

New Model for Statistical Simulation of High-Temperature Nonequilibrium Dissociation

Ye.A. Bondar and M.S. Ivanov

*Computational Aerodynamics Lab, Khristianovich Institute of Theoretical and Applied Mechanics SB RAS,
Institutskaya str. 4/1, Novosibirsk 630090, Russia*

Abstract. A model is developed to describe dissociation reactions in the DSMC method under conditions of strong thermal nonequilibrium, with vibrational temperature of the gas being significantly different from translational temperature. In contrast to conventional DSMC models, where the reaction cross section is obtained on the ground of the Arrhenius kinetics, the present model is based on two-temperature kinetics. Application of this model is illustrated by high-temperature dissociation of nitrogen.

Keywords: DSMC method, chemical reactions, dissociation cross sections

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INTRODUCTION

The direct simulation Monte Carlo (DSMC) [1] method is traditionally used to study rarefied hypersonic flows with a significant degree of thermal and chemical nonequilibrium. Presently, one of the most challenging problems in terms of the DSMC method development and improvement is related to the need to effectively and reliably simulate nonequilibrium chemical reactions. Many DSMC models of chemical reactions were suggested in the literature. The models differ in the area of applicability, derivation, and accuracy. Numerical studies by the DSMC method usually involve a simple and universal Total Collision Energy (TCE) model [1]. In this model, the probability of the chemical reaction as a function of the total energy of colliding particles (sum relative translational, rotational and vibrational energies) is determined from the known Arrhenius one-temperature dependence of the reaction rate constant. Some other chemical reaction models such as vibrationally favored model of Haas and Boyd [2] are also constructed in such a manner that they capture Arrhenius rate at thermal equilibrium.

The Arrhenius representation of the reaction rate

$$K_0(T) = AT^B \exp(-E_d/T) \quad (1)$$

provides an accurate description of chemical reactions in near-equilibrium flows, such as flows behind the shock waves at comparatively moderate temperatures within 5,000-6,000 K, when vibrations are completely excited before the beginning of dissociation. Behind strong shock waves, where temperatures are significantly higher (10,000-20,000 K) the Arrhenius description is invalid, and the reaction rate constant depends not only on translational T but also on vibrational T_v temperature, and the dissociation rate can differ by orders of magnitude from the Arrhenius rate (Hammerling, 1959; Marrone and Treanor, 1963). The thermally nonequilibrium dissociation rate constant is usually written in the form

$$K(T, T_v) = K_0(T)Z(T, T_v), \quad (2)$$

where Z is the coupling factor, which takes into account the deviation from the Arrhenius dependence due to retardation of vibrational temperature. There are many models for these factors of nonequilibrium; these models were derived on the basis of different assumptions about the kinetics of population and decay of vibrational states of reacting molecules (see [3] for details).

It is not possible to capture mentioned physical peculiarities of high-temperature dissociating flows in DSMC computations using only Arrhenius description as a basis for DSMC chemical reaction model. The major challenge of the present work was to develop a model for the DSMC method, which would describe nonequilibrium dissociation and could be applicable for high temperatures. It was suggested to develop the DSMC dissociation model on the basis of the two-temperature kinetics.

In contrast to numerical methods of continuum gas dynamics, information on the dependence of the reaction rate on the values of translational and vibrational temperatures is insufficient for the DSMC method. DSMC simulations of chemical reactions require the knowledge of the reaction cross section as a function of energies of different modes of the colliding molecules and also the law of energy distribution between different modes of molecules that are produced in the reaction.

In constructing the dissociation model for the DSMC method, we decided to use an approach based on seeking for the dissociation cross section as a function of the total energy of the colliding pair and vibrational energy of the dissociating molecule under the following condition: the dissociation rate under conditions of equilibrium population of vibrational levels of molecules (corresponding to the temperature T_v) and equilibrium velocity distribution function and population of rotational levels of molecules (corresponding to the temperature T) should coincide with the dissociation rate determined by the two-temperature nonequilibrium constant $K(T, T_v)$ in a wide range of values of T and T_v . Standard DSMC methodologies (e.g., those based on the Larsen-Borgnakke model) are proposed for the post-collision distribution of energy among the molecules and their different energy modes.

As a nonequilibrium constant $K(T, T_v)$, we decided to use the constant from Kuznetsov's model [3, 4]. The coupling factor in this model has the form

$$Z(T, T_v) = \frac{1 - \exp(-\theta_v/T_v)}{1 - \exp(-\theta_v/T)} \exp \left[-E_v^* \left(\frac{1}{kT_v} - \frac{1}{kT} \right) \right],$$

where E_v^* is approximately 0.7 of dissociation energy. This model is fairly well justified and, simultaneously, simple, convenient for computations and also effective for $T_v > T$ [3]. In addition to this advantage, this model possesses some important mathematical properties, which allow constructing models of the DSMC method on the basis of Kuznetsov's model.

STATEMENT OF THE PROBLEM

Let us consider dissociation of diatomic molecules A_1A_2 resulting from a collision with atom A_3 : $A_1A_2 + A_3 \longrightarrow A_1 + A_2 + A_3$. Further we use a continuous description of rotational energy and a discrete description of vibrational energy of molecules in accordance with the anharmonic oscillator (AHO) model. We assume that translational and rotational degrees of freedom of gas molecules are in equilibrium with each other. The distribution functions of velocities and rotational energy of molecules have the Maxwellian and Boltzmann form, respectively, and the translational-rotational temperature is T . The population of vibrational levels has the Boltzmann form corresponding to the vibrational temperature T_v , which is not equal to T in the general case.

Let us assume that, dissociation cross section σ_n for the molecule A_1A_2 at the vibrational level n is a function of the sum E of rotational energy of the molecule E_r and translational energy of relative motion of collision partners E_t : $\sigma_n = \sigma_n(E) = \sigma_n(E_r + E_t)$. Then the two-temperature constant $K(T, T_v)$ can be presented as

$$K(T, T_v) = \sum_{n=0}^{N_{max}} f_v(n, T_v) \int_0^\infty \int_0^\infty \sigma_n(E) \sqrt{\frac{2E_t}{m_r}} f_r(E_r, T) f_t(E_t, T) dE_r dE_t. \quad (3)$$

Here m_r is the reduced mass of the colliding particles, f_t , f_r and f_v are the Boltzmann distribution functions of relative translational, rotational, and vibrational energies, respectively.

If the two-temperature rate constant is known on some intervals of translational $[T_1, T_2]$ and vibrational $[T_{v1}, T_{v2}]$ temperatures, one can consider the equality 3 as an integral equation to be solved to find the set of vibrationally specific dissociation cross sections $\sigma_n(E)$, $n = 0, \dots, N_{max}$.

From the mathematical viewpoint, finding a solution of equation 3 is a complicated problem because of the following factors: 1) complicated form of the operator acting on $\sigma_n(E)$ (including operations of integration and summation); 2) high dimensionality of the problem (both the solution $\sigma_n(E)$ and the "right-hand side" $K(T, T_v)$ are functions of two variables); 3) ill-posedness and nonuniqueness of the solution (this issue will be discussed in detail later).

To overcome the first two difficulties, the problem will be subjected to transformations, and the solution will be sought in a special form. The two-temperature constant of Kuznetsov's model can be presented as the product

$$K(T, T_v) = g(T)g_v(T_v), \quad (4)$$

where the factors are given by

$$g(T) = AT^B \exp\left(-\frac{E_d - E_v^*}{kT}\right) [1 - \exp(-\theta_v/T)]^{-1}, \quad g_v(T_v) = \exp\left(-\frac{E_v^*}{kT_v}\right) [1 - \exp(-\theta_v/T_v)].$$

Here A and B are the Arrhenius constants and E_d is the dissociation energy.

Then, assuming the solution has also the form of the product

$$\sigma_n(E) = \beta(n) \sigma'_n(E), \quad n = 0, \dots, N_{max} \quad (5)$$

and applying some simple mathematical transformations, we can split the problem of determining set of cross sections into two independent stages with simpler equations being solved at each stage.

- **STAGE 1:** finding functions $\sigma_n(E)$ solving, for every vibrational level n , the equation

$$\int_{E_d - E_v(n)}^{\infty} \sigma'_n(E) \left(\frac{E}{kT}\right)^{\xi_r/2+1} \exp\left(-\frac{E}{kT}\right) dE = \frac{g(T)}{C(T)}, \quad (6)$$

where ξ_r is a number of rotational degrees of freedom and $C(T) = 8\sqrt{2/(\pi m_r kT)} / [\Gamma(\xi_r/2) \xi_r (\xi_r + 2)]$.

- **STAGE 2:** finding a function $\beta(n)$ solving the equation

$$\sum_{n=0}^{N_{max}} \beta(n) f_v(n, T_v) = g_v(T_v). \quad (7)$$

In terms of its structure Eq. 6, it is the Fredholm equation of the first kind. The problem of seeking for its solution belongs to the class of ill-posed inverse problems, which can be solved by using regularization algorithms and data based on the physical analysis of the problem [6]. The same algorithms can be used to solve Eq. 7 (in what follows, we confine ourselves to the description of algorithms as applied to solving equations of the type 6). As a result of solving these equations, we obtain the sought set of the cross sections $\sigma_n(E)$, $n = 0, \dots, N_{max}$. The procedure of using Tikhonov's regularization method [6] for solving the problem posed here is described in detail in the next section.

Note that this method has been successfully applied in [7] to compute the vibrationally specific cross sections of dissociation. The formulation of the initial problem in that study, however, was significantly different from the present formulation. First, Osipov and Shelepin [7] ignored rotational energy of molecules; second, the conventional one-temperature Arrhenius constant was used in Eq. 3 instead of the two-temperature constant, and the problem was solved under "one-temperature" equilibrium conditions (i.e., $T = T_v$), which is a much simpler case.

METHOD OF THE SOLUTION

Let us write the integral equation to be solved in the operator form

$$Az = u. \quad (8)$$

In Tikhonov's regularization method [6], the initial problem 8 is replaced by the problem of minimizing the functional

$$M^\alpha[z, u] = \|Az - u\|_{L_2[c, d]}^2 + \alpha \Omega[z], \quad (9)$$

where α is a regularization parameter chosen in a certain manner and $\Omega[z]$ is a stabilizing functional (stabilizer). In solving the Fredholm equation of the first kind by this method, the approximate solution is sought in the class of smooth functions, and the stabilizer is taken in the form

$$\Omega[z] = \int_a^b \sum_{r=0}^p q_r(s) \left(\frac{d^r z(s)}{ds^r} \right)^2 ds. \quad (10)$$

Here $q_0(s), \dots, q_p(s)$ are prescribed non-negative continuous functions (functional coefficients) and $q_p(s) > 0$.

According to the theory of variational calculus, it is possible to minimize the functional $M^\alpha[z, u]$ by solving an appropriate Euler equation

$$A^*Az + \alpha\Omega'[z] = A^*u, \quad (11)$$

where A^* is an operator conjugate to the operator A , and $\Omega'[z]$ is the Frechet derivative of the stabilizer.

To solve Eq. 11 numerically, we construct its finite-difference approximation, which is a system of linear algebraic equations (the number of equations equals the number of unknowns) and which has a unique solution if the determinant of the system differs from zero.

Let us now consider the procedure of choosing the regularization parameter α . The form of the sought solution is chosen from physical considerations. For instance, we can seek for the cross sections in the form of non-decreasing bounded functions, i.e., the solution $z(s)$ of Eq. 8 should satisfy the following conditions: $z(s_1) \leq z(s_2)$, $s_1 < s_2$; $0 \leq z(s) \leq z_0$. A useful property of the set of solutions that satisfy these conditions is the fact that this solution is a compact set in $L_p[c, d]$, $p > 1$. In this case, the solution z^α of Eq. 11 approaches the exact solution if we can minimize the residue $\|Az^\alpha - u\|_{L_2[c, d]}$. In this case, one of the most suitable methods of choosing the regularization parameter is the following procedure:

- a set of functional coefficients $q_0(s), \dots, q_p(s)$ is chosen;
- the possible values of α are taken in the form of a decreasing geometric progression (interrupted after a certain element); the parameters of this progression are chosen experimentally;
- the solutions z^α of Eq. 11 are found for all chosen values of α ;
- among the entire set of solutions, those solutions that belong to the compact set in which the problem is considered are chosen;
- among all other solutions, the solution with the minimum residue is found (if the value of the residue is not satisfactory, we go back to the first step and choose a new set of functional coefficients).

If the value of the residue is satisfactory, the chosen z^α is the sought approximate stable solution of Eq. 8.

Methods of choosing the regularization parameter are described in more detail in [6, 7]. Let us recall that the regularization method can be applied in a similar manner to seeking for the approximate solution of Eq. 7.

N₂ DISSOCIATION

The present section describes application of the approach outlined in the previous two sections to finding vibrationally specific cross sections of the dissociation process $N_2 + N \longrightarrow 3N$. The Arrhenius constants for this reaction are $A = 6.9 \times 10^8 \text{ # } m^3/s$ and $B = -1.5$ in accordance with [9]. The dissociation energy of nitrogen is $E_d = 1.611 \times 10^{-18} \text{ J}$ and the characteristic temperature of vibration is $\theta_v = 3371 \text{ K}$. Vibrations of the N_2 molecule in the present study were described on the basis of the anharmonic oscillator model. The value of the anharmonicity parameter $\eta = 0.9995$ was chosen to ensure the best fit of the energy of vibrational levels to the results computed in [8]. For this value of η , the last vibrational level is $N_{max} = 67$. The two stages of finding a set of N_2 dissociation cross sections are consecutively considered further.

STAGE 1: Finding the functions $\sigma'_n(E)$.

In accordance with the approach described in the previous section, instead of Eq. 8, we solve the corresponding Euler equation 11. For this equation to be solved numerically, it is necessary to construct its finite-difference approximation.

For this purpose, we introduce uniform grids $\{s_j\}_{j=1}^{j_0}$ and $\{x_i\}_{i=1}^{i_0}$ on segments $[E_1, E_2]$ and $[T_1, T_2]$ with steps h_s and h_x , respectively, and construct finite-difference approximations for all integral and differential operators. In particular, if \mathbf{A}_{ij} is the matrix corresponding to finite-difference approximation of the operator A (see Eq. 8), and \mathbf{z}_j and \mathbf{u}_i are the vector columns corresponding to the values of the functions $z(s)$ and $u(x)$, the finite-difference approximation of the initial integral equation 8 in the matrix form acquires the form $\mathbf{A}\mathbf{z} = \mathbf{u}$. We supplement this system of linear equations by equations that express the boundary conditions; we denote the expanded matrix and right-hand column by $\tilde{\mathbf{A}}_{ij}$ and $\tilde{\mathbf{u}}_i$ and further use them instead of \mathbf{A}_{ij} and \mathbf{u}_i . As a result, the problem of solving the integrodifferential Euler equation 11 with allowance for the boundary conditions reduces to solving a system of linear algebraic equations

$$[\tilde{\mathbf{A}}^T \tilde{\mathbf{A}} + \alpha \mathbf{C}]\mathbf{z} = \tilde{\mathbf{A}}^T \tilde{\mathbf{u}}. \quad (12)$$

System 12 consists of j_0 algebraic equations with j_0 unknowns, and the matrix $[\tilde{\mathbf{A}}^T \tilde{\mathbf{A}} + \alpha \mathbf{C}]_{ij}$ is symmetric. If its determinant is other than zero, it has only one solution \mathbf{z}_j . To solve the initial equation 8 by Tikhonov's regularization

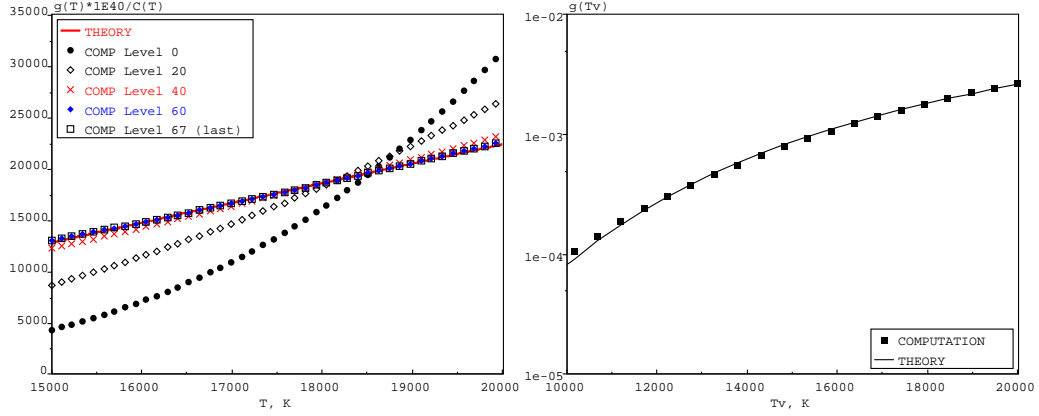


FIGURE 1. Functions $g(T)/C(T)$ (left) and $g_v(T_v)$ (right).

method, we use an iterative procedure described at the end of the previous chapter; each stage of this procedure (for each α) involves solving system 12 for finding the solution z^α .

As a result, for the reaction $N_2 + N \rightarrow 3N$ the optimal form of the functional coefficients $q_r(s)$ (for $p = 2$) was found: $q_0(s) = 0$, $q_1(s) = 0$, $q_2(s) = [(E_2 - E_1)/(s - E_1)]^2$. The following boundaries of the temperature range were used in the present computations: $c = T_1 = 15000$ K, $d = T_2 = 20000$ K. Left boundary of the energy interval was determined from the condition of the minimum energy sufficient for dissociation; the right boundary was chosen sufficiently large for the value of the integral to remain essentially unchanged with a further increase in its value: $E_1 = E_d - E_v(n)$, $E_2 = 40kT_2$.

The finite-difference approximation was constructed with a 300×300 grid. Based on the physical concepts of the shape of cross sections, only non-decreasing bounded functions were chosen among all solutions z^α in accordance with the iterative procedure (the set of such functions is compact, see the previous section), and the boundary conditions had the form: $z(E_1) = 0$, $z'(E_1) = 0$, $z'(E_2) = 0$, $z''(E_2) = 0$.

The accuracy of the resultant solution can be estimated by the graphs in Fig. 1, which shows the values of the left-hand side of Eq. 6 with substitution of the approximate solution $\sigma'_n(E) = z(s)$ for different values of n into the integral; these values are compared with the exact “theoretical” value $g(T)/C(T)$. Though the value of the integral is substantially different from the theoretical solution for low levels, excellent agreement between the computed and theoretical values of the integral is provided for high levels ($n > 40$) from which dissociation predominantly occurs.

STAGE 2: Finding the function $\beta(n)$.

We construct a finite-difference analog of Eq. 7. For this purpose, we use a uniform grid $\{x_i\}_{i=1}^{i_0}$ with a step h_x in the temperature interval $[T_{v1}, T_{v2}]$. On this grid, Eq. 7 reduces to a system of linear algebraic equations

$$\sum_{n=0}^{N_{max}} \beta(n) f_v(n, x_i) = g_v(x_i), \quad i = 1, \dots, i_0. \quad (13)$$

We solve system 13 by Tikhonov’s regularization method, using the solution of the Euler equation and the iterative procedure described above. As a result of the numerical experiments performed, the optimal form of the functional coefficients $q_r(n)$ (for $p = 2$) was found for the nitrogen dissociation reaction examined: $q_0(n) = 0$, $q_1(n) = 0$, $q_2(n) = [N_{max}/(N_{max} - n)]^6$. The following boundaries of the temperature range were used in the present computations: $T_{v1} = 5000$ K, $T_{v2} = 20000$ K. In constructing the finite-difference approximation, we used the value $i_0 = 300$ and assumed that $\beta(n)$ is a nondecreasing bounded function.

Figure 1 shows a comparison of the value of the left-hand side of Eq. 7 with the numerical solution for $\beta(n)$ substituted into this equation and the “theoretical” value of $g_v(T_v)$. It is clearly seen that the numerical solution predicts the value of $g_v(T_v)$ very accurately.

Cross sections of dissociation $\sigma_n(E)$.

In accordance with Eq. 5, the dissociation cross sections are sought in the form $\sigma_n(E) = \beta(n) \sigma'_n(E)$. The values of $\sigma_n(E)$ for different values of n are plotted in Fig. 2. The reaction rate constant obtained by finding these cross sections numerically on the basis of the equilibrium distributions of translational, rotational, and vibrational energies is compared in Fig. 2 with the rates obtained by Kuznetsov’s two-temperature model in a wide range of temperatures

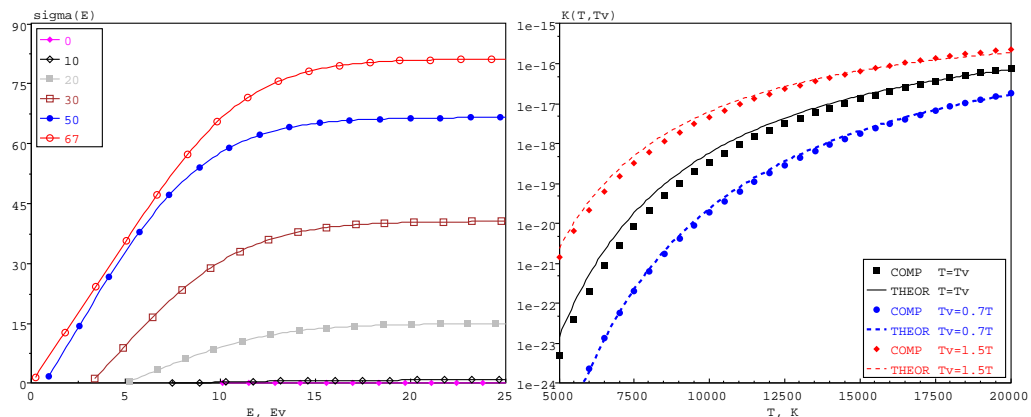


FIGURE 2. Cross sections (left), \AA^2 , and two-temperature constant (right), $\# m^3/s$, of the N_2 dissociation.

for different ratios of the translational and vibrational temperatures. It is seen that the cross sections obtained allow reaching almost complete coincidence with Kuznetsov's model in the case of equilibrium distributions.

SUMMARY AND CONCLUSIONS

A new dissociation model for DSMC computations of high-temperature nonequilibrium flows is developed. In the model, the vibrationally specific cross sections of dissociation are obtained as functions of the sum of translational and rotational energies on the basis of the known two-temperature dissociation rate constant $K(T, T_v)$. The model provides DSMC reaction rates, which are in excellent agreement with two-temperature kinetics in conditions of rotational-translational equilibrium and Boltzmann distribution of vibrational energy.

An important feature of the proposed model is the possibility of its use in hybrid continuum/DSMC codes. In this case, chemical reactions in the continuum module are modeled by the two-temperature model with the rate constant $K(T, T_v)$, which is a procedure typical for continuum approaches, whereas the model suggested here is used in DSMC computations. Such an approach allows taking into account the processes of high-temperature dissociation in hybrid codes. Thus, the two-temperature chemical model of the DSMC method can bridge the gap in creating a hybrid CFD/DSMC code.

Note that the approach to solving integral equations used in the present study can be also used to construct a DSMC model for recombination, which is consistent with the present model in terms of the detailed balance principle.

Generalization of the model to polyatomic molecules and a further analysis through comparisons with other DSMC models and experimental data is planned in the near future.

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