

Modeling of dissociation–recombination in nozzles using strongly non-equilibrium vibrational distributions

A. Chikhaoui^{a,*}, E.A. Nagnibeda^b, E.V. Kustova^b, T.Yu. Alexandrova^a

^a IUSTI – MHEQ, Université de Provence, Technopole de Chateau-Gombert, 5, rue Enrico Fermi, 13453 Marseille Cedex 13, France

^b Math. and Mech. Dept., St. Petersburg University, 198904 St. Petersburg, Russian Federation

Received 7 April 2000; in final form 27 September 2000

Abstract

The paper presents a quasi-stationary model for dissociation, recombination and vibrational kinetics in a nozzle expansion of (N₂, N) mixture. The model is based on strongly non-equilibrium non-Boltzmann and non-Treanor vibrational distributions. The closed set of equations for gas dynamic parameters is derived, the flow field parameters and vibrational distributions are computed in different sections of the nozzle for various reservoir conditions. The influence of vibrational distributions on gas parameters in the nozzle is discussed as well as the dissociation–recombination effects. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Modeling of vibrational and dissociation–recombination kinetics in nozzle flows is important for many practical problems of physical gas dynamics. The peculiarity of the rapid expansion of an initially heated gas mixture is that chemical reactions proceed in strongly vibrationally excited gas. Actually, the vibrational energy in a nozzle occurs much higher than the translational–rotational one because of rapid decrease of the gas temperature and different times of the translational–rotational and vibrational relaxation. Such a situation requires adequate models of vibra-

tional-chemical coupling in the flow. The first calculations of chemically non-equilibrium expanding flows were performed in the 60s [1–4], then different models of chemical and vibrational non-equilibrium have been elaborated.

The most rigorous approach consists in considering the state-to-state vibrational and chemical kinetics on the basis of the equations for vibrational level populations and atomic concentrations coupled with the gas dynamics equations. This approximation has been essentially advanced during the last decade and applied for different gas flows. For a nozzle flow the state-to-state model is developed in Refs. [5–10], and the important features of strongly non-equilibrium kinetics are shown. Another approach is based on the quasi-stationary vibrational distributions [11,12]. In this case the equations for vibrational level populations are reduced to the less number of the equations for macroscopic parameters. This approach

* Corresponding author. Tel.: +33-4-91-106869; fax: +33-4-91-106969.

E-mail address: aziz@iusti.univ-mrs.fr (A. Chikhaoui).

is essentially simpler than the state-to-state one and therefore is attractive for practical use. The most often used quasi-stationary models, based on the non-equilibrium Boltzmann or Treanor distributions [13], are not sufficiently good for nozzle flows. Indeed, due to strong vibrational excitation in a nozzle, not only low lying vibrational levels, but also intermediate and high vibrational states play an important role in the relaxation process. This situation cannot be described correctly by the Boltzmann or Treanor distributions. Thus, the Boltzmann distribution (with the vibrational temperature different from the translational–rotational one) is valid only for harmonic oscillator model and cannot take into account the real non-equidistant anharmonic vibrational spectrum, which is important for the high levels. The Treanor distribution takes into account the real vibrational spectrum but is applicable only for the low levels in strong vibrationally excited gas and gives unreal populations of high levels. Experiments in high enthalpy conditions with vibrational energy storage exceeding the translational–rotational one [14,15] show that the populations at intermediate and high levels are quite different from the Treanor distribution.

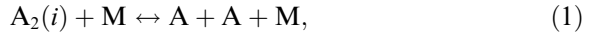
The non-equilibrium quasi-stationary vibrational distributions valid for all levels in the one-component chemically non-reactive gas have been found in Refs. [14,15] as an approximate solution of master equations, and in Refs. [16,17] such distributions have been obtained from the kinetic equation for distribution functions. These distributions reflect the complex mechanism of vibrational energy exchanges in a strongly excited gas.

In the present paper we generalize the model given in Refs. [16,17] for a dissociating gas mixture and apply it to a nozzle flow of (N₂, N) mixture. The aim of this paper is the elaboration of a generalized two-temperature model describing the dynamics of a strong vibrationally non-equilibrium flow with dissociation and recombination taking into account different channels of vibrational relaxation for various groups of vibrational levels. The accuracy of more simple models based on the Boltzmann and Treanor distributions in a nozzle expansion is estimated.

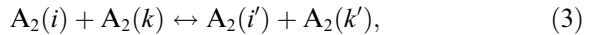
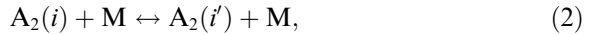
2. Kinetic model

2.1. Equations of the state-to-state kinetics

We consider the flow of a binary mixture of diatomic molecules and atoms with dissociation and recombination



and with VT(TV) and VV vibrational energy transitions



here $A_2(i)$ is a molecule at the i th vibrational level, an inert partner M can be a molecule or an atom A . The translational and rotational energies are known to equilibrate faster than the vibrational relaxation and dissociation–recombination processes proceed, and therefore the following conditions for characteristic relaxation times take place:

$$\tau_{tr} \leq \tau_{rot} \ll \tau_{vibr} < \tau_{dis-rec} \sim \theta, \quad (4)$$

here τ_{tr} , τ_{rot} , τ_{vibr} , $\tau_{dis-rec}$ are the mean times of translational, rotational, vibrational relaxation and dissociation–recombination processes, θ is the macroscopic characteristic time.

Under condition (4) the state-to-state model of non-equilibrium flow is valid. The equations of the state-to-state kinetics coupled with the gas dynamic conservation equations in the Euler approximation of a non-viscous non-conductive gas [18,19] have the form:

$$\frac{\partial n_i}{\partial t} + \sum_s \frac{\partial (n_i v_s)}{\partial x_s} = R_i, \quad i = 0, \dots, L, \quad (5)$$

$$\frac{\partial n_{at}}{\partial t} + \sum_s \frac{\partial (n_{at} v_s)}{\partial x_s} = R_a, \quad (6)$$

$$\rho \left(\frac{\partial v_j}{\partial t} + \sum_s v_s \frac{\partial v_j}{\partial x_s} \right) + \frac{\partial p}{\partial x_j} = 0, \quad (7)$$

$$\left(\frac{\partial}{\partial t} + \sum_s v_s \frac{\partial}{\partial x_s} \right) E + (p + E) \sum_s \frac{\partial v_s}{\partial x_s} = 0. \quad (8)$$

Here n_i is the i th level population, L is the total number of excited levels, v_j ($j = 1, 2, 3$) are the gas velocity components, E is the total energy per unit volume, p is the pressure, $\rho = n_{\text{mol}}m_{\text{mol}} + n_{\text{at}}m_{\text{at}}$, m_{mol} , m_{at} are the molecular and atomic masses, n_{at} and n_{mol} are the atom and molecule number densities.

The right-hand side of Eq. (5) describes the change of n_i as a result of VT(TV), VV vibrational energy transitions, dissociation and recombination:

$$R_i = R_i^{\text{vibr}} + R_i^{\text{dis-rec}}, \quad (9)$$

R_a describes the atom number density change:

$$R_a = -2 \sum_i R_i^{\text{dis-rec}}. \quad (10)$$

The expressions for R_i^{vibr} and $R_i^{\text{dis-rec}}$ have the form:

$$\begin{aligned} R_i^{\text{vibr}} = & \sum_{k,k',i'(k' \neq k, i' \neq i)} (k_{i'i}^{k'k} n_{i'} n_{k'} - k_{i'i'}^{kk'} n_i n_k) \\ & + n_{\text{mol}} \sum_{k \neq i} (k_{ki}^{\text{mol}} n_k - k_{ik}^{\text{mol}} n_i) \\ & + n_{\text{at}} \sum_{k \neq i} (k_{ki}^{\text{at}} n_k - k_{ik}^{\text{at}} n_i), \end{aligned}$$

$$R_i^{\text{dis-rec}} = R_i^{\text{dis}} + R_i^{\text{rec}},$$

$$R_i^{\text{dis}} = -n_i (n_{\text{mol}} k_{\text{dis},i}^{\text{mol}} + n_{\text{at}} k_{\text{dis},i}^{\text{at}}),$$

$$R_i^{\text{rec}} = n_a^2 (n_{\text{mol}} k_{\text{rec},i}^{\text{mol}} + n_{\text{at}} k_{\text{rec},i}^{\text{at}}).$$

Here $k_{ik}^{\text{mol}}(T)$, $k_{ik}^{\text{at}}(T)$, $k_{i'i'}^{kk'}(T)$ are the rate coefficients of VV and VT exchanges:

$$k_{i'i'}^{kk'}(T) = \frac{1}{n_{\text{mol}}} Z^{\text{mol}} Q_{i'i'}^{kk'}(T),$$

$$k_{ik}^{\text{mol}}(T) = \frac{1}{n_{\text{mol}}} Z^{\text{mol}} P_{ik}^{\text{mol}}(T),$$

$$k_{ik}^{\text{at}}(T) = \frac{1}{n_{\text{at}}} Z^{\text{at}} P_{ik}^{\text{at}}(T),$$

where Z^{mol} , Z^{at} are the numbers of collisions with molecules or atoms per unit time, $Q_{i'i'}^{kk'}(T)$, $P_{ik}^{\text{mol}}(T)$, $P_{ik}^{\text{at}}(T)$ are the probabilities of VV and VT transitions (we do not take into account TRV transi-

tions as they are less probable), $k_{\text{dis},i}^{\text{mol}}(T)$ and $k_{\text{dis},i}^{\text{at}}(T)$ are the rate coefficients of dissociation from the i th level at the collision with a molecule or an atom, $k_{\text{rec},i}^{\text{mol}}(T)$ and $k_{\text{rec},i}^{\text{at}}(T)$ are the rate coefficients of recombination to the i th level.

Eqs. (5)–(8) represent the closed set of the non-equilibrium gas dynamic equations for n_i , n_{at} , \mathbf{v} , T .

2.2. Quasi-stationary vibrational distributions

There exist the conditions when Eq. (5) can be reduced to the less number of the equations for macroscopic parameters. Such a procedure is performed in Ref. [18] for a reacting mixture and in Refs. [16,17] for a one-component gas with strong vibrational non-equilibrium. The reducing of the equations of state-to-state kinetics is based on the quasi-stationary solutions of Eq. (5). The existence of quasi-stationary distributions is determined by the relation between characteristic times of the considered processes. Usually these distributions are found from the equations

$$R_i^{\text{rap}} = 0, \quad (11)$$

where R_i^{rap} is the part of the collisional production term R_i in Eq. (5) for level populations, describing the dominant process with the shortest relaxation time.

Thus, from experimental results concerning relaxation times [20] it is known that at moderate temperatures which do not exceed strongly the characteristic vibrational temperature, the exchange of vibrational quanta between two molecules occurs more often than collisions with VT(TV) transitions, dissociation and recombination. Therefore the relaxation times for VV, VT(TV) and dissociation–recombination processes satisfy the condition

$$\tau_{\text{VV}} \ll \tau_{\text{VT}} \leq \tau_{\text{dis-rec}}. \quad (12)$$

Under condition (12) the quasi-stationary solution of Eq. (5) have the form of the Boltzmann or Treanor distribution [13]. It is well known that the Boltzmann non-equilibrium distribution with the vibrational temperature T_v different from T is valid only for the harmonic oscillator model, this distribution establishes as a result of rapid resonant VV exchanges between harmonic oscillators.

The Treanor distribution takes into account anharmonic vibrational spectrum and describes the non-resonant quanta exchanges. It was used by many authors for the investigation of the non-equilibrium vibrational kinetics. In the papers [18,21] the generalized multi-temperature model of the reacting air mixture is elaborated on the basis of the Treanor distribution for molecular components and applied for the conditions behind shock waves [21].

Such a model occurs not sufficiently rigorous for nozzle flows because in a strongly vibrationally excited gas the Treanor distribution is correct only at the lower levels. The distributions taking into account strong vibrational excitation and valid for all levels are obtained in Refs. [16,17] for a one-component non-reacting gas. In the present paper we generalize this model for a reacting mixture consideration.

The peculiarity of a strongly vibrationally excited gas is that the mechanism of vibrational energy transitions is different at various groups of levels. It follows both from experimental results and theoretical calculations concerning the transition probabilities [13–15]. Thus, at lower levels ($i < i^*$) the most rapid process is the non-resonant exchange of vibrational quanta between colliding molecules:

$$i + k = (i \pm m) + (k \mp m), \quad (13)$$

(m is the number of transferred quanta).

For the intermediate levels $i^* \leq i < i^{**}$ the resonant exchange of vibrational quanta between the neighboring levels proceeds more rapidly:

$$i + (i \pm 1) = (i \pm 1) + i. \quad (14)$$

For high levels the rates of all vibrational energy transitions are of the same order and remain much less than the rates of dissociation and recombination. Corresponding relations between relaxation times are:

$$\tau_{VV}^{\text{nonres}} \ll \tau_{VT} \leq \tau_{\text{dis-rec}} \sim \theta, \quad 0 \leq i < i^*,$$

$$\tau_{VV}^{\text{res}} \ll \tau_{VT} \leq \tau_{\text{dis-rec}} \sim \theta, \quad i^* < i \leq i^{**},$$

$$\tau_{VV} \sim \tau_{VT} \ll \tau_{\text{dis-rec}} \sim \theta, \quad i^{**} < i \leq L.$$

Under these conditions the expressions for R_i^{rap} in Eq. (11) are different for various groups of levels. Actually, at low levels R_i describe non-resonant exchanges (13), at intermediate levels R_i contain the terms corresponding to the resonant exchanges (14) and at high levels R_i describe all vibrational energy transitions. The solution of Eq. (11) in this case is obtained in Refs. [16,17] in the form:

$$\begin{aligned} n_i &= \frac{C_1}{Z_{\text{vibr}}^{\text{Tr}}} \exp\left(-\frac{\varepsilon_i - i\varepsilon_1}{kT} - \frac{i\varepsilon_1}{kT_1}\right), \quad 0 < i \leq i^*, \\ n_i &= \frac{\Gamma}{i+1}, \quad i^* < i \leq i^{**}, \\ n_i &= \frac{C_2}{Z_{\text{vibr}}^{\text{B}}} \exp\left(-\frac{\varepsilon_i}{kT}\right), \quad i^{**} < i \leq L. \end{aligned} \quad (15)$$

Here the coefficients C_1 , C_2 , Γ are found from the normalizing conditions for n_i and the continuity conditions at $i = i^*$, $i = i^{**}$,

$$Z_{\text{vibr}}^{\text{Tr}}(T, T_1) = \sum_{i=0}^{i^*} \exp\left(-\frac{\varepsilon_i - i\varepsilon_1}{kT} - \frac{i\varepsilon_1}{kT_1}\right), \quad (16)$$

$$Z_{\text{vibr}}^{\text{B}}(T) = \sum_{i=i^{**}}^L \exp\left(-\frac{\varepsilon_i}{kT}\right), \quad (17)$$

are the truncated Treanor and Boltzmann partition functions correspondingly, T_1 is the vibrational temperature of the first vibrational level, $\varepsilon_i = \varepsilon_1 i - \Delta\varepsilon i(i-1)$ is the vibrational energy of an anharmonic oscillator, $\varepsilon_1 = hc(w_e - 2w_e x_e)$, $\Delta\varepsilon = hcw_e x_e$, k is the Boltzmann constant, h is the Plank constant, c is the light speed, w_e and $w_e x_e$ are the spectroscopic constants ($w_e x_e$ is the anharmonicity), energies are calculated from the energy of the zeroth vibrational level.

Level populations (15) depend on two temperatures T , T_1 . One can see that at the low levels n_i are described by the Treanor distribution with the coefficient C_1 , at the intermediate levels populations have a form of a slopping plateau, and at the high levels they are described by the one-temperature Boltzmann distribution with the coefficient C_2 . The value i^* corresponds to the minimum of the Treanor distribution:

$$i^* = \frac{\varepsilon_1 T}{2\Delta\varepsilon T_1} + \frac{1}{2},$$

i^{**} is taken from the comparison of probabilities of VV and VT transitions: at $i > i^{**}$ probabilities of VV and VT transitions are of the same order. In Ref. [14] i^{**} is obtained in the form:

$$i^{**} = i^* + \frac{\varepsilon_1}{2\delta} \left(\frac{1}{kT} - \frac{1}{kT_1} \right),$$

$$\delta = \frac{8}{3}\pi^2 \frac{\Delta\varepsilon}{ha} \sqrt{\frac{\mu}{2kT}},$$

here μ is the reduced mass of colliding particles, a is the constant of exponential interaction potential. The last vibrational level L is found from the condition $\varepsilon_L \simeq D$, where D is the dissociation energy.

It can be easily shown that if $T_1 < T$ the value of i^* is close to the last level L and the Treanor distribution is valid practically for all levels. Such conditions are realized in the relaxation zone behind shock waves [21].

If anharmonic effects are negligible, $\varepsilon_i = i\varepsilon_1$, distribution (15) comes to the non-equilibrium Boltzmann distribution with vibrational temperature $T_1 = T_v \neq T$:

$$n_i = \frac{n_{\text{mol}}}{Z_{\text{vibr}}(T_v)} \exp\left(-\frac{\varepsilon_i}{kT_v}\right), \quad (18)$$

$$Z_{\text{vibr}}(T_v) = \sum_{i=0}^L \exp\left(-\frac{\varepsilon_i}{kT_v}\right). \quad (19)$$

If $T_v = T$ one obtains the thermal equilibrium Boltzmann distribution.

3. Macroscopic equations in the quasi-stationary approximation

Now we substitute distributions (15) into Eqs. (5) and (8). After summation of Eq. (5) over i we obtain the equation for molecular number density n_{mol} :

$$\frac{\partial n_{\text{mol}}}{\partial t} + \sum_s \frac{\partial(n_{\text{mol}}v_s)}{\partial x_s} = R^{\text{dis}} + R^{\text{rec}}. \quad (20)$$

Here

$$\begin{aligned} R^{\text{dis}} &= \sum_i R_i^{\text{dis}} = -n_{\text{mol}}(n_{\text{at}}k_{\text{dis}}^{\text{at}} + n_{\text{mol}}k_{\text{dis}}^{\text{mol}}), \\ R^{\text{rec}} &= \sum_i R_i^{\text{rec}} = n_{\text{at}}^2(n_{\text{at}}k_{\text{rec}}^{\text{at}} + n_{\text{mol}}k_{\text{rec}}^{\text{mol}}), \end{aligned} \quad (21)$$

where $k_{\text{rec}}^{(\text{M})}(T)$ and $k_{\text{dis}}^{(\text{M})}(T, T_1)$ (M is an atom or a molecule) are the macroscopic dissociation and recombination rate coefficients:

$$k_{\text{dis}}^{(\text{M})}(T, T_1) = \frac{1}{n_{\text{mol}}} \sum_{i=0}^L n_i k_{\text{dis},i}^{(\text{M})}(T), \quad (22)$$

$$k_{\text{rec}}^{(\text{M})}(T) = \sum_{i=0}^L k_{\text{rec},i}^{(\text{M})}(T).$$

Multiplying Eq. (5) by i , after summation over i we obtain the equation

$$\frac{\partial W}{\partial t} + \sum_s \frac{\partial(Wv_s)}{\partial x_s} = R_w^{\text{vibr}} + R_w^{\text{dis-rec}}, \quad (23)$$

here $W(n_{\text{mol}}, T, T_1) = \sum_{i=0}^L i n_i$ is the number of vibrational quanta in the unit volume and

$$R_w^{\text{vibr}} = \sum_i i R_i^{\text{vibr}}, \quad R_w^{\text{dis-rec}} = R_w^{\text{dis}} + R_w^{\text{rec}}, \quad (24)$$

$$R_w^{\text{dis}} = \sum_i i R_i^{\text{dis}}, \quad R_w^{\text{rec}} = \sum_i i R_i^{\text{rec}}. \quad (25)$$

Distributions (15) should also be substituted to the energy equation (8). The total energy E is the sum of the translational, rotational and vibrational ones:

$$E = \left(\frac{5}{2}n_{\text{mol}}kT + \frac{3}{2}n_{\text{at}}kT + E_{\text{vibr}} + E_f\right),$$

$$E_{\text{vibr}} = E_{\text{vibr}}(n_{\text{mol}}, T, T_1) = \sum_i \varepsilon_i n_i,$$

E_f is the energy of atom formation, $n_i = n_i(n_{\text{mol}}, T, T_1)$.

Finally we obtain the closed set of Eqs. (6)–(8), (20) and (23) for the functions $n_{\text{mol}}(\mathbf{r}, t)$, $n_{\text{at}}(\mathbf{r}, t)$, $\mathbf{v}(\mathbf{r}, t)$, $T(\mathbf{r}, t)$, $T_1(\mathbf{r}, t)$ in the quasi-stationary approximation. The equations for vibrational populations are reduced to the equations for the number density of molecular species and total

number of vibrational quanta W , which are expressed in terms of n_{mol} , T , T_1 . Compared to the quasi-stationary model considered by us previously [18,21], in the present case we take into account not only non-Boltzmann but also non-Treanor distributions with strongly excited intermediate and upper levels.

4. Dissociation–recombination models

For the calculation of the dissociation–recombination rate coefficients (22) and production terms (21), (24) in the equations for the number density of molecules (20) and atoms (6) and for the total number of vibrational quanta (23) two models have been used: the ladder-climbing model and the Treanor–Marrone one.

4.1. Ladder-climbing model

According to the ladder-climbing model molecules dissociate only from the last level and appear at this level as a result of recombination. In this case:

$$R^{\text{dis}} = R_L^{\text{dis}} = -n_L \left(n_{\text{at}} k_{\text{dis},L}^{\text{at}} + n_{\text{mol}} k_{\text{dis},L}^{\text{mol}} \right), \quad (26)$$

$$R^{\text{rec}} = R_L^{\text{rec}} = n_{\text{at}}^2 \left(n_{\text{at}} k_{\text{rec},L}^{\text{at}} + n_{\text{mol}} k_{\text{rec},L}^{\text{mol}} \right). \quad (27)$$

Dissociation rate is defined by the number of molecules leaving the last level L for the continuum spectrum. Following Ref. [22] the pseudo-level L' above L has been introduced, and it is assumed that dissociation and recombination go through the level L' . Thus,

$$R_L^{\text{dis}} = -n_L \left(k_{L,L+1}^{\text{mol}} n_{\text{mol}} + k_{L,L+1}^{\text{at}} n_{\text{at}} + \sum_{i=0}^L k_{L,L+1}^{i,i-1} n_i \right).$$

Therefore

$$k_{\text{dis},L}^{\text{mol}} = k_{L,L+1}^{\text{mol}} + \frac{1}{n_{\text{mol}}} \sum_{i=0}^L k_{L,L+1}^{i,i-1} n_i,$$

$$k_{\text{dis},L}^{\text{at}} = k_{L,L+1}^{\text{at}}.$$

The recombination rate coefficients $k_{\text{rec},L}^{\text{at}}$ and $k_{\text{rec},L}^{\text{mol}}$ are expressed in terms of $k_{\text{dis},L}^{\text{at}}$ and $k_{\text{dis},L}^{\text{mol}}$ using the detailed balance principle for the collisions with dissociation–recombination [23–25]:

$$k_{\text{rec},i}^{(\text{M})} = k_{\text{dis},i}^{(\text{M})} K_i(T),$$

$$K_i(T) = \left(\frac{m_{\text{mol}}}{m_{\text{at}}^2} \right)^{3/2} h^3 (2\pi kT)^{-3/2} Z_{\text{rot}} \times \exp \left(-\frac{\varepsilon_i - D}{kT} \right). \quad (28)$$

Z_{rot} is the rotational partition function.

Finally in the frame of the ladder-climbing model the dissociation and recombination rates are defined by the probabilities of vibrational energy transitions.

The expression for $R_w^{\text{dis-rec}}$ on the right-hand side of Eq. (23) for W in this case has the form:

$$R_w^{\text{dis-rec}} = LR_L^{\text{dis-rec}} = L(R_L^{\text{dis}} + R_L^{\text{rec}})$$

with R_L^{dis} and R_L^{rec} given by Eqs. (26) and (27).

4.1.1. Vibrational energy transitions

For the calculations of the production terms due to vibrations we take into account only one-quantum vibrational energy transitions as the more probable ones. The vibrational transition probabilities are computed using the SSH theory generalized for anharmonic vibrations [14,15].

It is known that at low temperatures the SSH theory underestimates significantly the efficiency of atoms in the VT exchange [26]. On the contrary, at high temperatures it gives overestimated values of probabilities of VT transfers from highly excited states (compared, for instance, to the values of Ref. [27]). However, the objective of the present paper is a comparative analysis of different models for the quasi-stationary vibrational distributions and their influence on the macroscopic parameters. For this purpose one can use a more simple SSH model for the rate coefficients of vibrational transitions. Further validation of the model and various transition probabilities should be based on the comparison with experimental data.

4.2. Treanor–Marrone model

Now we will calculate the dissociation and recombination rate coefficients and the production terms R^{dis} , R^{rec} and R_w^{dis} and R_w^{rec} on the right-hand sides of Eqs. (20) and (23) using the Treanor–Marrone model [28]. The Treanor–Marrone model permits the dissociation from any level.

In the approximation (15) the dissociation rate coefficients $k_{\text{dis}}^{(M)}$ defined by Eq. (22) depend on two temperatures T , T_1 . They can be presented in terms of the equilibrium rate coefficients $k_{\text{dis}}^{\text{eq}(M)}(T)$ and the non-equilibrium factor $\mathbf{Z}_f^{(M)}(T, T_1)$:

$$k_{\text{dis}}^{(M)}(T, T_1) = k_{\text{dis}}^{\text{eq}(M)}(T) \mathbf{Z}_f^{(M)}(T, T_1). \quad (29)$$

For calculation of $\mathbf{Z}_f^{(M)}(T, T_1)$ we use the Treanor–Marrone model. Previously [21], we have calculated $\mathbf{Z}_f^{(M)}(T, T_1)$ for the conditions behind a shock wave where $T \geq T_1$, correspondingly i^* is close to L , and therefore the Treanor distribution is correct for all levels. Now, following Refs. [28,21], we obtain $\mathbf{Z}_f^{(M)}(T, T_1)$ for strongly non-equilibrium distributions (15). Thus, in Ref. [28], the probability of the fact that a dissociated molecule was at the i th level

$$p_i^{(M)} = \frac{n_i k_{\text{dis},i}^{(M)}}{n_{\text{mol}} k_{\text{dis}}^{(M)}} \quad (30)$$

is presented in the form:

$$p_i = C n_i \exp\left(-\frac{D - \varepsilon_i}{kU}\right) \exp\left(-\frac{D - \varepsilon_i}{kT}\right). \quad (31)$$

Here U is the parameter of the model which can be found by fitting the experimental results, C is the normalizing coefficient:

$$C = \left(\sum_{i=0}^L n_i \exp\left(-\frac{D - \varepsilon_i}{kU}\right) \times \exp\left(-\frac{D - \varepsilon_i}{kT}\right) \right)^{-1}. \quad (32)$$

It should be noted that in our case the summation is performed over three different intervals of i with various n_i at these intervals.

Keeping in mind that $k_{\text{dis},i}^{(M)}$ does not depend on the vibrational distribution we have

$$k_{\text{dis},i}^{(M)} = \frac{p_i n_{\text{mol}} k_{\text{dis}}^{(M)}}{n_i} = \frac{p_i^{\text{eq}} n_{\text{mol}} k_{\text{dis}}^{\text{eq}(M)}}{n_i^{\text{eq}}}, \quad (33)$$

$$\mathbf{Z}_f(T, T_1) = \frac{k_{\text{dis}}^{(M)}(T, T_1)}{k_{\text{dis}}^{\text{eq}(M)}(T)} = \frac{p_i^{\text{eq}} n_i}{p_i n_i^{\text{eq}}} = \frac{C^{\text{eq}}}{C}, \quad (34)$$

where p_i^{eq} and C^{eq} denote the expressions for p_i and C with substituted equilibrium distributions $n_i = n_i^{\text{eq}}(T)$.

Taking into account the different form of distribution (15) at various levels we can write the final expression for $\mathbf{Z}_f(T, T_1)$ in our case:

$$\mathbf{Z}_f(T, T_1) = \frac{Z_{\text{vibr}}(T)}{Z_{\text{vibr}}(-U)} S(T, T_1),$$

where

$$\begin{aligned} S(T, T_1) &= \frac{1}{n_{\text{mol}}} \frac{C_1}{Z_{\text{vibr}}^{\text{Tr}}} \sum_{i=0}^{i^*} \exp\left(i\varepsilon_1 \left(\frac{1}{kT} - \frac{1}{kT_1}\right) + \frac{\varepsilon_i}{kU}\right) \\ &+ \frac{1}{n_{\text{mol}}} \Gamma \sum_{i=i^*}^{i^{**}} \frac{1}{i+1} \exp\left(\varepsilon_i \left(\frac{1}{kT} + \frac{1}{kU}\right)\right) \\ &+ \frac{1}{n_{\text{mol}}} \frac{C_2}{Z_{\text{vibr}}^{\text{B}}} \sum_{i^*}^L \exp\left(\frac{\varepsilon_i}{kU}\right), \end{aligned} \quad (35)$$

$$Z_{\text{vibr}}(T) = \sum_{i=0}^L \exp\left(-\frac{\varepsilon_i}{kT}\right).$$

This expression comes to the one obtained in Ref. [21] if the Treanor distribution is supposed to be valid for all levels. Actually, in this case i^* is close to L and from Eq. (35) it follows:

$$S(T, T_1) = \frac{S^{\text{Tr}}(T, T_1)}{Z_{\text{vibr}}^{\text{Tr}}(T, T_1)},$$

where

$$S^{\text{Tr}}(T, T_1) = \sum_{i=0}^L \exp\left(i\varepsilon_1 \left(\frac{1}{kT} - \frac{1}{kT_1}\right) + \frac{\varepsilon_i}{kU}\right),$$

$Z_{\text{vibr}}^{\text{Tr}}(T, T_1)$ is given by Eq. (16) where $i^* = L$. The equation for $\mathbf{Z}_f(T, T_1)$ can be easily reduced to the commonly used formula [12,28] if the anharmonic effects are neglected.

Finally the expression for R^{dis} reads:

$$R^{\text{dis}} = -n_{\text{mol}} \left(n_{\text{at}} k_{\text{dis}}^{\text{eq,at}}(T) + n_{\text{mol}} k_{\text{dis}}^{\text{eq,mol}}(T) \right) \times \mathbf{Z}_f(T, T_1). \quad (36)$$

Now we consider the term R_w^{dis} given by Eq. (25). Substituting $k_{\text{dis},i}^{(M)}$ from Eq. (33) and using Eqs. (31) and (34) we can rewrite R_w^{dis} in the form:

$$R_w^{\text{dis}} = -n_{\text{mol}} \left(n_{\text{mol}} k_{\text{dis}}^{\text{eq,mol}} + n_{\text{at}} k_{\text{dis}}^{\text{eq,at}} \right) \times \mathbf{Z}_f(T, T_1) G_{\text{dis}}(T, T_1). \quad (37)$$

Here

$$G_{\text{dis}}(T, T_1) = \frac{\sum_{i=0}^L n_i \left(\exp \left(\varepsilon_i \left(\frac{1}{kT} + \frac{1}{kU} \right) \right) \right)}{\sum_{i=0}^L n_i \left(\exp \left(\varepsilon_i \left(\frac{1}{kT} + \frac{1}{kU} \right) \right) \right)} = \frac{V(T, T_1)}{S(T, T_1)}, \quad (38)$$

$$V(T, T_1) = \frac{1}{n_{\text{mol}}} \frac{C_1}{Z_{\text{vibr}}^{\text{Tr}}} \sum_{i=0}^{i^*} i \exp \left(i \varepsilon_i \left(\frac{1}{kT} - \frac{1}{kT_1} \right) + \frac{\varepsilon_i}{kU} \right) + \frac{1}{n_{\text{mol}}} \Gamma \sum_{i=i^*}^{i^{**}} \frac{i}{i+1} \exp \left(\varepsilon_i \left(\frac{1}{kT} + \frac{1}{kU} \right) \right) + \frac{1}{n_{\text{mol}}} \frac{C_2}{Z_{\text{vibr}}^{\text{B}}} \sum_{i=i^*}^L i \exp \left(\frac{\varepsilon_i}{kU} \right), \quad (39)$$

and $S(T, T_1)$ is given by Eq. (35).

This expression comes to the one obtained in Ref. [21] in the case if we have only the Treanor distribution for all levels, then

$$V(T, T_1) = \sum_{i=0}^L i \exp \left(i \varepsilon_i \left(\frac{1}{kT} - \frac{1}{kT_1} \right) + \frac{\varepsilon_i}{kU} \right).$$

Eqs. (36) and (37) express R^{dis} and R_w^{dis} in terms of $k_{\text{dis}}^{\text{eq}(M)}(T)$, $\mathbf{Z}_f(T, T_1)$ and $G_{\text{dis}}(T, T_1)$. The equilibrium rate coefficients are given by the generalized Arrhenius law:

$$k_{\text{dis}}^{\text{eq}(M)} = AT^n \exp \left(-\frac{D}{kT} \right),$$

where values n , A are taken from Ref. [29] ($n = -1.6$, $A = 3.7 \times 10^{15}$ if M is a molecule and $A = 1.6 \times 10^{16}$ if M is an atom). The units of this coefficient are $\text{cm}^3/(\text{mole} \cdot \text{s})$.

Now we have to calculate the recombination rate coefficients and the terms R^{rec} and R_w^{rec} in Eqs. (20) and (23). We use for that the detailed balance equations (28) for the state-to-state rates of dissociation and recombination. We would like to note that we use here a more rigorous way for the connection of the coefficients of forward and backward reactions compared to the commonly used method in the multi-temperature models. In fact, non-equilibrium two-temperature coefficients of forward and backward reactions are often connected using the expression for the equilibrium constant $K(T)$ obtained for the equilibrium conditions. We also followed this approximate way in our previous paper [21]. Now we use Eq. (28) connecting $k_{\text{dis},i}^{(M)}$ and $k_{\text{rec},i}^{(M)}$ which follows from the rigorous detailed balance principle for the collisional differential balance cross-sections after averaging only over the velocity Maxwellian distribution and the rotational energy Boltzmann distribution. Therefore $K_i(T)$ does not depend on the vibrational distributions and depends only on T .

In so doing we write the recombination rate coefficients (22) in the form:

$$k_{\text{rec}}^{(M)}(T) = \sum_{i=0}^L k_{\text{dis},i}^{(M)}(T) K_i(T). \quad (40)$$

From Eq. (33) we can write $k_{\text{dis},i}^{(M)}(T)$ in the form [30]:

$$k_{\text{dis},i}^{(M)}(T) = k_{\text{dis}}^{\text{eq}(M)} \frac{Z_{\text{vibr}}(T)}{Z_{\text{vibr}}(-U)} \exp \left(\varepsilon_i \left(\frac{1}{kU} + \frac{1}{kT} \right) \right)$$

and obtain the expression for $k_{\text{rec}}^{(M)}(T)$:

$$k_{\text{rec}}^{(M)}(T) = k_{\text{dis}}^{\text{eq}(M)}(T) \frac{Z_{\text{vibr}}(T)}{Z_{\text{vibr}}(-U)} \times \sum_{i=0}^L \exp \left(\varepsilon_i \left(\frac{1}{kU} + \frac{1}{kT} \right) \right) K_i(T), \quad (41)$$

where $K_i(T)$ is given by Eq. (28).

Finally the term R^{rec} reads:

$$R^{\text{rec}} = n_{\text{at}}^2 \left(n_{\text{at}} k_{\text{dis}}^{\text{eq,at}}(T) + n_{\text{mol}} k_{\text{dis}}^{\text{eq,mol}}(T) \right) \times \frac{Z_{\text{vibr}}(T)}{Z_{\text{vibr}}(-U)} \sum_{i=0}^L \exp \left(\varepsilon_i \left(\frac{1}{kU} + \frac{1}{kT} \right) \right) K_i(T). \quad (42)$$

Now we have to consider the expression for R_w^{rec} on the right-hand side of Eq. (23) for the mean number of vibrational quanta:

$$R_w^{\text{rec}} = \sum_M n^{(M)} n_{\text{at}}^2 \sum_{i=0}^L i k_{\text{rec},i}^{(M)} \quad (43)$$

The term R_w^{rec} is also calculated using the detailed balance principle (33). Doing so, we find:

$$\begin{aligned} R_w^{\text{rec}} &= \sum_{i=0}^L i n_{\text{at}}^2 \left(n_{\text{mol}} k_{\text{rec},i}^{\text{mol}} + n_{\text{at}} k_{\text{rec},i}^{\text{at}} \right) \\ &= n_{\text{at}}^2 \left(n_{\text{mol}} k_{\text{dis}}^{\text{eq,mol}} + n_{\text{at}} k_{\text{dis}}^{\text{eq,at}} \right) \mathbf{Z}_f(T, T_1) G_{\text{rec}}(T), \\ G_{\text{rec}}(T) &= \frac{\sum_{i=0}^L i (K_i(T) \exp(\varepsilon_i (\frac{1}{kT} + \frac{1}{kU})))}{S(T, T_1)} \\ &= \frac{Z_{\text{vibr}}(T)}{Z_{\text{vibr}}(-U)} \sum_{i=0}^L i \exp\left(\varepsilon_i \left(\frac{1}{kU} + \frac{1}{kT}\right)\right) K_i(T). \end{aligned} \quad (44)$$

Finally, the equations for R^{rec} and R_w^{rec} are presented in terms of $k_{\text{dis}}^{\text{eq}(M)}$, $\mathbf{Z}_f(T, T_1)$ and $G_{\text{rec}}(T)$.

5. Application to a nozzle flow

The equations for macroscopic parameters n_{mol} , n_{at} , T , T_1 , \mathbf{v} derived above have been applied for the investigation of a nozzle expansion using the steady-state quasi-one-dimensional approximation. In this case the system of governing equations reads:

$$\begin{aligned} \frac{d(n_{\text{mol}} v S)}{dx} &= S R^{\text{dis-rec}}, \\ \frac{d(n_{\text{at}} v S)}{dx} &= -2 S R^{\text{dis-rec}}, \\ \rho v \frac{dv}{dx} &= -\frac{dp}{dx}, \\ S v \frac{dE}{dx} + (E + p) \frac{d(Sv)}{dx} &= 0, \\ \frac{d(SvW)}{dx} &= S(R_w^{\text{rel}} + R_w^{\text{dis-rec}}). \end{aligned} \quad (45)$$

Here $S(x)$ is the nozzle cross-section, x is the coordinate along the nozzle axis, v is the velocity along the nozzle axis.

The numerical calculations have been performed for the (N_2, N) mixture flow in the expanding nozzle of a conic profile with the angle 21° for the following conditions in the reservoir: $T_0 = 5375, 7525$ K, $p_0 = 1.74, 17.4, 174$ atm, the radius of the critical cross-section is 1 mm.

In the reservoir, as well as in the critical cross-section, the mixture is supposed to be at the thermal and chemical equilibrium. Number densities of molecular and atomic species in the reservoir are found in terms of T_0 , p_0 using the law of acting masses and the Dalton law:

$$\begin{aligned} \frac{\xi_{\text{at},0}^2}{\xi_{\text{mol},0}} &= \frac{kT_0}{p_0} \left(\frac{m_{\text{at}}^2}{m_{\text{mol}}} \right)^{3/2} h^{-3} (2\pi kT_0)^{3/2} \\ &\times (Z_{\text{int}}(T_0))^{-1} \exp\left(-\frac{D}{kT_0}\right), \end{aligned} \quad (46)$$

$$\xi_{\text{at},0} + \xi_{\text{mol},0} = 1,$$

where ξ_{mol} and ξ_{at} are the atomic and molecular molar fractions:

$$\xi_{\text{at}} = \frac{n_{\text{at}}}{n_{\text{at}} + n_{\text{mol}}}, \quad \xi_{\text{mol}} = \frac{n_{\text{mol}}}{n_{\text{at}} + n_{\text{mol}}},$$

$$Z_{\text{int}}(T) = Z_{\text{rot}}(T) Z_{\text{vibr}}(T).$$

The rotational partition function for diatomic molecules in the frame of the rigid rotator model is

$$Z_{\text{rot}} = \frac{8\pi J k T}{\sigma h^2},$$

where σ is a symmetrical factor, $\sigma = 2$ for homonuclear molecules, J is the inertia momentum, the data for N_2 are taken from Ref. [31].

The parameters in the critical section have been calculated in terms of reservoir parameters using the equation

$$\frac{1}{2} \gamma_* R T_* + h_* = h_0 \quad (47)$$

coupled with the equation of the law of acting mass and the Dalton one written for the parameters in the critical cross-section.

In Eq. (47) h_* , h_0 are the specific enthalpies in the critical cross-section and in the reservoir, subscript (*) denotes the values in the critical cross-section, $\gamma = c_p/c_v$, c_p , c_v are the specific heats at the constant pressure and constant volume.

The enthalpy of a mixture is

$$h = h_{\text{at}} Y_{\text{at}} + h_{\text{mol}} Y_{\text{mol}},$$

where h_{at} , h_{mol} are specific enthalpies of atoms and molecules, $Y_{\text{at}} = \rho_{\text{at}}/\rho$, $Y_{\text{mol}} = \rho_{\text{mol}}/\rho$ are the mass fractions of atoms and molecules.

Therefore

$$h = \frac{p}{\rho} + \frac{3}{2} \frac{R}{M} T + Y_{\text{at}} h_{\text{f}} + Y_{\text{mol}} \frac{R}{M_{\text{mol}}} T + Y_{\text{mol}} c_{v,\text{vibr}},$$

$$\frac{1}{M} = \frac{1}{M_{\text{at}}} + \frac{1}{M_{\text{mol}}},$$

M_{at} , M_{mol} are the atomic and molecular weights, h_{f} is the specific enthalpy of atom formation, $c_{v,\text{vibr}}$ is the vibrational specific heat at the constant volume.

The values γ and $c_{v,\text{vibr}}$ are found from the expressions:

$$\gamma = \frac{\frac{5}{2} + \zeta_{\text{mol}} + Y_{\text{mol}} c_{v,\text{vibr}}}{\frac{3}{2} + \zeta_{\text{mol}} + Y_{\text{mol}} c_{v,\text{vibr}}},$$

$$c_{v,\text{vibr}} = \frac{1}{k} \frac{\partial}{\partial T} \left(\frac{1}{Z_{\text{vibr}}(T)} \sum_i \varepsilon_i \exp\left(-\frac{\varepsilon_i}{kT}\right) \right).$$

The results presented below are obtained using the Treanor–Marrone model with the parameter $U = D/3k$.

6. Results

In this section we will discuss the results of numerical calculations. The macroscopic parameters n_{at} , n_{mol} , T , T_1 have been found as a numerical solution of Eq. (45) and presented at different distances from the critical cross-section along the axis. Then vibrational distributions (15) are calculated using the obtained values of macroscopic parameters. The results are compared with the ones obtained on the basis of

(1) the non-equilibrium Boltzmann distribution (18) (for harmonic oscillators with $T_v \neq T$),

(2) the Treanor two-temperature distribution (up to the level i^* and neglecting populations at $i > i^*$),

(3) the equilibrium Boltzmann distribution ($T_v = T$).

The influence of different vibrational distributions on the macroscopic parameters and dissociation–recombination processes is investigated for various values of pressure and gas temperature in the reservoir. The calculations have been done also neglecting dissociation and recombination in order to understand the role of these processes under the conditions considered. The results are presented in Figs. 1–12.

Figs. 1–4 plot the change of the gas temperature T and vibrational temperature of the first level T_1 along the nozzle axis in dependence of the distance from the critical cross-section (x is related to the radius R of the critical cross-section) for different reservoir conditions.

One can see the essential influence of vibrational distributions on T_1 , this effect on T is very weak. Neglecting the anharmonism of molecular vibrations and using the Boltzmann distribution lead to an overestimation of T_1 , lower values of T and more rapid freezing of both the temperatures. The Treanor distribution, taking into account anharmonic effects, gives the values of T_1 much closer to the ones obtained using distributions (15). The difference between the values found on the basis of Eq. (15) and the Boltzmann distribution is about 31% for T_1 and 6% for T in the case $T_0 = 7525$ K, $p_0 = 17.4$ atm.

In order to estimate the role of dissociation and recombination processes on the temperature we calculated T and T_1 in the following cases: (a) neglecting dissociation (with recombination and VV, VT(TV) processes), (b) neglecting recombination (with dissociation and VV, VT(TV) processes) and (c) neglecting dissociation and recombination (with VV and VT(TV) exchanges only). The results are presented in Figs. 3 and 4. Fig. 4 shows that in the case $p_0 = 174$ atm, $T_0 = 7525$ K neglecting dissociation–recombination and taking into account only VV and VT(TV) vibrational energy exchanges we have the higher values of T and lower T_1 values. Quantitatively this effect is rather

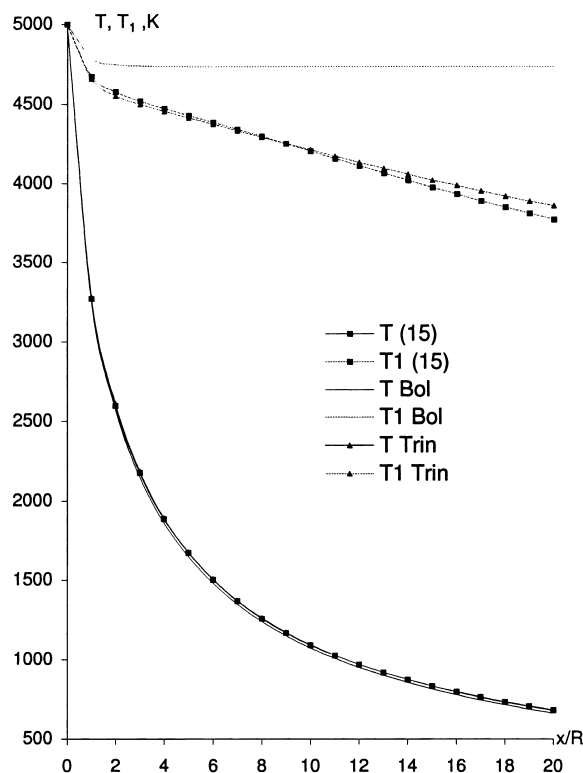


Fig. 1. T , T_1 versus x/R for different vibrational distributions; $T_0 = 5375$ K, $p_0 = 17.4$ atm.

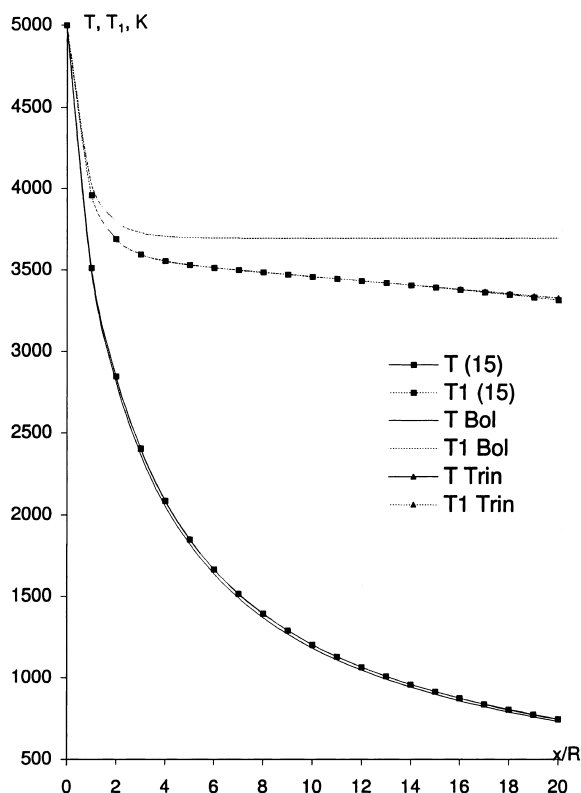


Fig. 2. T , T_1 versus x/R for different vibrational distributions; $T_0 = 5375$ K, $p_0 = 174$ atm.

small because dissociation–recombination processes go slightly in the expanding (N_2 , N) mixture under conditions considered.

Figs. 5–7 present the ratio T_1/T versus x/R for various models and different reservoir conditions. The ratio T_1/T characterizes the degree of non-equilibrium in the flow. Fig. 5 shows the highest T_1/T in the case of the Boltzmann non-equilibrium distribution, the Treanor distribution gives the value of T_1/T closer to the one obtained on the basis of distribution (15), but still exceeds the last one. The same figure presents T_1/T calculated with the distribution (15) taking into account the complete kinetics (curve (15)), neglecting dissociation (curve ((15)rec)), neglecting recombination (curve ((15)dis)), and neglecting both dissociation and recombination (curve ((15)VV, VT)). Neglecting dissociation–recombination causes lower T_1/T values in the case $p_0 = 174$ atm, $T_0 = 7525$ K. The ratio T_1/T increases with x rising.

Figs. 6 and 7 plot T_1/T calculated on the basis of Eq. (15) and the Boltzmann distribution correspondingly, for different reservoir conditions. The lowest T_1/T values are in the case $T_0 = 7525$ K, $p_0 = 174$ atm. One can see the higher values of T_1/T calculated using the Boltzmann distribution compared to distribution (15).

The molar fractions of atoms $n_{at}/(n_{at} + n_{mol})$ versus x/R is given in Figs. 8–10. The most essential recombination effect is found in the case $T_0 = 7525$ K, $p_0 = 174$ atm. The competition of dissociation and recombination is seen in Figs. 9 and 10, which are given in the other scale. Recombination plays the dominant role at the high pressure in the reservoir and is less important at the lower pressure.

Comparison of the values $n_{at}/(n_{at} + n_{mol})$ calculated on the basis of Eq. (15) and Boltzmann distribution (18) shows the higher role of

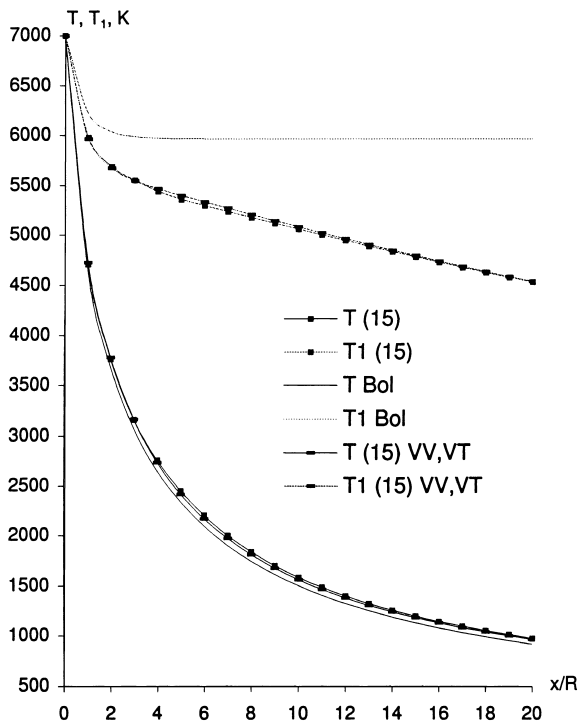


Fig. 3. T , T_1 versus x/R for distribution (15) and Boltzmann distribution (Bol) for the complete kinetics and neglecting dissociation–recombination ((15)VV, VT): $T_0 = 7525$ K, $p_0 = 17.4$ atm.

dissociation in the first case. It is not surprising because Eq. (15) gives more excited intermediate and upper levels which are important for dissociation. It should be noted, that the results obtained show the very weak change of atomic molar fraction in the expanding (N_2 , N) mixture. It is similar to the behavior found in Ref. [9] for the same mixture. It is explained by the low rate of dissociation–recombination in this case. Actually, the expanding of the flow results in the rapid decrease of both the gas temperature and pressure. Because of the temperature rapid decrease, the role of the dissociation becomes weak, and low pressure causes very slight recombination which goes through triple collisions. Experiments show the stronger decrease of $n_{at}/(n_{at} + n_{mol})$ in the air nozzle expansion [2]. It is explained by the fact that the change of nitrogen atom density in the air mixture goes mostly through the exchange reactions which

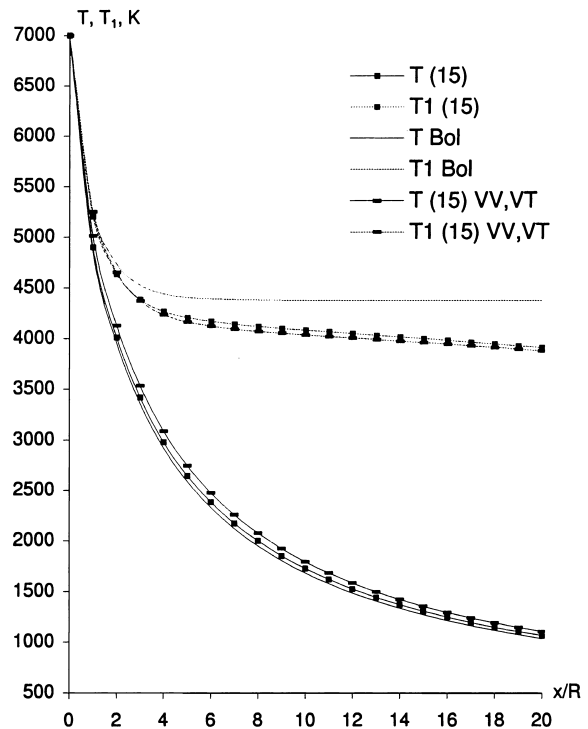


Fig. 4. T , T_1 versus x/R for distribution (15) and Boltzmann distribution (Bol) for the complete kinetics and neglecting dissociation–recombination ((15)VV, VT): $T_0 = 7525$ K, $p_0 = 17.4$ atm.

rates exceed the N_2 dissociation rate and the rate of N_2 formation due to recombination.

Our calculations show the effect of non-Boltzmann distribution on the dissociation–recombination processes, this role decreases at the higher pressure because in this case, as it is seen from Fig. 6, the deviation from the thermal equilibrium is less.

Figs. 11 and 12 represent the vibrational distributions n_i/n_{mol} versus i in two sections of the nozzle: $x/R = 3$ and $x/R = 15$. Distribution (15) is compared with the Treanor distribution, non-equilibrium Boltzmann distribution and one-temperature equilibrium Boltzmann distribution. The populations have been calculated using the gas parameters obtained from the macroscopic equations based on the approximation (15), Treanor distributions and Boltzmann distributions correspondingly.

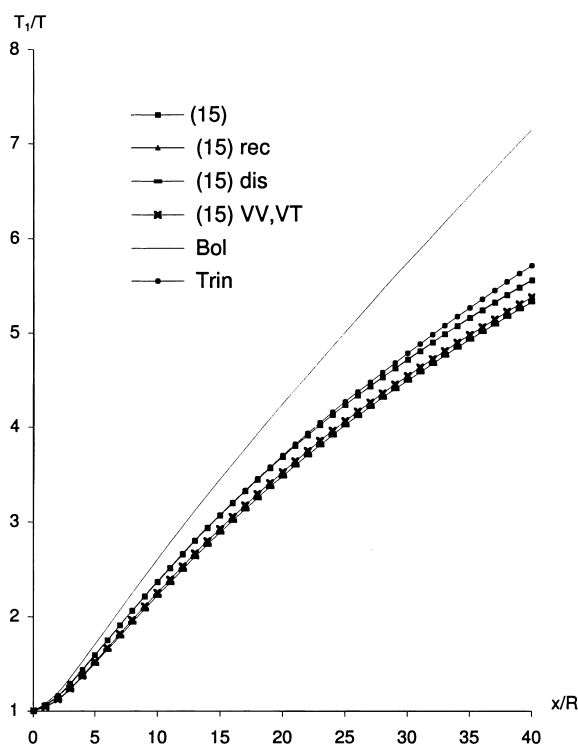


Fig. 5. T_1/T versus x/R for distribution (15): complete kinetics, neglecting dissociation ((15)rec), recombination ((15)dis), dissociation–recombination ((15)VV, VT) and for Boltzmann and Treanor distributions, complete kinetics. $T_0 = 7525$ K, $p_0 = 174$ atm.

One can see that close to the critical cross-section when T_1/T only slightly exceeds 1, the Treanor distribution is close to Eq. (15) practically at all levels. Anharmonism of vibrations manifests itself already at $i > 7$ and Boltzmann distribution gives underpopulation of the levels at $i > 7$. The thermal equilibrium Boltzmann distribution with $T_v = T$ gives much lower vibrational populations. At $x/R = 15$ the Treanor distribution is valid only up to $i^* = 17$ and distribution (15) gives populations of intermediate and upper levels quite different from the Treanor one.

7. Conclusions

In this paper the non-equilibrium gas dynamic model for binary (N_2 , N) mixture with dissociation and recombination is presented. The closed set of

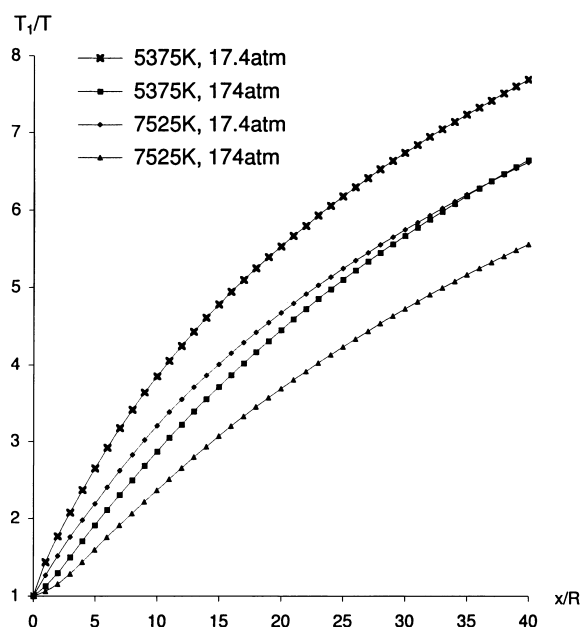


Fig. 6. Comparison of T_1/T for distribution (15) under different source conditions.

the equations for macroscopic parameters n_{mol} , n_{at} , T , T_1 , v is derived on the basis of quasi-stationary vibrational distributions. These distributions take into account strong vibrational excitation and differ from the Boltzmann and Treanor ones.

The model is applied to a nozzle expansion of (N_2 , N) mixture. The flow parameters and vibrational distributions are computed for different conditions in the reservoir. The results are compared with the ones obtained using the Boltzmann and Treanor distributions and the accuracy of the last ones in a nozzle flow is estimated.

It is shown that in a nozzle expansion of the mixture considered in the paper the essentially non-Boltzmann and non-Treanor distributions appear, the intermediate levels are excited due to VV vibrational energy exchange. The Boltzmann distribution gives an underestimation of level population and differs strongly from the Treanor distribution and distribution (15) obtained in our paper. It shows the importance of anharmonic effects in a nozzle flow. The Treanor distribution gives satisfactory approximation of all levels only in the very beginning of a nozzle, at small x , and then with x growing leads to unreal populations of

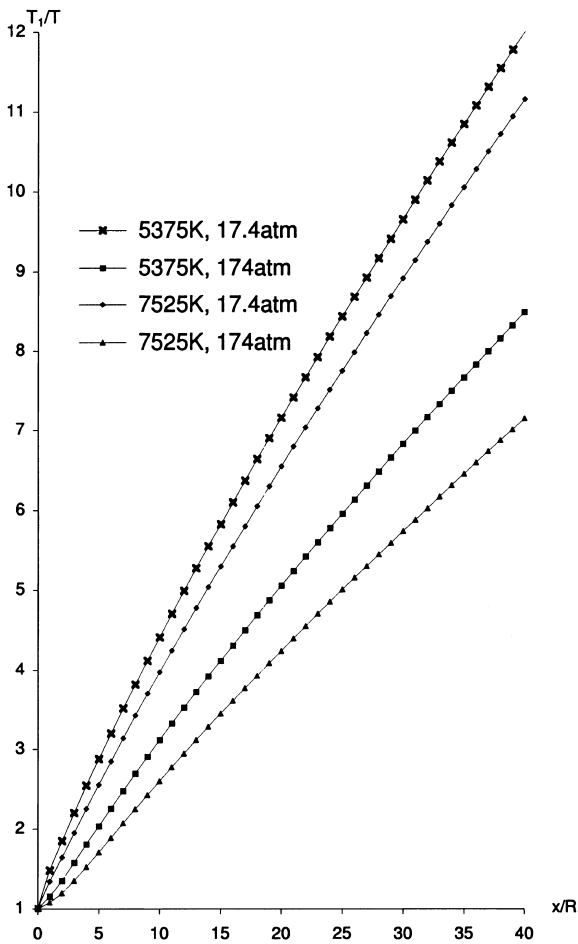


Fig. 7. Comparison of T_1/T for Boltzmann distribution (15) under different source conditions.

intermediate and upper levels. The difference between distribution (15) and the Treanor one increases noticeably with x rising.

The model of vibrational level populations influences significantly T_1 and non-equilibrium parameter T_1/T whereas its effect on the gas temperature is weak, the Boltzmann distribution causes an overestimation of T_1 and T_1/T and lower values of T .

The ratio T_1/T increases noticeably with x .

The influence of dissociation–recombination on T , T_1 , T_1/T and atomic molar fraction is also studied in this paper. However, this effect occurs small in the expanding (N_2 , N) mixture. Actually, the dissociation role decreases due to the rapid

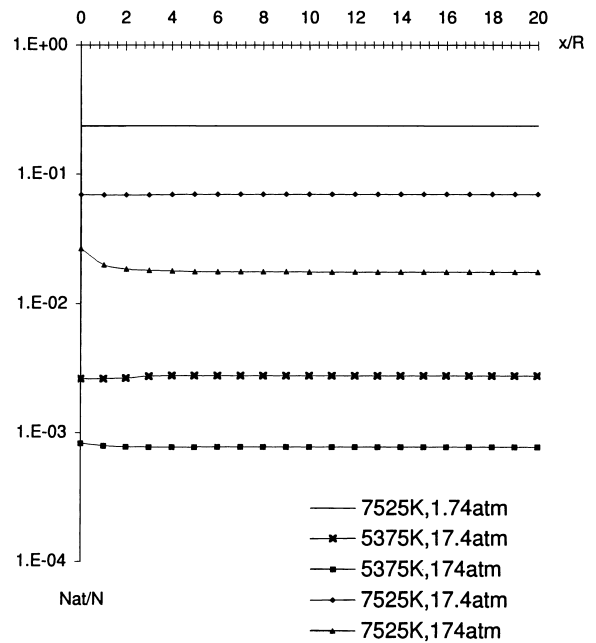


Fig. 8. N_{at}/N for distribution under different source conditions.

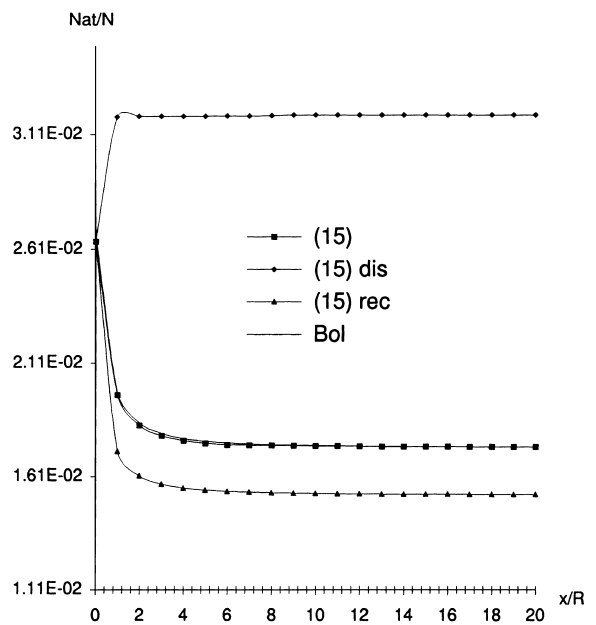


Fig. 9. N_{at}/N for distribution (15) with complete kinetics, neglecting recombination ((15)dis), neglecting dissociation ((15)rec) and for Boltzmann distribution. $T_0 = 7525$ K, $p_0 = 174$ atm.

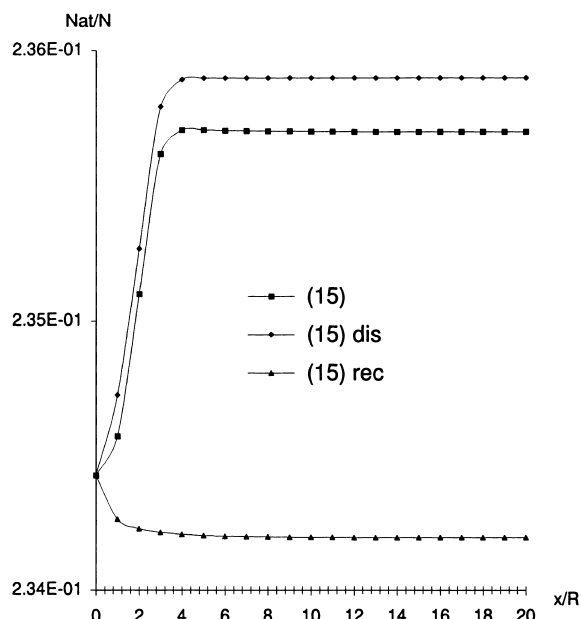


Fig. 10. N_{at}/N for distribution (15) with complete kinetics, neglecting recombination ((15)dis), neglecting dissociation ((15)rec). $T_0 = 7525$ K, $p_0 = 1.74$ atm.

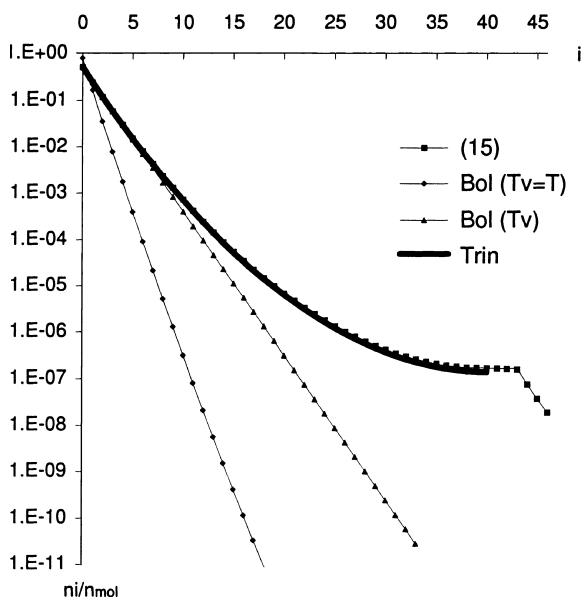


Fig. 11. Different distributions in the cross-section $x/R = 3$, $T_0 = 5375$ K, $p_0 = 17.4$ atm.

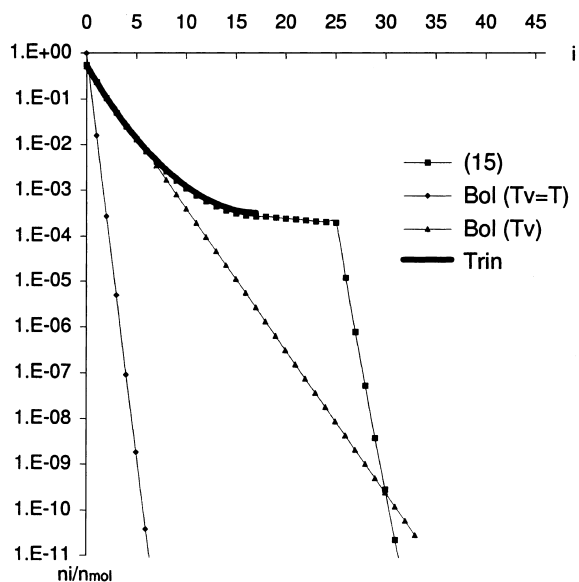


Fig. 12. Different distributions in the cross-section $x/R = 15$, $T_0 = 5375$ K, $p_0 = 17.4$ atm.

temperature falling and the recombination effect, which could be expected at low temperature, occurs small because of pressure decrease due to expansion. In order to see a more noticeable change of nitrogen atom number density in a nozzle flow, not only dissociation–recombination, but also bimolecular exchange reaction should be taken into account. For the mixture considered in this paper it is shown that neglecting dissociation and recombination at $p_0 = 174$ atm, $T_0 = 7525$ K leads to the lower values of T_1 and T_1/T and to the gas temperature overestimation.

We would like to note that the estimations presented above have a qualitative character. It is due to the uncertainty of data on rate coefficients for vibrational energy transitions and dissociation and because only quasi-stationary distributions are used in our paper. For the further validation of our model a comparison with the more rigorous state-to-state solution and with experimental data is required.

Acknowledgements

The authors thank C.N.R.S. for the support of collaboration between I.U.S.T.I. and

St. Petersburg University. The work has been supported by INTAS (99-00464).

References

- [1] K.N.C. Bray, *Fluid Mech.* VII 6 (1) (1959) 1.
- [2] A.Q. Eschenroeder, D.W. Boyer, J.G. Hall, *Phys. Fluids* V (5) (1962) 615.
- [3] H.T. Nagamatsu, R.E. Sheer, Vibrational relaxation and recombination of nitrogen and air in hypersonic nozzle flows, *AIAA* 3 (8) (1965) 1386.
- [4] R.E. Duffy, Experimental study of nonequilibrium expanding flows, *AIAA* 3 (2) (1965) 237.
- [5] S. Sharma, S. Ruffin, W. Gillespie, S. Meyer, J. Thermophys. Heat Transfer 7 (4) (1993) 697.
- [6] C.G. de Roany, A. Flament, C. Rich, J.W. Subramaniam, V.V. Warren, Strong vibrational nonequilibrium in supersonic nozzle flows, *AIAA* 31 (1) (1993) 119.
- [7] B. Shizgal, F. Lordet, *J. Chem. Phys.* 104 (10) (1996) 3579.
- [8] G. Colonna, M. Tuttafesta, M. Capitelli, D. Giordano, Influence of dissociation rates on the state-to-state vibrational kinetics in nozzle expansion, in: R. Brun et al. (Eds.), *Rarefied Gas Dynamics* 21, vol. 2, 1999, CEPADUES, Toulouse, p. 281–288.
- [9] M. Capitelli, G. Colonna, D. Giordano, E. Kustova, E. Nagnibeda, M. Tuttafesta, D. Bruno, The influence of state-to-state kinetics on transport properties in a nozzle flow, *Math. Model.* 11 (3) (1999) 45 (in Russian).
- [10] J. William, Thesis: Étude des processus physico-chimiques dans les écoulements détendus à haute enthalpie: Application à la soufflerie à A R C F4 1999, Université de Provence, I.U.S.T.I.
- [11] O. Knab, H.-H. Fruhauf, E.W. Messerschmid, *Thermophys. Heat Transfer* 9 (2) (1995) 219.
- [12] E.A. Kovach, S.A. Losev, A.L. Sergievskaya, *Chem. Phys. Reprints* 14 (1995) 1353.
- [13] C.E. Treanor, I.W. Rich, R.G. Rehm, *J. Chem. Phys.* 48 (1968) 1798.
- [14] B.F. Gordiets, S.A. Zhdanok, Analytical theory of vibrational kinetics of anharmonic oscillator, in: M. Capitelli (Ed.), *Nonequilibrium Vibrational Kinetics*, Springer, Berlin, 1986, p. 47.
- [15] B.F. Gordiets, A.I. Osipov, L.A. Shelepin, *Kinetic Processes in Gases and Molecular Lasers*, Gordon and Breach, Amsterdam, 1988.
- [16] E.V. Kustova, E.A. Nagnibeda, The Influence of non-Boltzmann vibrational distribution on thermal conductivity and viscosity, in: M. Capitelli (Ed.), *Molecular Physics and Hypersonic Flows*, Kluwer Academic Publishers, Dordrecht, 1996, p. 383.
- [17] E.V. Kustova, E.A. Nagnibeda, New kinetic model of transport processes in the strong nonequilibrium gas, in: J. Harvey, G. Lord (Eds.), *Rarefied Gas Dynamics* 19, vol. 1, Oxford University Press, Oxford, 1995, p. 78.
- [18] A. Chikhaoui, J.P. Dudon, E.V. Kustova, E.A. Nagnibeda, *Physica A* 247 (1–4) (1997) 526.
- [19] E.V. Kustova, E.A. Nagnibeda, *Chem. Phys.* 233 (1998) 57.
- [20] Ye.V. Stupochenko, S.A. Losev, A.I. Osipov, *Relaxation in Shock Waves*, Springer, Berlin, 1967.
- [21] A. Chikhaoui, J.P. Dudon, S. Genieys, E.V. Kustova, E.A. Nagnibeda, *Phys. Fluids* 12 (1) (2000) 220.
- [22] M. Capitelli, I. Armenise, C. Gorse, *J. Thermophys. Heat Transfer* 11 (4) (1997) 570.
- [23] E.A. Nagnibeda, M.A. Rydalevskaya, The derivation of the equations for macroparameters from the kinetic equations in the mixture of dissociating gases, *Aerodinamika Razrezhennykh Gazov*, vol. IX, Leningrad University Press, Leningrad, 1977 (in Russian), p. 29.
- [24] I. Kuvšcer, *Physica A* 176 (1991) 542.
- [25] E.V. Kustova, E.A. Nagnibeda, A. Chauvin, *Chem. Phys.* 248 (2–3) (1999) 221.
- [26] I. Armenise, M. Capitelli, R. Celiberto, G. Colonna, C. Gorse, A. Lagana, *Chem. Phys. Lett.* 227 (1994) 157.
- [27] G.D. Billing, *Topics Current Phys.* 39 (1986) 85.
- [28] P.V. Marrone, C.E. Treanor, *Phys. Fluids* IX 6 (9) (1963) 1215.
- [29] W. Gardiner Jr., *Combustion Chemistry*, Springer, Berlin, 1984.
- [30] E.V. Kustova, E.A. Nagnibeda, The influence of the state-to-state distributions behind shock wave on the dissociation rates, in: G.J. Ball, R. Hillier, G.T. Roberts (Eds.), *Proceedings of the 22nd International Symposium on Shock Waves*, paper 1151, Imperial College, London, 1999, p. 783.
- [31] M. Capitelli, G. Colonna, C. Gorse, D. Giordano, Survey of methods of calculating high-temperature thermodynamic properties of air species, Technical report, STR-236 ESA, The Netherlands, 1994, p. 1.