Comparison of nonequilibrium dissociation models in the direct simulation Monte Carlo method

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Abstract. Various chemical dissociation reactions models (Total collision energy model – TCE, Quantum Kinetic model – QK and Extended vibrational bias model – EVB) were implemented in the direct simulation Monte Carlo code SMILE++. It was shown that the dissociation models considered predict the same reaction rate over a wide range of temperatures in thermal equilibrium case. The analysis for the nonequilibrium case was carried out on the basis of dissociating nitrogen gas flow modelling around the wedge for the Hornung and Smith experiments conditions. All dissociation models proposed predict various results both in the standoff distance of the bow shock wave and in the temperature values behind it. It was generally shown, that taking into account the vibrational favoring (during dissociation) results in decreasing the reaction rate, which can be manifested in increasing the shock wave standoff distance.

1. Introduction

Nowadays, the direct simulation Monte Carlo (DSMC) [1] method proposed by Graeme Bird in the early sixties is the main tool for studying aerodynamics at high-altitudes above about 80 km, when the free mean path of gas particles becomes comparable with the linear size of space vehicle. The underlying ideas of the method are that, firstly, the rarefied gas flow is considered as a set of \(10^5 - 10^{10}\) modelling particles (each of them represents a large number of real gas molecules), and secondly, continuous motion and collisions of gas particles are divided into two consecutive stages. Flow fields of different parameters are obtained by averaging of molecular properties in cells of the computational domain.

It is important to note that the thermal nonequilibrium that occurs in the viscous layer behind the bow shock wave when a spacecraft enters the upper atmospheric layers complicates the gas flow structure and has a strong effect on the chemical reactions rates, including dissociation, which primarily determines the degree of thermal loads exerted on a space vehicle. Thus, correct modelling of chemical reactions in the DSMC method [2] is an essential objective for high-altitude aerodynamics calculations, since nonequilibrium chemical reactions have a significant effect on aerothermodynamic characteristics of the spacecraft. It should be noted, that in the DSMC method chemical reactions are implemented during the binary collision stage and it is necessary to know the reaction probability as a function of colliding particles parameters.

One of the most widely used software systems for rarefied gas flows calculation using the DSMC method is SMILE (Statistical Modeling In Low-density Environment) [3]. It is a software tool developed in the laboratory of computational aerodynamics of the Institute of Theoretical and Applied
Mechanics of the Siberian Branch of the Russian Academy of Sciences. Its more modern and flexible version is the SMILE++ \cite{4, 5} code, which is being actively developed at the moment.

The main objectives of this work are implementation and validation of existing molecular models of chemical dissociation reactions in the SMILE++ software system, as well as their analysis in the case of nonequilibrium supersonic flow around a wedge.

2. Dissociation reaction models
In this work, the following chemical dissociation reactions ($A_iA_j + R \rightarrow A_i + A_j + R$) models were considered:

1. Total Collision Energy (TCE) model \cite{6}. In this model the probability of chemical dissociation reaction depends on the total energy of colliding particles:

$$P_d(E_c) = C \frac{(E_c - E_d)^{x+\xi_c+1}}{E_c^{\xi_c+1}},$$

where $E_c = E_{tr} + E_{int}$ is the total energy of the colliding pair, $E_{tr}$ is the relative translational energy, $E_{int}$ is the internal energy of the colliding particles equal to the sum of rotational and vibrational energies of both molecules, $E_d$ is the reaction threshold energy, $\xi_c$ is the sum of the translational and internal degrees of freedom of the colliding pair; the constants $C, x$ are related to the constants in the Arrhenius law.

The TCE model is widely used in practice, since the Arrhenius law constants are known for a large number of chemical reactions. However, a significant drawback of this model is that it does not take into account the favoring of the vibrational energy over the translational energy in the dissociation process.

2. Quantum Kinetic (QK) model \cite{7, 8}. In this model dissociation always occurs when the total energy of the colliding particles exceeds the molecule dissociation energy, i.e. when the following condition is true:

$$\left| \frac{E_c}{k\theta_v} \right| > \frac{\theta_d}{\theta_v},$$

where $E_c, \theta_v, \theta_d$ are characteristic vibration and dissociation temperatures; $E_c = E_{tr} + E_v$ is the sum of the relative translational energy $E_{tr}$ of the colliding pair and the vibrational energy $E_v$ of the particle that may dissociate, $k$ is the Boltzmann constant and square brackets denote truncation.

The main advantage of the QK model is the absence of any empirical coefficients. Thus, the model can be used in situations when there is no experimental data necessary to determine the parameters of other models.

3. Extended vibrational bias (EVB) model \cite{9}. In this model the probability of dissociation strongly depends on the vibrational level of a molecule, and it can be represented as follows:

$$P_d = A_d \left( 1 - \frac{E_d - E_v}{E_{tr} + E_r} \right) \exp \left( \lambda \left( \frac{E_v}{E_d} - 1 \right) \right),$$

where $E_r, E_v$ are rotational and vibrational energies of the dissociating molecule, $A_d$ is the calibration constant, $\lambda$ is the degree of vibrational favoring.

A number of studies noted \cite{9, 10} that the EVB model provides better agreement with known equilibrium and nonequilibrium reaction rates than other widely used models due to the fact that it takes into account the vibrational level (vibrational favoring) of molecules. The calibration constants values for various chemical reactions are given in \cite{10}. 

3. Numerical results
To perform the comparative analysis of physico-chemical models the QK and EVB dissociation models were implemented in the SMILE++ software system (the TCE model had been implemented before in this system [11] as the basic chemical model and, therefore, did not require any addition coding). Verification results and analysis of the models implemented in the SMILE++ software system for the homogeneous gas case as in [2] are presented below. To verify the correctness of the chemical dissociation reactions models implementation in the program, isothermal reservoir case calculations for a temperature range of 8000 – 20000 K were performed and the chemical dissociation rates under thermal equilibrium conditions were obtained for the following reactions: $N_2 + N \rightarrow N + N + N$ and $N_2 + N_2 \rightarrow N_2 + N + N$.

The verification results are shown in figure 1. It can be seen that an excellent agreement was obtained between the reaction rates of the implemented dissociation models with the Arrhenius law, which confirms the correctness of the dissociation models description under thermal equilibrium condition.

![Figure 1](image_url)

**Figure 1.** Dissociation reactions rates for $N_2 + N \rightarrow N + N + N$ (a) and $N_2 + N_2 \rightarrow N_2 + N + N$ (b). Symbols – calculated rates, lines – Arrhenius rates.

| Table 1. Freestream conditions for the supersonic flow around the wedge. |
|---------------------------------------------|
| Parameter               | Value          |
| $T_{\infty}, K$          | 1100           |
| $V_{\infty}, m/s$        | 5500           |
| $\rho_{\infty}, kg/m^3$ | 0.0026         |
| $p_{\infty}, Pa$         | 940            |
| $Kn_{\infty}$           | $6.52 \times 10^{-4}$ |
| Wedge length, m         | 0.051          |
| Wedge angle, °          | 62.5           |
| Composition, mol/kg     | $N_2 – 31.9; N – 7.7$ |

The physico-chemical dissociation models were also verified on the problem of nonequilibrium high-enthalpy supersonic flow about a wedge for the Hornung and Smith experiments conditions [12] with $N_2 + N \rightarrow N + N + N$ and $N_2 + N_2 \rightarrow N_2 + N + N$ chemical reactions. The gas flow parameters were set similarly to the parameters given in the [13] and are shown in table 1. Elastic collisions were
calculated using the Variable Soft Sphere (VSS) model \[14\]. The Larsen-Borgnakke (LB) model \[15\] was used for inelastic collisions modelling and the TCE, QK and EVB models were considered for dissociation modelling. The general flow structure obtained with all three models is demonstrated by the flowfields of translational temperature in figure 2. Numerical results for various chemical models differ both in temperature flowfields and in standoff distance of the shock wave (both QK and EVB models predict equal shock standoff distance which is more than 10% lower for the TCE model).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Translational temperature field.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Translational (\(T_{tr}\)), rotational (\(T_{rot}\)) and vibrational (\(T_{vib}\)) temperatures along the stagnation streamline for the considered dissociation models.}
\end{figure}
Figure 4 Translational ($T_{tr}$), rotational ($T_{rot}$) and vibrational ($T_{vib}$) temperatures of the nitrogen gas mixture along the stagnation streamline.

Translational, rotational and vibrational temperatures along the stagnation streamline for all considered dissociation models are shown in figure 3. The flow direction coincides with the X-axis direction, and the stagnation point was at $1.5 \times 10^{-3}$ m from the origin. From these plots we can conclude, that chemical dissociation models predict the same picture from the qualitative point of view. But, from the quantitative perspective, the results obtained by different models are different. It can be seen from the figure 3 that the translational, rotational and vibrational temperatures differ significantly from each other due to the strong thermal nonequilibrium in the shock layer. Also, it should be noted that at a distance of approximately $6 \times 10^{-3}$ m from the wedge a thermal equilibrium is reached. However, when approaching the wedge an area with the vibrational nonequilibrium appears again.

Figure 4 shows the comparison of temperatures of different modes obtained with different models. The maximum gas flow temperature in the QK model is lowest among three models. The highest temperature is observed for the EVB model. It is interesting to note that the maximum value of the translational temperature is about 14000 K and is nearly identical for all three models.

4. Conclusion
The implementation in the SMILE++ software system and verification of existing molecular models of dissociation were carried out. In the process of a qualitative analysis of dissociation models, it was revealed, that while in the isothermal equilibrium case, the considered models predict the same dissociation rate, the results for the nonequilibrium flow over the wedge are substantially different both in terms of bow shock standoff distance and the values of gas-dynamic parameters, such as temperatures of different modes. To access the accuracy of the models validation studies should be performed for available ground-based or in-flight experimental data as in [13, 16-23].

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