

# On the simplified state-to-state transport coefficients

E.V. Kustova \*

*Department of Mathematics and Mechanics, Saint Petersburg University, Bibliotechnaya pl. 2, 198904 Saint Petersburg, Petrodvoretz, Russia*

Received 6 December 2000; in final form 21 March 2001

---

## Abstract

Simplified expressions for the state-to-state transport coefficients are proposed. The main stress is on the diffusion of vibrational energy. The state-to-state diffusion coefficients are compared to the commonly used diffusion coefficients, and the role of non-equilibrium vibrational distributions in the diffusion process and heat transfer is estimated. © 2001 Elsevier Science B.V. All rights reserved.

*PACS:* 51.10.+y; 51.20.+d; 82.20.Mj; 82.20.Rp

*Keywords:* State-to-state vibrational kinetics; Transport properties; Diffusion coefficients

---

## 1. Introduction

Recent advancement of state-to-state kinetic theory can be explained by the growing interest to different kinds of non-equilibrium flows. It is well known that in many real gas flows the strongly non-equilibrium conditions arise, so that widely used quasi-stationary distributions over vibrational energies are not valid. Excellent examples are the flows behind shock waves [1–3], expanding flows [4–7], flows in the boundary layer under re-entry conditions [8,9]. In the papers cited above the master equations for the vibrational level populations have been solved and noticeable deviations from the Boltzmann vibrational distribu-

tion have been found in some regions of the flow field.

Another important aspect of the state-to-state kinetic theory is the evaluation of transport properties under non-equilibrium conditions. The formal transport kinetic theory in the case of strong vibrational and chemical non-equilibrium has been developed in Ref. [10]. In the more recent papers [11–14] the effect of non-equilibrium vibrational distributions on the heat transfer and diffusion in different flows is estimated. In particular, it has been shown that the vibrational energy transport by diffusion makes a significant contribution to the total heat flux behind shock waves and in the boundary layer.

The investigation of transport properties in papers [11–14] has been performed using an approximate approach. First, the macroscopic parameters (vibrational distributions, species concentrations, temperature, pressure) are computed either in the Euler approach [11,13] or on the basis

---

\* Fax: +7-812-428-6649.

*E-mail addresses:* elena\_kustova@mail.ru, elena.kustova@pobox.spbu.ru (E.V. Kustova).

of essentially simplified models for transport coefficients [12]. In the paper [14] the state-to-state distributions are derived by the DSMC method. Then the calculated macroscopic parameters are used as input for the transport properties evaluation. The reason for invoking such an approximate scheme is that the practical implementation of the state-to-state transport coefficients in the computational fluid dynamics (CFD) is extremely difficult, re-calculation of these coefficients at the each step of numerical code leads to very high consumption of computational time. The computational cost of the linear transport systems solution is discussed in Section 3.

The aim of the present paper is to derive the simplified linear transport systems and thus reduce noticeably the time for the transport coefficients calculation. The obtained systems consist of few equations, it makes possible to solve them at the each step of CFD code, and therefore to get more self-consistent results. Another objective is to check the validity of some commonly used models for the diffusion coefficients.

## 2. Transport terms in the state-to-state approach

The state-to-state transport kinetic theory is developed in Ref. [10] on the basis of the generalized Chapman–Enskog method. An experimentally observed relationship between the characteristic times of main processes [15]

$$\tau_{\text{el}} < \tau_{\text{rot}} \ll \tau_{\text{vibr}} < \tau_{\text{react}} \sim \theta, \quad (1)$$

( $\tau_{\text{el}}$ ,  $\tau_{\text{rot}}$ ,  $\tau_{\text{vibr}}$ ,  $\tau_{\text{react}}$  are respectively the mean times of translational, rotational and vibrational relaxation and chemical reactions,  $\theta$  is the macroscopic time) provides a strong vibrational–chemical coupling. In this case no quasi-stationary vibrational distributions exist, and the zero order distribution function  $f_{cij}^{(0)}$  ( $c$ ,  $i$ ,  $j$  denote chemical species, vibrational and rotational quantum numbers) is obtained under the form of Maxwell–Boltzmann distribution over velocities and rotational energy depending on the non-equilibrium vibrational level populations and chemical species concentrations:

$$f_{cij}^{(0)} = \left( \frac{m_c}{2\pi kT} \right)^{3/2} \frac{n_{ci} s_j^{ci}}{Z_{\text{rot}}^{ci}} \exp \left( -\frac{m_c c_c^2}{2kT} - \frac{\varepsilon_j^{ci}}{kT} \right), \quad (2)$$

$m_c$  is the molecular mass,  $k$  is the Boltzmann constant,  $T$  is the gas temperature,  $n_{ci}$  are the non-equilibrium vibrational level populations,  $\mathbf{c}_c = \mathbf{u}_c - \mathbf{v}$  is the peculiar velocity,  $\mathbf{v}$  is the macroscopic gas velocity,  $s_j^{ci}$ ,  $\varepsilon_j^{ci}$  are the statistic weight and energy of the  $j$ th rotational state corresponding to the vibrational level  $i$  of chemical species  $c$ ,  $Z_{\text{rot}}^{ci}$  is the rotational partition function.

The first order distribution functions are given by the expression [10]:

$$f_{cij}^{(1)} = f_{cij}^{(0)} \left( -\frac{1}{n} \mathbf{A}_{cij} \cdot \nabla \ln T - \frac{1}{n} \sum_{dk} \mathbf{D}_{cij}^{dk} \cdot \mathbf{d}_{dk} - \frac{1}{n} \mathbf{B}_{cij} : \nabla \mathbf{v} - \frac{1}{n} F_{cij} \nabla \cdot \mathbf{v} - \frac{1}{n} G_{cij} \right), \quad (3)$$

$n$  is the total number density,  $\mathbf{d}_{ci}$  are the diffusion driving forces for each chemical and vibrational species:

$$\mathbf{d}_{ci} = \nabla \left( \frac{n_{ci}}{n} \right) + \left( \frac{n_{ci}}{n} - \frac{\rho_{ci}}{\rho} \right) \nabla \ln p, \quad (4)$$

$\rho_{ci} = m_c n_{ci}$ ,  $\rho = \sum_c m_c \sum_i n_{ci}$ ,  $p$  is the pressure.

Functions  $\mathbf{A}_{cij}$ ,  $\mathbf{B}_{cij}$ ,  $\mathbf{D}_{cij}^{dk}$ ,  $F_{cij}$  and  $G_{cij}$  are found from the linear integral equations derived in Ref. [10].

A closed set of macroscopic equations for the macroscopic parameters  $n_{ci}$ ,  $\mathbf{v}$ ,  $T$  is obtained in Refs. [10,16] and consists of the conservation equations for the momentum and total energy coupled with the equations of detailed vibration–chemical kinetics for the vibrational level populations  $n_{ci}$ .

The first order transport terms are determined by the first order distribution functions. The pressure tensor  $\mathbf{P}$  has been obtained in the following form:

$$\mathbf{P} = (p - p_{\text{rel}}) \mathbf{I} - 2\mu \mathbf{S} - \eta \nabla \cdot \mathbf{v} \mathbf{I}. \quad (5)$$

Here  $\mathbf{I}$  is the unit tensor,  $\mathbf{S}$  is the tensor of deformation velocities,  $\mu$ ,  $\eta$  are the shear and bulk viscosity coefficients,  $p_{\text{rel}}$  is the relaxation pressure:

$$\mu = \frac{kT}{10} [\mathbf{B}, \mathbf{B}], \quad \eta = kT[F, F], \quad p_{\text{rel}} = kT[F, G]. \quad (6)$$

The bracket integrals  $[A, B]$  introduced in Refs. [10,16] are determined by the cross-sections of the most frequent collisions, i.e. the elastic collisions and those leading to the rotational energy exchange (see Appendix A.1 for definition). Therefore these bracket integrals differ from the ones defined in the classical thermal equilibrium one-temperature approach. In the latter case the bracket integrals depend also on the cross-sections of vibrational energy exchanges.

The diffusion velocity of the molecules of each chemical and vibrational species has been found in Ref. [10] under the form:

$$\mathbf{V}_{ci} = - \sum_{dk} D_{cidk} \mathbf{d}_{dk} - D_{\text{Tci}} \nabla \ln T, \quad (7)$$

where  $D_{cidk}$  and  $D_{\text{Tci}}$  are the diffusion and thermal diffusion coefficients for every chemical and vibrational species:

$$D_{cidk} = \frac{1}{3n} [\mathbf{D}^{ci}, \mathbf{D}^{dk}], \quad D_{\text{Tci}} = \frac{1}{3n} [\mathbf{D}^{ci}, \mathbf{A}]. \quad (8)$$

The expression for the total heat flux in the first order approximation takes the following form:

$$\mathbf{q} = -\lambda' \nabla T - p \sum_{ci} D_{\text{Tci}} \mathbf{d}_{ci} + \sum_{ci} \left( \frac{5}{2} kT + \langle \varepsilon_j^{ci} \rangle_r + \varepsilon_i^c + \varepsilon^c \right) n_{ci} \mathbf{V}_{ci}, \quad (9)$$

where  $\langle \varepsilon_j^{ci} \rangle_r$  is the mean rotational energy of  $c$  species at the vibrational level  $i$ ,  $\varepsilon_i^c$ ,  $\varepsilon^c$  are the vibrational energy of the  $i$ th level and energy of formation of chemical species  $c$ ,

$$\lambda' = \lambda_t + \lambda_r = \frac{k}{3} [\mathbf{A}, \mathbf{A}] \quad (10)$$

is the coefficient of thermal conductivity. The coefficients  $\lambda_t$  and  $\lambda_r$  express thermal conductivity connected with elastic and inelastic translational–rotational TR energy transfers. It is important to emphasize that vibrational energy does not contribute to the thermal conductivity in this approach.

The expressions for the heat flux and diffusion velocity contain not only the gradient of the gas temperature but also the gradients of all level populations of different molecular species and number densities of atoms with corresponding diffusion and thermal diffusion coefficients. In the general case these coefficients are different for various vibrational and chemical species.

Following the procedure proposed in Ref. [10], the functions  $\mathbf{A}_{cij}$ ,  $\mathbf{D}_{cij}^{dk}$  and  $\mathbf{B}_{cij}$  are expanded into finite series of Sonine and Waldmann–Trübenbacher orthogonal polynomials over reduced translational and rotational energy correspondingly:

$$\mathbf{A}_{cij} = - \frac{m_c \mathbf{c}_c}{2kT} \sum_{rp} a_{ci,rp} S_{3/2}^{(r)} \left( \frac{m_c \mathbf{c}_c^2}{2kT} \right) P_j^{(p)} \left( \frac{\varepsilon_j^{ci}}{kT} \right), \quad (11)$$

$$\mathbf{D}_{cij}^{dk} = \frac{m_c \mathbf{c}_c}{2kT} \sum_r d_{ci,r}^{dk} S_{3/2}^{(r)} \left( \frac{m_c \mathbf{c}_c^2}{2kT} \right), \quad (12)$$

$$\mathbf{B}_{cij} = \frac{m_c}{2kT} \left( \mathbf{c}_c \mathbf{c}_c - \frac{1}{3} c_c^2 \mathbf{I} \right) \sum_r b_{ci,r} S_{5/2}^{(r)} \left( \frac{m_c \mathbf{c}_c^2}{2kT} \right). \quad (13)$$

The transport coefficients can be easily expressed in terms of the first non-vanishing coefficients of expansions (11)–(13):

$$\lambda' = \sum_{ci} \frac{5}{4} k \frac{n_{ci}}{n} a_{ci,10} + \sum_{ci} \frac{k}{2} \frac{n_{ci}}{n} c_{\text{rot},ci} a_{ci,01}, \quad (14)$$

$$D_{cidk} = \frac{1}{2n} d_{dk,0}^{ci}, \quad (15)$$

$$D_{\text{Tci}} = - \frac{1}{2n} a_{ci,00}, \quad (16)$$

$$\mu = \frac{kT}{2} \sum_{ci} \frac{n_{ci}}{n} b_{ci,0}. \quad (17)$$

Here  $c_{\text{rot},ci}$  is the dimensionless (divided by the factor  $k/m_c$ ) rotational specific heat of  $c$  species at the  $i$ th vibrational level:

$$c_{\text{rot},ci} = \frac{m_c}{k} \frac{\partial E_r^{ci}}{\partial T}, \quad \rho_{ci} E_r^{ci} = \sum_j \int \varepsilon_j^{ci} f_{cij} \mathbf{d}\mathbf{u}_c.$$

Using the polynomial expansions, the integral equations for functions  $\mathbf{A}_{cij}$ ,  $\mathbf{D}_{cij}^{dk}$ ,  $\mathbf{B}_{cij}$  can be reduced to the systems of linear algebraic equations. Thus the system of equations for the expansion coefficients  $a_{ci,rp}$  has the following form [10]:

$$\sum_{dk} \sum_{r'p'} A_{rr'pp'}^{cidk} a_{dk,r'p'} = \frac{15kT}{2} \frac{n_{ci}}{n} \delta_{r1} \delta_{p0} + 3kT \frac{n_{ci}}{n} c_{\text{rot},ci} \delta_{r0} \delta_{p1}, \quad (18)$$

$$c = 1, \dots, L, \quad i = 0, 1, \dots, L_c, \quad r, p = 0, 1, \dots$$

Here  $L$  is the number of chemical species,  $L_c$  is the total number of vibrational energy levels in molecular species  $c$ .

The coefficients of system (18) are expressed in terms of level populations and partial bracket integrals:

$$A_{rr'pp'}^{cidk} = \sqrt{m_c m_d} \left( \delta_{cd} \delta_{ik} \sum_{bl} \frac{n_{ci} n_{bl}}{n^2} \left[ Q^{rp}, Q^{r'p'} \right]'_{cibl} + \frac{n_{ci} n_{dk}}{n^2} \left[ Q^{rp}, Q^{r'p'} \right]''_{cidk} \right), \quad (19)$$

$$Q^{rp} = \sqrt{\frac{m_c}{2kT}} \mathbf{c}_c S_{3/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) P_j^{(p)} \left( \frac{\varepsilon_j^{ci}}{kT} \right).$$

Eq. (18) occurs not to be linearly independent in the case  $r = p = 0$ , and therefore must be solved using a constraint obtained in Ref. [10]:

$$\sum_{ci} \frac{\rho_{ci}}{\rho} a_{ci,00} = 0. \quad (20)$$

Similarly the equations for the coefficients  $d_{ci,r}^{dk}$  can be written:

$$\sum_{dk} \sum_{r'} \gamma_{rr'}^{cidk} d_{dk,r'}^{bl} = 3kT \left( \delta_{cb} \delta_{il} - \frac{\rho_{ci}}{\rho} \right) \delta_{r0}, \quad (21)$$

$$b, c = 1, \dots, L, \quad i, l = 0, 1, \dots, L_c(L_b),$$

$$r = 0, 1, \dots,$$

where  $\gamma_{rr'}^{cidk}$  represent the particular case of the bracket integrals  $A_{rr'pp'}^{cidk}$  at  $p = p' = 0$ :  $\gamma_{rr'}^{cidk} = A_{rr'00}^{cidk}$ .

A linearly independent system is obtained taking into account constraints for the coefficients  $d_{ci,r}^{dk}$ :

$$\sum_{ci} \frac{\rho_{ci}}{\rho} d_{ci,0}^{dk} = 0, \quad d = 1, \dots, L, \quad k = 0, 1, \dots, L_d. \quad (22)$$

The equations for the coefficients  $b_{ci,r}$  are found in the form:

$$\sum_{dk} \sum_{r'} H_{rr'}^{cidk} b_{dk,r'} = \frac{2}{kT} \frac{n_{ci}}{n} \delta_{r0}, \quad (23)$$

$$c = 1, \dots, L, \quad i = 0, 1, \dots, L_c, \quad r = 0, 1, \dots,$$

where

$$H_{rr'}^{cidk} = \frac{2}{5kT} \left( \delta_{cd} \delta_{ik} \sum_{bl} \frac{n_{ci} n_{bl}}{n^2} \left[ Q^r, Q^{r'} \right]'_{cibl} + \frac{n_{ci} n_{dk}}{n^2} \left[ Q^r, Q^{r'} \right]''_{cidk} \right), \quad (24)$$

$$Q^r = \frac{m_c}{2kT} S_{5/2}^{(r)} \left( \frac{m_c c_c^2}{2kT} \right) \left( \mathbf{c}_c \mathbf{c}_c - \frac{1}{3} c_c^2 \mathbf{I} \right).$$

This is the general method for the calculation of state dependent transport coefficients based on the rigorous kinetic theory approach [10]. Until this point no additional assumptions have been introduced to simplify this procedure.

### 3. Simplified expressions for transport coefficients

Let us remind the main problems which arise during the practical calculation of the state-to-state transport coefficients. First, several kinds of bracket integrals for each chemical and vibrational species must be computed. It requires the data on the cross-sections of elastic collisions and TR processes depending on the vibrational states of colliding particles. Another difficulty encountered in reaching this goal is the great amount of linear algebraic equations which have to be solved for every value of temperature and each distribution over vibrational energies and chemical species. Let  $N_{\text{tot}}$  be the total number of chemical and vibrational species ( $N_{\text{tot}} = \sum_{c=1}^{L_{\text{mol}}} L_c + L_{\text{at}}$ ,  $L_{\text{mol}}$  is the

number of molecular species,  $L_c$  is the total number of vibrational energy levels in molecular species  $c$ ,  $L_{at}$  is the number of atomic species),  $N_v = \sum_{c=1}^{L_{mol}} L_c$  denotes the total number of vibrational states in a mixture. In order to deduce the thermal conductivity coefficient  $\lambda'$  one must solve a system consisting of  $3N_v + 2L_{at}$  algebraic equations, the system for the shear viscosity coefficient calculation contains  $N_{tot}$  equations. The worst case is the computation of diffusion coefficients: there are  $N_{tot}^2$  coefficients  $D_{cidk}$  in the mixture, for each coefficient the system of  $N_{tot}$  algebraic coefficients has to be solved. Strictly speaking, the number of independent diffusion coefficients is  $N_{tot}(N_{tot} + 1)/2$  because  $D_{cidk} = D_{dkci}$ . However, despite this fact the total number of diffusion coefficients remains tremendous. A simple example: in a mixture ( $N_2/N$ ) taking into account 46 vibrational levels of nitrogen, one obtains 1128 independent diffusion coefficients, each of them is found solving the system of 47 algebraic equations. In the same mixture, for the computation of thermal conductivity and shear viscosity coefficients the systems of 140 and 47 equations should be considered respectively.

It is obvious that such a computational scheme cannot be implemented to any CFD code, re-calculation of all transport coefficients at the each step of numerical code will make it too much time consumable. In order to maintain the advantages of the state-to-state transport theory and simplify the procedure of transport coefficients calculation some additional assumptions are required. In the present work the following assumptions are introduced:

(1) The rotational motion of a molecule is described by the rigid rotator model. It allows to consider the rotational energy independently from the vibrational state ( $\epsilon_j^{ci} = \epsilon_j^c$ ) and therefore to put  $c_{rot,ci} = c_{rot,c}$ . This fact simplifies noticeably the thermal conductivity computation.

(2) Usual assumptions of Monchick et al. [17] for the calculation of bracket integrals are introduced: first, all complex collisions are neglected, and second, the internal and translational motions are considered as the uncorrelated ones. These assumptions allow one to express all bracket integrals as linear combinations of the elastic colli-

sion integrals and the integrals depending on the change of rotational energy  $\Delta \epsilon_{rot}^{cidk}$  at the inelastic collisions.

(3) All collision integrals depending on  $\Delta \epsilon_{rot}^{cidk}$  are supposed to be much smaller than the elastic collision integrals. This assumption was discussed in details and proved in Refs. [10,18]: the contribution of the collision integrals depending on  $\Delta \epsilon_{rot}^{cidk}$  to the thermal conductivity coefficients is found to be less than 1–2%.

(4) The cross-sections of elastic collisions are assumed to be 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, Ref. [19]). The validity of this assumption is discussed in Ref. [14]. 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.

Applying these assumptions one can simplify significantly the procedure of transport coefficients calculation. First, assumptions (2)–(4) permit to express all the bracket integrals in terms of the vibrational level populations, atomic number densities and reduced elastic collision integrals  $\Omega_{cd}^{(l,r)*}$  (see Refs. [20–23] for definition and Ref. [24] for the most reliable data on these integrals). The final expressions for the bracket integrals are obtained in Ref. [10] and are given in Appendix A.2 in the simplified form ((A.2)–(A.12)).

The next result concerns the simplification of systems (18) and (20)–(23). Let us consider first the most simple system (23) for the coefficients  $b_{ci,r}$ . Due to assumption (4) the bracket integrals  $H_{rr}^{cidk}$  depend on the vibrational level  $i$  only through the vibrational level populations  $n_{ci}$  (see Appendix A.2). Then, after some algebra, from system (23) it follows that coefficients  $b_{ci,r}$  do not depend on the vibrational level:  $\forall i = 0, \dots, L_c$   $b_{ci,r} = b_{c,r}$ . Keeping only the first non-vanishing terms of expansion (13) one can reduce the calculation of the shear viscosity coefficient to the simple formula:

$$\mu = \frac{kT}{2} \sum_c \frac{n_c}{n} b_{c,0}. \quad (25)$$

Coefficients  $b_{c,0}$  are found from the simplified system:

$$\sum_d H_{00}^{cd} b_{d,0} = \frac{2}{kT} \frac{n_c}{n}, \quad c = 1, \dots, L. \quad (26)$$

As it is seen, system (26) contains only  $L$  equations instead of  $N_{\text{tot}}$  in system (23). This solution coincides formally with the one obtained in the quasi-stationary local thermal equilibrium one-temperature approach described in Refs. [16,23], the bracket integrals  $H_{00}^{cd}$  for the one-temperature solution are given in many classical works on the transport theory in terms of standard  $\Omega_{cd}^{(l,r)*}$  integrals and fictitious viscosity and heat conductivity coefficients [21–23]. However, the principal difference exists: as the transport coefficients are determined by the cross-sections of rapid processes, the  $\Omega_{cd}^{(l,r)*}$  integrals in the state-to-state model depend on the cross-sections of elastic collisions and TR exchanges; in the one-temperature approach they depend also on the cross-sections of vibrational energy exchanges.

Finally one can conclude that shear viscosity does not depend on the vibrational distributions. It is reasonable because this coefficient describes the transfer of momentum which depends significantly on the velocities but not on the internal state of particles.

The bulk viscosity coefficient as well as relaxation pressure are determined by the integrals depending on  $\Delta_{\text{rot}}^{c,dk}$  and, consequently, cannot be calculated using assumption (3) proposed above. In some cases these coefficients can be expressed in terms of the rotational relaxation times. For a pure diatomic gas bulk viscosity in the state-to-state approach is obtained in Ref. [25].

Now, let us consider the coefficients making part of the diffusion velocities and total energy flux. Proceeding in a similar way and invoking also assumption (1), the expression for the thermal conductivity coefficient has been simplified:

$$\lambda' = \sum_c \frac{5}{4} k \frac{n_c}{n} a_{c,10} + \sum_c \frac{k}{2} \frac{n_c}{n} c_{\text{rot},c} a_{c,01}, \quad (27)$$

coefficients  $a_{c,10}$  and  $a_{c,01}$  are found from the system:

$$\begin{aligned} \sum_d (A_{0000}^{cd} a_{d,00} + A_{0100}^{cd} a_{d,10} + A_{0001}^{cd} a_{d,01}) &= 0, \\ \sum_d (A_{1000}^{cd} a_{d,00} + A_{1100}^{cd} a_{d,10} + A_{1001}^{cd} a_{d,01}) &= \frac{15kT}{2} \frac{n_c}{n}, \\ \sum_d (A_{0010}^{cd} a_{d,00} + A_{0110}^{cd} a_{d,10} + A_{0011}^{cd} a_{d,01}) &= 3kT \frac{n_c}{n} c_{\text{rot},c}, \\ c &= 1, \dots, L. \end{aligned} \quad (28)$$

System (28) must be solved together with the constraint obtained from Eq. (20) after summation over  $i$ :

$$\sum_c \frac{\rho_c}{\rho} a_{c,00} = 0. \quad (29)$$

Again, compared to systems (18) and (20) the number of equations is significantly reduced: there are only  $3L_{\text{mol}} + 2L_{\text{at}}$  equations instead of  $3N_v + 2L_{\text{at}}$ .

This result is also close to the one given by the one-temperature model [16,23] except two points: the first one, concerning the inelastic cross-sections is discussed above, and the second point is that in the state-to-state approach only rotational degrees of freedom make contribution to the internal thermal conductivity whereas in the one-temperature approach both rotational and vibrational energy contribute to this coefficient. Therefore in the latter case the internal specific heat  $c_{\text{int},c}$  appears in Eqs. (27) and (28) instead of rotational specific heat  $c_{\text{rot},c}$ . The reason for this is that thermal conductivity as well as viscosity are determined by the rapid processes. Finally in the state-to-state approach the thermal conductivity coefficient does not depend on the vibrational distribution. The transport of vibrational energy is described by introducing diffusion coefficients for every vibrational state.

Due to the fact that  $a_{ci,00} = a_{c,00}, \forall i$ , the thermal diffusion coefficients are also independent from the vibrational state ( $D_{\text{T}ci} = D_{\text{T}c}, \forall i$ ), and the term  $\sum_{ci} D_{\text{T}ci} \mathbf{d}_{ci}$  entering to the total heat flux is equal to  $\sum_c D_{\text{T}c} \mathbf{d}_c$ , where  $\mathbf{d}_c = \sum_i \mathbf{d}_{ci}$ .

The situation is more complicated for the diffusion coefficients. Actually, system (21) cannot be simplified in the same way as the previous ones because of the structure of its right-hand sides. However, it is easy to show that the main part of

coefficients  $d_{dk,r}^{bl}$  do not depend on the vibrational quantum number except the coefficients  $d_{bl,r}^{bl}$ . Therefore,  $d_{dk,r}^{bl} = d_{d,r}^b, \forall d \neq b, \forall k, l$ , and  $d_{bk,r}^{bl} = d_{b,r}^b, \forall l, \forall k \neq l$ . Keeping the first non-vanishing terms in expansion (12), i.e., the terms corresponding to  $r = 0$ , system (21) can be written in the reduced form:

for  $c = b, i = l$ :

$$\begin{aligned} \gamma_{00}^{blbl} d_{bl,0}^{bl} + \sum_{k \neq l} \gamma_{00}^{bikk} d_{b,0}^b + \sum_{d \neq b} d_{d,0}^b \sum_k \gamma_{00}^{bidk} \\ = 3kT \left( 1 - \frac{\rho_{bl}}{\rho} \right), \end{aligned} \quad (30)$$

for  $c = b, i = 0, \dots, l-1, l+1, \dots, L_b$ :

$$\begin{aligned} \sum_{i \neq l} \left( \gamma_{00}^{bibl} d_{bl,0}^{bl} + \sum_{k \neq l} \gamma_{00}^{bikk} d_{b,0}^b + \sum_{d \neq b} d_{d,0}^b \sum_k \gamma_{00}^{bidk} \right) \\ = -3kT \frac{\rho_b - \rho_{bl}}{\rho}, \end{aligned} \quad (31)$$

for  $c = 1, \dots, b-1, b+1, \dots, L, i = 0, \dots, L_c$ :

$$\begin{aligned} \sum_i \left( \gamma_{00}^{cibl} d_{bl,0}^{bl} + \sum_{k \neq l} \gamma_{00}^{cikk} d_{b,0}^b + \sum_{d \neq b} d_{d,0}^b \sum_k \gamma_{00}^{cidk} \right) \\ = -3kT \frac{\rho_c}{\rho}, \end{aligned} \quad (32)$$

$b = 1, \dots, L, l = 0, \dots, L_b$ .

The constraint (22) is replaced by the following equation:

$$\begin{aligned} \frac{\rho_{bl}}{\rho} d_{bl,0}^{bl} + \frac{\rho_b - \rho_{bl}}{\rho} d_{b,0}^b + \sum_{d \neq b} \frac{\rho_d}{\rho} d_{d,0}^b = 0, \\ b = 1, \dots, L, l = 0, 1, \dots, L_b. \end{aligned} \quad (33)$$

System (30)–(33) contains only  $L + 1$  equations instead of  $N_{\text{tot}}$  in the case of systems (21) and (22). Finally the system of diffusion coefficients is reduced to the following: there are  $N_v$  coefficients  $D_{cici}$  which are different for any vibrational level  $i$  of species  $c$ ,  $L_{\text{mol}}$  coefficients  $D_{cc} = D_{cick}, \forall i, \forall k \neq i$ , and  $L^2$  coefficients  $D_{cd} = D_{cidk}, \forall d \neq c, \forall i, k$ . The total number of independent diffusion coefficients is  $N_v + L_{\text{mol}} + L(L + 1)/2$ .

Coming back to the ( $\text{N}_2/\text{N}$ ) mixture mentioned at the beginning of this section, after simplifica-

tions proposed above, one obtains only 49 independent diffusion coefficients, each of them is found from the system of three equations. For the computation of thermal conductivity and shear viscosity coefficients the systems of five and two equations are to be solved respectively.

Finally, computation of the transport coefficients is reduced to the solution of linear algebraic systems (26), (28), (29) and (30)–(33). Coefficients of these systems represent the partial bracket integrals determined by the cross-sections of elastic collisions and translation–rotation energy exchange. The expressions for the bracket integrals  $H_{00}^{cd}, A_{rr'pp'}^{cd}, \gamma_{00}^{cd}$  are summarized in Appendix A.3 ((A.13)–(A.22)). These formulas are close to the classical ones [21–23]. Nevertheless, one should keep in mind that in the state-to-state approach  $\Omega_{cd}^{(l,r)*}$  integrals as well as the bracket integrals depend on the cross-sections of elastic and TR collisions (while in the well known one-temperature case they depend also on the cross-sections of vibrational energy transitions). However, for the practical calculations of  $\Omega_{cd}^{(l,r)*}$  integrals, the inelastic cross-sections are usually substituted by the elastic ones. The influence of the inelastic cross-sections on these integrals occurs to be weak (see, for instance, Ref. [26]).

Various methods of solution of transport linear systems have been elaborated since the work of Chapman and Cowling [20]. The most evident way is the direct solution of algebraic systems by the Cramer's rule which allows one to express the transport coefficients explicitly as ratios of determinants [20–22,27]. Nevertheless, solving the linear systems by this method is extremely computationally expensive. Another direct method using the Gaussian elimination is considered, for instance, in Ref. [28]. This method is noticeably less time consumable but still not satisfactory as a majority of direct methods. Recently the mathematical properties of transport linear systems have been studied comprehensively in Ref. [23] and new efficient iterative algorithms have been proposed. This technique provides very fast and accurate evaluation of transport properties.

It should be emphasized that the resemblance of systems (26), (28) and (29) to the classical one-temperature ones remains only formal, it is seen

from the definition of partial bracket integrals (see Appendix A.1) and from the fact that vibrational degrees of freedom do not contribute to the transport coefficients. Strictly speaking, the independence of some transport coefficients of the vibrational distributions is not an evident fact, and application of the state-to-state transport theory must in essence be based on the complete systems (18) and (20)–(23). Thus, the analysis of transport properties performed in Refs. [11–14] is carried out in this way, and it was a rather lengthy procedure, even using an approximate method mentioned in Section 1.

A possibility of getting simplified transport linear systems in the state-to-state approach is discussed in Ref. [10], but their validity has never been proved before. The derivation of transport linear systems (26), (28)–(33) is the first step to the implementation of state-to-state transport theory to the computational fluid dynamics.

#### 4. Diffusion coefficients

In this section the diffusion coefficients are considered in some more details. The diffusion coefficients for each vibrational state have been introduced recently in Ref. [10], they are required for the estimation of vibrational energy transport in the absence of quasi-stationary vibrational distributions.

For a mixture of diatomic gas  $A_2$  and atoms  $A$  the analytical expressions for the diffusion coefficients can be derived from Eqs. (30)–(33). Finally all diffusion coefficients are expressed in terms of mass fractions of species  $c_d = \rho_d/\rho$  and binary and self-diffusion coefficients:

$$\mathcal{D}_{cd} = \frac{3}{16nm_{cd}} \frac{(2\pi m_{cd}kT)^{1/2}}{\pi \bar{\sigma}_{cd}^2 \Omega_{cd}^{(1,1)*}},$$

$$\mathcal{D}_c = \frac{3}{8nm_c} \frac{(\pi m_c kT)^{1/2}}{\pi \bar{\sigma}_c^2 \Omega_c^{(1,1)*}}$$

$m_{cd}$  is the reduced mass,  $\bar{\sigma}_{cd}$  is the collision diameter. Thus for the ( $N_2/N$ ) mixture the diffusion coefficients are given by:

$$D_{N_2iN_2i} = \mathcal{D}_{NN_2} \left( \frac{m_N}{\rho/n} \right)^2 \times \frac{\frac{c_N}{\mathcal{D}_{N_2}} + \frac{2}{\mathcal{D}_{NN_2}} \left( \frac{1}{c_{N_2i}} - c_N - 1 \right)}{\frac{c_{N_2}}{2\mathcal{D}_{N_2}} + \frac{c_N}{\mathcal{D}_{NN_2}}},$$

$$i = 0, \dots, 45, \quad (34)$$

$$D_{N_2N_2} = D_{N_2iN_2k} = \mathcal{D}_{NN_2} \left( \frac{m_N}{\rho/n} \right)^2 \times \frac{\frac{c_N}{\mathcal{D}_{N_2}} - \frac{2}{\mathcal{D}_{NN_2}} (c_N + 1)}{\frac{c_{N_2}}{2\mathcal{D}_{N_2}} + \frac{c_N}{\mathcal{D}_{NN_2}}}, \quad \forall k \neq i, \quad (35)$$

$$D_{NN_2} = -\mathcal{D}_{NN_2} \frac{m_N m_{N_2}}{(\rho/n)^2}, \quad (36)$$

$$D_{NN} = \mathcal{D}_{NN_2} \frac{m_N m_{N_2}}{(\rho/n)^2} \left( \frac{1}{c_N} - 1 \right). \quad (37)$$

One can notice that expressions for  $D_{NN_2}$  and  $D_{NN}$  are similar to the well-known formulas given by Ferziger and Kaper [22] for a binary mixture (again, the difference is in the cross-sections determining the  $\Omega_{cd}^{(1,1)*}$  integrals). The state specific diffusion coefficients  $D_{N_2iN_2i}$  depend on the mass fractions of chemical species and population of the corresponding level. Due to assumption (4) of the previous section, these coefficients are the only ones determined by the non-equilibrium state-to-state distributions. In the limit of a pure diatomic gas ( $c_N = 0$ ) coefficients  $D_{N_2iN_2i}$  and  $D_{N_2N_2}$  take the form obtained in Ref. [25]:

$$D_{N_2iN_2i} = \mathcal{D}_{N_2} \left( \frac{1}{c_{N_2i}} - 1 \right), \quad D_{N_2N_2} = -\mathcal{D}_{N_2}.$$

The state-to-state vibrational distributions as well as transport coefficients and heat flux have been investigated in the previous papers [11–13] for three different flows of a ( $N_2, N$ ) mixture: (1) flow behind a strong shock wave (initial conditions are:  $M_0 = 15$ ,  $T_0 = 293$  K,  $p_0 = 100$  Pa), (2) flow in a hypersonic boundary layer (temperature and pressure at the edge of the boundary layer are  $T_c = 5000$  K,  $p_c = 1000$  Pa, the wall temperature is  $T_w = 300$  K), and (3) expanding flow in the F4



nozzle used in ONERA (reservoir conditions are:  $T_0 = 6000$  K,  $p_0 = 10^5$  Pa).

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 [11,13] or on the basis of very simple models for transport coefficients [12]. The numerical methods are described in details in Refs. [6–9,11]. Then the calculated macroscopic parameters are used as input for the transport coefficients and heat transfer evaluation. This approach permits to estimate qualitatively the influence of state-to-state vibrational kinetics on the transport properties. Certainly, in order to understand the mutual effect of non-equilibrium kinetics and state dependent transport properties, it is necessary to use the equations of viscous and heat conductive gas flow and compute the state-to-state coefficients at the each time and space cell. Up to now, the computational cost of such a scheme was extremely high, and the practical incorporation of the state-to-state linear transport systems to the numerical codes has not been accomplished. The implementation of simplified systems proposed in the present paper makes this goal attainable. A simple illustration: in the present study the transport coefficients and heat fluxes in ( $N_2, N$ ) mixture flows are calculated using the same macroscopic parameters as in Refs. [11–13] but applying reduced systems (26), (28)–(33) in contrast to the previous papers where complete systems (18) and (20)–(23) have been solved. The computational time for each step is now 100–150 times less, the accuracy of calculations remains the same. The gain of time is expected to be much higher for multi-component mixtures. This can encourage one to consider simultaneously the state-to-state kinetics and transport theory and by this means get more comprehensive results.

The following discussion serves as a warning against an over-simplification of the diffusion coefficients. The main factor which affects the state specific diffusion coefficients  $D_{cici}$  is the non-equilibrium vibrational kinetics,  $D_{cici}$  appear to be approximately inverse proportional to  $n_{ci}$  (see Refs. [11–13]). The similar dependence of usual self-

diffusion coefficients on the concentration of corresponding chemical species has been predicted by Ferziger and Kaper [22]. It is known that vibrational level populations can vary within several orders of magnitude, therefore, the inverse proportional dependence leads to very strong variations of diffusion coefficients as far as one computes them as functions of  $i$ . For the practical calculations sometimes it is more convenient to deal with slowly varying coefficients. Consequently, it is useful to introduce the coefficients  $\tilde{D}_{cici}$  in the following way:

$$\tilde{D}_{cici} = \frac{n_{ci}}{n} D_{cici}, \quad (38)$$

and insert  $\tilde{D}_{cici}$  to the macroscopic equations instead of  $D_{cici}$ . Various definitions of diffusion velocity are discussed in Ref. [22], and it is shown that definitions like (7) are more self-consistent. However, coefficients  $\tilde{D}_{cici}$  vary much slower with the vibrational quantum number compared to  $D_{cici}$ , this makes easier to use them for rapid estimations. Moreover, weak variation of  $\tilde{D}_{cici}$  allows one to suppose that these coefficients do not depend on the vibrational state and can be replaced by a unique coefficient  $\tilde{D}$ , which, for a mixture ( $N_2, N$ ), is connected with a simple binary diffusion coefficient:

$$\tilde{D} = \tilde{D}_{N_2iN_2i} = \frac{n_{N_2}}{n} \mathcal{D}_{NN_2}, \quad \forall i. \quad (39)$$

Such an assumption is often used in the state-to-state calculations in order to incorporate the vibrational energy transport by diffusion to the master equations and to treat it in the most simple way [8,9,29,30]. By this means the constant Lewis and Schmidt numbers can be introduced, it facilitates significantly the numerical algorithms [8,9]. However, assumption (39) requires further verification. The limits of its validity as well as the impact of vibrational distributions on the diffusion coefficients are discussed hereafter.

In Figs. 1–7 the vibrational distributions and state specific diffusion coefficients (38) are given for different conditions. For a comparison the values of coefficient  $\tilde{D}$  (39) independent on the vibrational state are also plotted.

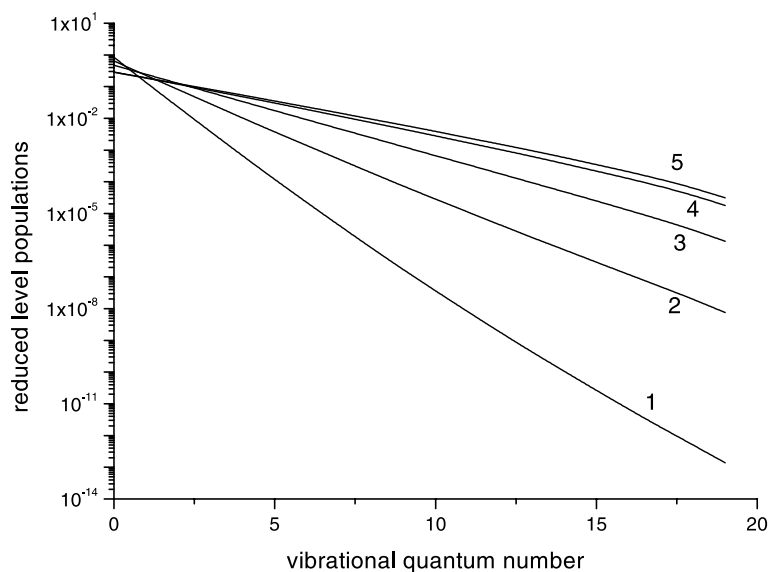


Fig. 1. Vibrational distributions  $n_i/n$  behind a shock wave at different distances  $x$  from the shock front. (1)  $x = 0.015$  cm; (2)  $x = 0.05$  cm; (3)  $x = 0.1$  cm; (4)  $x = 1$  cm; (5)  $x = 2$  cm.

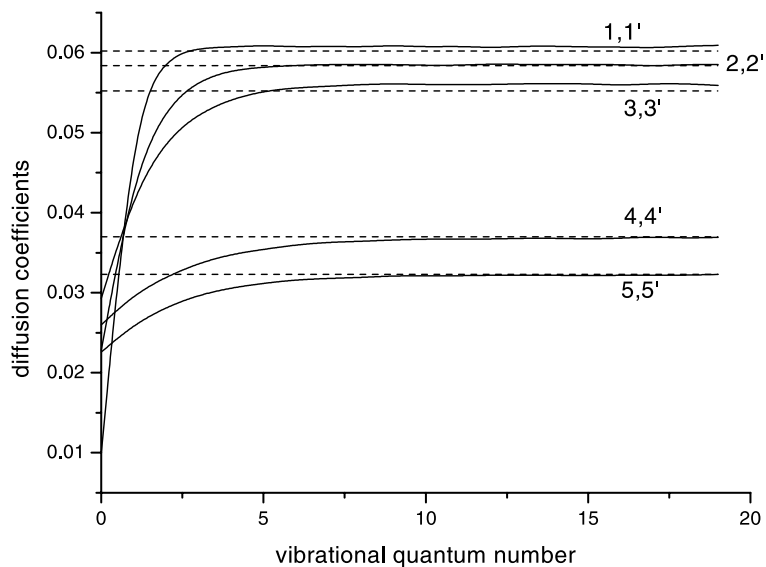


Fig. 2. Diffusion coefficients  $D_{N_2iN_2i}$ ,  $\text{m}^2/\text{s}$ , behind a shock wave at different distances  $x$  from the shock front. Solid lines – state-to-state approach, dashed lines – coefficient  $\bar{D}$ . 1,1' –  $x = 0.015$  cm; 2,2' –  $x = 0.05$  cm; 3,3' –  $x = 0.1$  cm; 4,4' –  $x = 1$  cm; 5,5' –  $x = 2$  cm.

The process of vibrational relaxation behind a shock wave is illustrated by Fig. 1. The initial Boltzmann distribution over vibrational energies evolves towards the final equilibrium state through

the series of non-equilibrium state-to-state distributions. They are formed by translation–vibration TV excitation of low levels and consecutive vibrational energy re-distribution by VV exchange

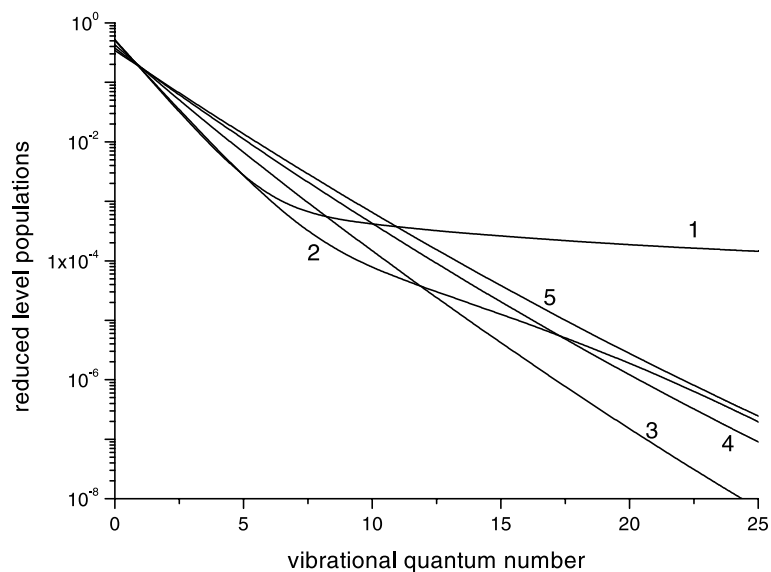


Fig. 3. Vibrational distributions  $n_i/n$  in a boundary layer at different distances  $\eta$  from the wall. (1)  $\eta = 0$ ; (2)  $\eta = 1$ ; (3)  $\eta = 2$ ; (4)  $\eta = 3$ ; (5)  $\eta = 4$ .

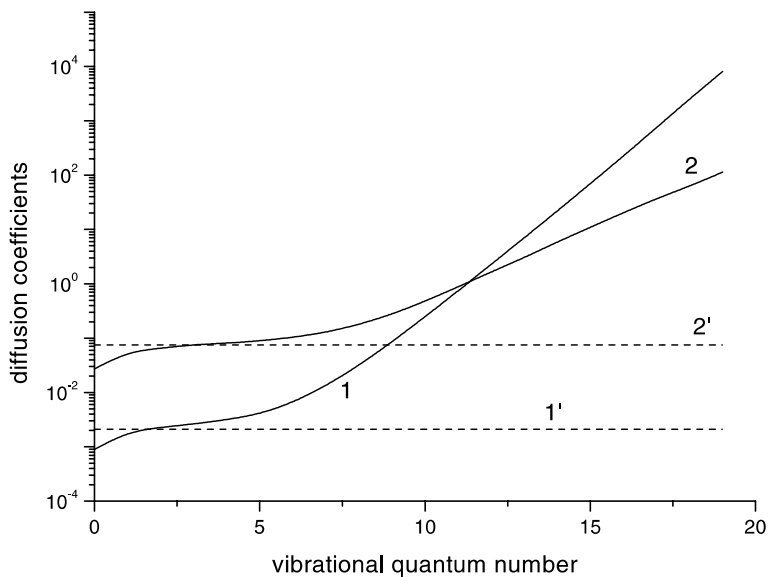


Fig. 4. Diffusion coefficients  $D_{N_2/N_2i}$ ,  $m^2/s$ , in a boundary layer at different distances  $\eta$  from the wall. Solid lines – state-to-state approach, dashed lines – coefficient  $\bar{D}$ . 1,1' –  $\eta = 0$ ; 2,2' –  $\eta = 1$ .

between vibrational states. The high levels are slightly depleted because of dissociation process. Similar shapes of the distributions behind a shock wave are found also in Refs. [2,3]. It is shown in

Refs. [2,11] that in the vicinity of the shock front the quasi-stationary Boltzmann distributions remain higher than the corresponding state-to-state ones. With distance from the shock front

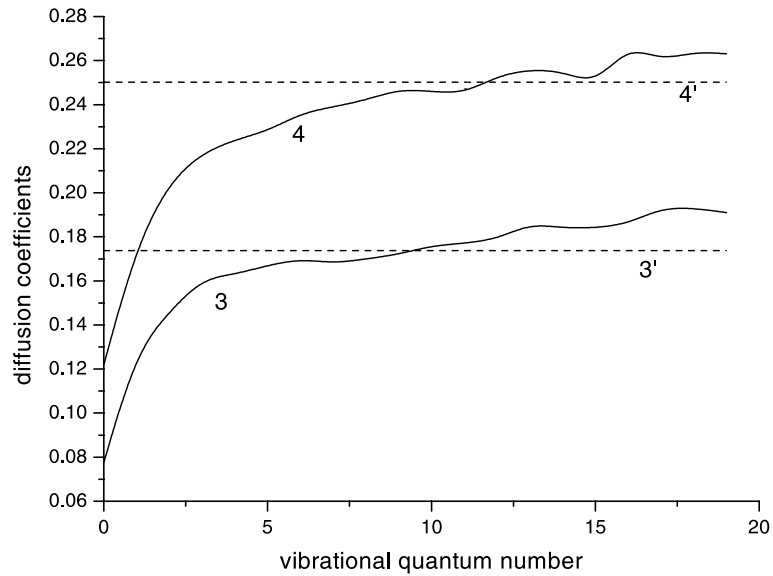


Fig. 5. Diffusion coefficients  $D_{N_2/N_2i}$ ,  $m^2/s$ , in a boundary layer at different distances  $\eta$  from the wall. Solid lines – state-to-state approach, dashed lines – coefficient  $\bar{D}$ . 3,3' –  $\eta = 2$ ; 4,4' –  $\eta = 3$ .

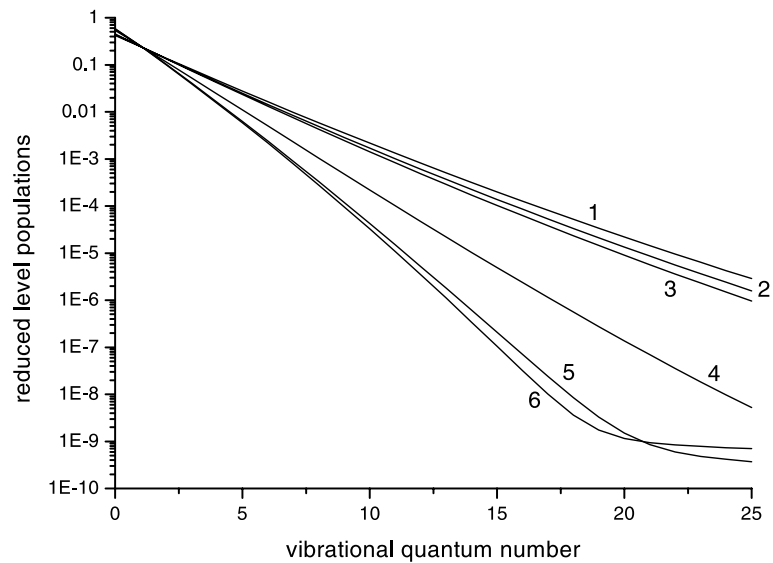


Fig. 6. Vibrational distributions  $n_i/n$  in a nozzle at different distances  $x$  from reservoir ( $x_{\text{throat}} = 0.5$  m). (1)  $x = 0$ ; (2)  $x = 0.5$  m; (3)  $x = 0.51$  m; (4)  $x = 0.55$  m; (5)  $x = 0.6$  m; (6)  $x = 2$  m.

all quasi-stationary and state-to-state distributions converge. The diffusion coefficients  $\tilde{D}_{N_2i/N_2i}$  behind the shock are presented in Fig. 2 as functions of the vibrational quantum number  $i$ . One can notice

that the coefficient  $\tilde{D}$  is significantly higher than state-to-state coefficients for low vibrational states ( $i < 5-7$ ), especially in the beginning of the relaxation zone where the quasi-stationary distributions

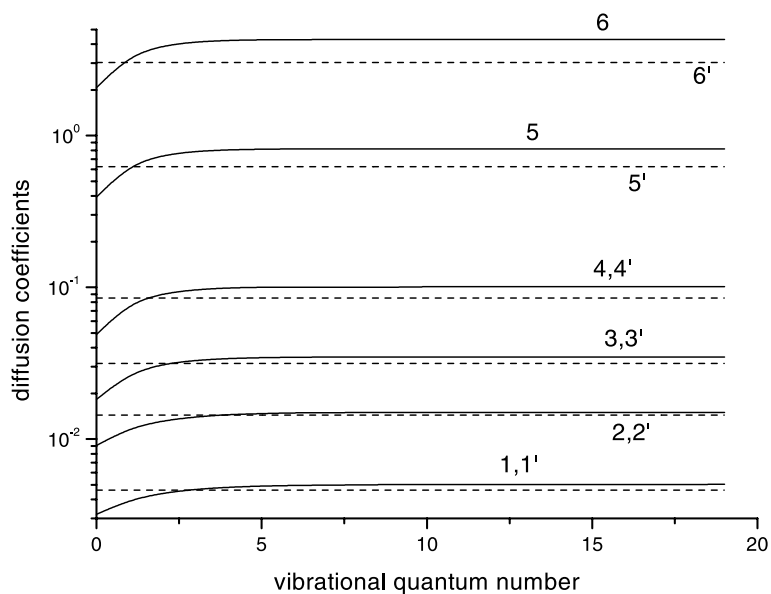


Fig. 7. Diffusion coefficients  $D_{N_2, iN_2i}$ ,  $m^2/s$ , in a nozzle at different distances  $x$  ( $x_{\text{throat}} = 0.5$  m). Solid lines – state-to-state approach, dashed lines – coefficient  $\tilde{D}$ . 1,1' –  $x = 0$ ; 2,2' –  $x = 0.5$  m; 3,3' –  $x = 0.55$  m; 4,4' –  $x = 0.6$  m; 5,5' –  $x = 0.8$  m; 6,6' –  $x = 2$  m.

do not exist. Approaching to the thermal equilibrium state this discrepancy decreases noticeably. Concerning the high levels, the difference between  $\tilde{D}_{N_2, iN_2i}$  and  $\tilde{D}$  does not exceed 10% even in the range of strong vibrational non-equilibrium. It can be connected with the fact that the shape of distributions remains close to the Boltzmann one and, therefore, high states are not populated sufficiently to give a noticeable contribution to the diffusion coefficients.

Quite different behaviour of diffusion coefficients has been found in a boundary layer, where the vibrational distributions are essentially non-Boltzmann. The mechanism of formation of these distributions is the following: dissociation in the gas flow near the high-temperature edge of the boundary layer produces nitrogen atoms which diffuse towards the cool surface. Recombination near the surface pumps the populations of the high vibrational states. As the result of this process and VV and VT exchange the strong non-equilibrium distribution with a plateau part at the intermediate and upper levels appears just near the wall (see Fig. 3). This effect has been studied in Refs. [8,9,29] and the role of recombination and VV

exchange is found to be particularly important in this flow. The non-Boltzmann character of vibrational distributions influences dramatically the diffusion coefficients: close to the surface, at  $i > 5$  the ratio  $\tilde{D}_{N_2, iN_2i}/\tilde{D}$  reaches several thousands (Fig. 4). The over-population of high states leads to very large values of corresponding diffusion coefficients.

Again, coming to equilibrium at the external edge of boundary layer, this ratio decreases, and finally the discrepancy between  $\tilde{D}_{N_2, iN_2i}$  and  $\tilde{D}$  for high levels tends to 5–10% (Fig. 5).

Another example of non-equilibrium flow is a nozzle expansion. Characteristic vibrational distributions and diffusion coefficients in the F4 nozzle [7,13] are shown in Figs. 6 and 7. In the initial part of the nozzle the distributions are close to the Boltzmann ones and then a plateau develops at the intermediate and upper levels as a result of VT deactivation, VV exchange and recombination. The region of major change of the level populations is in the beginning of the expanding part just after the throat ( $x < 0.6$  m). Then the populations (except very high levels) change weakly and approach the constant frozen values. This character of the distributions has been found in Ref. [7], in

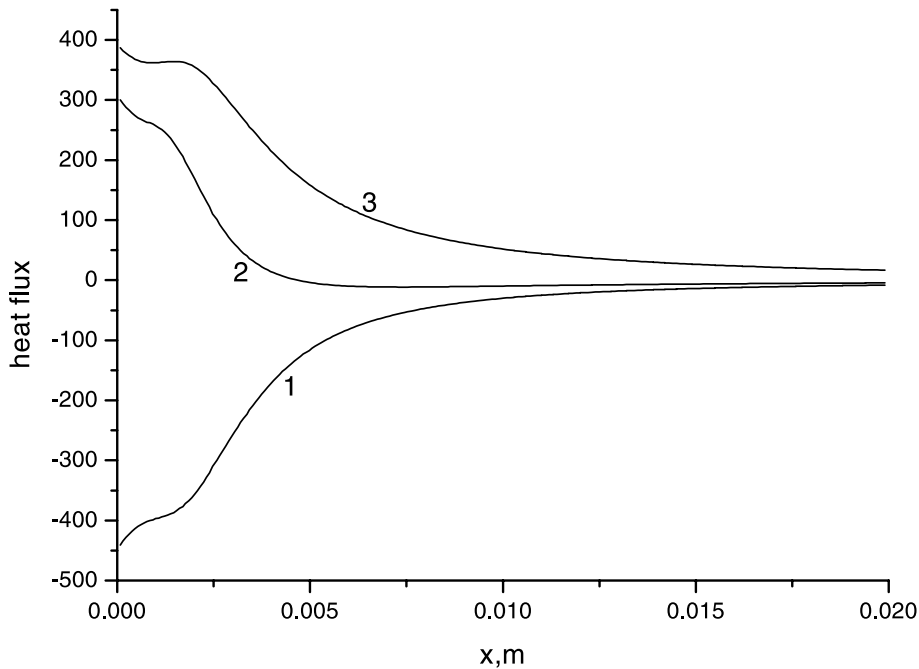


Fig. 8. Heat flux  $q$ , kW/m<sup>2</sup>, behind a shock wave as a function of  $x$  calculated using coefficients  $\tilde{D}_{N_2iN_2i}$  and  $\tilde{D}$  (curves 1 and 2). Curve 3 – flux Fourier.

this paper a comparison of the calculated distributions with the experimental ones [31] is given and a qualitative agreement is observed. In the vicinity of the throat, where the distributions have an approximately Boltzmann shape, the state dependent diffusion coefficients are not far from  $\tilde{D}$ . The difference increases with  $x$  from 5% at  $x = 0.5$  m up to 50% at  $x = 2$  m. It should be noted that for the calculation of diffusion coefficients only the lowest 20 levels have been retained. At higher levels the distributions in this kind of nozzle take more complicated form [7,13], it can change also the diffusion coefficients.

The general tendency can be formulated in the following way: average coefficient  $\tilde{D}$  overestimates state-to-state diffusion coefficients at low vibrational levels, and underestimates them for the high states. The discrepancy between these coefficients decreases significantly approaching to the thermal equilibrium conditions.

Let us consider now a qualitative behaviour of the total heat flux calculated for the flows discussed above using the state dependent and con-

stant diffusion coefficients  $\tilde{D}_{N_2iN_2i}$  and  $\tilde{D}$ . Figs. 8–10 present respectively the heat fluxes behind a shock wave, in a boundary layer, and in a nozzle. Curves denoted as “1” in these figures correspond to the results obtained with coefficients  $\tilde{D}_{N_2iN_2i}$ , “2” are calculated with the state independent coefficient  $\tilde{D}$ .

The role of diffusion in a shock heated gas flow is found to be very important [11], even the qualitative behaviour of the total energy flux and Fourier flux caused by heat conductivity ( $\mathbf{q}_F = -\lambda' \nabla T$ ) differs in the relaxation region. Curve “3” in Fig. 8 denotes the Fourier flux. Under these conditions the employment of averaged coefficients  $\tilde{D}$  gives only a very rough approximation for the heat flux. Such a discrepancy can be explained in the following way. The only positive diffusion velocity in this case is that of the ground vibrational state  $V_0$  (the population of the ground state is the only one which decreases during the relaxation process, remaining, however, much higher than the populations of other levels). Consequently, noticeable overestimation of the diffusion

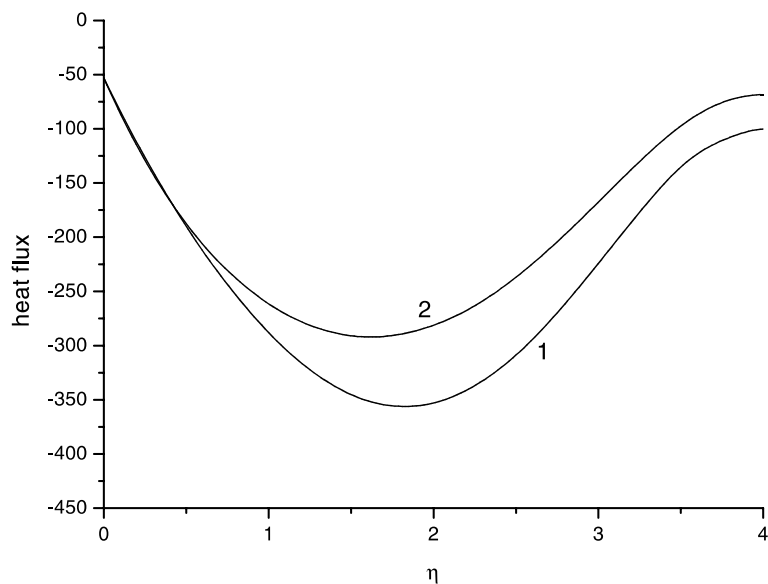


Fig. 9. Heat flux  $q$ ,  $\text{W/m}^2$ , in a boundary layer as a function of  $\eta$  calculated using coefficients  $\tilde{D}_{N_2iN_2i}$  and  $\tilde{D}$  (curves 1 and 2).

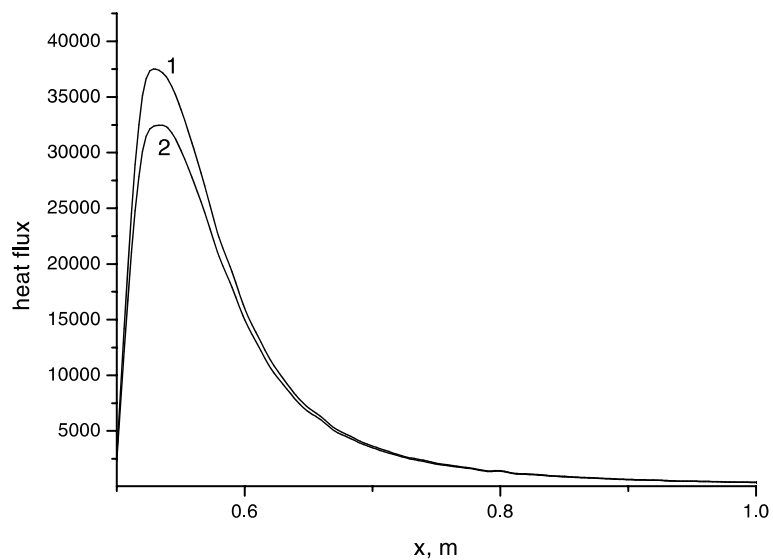


Fig. 10. Heat flux  $q$ ,  $\text{W/m}^2$ , in a nozzle as a function of  $x$  calculated using coefficients  $\tilde{D}_{N_2iN_2i}$  and  $\tilde{D}$  (curves 1 and 2).

coefficient  $\tilde{D}_{N_20N_20}$  (see Fig. 2) leads to overestimation of the  $V_0$  contribution to the heat flux. In the case of state dependent diffusion coefficients, the contribution of different levels to diffusion of vibrational energy is of the same order of magnitude, and negative diffusion velocities decrease

significantly the total energy flux compared to the previous case.

Looking at Figs. 4 and 5 one can expect a strong disagreement between the heat fluxes calculated in a boundary layer using two models for diffusion coefficients. Nevertheless, the difference

between two fluxes does not exceed 30% (see Fig. 9). The reason is that in the boundary layer with non-catalytic surface the contribution of the diffusion processes to the total energy flux is much less than in the shock heated flow, the heat transfer in this case is determined mainly by thermal conductivity. The heterogeneous reactions on the surface increase dramatically the role of diffusion [32], and in the case of catalytic wall the effect of diffusion coefficients on the heat flux should be greater.

Fig. 9 plots the heat fluxes computed in a nozzle. It is not surprisingly that the influence of state dependent diffusion coefficients on the heat flux is weak (the discrepancy is within 15% in a very narrow interval just near the throat and does not exceed 5% in other regions). This is explained by the fact that in this flow only the low vibrational levels contribute considerably to the heat transfer at  $x > 0.6$  m (the highly located states are populated very poorly). For low levels the discrepancy between  $\tilde{D}_{N_2iN_2i}$  and  $\tilde{D}$  is small, therefore, coefficient  $\tilde{D}$  gives a satisfactory description of vibrational energy diffusion in a nozzle.

One should keep in mind that the present results can be treated only as the qualitative ones because of approximations adopted for the heat flux calculation. A comparison with experimental data is necessary for the estimation of accuracy of the proposed method. Unfortunately, the lack of data on the heat transfer in the flows discussed above makes this task unattainable. Nevertheless, it can be pointed out that only state-to-state description gives an adequate shape of vibrational distributions in strongly non-equilibrium conditions. For instance, in papers [30,33,34] the experimentally measured vibrational distributions in optically pumped CO and other diatomic gases are compared with the state-to-state and quasi-stationary distributions. An excellent correlation between the state-to-state and measured distributions is observed, whereas all quasi-stationary models give a very poor agreement. This fact is a good reason to believe that the results of state-to-state simulation of the heat transfer in extremely non-equilibrium conditions will be much more accurate compared to the results obtained by means of quasi-stationary one-temperature or multi-temperature models.

## 5. Conclusions

The transport kinetic theory in the state-to-state approach is considered. The simplified algorithm for the viscosity, thermal conductivity and diffusion coefficients calculation is proposed. This algorithm reduces essentially the time of transport coefficients computation and thus encourages one to insert the obtained linear transport systems to the numerical codes for the solution of master equations.

The results concerning state specific diffusion coefficients which describe the transport of vibrational energy are presented, and the influence of non-equilibrium vibrational distributions on these coefficients is estimated. A comparison with the results obtained on the basis of the simple intuitive model is also given. This model gives a satisfactory agreement with the state-to-state approach only for weak deviations of vibrational distributions from the Boltzmann ones. Under strongly non-equilibrium conditions, state-to-state diffusion coefficients differ significantly from the average values. Using the constant diffusion coefficients instead of the state dependent ones may lead to an essential error in the values of diffusion velocities and total energy flux.

## Acknowledgements

This study is supported by INTAS (99-00464).

## Appendix A

### A.1. Definition of bracket integrals

$$[A, B] = \sum_{cldk} \frac{n_{ci}n_{dk}}{n^2} \left( [A, B]'_{cldk} + [A, B]''_{cldk} \right), \quad (\text{A.1})$$

the partial bracket integrals are introduced as follows:

$$[A, B]'_{cldk} = \frac{1}{2n_{ci}n_{dk}} \sum_{jlj'l'} \int f_{cij}^{(0)} f_{dkl}^{(0)} (B_{cij} - B_{cij'}) \times (A_{cij} - A_{cij'}) g \sigma_{cldk, jl}^{j'l'} d^2 \Omega d\mathbf{u}_c d\mathbf{u}_d,$$



$$[A, B]''_{cidk} = \frac{1}{2n_{ci}n_{dk}} \sum_{jlj'l'} \int f_{cij}^{(0)} f_{dkl}^{(0)} (B_{cij} - B_{cij'}) \times (A_{dkl} - A_{dkl'}) g \sigma_{cidk, jl}^{j'l'} d^2\Omega \mathbf{du}_c \mathbf{du}_d.$$

$\sigma_{cidk, jl}^{j'l'}$  is the cross-section of collision of two molecules  $c$  and  $d$  chemical species at  $i, k$  vibrational and  $j, l$  rotational states leading to the change of translational and rotational energy,  $d^2\Omega$  is the solid angle where the relative velocity after the collision can appear,  $\mathbf{g}$  is the relative velocity before the collision,  $j', l'$  are the rotational levels after collision.

### A.2. Bracket integrals depending on vibrational state [10]

The expressions obtained in Ref. [10] can be rearranged to the following form:

$$A_{0000}^{cici} = \gamma_{00}^{cici} = \frac{75k^2 T x_{ci}}{16} \left( \sum_b \frac{x_b}{A_{cb}^* \lambda_{cb}} - \frac{x_{ci}}{A_{cc}^* \lambda_{cc}} \right), \quad (\text{A.2})$$

$$A_{0000}^{cidk} = \gamma_{00}^{cidk} = -\frac{75k^2 T}{16} \frac{x_{ci} x_{dk}}{A_{cd}^* \lambda_{cd}}, \quad c \neq d \text{ or } i \neq k, \quad (\text{A.3})$$

$$A_{1000}^{cici} = -\frac{75k^2 T x_{ci}}{32} \left( \sum_b \frac{x_b}{A_{cb}^* \lambda_{cb}} \frac{m_b (6C_{cb}^* - 5)}{m_c + m_b} - \frac{x_{ci} (6C_{cc}^* - 5)}{2A_{cc}^* \lambda_{cc}} \right), \quad (\text{A.4})$$

$$A_{1000}^{cidk} = \frac{75k^2 T}{32} \frac{x_{ci} x_{dk}}{A_{cd}^* \lambda_{cd}} \frac{m_c}{m_c + m_d} (6C_{cd}^* - 5), \quad c \neq d \text{ or } i \neq k, \quad (\text{A.5})$$

$$A_{1100}^{cici} = \frac{75k^2 T x_{ci}}{16} \left( \frac{x_{ci}}{4A_{cc}^* \lambda_{cc}} \left( 4A_{cc}^* - \frac{55}{4} + 3B_{cc}^* \right) + \sum_b \frac{x_b}{A_{cb}^* \lambda_{cb}} \times \frac{\frac{15}{2} m_c^2 + \frac{25}{4} m_b^2 - 3m_b^2 B_{cb}^* + 4m_c m_b A_{cb}^*}{(m_c + m_b)^2} \right), \quad (\text{A.7})$$

$$A_{1100}^{cidk} = -\frac{75k^2 T}{16} \frac{x_{ci} x_{dk}}{A_{cd}^* \lambda_{cd}} \frac{m_c m_d}{(m_c + m_d)^2} \times \left( \frac{55}{4} - 3B_{cd}^* - 4A_{cd}^* \right), \quad c \neq d \text{ or } i \neq k, \quad (\text{A.8})$$

$$A_{0011}^{cici} = \frac{75k^2 T x_{ci}}{16} c_{\text{rot}, ci} \sum_b \frac{x_b}{A_{cb}^* \lambda_{cb}}, \quad (\text{A.9})$$

$$A_{0011}^{cidk} = 0, \quad c \neq d \text{ or } i \neq k, \quad (\text{A.10})$$

$$H_{00}^{cici} = x_{ci} \left( \sum_b \frac{2x_b}{\mu_{cb}} \frac{m_c m_b}{(m_c + m_b)^2} \left( \frac{5}{3A_{cb}^*} + \frac{m_b}{m_c} \right) - \frac{x_{ci}}{2\mu_{cc}} \left( \frac{5}{3A_{cc}^*} - 1 \right) \right), \quad (\text{A.11})$$

$$H_{00}^{cidk} = -\frac{2x_{ci} x_{dk}}{\mu_{cd}} \frac{m_c m_d}{(m_c + m_d)^2} \left( \frac{5}{3A_{cd}^*} - 1 \right), \quad c \neq d \text{ or } i \neq k, \quad (\text{A.12})$$

where  $x_{ci} = n_{ci}/n$  is the molar fraction of  $c$  species at the vibrational state  $i$ ,

$$\lambda_{cd} = \frac{75k}{128m_{cd}} \frac{(2\pi m_{cd} kT)^{1/2}}{\pi \bar{\sigma}_{cd}^2 \Omega_{cd}^{(2,2)*}},$$

$$\mu_{cd} = \frac{5}{16} \frac{(2\pi m_{cd} kT)^{1/2}}{\pi \bar{\sigma}_{cd}^2 \Omega_{cd}^{(2,2)*}}$$

are the fictitious thermal conductivity and viscosity coefficients. Functions  $A_{cd}^*$ ,  $B_{cd}^*$ ,  $C_{cd}^*$  are defined in Refs. [21–23]:

$$A_{cd}^* = \frac{\Omega_{cd}^{(2,2)*}}{\Omega_{cd}^{(1,1)*}}, \quad B_{cd}^* = \frac{5\Omega_{cd}^{(1,2)*} - 4\Omega_{cd}^{(1,3)*}}{\Omega_{cd}^{(1,1)*}},$$

$$C_{cd}^* = \frac{\Omega_{cd}^{(1,2)*}}{\Omega_{cd}^{(1,1)*}}.$$

$\Omega_{cd}^{(l,r)*}$  integrals can be computed using the data from [24].

## A.3. Classical bracket integrals [22]

$$A_{0000}^{cc} = \gamma_{00}^{cc} = \frac{75k^2T}{16} \sum_{b \neq c} \frac{x_c x_b}{A_{cb}^* \lambda_{cb}}, \quad (\text{A.13})$$

$$A_{0000}^{cd} = \gamma_{00}^{cd} = -\frac{75k^2T}{16} \frac{x_c x_d}{A_{cd}^* \lambda_{cd}}, \quad c \neq d, \quad (\text{A.14})$$

$$A_{1000}^{cc} = -\frac{75k^2T}{32} \sum_{b \neq c} \frac{x_c x_b}{A_{cb}^* \lambda_{cb}} \frac{m_b}{m_c + m_b} (6C_{cb}^* - 5), \quad (\text{A.15})$$

$$A_{1000}^{cd} = \frac{75k^2T}{32} \frac{x_c x_d}{A_{cd}^* \lambda_{cd}} \frac{m_c}{m_c + m_d} (6C_{cd}^* - 5), \quad c \neq d, \quad (\text{A.16})$$

$$A_{1100}^{cc} = \frac{75k^2T}{8} \left( \frac{x_c^2}{\lambda_{cc}} + \sum_{b \neq c} \frac{x_c x_b}{2A_{cb}^* \lambda_{cb}} \times \frac{\frac{15}{2}m_c^2 + \frac{25}{4}m_b^2 - 3m_b^2 B_{cb}^* + 4m_c m_b A_{cb}^*}{(m_c + m_b)^2} \right), \quad (\text{A.17})$$

$$A_{1100}^{cd} = -\frac{75k^2T}{16} \frac{x_c x_d}{A_{cd}^* \lambda_{cd}} \frac{m_c m_d}{(m_c + m_d)^2} \times \left( \frac{55}{4} - 3B_{cd}^* - 4A_{cd}^* \right), \quad c \neq d, \quad (\text{A.18})$$

$$A_{0011}^{cc} = \frac{75k^2T}{16} c_{\text{rot},c} \left( \frac{x_c^2}{A_{cc}^* \lambda_{cc}} + \sum_{b \neq c} \frac{x_c x_b}{A_{cb}^* \lambda_{cb}} \right), \quad (\text{A.19})$$

$$A_{0011}^{cd} = 0, \quad c \neq d, \quad (\text{A.20})$$

$$H_{00}^{cc} = \frac{x_c^2}{\mu_{cc}} + \sum_{b \neq c} \frac{2x_c x_b}{\mu_{cb}} \frac{m_c m_b}{(m_c + m_b)^2} \left( \frac{5}{3A_{cb}^*} + \frac{m_b}{m_c} \right), \quad (\text{A.21})$$

$$H_{00}^{cd} = -\frac{2x_c x_d}{\mu_{cd}} \frac{m_c m_d}{(m_c + m_d)^2} \left( \frac{5}{3A_{cd}^*} - 1 \right), \quad c \neq d, \quad (\text{A.22})$$

$$x_c = \sum_i n_{ci} / n = n_c / n.$$

## References

- [1] E. Nagnibeda, The structure of the relaxation zone behind shock waves in the reacting gas flows, in: J. Hunt (Ed.), *Aerothermodynamics for Space Vehicles*, ESA Publication Division, ESTEC, Noordwijk, The Netherlands, 1995.
- [2] F. Lordet, J. Meolans, A. Chauvin, R. Brun, Nonequilibrium vibration dissociation phenomena behind a propagating Shock Waves 4 (1995) 299.
- [3] I. Adamovich, S. Macheret, J. Rich, C. Treanor, *AIAA J.* 33 (6) (1995) 1064.
- [4] S. Ruffin, C. Park, Vibrational relaxation of anharmonic oscillators in expanding flows, *AIAA paper* 92-0806.
- [5] A. Chiroux de Gavelle de Roany, C. Flament, J.W. Rich, V.V. Subramaniam, W.R. Warren Jr., *AIAA J.* 31 (1) (1993) 119.
- [6] B. Shizgal, F. Lordet, *J. Chem. Phys.* 104 (10) (1996) 3579.
- [7] G. Colonna, M. Tuttafesta, M. Capitelli, D. Giordano, Influence of dissociation rates on the state-to-state vibrational kinetics in nozzle expansions, *Rarefied Gas Dynamics* 21, vol. 2, CEPADUES, Toulouse, France, 1999, p. 281.
- [8] I. Armenise, M. Capitelli, G. Colonna, C. Gorse, *J. Thermophys. Heat Transfer* 10 (3) (1996) 397.
- [9] M. Capitelli, I. Armenise, C. Gorse, *J. Thermophys. Heat Transfer* 11 (4) (1997) 570.
- [10] E. Kustova, E. Nagnibeda, *Chem. Phys.* 233 (1998) 57.
- [11] E. Kustova, E. Nagnibeda, State-to-state approach in the transport kinetic theory, *Rarefied Gas Dynamics* 21, vol. 1, CEPADUES, Toulouse, France, 1999, p. 231.
- [12] I. Armenise, M. Capitelli, E. Kustova, E. Nagnibeda, *J. Thermophys. Heat Transfer* 13 (2) (1999) 210.
- [13] M. Capitelli, G. Colonna, D. Giordano, E. Kustova, E. Nagnibeda, M. Tuttafesta, D. Bruno, *Mathematical Modelling* 11 (3) (1999) 45.
- [14] D. Bruno, M. Capitelli, E. Kustova, E. Nagnibeda, *Chem. Phys. Lett.* 308 (1999) 463.
- [15] Y. Stupochenko, S. Losev, A. Osipov, *Relaxation in Shock Waves*, Springer, Berlin, 1967.
- [16] A. Chikhaoui, J. Dudon, E. Kustova, E. Nagnibeda, *J. Physica A* 247 (1–4) (1997) 526.
- [17] L. Monchick, A. Pereira, E. Mason, *J. Chem. Phys.* 42 (1965) 3241.
- [18] E. Kustova, E. Nagnibeda, *Chem. Phys.* 208 (3) (1996) 313.
- [19] S. Kang, J. Kunc, *J. Phys. Chem.* 95 (1991) 6971.
- [20] S. Chapman, T. Cowling, *The Mathematical Theory of Non-uniform Gases*, Cambridge University Press, Cambridge, 1970.
- [21] J. Hirschfelder, C. Curtiss, R. Bird, *The Molecular Theory of Gases and Liquids*, Wiley, New York, 1954.
- [22] J. Ferziger, H. Kaper, *Mathematical Theory of Transport Processes in Gases*, North-Holland, Amsterdam, London, 1972.
- [23] A. Ern, V. Giovangigli, *Multicomponent Transport Algorithms*, Lecture Notes in Physics, Series monographs, M24, 1994.
- [24] M. Capitelli, C. Gorse, S. Longo, D. Giordano, Transport properties of high temperature air species, *AIAA Paper*

- 98-2936, 7th AIAA/ASME Joint Thermophysics and Heat Transfer Conference.
- [25] E. Kustova, F. Mallinger, Level kinetics approach in the case of strong vibrational nonequilibrium for a pure diatomic gas, Research Report No. 3557, INRIA, Rocquencourt, December 1998.
- [26] Y. Gershenzon, V. Rozenshtein, S. Umanskii, *Doklady Akademii Nauk SSSR* 223 (3) (1975) 629.
- [27] L. Monchick, K. Yun, E. Mason, *J. Chem. Phys.* 39 (1963) 654.
- [28] R. Kee, G. Dixon-Lewis, J. Warnatz, M. Coltrin, J. Miller, A Fortran computer code package for the evaluation of gas-phase multicomponent transport properties, SAND86-8246, SANDIA National Laboratories Report, 1986.
- [29] V. Doroshenko, N. Kudryavtsev, S. Novikov, V. Smetnin, *High Temperature* 28 (1990) 82.
- [30] E. Plönjes, P. Palm, A. Chernukho, I. Adamovich, J. Rich, *Chem. Phys.* 256 (2000) 315.
- [31] S. Sharma, S. Ruffin, W. Gillespie, S. Meyer, J. Thermophys. Heat Transfer 7 (4) (1993) 697.
- [32] I. Armenise, M. Cacciatore, M. Capitelli, E. Kustova, E. Nagnibeda, M. Rutigliano, The influence of nonequilibrium vibrational and dissociation-recombination kinetics on the heat transfer and diffusion in the boundary layer under reentry conditions, *Rarefield Gas Dynamics* 21, vol. 2, CEPADUES, Toulouse, France, 1999.
- [33] R. Deleon, J. Rich, *Chem. Phys.* 107 (1986) 283.
- [34] E. Plönjes, P. Palm, W. Lee, M. Chidley, I. Adamovich, W. Lempert, J. Rich, *Chem. Phys.* 260 (2000) 353.