start rapidly increasing. All the temperatures are relaxing to the same value, which equals the equilibrium value obtained by solving the chemical kinetic equations. The ignition delay obtained in DSMC simulations also agrees well with the macroscopic model and equals approximately 1 μs . The difference between the approaches is observed only for

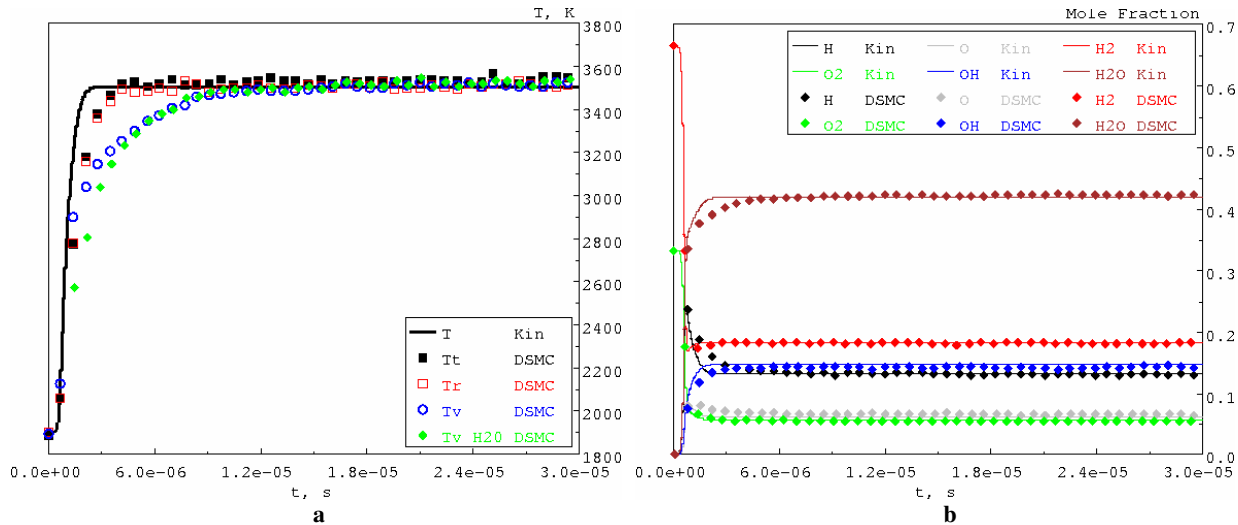


FIGURE 1. Temperatures of different modes (a) and species mole fractions (b). **Kin** – solution of the system of kinetic equations, **DSMC** – results of the DSMC simulations.

times between $1 \mu\text{s}$ and $10 \mu\text{s}$ when non-equilibrium chemical reactions occur. The time dependences of the species mole fractions obtained by particle simulation and by solving the kinetic equations (see Figure 1b) are in excellent agreement, except for a small nonequilibrium segment immediately after the ignition. The results clearly demonstrate that the modified DSMC models provide a correct state of chemical equilibrium in complicated reacting mixtures including polyatomic molecules and provide the verification of the DSMC implementation of the ONERA kinetic mechanism.

Propagation of a detonation wave over an H_2/O_2 mixture was simulated by the SMILE software system in one-dimensional formulation. Conditions of specular reflection were imposed on the left and right boundaries of the computational domain. The detonation wave was initiated by the breakdown of a diaphragm (discontinuity decay) at the point $X=0$ between the channels of low ($0 < X < X_l$) and high ($X_2 < X < 0$) pressure. At the initial time, both channels were filled with the $\text{H}_2/\text{O}_2 = 2/1$ mixture under the following conditions: $P=100 \text{ kPa}$ and $T=300 \text{ K}$ in the low-pressure channel; $P=3335 \text{ kPa}$ and $T=2000 \text{ K}$ in the high-pressure channel.

After diaphragm breakdown, a shock wave starts propagating in the low pressure channel; this shock wave compresses and ignites the gas. In about $1 \mu\text{s}$ after the breakdown, an unsupported detonation wave is formed; the velocity of its propagation coincides with the Chapman-Jouguet velocity (2841 m/s). The profiles of temperature and atomic hydrogen mass fraction for different time instants in the wave-front-fitted coordinate system are compared in Fig. 2. All parameters exhibit good coincidence at different time instants. Figure 2 also shows the solution for the detonation-wave structure calculated on the basis of the ZND theory by the Cantera code [17]. The structure of the detonation-wave front obtained in DSMC computations qualitatively agrees with the structure predicted by the ZND theory. Note that significant differences were observed in previous DSMC studies in terms of equilibrium values of some parameters behind the detonation wave. The present DSMC results excellently agree with the ZND theory in terms of parameters behind the detonation front (see the values at $X=-0.002 \text{ m}$).

CONCLUSIONS

The DSMC chemistry models were modified to correctly reproduce the combustion process in a hydrogen-oxygen mixture. The main attention was paid to making the models of forward and reverse reactions consistent in terms of detailed balance. It was done for the first time for reactions of polyatomic molecules, which are especially important for the case considered, because the triatomic molecule H_2O is one of the combustion products. Modified models are able to correctly reproduce the adiabatic autoignition processes with a correct ignition delay and final equilibrium state. They were used for DSMC modeling of propagation of a detonation wave initiated by breakdown of the diaphragm between channels with different pressures. An unsupported Chapman-Jouguet detonation was obtained. The simulation results on the internal structure of the detonation wave are in qualitative agreement with the Zeldovich – von Neumann – Doering theory and provide a correct equilibrium state downstream of the wave front.

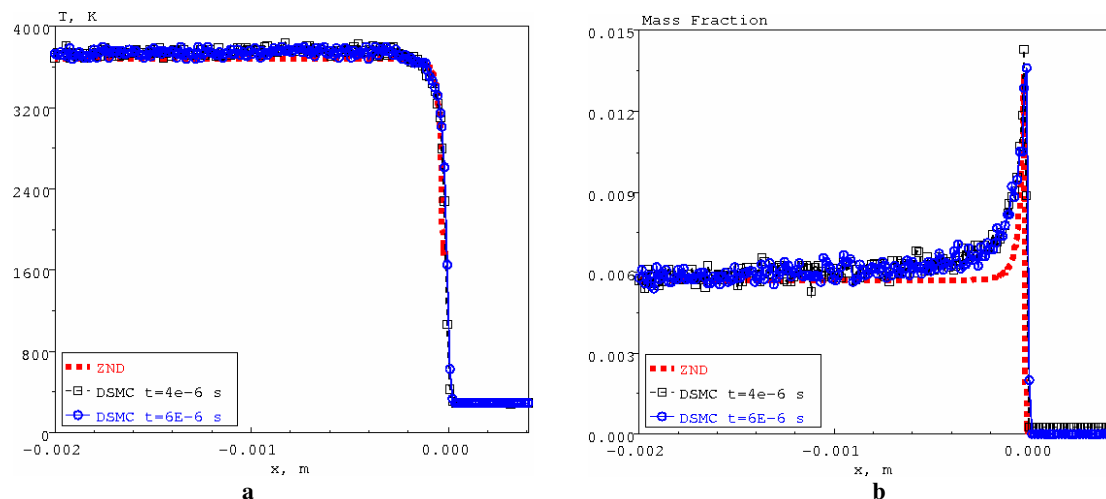


FIGURE 2. Profiles of translational temperature (a) and atomic hydrogen mass fraction (b) at different time instants obtained in DSMC computations and based on the ZND theory in the coordinate system fitted to the detonation-wave front.

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