Non-equilibrium dissociation and relaxation behind the shock wave within two-temperature approach

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Abstract. Within the recently proposed asymptotic method for solving the Boltzmann equation for chemically reacting gas mixture, the equations for a dissociating diatomic gas have been derived assuming two-temperature (translational-rotational + vibrational) approximation. Corresponding expressions for the reaction and relaxation rates, determined by the quasi-stationary vibrational distributions, have been obtained under assumption of dissociation from the highest vibrational level. Cut-off harmonic oscillator approximation for the diatomic molecules is assumed. It is shown that all reaction rates are the complex functions of the species densities. Analysis of a flow behind a shock wave is performed in a wide range of the flow parameters. It is shown that under strong non-equilibrium condition the dissociation rate is determined not by the dissociation probability, but by the vibration probability, since the excitation of highest vibrational levels is the bottleneck of dissociation process. This means that the procedure of obtaining the data on dissociation rates needs the accurate revision.

1. Introduction
Simulation of the high-speed entry of the spacecrafts into a planetary atmosphere, low temperature plasma installations for material processing and manufacturing needs the non-equilibrium flow models. The most detailed description of such flows available for the modern computers consists in state-to-state models. Still, the continuum models are in demand and their possibilities to describe the complex reactive flows are far from exhausting.

Recent results based on the asymptotic solution of the Boltzmann equation for the mixture of reacting gases yield the transport equations describing the non-equilibrium effects in the zeroth-order approximation, i.e. corresponding Euler equations contain non-equilibrium reaction and relaxation rates [1, 2, 3, 4, 5]. This is due to discarding the approximation, which is the foundation for all modern models of chemically reacting gas flows, derived from kinetic equations. The assumption that perturbation of the collision integral by chemical reactions is small, i.e. of the order of Knudsen number [6] is avoided. This is important, for instance, for considering the dissociation reactions, since the deviation of vibrational distribution from the equilibrium one for the high vibrational levels (close to the dissociation threshold) is of the order of the distribution function itself, but not of the order of the Knudsen number [7]. The proposed method is based on the following positions [1, 2, 3, 4, 5]:

1) fast and slow variables are separated according to the rule based on the small value of the Knudsen number (approximate summational invariants concept),
(2) the collisional integral of the corresponding Boltzmann equation is not expanded into the series using small parameter, 

(3) the distribution function is represented as a sum of ‘slow’ and ‘fast’ parts and equations for them are represented as a singularly perturbed set of equations and solved using the procedure similar to Chapman–Enskog.

The set of gas-dynamic variables \{Γ_i\} is determined via the approximate summational invariants (ASI) ψ_i by the relationships

\[ ⟨ψ_i, I_α⟩ = λ, \quad Γ_i = ⟨ψ_i, F_α⟩, \quad ⟨...⟩ = \sum_{α,s_α} \int dν_α... \tag{1} \]

where α indicates the species, \( I_α \) are corresponding collisional integrals, \( λ \) is the small parameter, \( F_α \) is the distribution function, \( k_α \) and \( ν_α \) are the quantum numbers characterizing the internal state and velocity of the molecule of sort \( α \), respectively.

According the maximum entropy principle the quasi-equilibrium distribution has the form [8]:

\[ F_{α}^{qe} = \exp \left( \ln s_α (k_α) - \sum_{i=1}^{M} γ_i ⟨ν_i, k_α⟩ \right) \tag{2} \]

where \( s_α(k_α) \) is the statistical weight of the quantum level \( k_α \), \( γ_i \) are the intensive thermodynamic variables connected with the extensive, \( Γ_i \), by the relationships (1), where \( F_α \) is replaced by \( F_{α}^{qe} \). Function \( F_{α}^{qe} \) is considered as a ‘slow’ part of the distribution function \( F_α \), while its ‘fast’ part \( F = F_α - F_{α}^{qe} \) is determined by the equation [1, 8]

\[ J'_{F^{qe}, α}(F^{qe})Φ = -J_{F^{qe}, α}(F^{qe}) + \sum_{i=1}^{M} \frac{∂ F_{α}^{qe}}{∂ Γ_i} \left[ ∇ Γ_i - ∇ ⟨ψ_i, F_α^{qe}⟩ \right] \tag{3} \]

where \( J_{F^{qe}} \) is the Kolesnichenko’s collision operator

\[ J_{F^{qe}}(F) = I(F) - \sum_{i} \left( \frac{∂ F^{qe}}{∂ Γ_i} \right) ⟨ψ_i, I(F)⟩ = I(F) - \sum_{i} \left( \frac{∂ F^{qe}}{∂ Γ_i} \right) R_i \tag{4} \]

\( J'_{F^{qe}} \) is its linearized form, the summation is performed over all gas-dynamic variables. Generalized relaxation (reaction and relaxation) rates (GRR) defined as \( R_i = ⟨ψ_i, I(F)⟩ \) vanish when ψ_i are the exact summational invariants (ESI).

Due to linearity of the equation (3) function Φ can be represented as a sum of terms that are proportional to the gradients of all gas-dynamic variables (spatially inhomogeneous terms) and a term which does not depend on those gradients (spatially homogeneous term). As discussed in the next section, within the applied approximations spatially inhomogeneous terms do not contribute the GRRs, thus the equation (3) can be reduced to

\[ J'_{F^{qe}, α}(F^{qe})Φ = -J_{F^{qe}, α}(F^{qe}) \tag{5} \]

Within the developed approach the following set of the zeroth-order (Euler) equations have been derived [1, 8]:

\[ \frac{∂ n_α}{∂ t} + ∇ \cdot (n_α u) = R_α(\{n_β\}, u, E, Γ_j), \quad R_α = \left\{ δ_{αβ}I_β(F^{qe}) + \left( δ_{αβ}l^i(F^{qe})Φ \right) \right\} = R_{α}^{qe} + R_{α}^{ne}, \tag{6} \]

\[ \frac{∂ ρ u}{∂ t} + ∇ \cdot (ρ uu) + ∇ p = 0, \quad p = n/γ_E, \quad γ_E = 1/k_B T, \tag{7} \]
where \( n_\alpha \) is the species \( \alpha \) number density, \( P \) and \( n \) are the mass and number densities of mixture, \( u \) is the mixture velocity, \( p \) and \( T \) are the mixture pressure and temperature, respectively, \( k_B \) is the Boltzmann constant, \( E \) is the total energy density, \( \Gamma_{\alpha j} \) is the set of other gas-dynamic variables which correspond to \( \alpha \)-species ASI that is the vibrational energy \( \gamma \) correspond to the quasi-stationary distributions, so that they contain the non-equilibrium effects. As expected and shown by simulations, the deviation of RRRs from their equilibrium values may significantly exceed corresponding equilibrium values.

The goal of the present work is to study the structure of relaxation zone behind the shock wave within the new proposed approach. The paper is organized as follows. The next section contains the description of considered problem and corresponding set of equations to be solved. The third section contains equations for the dissociation and relaxation rates, calculated for the cut-off harmonic oscillator model, and their analysis. The simulation results and their discussion are presented in the fourth section. Conclusions are concentrated in the last section.

2. Problem statement and governing equations

Aiming to study the relaxation processes in dissociating diatomic gases behind a shock, we consider a mixture of molecules \( A_2 \) and atoms \( A \). Corresponding reactions are

\[
R_1 : A_2 + A_2 \leftrightarrow A_2 + 2A, \quad R_2 : A_2 + A \leftrightarrow 3A.
\]

According to the proposed asymptotic method of deriving the gas-dynamic equations a set of ASIs should be chosen. Kronecker’s symbol as the ASI corresponds to the species number density \( \psi_n(\beta) = \delta_{\alpha \beta}, \alpha, \beta = A, A, \Gamma_n = \delta_{\alpha \alpha} \). Those densities evolution is governed by the equations (6) with the corresponding reaction rates \( R_k \) and \( R_\alpha \). Another ASIs (which really are the exact invariants (ESI)) corresponding GRRs, \( R^e_{\alpha j} \) are corresponding non-equilibrium parts. Since momentum \( m_\alpha v_\alpha \) and total energy \( \epsilon^{e}_{\alpha j} \) are the exact summation invariants (ESI) corresponding GRRs, the right-hand sides of the equations (7) and (8) are zero. Zeroth order approximation leads to the equations with the reaction and relaxation rates (RRRs) determined by the quasi-stationary densities, so that they contain the non-equilibrium effects.

For our specific case, when only one diatomic molecule is considered, the subscript in the expressions concerning the internal energy characteristics can be omitted and we can write \( E^v = n_{2A}E^v_{2A} \). For further simplification, the cut-off harmonic oscillator model is employed for the molecule oscillations description. Thus, \( \psi_{E^v} = \epsilon^{v}_{\alpha j} = h c \omega_a(q + 1/2), E^{v}_{\alpha j} = h c \omega_a(\bar{q} + 1/2) \), where \( \bar{q} = \langle q, E^v_\alpha \rangle / n_{2A} \) is the usual mean vibrational quantum number, \( h \) is the Planck constant, \( c \) is the light speed in vacuum, \( \omega_a \) is the spectroscopic constant of \( A_2 \) molecule. Instead of \( \psi_{E^v} \) it is convenient to use \( \psi_v = q \) as an
Here $\mathbf{c}_\alpha = \mathbf{v}_\alpha - \mathbf{u}$ is the particle peculiar velocity, $Q^\alpha_{\Gamma v}$ are the translational, rotational and vibrational partition functions, respectively.

To calculate the source terms in the transport equations we need solving equation (5). For that, the following approximations are exploited. Assuming translational-rotational equilibrium, after integration over velocity and summation over rotational quantum number, the equation (5) is reduced to

\[ I^V_q(X^{qe})\Psi = -I^V_q(X^{qe}) + \sum_i \frac{\partial X^{qe}_i}{\partial \Gamma_i} R_i, \quad X^{qe} = \sum_j \int F_{A_j} d\nu_{A_j}, \quad \Psi = \sum_i \Phi_{A_i} d\nu_{A_i}, \]

the solution of which can be sought in a form $\Psi_q = \Psi_{0h}^q + \sum_i \Psi^{av}_q R_i, \quad i = A_2, \quad v$. From $R_{A_2} = -2R_A$ it follows $\sum_i \frac{\partial X^{qe}_i}{\partial \Gamma_i} R_i = R_{A_2} \left( \frac{\partial}{\partial n_{A_2}} - 2 \frac{\partial}{\partial n_A} \right) X^{qe} + R_v \frac{\partial X^{qe}_v}{\partial \Gamma_v}$. Then, from the definitions (6) and (8) for the reaction and relaxation rates, $\mathbf{R} = \{R_{A_2}, R_v\}^T$, the following equations can be obtained

\[ \mathbf{R} = \mathbf{R}^{qe} + \mathbf{R}^{0h} + \mathbf{A} \cdot \mathbf{R}, \quad \mathbf{R}^{0h} = \{R^{0h}_{A_2}, R^{0h}_v\}^T, \quad \mathbf{A} = \begin{pmatrix} A_{A_2 A_2} & A_{A_2 v} \\ A_{v A_2} & A_{v v} \end{pmatrix}, \]

\[ R^{0h}_{A_2} = \sum_{q=0}^{q_m} I^V_q(X^{qe})\Psi_{0h}^q, \quad R^{0h}_v = \sum_{q=0}^{q_m} qI^V_q(X^{qe})\Psi_{0h}^q, \quad A_{A_2 A_2} = \sum_{q=0}^{q_m} I^V_q(X^{qe})\Psi^{av}_{A_2}, \]

\[ A_{A_2 v} = \sum_{q=0}^{q_m} I^V_q(X^{qe})\Psi^{av}, \quad A_{v A_2} = \sum_{q=0}^{q_m} qI^V_q(X^{qe})\Psi^{av}_{A_2}, \quad A_{v v} = \sum_{q=0}^{q_m} qI^V_q(X^{qe})\Psi^{av}, \]

$q_m$ is the highest vibrational level. Thus, the non-equilibrium reaction and relaxation rates can be expressed via their equilibrium parts, $\mathbf{R}^{qe}$, reduced correction parts, $\mathbf{R}^{0h}$, and the resolvent of the renormalizing matrix $\mathbf{A}$:

\[ \mathbf{R} = (\mathbf{I} - \mathbf{A})^{-1} \cdot \mathbf{R}^0 = (\mathbf{I} - \mathbf{A})^{-1} \cdot (\mathbf{R}^{qe} + \mathbf{R}^{0h}). \]
\[ R_{A_2}^{0h} = -\frac{P_{d_{eq}}X_{q}^{0e}(e^{\theta_{v}} - 1)}{(1 + \beta_{v}^{-1})a_{1}}, \quad [a_{1}] = \frac{a_{1}^{-e_{\theta_{v}}}}{a_{1} - 1} - a_{1}^{-e_{\theta_{v}} - 1}, \quad R_{v}^{0h} = q_{m}R_{A_{2}}^{0h}\left(1 + \frac{P_{01}}{P_{d_{eq}}Q_{10}}\right), \]

\[ A_{A_2A_2} = -\frac{(P_{d_{eq}}/P_{01})e^{-\theta_{v}}}{q_{m}(1 + \beta_{v}^{-1})(1 - a_{1}e^{-\theta_{v}})}, \quad A_{vA_{2}} = q_{m}\left(1 + \frac{P_{01}}{P_{d_{eq}}Q_{10}}\right)A_{A_2A_2} = -\frac{(P_{d_{eq}}/P_{01})e^{-\theta_{v}}}{(1 + \beta_{v}^{-1})(1 - a_{1}e^{-\theta_{v}})}, \]

\[ A_{vv} = q_{m}\left(\frac{P_{d_{eq}}/P_{01} + 1}{c_{10}\pi V q_{m}e^{\theta_{v}}(1 + \beta_{v}^{-1})[a_{1}]}\right), \quad A_{vA_{2}} = \frac{A_{v}}{q_{m}(1 + P_{01}/P_{d_{eq}}Q_{10})} = \frac{(P_{d_{eq}}/P_{01})e^{-\theta_{v}}}{c_{10}\pi V q_{m}e^{\theta_{v}}(1 + \beta_{v}^{-1})[a_{1}]}, \]

\[ a_{1} = (e^{\theta_{v}} + \beta_{v}^{-1})/(1 + \beta_{v}^{-1}), \quad \beta_{v}^{-1} = Q_{10}^{01}\Gamma_{v}e^{\theta_{v}}/P_{01}, \quad \Gamma_{v} = n_{A_{2}}\Gamma_{vA_{2}} \approx \frac{n_{A_{2}}}{\exp(\theta_{v}) - 1}, \]

\[ P_{d_{eq}} = P_{d_{eq}}^{A_{2}} + P_{d_{eq}}^{A_{2}} = P_{d_{eq}}^{A_{2}}Z_{A} + P_{d_{eq}}^{A_{2}}Z_{A_{2}}, \quad Z_{A,A_{2}} = n_{A_{2}}\pi r_{0_{A_{2}}}^{2}\sqrt{8k_{B}T/(\pi \mu_{A,A_{2}})}, \]

\[ P_{d_{eq}}^{A_{2}} = A_{d}^{A_{2}}T^{B_{A_{2}}}(1 - e^{-\theta_{v}})^{-1}\exp(-\theta_{v}E_{d}(1 - \theta_{v}E_{d}^{2}Q_{10}^{01})). \tag{14} \]

where \(\theta_{v} = \hbar c\omega_{v}/(k_{B}T)\), \(\theta_{t} = \hbar c\omega_{t}/(k_{B}T)\); \(P_{q,q+1} = (q + 1)P_{01}\) and \(Q_{q,q+1}^{01} = (q + 1)(I + 1)Q_{01}^{01}\) are corresponding rate constants of VT- and VV-transitions; \(P_{d_{eq}}^{A_{2}}\) are the dissociation probability of the considered molecule from level \(q\) when colliding with \(A_{2}\) or \(A_{2}\), \(Z_{A,A_{2}}\) is the collision frequency with \(A_{2}\) or \(A_{2}\), \(r_{0_{A_{2}}}^{2}\) are the Lennard–Jones potential parameters for interaction with \(A_{2}\) or \(A_{2}\), \(\mu_{A,A_{2}}\) is the corresponding reduced mass of colliding particles, \(P_{d_{eq}}\) is the corresponding recombination frequency with formation of the molecule in the vibrational state \(q\). Thus, the equations for quasi-stationary reaction, \(R_{A_{2}}^{eq}\), and relaxation, \(R_{v}^{eq}\), rates read as:

\[ R_{A_{2}}^{eq} = \frac{(1 - A_{v})(R_{A_{2}}^{eq} + R_{A_{2}}^{0h}) + A_{A_{2}v}(R_{v}^{eq} + R_{v}^{0h})}{1 - A_{A_{2}A_{2}} - A_{vv}}, \quad R_{v}^{eq} = \frac{(1 - A_{A_{2}A_{2}})(R_{v}^{eq} + R_{v}^{0h}) + A_{vA_{2}}(R_{v}^{eq} + R_{v}^{0h})}{1 - A_{A_{2}A_{2}} - A_{vv}}. \tag{15} \]

3. Numerical Procedure

The governing equations were solved numerically using ANSYS Fluent for simulation of a flow around a cylinder and Matlab for simulation of a 1D-shock. The finite volume flow-solver ANSYS Fluent was coupled with User Defined Functions (UDF) to describe the thermochemical phenomena. The governing equations were slightly modified in order to satisfy the requirements of the flow-solver (details are going to be provided in the future paper). In general, UDF implementation repeats the implementation described in [9]. The key difference is the computation of reaction, \(R_{A_{2}}^{eq}\), \(R_{A_{2}}^{eq}\), and relaxation, \(R_{v}^{eq}\), \(R_{v}^{eq}\), rates. The presented model gives expressions for the net reaction and relaxation rates that take into account all four chemical reaction rates, all VT- and VV-exchanges, vibrational energy depletion, and the influence of the chemical reactions on the vibrational relaxation rate. Due to the complexity of writing a reaction rate of one independent process (like dissociation rate \(N_{2} + N_{2} \rightarrow N_{2} + 2\)), we calculate expressions for \(R_{v}^{eq}\), \(R_{v}^{eq}\) or \(R_{v}^{eq}\), \(R_{v}^{eq}\) in DEFINE_VR_RATE macro for the one virtual chemical reaction \(N_{2} \rightarrow 2\). The value of \(R_{v}^{eq}\) or \(R_{v}^{eq}\) is passed to the flow-solver directly from DEFINE_VR_RATE to compute the mixture composition. Then, both \(R_{v}^{eq}\) (or \(R_{v}^{eq}\)) and \(R_{v}^{eq}\) (or \(R_{v}^{eq}\)) are stored in the User Defined Memory for further use inside DEFINE_SOURCE macro to compute source terms in the energy conservation equations. The Fluent flow-solver was used for the simulation of binary nitrogen flow around a cylinder. It is necessary to note that coefficients of viscosity, thermal conductivity and diffusion were calculated using standard model implemented in Fluent (details are given in [9]).
Figure 1. Numerical results for cylinder flow. Computational domain and translational-rotational temperature iso-lines (a) for computation with $R_{A_1}$, $R_{A_2}$. Stagnation profiles of translational-rotational and vibrational temperature computed using $R_{A_1}^{qs}$, $R_{A_2}^{qs}$ (b) and $R_{A_1}^{qe}$, $R_{A_2}^{qe}$ (c). Stagnation profiles of $|A_{mun}|$ computed using $R_{A_1}^{qs}$, $R_{A_2}^{qs}$ (d). Stagnation profiles of mass fraction of atomic component computed using $R_{A_1}^{qs}$, $R_{A_2}^{qs}$ (e) and $R_{A_1}^{qe}$, $R_{A_2}^{qe}$ (f).

The Matlab package was used to compute macroparameters behind 1D shock in a binary mixture of oxygen. The built-in function ode15s was used for solution of stiff ordinary differential equations on the basis of variable-order method.

4. Results

The presented model was used to simulate flows behind the planar and curved shock waves (1D flow and flow around the cylinder) for various free stream conditions. An impact of the reaction and relaxation rates on gas-dynamic parameters was analyzed. From equation (15) it can be seen that both $R_{A_1}^{qs}$ and $R_{A_2}^{qs}$ values crucially depends on whether $|A_{A_2} + A_{v_1}|$ is greater or smaller than 1. Under all considered conditions $|A_{v_1}| \ll |A_{A_2}|$, therefore only the dependence on $|A_{A_2}|$ value is considered and impact of the $|A_{A_2}|$ on the flow parameters is studied here. When $|A_{A_2}| \ll 1$, both rates are determined by the $R_{V}^{qs}$ and as a consequence by $P_{d_{1}}$, while at $|A_{A_2}| \gg 1$ ($P_{d_{1}}/P_{0_1} \gg 1$) the $P_{d_{1}}$ which is in the numerator and denominator (see (14)) reduces. Thus, corresponding rates become function not of $P_{d_{1}}$, but of $P_{0_1}(1 + \beta^{-1}) = P_{0_1} + Q_{1_0}^{1_0} d^{1} T_{v}$.

A flow around a cylinder was simulated in the computational domain shown in Fig. 1a. The segment AB is an inflow, where the free-stream conditions were applied. The free-stream is pure molecular nitrogen at Mach number equal to 25; static pressure and temperature are 15 Pa and 200 K, respectively. The segment BC is a supersonic outflow, i.e. all variables were extrapolated from the computational domain. The segment CD is a no-slip non-catalytic iso-thermal wall at 1000 K. The segment DA is a symmetry plane (the computational domain is 2D planar). The computations used hexa-mesh that refines towards the wall to resolve the boundary layer. The mesh was refined several times to reach grid...
In order to demonstrate the sensitivity of the numerical solution to the variation of the Arrheniuslaw parameters (and of the $P_{d_{qA}}$ as a whole), we computed the same case for different dissociation probabilities based on the various literature data. The Arrhenius law parameters are listed in Table 1. The computed profiles of the translational-rotational and vibrational temperatures and mass fraction of an atomic nitrogen along the stagnation line are given in Fig. 1b, 1c, 1e and 1f. It is seen that profiles for all Arrhenius coefficients are close to each other if quasi-stationary reaction $R_{A2}$, and relaxation, $R_{aq}$, rates are used. The profiles computed using quasi-equilibrium reaction $R_{aq}$, and relaxation, $R_{aq}$, rates depend on Arrhenius coefficients. In particular, the shock stand-off distance, peaks of the vibrational temperature and mixture composition are noticeable different. Figure 1d shows profiles of $[A_{A2:A2}]$ along the stagnation line. It is seen that $[A_{A2:A2}]$ is less than unity only in the free-stream for all Arrhenius coefficients excluding the Mankodi case. Inside the bow shock $[A_{A2:A2}]$ has a peak, which position correlates with the position of the translational temperature maximum. The quantity $[A_{A2:A2}]$ increases towards the cylinder’ wall keeping its value not smaller than 5.

For the numerical simulation of a high Mach number flow, it is also possible to assume that the probability of dissociation from the last vibrational level is equal to unity, i.e. $p_{d_{qA}} = p_{d_{ AQ}} = 1$, see (14). The curve, corresponding to this case, is denoted as ‘pd=1’ in Fig. 1. The computed ‘pd=1’ temperatures profiles coincide with all curves computed with the different Arrhenius law coefficients (Fig. 1b). The computed ‘pd=1’ mass fraction curve is slightly different from the curves computed with different Arrhenius law coefficients (Fig. 1e). For the case ‘pd=1’ the value of $[A_{A2:A2}]$ is significantly higher than unity. At the same time, the value of $[A_{A2:A2}]$ is smaller than that for any previous case.

In order to study the influence of the chemical reaction rate on the numerical solution we performed a simulation using Park’s set of the Arrhenius law coefficients reduced in million times. This case is denoted as ‘Park, A*1E-6’. It is seen that for ‘Park, A*1E-6’ the shock stand-off distance is higher than for all previous cases (Fig. 1b). The mixture composition along the stagnation line (Fig. 1e) is close to the other curves. The value of $[A_{A2:A2}]$ is much smaller than unity.

As mentioned above, the dissociation rate at high Mach numbers does not depend on $P_{d_{qA}}$. Hence, variation of the parameters determining $P_{d_{qA}}$, that are $A_{A2}$, $A_A$, $B_{A2}$ and $B_A$, is not important in that Mach number range. Thus, assumption ‘pd=1’ can also be used in the wide range of the Mach numbers. This conclusion agrees with the conclusion previously made in [10]. $P_{d_{qA}}$ decreases as the free-stream Mach number decreases. Starting at a certain Mach number, $P_{d_{qA}}$ becomes small, so that the dissociation rate becomes proportional to $P_{d_{qA}}$, as with the traditional approach. At the same time, due to the small value of $P_{d_{qA}}$, the effect of dissociation becomes insignificant. Thus, variation of $P_{d_{qA}}$ in the whole range of Mach numbers does not impact the flow parameters.

**Table 1.** The Arrhenius law parameters used in the computations.

| Notation | Source | Reaction | $A$, m$^3$/s | $B$ | $E_d$, K |
|----------|--------|----------|--------------|-----|---------|
| Chaudhry | [11]   | $N_2 + N_2$
$N_2 + N$          | 3.1458 \cdot 10^{-12}
7.6331 \cdot 10^{-13} | -0.6843
-0.5108 | 113200  |
| Mankodi  | [12, 13]| $N_2 + N_2$
$N_2 + N$          | 1.8048 \cdot 10^{-12}
8.5145 \cdot 10^{-12} | -0.5703
-0.7116 | 109920  |
| Park     | [14]   | $N_2 + N_2$
$N_2 + N$          | 1.1624 \cdot 10^{-8}
4.9817 \cdot 10^{-8} | -1.6
-1.6 | 113200  |
| Scanlon  | [15]   | $N_2 + N_2$
$N_2 + N$          | 4.1 \cdot 10^{-12}
1.0 \cdot 10^{-11} | -0.62
-0.68 | 113490  |
Figure 2 shows a comparison between profiles along the stagnation line computed using quasi-stationary and quasi-equilibrium reaction and relaxation rates. Using of quasi-stationary reaction and relaxation rates increases the shock stand-off distance, and increases the peak of the vibrational temperature (Fig. 2a). In the case of quasi-equilibrium reaction and relaxation rates, atomic mass fraction grows faster behind the shock. Then it drops down near the wall (Fig. 2b). This behavior is caused by the fast recombination rate in the boundary layer. Comparison between quasi-stationary and quasi-equilibrium reaction rates is given in Fig. 2c. $R^e_{qs}$ goes down near the wall ($x = 0$) indicating fast recombination rate. It is also necessary to note that the peak of $R^e_{qs}$ is higher than the peak of $R^e_{qe}$, which agrees with the numerical results obtained in [16] for one-temperature flow. Comparison between quasi-stationary and quasi-equilibrium relaxation rate is given in Fig. 2d. Both relaxation rate have qualitatively the same behavior.

The presented model is almost not sensitive to the variation of the probability of the dissociation rate. So, the dissociation rate depends on how fast the last vibrational level populates. The population of the last vibrational level is determined by the rate of the energy transfer, which within the harmonic oscillator model, is determined by the rate constants of VT excitation from the ground state to the first vibrational level, $R_{01}$, and of VV energy exchange, $Q_{10}^{10}$. Parameters $P_{01}$ and $Q_{01}^{10}$ can be computed using different models of vibrational-translation energy exchange.

In this study, we used SSH [17, 18] and FHO [19] models to assess their influence on the dissociation rate as well as on the macroparameters behind 1D shock in oxygen ($\text{O}_2$). Computations of the macroparameters behind 1D shock were done as follows. The gas mixture was assumed inviscid, hence, the shock is a line without internal structure. It was assumed that the vibrational excitation and chemical reactions are frozen across the shock, hence, classical Rankine–
Hugoniot conditions are valid to compute the macroparameters just behind the shock before relaxation starts. Therefore, in the next figure the left boundary of the computational domain corresponds to the parameters computed by the Rankine–Hugoniot conditions. Vibrational-translational energy exchange and chemical reactions are active starting from the left boundary of the computational domain. The right (outflow) boundary was placed downstream far enough for the mixture to reach the equilibrium state.

Figure 3 shows profiles computed behind 1D shock in O2/O mixture with next free steam conditions: pressure $p = 1$ Torr, gas temperature and vibrational temperature $T = T_v = 300$ K, Mach number $M = 15, 20, 25$, mixture composition contains 100% molecules. It can be seen that vibrational-translation energy exchange affects the temperature profiles and the length of the relaxation zone (Fig. 3a). Molar fraction behind the shock is highly affected by the rate of the last vibrational level population and as a consequence by the VT-model (Fig. 3b). It should be noted that the same probability of dissociation reactions based on the Park’s data [14] was used to compute all profiles behind the shock. As it can be seen in Fig. 3c in the majority of cases $|A_{A_2A_1}| \gg 1$ except the zone just behind the shock for the high Mach number cases ($M = 20$ and 25) with using SSH model. Such distinction is connected to the fact that the SSH model gives overestimated values of $P_{01}$ at high temperatures. This can be seen in Fig. 3d where the value of $P_{d_0}/P_{01}$ is significantly lower in ‘SSH’ case than in ‘FHO’ in the beginning of relaxation.
zone.

Performed simulations have shown that along with dissociation and vibration excitation probabilities, $|A_{A_2A_2}|$ is the key parameter of the model. When $|A_{A_2A_2}| \gg 1$ the system behavior is governed not by the $P_{dqm}$, but by the $P_{01} + Q_{10}e^{\theta_v}$.\Gamma_v$.

5. Conclusion
The reaction and relaxation rates derived within the new asymptotic method of solving the Boltzmann equation for the reacting mixture have been employed for studying the dissociation processes behind the shock wave. Analysis of the equations (15) and performed simulations have shown that in a wide range of flow parameters behind the shock the dissociation is controlled not by the dissociation probability, but by the vibration excitation probability (assuming the dissociation from the last vibrational level). This is because the population of the highest vibrational levels is the bottleneck of the dissociation process. This means that the attempts to describe the experimental data by varying the dissociation probability will not allow achieving the goal. It is shown that the dissociation probability can be considered equal to one, while the equations for excitation probabilities need to be specified. Further refining of the model is planned by including the anharmonicity effects and considering more complex mixtures.

Acknowledgments
The research was partly supported by the Russian Science Foundation (Grant No. 17-19-01375).

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