Transport properties of a reacting gas mixture with strong vibrational and chemical nonequilibrium

E.V. Kustova, E.A. Nagnibeda

St. Petersburg University, Math. and Mech. Dept., 198904 St. Petersburg, Petrodvorets, Russia

Abstract

Transport properties of multi-component reacting gas mixtures are studied on the basis of the kinetic theory in the case of strong vibrational and chemical nonequilibrium. Considered are the conditions when quasi-stationary distributions of the molecules over vibrational levels do not exist and level kinetic approach is developed. The formulas for the viscosity, diffusion and thermal conductivity coefficients in terms of the nonequilibrium level populations, gas temperature and elastic collision integrals are derived. The practical algorithm for the calculation of these coefficients is given and applied for the investigation of the heat transfer behind a plane shock wave. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The theoretical models of transport processes of reacting gas mixtures are needed for the prediction of flow-field parameters near space crafts, in nozzles, in high enthalpy facilities and in other problems of aerothermochemistry and nonequilibrium gas dynamics. In particular the influence of chemical-vibrational nonequilibrium on heat transfer is very important in high temperature and high enthalpy flows.

The transport kinetic theory of reacting flows is based on the asymptotic solution of the generalized Boltzmann equations. The most commonly used are the one-temperature and multi-temperature approaches which are based on the quasi-stationary distributions of molecules over vibrational levels: the equilibrium Boltzmann distribution in the first case and the nonequilibrium multi-temperature distribution in the latter case. But there exist the conditions when the quasi-stationary distributions over vibrational energy are not valid due to the strong vibrational-chemical coupling. Actually the experimental data concerning the relaxation times of different processes in reacting mixtures [1] show that in many cases of practical interest the following relation between the relaxation times is valid:

$$\tau_{el} < \tau_{r} \ll \tau_{vibr} < \tau_{react} \sim \theta, \tag{1}$$

where τ_{el}, τ_{r}, τ_{vibr}, τ_{react} are the mean times between the collisions with the translational, rotational and vibrational energy transfer and those with chemical reactions, θ is the macroscopic time. Translational energy

distribution is known to equilibrate fast and the rotational relaxation time is of the same order as the translational one and much smaller in comparison to the vibrational and chemical relaxation time. Therefore processes of translational and rotational relaxation may be considered as rapid processes and on the contrary vibrational and chemical relaxation as the slow ones. The mean time of slow processes is comparable with the macroscopic time and these processes are strongly nonequilibrium. The condition given in (1) provides the so-called level approach in nonequilibrium gas dynamics which describes the simultaneous processes of the vibrational and chemical relaxation. In this case the macroscopic conservation equations for mass, momentum and total energy should be considered together with the equations for level populations of different chemical species. This model is important for the study of vibrational-chemical coupling in the boundary layer, in the short relaxation zone behind a shock wave where steady-state vibrational distributions do not establish. Level approach can give the limits of the validity of the multi-temperature and one-temperature models.

In the recent years the level approach was used by several researches in a study of vibrational-chemical coupling behind a shock wave [2–7], in expanding flows and nozzles [8,9], in a nonequilibrium boundary layer near re-entering bodies [10–12] and in a shock layer [13]. The brief review and bibliography of the papers concerning the vibrational relaxation coupled to reactive processes in flowing systems is given in Ref. [8]. These investigations were performed in the frame of the master equations for vibrational level populations in different flows and the influence of vibrational-chemical coupling on level populations was examined. In these codes the effect of vibrational-chemical nonequilibrium on transport coefficients was neglected: either non-viscous flows were considered or very simple models for the transport coefficients were used.

The present paper deals with the study of transport properties of a reacting mixture in the level approach and the influence of vibrational-chemical coupling on the transport properties is considered. Previously this approach was developed by us in the case of pure vibrationally excited gas [14,15], in the case of two-component mixture consisted of atoms and dissociating molecules [6] and was applied to the flow behind a shock wave [6]. In the present paper the transport kinetic theory of multi-component reacting mixtures is developed under the condition (1). Heat transfer and diffusion are studied in the case of strong vibrational and chemical nonequilibrium. The practical algorithms for the calculation of the heat conductivity, viscosity and all diffusion coefficients are given. The results of the calculation of the gas temperature and total heat flux in the relaxation zone behind a plane shock wave are shown.

2. Zero order distribution functions

We consider a multi-component reacting gas mixture with rapid and slow processes. The kinetic equations for distribution functions $f_{cij}(\boldsymbol{r}, \boldsymbol{u}_c, t)$ for every chemical species c, vibrational i and rotational energy level j over the velocities $\boldsymbol{u}_c$, the spatial and temporal co-ordinates have a form [16]:

$$\frac{\partial f_{cij}}{\partial t} + \boldsymbol{u}_c \frac{\partial f_{cij}}{\partial \boldsymbol{r}} = \frac{1}{\varepsilon} J_{cij}^{\text{rap}} + J_{cij}^{\text{sl}}. \tag{2}$$

Here J_{cij}^{rap}, J_{cij}^{sl} are the collision operators of rapid and slow processes, $\varepsilon = \tau_{\text{rap}} / \tau_{\text{sl}}$ is the small parameter, τ_{rap}, τ_{sl} are the average times between the frequent and rare collisions respectively. The condition (1) provides the following form of the collision operators in (2):

$$J_{cij}^{\text{rap}} = J_{cij}^{\text{el}} + J_{cij}^{\text{r}}, \quad J_{cij}^{\text{sl}} = J_{cij}^{\text{vibr}} + J_{cij}^{\text{react}},$$

where collision integrals J_{cij}^{el}, J_{cij}^{r}, J_{cij}^{vibr}, J_{cij}^{react} correspond to the elastic collisions and those including rotational, vibrational energy transfers and chemical reactions respectively. The collision integral J_{cij}^{vibr} describes the exchange of vibrational energy within every mode and between different modes and also the vibrational-ro-

tational-translational energy exchange. The collision integral J_{cij}^{react} describes the binary collisions with chemical exchange reactions and collisions with dissociation and recombination. The expressions for all collision integrals can be found in Refs. [16–20]

For the solution of Eq. (2) the Chapman-Enskog method generalized for reacting mixtures with rapid and slow processes is used [16,20]. The distribution functions $f_{cij}(\mathbf{r},\mathbf{u}_c,t)$ are expanded in a power series of the parameter ε ($\varepsilon \ll 1$). The peculiarity of this expansion is that the zero order distribution functions are already nonequilibrium. Actually, the equations for the zero order distribution functions $f_{cij}^{(0)}$ contain only the integral operator of rapid processes and have the following form:

$$J_{cij}^{\text{el}}\left(f^{(0)},f^{(0)}\right) + J_{cij}^{\text{r}}\left(f^{(0)},f^{(0)}\right) = 0. \tag{3}$$

The solution of these equations is obtained in Refs. [16,20]. For molecular species it is given by

$$f_{cij}^{(0)} = \left(\frac{m_c}{2\pi kT}\right)^{3/2} s_j^{ci} \frac{n_{ci}}{Z_{ci}^{\text{rot}}(T)} \exp\left(-\frac{m_c c_c^2}{2kT} - \frac{\varepsilon_j^{ci}}{kT}\right). \tag{4}$$

and for atomic species

$$f_c^{(0)} = \left(\frac{m_c}{2\pi kT}\right)^{3/2} n_c \exp\left(-\frac{m_c c_c^2}{2kT}\right). \tag{5}$$

Here m_c is the molecular mass, s_j^{ci} is the statistical weight, n_{ci} is the number density of the molecules of c species at the ith vibrational level, n_c is the number density of chemical species, k is the Boltzmann constant, $\mathbf{c}_c = \mathbf{u}_c - \mathbf{v}$, $\mathbf{v}$ is the macroscopic gas velocity, T is the gas temperature, Z_{ci}^{rot} is the rotational partition function.

The distribution functions (4), (5) describe the equilibrium Maxwell-Boltzmann distribution over velocities and rotational energy and nonequilibrium distribution over vibrational energy and chemical species.

The distribution functions Eq. (4) are defined in terms of the macroscopic parameters $n_{ci}(\mathbf{r},t)$, $\mathbf{v}(\mathbf{r},t)$, $T(\mathbf{r},t)$ and are normalized in such a form:

$$\sum_j \int f_{cij}\,\mathrm{d}\mathbf{u}_c = \sum_j \int f_{cij}^{(0)}\,\mathrm{d}\mathbf{u}_c = n_{ci}, \quad c = 1,2,\dots,L, i = 0,1,\dots L_c,$$

$$\sum_{cij} m_c \int \mathbf{u}_c f_{cij}\,\mathrm{d}\mathbf{u}_c = \sum_{cij} m_c \int \mathbf{u}_c f_{cij}^{(0)}\,\mathrm{d}\mathbf{u}_c = \rho\mathbf{v}, \tag{6}$$

$$\sum_{cij} \int \left(\frac{m_c c_c^2}{2} + \varepsilon_i^c + \varepsilon_j^{ci} + \varepsilon^c\right) f_{cij}\,\mathrm{d}\mathbf{u}_c = \sum_{cij} \int \left(\frac{m_c c_c^2}{2} + \varepsilon_i^c + \varepsilon_j^{ci} + \varepsilon^c\right) f_{cij}^{(0)}\,\mathrm{d}\mathbf{u}_c$$

$$= \tfrac{3}{2}nkT + \rho E_{\text{r}} + \rho E_v + \rho E_f.$$

Here $n = \sum_{ci} n_{ci}$ is the total number of particles, $\rho = \sum_{cc}\sum_i n_{ci}$ is the gas density, L is the number of chemical species, L_c is the number of excited vibrational levels of species c, ε_i^c is the vibrational energy of a molecule of species c, counted from the minimum of its potential curve, $\varepsilon^c = -D_c$, D_c is the energy of dissociation of molecular species c,

$$\rho E_{\text{r}}(T) = \sum_{cij} \int \varepsilon_j^{ci} f_{cij}\,\mathrm{d}\mathbf{u}_c, \quad \rho E_v = \sum_{ci} \varepsilon_i^c n_{ci}, \quad \rho E_f = \sum_c \varepsilon^c n_c,$$

$n_c = \sum_i n_{ci}$, E_{r} and E_v are, respectively, the rotational and vibrational energy per unit mass.

3. The macroscopic equations

The closed system of macroscopic equations for n_{ci}, $\boldsymbol{v}$, T follows from the kinetic equation (2) and contains the equations of nonequilibrium kinetics and conservation equations of the momentum and total energy. The equations for level populations are obtained after integration of Eq. (2) over velocities and summation over rotational levels. Finally we derive:

$$\frac{\mathrm{d} n_{ci}}{\mathrm{d} t} + n_{ci}\nabla \cdot \boldsymbol{v} + \nabla \cdot (n_{ci}\boldsymbol{V}_{ci}) = R_{ci}, \quad c = 1,..,L, \; i = 0,1,\ldots, L_c, \tag{7}$$

$$\rho \frac{\mathrm{d}\boldsymbol{v}}{dt} + \nabla \cdot \mathbf{P} = 0, \tag{8}$$

$$\rho \frac{\mathrm{d}U}{\mathrm{d}t} + \nabla \cdot \boldsymbol{q} + \mathbf{P}{:}\nabla\boldsymbol{v} = 0. \tag{9}$$

Here U is the total energy per unit mass:

$$\rho U = \tfrac{3}{2} nkT + \rho E_{\mathrm{r}} + \rho E_v + \rho E_f.$$

Eqs. (7) contain the production terms

$$R_{ci} = \sum_j \int J^{\mathrm{sl}}_{cij} \, \mathrm{d}\boldsymbol{u}_c = R^{\mathrm{vibr}}_{ci} + R^{\mathrm{react}}_{ci}, \tag{10}$$

and the diffusion velocity $\boldsymbol{V}_{ci}$ of c chemical species at the ith vibrational level:

$$n_{ci}\boldsymbol{V}_{ci} = \sum_j \int \boldsymbol{c}_c f_{cij} \, \mathrm{d}\boldsymbol{u}_c. \tag{11}$$

$\mathbf{P}$ is the tensor of pressure:

$$\mathbf{P} = \sum_{cij} \int m_c \boldsymbol{c}_c \boldsymbol{c}_c f_{cij} \, \mathrm{d}\boldsymbol{u}_c, \tag{12}$$

$\boldsymbol{q}$ is the heat flux:

$$\boldsymbol{q} = \sum_{cij} \int \left(\frac{m_c c_c^2}{2} + \varepsilon_j^{ci} + \varepsilon_i^c + \varepsilon^c \right) \boldsymbol{c}_c f_{cij} \, \mathrm{d}\boldsymbol{u}_c. \tag{13}$$

In the zero approximation $\boldsymbol{q}^{(0)} = 0$, $\boldsymbol{V}_{ci}^{(0)} = 0$, $\mathbf{P}^{(0)} = p\mathbf{I}$, $\mathbf{I}$ is the unit tensor, p is the pressure,

$$R_{ci}^{(0)} = \sum_j \int J^{\mathrm{sl}(0)}_{cij} \, \mathrm{d}\boldsymbol{u}_c,$$

$J^{\mathrm{sl}(0)}_{cij}$ corresponds to the collision operator of slow processes after the substitution of the zero order distribution function $f_{cij}^{(0)}$.

The expressions for R^{vibr}_{ci} and R^{react}_{ci} are given in Refs. [16,21] in the zero and the first order approximation. In the zero order approximation $R_{ci}^{(0)}$ contain the microscopical rate constants of vibrational transitions, dissociation from each vibrational level and recombination on each vibrational level and also the microscopical rate constants of exchange reactions depending on vibrational levels of molecules before and after collision. In the first order approximation the expressions for the rate constants take into account weak deviations from the Maxwell-Boltzmann distribution over translational-rotational energy and contain the terms proportional to $\nabla \cdot \boldsymbol{v}$.

Eqs. (7)–(9) describe the flow of a multi-component reacting gas mixture in the case of strong vibrational and chemical nonequilibrium.

4. First order distribution functions and transport terms

Now we consider the linear integral equations for the first order distribution functions $f_{cij}^{(1)} = f_{cij}^{(0)}\phi_{cij}$ which follow from Eq. (2):

$$-\sum_{dk} n_{ci}n_{dk} I_{cijdk}(\phi) = \frac{\mathrm{d}f_{cij}^{(0)}}{\mathrm{d}t} - J_{cij}^{\mathrm{sl}(0)}. \tag{14}$$

Here I_{cijdk} is the linearized operator of rapid processes:

$$I_{cijdk}(\phi) = \frac{1}{n_{ci}n_{dk}} \sum_{lj'l'} \int f_{cij}^{(0)} f_{dkl}^{(0)} (\phi_{cij} + \phi_{dkl} - \phi_{cij'} - \phi_{dkl'}) g\,\sigma_{cidk,jl}^{j'l'}\,\mathrm{d}^2\Omega\,\mathrm{d}u_d. \tag{15}$$

Here $\sigma_{cidk,jl}^{j'l'}$ is the cross section of the collision of two molecules c and d chemical species at the ith and kth vibrational and jth and lth rotational levels leading to the change of translational and rotational energy, $\mathrm{d}^2\Omega$ is the solid angle where the relative velocity after the collision can appear, g is the relative velocity before the collision, j', l' are the rotational levels after the collision. This integral operator describes the elastic collisions if $j = j'$, $l = l'$.

The expression for $\mathrm{d}f_{cij}^{(0)}/\mathrm{d}t$ in Eq. (14) is obtained using Eq. (4):

$$\frac{\mathrm{d}f_{cij}^{(0)}}{\mathrm{d}t} = f_{cij}^{(0)}\left\{ \left(\frac{m_c c_c^2}{2kT} - \frac{5}{2} + \left[\frac{\varepsilon_j^{ci}}{kT}\right]_{\mathrm{r}}'\right) c_c \cdot \nabla \ln T + \frac{n}{n_{ci}} c_c \cdot d_{ci} + \frac{m_c}{kT}\left(c_c c_c - \tfrac{1}{3}c_c^2 \mathbf{I}\right){:}\nabla v \right.$$
$$+ \left(\frac{m_c c_c^2}{3kT} - 1 - \frac{p}{\rho T(c_{\mathrm{tr}} + c_{\mathrm{rot}})}\left(\frac{m_c c_c^2}{2kT} - \frac{3}{2} + \left[\frac{\varepsilon_j^{ci}}{kT}\right]_{\mathrm{r}}'\right)\right)\nabla \cdot v + \frac{R_{ci}^{(0)}}{n_{ci}}$$
$$\left. - \frac{\sum\limits_{ci} R_{ci}^{(0)}\left(\tfrac{3}{2}kT + \langle\varepsilon_j^{ci}\rangle_{\mathrm{r}} + \varepsilon_i^c + \varepsilon^c\right)}{\rho T(c_{\mathrm{tr}} + c_{\mathrm{rot}})}\left(\frac{m_c c_c^2}{2kT} - \frac{3}{2} + \left[\frac{\varepsilon_j^{ci}}{kT}\right]_{\mathrm{r}}'\right)\right\}. \tag{16}$$

Here d_{ci} are the diffusion driving forces for each chemical and vibrational species:

$$d_{ci} = \nabla\left(\frac{n_{ci}}{n}\right) + \left(\frac{n_{ci}}{n} - \frac{\rho_{ci}}{\rho}\right)\nabla \ln p, \tag{17}$$

$\rho_c = m_c\sum_i n_{ci}$, $n_{ci} = n_c$ for atomic species. c_{tr} and c_{rot} denote the translational and rotational specific heats at constant volume:

$$c_{\mathrm{tr}} = \frac{3k}{2}\frac{n}{\rho}, \quad c_{\mathrm{rot}} = \frac{\partial E_{\mathrm{r}}}{\partial T}.$$

In Eq. (16) the notation $[\zeta_{ij}]_{\mathrm{r}}' = \zeta_{ij} - \langle\zeta_{ij}\rangle_{\mathrm{r}}$ is introduced, $\langle\zeta_{ij}\rangle_{\mathrm{r}}$ is the averaged value of ζ_{ij} over a rotational spectrum:

$$\langle\zeta_{ij}\rangle_{\mathrm{r}} = \frac{\sum\limits_{j} s_j^{ci}\zeta_{ij}\exp\left(-\varepsilon_j^{ci}/kT\right)}{\sum\limits_{j} s_j^{ci}\exp\left(-\varepsilon_j^{ci}/kT\right)}.$$

Taking into account Eq. (16) the solution of Eq. (14) may be found under the form:

$$f_{cij}^{(1)} = f_{cij}^{(0)}\left(-\frac{1}{n}A_{cij} \cdot \nabla \ln T - \frac{1}{n}\sum_{dk} D_{cij}^{dk} \cdot d_{dk} - \frac{1}{n}\mathbf{B}_{cij}{:}\nabla v - \frac{1}{n}F_{cij}\nabla \cdot v - \frac{1}{n}G_{cij}\right). \tag{18}$$

The distribution functions $f_{cij}^{(1)}$ contain the gradients of vibrational level populations of all molecular species n_{ci} and number densities of atoms through the diffusion driving forces. The scalar term G_{cij} is connected with slow processes: nonequilibrium chemical reactions and vibrational relaxation.

Equations for the functions A_{cij}, B_{cij}, D_{cij}^{dk}, F_{cij} and G_{cij} follow from Eq. (14) after substituting Eq. (18) into Eq. (14) and identifying the coefficients at the gradients of the same macroscopic parameters. Finally we obtain the linear integral equations for the functions A_{cij}, B_{cij}, D_{cij}^{dk}, F_{cij} and G_{cij} ($c = 1, \ldots, L$, $i = 0,1, \ldots, L_c$, $j = 0,1,\ldots$):

$$\sum_{dk} \frac{n_{ci} n_{dk}}{n^2} I_{cijdk}(A) = \frac{1}{n} f_{cij}^{(0)} \left(\frac{m_c c_c^2}{2kT} - \frac{5}{2} + \left[\frac{\varepsilon_j^{ci}}{kT} \right]_r' \right) c_c, \tag{19}$$

$$\sum_{dk} \frac{n_{ci} n_{dk}}{n^2} I_{cijdk}(D^{bn}) = \frac{1}{n_{ci}} f_{cij}^{(0)} \left(\delta_{cb} \delta_{in} - \frac{\rho_{ci}}{\rho} \right) c_c, \quad b = 1, \ldots, L, \; n = 0,1, \ldots, L_c, \tag{20}$$

$$\sum_{dk} \frac{n_{ci} n_{dk}}{n^2} I_{cijdk}(\mathbf{B}) = \frac{m_c}{nkT} f_{cij}^{(0)} \left(c_c c_c - \tfrac{1}{3} c_c^2 \mathbf{I} \right), \tag{21}$$

$$\sum_{dk} \frac{n_{ci} n_{dk}}{n^2} I_{cijdk}(F) = \frac{1}{n} f_{cij}^{(0)} \left(\frac{m_c c_c^2}{3kT} - 1 - \frac{p}{\rho T (c_{\text{tr}} + c_{\text{rot}})} \left(\frac{m_c c_c^2}{2kT} - \frac{3}{2} + \left[\frac{\varepsilon_j^{ci}}{kT} \right]_r' \right) \right), \tag{22}$$

$$\sum_{dk} \frac{n_{ci} n_{dk}}{n^2} I_{cijdk}(G) = -J_{cij}^{\text{sl}(0)} + \frac{1}{n} f_{cij}^{(0)} \left(\frac{R_{ci}^{(0)}}{n_{ci}} - \frac{\sum_{ci} R_{ci}^{(0)} \left(\tfrac{3}{2} kT + \langle \varepsilon_j^{ci} \rangle_r + \varepsilon_i^c + \varepsilon^c \right)}{\rho T (c_{\text{tr}} + c_{\text{rot}})} \right.$$
$$\left. \times \left(\frac{m_c c_c^2}{2kT} - \frac{3}{2} + \left[\frac{\varepsilon_j^{ci}}{kT} \right]_r' \right) \right). \tag{23}$$

One can see that the equations for the functions A_{cij}, B_{cij}, D_{cij}^{dk}, F_{cij} contain only the linearized integral operator of rapid processes whereas the equation for G_{cij} depend on both operators of rapid and slow processes.

For the unity of the solution of integral equations (19)–(23) the following additional constraints on the functions $A_{cij} = A_{cij}(c_c) c_c$, $D_{cij}^{dk} = D_{cij}^{dk}(c_c) c_c$, F_{cij}, G_{cij} can be obtained from the normalization conditions Eq. (6):

$$\sum_{cij} m_c \int f_{cij}^{(0)} A_{cij} c_c^2 \, d\mathbf{u}_c = 0, \tag{24}$$

$$\sum_{cij} m_c \int f_{cij}^{(0)} D_{cij}^{dk} c_c^2 \, d\mathbf{u}_c = 0, \quad d = 1, \ldots, L, \; k = 0,1, \ldots, L_d, \tag{25}$$

$$\sum_j \int f_{cij}^{(0)} F_{cij} \, d\mathbf{u}_c = 0, \quad c = 1, \ldots, L, \; i = 0,1, \ldots, L_c, \tag{26}$$

$$\sum_j \int f_{cij}^{(0)} G_{cij} \, d\mathbf{u}_c = 0, \quad c = 1, \ldots, L, \; i = 0,1, \ldots, L_c, \tag{27}$$

$$\sum_{cij} \int f_{cij}^{(0)} \left(\frac{m_c c_c^2}{2} + \varepsilon_j^{ci} + \varepsilon_i^c \right) F_{cij} \, d\mathbf{u}_c = 0, \tag{28}$$

$$\sum_{cij} \int f_{cij}^{(0)} \left(\frac{m_c c_c^2}{2} + \varepsilon_j^{ci} + \varepsilon_i^c \right) G_{cij} \, d\mathbf{u}_c = 0. \tag{29}$$

Similarly to [22] the additional condition for $\boldsymbol{D}_{cij}^{dk}$ should be added to Eq. (25):

$$\sum_{dk} \frac{\rho_{dk}}{\rho} \boldsymbol{D}_{cij}^{dk} = 0. \tag{30}$$

Eq. (30) is needed because the diffusion driving forces (17) are not linearly independent ($\sum_{ci} \boldsymbol{d}_{ci} = 0$) due to the relations $\sum_{ci} n_{ci}/n = 1$ and $\sum_{ci} \rho_{ci}/\rho = 1$.

The first order distribution functions (18) correspond to weak deviation from the equilibrium over velocities and rotational energy and strong vibrational and chemical nonequilibrium. Substituting (18) into the expression (12) for the pressure tensor we obtain:

$$\mathbf{P} = (p - p_{\text{rel}})\mathbf{I} - 2\mu\mathbf{S} - \eta\nabla \cdot \boldsymbol{v}\mathbf{I} \tag{31}$$

Here $\mathbf{S}$ is the tensor of deformation velocities, μ, η are the shear and bulk viscosity coefficients, p_{rel} is the relaxation pressure:

$$\mu = \frac{kT}{10}[\mathbf{B},\mathbf{B}], \quad \eta = kT[F,F], \quad p_{\text{rel}} = kT[F,G]. \tag{32}$$

The bracket integral $[A,B]$ is defined by analogy with [22] as

$$[A,B] = \sum_{cidk} \frac{n_{ci}n_{dk}}{n^2}([A,B]'_{cidk} + [A,B]''_{cidk}), \tag{33}$$

the partial bracket integrals are introduced as follows:

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

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

The bracket integrals contain the cross sections of the most frequent collisions: the elastic collisions and those leading to the rotational energy exchange.

The additional terms in the pressure tensor such as the relaxation pressure and bulk viscosity appear in this case due to the inelastic translational-rotational TR energy transfers in the collisions between molecules of different vibrational and chemical species.

The first order distribution function provides the following expression for the diffusion velocity of the molecules of each chemical and vibrational species:

$$\boldsymbol{V}_{ci} = - \sum_{dk} D_{cidk} \boldsymbol{d}_{dk} - D_{Tci}\nabla \ln T, \tag{34}$$

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

$$D_{cidk} = \frac{1}{3n}[\boldsymbol{D}^{ci},\boldsymbol{D}^{dk}], \quad D_{Tci} = \frac{1}{3n}[\boldsymbol{D}^{ci},A]. \tag{35}$$

The expression for the total heat flux in the first order approximation has the next form:

$$\boldsymbol{q} = -\lambda'\nabla T - p\sum_{ci} D_{Tci}\boldsymbol{d}_{ci} + \sum_{ci}\left(\tfrac{5}{2}kT + \langle \varepsilon_j^{ci} \rangle_{\text{r}} + \varepsilon_i^c + \varepsilon^c\right)n_{ci}\boldsymbol{V}_{ci}, \tag{36}$$

where

$$\lambda' = \lambda_{\text{t}} + \lambda_{\text{r}} = \frac{k}{3}[A,A] \tag{37}$$

is the coefficient of thermal conductivity. The coefficients λ_t and λ_r express thermal conductivity connected with elastic and inelastic translational-rotational *TR* energy transfers. From Eqs. (34), (36), (17) one can see that 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 molecules of the different species and number density of atoms with corresponding diffusion coefficients which are different for various vibrational and chemical species.

The expressions for V_{ci}, q reported above differ from those in a multi-component mixture with frozen chemical reactions [22]. In the latter case the number densities of all chemical species are found from the conservation equations for number density of chemical species. In our case nonequilibrium level populations n_{ci} should be found from the equations of detailed vibrational and chemical kinetics coupled with the macroscopic conservation equations (8)–(9).

The expressions (34) and (36) differ also from the formulas for the diffusion velocity and heat flux in the one-temperature and multi-temperature approaches considered by us previously [20]. In the one-temperature approach the heat flux is defined by the gradients of the gas temperature T and number density of chemical species n_c which are obtained as a solution of the equations of one-temperature chemical kinetics based on the Boltzmann distribution over vibrational levels with the gas temperature T. In the multi-temperature approach T, n_c and vibrational temperatures of molecular species $T_v^{(c)}$ satisfy to the equations of nonequilibrium gas dynamics in the multi-temperature approach based on the quasi-stationary nonequilibrium multi-temperature distribution over vibrational levels.

In the case of equilibrium chemical reactions number density of species are the functions of the gas temperature and may be found from the equations of equilibrium chemical kinetics. The transport coefficients in this approach are calculated in Refs. [23–25].

5. The transport coefficients

In this section we derive the expressions for the shear viscosity, thermal conductivity, diffusion and thermal diffusion coefficients using Eqs. (19)–(21) for the functions A_{cij}, D_{cij}^{dk} and B_{cij}. The functions are expanded into finite series of Sonine and Waldmann-Trübenbacher [26] orthogonal polynomials over reduced translational and rotational energy correspondingly:

$$A_{cij} = -\frac{m_c c_c}{2kT} \sum_{rp} a_{ci,rp} S_{3/2}^{(r)}\left(\frac{m_c c_c^2}{2kT}\right) P_j^{(p)}\left(\frac{\varepsilon_j^{ci}}{kT}\right), \tag{38}$$

$$D_{cij}^{dk} = \frac{m_c c_c}{2kT} \sum_{r} d_{ci,r}^{dk} S_{3/2}^{(r)}\left(\frac{m_c c_c^2}{2kT}\right), \tag{39}$$

$$B_{cij} = \frac{m_c}{2kT}\left(c_c c_c - \frac{1}{3} c_c^2 \mathbf{I}\right) \sum_{r} b_{ci,r} S_{5/2}^{(r)}\left(\frac{m_c c_c^2}{2kT}\right). \tag{40}$$

To derive the equations for the coefficients $a_{ci,rp}$, $d_{ci,r}^{dk}$, $b_{ci,r}$ one can substitute the series (38)–(40) into integral equations (19)–(21) and multiply them by the velocity. After the integration over the velocities and summation over the rotational, vibrational quantum numbers and chemical species the systems of the linear algebraic equations are obtained. Thus the system of equations for the expansion coefficients $a_{ci,rp}$ has the following form:

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

$$c = 1,\ldots,L, \ i = 0,1,\ldots,L_c, \ r,p = 0,1,\ldots. \tag{41}$$

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

$$c_{\mathrm{rot},ci} = \frac{m_c}{k} \frac{\partial E_{\mathrm{r}}^{ci}}{\partial T}, \quad \rho_{ci} E_{\mathrm{r}}^{ci} = \sum_j \int \varepsilon_j^{ci} f_{cij}\, \mathrm{d}\boldsymbol{u}_c.$$

In the case when the rotational and vibrational energy of a molecule are considered independently the specific heats $c_{\mathrm{rot},ci}$ are equal one to another for any vibrational level: $c_{\mathrm{rot},ci} = c_{\mathrm{rot},c}$. The calculations also show that the coefficients of the expansions (38), (40) for $\boldsymbol{A}_{cij}$ and $\boldsymbol{B}_{cij}$ do not depend on the vibrational level in this particular case. This fact gives an essential simplification of the algebraic equations and the algorithm of their solution.

In the general case the coefficients of the system (41) are expressed in terms of bracket integrals defined by (33) and level populations:

$$\Lambda_{rr'pp'}^{cidk} = \sqrt{m_c m_d}\left(\delta_{cd}\delta_{ik} \sum_{bl} \frac{n_{ci}n_{bl}}{n^2}[Q^{rp}, Q^{r'p'}]_{cibl} + \frac{n_{ci}n_{dk}}{n^2}[Q^{rp}, Q^{r'p'}]_{cidk}'' \right), \tag{42}$$

and

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

Eqs. (41) occur not to be linear independent in the case $r = p = 0$. It follows from the momentum conservation and the symmetry of the bracket integrals: $\Lambda_{rr'pp'}^{cidk} = \Lambda_{r'rp'p}^{dkci}$. Taking into account the normalizing conditions (24) one can derive the additional equation for the coefficients $a_{ci,rp}$:

$$\sum_{ci} \frac{\rho_{ci}}{\rho} a_{ci,00} = 0. \tag{43}$$

The system (41) completed by Eq. (43) has a unique solution.

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

$$\sum_{dk} \sum_{r'} \gamma_{rr'}^{cidk} d_{dk,r'}^{bl} = 3kT\left(\delta_{cb}\delta_{il} - \frac{\rho_{ci}}{\rho} \right)\delta_{r0}, \quad b,c = 1,\ldots, L,\ i,l = 0,1,\ldots, L_c,\ r = 0,1,\ldots, \tag{44}$$

where

$$\gamma_{rr'}^{cidk} = \sqrt{m_c m_d}\left(\delta_{cd}\delta_{ik} \sum_{bl} \frac{n_{ci}n_{bl}}{n^2}[Q^r, Q^{r'}]_{cibl} + \frac{n_{ci}n_{dk}}{n^2}[Q^r, Q^{r'}]_{cidk}'' \right), \tag{45}$$

$$Q^r = \sqrt{\frac{m_c}{2kT}}\, c_c S_{3/2}^{(r)}\left(\frac{m_c c_c^2}{2kT}\right).$$

It is obvious that the bracket integrals $\gamma_{rr'}^{cidk}$ represent the particular case of the bracket integrals $\Lambda_{rr'pp'}^{cidk}$ at $p = p' = 0$ due to the normalizing conditions of the Waldmann-Trübenbacher polynomials:

$$\gamma_{rr'}^{cidk} = \Lambda_{rr'00}^{cidk} \tag{46}$$

Linear independent system can be derived taking into account constraints (25) which have the next form in terms of coefficients $d_{ci,r}^{dk}$:

$$\sum_{ci} \frac{\rho_{ci}}{\rho} d_{ci,0}^{dk} = 0,\ d = 1,\ldots, L,\ k = 0,1,\ldots, L_d. \tag{47}$$

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

$$\sum_{dk} \sum_{r'} H_{rr'}^{cidk} b_{dk,r'} = \frac{2}{kT} \frac{n_{ci}}{n} \delta_{r0}, \quad c = 1, \ldots, L, \ i = 0,1,\ldots, L_c, \ r = 0,1,\ldots, \tag{48}$$

where

$$H_{rr'}^{cidk} = \frac{2}{5kT} \left(\delta_{cd} \delta_{ik} \sum_{bl} \frac{n_{ci} n_{bl}}{n^2} [Q^r, Q^{r'}]_{cibl} + \frac{n_{ci} n_{dk}}{n^2} [Q^r, Q^{r'}]''_{cidk} \right), \tag{49}$$

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

One can see that the coefficients of the linear algebraic equations (41), (44) and (48) are expressed in terms of partial bracket integrals of the most rapid processes. They depend on the cross sections of the elastic collisions and the collisions with the rotational energy exchange.

Substituting the expansions (38)–(39) into Eqs. (37), (35), (31) and using the normalizing conditions for the polynomials, one can express the thermal conductivity, diffusion and thermal diffusion coefficients and the shear viscosity coefficient in terms of the expansion coefficients:

$$\lambda' = \sum_{ci} \frac{5}{4k} \frac{n_{ci}}{n} a_{ci,10} + \sum_{ci} \frac{k}{2} \frac{n_{ci}}{n} c_{\text{rot},ci} a_{ci,01}, \tag{50}$$

$$D_{cidk} = \frac{1}{2n} d_{dk,0}^{ci}, \tag{51}$$

$$D_{Tci} = -\frac{1}{2n} a_{ci,00}, \tag{52}$$

$$\mu = \frac{kT}{2} \sum_{ci} \frac{n_{ci}}{n} b_{ci,0}. \tag{53}$$

One can see that just zero order terms of the expansions appear in the formulas for the diffusion and thermal diffusion coefficients. However, maintaining only the equations for $a_{ci,00}$ in the system (41) leads to the zero values of thermal diffusion coefficients. The simplest way to yield nonzero thermal diffusion is to keep the terms involving the coefficients $a_{ci,00}$, $a_{ci,01}$ and $a_{ci,01}$ for the determination of $D_{T_{ci}}$ [22]. The resulting system must be solved for $a_{ci,00}$.

6. The bracket integrals

In the previous section the expressions for all transport coefficients are given in terms of the coefficients of polynomial expansions (38)–(40). These coefficients should be found from the systems of algebraic equations (41), (44), (48). The coefficients of these equations depend on the bracket integrals and level populations. In this section the bracket integrals are considered and the simple formulas for their calculation are presented.

First, we keep only the first non-vanishing terms of the expansions (38)–(40). Also, following [27], all complex collisions are assumed to be rare and are neglected, i.e. we neglect the collisions in which the internal states of both colliding molecules change, or in which both internal modes of one of the molecules change in one collision. Furthermore like in Ref. [27] we consider the internal and translational motions as the uncorrelated ones. Therefore one can suppose that

$$\left(\varepsilon_{j'}^{ci} - \varepsilon_{l'}^{ci} \right) g' = \left(\varepsilon_{j}^{ci} - \varepsilon_{l}^{ci} \right) g.$$

These assumptions allow us to express all bracket integrals as a linear combination of the elastic collision integrals and the integrals depending on the change of the rotational energy $\Delta\varepsilon_{\text{rot}}^{cidk}$ at the inelastic collisions:

$$\Delta\varepsilon_{\text{rot}}^{cidk} = \varepsilon_{j'}^{ci} + \varepsilon_{l'}^{dk} - \varepsilon_j^{ci} - \varepsilon_l^{dk}.$$

It is known [22] that the rotational quantum for gases at ordinary temperatures is much smaller than the relative kinetic energy of a colliding pair. And in collisions between rotating molecules generally only one or few quanta of rotational energy are exchanged. Therefore one can expect $\Delta\varepsilon_{\text{rot}}^{cidk}$ to be close to zero. This fact permits us to suppose that all collision integrals depending on $\left(\Delta\varepsilon_{\text{rot}}^{cidk}\right)^2$, are much less compared to the elastic collision integrals. This assumption was proved in Refs. [28,29], it was shown that the contribution of the collision integrals depending on $\left(\Delta\varepsilon_{\text{rot}}^{cidk}\right)^2$ to the thermal conductivity coefficients does not exceed 1–2%. It should be noticed that neglecting $\Delta\varepsilon_{\text{rot}}^{cidk}$ cannot be allowed at the calculation of rotational bulk viscosity because this coefficient appears only in the case when $\Delta\varepsilon_{\text{rot}}^{cidk} \neq 0$.

Finally the rather simple approximate expressions for the bracket integrals and correspondingly for the coefficients of algebraic equations are obtained:

$$\Lambda_{rr'pp'}^{cidk} = \Lambda_{r'rp'p}^{dkci}, \tag{54}$$

$$\Lambda_{0000}^{cici} = \frac{75k^2T}{16} \sum_{\substack{b \neq c \\ n \neq i}} \frac{x_{ci}x_{bn}}{A_{cibn}^*\lambda_{cibn}}, \tag{55}$$

$$\Lambda_{0000}^{cidk} = -\frac{75k^2T}{16} \frac{x_{ci}x_{dk}}{A_{cidk}^*\lambda_{cidk}}, \quad c \neq d \text{ or } i \neq k \tag{56}$$

$$\Lambda_{1000}^{cici} = -\frac{75k^2T}{32} \sum_{\substack{b \neq c \\ n \neq i}} \frac{x_{ci}x_{bn}}{A_{cibn}^*\lambda_{cibn}} \frac{m_b}{m_c + m_b}(6C_{cibn}^* - 5), \tag{57}$$

$$\Lambda_{1000}^{cidk} = \frac{75k^2T}{32} \frac{x_{ci}x_{dk}}{A_{cidk}^*\lambda_{cidk}} \frac{m_c}{m_c + m_d}(6C_{cidk}^* - 5), \quad c \neq d \text{ or } i \neq k \tag{58}$$

$$\Lambda_{1100}^{cici} = \frac{75k^2T}{8}\left(\frac{x_{ci}^2}{\lambda_{ci}} + \sum_{\substack{b \neq c \\ n \neq i}} \frac{x_{ci}x_{bn}}{2A_{cibn}^*\lambda_{cibn}} \frac{\frac{15}{2}m_c^2 + \frac{25}{4}m_b^2 - 3m_b^2 B_{cibn}^* + 4m_c m_b A_{cibn}^*}{(m_c + m_b)^2} \right) \tag{59}$$

$$\Lambda_{1100}^{cidk} = -\frac{75k^2T}{16} \frac{x_{ci}x_{dk}}{A_{cidk}^*\lambda_{cidk}} \frac{m_c m_d}{(m_c + m_d)^2}\left(\tfrac{55}{4} - 3B_{cidk}^* - 4A_{cidk}^* \right), \quad c \neq d \text{ or } i \neq k, \tag{60}$$

$$\Lambda_{0011}^{cici} = 4x_{ci}^2 m_c c_{\text{rot},ci}\Omega_{ci}^{(1,1)} + 8\sum_{\substack{b \neq c \\ n \neq i}} x_{ci}x_{bn}c_{\text{rot},ci}\frac{m_c m_b}{m_c + m_b}\Omega_{cibn}^{(1,1)}, \tag{61}$$

$$\Lambda_{0011}^{cidk} = 0, \quad c \neq d \text{ or } i \neq k. \tag{62}$$

All the remaining integrals $\Lambda_{rr'pp'}^{cidk}$ are equal to zero.

Here the following notations are introduced: $x_{ci} = n_{ci}/n$ is the dimensionless number density of molecules of c chemical species at the ith vibrational level, λ_{ci} and λ_{cidk} are the following coefficients:

$$\lambda_{ci} = \frac{75k}{64m_c} \frac{(\pi m_c kT)^{1/2}}{\pi \overline{\sigma}_{ci}^2 \Omega_{ci}^{(2,2)*}}, \tag{63}$$

$$\lambda_{cidk} = \frac{75k}{128m_{cd}} \frac{(2\pi m_{cd}kT)^{1/2}}{\pi \overline{\sigma}_{cidk}^2 \Omega_{cidk}^{(2,2)*}}, \tag{64}$$

$\overline{\sigma}_{cidk}$ is the collision diameter, m_{cd} is the reduced mass:

$$m_{cd} = \frac{m_c m_d}{m_c + m_d}.$$

The coefficients λ_{ci} and λ_{cidk} have the form similar to the expressions for the heat conductivity coefficients in a pure gas and in a binary mixture and may be considered as the fictitious heat conductivity coefficients.

The collision integrals $\Omega_{cidk}^{(l,r)}$ are introduced as follows:

$$\Omega_{cidk}^{(1,r)} = \left(\frac{kT}{2\pi m_{cd}}\right)^{1/2} \int_0^\infty \exp(-g^2) g^{2r+3} \mathscr{Q}_{cidk}^{(l)} \, \mathrm{d}g, \tag{65}$$

$$\mathscr{Q}_{cidk}^{(l)} = 2\pi \int \left(1 - \cos^l \chi_{cidk}(b,g)\right) b \, \mathrm{d}b.$$

Here $\chi_{cidk}(b,g)$ is the deflection angle, b is the impact parameter.

The functions A_{cidk}^*, B_{cidk}^*, C_{cidk}^* are given by analogy to [22]:

$$A_{cidk}^* = \frac{\Omega_{cidk}^{(2,2)*}}{\Omega_{cidk}^{(1,1)*}}, \tag{66}$$

$$B_{cidk}^* = \frac{5\Omega_{cidk}^{(1,2)*} - 4\Omega_{cidk}^{(1,3)*}}{\Omega_{cidk}^{(1,1)*}}, \tag{67}$$

$$C_{cidk}^* = \frac{\Omega_{cidk}^{(1,2)*}}{\Omega_{cidk}^{(1,1)*}}, \tag{68}$$

where the reduced collision integrals $\Omega_{cidk}^{(l,r)*}$ have such a form:

$$\Omega_{cidk}^{(l,r)*} = \frac{\Omega_{cidk}^{(1,r)}}{\left(\Omega_{cidk}^{(1,r)}\right)_{\mathrm{h.s.}}} \tag{69}$$

the collision integrals $\left(\Omega_{cidk}^{(1,r)}\right)_{\mathrm{h.s.}}$ are calculated for the hard spheres model:

$$\left(\Omega_{cidk}^{(1,r)}\right)_{\mathrm{h.s.}} = \left(\frac{kT}{2\pi m_{cd}}\right)^{1/2} \frac{(r+1)!}{2} \left[1 - \frac{1 + (-1)^l}{2(l+1)}\right] \pi \overline{\sigma}_{cidk}^2. \tag{70}$$

Hereafter we suppose that the collision diameter $\overline{\sigma}_{cidk}$ and deflection angle $\chi_{cidk}(b,g)$ do not depend on the vibrational level of the molecule. Therefore the cross sections of the most frequent collisions are independent from the vibrational state and one can write:

$$\lambda_{ci} = \lambda_c, \ \lambda_{cidk} = \lambda_{cd}, \ \Omega_{ci}^{(1,r)} = \Omega_c^{(1,r)}, \ \Omega_{cidk}^{(1,r)} = \Omega_{cd}^{(1,r)}, \ \Omega_{cidk}^{(l,r)*} = \Omega_{cd}^{(l,r)*},$$
$$A_{cidk}^* = A_{cd}^*, \ B_{cidk}^* = B_{cd}^*, \ C_{cidk}^* = C_{cd}^*.$$

In this case the collision integrals (65) and their combinations (66)–(70) do not depend on the number of vibrational level. Using this simplification the final formulas for the bracket integrals are obtained in the form:

$$\Lambda_{0000}^{cici} = \frac{75k^2T}{16} \sum_{\substack{b \neq c \\ n \neq i}} \frac{x_{ci}x_{bn}}{A_{cb}^*\lambda_{cb}}, \tag{71}$$

$$\Lambda_{0000}^{cidk} = -\frac{75k^2T}{16} \frac{x_{ci}x_{dk}}{A_{cd}^*\lambda_{cd}}, \quad c \neq d \text{ or } i \neq k, \tag{72}$$

$$\Lambda_{1000}^{cici} = -\frac{75k^2T}{32} \sum_{\substack{b \neq c \\ n \neq i}} \frac{x_{ci}x_{bn}}{A_{cb}^*\lambda_{cb}} \frac{m_b}{m_c + m_b}\left(6C_{cb}^* - 5\right), \tag{73}$$

$$\Lambda_{1000}^{cidk} = \frac{75k^2T}{32} \frac{x_{ci}x_{dk}}{A_{cd}^*\lambda_{cd}} \frac{m_c}{m_c + m_d}\left(6C_{cd}^* - 5\right), \quad c \neq d \text{ or } i \neq k, \tag{74}$$

$$\Lambda_{1100}^{cici} = \frac{75k^2T}{8}\left(\frac{x_{ci}^2}{\lambda_c} + \sum_{\substack{b \neq c \\ n \neq i}} \frac{x_{ci}x_{bn}}{2A_{cb}^*\lambda_{cb}} \frac{\frac{15}{2}m_c^2 + \frac{25}{4}m_b^2 - 3m_b^2 B_{cb}^* + 4m_c m_b A_{cb}^*}{(m_c + m_b)^2}\right), \tag{75}$$

$$\Lambda_{1100}^{cidk} = -\frac{75k^2T}{16} \frac{x_{ci}x_{dk}}{A_{cd}^*\lambda_{cd}} \frac{m_c m_d}{(m_c + m_d)^2}\left(\frac{55}{4} - 3B_{cd}^* - 4A_{cd}^*\right), \quad c \neq d \text{ or } i \neq k, \tag{76}$$

$$\Lambda_{0011}^{cici} = 4x_{ci}^2 m_c c_{\mathrm{rot},ci}\Omega_c^{(1,1)} + 8 \sum_{\substack{b \neq c \\ n \neq i}} x_{ci}x_{bn}c_{\mathrm{rot},ci}\frac{m_c m_b}{m_c + m_b}\Omega_{cb}^{(1,1)}, \tag{77}$$

$$\Lambda_{0011}^{cidk} = 0, \quad c \neq d \text{ or } i \neq k. \tag{78}$$

It is seen that now in the formulas (71)–(78) the bracket integrals depend on the vibrational level only through the level populations of species x_{ci} and not through the collision integrals. For the calculation of $\Omega_{cd}^{(1,r)}$-integrals and functions A_{cd}^*, B_{cd}^*, C_{cd}^* the existing tables or approximate formulas ([22,30–32] and others) may be used.

Table 1
Potential parameters for interactions in an (N_2,N) mixture

Interaction	Lennard-Jones potential			Repulsive potential		
	ϵ/k, K	$\bar{\sigma}$, Å	Source	V_0, eV	β, Å^{-1}	Source
N_2–N_2	97.53	3.621	[33]	415.7	2.573	[35]
N_2–N	82.904	3.459		184.9	2.614	[34]
N–N	71.4	3.298	[33]	86.0	2.68	[35]

Similarly the expression for the integral bracket H_{00}^{cidk} is derived:

$$H_{00}^{cici} = \frac{x_{ci}^2}{\mu_c} + \sum_{\substack{b \neq c \\ n \neq i}} \frac{2\,x_{ci}x_{bn}}{\mu_{cb}} \frac{m_c m_b}{(m_c + m_b)^2} \left(\frac{5}{3A_{cb}^*} + \frac{m_b}{m_c} \right), \tag{79}$$

$$H_{00}^{cidk} = -\frac{2\,x_{ci}x_{dk}}{\mu_{cd}} \frac{m_c m_d}{(m_c + m_d)^2} \left(\frac{5}{3A_{cd}^*} - 1 \right), \quad c \neq d, i \neq k, \tag{80}$$

where

$$\mu_c = \frac{5}{16} \frac{(\pi m_c kT)^{1/2}}{\pi \overline{\sigma}_c^2 \Omega_c^{(2,2)*}}, \tag{81}$$

$$\mu_{cd} = \frac{5}{16} \frac{(2\pi m_{cd} kT)^{1/2}}{\pi \overline{\sigma}_{cd}^2 \Omega_{cd}^{(2,2)*}}, \tag{82}$$

are the fictitious viscosity coefficients.

Thus all transport coefficients are expressed in terms of the $\Omega_{cd}^{(1,r)}$ collision integrals which can be easily calculated using numerous existing data and in terms of nonequilibrium level populations n_{ci} which should be found from the equations of nonequilibrium gas dynamics (7)–(9) for different flows.

For the calculation of $\Omega_{cd}^{(1,r)}$ integrals some assumptions about the character of molecular interaction should be made. At the moderate gas temperature ($T < 1000$ K) using the Lennard-Jones interaction potential provides a good agreement with experimental data. The values of the potential parameters (its well depth ϵ/k and collision diameter $\overline{\sigma}$) are usually found from the fitting of the experimental data for shear viscosity or second virial coefficient. The calculation of the transport coefficients for different gases shows that the parameters of the Lennard-Jones potential from Ref. [33] appear to be more precise than those from Ref. [30] and may be recommended for practical use. With the gas temperature rising using the Lennard-Jones potential for the calculation of $\Omega_{cd}^{(1,r)}$ integrals leads to an underestimation of transport coefficients. At the condition $kT/\epsilon > 10$ we apply a repulsive model of interaction potential V in the form suggested in Ref. [34]:

$$V = V_0 \exp(-\beta r),$$

where r is the distance between the centers of mass of interacting molecules, V_0 and β are the parameters. The approximate formulas for $\Omega_{cd}^{(1,r)}$ given in Ref. [31] with the parameters of repulsive potential taken from Ref. [35] give a good agreement with experimental data on the transport coefficients in high-temperature gas mixtures. The set of the potential parameters which we use in the present study for the calculation of transport coefficients in an (N_2,N) mixture is given in Table 1. The parameters of the Lennard-Jones potential for N_2–N interaction are computed using combining rules [22]:

$$\overline{\sigma}_{N_2-N} = \tfrac{1}{2}\left(\overline{\sigma}_{N_2} + \overline{\sigma}_N \right), \quad \epsilon_{N_2-N}\overline{\sigma}_{N_2-N}^6 = \left(\epsilon_{N_2}\overline{\sigma}_{N_2}^6 \epsilon_N \overline{\sigma}_N^6 \right)^{1/2}.$$

It should be noticed that the assumption about the independence of the cross sections of elastic collisions from the vibrational level reduces essentially the number of independent diffusion and thermal diffusion coefficients. Substituting the final expressions (71)–(78) for the bracket integrals into the linear algebraic systems (44), (47) for the coefficients $d_{dk,r}^{ci}$ one can found that the coefficients $d_{dk,r}^{ci}$ depend on the vibrational level only if $c = d$ and $i = k$. It leads to the different self-diffusion coefficients D_{cici} for each vibrational level in the molecular species. On the contrary, if $c \neq d$ or $i \neq k$ the diffusion coefficients D_{cidk} do not depend on i and k. Consequently, all coefficients D_{cick} are equal one to another if $i \neq k$. ($D_{cick} = D_{cc}$, $i \neq k$). The coefficients $D_{cidi} = D_{cidk} = D_{cd}$. Similarly one can deduce that the thermal diffusion coefficients are also

independent of the vibrational level and all $D_{T_{ci}} = D_{T_c}$. Taking into account this simplification the expressions (34) and (36) for the diffusion velocity and total heat flux may be written in such a form:

$$V_{ci} = -D_{cici}d_{ci} - D_{cc}\sum_{k \neq i}d_{ck} - \sum_{d \neq c}D_{cd}d_d - D_{Tc}\nabla\ln T, \tag{83}$$

$$q = -\lambda'\nabla T - p\sum_c D_{Tc}d_c + \sum_{ci}\left(\tfrac{5}{2}kT + \langle \varepsilon_j^{ci}\rangle_r + \varepsilon_i^c + \varepsilon^c\right)n_{ci}V_{ci}. \tag{84}$$

Here

$$d_c = \sum_i d_{ci} = \nabla\left(\frac{n_c}{n}\right) + \left(\frac{n_c}{n} - \frac{\rho_c}{\rho}\right)\nabla\ln p. \tag{85}$$

Finally in a multi-component mixture under the assumption $\bar{\sigma}_{cidk} = \bar{\sigma}_{cd}$, $\chi_{cidk} = \chi_{cd}$ we have the following system of the diffusion coefficients: the thermal diffusion coefficients for different chemical species D_{T_c}, the multi-component diffusion coefficients of the molecules of c and d chemical species D_{cd}, the diffusion coefficients of the molecules of the same chemical species c at different vibrational levels D_{cc}, and the self-diffusion coefficients for the molecule of c species at the ith vibrational level D_{cici}. The number of the diffusion coefficients in Eqs. (83), (84) is much less compared to (34)–(36) in the general case taking into account the dependence of the cross sections on i. Therefore the assumption $\bar{\sigma}_{cidk} = \bar{\sigma}_{cd}$, $\chi_{cidk} = \chi_{cd}$ gives a noticeable reduction of the computation time. This assumption is usually accepted in the transport kinetic theory. However the fact that molecules in vibrationally excited states have a larger effective radius than ground state molecules is well established [36–38]. In particular in Ref. [38] it is indicated that nitrogen molecules with vibrational quantum number greater than about 38 occur more than 50% larger compared to molecules in the
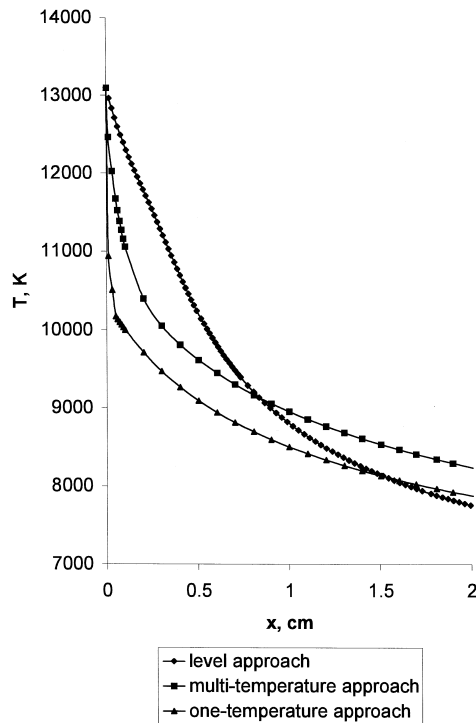

Fig. 1. Gas temperature behind a shock wave in (N_2, N) mixture calculated in different approaches. $M_0 = 15$, $T_0 = 293$ K, $p_0 = 100$ Pa.

ground state. But in many cases the population of high vibrational levels in a gas flow is less than the population of intermediate and low levels and therefore molecules with high vibrational quantum number do not effect significantly macroscopic gas parameters and transport properties.

7. Results and discussion

The approach developed above was applied to the calculation of the heat flux in a dissociating (N_2–N) mixture behind a plane shock wave. The results are compared to the ones obtained in the two-temperature and one-temperature approaches based on the steady-state Boltzmann distributions over vibrational energy. The one-temperature approach corresponds to thermal equilibrium in a dissociating gas, in this case there exists the equilibrium Boltzmann distribution over internal energy with the gas temperature. In the two-temperature model the existence of the nonequilibrium Boltzmann distribution with the vibrational temperature T_v for molecular species due to the dominant resonant VV vibrational energy exchange was assumed. The macroscopic parameters in the one-temperature and multi-temperature approaches are computed using the code described in Ref. [39]. In the level approach the system of the macroscopic equations is solved using the Gear method. The distribution of the molecules over vibrational levels in free stream is assumed to be the Boltzmann one, 20 excited vibrational levels in N_2 are taken into account. The molecular spectra are simulated as anharmonic oscillators. The transition probabilities are calculated using the SSH-theory generalized for anharmonic oscillators [40]. The Treanor-Marrone model [41] is applied for the computation of the probability of dissociation from each vibrational level. The following conditions in the free stream are considered: $T_0 = 293$ K, $p_0 = 100$ Pa, $M_0 = 15$, $n_{N_2}^{(0)}/n^{(0)} = 1$.
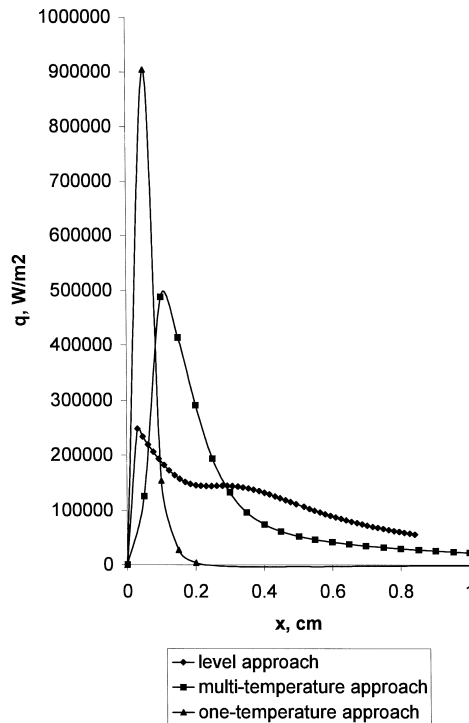

Fig. 2. Total heat flux q, W/m^2, behind a shock wave calculated in different approaches for the conditions of Fig. 1.

The gas temperature distribution behind a shock wave calculated using three different approach is given in Fig. 1 as a function of the distance from the shock front x. The curves are cut at $x = 2$ cm before the total equilibrium is established because at $x > 2$ cm the gradients of the macroscopic parameters are rather small and therefore their behaviour is not important for the analysis of the total heat flux. It is seen that in the beginning of the relaxation zone both two-temperature and one-temperature approaches give an underestimation of the gas temperature compared to the level approach. With increasing the distance from the shock front the temperatures calculated on the basis of all three approaches become close to each other.

The total heat flux behind a shock wave calculated for the same free stream conditions in the level, multi-temperature and one-temperature approaches is presented in Fig. 2 as a function of x. One can conclude that the total heat flux decreases approaching to the equilibrium. At $x > 1$ cm all three approaches give the close values of q. On the contrary, in the beginning of the relaxation zone there exists an essential discrepancy between the heat fluxes calculated using different models. The one-temperature approach provides a very strong peak of the heat flux just behind the shock front. This effect can be explained by the fact that the one-temperature approach does not describe the process of the vibrational excitation of the molecules just after the shock. It leads to a more sharp decrease of the gas temperature in the very beginning of the relaxation zone compared to the two other approaches (see Fig. 1) and therefore to the very high values of the temperature gradient. The two-temperature approach yields a more smooth behaviour of the macroscopic parameter gradients and the heat flux but there remains a noticeable distinction between q calculated using the level and two-temperature approach. Thus in the zone of vibrational excitation where the steady-state vibrational distributions do not exist the more rigorous level approach should be used for the evaluation of heat transfer in a reacting gas mixture.

8. Conclusions

The transport kinetic theory of reacting gas mixtures is developed in the case of strong chemical-vibrational nonequilibrium. The influence of chemical-vibrational coupling on heat transfer is studied. It is shown that the heat flux in a nonequilibrium reacting gas mixture is determined by the gradients of the gas temperature, number densities of atomic species and nonequilibrium populations of all vibrational levels of molecular species. The comparison with the expression for the heat flux derived in the case of multi-component mixture with frozen chemical reactions and with the one obtained in the one-temperature and multi-temperature approaches is given. The closed system of the macroscopic equations for nonequilibrium level populations, gas velocity and gas temperature is obtained. The equations for level populations contain the diffusion velocities for each vibrational level of molecular species. The formulas for the shear and bulk viscosity, thermal conductivity and diffusion coefficients different for various vibrational levels are derived. It is shown that in the level approach all transport coefficients depend on the cross sections of the most frequent collisions: elastic collisions and the ones leading to the rotational energy change. The simplified algorithm for the calculation of the shear viscosity, heat conductivity and diffusion coefficients is developed and the final formulas for the transport coefficients are given in terms of the elastic collision integrals ($\Omega_{cd}^{(1,r)}$-integrals) and nonequilibrium level populations, number densities of atomic species and gas temperature.

The formulas obtained may be easily inserted into a numerical code for the solution of the Navier-Stokes equations for reacting gas mixtures with vibrational relaxation coupled to nonequilibrium chemical reactions. This approach is particularly important in the case of strong vibrational excitation due to recombination, intensive VV vibrational energy exchange, expansion of the flow or some kind of vibrational energy pumping.

The calculation of heat transfer in a dissociating gas mixture behind a strong shock wave shows a significant difference between the total heat fluxes computed using the level, two-temperature and one-temperature approaches. In the beginning of the relaxation zone where the process of vibrational excitation is of the importance the more detailed level approach should be used. Both one-temperature and two-temperature models lead to an unlikely rise of the heat flux just behind the shock front.

Acknowledgements

The authors thank ESA ESTEC for the support of this work.

References

[1] Ye.V. Stupochenko, S.A. Losev, A.I. Osipov, Relaxation in Shock Waves, Springer, Berlin, Heidelberg, New York, 1967.

[2] P.L. Varghese, D.A. Gonzales, Non-equilibrium chemistry models for shock-heated gases, in: M. Capitelli (Ed.), Molecular Physics and Hypersonic Flows, Kluwer Acad. Publishers, Netherlands, 1996.

[3] E.A. Nagnibeda, The structure of the relaxation zone behind shock waves in the reacting gas flows, in: J.J. Hunt (Ed.), Aerothermodynamics for Space Vehicles, ESA Publication Division, ESTEC, Noordwijk, The Netherlands, 1995.

[4] J.G. Meolans, M. Mouti, F. Lordet, A.H. Chauvin, Vibration-dissociation coupling behind a plane shock wave, in: J. Harvey, G. Lord (Eds.), Rarefied Gas Dynamics 19, vol. 1, Oxford Univ. Press, Oxford, New York, Tokyo, 1995.

[5] E.A. Nagnibeda, J.G. Meolans, M. Mouti, A.H. Chauvin, Various models of coupling of vibrational-dissociational kinetics behind shock wave, in: Proc. 20th International Symposium on Shock Waves, Pasadena, 1995, in press.

[6] E.V. Kustova, E.A. Nagnibeda, The effect of level nonequilibrium kinetics on transport properties of dissociating gas flow behind a shock wave, in: Proc. 21st International Symposium on Shock Waves, Great Keppel Island, Australia, 1997, in press.

[7] J. Warnatz, U. Riedel, R. Schmidt, Different levels of air dissociation chemistry and its coupling with flow models, in: J.J. Bertin, J. Periaux, J. Ballmann (Eds.), Advanced in Hypersonic Flows, vol. 2: Modeling Hypersonic Flows, Birhauser, Boston, 1992.

[8] D. Shizgal, F. Lordet, J. Chem. Phys. 104 (1996) 3579.

[9] S.M. Ruffin, C. Park, Vibrational relaxation of anharmonic oscillatos in expanding flows, AIAA paper 92-0806, 1992.

[10] I. Armenise, M. Capitelli, C. Gorse, On the coupling of non-equilibrium vibrational kinetics and dissociation-recombination processes in the boundary layer surrounding an hypersonic reentry vehicle, in: J.J. Hunt (Ed.), Aerothermodynamics for Space Vehicles ESA Publication Division, ESTEC, Noordwijk, The Netherlands, 1995.

[11] I. Armenise, M. Capitelli, G. Colonna, C. Gorse, J. Thermophysics and Heat Transfer 10 (1996) 397.

[12] I. Armenise, M. Capitelli, R. Celiberto, G. Colonna, C. Gorse, A. Lagana, Chem. Phys. Lett. 227 (1994) 157.

[13] G.V. Candler, J. Olejniczak, B. Harrold, Phys. Fluids 9 (1997) 2108.

[14] S.Yu. Doronova, E.A. Nagnibeda, Vestnik Leningr. Universiteta Math. Mech. Astr. 19 (1974) 86, in Russian.

[15] E.A. Nagnibeda, S.Yu. Doronova, Vestnik Leningr. Universiteta Math. Mech. Astr. 19 (1977) 93, in Russian.

[16] S.V. Vallander, E.A. Nagnibeda, M.A. Rydalevskaya, Some Questions of the Kinetic Theory of the Chemical Reacting Gas Mixture Leningrad University Press, Leningrad, 1977, in Russian. Translation: US AirForce FASTC–ID (RS) TO–0608–93.

[17] G. Ludwig, M. Heil, Boundary layer theory with dissociation and ionization, in: Advances in Applied Mechanics, vol. VI, Academic Press, New York, 1960.

[18] E.A. Nagnibeda, M.A. Rydalevskaya, The derivation of the equations for macroparameters from the kinetic equations in the mixture of dissociating gases, in: Aerodinamika Razrezhennykh Gazov, vol. IX, Leningrad University Press, Leningrad, 1977, in Russian.

[19] I. Kuščer, Transport Theory and Statistical Physics 24 (1995) 347.

[20] A. Chikhaoui, J.P. Dudon, E.V. Kustova, E.A. Nagnibeda, J. Physica A 247 (1997) 526.

[21] E.A. Nagnibeda, M.A. Rydalevskaya, The equations describing a mixture of nonequilibrium viscous dissociating gases, in: Aerodinamika Razrezhennykh Gazov, vol. X, Leningrad University Press, Leningrad, 1980, in Russian.

[22] J.H. Ferziger, H.G. Kaper, Mathematical Theory of Transport Processes in Gases, North-Holland, Amsterdam, London, 1972.

[23] J.N. Butler, R.S. Brokaw, J. Chem. Phys. 26 (1957) 1636.

[24] R.S. Brokaw, J. Chem. Phys. 32 (1960) 1005.

[25] R.S. Brokaw, J. Chem. Phys. 47 (1967) 3236.

[26] L. Waldmann, E. Trübenbacher, Z. Naturforsch 17a (1962) 364.

[27] L. Monchick, A.N.G. Pereira, E.A. Mason, J. Chem. Phys. 42 (1965) 3241.

[28] E.V. Kustova, E.A. Nagnibeda, The influence of non-Boltzmann vibrational distribution on thermal conductivity and viscosity, in: M. Capitelli (Ed.), Molecular Physics and Hypersonic Flows, Kluwer Acad. Publishers, Netherlands, 1996.

[29] E.V. Kustova, E.A. Nagnibeda, Chem. Phys. 208 (1996) 313.

[30] J.O. Hirschfelder, C.F. Curtiss, R.B. Bird, The Molecular Theory of Gases and Liquids, Wiley, New York, 1954.

[31] J. Bzowski, J. Kestin, E.A. Mason, F.J. Uribe, J. Phys. Chem. Ref. Data 19 (1990) 1179.

[32] R.N. Gupta, J.M. Yos, R.A. Thompson, K.P. Lee, A review of reaction rates and thermodynamic and transport properties for an 11-species air model for chemical and thermal nonequilibrium calculations to 30000 K, NASA reference publication 1232, 1990.

[33] R.J. Kee, J.A. Miller, T.N. Jefferson, Chemkin: A General-Purpose, Problem-Independent, Transportable, Fortran Chemical Kinetics Code Package, Sand80-8003, Sandia National Laboratories, 1980.

[34] S.J. Cubley, E.A. Mason, Phys. Fluids 18 (1975) 1109.

[35] V.V. Riabov, Journ. of Thermophysics, Heat Transfer 10 (1996) 209.

[36] M.P. Fewell, S.C. Haydon, A.D. Ernest, Chem. Phys. 206 (1996) 257.

[37] S.H. Kang, J.A. Kunc, J. Phys. Chem. 95 (1991) 6971.

[38] A. Loftus, P.H. Krupenie, J. Phys. Chem. Ref. Data 6 (1977) 113.

[39] S. Seror, M.C. Druguet, E. Schall, D. Zeitoun, AIAA Paper 97-2556, 1997.

[40] B.F. Gordietz, S.A. Zhdanok, Analytical theory of vibrational kinetics of anharmonic oscillators, in: M. Capitelli (Ed.), Nonequilibrium Vibrational Kinetics, Springer, Berlin, Heidelberg, New York, Tokyo, 1986.

[41] P.V. Marrone, C.E. Treanor, Phys. of Fluids 6 (1963) 1215.