

On the non-equilibrium kinetics and heat transfer in nozzle flows

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Abstract

In this paper the influence of different vibrational distributions on heat transfer and diffusion in expanding nozzle flows is studied. Non-equilibrium flows of N₂/N and O₂/O mixtures with dissociation, recombination and excitation of vibrational levels are considered. Vibrational distributions, gas dynamic parameters as well as the transport coefficients and total energy flux are computed along the nozzle axis using four approaches of the transport kinetic theory: a rigorous state-to-state approximation, quasi-stationary two-temperature models for harmonic and anharmonic oscillators and a thermal equilibrium one-temperature model. A comparison of vibrational distributions and transport properties obtained in different approaches is presented. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Adequate models of heat transfer in reacting real gas flows should take into account the kinetics of numerous non-equilibrium processes. Appropriate models of non-equilibrium kinetics depend on specific flow conditions and relations between relaxation times of various processes. Thus, under conditions of strong vibrational and chemical non-equilibrium, the commonly used kinetic models

based on quasi-stationary one-temperature and multi-temperature distributions over vibrational levels become not to be valid, and more rigorous state-to-state approximation is needed. It is particularly important in expanding flows of initially heated gas. As a matter of fact, in such a flow the gas temperature drops fast and vibrational energy becomes higher than the translational one. As a result, recombination and vibrational energy exchanges lead to formation of non-Boltzmann non-equilibrium distributions.

Particular features of state-to-state distributions in nozzle flows have been recently studied in [1–3], and a rather strong difference between state-to-state populations and quasi-stationary distributions in all cases has been found. The transport

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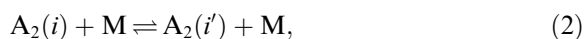
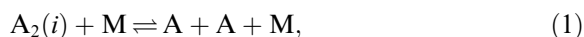
kinetic theory in the state-to-state and several multi-temperature approximations has been developed in [4–6], and in [7,8] the heat transfer in nozzle flows has been investigated on the basis of state-to-state distributions. However, up to now it is not sufficiently clear how the various vibrational distributions can influence the gas dynamic parameters and transport properties. This problem is very important for practical applications: understanding the role of non-equilibrium kinetics in the heat transfer allows one to choose an appropriate model of non-equilibrium gas dynamics for particular conditions. The implementation of the state-to-state model requires solution of a large number of master equations for vibrational level populations coupled with the gas dynamic equations. In order to find the heat flux in this approach, one should calculate state dependent transport coefficients, among them the diffusion coefficients for each vibrational level [6]. Moreover, transport coefficients should be recalculated at each step of the numerical code. Such a procedure consumes a lot of computational time even for the case of simple gas mixtures. From this point of view the employment of quasi-stationary models gives a considerable benefit. Therefore it is interesting to distinguish the conditions where both the rigorous state-to-state model and more simple quasi-stationary ones provide similar results when applied to a gas dynamic problem. This question is discussed in the present paper.

The aim of the paper is the investigation of non-equilibrium vibrational distributions and heat transfer in expanding flows of N_2/N and O_2/O mixtures in a nozzle on the basis of several models: the state-to-state approach, the quasi-stationary multi-temperature models for harmonic and anharmonic oscillators and, finally, one-temperature thermal equilibrium model. First, the non-equilibrium distributions and gas dynamic parameters along the nozzle axis are calculated on the basis of these four models in the Euler approximation. After that, their influence on the transport coefficients and heat transfer is estimated using an approximate method proposed in [9] and then applied for the evaluation of transport properties in various non-equilibrium flows [6–8,10–13].

2. State-to-state approximation

2.1. Non-equilibrium kinetics

In the present paper we study a binary mixture of diatomic molecules $A_2(i)$ and atoms A with dissociation, recombination, vibration–translation (VT) and vibration–vibration (VV) energy transitions:



where $A_2(i)$ is a molecule at the vibrational level i , an inert partner M can be a molecule or an atom A .

The state-to-state approach is commonly applied when the characteristic times of vibrational and chemical relaxation τ_{vibr} and τ_{react} are comparable with the mean time of changing of macroscopic gas flow parameters θ and exceed essentially the times of translational and rotational relaxation τ_{el} , τ_{rot} :

$$\tau_{\text{el}} < \tau_{\text{rot}} \ll \tau_{\text{vibr}} < \tau_{\text{react}} \sim \theta. \quad (4)$$

Under condition (4) in the zero-order approximation of the generalized Chapman–Enskog method for the distribution functions one obtains the Maxwell distribution over velocities and the Boltzmann distribution over rotational energies while no quasi-stationary distributions over vibrational energy levels exist. The vibrational level populations n_i and number densities of atoms n_{at} are found from the equations of detailed vibration–chemical kinetics coupled to the conservation equations of momentum and total energy [6].

A closed set of equations describing a non-viscous non-conductive gas flow in a nozzle in the state-to-state approach has been derived in [2,3,14]. For a binary mixture of molecules and atoms it has the form:

$$\frac{d}{dx}(n_i v S) = S(R_i^{\text{vibr}} + R_i^{\text{diss-rec}}), \quad i = 0, 1, \dots, L, \quad (5)$$

$$\frac{d}{dx}(n_{\text{at}} v S) = -2S \sum_i R_i^{\text{diss-rec}}, \quad (6)$$

$$\rho v \frac{dv}{dx} + \frac{dp}{dx} = 0, \quad (7)$$

$$\frac{dh}{dx} + v \frac{dv}{dx} = 0, \quad (8)$$

where n_i is the population of molecular vibrational level i , n_{at} is the number density of atoms, x is the distance from the reservoir along the nozzle axis, $S(x)$ is the nozzle cross-section, v is the macroscopic gas velocity, L is the number of excited vibrational states, ρ is the density, p is the pressure, h is the enthalpy per unit mass:

$$h = h_{\text{mol}} \frac{\rho_{\text{mol}}}{\rho} + h_{\text{at}} \frac{\rho_{\text{at}}}{\rho}, \quad (9)$$

$\rho_{\text{mol}} = m_{\text{mol}} \sum_i n_i = m_{\text{mol}} n_{\text{mol}}$, $\rho_{\text{at}} = m_{\text{at}} n_{\text{at}}$, m_c is the mass of species c ,

$$h_{\text{at}} = \frac{5}{2} \frac{kT}{m_{\text{at}}} + h_{\text{f}}^{\text{at}}, \quad h_{\text{mol}} = \frac{5}{2} \frac{kT}{m_{\text{mol}}} + E^{\text{rot}} + E^{\text{vibr}},$$

k is the Boltzmann constant, T is the gas temperature, h_{f}^{at} is the enthalpy of atom formation, E^{rot} , E^{vibr} are the rotational and vibrational energies per unit mass. In the present case,

$$E^{\text{rot}} = \frac{kT}{m_{\text{mol}}}, \quad E^{\text{vibr}} = \frac{1}{\rho_{\text{mol}}} \sum \varepsilon_i n_i,$$

ε_i is the vibrational energy of a molecule at the i th level. One can see that the specific enthalpy in the state-to-state approach depends on the species concentrations, gas temperature and populations of all vibrational levels.

The production terms R_i^{vibr} , $R_i^{\text{diss-rec}}$ in Eqs. (5) and (6) describe the change of vibrational level populations and atomic concentrations due to VV, VT energy exchanges and chemical reactions. They are given, for instance, in [14]. In the present study we use the rate coefficients for all vibrational energy transitions reported in [15] where the interpolating formulas for the rate coefficients obtained by means of molecular dynamics methods [16,17] are proposed. Dissociation rate coefficients are calculated on the basis of the Treanor–Marrone model [18] extended in [19] to the case of state-to-state approach. The rate coefficients of recombination are evaluated using the detailed balance principle for the state-to-state coefficients (see [14]).

2.2. Transport terms

The first-order approximation of the generalized Chapman–Enskog method under condition (4) has been considered in [6] in the general case of a multi-component reacting mixture. In the latter paper the first-order perturbation term has been expressed in terms of the gradients of macroscopic flow parameters: n_{ci} (number densities of species c at the vibrational level i), \mathbf{v} (gas velocity), T (gas temperature). On the basis of the first-order distribution function the diffusion velocities of molecules at each vibrational state and the total heat flux have been derived. Thus the diffusion velocity of the molecules of each chemical species c at the vibrational level i reads [6]:

$$\mathbf{V}_{ci} = - \sum_{dk} D_{cick} \mathbf{d}_{dk} - D_{Tci} \nabla \ln T, \quad (10)$$

where D_{cick} and D_{Tci} are the diffusion and thermal diffusion coefficients for every chemical and vibrational species, \mathbf{d}_{ci} are the diffusion driving forces for each chemical and vibrational species:

$$\mathbf{d}_{ci} = \nabla \left(\frac{n_{ci}}{n} \right) + \left(\frac{n_{ci}}{n} - \frac{\rho_{ci}}{\rho} \right) \nabla \ln p. \quad (11)$$

It is clear that the number of independent diffusion and thermal diffusion coefficients in this approximation is very large (see estimations in [20]). The expressions for diffusion velocities can be simplified invoking some additional assumptions. In [6,20] it has been supposed that the cross-sections of elastic collisions are independent of the vibrational states of colliding particles. This assumption is usually accepted in the transport kinetic theory despite the fact that molecules in vibrationally excited states may have a larger effective radius than ground state molecules (see, for instance, [21]). The validity of this assumption is discussed in [13], where it is shown that taking into account the dependence of elastic cross-sections on the vibrational quantum number provides only a very small correction to the transport coefficients. Finally, using this assumption, the system of diffusion coefficients is reduced to the following system: there remain coefficients D_{cici} which are different for any vibrational level i of species c , coefficients $D_{cc} = D_{cick} \forall i, \forall k \neq i$,

coefficients $D_{cd} = D_{cidk} \forall d \neq c, \forall i, k$, and thermal diffusion coefficients $D_{Tci} = D_{Tc}, \forall i$.

For a binary mixture considered in the present paper, the diffusion velocities of vibrationally excited molecules \mathbf{V}_i and atoms \mathbf{V}_{at} , after simplification discussed above, have the form:

$$\mathbf{V}_i = -D_{ii}\mathbf{d}_i - D_{mm} \sum_{k \neq i} \mathbf{d}_k - D_{\text{ma}}\mathbf{d}_{\text{at}} - D_{T_{\text{mol}}}\nabla \ln T, \quad (12)$$

$$\mathbf{V}_{\text{at}} = -D_{\text{aa}}\mathbf{d}_{\text{at}} - D_{\text{ma}}\mathbf{d}_{\text{mol}} - D_{T_{\text{at}}}\nabla \ln T. \quad (13)$$

Here D_{ma} is the binary diffusion coefficient for a mixture of molecules and atoms, D_{mm} is the diffusion coefficient of the molecules at different vibrational levels, D_{aa} is the self-diffusion coefficient of atomic species, and D_{ii} are the self-diffusion coefficients of molecular species at the same i th vibrational level, $D_{T_{\text{mol}}}$ and $D_{T_{\text{at}}}$ are the thermal diffusion coefficients of molecules and atoms correspondingly, $\mathbf{d}_{\text{mol}} = \sum_i \mathbf{d}_i$.

The total energy flux in the state-to-state approximation in the considered mixture reads

$$\begin{aligned} \mathbf{q} = & -\lambda_{\text{TR}}\nabla T - p(D_{T_{\text{mol}}}\mathbf{d}_{\text{mol}} + D_{T_{\text{at}}}\mathbf{d}_{\text{at}}) \\ & + \sum_i \left(\frac{5}{2}kT + \langle \varepsilon_j^i \rangle_r + \varepsilon_i \right) n_i \mathbf{V}_i \\ & + \left(\frac{5}{2}kT + \varepsilon^{\text{at}} \right) n_{\text{at}} \mathbf{V}_{\text{at}}, \end{aligned} \quad (14)$$

where ε^{at} is the energy of atom formation, $\langle \varepsilon_j^i \rangle_r$ is the rotational energy averaged over rotational spectrum. The coefficient of heat conductivity $\lambda_{\text{TR}} = \lambda_{\text{tr}} + \lambda_{\text{rot}}$ is due to translational and rotational degrees of freedom, vibrational modes do not contribute to thermal conductivity in this approach. The transport of vibrational energy is described in terms of diffusion coefficients introduced for each vibrational state.

It is important to note that the expressions for diffusion velocities depend on the gradients of all level populations and also on the gradients of gas temperature, pressure and number density of atoms. Consequently, the total energy transfer in the state-to-state approximation is determined by heat conductivity, thermal diffusion, mass diffusion of molecules and atoms and diffusion of vibrationally excited molecules. The last mentioned effect takes

place only in the state-to-state approximation. In order to estimate the role of different dissipative processes in the heat transfer it is useful to separate their contribution to the heat flux. First, let us define the diffusion velocities caused by mass diffusion of molecules and atoms:

$$\mathbf{V}_i^{\text{MD}} = \mathbf{V}_{\text{mol}}^{\text{MD}} = -D_{\text{mm}}\mathbf{d}_{\text{mol}} - D_{\text{ma}}\mathbf{d}_{\text{at}}, \quad (15)$$

$$\mathbf{V}_{\text{at}}^{\text{MD}} = -D_{\text{aa}}\mathbf{d}_{\text{at}} - D_{\text{ma}}\mathbf{d}_{\text{mol}}, \quad (16)$$

by thermal diffusion of molecules and atoms:

$$\mathbf{V}_i^{\text{TD}} = \mathbf{V}_{\text{mol}}^{\text{TD}} = -D_{T_{\text{mol}}}\nabla \ln T, \quad (17)$$

$$\mathbf{V}_{\text{at}}^{\text{TD}} = -D_{T_{\text{at}}}\nabla \ln T, \quad (18)$$

and finally, by diffusion of vibrational energy of excited molecules

$$\mathbf{V}_i^{\text{DVE}} = -(D_{ii} - D_{\text{mm}})\mathbf{d}_i. \quad (19)$$

It is evident that diffusion velocities due to mass and thermal diffusion do not depend on the vibrational state of molecules.

On the basis of these definitions one can introduce various contributions to the heat flux. In this way the total energy flux can be written as a sum of several terms:

$$\mathbf{q} = \mathbf{q}^{\text{HC}} + \mathbf{q}^{\text{MD}} + \mathbf{q}^{\text{TD}} + \mathbf{q}^{\text{DVE}}, \quad (20)$$

where \mathbf{q}^{HC} , \mathbf{q}^{MD} , \mathbf{q}^{TD} , \mathbf{q}^{DVE} are the fluxes determined respectively by heat conductivity, mass diffusion, thermal diffusion and diffusion of vibrational energy:

$$\mathbf{q}^{\text{HC}} = -\lambda_{\text{TR}}\nabla T, \quad (21)$$

$$\begin{aligned} \mathbf{q}^{\text{MD}} = & \sum_i \left(\frac{5}{2}kT + \langle \varepsilon_j^i \rangle_r + \varepsilon_i \right) n_i \mathbf{V}_i^{\text{MD}} \\ & + \left(\frac{5}{2}kT + \varepsilon^{\text{at}} \right) n_{\text{at}} \mathbf{V}_{\text{at}}^{\text{MD}} \\ = & \sum_{c=\text{mol,at}} \rho_c h_c \mathbf{V}_c^{\text{MD}}, \end{aligned} \quad (22)$$

$$\mathbf{q}^{\text{TD}} = \sum_{c=\text{mol,at}} (-pD_{Tc}\mathbf{d}_c + \rho_c h_c \mathbf{V}_c^{\text{TD}}), \quad (23)$$

$$\mathbf{q}^{\text{DVE}} = \sum_i \left(\frac{5}{2}kT + \langle \varepsilon_j^i \rangle_r + \varepsilon_i \right) n_i \mathbf{V}_i^{\text{DVE}}. \quad (24)$$

Sometimes it is convenient to eliminate the diffusion driving forces in Eq. (23) introducing the thermal diffusion ratios and rewrite \mathbf{q}^{TD} in another form (see [22]).

The expressions for the state-to-state transport coefficients in terms of bracket integrals and algorithms for their calculation are given in [6,20]. In particular, all transport coefficients are expressed in terms of vibrational level populations n_i , number density of atoms n_{at} , gas temperature T and collision integrals depending on the cross-sections of the most frequent collisions. Under condition (4), the most probable collisions are the elastic ones and inelastic collisions resulting in the RT rotational energy transitions. Moreover, as it is shown in [6,23], the influence of the inelastic collision integrals on the transport coefficients is weak. For instance, their contribution to the heat conductivity coefficient does not exceed 2% and occurs to be even less for the diffusion coefficients. Therefore, for the calculation of heat conductivity and diffusion coefficients only the data on the elastic collision integrals are required. As it is emphasized in [24–26], for low temperatures the Lennard–Jones potential gives a good agreement with experimental data; for high temperatures the employment of the repulsive potential yields a reasonable accuracy. In the present study the parameters of the Lennard–Jones and repulsive potentials recommended correspondingly in [27] and [28] have been used, this choice provides approximately the same accuracy as the formulas proposed in [25,26].

2.3. Approximate evaluation of heat transfer

Evaluation of transport properties in real gas flows on the basis of the rigorous kinetic theory requires solution of fluid dynamics equations coupled to the equations of non-equilibrium vibration-chemical kinetics in viscous and heat conductive gases. For the Navier–Stokes approximation, the closed system of equations in the state-to-state approach have been derived in [5,6] on the basis the generalized Chapman–Enskog method. These equations contain production and transport terms. The algorithms for evaluation of transport terms are given in [5,6], and production

terms containing first-order state-to-state rates of vibrational energy transitions and chemical reactions are given in [29]. In the state-to-state approach the tensor of pressure, heat flux and diffusion velocities for each vibrational level are determined by the transport coefficients depending on the vibrational state. For numerical simulations one has to compute the state-to-state coefficients at the each time and space cell. The computational cost of such a scheme is extremely high. Using the simplified expressions for the state dependent transport coefficients proposed in the recent paper [20] makes this goal attainable. However, up to now, the practical incorporation of the state-to-state transport coefficients to the numerical codes has not been accomplished.

Because of complexity of a rigorous scheme, in [7–13] an approximate way for the evaluation of the heat transfer in the state-to-state approach has been proposed. The analysis carried out in these papers is based on a simplified scheme: first, the vibrational distributions, species concentrations, temperature, pressure, velocity are computed either in the Euler approach of non-viscous and non-conductive gas flow [7–10,13] or on the basis of very simple models for transport coefficients [11,12]. Then the calculated macroscopic parameters are used as input for the transport coefficients and heat transfer evaluation using rigorous kinetic theory formulas. This approach permits to estimate the influence of state-to-state vibrational kinetics on the transport properties. Certainly, in order to understand the mutual effect of state-to-state kinetics and transport properties, it is necessary to consider the equations of non-equilibrium kinetics in viscous and heat conductive gas flow together with fluid dynamics equations containing precise transport coefficients. This could be an interesting perspective for future theoretical and numerical studies.

3. Quasi-stationary models

3.1. Quasi-stationary vibrational distributions

Since the number of equations constituting system (5)–(8) is very large, especially for a multi-

component mixture, it is useful to find conditions when this system can be reduced to a more simple one. In the case of significant vibrational excitation at moderate gas temperatures, VV exchanges (3) appear to be much more probable than VT transitions (2) [30,31]:

$$\tau_{\text{el}} < \tau_{\text{rot}} < \tau_{\text{VV}} \ll \tau_{\text{VT}} < \tau_{\text{react}} \sim \theta. \quad (25)$$

Under condition (25), the quasi-stationary multi-temperature distributions establish at the time scale τ_{VV} . In particular, if molecules are simulated using the harmonic oscillator model, then conservation of the vibrational energy ε_i of colliding molecules during VV exchanges takes place, and vibrational level populations have the form of the non-equilibrium Boltzmann distribution with vibrational temperature $T_v \neq T$:

$$n_i = \frac{n_{\text{mol}}}{Z^{\text{vibr}}(T_v)} s_i \exp\left(-\frac{\varepsilon_i}{kT_v}\right), \quad (26)$$

s_i is the vibrational statistical weight. Since for diatomic molecules $s_i = 1$, in further discussion it is omitted. The vibrational partition function in the present case reads

$$Z^{\text{vibr}}(T_v) = \sum_{i=0}^L \exp\left(-\frac{\varepsilon_i}{kT_v}\right). \quad (27)$$

If molecular vibrations are supposed to be anharmonic, then the VV exchange is non-resonant, and vibrational energy does not conserve in the most frequent collisions. However, as it is shown in [32], during VV transitions the number of vibrational quanta in a system of colliding molecules does not change, and therefore the value i can be chosen as an additional collision invariant of rapid processes. In this case, at the early stages of vibrational relaxation the Treanor distribution with the temperature of the first vibrational level T_1 establishes [32]

$$n_i = \frac{n_{\text{mol}}}{Z^{\text{vibr}}(T, T_1)} \exp\left(-\frac{\varepsilon_i - i\varepsilon_1}{kT} - \frac{i\varepsilon_1}{kT_1}\right), \quad (28)$$

$$Z^{\text{vibr}}(T, T_1) = \sum_{i=0}^L \exp\left(-\frac{\varepsilon_i - i\varepsilon_1}{kT} - \frac{i\varepsilon_1}{kT_1}\right). \quad (29)$$

The Treanor distribution describes correctly the vibrational kinetics only in the case of moderate

vibrational excitation or at $T_1 < T$. Under conditions of strong vibrational excitation, various mechanisms of vibrational relaxation dominate at different groups of vibrational levels [31]. Thus, at low levels the non-resonant VV' transitions are the most probable ones, at the intermediate levels near-resonant VV'' exchanges between the neighboring states dominate, and at the high levels, probabilities of all vibrational energy transitions become comparable. It leads to different relations between relaxation times along the vibrational spectrum. In this case, the vibrational distribution has different forms at various groups of vibrational levels [4,14]:

$$n_i = \begin{cases} \frac{N_1}{Z^{v1}} \exp\left(-\frac{\varepsilon_i - i\varepsilon_1}{kT} - \frac{i\varepsilon_1}{kT_1}\right), & 0 \leq i \leq i_*, \\ n_{\text{mol}} \frac{\Gamma}{i+1}, & i_* \leq i \leq i_{**}, \\ \frac{N_3}{Z^{v3}} \exp\left(-\frac{\varepsilon_i}{kT}\right), & i_{**} \leq i \leq L. \end{cases} \quad (30)$$

Level i_* corresponds to the minimum of the Treanor distribution, level i_{**} is defined from the ratio of probabilities of VV and VT transitions [31]. Parameters N_1 , N_3 , Γ can be defined in terms of T , T_1 and n_{mol} from the normalizing conditions and continuity of distribution at $i = i_*$, $i = i_{**}$; Z^{v1} , Z^{v3} are the partition functions:

$$Z^{v1} = \sum_{i=0}^{i_*} \exp\left(-\frac{\varepsilon_i - i\varepsilon_1}{kT} - \frac{i\varepsilon_1}{kT_1}\right), \quad (31)$$

$$Z^{v3} = \sum_{i=i_{**}}^L \exp\left(-\frac{\varepsilon_i}{kT}\right). \quad (32)$$

Distribution (30) represents the Treanor distribution at low levels, the declining plateau at the intermediate levels and the Boltzmann distribution at high levels. It has been obtained first in [31] as an approximate solution of balance equations for vibrational level populations in a pure gas, and then, it has been derived from the kinetic theory principles in [4,33]. In [14] the model has been extended for a dissociating gas.

On the basis of the analytical distributions introduced above the system of macroscopic equations (5)–(8) can be significantly simplified (see [5,34] for a detailed discussion). Substituting distributions (26), (28) or (30) into Eq. (5) and performing summation over vibrational levels, one obtains the equation of two-temperature chemical

kinetics for the concentration of molecules n_{mol} . Furthermore, multiplying (5) by the additional collision invariants and using quasi-stationary distributions, one can derive relaxation equations for the vibrational temperature T_v in the case of harmonic oscillators or for the temperature T_1 for anharmonic oscillators. Finally, instead of $L + 1$ equations for the vibrational level populations, one has only two additional relaxation equations. One should mention that the specific enthalpy in the energy conservation equation is now a function of n_{mol} , n_{at} , T , T_1 . The reduced systems of macroscopic equations are reported in [5,34] for a general case, and in [14] for a binary mixture flow in a nozzle.

In the case of thermal equilibrium, when all internal energy exchanges proceed much faster than chemical reactions,

$$\tau_{\text{el}} < \tau_{\text{int}} \ll \tau_{\text{react}} \sim \theta \quad (33)$$

(τ_{int} is the characteristic time of internal energy relaxation), vibrational level populations are described by the equilibrium Boltzmann distribution (26) with gas temperature $T = T_v$. Under condition (33) the system of macroscopic equations consists of two equations of one-temperature chemical kinetics for n_{mol} and n_{at} , and conservation equations (7) and (8). The specific enthalpy in this case is determined only by the gas temperature and concentrations of chemical species.

One should note that, contrary to the state-to-state distributions, the analytical quasi-stationary distributions described above are not perturbed directly by the recombination and dissociation processes. These processes are taken into account in the equations of two-temperature chemical kinetics for n_{mol} and n_{at} , and influence the vibrational distributions through the concentrations of chemical species and temperatures.

3.2. Transport terms in quasi-stationary approaches

The transport terms in various quasi-stationary approaches have been considered in [4,5,34]. For distribution (30), using the definitions of Section 2 one can write the total heat flux in the following form:

$$\mathbf{q} = -\lambda_{\text{TRV}} \nabla T - \lambda_v \nabla T_1 + \mathbf{q}^{\text{MD}} + \mathbf{q}^{\text{TD}}. \quad (34)$$

In this case the coefficient $\lambda_{\text{TRV}} = \lambda_{\text{tr}} + \lambda_{\text{rot}} + \lambda_{\text{vt}}$ describes the transport of translational, rotational energy and a small part of vibrational energy due to the non-resonant character of VV exchange (in a system of anharmonic oscillators vibrational levels are not equidistant and therefore a small fraction of vibrational energy is transferred to the translational mode during VV transitions). The coefficient λ_v is determined by the transport of the total number of vibrational quanta as well as by the loss or gain of vibrational energy in non-resonant VV exchange [5].

One can see that using the analytical vibrational distribution, the term \mathbf{q}^{DVE} is reduced to the term $\mathbf{q}^{\text{vibr}} = -\lambda_v \nabla T_1$ depending on the gradient of vibrational temperature T_1 instead of gradients of all vibrational level populations. The expressions for \mathbf{q}^{MD} and \mathbf{q}^{TD} are formally given by formulas (22) and (23). Nevertheless the principal difference exists: first, the specific enthalpy h as well as all transport coefficients in the two-temperature approach depend on n_{mol} , n_{at} , T and T_1 contrary to the state-to-state model, when these quantities are determined by the gas temperature T , n_{at} and all vibrational level populations n_i ; then, the coefficient D_{mm} in the present case denotes the self-diffusion coefficient of molecular species rather than diffusion coefficient of the molecules at different vibrational levels; and finally, all transport coefficients are determined by the cross-sections of not only elastic and RT collisions, but also by the cross-sections of VV transitions. However the last point is not of great importance because the contribution of collision integrals depending on the cross-sections of VV transitions to the heat conductivity and diffusion coefficients is found to be negligibly small [4,23], while the role of non-equilibrium specific heats defined on the basis of distribution (30) is shown to be decisive for the heat conductivity calculation.

If molecules are simulated by harmonic oscillators, then non-equilibrium Boltzmann distribution (26) takes place, and the total heat flux is given by the expression:

$$\mathbf{q} = -\lambda'_{\text{TR}} \nabla T - \lambda'_v \nabla T_v + \mathbf{q}^{\text{MD}} + \mathbf{q}^{\text{TD}}. \quad (35)$$

Again, like in Eq. (14), the heat conductivity coefficients λ'_{TR} at the temperature gradient is

determined only by translational and rotational degrees of freedom, $\lambda'_{\text{TR}} = \lambda_{\text{tr}} + \lambda_{\text{rot}}$ [5,35]. It is due to the fact that the coefficient λ_{vt} comes to zero in this approximation because the vibrational spectrum of harmonic oscillators is equidistant, and therefore VV exchange is resonant. The coefficient λ'_v describes the transport of vibrational energy.

In the case of thermal equilibrium the total heat flux takes the classical form [22]:

$$\mathbf{q} = -\lambda \nabla T + \mathbf{q}^{\text{MD}} + \mathbf{q}^{\text{TD}}. \quad (36)$$

The heat conductivity coefficient $\lambda = \lambda_{\text{tr}} + \lambda_{\text{int}}$ includes the coefficient λ_{int} describing the heat transfer due to all internal energy exchanges, which are supposed to be more rapid than chemical reactions in this case. Note, that the specific enthalpy h_{mol} depends now only on the gas temperature T , and the transport coefficients are expressed in terms of macroscopic quantities n_{mol} , n_{at} , T , elastic collision integrals and integrals of all inelastic non-reactive collisions. However, similarly to previous cases, the contribution of inelastic collision integrals to the transport coefficients is significantly less than that of the elastic ones.

The algorithms for the calculation of all transport coefficients in reacting gas mixtures on the basis of various quasi-stationary distributions have been elaborated in [4,5,34]. The transport properties in the flow are estimated in the present study using the approximate procedure described in Section 2.3.

4. Results

The flows of O_2/O and N_2/N mixtures in a conic nozzle with an angle 21° have been studied under different reservoir conditions using the state-to-state and three quasi-stationary models. The conditions in the critical cross-section for five cases considered are summarized in Table 1. The molar fractions of atoms in the throat are also given in the table. Distributions in the critical cross-section are assumed to be in thermal and chemical equilibrium.

First, let us discuss the peculiarities of the state-to-state vibrational populations. The evolution of state-to-state populations along the nozzle axis for

the conditions indicated above has been found after numerical integration of system (5)–(8). The typical behavior is presented in Figs. 1(a) and (b) where distributions versus i are given for the Cases 2 and 5. Different curves correspond to various dimensionless distances x/R from the throat (R is the radius of the critical cross-section). In both cases formation of essentially non-Boltzmann

Table 1
Conditions in the critical cross-section

Case	Mixture	T_* (K)	p_* (atm)	$(n_{\text{at}}/n)_*$
1	O_2/O	4000	1	0.290
2	O_2/O	4000	100	0.0339
3	O_2/O	6000	100	0.360
4	N_2/N	7000	1	0.234
5	N_2/N	7000	100	0.0264

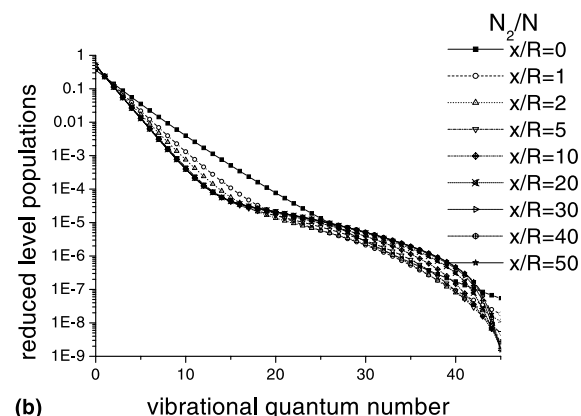
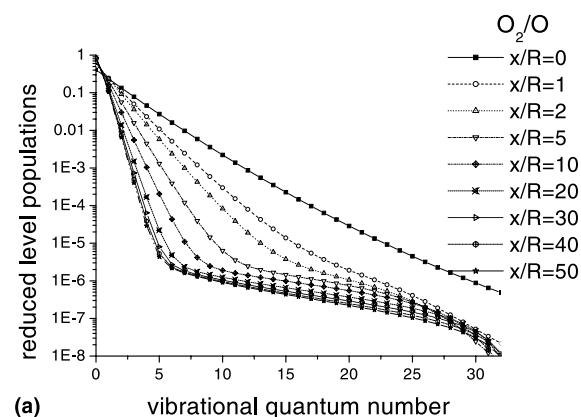


Fig. 1. Reduced level populations n_i/n versus i in different cross-sections x/R . (a) O_2/O , $T_* = 4000$ K, $p_* = 100$ atm; (b) N_2/N , $T_* = 7000$ K, $p_* = 100$ atm.

distributions with a distinct plateau part is observed, this part becomes longer with distance x rising; in oxygen the plateau is more pronounced than in nitrogen. A similar qualitative behavior of state-to-state distributions is found in other cases except Case 4 (N_2/N , $T_* = 7000$ K, $p_* = 1$ atm). In this case the populations of low and intermediate levels remain almost constant along the nozzle axis, only the populations of very high levels change slightly during the expansion. With temperature rising (Case 3) the plateau forms more rapidly compared to the low temperature conditions (Cases 1 and 2); it starts at very low levels ($i = 3$ –4) and appears to be longer.

Comparing the peculiarities of vibrational distributions in the present case to the ones reported in [3,7] one can see the qualitative similarity of the results. The existing deviations are explained, first, by the various nozzle profiles, and then, one should note that different models of dissociation–recombination processes have been used in these two studies: the ladder-climbing model in [3,7] and the Treanor–Marrone model in the present paper.

Figs. 2(a) and (b) give the variation of populations of selected vibrational states along the nozzle axis for the same cases; populations are given versus x/R . One can see that populations of low vibrational states change monotonously with x while the evolution of intermediate and high level populations is not always monotonous. For higher temperature (Case 3), contrary to Case 2, O_2 populations at upper levels ($i = 25$ –33) decrease noticeably with x . Under low pressure conditions (Cases 1 and 4) populations of all states vary monotonously except several very highly located levels. It can also be noted that in nitrogen values of level populations become frozen considerably faster than in oxygen.

An important role of recombination in the formation of non-equilibrium distributions can be seen from Figs. 3(a) and (b). In these figures we present a comparison of vibrational distributions at $x/R = 50$ calculated taking into account vibrational energy exchange and: (1) dissociation and recombination; (2) only dissociation; (3) only recombination; (4) without dissociation and recombination. It is seen that neglecting dissociation influences rather weakly the state-to-state distributions

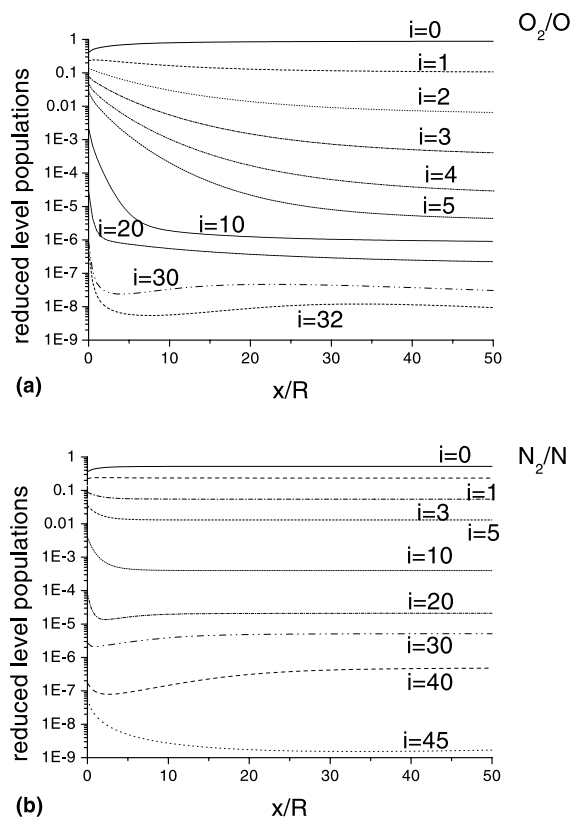
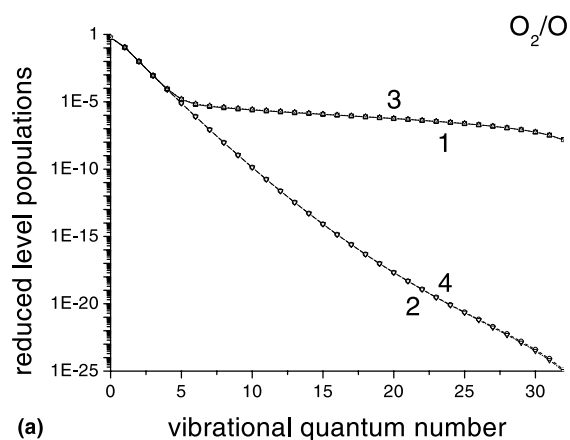


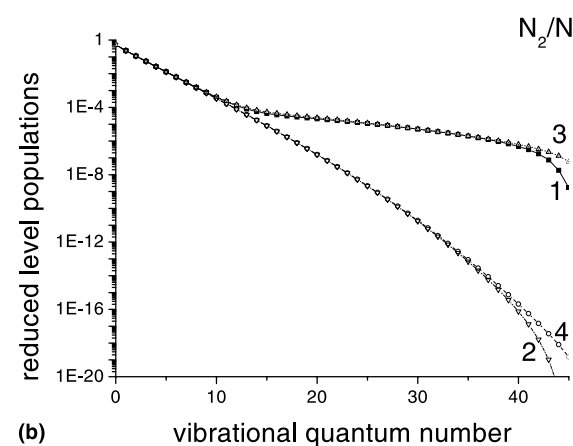
Fig. 2. Reduced level populations n_i/n versus x/R . (a) O_2/O , $T_* = 4000$ K, $p_* = 100$ atm; (b) N_2/N , $T_* = 7000$ K, $p_* = 100$ atm.

distributions in nozzles whereas neglecting recombination leads to a quite different shape of distributions and disappearing of their plateau parts.

Next figures show a comparison of vibrational distributions and temperatures calculated in different approaches (Cases 2 and 5). Figs. 4(a) and (b) present the level populations in the cross-section $x/R = 50$ where the discrepancy between various distributions is maximum. Curves 1 depict the state-to-state populations, and Curves 2, 3, 4 denote the non-equilibrium distributions of anharmonic and harmonic oscillators and thermal equilibrium Boltzmann distributions, respectively. One can observe the dramatic difference between the distributions in both mixtures; the qualitative picture is similar also in all remaining cases. As it is expected, thermal equilibrium one-temperature Boltzmann populations are located essentially



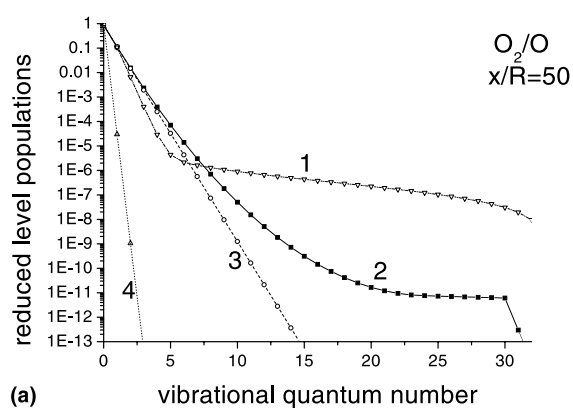
(a) vibrational quantum number



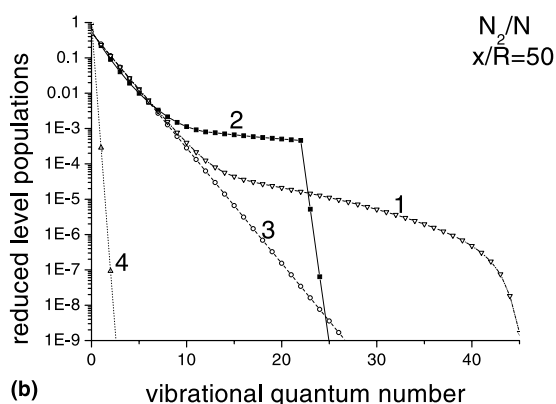
(b) vibrational quantum number

Fig. 3. Reduced level populations n_i/n versus i at $x/R = 50$. Curves 1: dissociation and recombination; 2: dissociation; 3: recombination; 4: no dissociation and recombination. (a) O_2/O , $T_* = 4000$ K, $p_* = 100$ atm; (b) N_2/N , $T_* = 7000$ K, $p_* = 100$ atm.

lower than the state-to-state and non-equilibrium quasi-stationary ones. Harmonic and anharmonic oscillator models provide a rather good indication of the distribution shape at the low levels whereas at the intermediate and high states the shape of state-to-state distributions is quite different. The harmonic oscillator approach based on distribution (26) underestimates significantly the level populations at $i > 7-8$ in oxygen and at $i > 12$ in nitrogen. The distributions obtained by means of the anharmonic oscillator model using distribution (30) have some resemblance to the state-to-state ones; however, their plateau parts and populations



(a) vibrational quantum number



(b) vibrational quantum number

Fig. 4. Reduced level populations n_i/n versus i at the cross-section $x/R = 50$ in different approaches. Curves 1: state-to-state model; 2: two-temperature anharmonic oscillator model; 3: two-temperature harmonic oscillator model; 4: one-temperature model. (a) O_2/O , $T_* = 4000$ K, $p_* = 100$ atm; (b) N_2/N , $T_* = 7000$ K, $p_* = 100$ atm.

of high levels have distinguishing features. It can be noted that the length of plateau and its starting level in the quasi-stationary approximation can be corrected using other points i_* and i_{**} for pasting together different parts of Treanor–plateau–Boltzmann distribution (30). The choice of these points can depend on the specific flow conditions and transition probabilities (see [4,31]), and the rigorous solution of master equations can be used in order to choose correctly values i_* and i_{**} . Finally, one can conclude that the state-to-state model gives the most appropriate behavior of vibrational distributions. It is confirmed by many experimental works (see, for instance, [36,37]).

The change of gas temperature and vibrational temperatures T_1 or T_v calculated in different approximations along the nozzle axis is presented in Figs. 5(a) and (b). In the state-to-state approach T_1 is given by the relation: $T_1 = \varepsilon_1/k \ln(n_0/n_1)$. The discrepancy between the values obtained in various approaches (except the one-temperature model) is found to be relatively weak. In Cases 1, 2, 4, 5 the thermal equilibrium model underestimates the gas temperature (the discrepancy reaches 47% for Case 2 and 24% for Case 5). A very sharp decrease of the gas temperature in the

vicinity of the throat is found for condition 3 (O_2/O , $T_* = 6000$ K, $p_* = 100$ atm), in this case the one-temperature model provides the temperature profile slightly distinct from the one obtained under conditions of lower initial temperature. Non-equilibrium quasi-stationary models give the values of T very close to those obtained by means of the state-to-state model (the maximum difference does not exceed 2% for anharmonic oscillators and 4% for the harmonic oscillator approach). In all cases, for the prediction of gas temperature, the anharmonic oscillator model represents some improvement of the harmonic oscillator approximation. Concerning T_1 and T_v for Cases 2 and 5, in oxygen all vibrational temperatures appear to be very close to each other whereas in nitrogen a noticeable difference (up to 15–20% in the anharmonic case) can be observed. Under low pressure conditions (Cases 1 and 4) the deviation of quasi-stationary vibrational temperatures from T_1 given by the state-to-state model is a little higher.

Now we will discuss the transport properties evaluated on the basis of the results presented above. Figs. 6(a) and (b) plot the heat conductivity coefficients versus x/R (Cases 2 and 5) computed using different models. Curves 1–4 denote the coefficient λ_{TR} , λ_{TRV} , λ'_{TR} or λ at the temperature gradient; Curves 2' and 3' designate the vibrational heat conductivity coefficients λ_v and λ'_v at the gradient of vibrational temperature. These coefficients appear only in the multi-temperature approaches (see formulas (34) and (35)); in the one-temperature model vibrational degrees of freedom are supposed to be in equilibrium, therefore the vibrational heat conductivity coefficient makes a part of the coefficient λ at ∇T ; in the state-to-state approach the transport of vibrational energy is connected with diffusion of vibrationally excited states rather than with heat conductivity. It is seen that the one-temperature approximation gives lower values of λ compared to other models, this fact is explained by lower temperature values obtained in this approach. In O_2/O mixtures coefficients λ'_{TR} and λ_{TRV} calculated by means of all thermal non-equilibrium models practically coincide, the same result is valid for coefficients λ_v and λ'_v obtained on the basis of harmonic and anharmonic oscillator models. It is connected with the

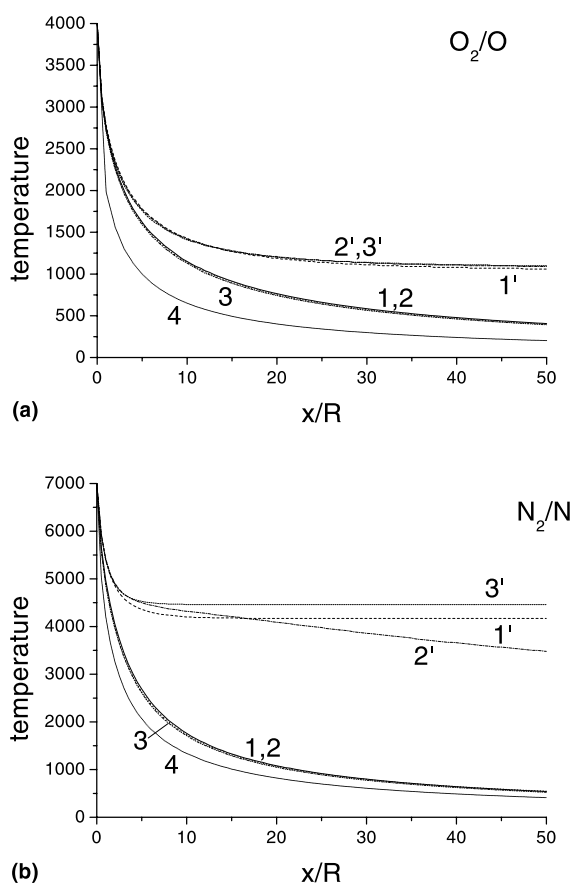
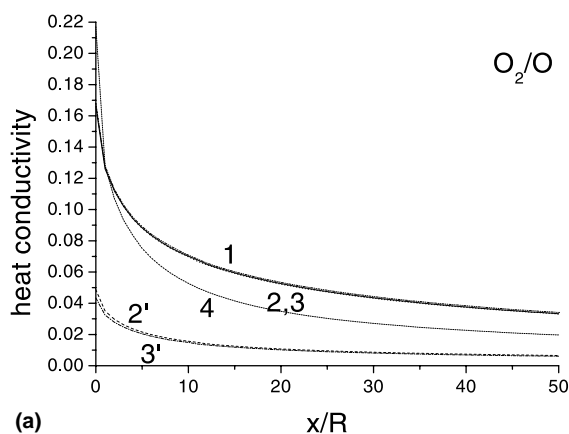
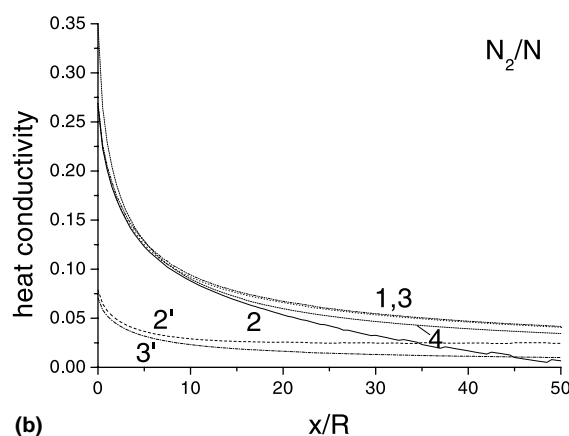


Fig. 5. Temperature and vibrational temperature versus x/R in different approaches. Curves 1–4 correspond to the gas temperature; 1', 2': T_1 ; 3': T_v . Curves 1,1': state-to-state model; 2,2': two-temperature anharmonic oscillator model; 3,3': two-temperature harmonic oscillator model; 4: one-temperature model. (a) O_2/O , $T_* = 4000$ K, $p_* = 100$ atm; (b) N_2/N , $T_* = 7000$ K, $p_* = 100$ atm.



(a)

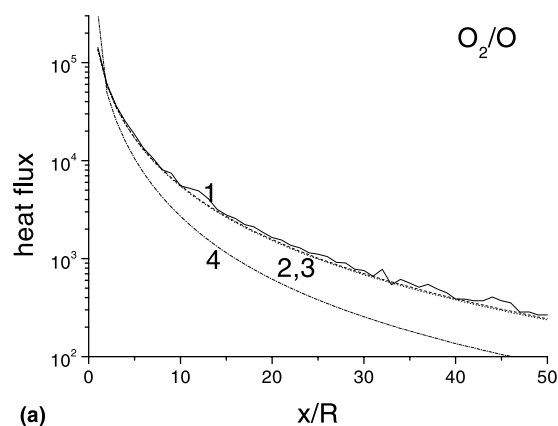


(b)

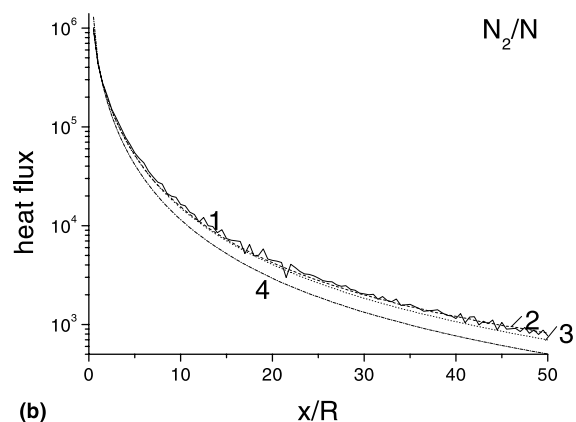
Fig. 6. Heat conductivity coefficients (W/m K) versus x/R in different approaches. Curves 1–4 correspond to λ_{TR} , λ_{TRV} , λ'_{TR} and λ ; 2', 3': λ_v , λ'_v . Curves 1: state-to-state model; 2, 2': two-temperature anharmonic oscillator model; 3, 3': two-temperature harmonic oscillator model; 4: one-temperature model. (a) O_2/O , $T_* = 4000$ K, $p_* = 100$ atm; (b) N_2/N , $T_* = 7000$ K, $p_* = 100$ atm.

fact that the ratio of temperatures T_1/T remains rather low, it does not exceed 3 throughout the flow. In N_2/N mixtures, where T_1/T reaches 8, the anharmonic effects are more important: the variation of coefficients λ_{TRV} , λ'_{TR} and λ_v , λ'_v with T_1/T rising is different for harmonic and anharmonic oscillators; a similar dependence of the coefficients on T_1/T in a pure gas has been reported in [4].

The total energy flux versus x/R obtained in four approximations is presented in Figs. 7(a) and (b) for Cases 2 and 5. In all remaining cases the behavior of the heat flux is analogous. Notations



(a)



(b)

Fig. 7. Heat flux q (W/m^2) versus x/R in different approaches. Curves 1: state-to-state model; 2: two-temperature anharmonic oscillator model; 3: two-temperature harmonic oscillator model; 4: one-temperature model. (a) O_2/O , $T_* = 4000$ K, $p_* = 100$ atm; (b) N_2/N , $T_* = 7000$ K, $p_* = 100$ atm.

are the same as in Fig. 4; different curves correspond to various approaches. The total energy flux decreases with x due to decreasing of macroscopic parameter gradients. Again, the thermal equilibrium model underestimates noticeably the heat flux, the deviation may reach several tens of percents. Non-equilibrium two-temperature models give heat flux values significantly closer to the rigorous state-to-state ones, the anharmonic approach provides a slightly better accuracy; the mean discrepancy between the state-to-state and quasi-stationary heat fluxes is about 7% and 10% for anharmonic and harmonic oscillators, respectively, in O_2/O mixtures (for N_2/N mixture we get 4% and 10% correspondingly).

Starting such a detailed study of the heat transfer in a nozzle flow, we expected to find a more appreciable influence of state-to-state distributions on the total energy flux. Thus, in a shock heated flow a substantial influence of state-to-state kinetics on the heat transfer has been demonstrated [10,24], although the shape of vibrational distributions behind the shock is not far from the Boltzmann one. On the contrary, in the present case the essentially non-Boltzmann distributions do not change significantly the heat flux. In order to understand the reason for this disparity, we have examined the contribution of various processes to the energy flux in the state-to-state approach. Figs. 8(a) and (b) report the different parts of the heat flux normalized to the total flux q . Curves 1 give the reduced Fourier flux q^{HC}/q ; Curves 2 correspond to the flux due to mass diffusion q^{MD}/q ; Curves 3 denote the ratio q^{DVE}/q (q^{DVE} is caused by diffusion of vibrational states); finally, Curves 4 are obtained taking into account only thermal diffusion (q^{TD}/q). One can see that the contribution of thermal diffusion to the heat flux is negligible in all cases, it confirms the commonly used assumption in the kinetic theory about small influence of this process. In O_2/O mixtures the heat transfer caused by heat conductivity prevails, its contribution comprises about 70–80% of the total flux; the role of mass diffusion and diffusion of vibrational energy is of the same order, the latter process loses its importance with x rising. In N_2/N mixtures close to the throat the picture is similar, however at some distance from the critical cross-section a strong competition between heat conductivity and mass diffusion takes place whereas the contribution of vibrational energy diffusion diminishes rapidly. This process is not negligible only in the vicinity of the throat. A similar tendency has been reported recently in [8] for an N_2/N mixture flow in a nozzle with different geometry. It is reasonable because in nitrogen the gradients of level populations are rather low except the very beginning of the expansion (see Fig. 2(b)). It is not the case in oxygen (Fig. 2(a)), where the freezing of level populations proceeds slower.

From the above discussion it is evident that in the general case diffusion of vibrational energy cannot be neglected throughout the flow. There-

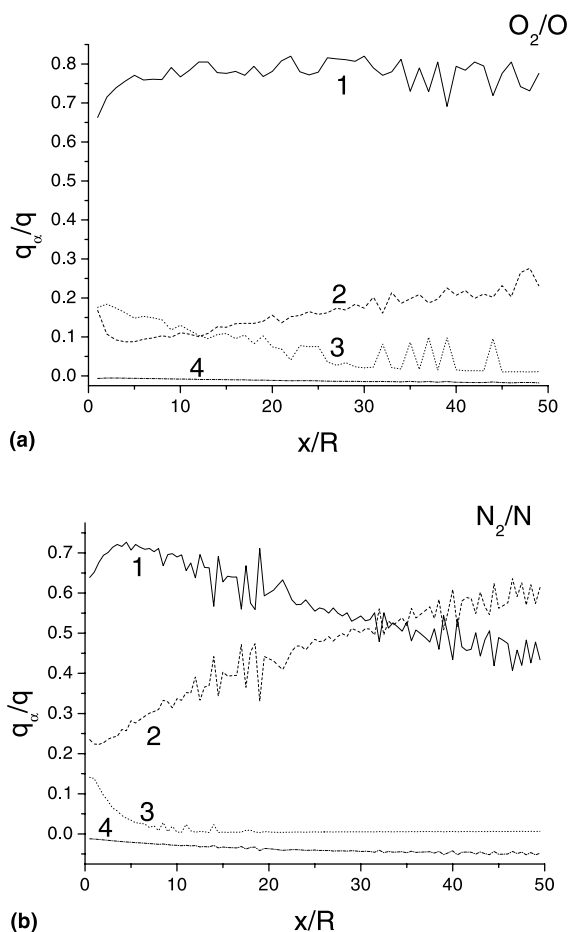


Fig. 8. Contribution of various processes to the total heat flux. Curves 1: q^{HC}/q ; 2: q^{MD}/q ; 3: q^{DVE}/q ; 4: q^{TD}/q . (a) O_2/O , $T_* = 4000$ K, $p_* = 100$ atm; (b) N_2/N , $T_* = 7000$ K, $p_* = 100$ atm.

fore, the question about the weak influence of non-Boltzmann distributions on the heat flux still remains open. The next point to check is the contribution of different vibrational states to the energy flux. In Figs. 9(a) and (b) the heat flux due to diffusion of vibrational states calculated using different number of levels is presented. Curves 1 are obtained taking into account the maximum number of vibrational states ($L = 33$ for O_2 and $L = 46$ for N_2). Curves 2, 3, 4 correspond to q^{DVE} calculated with use of 5, 10 and 20 levels, respectively. One can notice that only Curves 2 ($L = 5$) deviate noticeably from the accurate values. For oxygen

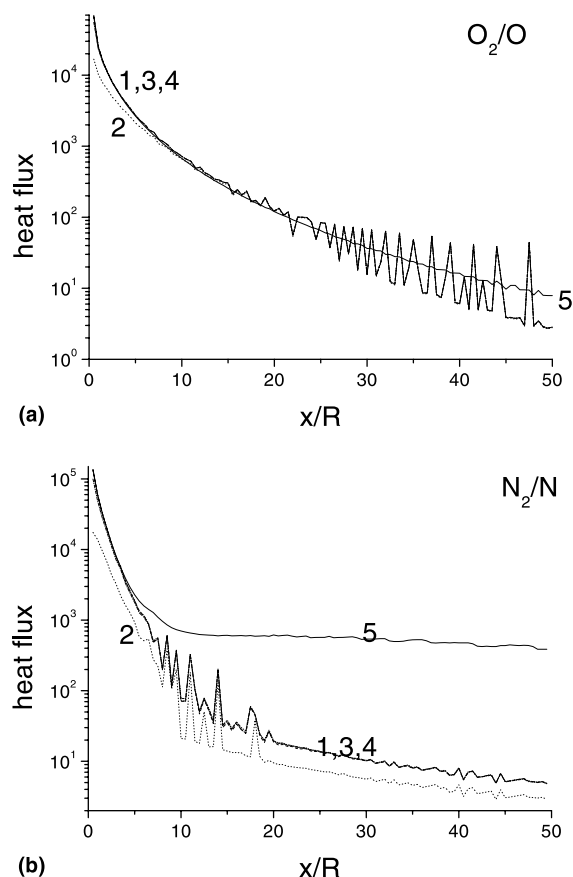


Fig. 9. Heat flux due to diffusion of vibrational energy q^{DVE} and q^{vibr} (W/m^2). Curves 1: q^{DVE} , $L = 33$ (46); 2: $L = 5$; 3: $L = 10$; 4: $L = 20$; 5: q^{vibr} . (a) O_2/O , $T_* = 4000$ K, $p_* = 100$ atm; (b) N_2/N , $T_* = 7000$ K, $p_* = 100$ atm.

taking into account only five levels leads to a 10% error in the vicinity of the throat, then this error tends to zero. The results obtained with $L = 10$ practically coincide with the ones calculated using $L = 33$. In nitrogen, using five levels is not enough for a correct prediction of q^{DVE} , 10 levels give a maximum discrepancy within 25%; finally, 15–20 levels are quite sufficient for the accurate calculation of q^{DVE} . Consequently, several lower levels give the main contribution to the heat flux. However, we have seen from Fig. 4 that at low levels the state-to-state distributions are relatively close to the quasi-stationary two-temperature ones. It allows us to suggest that the heat flux due to diffusion of vibrational energy represents in our case prac-

tically the same value as the heat flux due to vibrational heat conductivity, $q^{\text{vibr}} = -\lambda_v \partial T_1 / \partial x$. Curves 5 in Fig. 9 show the vibrational energy flux q^{vibr} . It is seen that for oxygen our assumption about the close agreement of q^{vibr} and q^{DVE} works rather well, q^{vibr} represents the average value of q^{DVE} . That is why the quasi-stationary models provide so good correspondence to the state-to-state approach. The situation is somewhat different in nitrogen: q^{vibr} coincides with q^{DVE} only close to the throat, then a significant deviation appears: it is connected with the discrepancy between state-to-state and quasi-stationary solutions at intermediate levels ($i = 10$ – 20) which in N_2 make some contribution to the energy flux. Nevertheless, in this case the role of diffusion of vibrational energy in the total heat flux at $x/R > 5$ tends to zero (see Fig. 8(b)), and in the region where q^{vibr} differs from q^{DVE} the state-to-state distributions again do not influence noticeably the total energy flux.

It is interesting to note that in a shock heated gas close to the shock front a significant distinction between heat fluxes calculated by means of state-to-state and quasi-stationary models is determined by the strong difference in the state-to-state and multi-temperature distributions at low vibrational levels. Under such conditions the role of diffusion of vibrational states becomes much more important than in the present case [10].

Finally, one can conclude that thermal non-equilibrium multi-temperature quasi-stationary models provide a good approximation for the gas temperature and heat flux evaluation in a nozzle flow, while for the correct prediction of vibrational distributions, the more rigorous state-to-state approach is required.

5. Conclusions

The vibration–chemical kinetics and heat transfer in a nozzle flow have been studied using four kinetic theory approaches: detailed state-to-state model; non-equilibrium two-temperature models for anharmonic and harmonic oscillators based on different quasi-stationary vibrational distributions; thermal equilibrium one-temperature model.

The influence of these approaches on the vibrational state populations, macroscopic gas flow parameters and transport properties has been estimated. It is shown that vibrational distributions depend essentially on the model: one-temperature distributions are very far from the state-to-state and other quasi-stationary ones; at the low levels state-to-state and two-temperature models give a similar behavior of distributions while at the intermediate and high levels only the state-to-state approach provides adequate shapes of distributions with a well pronounced plateau part.

The macroscopic flow parameters are rather weakly affected by the model; in all cases only the one-temperature approach leads to a considerable error, both harmonic and anharmonic oscillator models give results close to the ones obtained by means of the detailed state-to-state approach. The same conclusion is valid for the heat transfer; the one-temperature approach underestimates the heat flux whereas all remaining models give close agreement for the heat flux values. Such a weak influence of essentially non-equilibrium distributions on the energy flux is explained by a small contribution of intermediate and high levels to the heat transfer in the present case.

The role of various processes in the energy transfer has been examined. Thermal diffusion can be neglected in all the considered cases. The dominating role of heat conductivity and mass diffusion in the heat transfer is demonstrated.

Acknowledgements

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