

Transport properties in reacting mixture of polyatomic gases

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Abstract

The mathematical modeling of transport properties in reacting gases on the basis of kinetic equations for the distribution functions is given in this paper. Thermal and chemical nonequilibrium conditions are considered. The influence of rotational and vibrational excitation and chemical reactions on the pressure tensor, heat flux and diffusion velocity is investigated. The generalization of the Chapman–Enskog method is used at the different levels of the strong nonequilibrium mixture description. Three nonequilibrium models are presented: the level approach, the generalized multi-temperature approach and the one-temperature approach. The macroscopic equations for macroparameters are derived from the kinetic theory treatment, and the expressions for the pressure tensor, diffusion velocity and heat flux as well as for the transport coefficients are given. The role of the different rates of the various energy exchanges, the anharmonism of molecular vibrations and chemical reactions in the transport properties of reacting mixtures is discussed.

Keywords: Kinetic theory; Polyatomic gases; Reacting flows; Transport properties

1. Introduction

The prediction of macroscopic parameters in high-temperature reacting gas flows requires adequate models for the transport properties such as heat conductivity, viscosity and diffusion. The dissipative processes in gas mixtures with internal degrees of freedom and chemical reactions have been largely investigated on the basis of the kinetic theory of gases. The generalization of the classical Chapman–Enskog method and some algorithms for the calculation of transport coefficients in gases with internal modes were given in the papers [1,2]. The model developed herein was widely used

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for the investigation of dissipative properties in the case of weak deviation from the equilibrium when all inelastic processes are more rapid than the macroscopic processes corresponding to the macroparameters change. The conditions when the characteristic time of some relaxation processes becomes comparable with the macroscopic time were considered later by several authors in gases with rotational and vibrational excitation [3,4], in binary mixtures [5], and in mixtures with chemical reactions [3]. Actually, many papers devoted to the kinetic theory of reacting gases are reported in a recent bibliography [6], and the mathematical aspects of the transport theory in a multicomponent mixture are discussed in Ref. [7]. However, up to now the transport theory of reacting gas mixtures is not sufficiently advanced in order to estimate the impact of internal modes and chemical reactions on all transport coefficients. In particular, the influence of vibrational–chemical nonequilibrium on the heat flux, pressure tensor and diffusion vectors in a reacting mixture is still not clearly understood. In fact, the transport coefficients in reacting mixtures were mainly studied in the case of weak deviation from the one-temperature Boltzmann distribution over internal energies. In this case all the collisions with inelastic energy exchanges are supposed to be more frequent in comparison to the chemically active collisions. Nevertheless, it is important to take into account the different rates of various energy exchanges, because some of them can be comparable with the rates of chemical reactions. It becomes particularly significant in the case of strongly vibrationally excited gases when the storage of vibrational energy exceeds the translational and rotational ones. This fact leads to the non-Boltzmann distributions over internal energies and anharmonism of molecular vibrations becomes important. The influence of the non-Boltzmann distributions on transport processes in gases with rotational and vibrational excitation is considered in Ref. [8]. In the present study, the kinetic theory treatment of the heat conductivity, viscosity and diffusion in high-temperature reacting mixtures with rotational, vibrational excitation and chemical reactions is developed. Different rates of various energy exchanges and anharmonic effects in reacting mixtures are taken into account. The formulae for the calculation of the dissipative coefficients are derived for different relations between the characteristic times of the processes considered in the present work.

The experimental data concerning relaxation times [9] permit to consider the following three cases. First of them corresponds to the conditions

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

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. The condition Eq. (1) is valid because 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. However, this assumption is no longer valid for slow rotational relaxation of light molecules and in the case of hot-atom chemistry. The condition given in Eq. (1) provides the so-called level approach in nonequilibrium gas

dynamics which describes the simultaneous processes of the vibrational and chemical relaxation. This model can be used for the study of vibrational–chemical coupling in the boundary layer or in the short relaxation zone behind a shock wave where steady-state vibrational distributions do not exist.

In the second case, the collisions with vibrational energy exchanges have different frequencies

$$\tau_{el} < \tau_r < \tau_{VV_1} \ll \tau_{VV_2} < \tau_{RVT} < \tau_{react} \sim \theta. \quad (2)$$

here τ_{VV_1} is the mean time between the collisions with the exchange of vibrational quanta inside every vibrational mode, τ_{VV_2} is that for the exchanges between different modes, τ_{RVT} is the time between the collisions with the inelastic rotational–vibrational–translational transfer. Condition Eq. (2) is valid in vibrationally excited gases such as in nozzle streams and expanding flows. This condition corresponds to the generalized multi-temperature approach.

With increasing gas temperature, the relaxation times τ_{VV_1} and τ_{VV_2} become comparable and of the same order as τ_{RVT} , and the corresponding inelastic exchanges become more rapid, so that the following conditions take place, especially for the reactions with a high threshold or for slow reactions

$$\tau_{el} < \tau_r < \tau_{VV_1} \sim \tau_{VV_2} \sim \tau_{RVT} \ll \tau_{react} \sim \theta. \quad (3)$$

In this case the one-temperature approach follows from the kinetic equations. This model is widely used in chemical kinetics, particularly for the investigation of the relaxation zone behind a shock wave. Nevertheless, it does not allow to study the vibrational–chemical coupling in the vibrational nonequilibrium zone.

The comparison of the kinetic theory approach for the calculation of the transport coefficients using the different models is discussed hereafter.

2. Level kinetics approach

2.1. Zeroth order distribution functions

We consider the kinetic equations for distribution functions $f_{cij}(\mathbf{r}, \mathbf{u}_c, t)$ for every chemical species c , vibrational i and rotational energy level j over the velocities \mathbf{u}_c , the spatial and temporal coordinates [3]

$$\frac{\partial f_{cij}}{\partial t} + \mathbf{u}_c \frac{\partial f_{cij}}{\partial \mathbf{r}} = \frac{1}{\varepsilon} J_{cij}^{rap} + J_{cij}^{sl}. \quad (4)$$

Here J_{cij}^{rap} , J_{cij}^{sl} are the collision operators of rapid and slow processes, $\varepsilon = \tau_{rap}/\tau_{sl}$ is the small parameter, τ_{rap} , τ_{sl} are the average times between the frequent and rare collisions, respectively. Under Condition Eq. (1) the collision operators in Eq. (4)

can be written in the form:

$$J_{cij}^{rap} = J_{cij}^{el} + J_{cij}^r,$$

$$J_{cij}^{sl} = J_{cij}^{vibr} + J_{cij}^{react},$$

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 expression for J_{cij}^{vibr} has such a form

$$J_{cij}^{vibr} = \sum_{dkli'j'k'l'} \int \left(f_{ci'j'} f_{dk'l'} \frac{s_{ij}^c s_{kl}^d}{s_{i'j'}^c s_{k'l'}^d} - f_{cij} f_{dkl} \right) g \sigma_{cd,ijkl}^{i'j'k'l'} d^2\Omega d\mathbf{u}_d, \tag{5}$$

where $\sigma_{cd,ijkl}^{i'j'k'l'}$ is the inelastic collision cross-section of the molecules of chemical species c and d , respectively, at the i th and k th vibrational levels and j th and l th rotational ones, i' , j' , k' , l' are the numbers of the energy levels after the collision, \mathbf{g} is the relative velocity, $d^2\Omega$ is the solid angle in which the relative velocity after the collision can appear, s_{ij}^c is the statistical weight. It should be noted that the distribution functions and the cross-sections are averaged over the internal momentum orientations [10,11]. The expressions for J_{cij}^{el} and J_{cij}^r can be easily written using Eq. (5) Ref. [3].

The collision integral J_{cij}^{vibr} expresses the VV_1 and VV_2 exchanges of vibrational energy within every mode and between different modes and the rotational–vibrational–translational energy exchanges:

$$J_{cij}^{vibr} = J_{cij}^{VV_1} + J_{cij}^{VV_2} + J_{cij}^{RVT}.$$

The collision integral J_{cij}^{react} describes binary collisions (chemical exchange reactions) and collisions with dissociation and recombination

$$J_{cij}^{react} = J_{cij}^{react(2\leftrightarrow 2)} + J_{cij}^{react(2\leftrightarrow 3)}.$$

The collision operator $J_{cij}^{react(2\leftrightarrow 2)}$ has the form [3,7]:

$$J_{cij}^{react(2\leftrightarrow 2)} = \sum_{dc'd'kl'i'j'k'l'} \int \left(f_{c'i'j'} f_{d'k'l'} \frac{s_{ij}^c s_{kl}^d}{s_{i'j'}^c s_{k'l'}^d} \left(\frac{m_c m_d}{m_{c'} m_{d'}} \right)^3 - f_{cij} f_{dkl} \right) \times g \sigma_{cd,ijkl}^{c'd',i'j'k'l'} d^2\Omega d\mathbf{u}_d, \tag{6}$$

m_c is the molecular mass, $\sigma_{cd,ijkl}^{c'd',i'j'k'l'}$ is the cross-section of the chemically active collision. The expressions for $J_{cij}^{react(2\leftrightarrow 3)}$ are given in Ref. [12–15].

For the solution of Eq. (4) the generalized Chapman–Enskog method is used, so 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 zeroth approach gives the following relation:

$$J_{cij}^{el}(f^{(0)}, f^{(0)}) + J_{cij}^r(f^{(0)}, f^{(0)}) = 0$$

It traditionally follows that $\ln f_{cij}^{(0)} / s_j^{ci}$ (s_j^{ci} is the rotational statistical weight) has to be a linear combination of the summational invariants of the most frequent collisions

(eigenfunctions of the linearized collision operator of rapid processes J_{cij}^{rap}). The invariants of any collision are: $\psi_{cij}^{(1)} = 1$, $\psi_{cij}^{(v+1)} = m_c u_{cv}$ ($v = 1, 2, 3$ are the spatial indices), $\psi_{cij}^{(5)} = m_c u_c^2 / 2 + \varepsilon_j^{ci}$ (ε_j^{ci} is the rotational energy of the molecule of chemical species c at the i th vibrational level). Besides that there exist additional invariants of the most frequent collisions. In the conditions of slow vibrational exchange and chemical reactions, any variable a_{ci} independent of the velocity and the rotational energy level j and depending arbitrary on i and c is conserved: $\psi_{cij}^{(\lambda+5)} = a_{ci}$, ($\lambda = 1, \dots, N$, where $N = \sum_{ci} 1$). The conservation of the number of particles is a consequence of the conservation of $\psi_{cij}^{(\lambda+5)}$ ($\lambda = 1, \dots, N$). Therefore, there exist $N + 4$ independent collision invariants in this case. Hence, $f_{cij}^{(0)}$ is obtained in such a form [3]

$$f_{cij}^{(0)} = \left(\frac{m_c}{2\pi kT} \right)^{3/2} s_j^{ci} \frac{n_{ci}}{Z_{ci}^{rot}(T)} \exp \left(-\frac{m_c c_c^2}{2kT} - \frac{\varepsilon_j^{ci}}{kT} \right). \quad (7)$$

Here n_{ci} is the number density of the molecules of c species at the i th vibrational level, 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 normalization conditions may be classically written in such a form

$$\begin{aligned} \sum_j \int f_{cij} d\mathbf{u}_c &= \sum_j \int f_{cij}^{(0)} d\mathbf{u}_c = n_{ci}, \quad c = 1, 2, \dots, L, \quad i = 0, 1, \dots, L_c, \\ \sum_{cij} m_c \int \mathbf{u}_c f_{cij} d\mathbf{u}_c &= \sum_{cij} m_c \int \mathbf{u}_c f_{cij}^{(0)} d\mathbf{u}_c = \rho \mathbf{v}, \\ \sum_{cij} \int \left(\frac{m_c c_c^2}{2} + \varepsilon_i^c + \varepsilon_j^{ci} + \varepsilon^c \right) f_{cij} d\mathbf{u}_c &= \sum_{cij} \int \left(\frac{m_c c_c^2}{2} + \varepsilon_i^c + \varepsilon_j^{ci} + \varepsilon^c \right) f_{cij}^{(0)} d\mathbf{u}_c \\ &= \frac{3}{2} n kT + \rho E_r + \rho E_v + \rho E_f. \end{aligned} \quad (8)$$

Here $n = \sum_{ci} n_{ci}$ is the total number of particles, $\rho = \sum_c m_c \sum_i n_{ci}$ 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 ,

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

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

The nonequilibrium distribution functions, Eq. (7), are defined in terms of the macroparameters $n_{ci}(\mathbf{r}, t)$, $\mathbf{v}(\mathbf{r}, t)$, $T(\mathbf{r}, t)$. The corresponding macroscopic equations are

written as follows:

$$\frac{dn_{ci}}{dt} + n_{ci} \nabla \cdot \mathbf{v} + \nabla \cdot (n_{ci} \mathbf{V}_{ci}) = R_{ci}, \quad c = 1, \dots, L, \quad i = 0, 1, \dots \tag{9}$$

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \mathbf{P} = 0, \tag{10}$$

$$\rho \frac{dU}{dt} + \nabla \cdot \mathbf{q} + \mathbf{P} : \nabla \mathbf{v} = 0. \tag{11}$$

Here U is the total energy per unit mass:

$$\rho U = \frac{3}{2}nkT + \rho E_r + \rho E_v + \rho E_f.$$

The right-hand sides of the equations for n_{ci} are defined as

$$R_{ci} = \sum_j \int J_{cij}^{sl} d\mathbf{u}_c = R_{ci}^{vibr} + R_{ci}^{react}, \tag{12}$$

\mathbf{V}_{ci} is the diffusion velocity of c component molecules at the i th level

$$n_{ci} \mathbf{V}_{ci} = \sum_j \int \mathbf{c}_c f_{cij} d\mathbf{u}_c,$$

\mathbf{P} is the tensor of pressure

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

\mathbf{q} is the heat flux

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

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

$$R_{ci}^{(0)} = \sum_j \int J_{cij}^{sl(0)} d\mathbf{u}_c,$$

$J_{cij}^{sl(0)}$ corresponds to the collision operator of slow processes after the substitution of the zeroth-order distribution function $f_{cij}^{(0)}$.

The expressions for R_{ci}^{vibr} and R_{ci}^{react} are given in Ref. [3,16] in the zeroth- and the first-order approximation. In the first-order approximation $R_{ci}^{(1)}$ contains terms proportional to $\nabla \cdot \mathbf{v}$.

2.2. First-order distribution functions and transport terms

For the first-order distribution functions $f_{cij}^{(1)} = f_{cij}^{(0)}\phi_{cij}$ the linear integral equations follow from Eq. (4):

$$-\sum_{dk} n_{ci}n_{dk}I_{cidk}(\phi) = \frac{df_{cij}^{(0)}}{dt} - J_{cij}^{sl(0)}. \tag{13}$$

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

$$I_{cidk}(\phi) = \frac{1}{n_{ci}n_{dk}} \sum_{ij'l'} \int f_{cij}^{(0)} f_{dkl}^{(0)} (\phi_{cij} + \phi_{dkl} - \phi_{cij'} - \phi_{dkl'}) g\sigma_{cidk,jl}^{j'l'} d^2\Omega d\mathbf{u}_d.$$

Using the peculiar velocities \mathbf{c}_c and taking into account Eq. (7) the following expression is obtained for $df_{cij}^{(0)}/dt$:

$$\begin{aligned} \frac{df_{cij}^{(0)}}{dt} = f_{cij}^{(0)} & \left\{ \left(\frac{m_c c_c^2}{2kT} - \frac{5}{2} + \left[\frac{\varepsilon_j^{ci}}{kT} \right]'_r \right) \mathbf{c}_c \cdot \nabla \ln T \right. \\ & + \frac{n}{n_{ci}} \mathbf{c}_c \cdot \mathbf{d}_{ci} + \frac{m_c}{kT} (\mathbf{c}_c \mathbf{c}_c - \frac{1}{3} c_c^2 \mathbf{I}) : \nabla \mathbf{v} \\ & + \left(\frac{m_c c_c^2}{3kT} - 1 - \frac{p}{\rho T (c_{tr} + c_{rot})} \left(\frac{m_c c_c^2}{2kT} - \frac{3}{2} + \left[\frac{\varepsilon_j^{ci}}{kT} \right]'_r \right) \right) \nabla \cdot \mathbf{v} + \frac{R_{ci}^{(0)}}{n_{ci}} \\ & \left. - \frac{\sum_{ci} R_{ci}^{(0)} (3/2kT \langle \varepsilon_j^{ci} \rangle_r + \varepsilon_i^c + \varepsilon^c)}{\rho T (c_{tr} + c_{rot})} \left(\frac{m_c c_c^2}{2kT} - \frac{3}{2} + \left[\frac{\varepsilon_j^{ci}}{kT} \right]'_r \right) \right\}. \tag{14} \end{aligned}$$

Here the diffusion driving forces \mathbf{d}_{ci} are defined as follows:

$$\mathbf{d}_{ci} = \nabla \left(\frac{n_{ci}}{n} \right) + \left(\frac{n_{ci}}{n} - \frac{\rho_{ci}}{\rho} \right) \nabla \ln p, \tag{15}$$

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

$$c_{tr} = \frac{3k \sum_{ci} n_{ci}}{2 \sum_{ci} m_c n_{ci}}, \quad c_{rot} = \frac{\partial E_r}{\partial T},$$

and the following notation is used

$$[\zeta_{ij}]'_r = \zeta_{ij} - \langle \zeta_{ij} \rangle_r,$$

$\langle \zeta_{ij} \rangle_r$ is the averaged value of ζ_{ij} over a rotational spectrum

$$\langle \zeta_{ij} \rangle_r = \frac{\sum_j s_j^{ci} \zeta_{ij} \exp(-\varepsilon_j^{ci}/kT)}{\sum_j s_j^{ci} \exp(-\varepsilon_j^{ci}/kT)}.$$

Proceeding from Eq. (14) the solution of Eq. (13) may be found under the form:

$$f_{cij}^{(1)} = f_{cij}^{(0)} \left(-\frac{1}{n} \mathbf{A}_{cij} \cdot \nabla \ln T - \frac{1}{n} \sum_{dk} \mathbf{D}_{cij}^{dk} \cdot \mathbf{d}_{dk} - \frac{1}{n} \mathbf{B}_{cij} : \nabla \mathbf{v} - \frac{1}{n} F_{cij} \nabla \cdot \mathbf{v} - \frac{1}{n} G_{cij} \right). \tag{16}$$

The functions \mathbf{A}_{cij} , \mathbf{B}_{cij} , \mathbf{D}_{cij}^{dk} , F_{cij} and G_{cij} depend on the microscopic velocities \mathbf{u}_c and macroparameters $n_{ci}(\mathbf{r}, t)$, $\mathbf{v}(\mathbf{r}, t)$, $T(\mathbf{r}, t)$, and can be obtained from the linear integral equations which follow from Eq. (13) after the substitution of Eq. (16) into Eq. (13) and identifying the coefficients at the gradients of the same macroparameters. The following additional constraints on the functions $\mathbf{A}_{cij} = A_{cij}(\mathbf{c}_c)\mathbf{c}_c$, $\mathbf{D}_{cij}^{dk} = D_{cij}^{dk}(\mathbf{c}_c)\mathbf{c}_c$, F_{cij} , G_{cij} can be obtained from the normalization conditions, Eq. (8):

$$\sum_{cij} m_c \int f_{cij}^{(0)} A_{cij} c_c^2 d\mathbf{u}_c = 0, \tag{17}$$

$$\sum_{cij} m_c \int f_{cij}^{(0)} D_{cij}^{dk} c_c^2 d\mathbf{u}_c = 0, \quad d = 1, \dots, L, \quad k = 0, 1, \dots, L_d, \tag{18}$$

$$\sum_j \int f_{cij}^{(0)} F_{cij} d\mathbf{u}_c = 0, \quad c = 1, \dots, L, \quad i = 0, 1, \dots, L_c, \tag{19}$$

$$\sum_j \int f_{cij}^{(0)} G_{cij} d\mathbf{u}_c = 0, \quad c = 1, \dots, L, \quad i = 0, 1, \dots, L_c, \tag{20}$$

$$\sum_{cij} \int f_{cij}^{(0)} \left(\frac{m_c c_c^2}{2} + \varepsilon_j^{ci} + \varepsilon_i^c \right) F_{cij} d\mathbf{u}_c = 0, \tag{21}$$

$$\sum_{cij} \int f_{cij}^{(0)} \left(\frac{m_c c_c^2}{2} + \varepsilon_j^{ci} + \varepsilon_i^c \right) G_{cij} d\mathbf{u}_c = 0. \tag{22}$$

It is obvious that the diffusion driving forces Eq. (15) are not linearly independent because $\sum_{ci} \mathbf{d}_{ci} = 0$ due to the relations $\sum_{ci} n_{ci}/n = 1$ and $\sum_{ci} \rho_{ci}/\rho = 1$. Similar to Ref. [17] the additional condition for \mathbf{D}_{cij}^{dk} is easily obtained in the form:

$$\sum_{dk} \frac{\rho_{dk}}{\rho} \mathbf{D}_{cij}^{dk} = 0. \tag{23}$$

Now the functions \mathbf{A}_{cij} , \mathbf{D}_{cij}^{dk} , \mathbf{B}_{cij} , F_{cij} and G_{cij} are uniquely determined by the corresponding integral equations and constraints Eqs. (17)–(23).

The first-order distribution functions Eq. (16) provide the following expressions for the pressure tensor:

$$\mathbf{P} = (p - p_{rel})\mathbf{I} - 2\mu\mathbf{S} - \eta\nabla \cdot \mathbf{v}\mathbf{I}. \tag{24}$$

Here μ , η are the shear and bulk viscosity coefficients, p_{rel} is the relaxation pressure

$$\mu = \frac{kT}{10} [\mathbf{B}, \mathbf{B}], \quad \eta = kT[F, F], \quad p_{rel} = kT[F, G], \tag{25}$$

the bracket integral $[A, B]$ is defined by analogy with Ref. [17] as

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

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 diffusion velocity in the first approximation may be written as follows:

$$\mathbf{V}_{ci} = - \sum_{dk} D_{cidk} \mathbf{d}_{dk} - D_{Tci} \nabla \ln T, \quad (26)$$

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

$$D_{cidk} = \frac{1}{3n} [\mathbf{D}^{ci}, \mathbf{D}^{dk}] \quad D_{Tci} = \frac{1}{3n} [\mathbf{D}^{ci}, \mathbf{A}]. \quad (27)$$

The expression for the total heat flux has the next form:

$$\mathbf{q} = -\lambda' \nabla T - p \sum_{ci} D_{Tci} \mathbf{d}_{ci} + \sum_{ci} \left(\frac{5}{2} kT + \langle \varepsilon_j^{ci} \rangle_r + \varepsilon_i^c + \varepsilon^c \right) n_{ci} \mathbf{V}_{ci}, \quad (28)$$

where

$$\lambda' = \lambda_t + \lambda_r = \frac{k}{3} [\mathbf{A}, \mathbf{A}] \quad (29)$$

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.

Thus, at this stage we obtain the momentum and energy conservation equations and the equations for the populations of vibrational and chemical species. In the zeroth approximation the equations for n_{ci} are widely used in the investigation of vibrational and dissociation coupling [18–20]. However, in the case of multi-component vibrationally excited mixtures, such a detailed description becomes strongly difficult because of the large number of equations for n_{ci} , and the lack of data concerning the microscopic rate constants for vibrational–chemical reactions. A practical implementation of Eqs. (9)–(11) in the first approach for a multi-component mixture of viscous gases requires

the modeling of the kinetic coefficients Eq. (25), (27) and (29) for all energy levels and chemical components. Unfortunately, an experimental approach does not seem to be easy.

Therefore, the derivation of an adequate multi-temperature model and its validation has a great importance mainly for multi-component mixtures.

3. Generalized multi-temperature approach

3.1. Zeroth order approximation

The model developed in the previous section and based on the detailed description of level vibrational and chemical kinetics can be simplified due to the reduction of the number of macroparameters. It is possible in the case when there exist some additional rapid processes with additional summational invariants of the most frequent collisions. In vibrationally excited gases the various vibrational energy exchanges have different rates. Actually, it is known [21,22] that the VV_1 exchange of vibrational quanta within every vibrational mode occurs more often than the exchange between different modes. The collisions leading to the VV_1 exchange may be considered as the most frequent, together with the ones involving translational and rotational energy transfer.

Therefore, the operator J_{cij}^{rap} includes the collision integral $J_{cij}^{VV_1}$ with the exchange of vibrational quantum within every mode

$$J_{cij}^{rap} = J_{cij}^{el} + J_{cij}^r + J_{cij}^{VV_1} .$$

Besides the common summational invariants $\psi_{cij}^{(\lambda)}$, ($\lambda = 1, 2, \dots, 5$) there exist additional summational invariants of the most frequent collisions: $\psi_{cij}^{(\mu+5)} = i_c$ ($\mu = 1, \dots, L_{mol}$, L_{mol} is the number of molecular species), i_c is the number of vibrational quanta of the c th species, $\psi_{cij}^{(v+L_{mol}+5)} = a_c$ ($v = 1, \dots, L$), a_c is any variable independent of rotational and vibrational energy levels and depending arbitrarily on the chemical species. Invariants $\psi_{cij}^{(\mu+5)}$ ($\mu = 1, \dots, L_{mol}$) are connected with the conservation of the number of vibrational quanta of every molecular species, and $\psi_{cij}^{(v+L_{mol}+5)}$ ($v = 1, \dots, L$) appear because chemical reactions are frozen in the frequent collisions. There are $L_{mol} + L + 4$ independent collision invariants in this case because the conservation of the number of particles follows from the conservation of invariants $\psi_{cij}^{(v+L_{mol}+5)}$ ($v = 1, \dots, L$). We consider here the mixture of diatomic molecules where every molecule contains one vibrational mode. Proceeding from the set of collision invariants the zeroth order distribution functions have such a form:

$$f_{cij}^{(0)} = \frac{n_c}{Z_c} s_{ij}^c \exp \left(-\frac{m_c c_c^2}{2kT} - \frac{\epsilon_j^{ci}}{kT} - \frac{\epsilon_i^c}{kT} - \vartheta_c i_c \right) \quad (30)$$

and are expressed in terms of the macroparameters n_c , ϑ_c , T , \mathbf{v} . Here n_c is a number density of the molecules of c species, Z_c is the total partition function for c species,

ϑ_c is defined in terms of the total number of vibrational quantum W_c of c th component

$$\rho_c W_c = \sum_{ij} i \int f_{cij} d\mathbf{u}_c. \quad (31)$$

(Hereafter, the index c at i_c is omitted for the simplicity of designations.) Similarly to a one-component gas [21], it is possible to introduce the temperature of the first vibrational level for c species T_1^c as follows:

$$\vartheta_c = \frac{\tilde{\varepsilon}_1^c}{k} \left(\frac{1}{T_1^c} - \frac{1}{T} \right), \quad \tilde{\varepsilon}_1^c = \varepsilon_1^c - \varepsilon_0^c.$$

Vibrational and rotational energy spectra are simulated, respectively, as an anharmonic oscillator and a rigid rotator [23]. Then $Z_c = Z_c^{tr} Z_c^{rot} Z_c^{vibr}$, the vibrational partition functions Z_c^{vibr} are expressed as follows:

$$Z_c^{vibr} = Z_c^{vibr}(T, T_1^c) = \sum_i s_i^c \exp \left(-\frac{\varepsilon_i^c - i\tilde{\varepsilon}_1^c}{kT} - \frac{i\tilde{\varepsilon}_1^c}{kT_1^c} \right).$$

The set of normalization conditions has the following form:

$$\begin{aligned} \sum_{ij} \int f_{cij} d\mathbf{u}_c &= \sum_{ij} \int f_{cij}^{(0)} d\mathbf{u}_c = n_c, \quad c = 1, 2, \dots, L, \\ \sum_{cij} m_c \int \mathbf{u}_c f_{cij} d\mathbf{u}_c &= \sum_{cij} m_c \int \mathbf{u}_c f_{cij}^{(0)} d\mathbf{u}_c = \rho \mathbf{v}, \end{aligned} \quad (32)$$

$$\begin{aligned} \sum_{cij} \int \left(\frac{m_c c_c^2}{2} + \varepsilon_i^c + \varepsilon_j^c + \varepsilon^c \right) f_{cij} d\mathbf{u}_c &= \sum_{cij} \int \left(\frac{m_c c_c^2}{2} + \varepsilon_i^c + \varepsilon_j^c + \varepsilon^c \right) f_{cij}^{(0)} d\mathbf{u}_c \\ &= \frac{3}{2} n k T + \rho E_r + \sum_c \rho_c E_v^c(T, T_1^c) + \rho E_f, \end{aligned}$$

$$\sum_{ij} i \int f_{cij} d\mathbf{u}_c = \sum_{ij} i \int f_{cij}^{(0)} d\mathbf{u}_c = \rho_c W_c, \quad c = 1, 2, \dots, L_{mol}.$$

Proceeding from Eq. (30) the level populations can be expressed as

$$n_{ci} = \frac{n_c}{Z_c^{vibr}(T, T_1^c)} s_i^c \exp \left(-\frac{\varepsilon_i^c - i\tilde{\varepsilon}_1^c}{kT} - \frac{i\tilde{\varepsilon}_1^c}{kT_1^c} \right). \quad (33)$$

In fact Eq. (33) describes the Treanor distribution [21] in a multicomponent mixture. It should be pointed out that the Treanor distribution is valid only at the levels $i_c \leq i_{c*}$, where i_{c*} corresponds to the minimum of the function n_{ci} over i for every mode because the additional summational invariant $\psi_{cij} = i_c$ exists only at the levels $i_c \leq i_{c*}$. The magnitude of i_{c*} may be easily found from the equation

$$\left| \frac{\partial n_{ci}}{\partial i} \right|_{i_{c*}} = 0$$

and equals [22]

$$i_{c*} = \frac{\tilde{\epsilon}_1^c}{2\alpha_c \hbar \nu_c} \frac{T}{T_1^c} + \frac{1}{2}.$$

Here \hbar is the Planck constant, ν_c is the frequency of molecular vibrations, α_c is the anharmonism parameter.

At higher temperatures when $T \gg T_1^c$ the level i_{c*} appears to be close to the last vibrational level $i_c = L_c$, which can be found by equating the vibrational energy $\epsilon_{L_c}^c$ to the energy of dissociation D_c . Therefore, in the case $T \gg T_1^c$ the Treanor distribution is valid practically up to the higher levels.

For strongly vibrationally excited gases with $T_1^c \gg T$ the refinement of the distributions Eq. (30), and Eq. (33) is considered in Refs. [24,25].

If the anharmonic effects are negligible, $\epsilon_i^c = \epsilon_0^c + i\tilde{\epsilon}_1^c$, the distribution expressed in Eq. (33) becomes

$$n_{ci} = \frac{n_c}{Z_c^{vibr}} s_i^c \exp\left(-\frac{\epsilon_i^c}{kT_1^c}\right) \tag{34}$$

with

$$Z_c^{vibr} = Z_c^{vibr}(T_1^c) = \sum_i s_i^c \exp\left(-\frac{\epsilon_i^c}{kT_1^c}\right),$$

which is the multi-temperature Boltzmann distribution with the vibrational temperatures of components $T_v^c = T_1^c$.

In the equilibrium case ($T = T_1^c$) from Eq. (33) we obtain the one-temperature Boltzmann distribution:

$$n_{ci} = \frac{n_c}{Z_c^{vibr}} s_i^c \exp\left(-\frac{\epsilon_i^c}{kT}\right), \tag{35}$$

$$Z_c^{vibr} = Z_c^{vibr}(T) = \sum_i s_i^c \exp\left(-\frac{\epsilon_i^c}{kT}\right).$$

3.2. Macroscopic equations

The nonequilibrium distribution functions, Eq. (30) are determined in terms of the macroparameters: $n_c(\mathbf{r}, t)$, $\mathbf{v}(\mathbf{r}, t)$, $T(\mathbf{r}, t)$, $T_1^c(\mathbf{r}, t)$, which are governed by the macroscopic equations:

$$\frac{dn_c}{dt} + n_c \nabla \cdot \mathbf{v} + \nabla \cdot (n_c \mathbf{V}_c) = R_c^{react}, \quad c = 1, \dots, L, \tag{36}$$

where

$$R_c^{react} = \sum_{ij} \int J_{cij}^{react} d\mathbf{u}_c, \quad n_c \mathbf{V}_c = \sum_{ij} \int \mathbf{c}_c f_{cij} d\mathbf{u}_c.$$

The momentum and total energy conservation equations coincide with Eqs. (10) and (11). In this case the vibrational energy is a function of the temperatures T and T_1^c :

$$\rho E_v = \sum_c \rho_c E_v^c(T, T_1^c) = \sum_{ci} \varepsilon_i^c n_{ci}(T, T_1^c).$$

The additional relaxation equations for the number of vibrational quanta W_c of the c th species take the form

$$\rho_c \frac{dW_c}{dt} + \nabla \cdot \mathbf{q}_w^c = R_c^w - W_c m_c R_c^{\text{react}} + W_c \nabla \cdot (\rho_c \mathbf{V}_c), \quad c = 1, 2, \dots, L_{\text{mol}}, \quad (37)$$

$$R_c^w = \sum_{ij} i \int J_{cij}^{sl} d\mathbf{u}_c, \quad \mathbf{q}_w^c = \sum_{ij} i \int \mathbf{c}_c f_{cij} d\mathbf{u}_c,$$

\mathbf{q}_w^c is the flux of vibrational quanta.

Thus, the equations for the number densities of chemical species, momentum and energy conservation equations and relaxation equations for the number of vibrational quanta of every component are obtained.

In the zeroth approximation $\mathbf{q}_w^{c(0)} = 0$, $\mathbf{V}_c^{(0)} = 0$, $\mathbf{P}^{(0)} = p\mathbf{I}$,

$$R_c^{w(0)} = \sum_{ij} \int i J_{cij}^{sl(0)} d\mathbf{u}_c,$$

$$R_c^{\text{react}(0)} = \sum_{ij} \int J_{cij}^{\text{react}(0)} d\mathbf{u}_c.$$

3.3. First-order solution

In the generalized multi-temperature approach the linear integral equations for the first order distribution functions take the next form

$$-\sum_d n_c n_d I_{cd}(\phi) = \frac{d f_{cij}^{(0)}}{dt} - J_{cij}^{sl(0)} \quad (38)$$

with the following linearized operator of the rapid processes:

$$I_{cd}(\phi) = \frac{1}{n_c n_d} \sum_{ijkl'j'k'l'} \int f_{cij}^{(0)} f_{dkl}^{(0)} (\phi_{cij} + \phi_{dkl} - \phi_{ci'j'} - \phi_{dk'l'}) g \sigma_{cd,ijkl}^{i'j'k'l'} d^2 \Omega d\mathbf{u}_d.$$

The expression (Eq. (14)) of $d f_{cij}^{(0)}/dt$ becomes

$$\begin{aligned} \frac{d f_{cij}^{(0)}}{dt} = f_{cij}^{(0)} & \left\{ \left(\frac{m_c c_c^2}{2kT} - \frac{5}{2} + \left[\frac{\varepsilon_j^c}{kT} \right]_r + \left[\frac{\varepsilon_i^c - i\tilde{\varepsilon}_1^c}{kT} \right]_v \right) \mathbf{c}_c \cdot \nabla \ln T \right. \\ & \left. + \left[\frac{i\tilde{\varepsilon}_1^c}{kT_1^c} \right]_v \mathbf{c}_c \cdot \nabla \ln T_1^c + \frac{n}{n_c} \mathbf{c}_c \cdot \mathbf{d}_c + \frac{m_c}{kT} \left(\mathbf{c}_c \mathbf{c}_c - \frac{1}{3} c_c^2 \mathbf{I} \right) : \nabla \mathbf{v} \right\} \end{aligned}$$

$$\begin{aligned}
 & + \left(\frac{m_c c_c^2}{2kT} - \frac{3}{2} + \left[\frac{\varepsilon_j^c}{kT} \right]_r + \left[\frac{\varepsilon_i^c - i\tilde{\varepsilon}_1^c}{kT} \right]_v \right) \frac{1}{T} \frac{dT}{dt} \\
 & + \left\{ \left[\frac{i\tilde{\varepsilon}_1^c}{kT_1^c} \right]_v \frac{1}{T_1^c} \frac{dT_1^c}{dt} + \left(\frac{m_c c_c^2}{3kT} - 1 \right) \nabla \cdot \mathbf{v} + \frac{R_c^{react(0)}}{n_c} \right\}. \tag{39}
 \end{aligned}$$

Here

$$\mathbf{d}_c = \nabla \left(\frac{n_c}{n} \right) + \left(\frac{n_c}{n} - \frac{\rho_c}{\rho} \right) \nabla \ln p,$$

Notation $[\zeta_i]_v'$ corresponds to $\zeta_i - \langle \zeta_i \rangle_v$. The averaging over vibrational and rotational spectra in this case is performed as follows:

$$\langle \zeta_i \rangle_v = \frac{\sum_i s_i^c \zeta_i \exp(-(\varepsilon_i^c - i\tilde{\varepsilon}_1^c)/kT - (i\tilde{\varepsilon}_1^c/kT_1^c))}{\sum_i s_i^c \exp(-(\varepsilon_i^c - i\tilde{\varepsilon}_1^c)/kT - (i\tilde{\varepsilon}_1^c/kT_1^c))}, \quad \langle \zeta_j \rangle_r = \frac{\sum_j s_j^c \zeta_j \exp(-\varepsilon_j^c/kT)}{\sum_j s_j^c \exp(-\varepsilon_j^c/kT)}$$

The system of the equations for the determination of dT/dt and dT_1^c/dt follows from Eq. (11) and Eq. (37):

$$\rho c_u \frac{dT}{dt} + \sum_c \rho_c c_v^T \frac{dT_1^c}{dt} = -p \nabla \cdot \mathbf{v} - \sum_c R_c^{react(0)} U_c, \tag{40}$$

$$\rho_c c_{w,c}^T \frac{dT}{dt} + \rho_c c_{w,c}^T \frac{dT_1^c}{dt} = R_c^{e(0)}, \quad c = 1, \dots, L_{mol}. \tag{41}$$

where

$$U_c = \frac{3}{2}kT + \langle \varepsilon_j \rangle_r + \langle \varepsilon_i \rangle_v + \varepsilon^c, \quad R_c^{e(0)} = \tilde{\varepsilon}_1^c R_c^{w(0)} - R_c^{react(0)} \langle i\tilde{\varepsilon}_1^c \rangle_v.$$

The following notations are used for the modified specific heats:

$$c_u = c_{tr} + c_{rot} + c_v^T, \quad c_v^T = \frac{\partial E_v}{\partial T} = \frac{1}{\rho} \sum_c \rho_c c_{v,c}^T = \frac{1}{\rho} \sum_c \rho_c \frac{\partial E_v^c}{\partial T},$$

$$c_{v,c}^T = \frac{\partial E_v^c}{\partial T_1^c}, \quad c_{w,c}^T = \frac{\partial(\tilde{\varepsilon}_1^c W_c)}{\partial T}, \quad c_{w,c}^T = \frac{\partial(\tilde{\varepsilon}_1^c W_c)}{\partial T_1^c}.$$

The derivatives dT/dt , dT_1^c/dt can be found from Eqs. (40) and (41) in the explicit form

$$\frac{dT}{dt} = \frac{-p \nabla \cdot \mathbf{v} - \sum_c R_c^{react(0)} U_c - \sum_c (c_v^T / c_{w,c}^T) R_c^{e(0)}}{\rho c_u - \sum_c \rho_c c_{w,c}^T (c_v^T / c_{w,c}^T)},$$

$$\frac{dT_1^c}{dt} = \frac{\rho_c c_{w,c}^T (p \nabla \cdot \mathbf{v} + \sum_c R_c^{react(0)} U_c) + \rho_c c_u R_c^{e(0)} + \rho_c c_{w,c}^T - R_c^{e(0)} \sum_{b \neq c} \rho_b c_{w,b}^T (c_v^T / c_{w,b}^T)}{\rho_c c_{w,c}^T \left(\rho c_u - \sum_b \rho_b c_{w,b}^T (c_v^T / c_{w,b}^T) \right)}$$

$$c = 1, 2, \dots, L_{mol}.$$

The positiveness of the determinant of the system (40) and (41) is evident for the harmonic oscillator model, when $c_{w,c}^T = c_v^T = 0$. When ε_i^c is simulated by an anharmonic

oscillator, the positiveness of the determinant is proved starting from the properties of the modified specific heats introduced above. It is seen that the derivatives dT/dt , dT_1^c/dt are linear functions of $\nabla \cdot \mathbf{v}$, $R_c^{w(0)}$ and $R_c^{react(0)}$.

Using the solution of the system (40) and (41) and Eq. (39), the first-order distribution functions are found under the form

$$f_{cij}^{(1)} = f_{cij}^{(0)} \left(-\frac{1}{n} \mathbf{A}_{cij} \cdot \nabla \ln T - \frac{1}{n} \sum_d \mathbf{A}_{cij}^{d(1)} \cdot \nabla \ln T_1^d - \frac{1}{n} \sum_d \mathbf{D}_{cij}^d \cdot \mathbf{d}_d - \frac{1}{n} \mathbf{B}_{cij} : \nabla \mathbf{v} - \frac{1}{n} F_{cij} \nabla \cdot \mathbf{v} - \frac{1}{n} G_{cij} \right). \quad (42)$$

The equations for \mathbf{A}_{cij} , $\mathbf{A}_{cij}^{d(1)}$, \mathbf{B}_{cij} , \mathbf{D}_{cij}^d , F_{cij} and G_{cij} are obtained substituting Eq. (39) into Eq. (38) and equalizing the coefficients of the gradients of the same macro-parameters.

The set of the normalization conditions, Eq. (32), gives the following additional constraints:

$$\sum_{cij} \int m_c f_{cij}^{(0)} A_{cij}^{d(1)} c_c^2 d\mathbf{u}_c = 0, \quad d = 1, \dots, L_{mol}, \quad (43)$$

$$\sum_{cij} m_c \int f_{cij}^{(0)} A_{cij} c_c^2 d\mathbf{u}_c = 0, \quad (44)$$

$$\sum_{cij} m_c \int f_{cij}^{(0)} D_{cij}^d c_c^2 d\mathbf{u}_c = 0, \quad d = 1, \dots, L, \quad (45)$$

$$\sum_{ij} \int f_{cij}^{(0)} F_{cij} d\mathbf{u}_c = 0, \quad c = 1, \dots, L, \quad (46)$$

$$\sum_{ij} \int f_{cij}^{(0)} G_{cij} d\mathbf{u}_c = 0, \quad c = 1, \dots, L, \quad (47)$$

$$\sum_{cij} \int f_{cij}^{(0)} \left(\frac{m_c c_c^2}{2} + \varepsilon_j^c + \varepsilon_i^c \right) F_{cij} d\mathbf{u}_c = 0, \quad (48)$$

$$\sum_{cij} \int f_{cij}^{(0)} \left(\frac{m_c c_c^2}{2} + \varepsilon_j^c + \varepsilon_i^c \right) G_{cij} d\mathbf{u}_c = 0, \quad (49)$$

$$\sum_{ij} i \int f_{cij}^{(0)} F_{cij} d\mathbf{u}_c = 0, \quad c = 1, \dots, L_{mol}, \quad (50)$$

$$\sum_{ij} i \int f_{cij}^{(0)} G_{cij} d\mathbf{u}_c = 0, \quad c = 1, \dots, L_{mol}. \quad (51)$$

The expression (Eq. (23)) in this case has the form:

$$\sum_d \frac{\rho_d}{\rho} \mathbf{D}_{cij}^d = 0. \quad (52)$$

3.4. Transport terms

Now, we consider the transport terms in Eq. (36), (37), (10) and (11) and write them in a generalized multi-temperature approach on the basis of Eq. (42). The expression for the pressure tensor coincides with Eq. (24) with the same definition of the corresponding transport coefficients Eq. (25). In the present case the bracket integrals $[A, B]$ are written in the form

$$[A, B] = \sum_{cd} \frac{n_c n_d}{n^2} ([A, B]_{cd}' + [A, B]_{cd}''), \tag{53}$$

where

$$\begin{aligned}
 [A, B]_{cd}' &= \frac{1}{2n_c n_d} \sum_{ijkl'j'k'l'} \int f_{cij}^{(0)} f_{dki}^{(0)} (B_{cij} - B_{ci'j'}) \\
 &\quad \times (A_{cij} - A_{ci'j'}) g \sigma_{cd,ijkl}^{i'j'k'l'} d^2 \Omega d\mathbf{u}_c d\mathbf{u}_d, \\
 [A, B]_{cd}'' &= \frac{1}{2n_c n_d} \sum_{ijkl'j'k'l'} \int f_{cij}^{(0)} f_{dki}^{(0)} (B_{cij} - B_{ci'j'}) \\
 &\quad \times (A_{dki} - A_{dk'l'}) g \sigma_{cd,ijkl}^{i'j'k'l'} d^2 \Omega d\mathbf{u}_c d\mathbf{u}_d.
 \end{aligned}$$

The linear integral equations for the functions F_{cij} and G_{cij} are determined by Eq. (39) and differ from those obtained in the level approach. Here the relaxation pressure p_{rel} and the bulk viscosity η are expressed as a sum of two terms

$$\eta = \eta_r + \eta_v, \quad p_{rel} = p_{rel}^r + p_{rel}^v,$$

which are related in this case to the inelastic TR and VV_1 energy exchanges inside every mode.

The diffusion velocity in the first order approximation takes the next form

$$\mathbf{V}_c = - \sum_d D_{cd} \mathbf{d}_d - D_{Tc} \nabla \ln T - \sum_d D_{Tc}^{d(1)} \nabla \ln T_1^d, \tag{54}$$

the diffusion and thermal diffusion coefficients, D_{cd} and D_{Tc} for chemical species become

$$D_{cd} = \frac{1}{3n} [\mathbf{D}^c, \mathbf{D}^d], \quad D_{Tc} = \frac{1}{3n} [\mathbf{D}^c, \mathbf{A}], \tag{55}$$

and the additional thermal diffusion coefficients $D_{Tc}^{d(1)}$ appear due to the temperature T_1^c gradients

$$D_{Tc}^{d(1)} = \frac{1}{3n} [\mathbf{D}^c, \mathbf{A}^{d(1)}]. \tag{56}$$

The heat flux and the flux of vibrational quanta contain the gradients of T , vibrational temperatures of the first level of every component T_1^c and gradients of n_c through \mathbf{d}_c

$$\mathbf{q} = - \left(\lambda' + \sum_c \lambda_{vt}^c \right) \nabla T - \sum_c \left(\lambda_{tw}^c \nabla T_1^c + \sum_d \lambda_{vw}^{cd} \nabla T_1^d \right) - p \sum_c D_{Tc} \mathbf{d}_c - p \sum_c \frac{T_1^c}{T} \sum_d D_{Tc}^{d(1)} \mathbf{d}_d + \sum_c \left(\frac{5}{2} kT + \langle \varepsilon_j^c \rangle_r + \langle \varepsilon_i^c \rangle_v + \varepsilon^c \right) n_c \mathbf{V}_c, \quad (57)$$

and

$$\tilde{\varepsilon}_1^c \mathbf{q}_w^c = - \lambda_{vt}^c \nabla T - \sum_d \lambda_{vw}^{cd} \nabla T_1^d - p \frac{T_1^c}{T} \tilde{\varepsilon}_1^c \sum_d D_{Tc}^{d(1)} \mathbf{d}_d. \quad (58)$$

The thermal conductivity coefficients are defined as follows:

$$\lambda' = \frac{k}{3} [\mathbf{A}, \mathbf{A}], \quad \lambda_{vt}^c = \frac{kT_1^c}{3T} [\mathbf{A}^{c(1)}, \mathbf{A}],$$

$$\lambda_{tw}^c = \frac{kT}{3T_1^c} [\mathbf{A}, \mathbf{A}^{c(1)}], \quad \lambda_{vw}^{cd} = \frac{k}{3} [\mathbf{A}^{d(1)}, \mathbf{A}^{c(1)}]. \quad (59)$$

In this case, the additional thermal conductivity coefficients appear due to the vibrational energy change in the rapid process. For harmonic oscillator $\lambda_{vt}^c = \lambda_{tw}^c = 0$.

It may be noticed that in the case when the vibrational quanta of various components do not differ considerably, the next condition

$$\tau_{VV_1} \sim \tau_{VV_2} \ll \tau_{TRV}$$

can take place. In this case the parameters ϑ_c in Eq. (30) are close to each other. Therefore, the temperatures are not independent and are determined by the condition following from the equality of the parameters ϑ_c . For harmonic oscillators a two-temperature distribution with $T_v^c = T_v$ takes place in that case. Such a suggestion of equal vibrational temperatures of different modes is convenient for a practical use, however, the range of its validity is limited. The empirical two-temperature models for reacting mixtures are given in Refs. [26,27].

3.4.1. Thermal conductivity, diffusion and thermal diffusion coefficients

In order to calculate the transport coefficients the integral equations for the functions \mathbf{A}_{cij} , $\mathbf{A}_{cij}^{d(1)}$, \mathbf{B}_{cij} , \mathbf{D}_{cij}^d , F_{cij} and G_{cij} following from Eq. (38) have to be solved.

The linear integral equations for the functions \mathbf{A}_{cij} , $\mathbf{A}_{cij}^{d(1)}$ and \mathbf{D}_{cij}^d defining the thermal conductivity, diffusion and thermal diffusion coefficients have the form:

$$\sum_d \frac{n_c n_d}{n^2} I_{cd}(\mathbf{A}) = \frac{1}{n} f_{cij}^{(0)} \left(\frac{m_c c_c^2}{2kT} - \frac{5}{2} + \left[\frac{\varepsilon_j^c}{kT} \right]'_r + \left[\frac{\varepsilon_i^c - i\tilde{\varepsilon}_1^c}{kT} \right]'_v \right) \mathbf{c}_c, \quad c = 1, \dots, L, \quad (60)$$

$$\sum_d \frac{n_c n_d}{n^2} I_{cd}(\mathbf{A}^{b(1)}) = \frac{1}{n} f_{cij}^{(0)} \left(\left[\frac{i\tilde{\epsilon}_1^c}{kT_1^c} \right]_v' \right) \mathbf{c}_c, \quad b, c = 1, \dots, L_{mol}, \quad (61)$$

$$\sum_d \frac{n_c n_d}{n^2} I_{cd}(\mathbf{D}^b) = \frac{1}{n_c} f_{cij}^{(0)} \left(\delta_{cb} - \frac{\rho_c}{\rho} \right) \mathbf{c}_c, \quad b, c = 1, \dots, L. \quad (62)$$

In order to solve these equations the functions are expanded into finite series of Sonine and Waldmann-Trübenbacher orthogonal polynomials. The following polynomial systems are used:

$$\mathbf{A}_{cij} = \frac{m_c \mathbf{c}_c}{2kT} \sum_{rpq} a_{c,rpq} S_{3/2}^{(r)} \left(\frac{m_c c_c^2}{2kT} \right) P_j^{(p)} \left(\frac{\epsilon_j^c}{kT} \right) P_i^{(q)} \left(\frac{\epsilon_i^c - i\tilde{\epsilon}_1^c}{kT} \right), \quad (63)$$

$$\mathbf{A}_{cij}^{d(1)} = \frac{m_c \mathbf{c}_c}{2kT} \sum_r a_{c,r}^{d(1)} P_i^{(r)} \left(\frac{i\tilde{\epsilon}_1^c}{kT_1^c} \right), \quad (64)$$

$$\mathbf{D}_{cij}^d = \frac{m_c \mathbf{c}_c}{2kT} \sum_r d_{c,r}^d S_{3/2}^{(r)} \left(\frac{m_c c_c^2}{2kT} \right). \quad (65)$$

The systems of linear algebraic equations for the expansion coefficients $a_{c,rpq}$, $a_{c,r}^{d(1)}$, $d_{c,r}^d$ are given in Appendix A.

Substituting the expansions (63)–(65) into Eq. (59), and using the normalizing conditions for the polynomials, one can express the thermal conductivity coefficients in terms of the expansion coefficients:

$$\lambda' = \sum_c \frac{5}{4} k \frac{n_c}{n} a_{c,100} + \sum_c \frac{k}{2} \frac{n_c}{n} c_{r,c} a_{c,010} + \sum_c \frac{k}{2} \frac{n_c}{n} c_{a,c}^T a_{c,001},$$

$$\lambda_{vt}^c = \frac{k}{2} \frac{n_c}{n} c_{w,c}^T a_{c,001}, \quad \lambda_{tv}^c = \frac{k}{2} \frac{n_c}{n} c_{a,c}^{T_1^c} a_{c,1}^{c(1)}, \quad \lambda_{vv}^{cd} = \delta_{cd} \lambda_{vv}^c, \quad \lambda_{vv}^c = \frac{k}{2} \frac{n_c}{n} c_{w,c}^{T_1^c} a_{c,1}^{c(1)},$$

where

$$c_{r,c} = \frac{\partial E_r^c}{\partial T}, \quad c_{a,c}^T = \frac{\partial (E_v^c - \tilde{\epsilon}_1^c W_c)}{\partial T}, \quad c_{a,c}^{T_1^c} = \frac{\partial (E_v^c - \tilde{\epsilon}_1^c W_c)}{\partial T_1^c},$$

$c_{r,c}$ is the dimensionless rotational specific heat (divided by the factor k/m_c), $c_{a,c}^T$ and $c_{a,c}^{T_1^c}$ are the modified dimensionless specific heats, connected with anharmonism of molecular vibrations. One can see that $c_{a,c}^T = c_{v,c}^T - c_{w,c}^T$ and $c_{a,c}^{T_1^c} = c_{v,c}^{T_1^c} - c_{w,c}^{T_1^c}$. Finally, one can express the thermal conductivity coefficients of the gradients of the temperatures T and T_1^c , respectively, in the following form

$$\lambda'_{trv} = \lambda' + \sum_c \lambda_{vt}^c = \sum_c \frac{5}{4} k \frac{n_c}{n} a_{c,100} + \sum_c \frac{k}{2} \frac{n_c}{n} c_{r,c} a_{c,010} + \sum_c \frac{k}{2} \frac{n_c}{n} c_{v,c}^T a_{c,001}, \quad (66)$$

$$\lambda_v^c = \lambda_{tv}^c + \lambda_{vv}^c = \frac{k}{2} \frac{n_c}{n} c_{v,c}^{T_1^c} a_{c,1}^{c(1)} \quad (67)$$

and write the heat flux as follows:

$$\mathbf{q} = -\lambda'_{rv} \nabla T - \sum_c \lambda_v^c \nabla T_1^c - p \sum_c D_{Tc} \mathbf{d}_c - p \sum_c \frac{T_1^c}{T} \sum_d D_{Tc}^{d(1)} \mathbf{d}_d + \sum_c \left(\frac{5}{2} kT + \langle \varepsilon_j \rangle_r + \langle \varepsilon_i \rangle_c + \varepsilon^c \right) n_c \mathbf{V}_c. \quad (68)$$

The nonequilibrium number densities of species n_c are found from the equations of chemical kinetics Eq. (36) which are considered together with Eqs. (10), (11) and (37).

It can be pointed out that the trial functions of the Waldmann–Trübenbacher polynomials in expansions, Eqs. (63) and (64) differ from those commonly used for the derivation of the transport coefficients [1,2,5,28]. They are chosen in accordance with the right-hand sides of Eqs. (60) and (61), which depend on $df_{cij}^{(0)}/dt$, and therefore, on the collision invariants of the collision operator of rapid processes J_{cij}^{rap} . In the case of weak deviation from the equilibrium using the Waldmann–Trübenbacher polynomials over the total internal energy gives a good convergence. The problem of choosing the trial functions was discussed before by several authors [29,30]. In the case of the Boltzmann nonequilibrium multi-temperature distribution $f_{cij}^{(0)}$ in a system of harmonic oscillators, it is reasonable to use the Waldmann–Trübenbacher polynomials over the rotational and vibrational energies [5]. In the case of strong vibrational nonequilibrium in a system of anharmonic oscillators and the non-Boltzmann distribution $f_{cij}^{(0)}$, the trial functions chosen in the present paper (see also Refs. [8,31]) permit to get more simple systems for the coefficients of the expansions and obtain the main expressions for the transport coefficients in terms of the first nonvanishing members of series, Eqs. (63) and (64). The thermal conductivity coefficients in this case have been calculated both on the basis of expansions, Eqs. (63) and (64) and the expansions similar to those suggested in Ref. [5]. In the first-order approximation of the Chapman–Enskog method these calculations give exactly the same results. However, in the first case more simple systems are to be solved.

The diffusion and thermal diffusion coefficients can also be expressed in terms of the expansion coefficients:

$$D_{cd} = \frac{1}{2n} d_{d,0}^c, \quad (69)$$

$$D_{Tc} = -\frac{1}{2n} a_{c,000}, \quad (70)$$

$$D_{Tc}^{d(1)} = -\frac{1}{2n} a_{c,0}^{d(1)}. \quad (71)$$

One can see that just zeroth-order terms of the expansions appear in the formulae for the diffusion and thermal diffusion coefficients. However, maintaining only the equations for $a_{c,000}$ and $a_{c,0}^{d(1)}$ in the systems (A.1) and (A.4), leads to zero values of thermal

diffusion coefficients. The simplest way to yield nonzero thermal diffusion is to keep terms involving the coefficients $a_{c,000}$, $a_{c,100}$, $a_{c,010}$ and $a_{c,001}$ for the determination of D_{T_c} and $a_{c,0}^{d(1)}$ and $a_{c,1}^{d(1)}$ for the calculation of $D_{T_c}^{d(1)}$ [32,17]. The resulting systems must be solved for $a_{c,000}$ and $a_{c,0}^{d(1)}$, respectively.

4. One-temperature approach

4.1. Zeroth order approximation

Now, we consider the case when τ_{VV_1} is much less than τ_{react} and is comparable with the mean time between the collisions with the VV_2 exchanges of vibrational energies of different modes and with the VTR exchanges. In this case

$$J_{cij}^{rap} = J_{cij}^{el} + J_{cij}^r + J_{cij}^{vibr},$$

$$J_{cij}^{sl} = J_{cij}^{react}.$$

The rapid vibrational exchange between the various modes results in equalizing the vibrational temperatures and the VTR exchanges lead to the one-temperature distribution.

The zeroth-order solution $f_{cij}^{(0)}$ has the following form:

$$f_{cij}^{(0)} = \frac{n_c}{Z_c(T)} s_{ij}^c \exp\left(-\frac{m_c c_c^2}{2kT} - \frac{\epsilon_j^{ci} + \epsilon_i^c}{kT}\right), \quad (72)$$

$$Z_c = Z_c^r Z_c^{int}(T), \quad Z_c^{int} = \sum_{ij} s_{ij}^c \exp\left(-\frac{\epsilon_j^{ci} + \epsilon_i^c}{kT}\right).$$

The vibrational level populations are described by the one-temperature equilibrium Boltzmann distribution Eq. (35).

The equations for $n_c(\mathbf{r},t)$, $\mathbf{v}(\mathbf{r},t)$, $T(\mathbf{r},t)$ can be obtained in the form given in Eqs. (36), (10) and (11). In the zeroth approach we have the system of equations for one-temperature chemical kinetics, Eq. (36) in the present case contain the one-temperature equilibrium rate constants for dissociation, recombination and binary reactions, Eq. (11) involves the vibrational energy $\rho E_v = \rho E_v(T)$,

$$\rho E_v = \sum_c \rho_c E_v^c = \sum_c \frac{n_c}{Z_c^{vibr}(T)} \sum_i \epsilon_i^c \exp\left(-\frac{\epsilon_i^c}{kT}\right), \quad (73)$$

$$Z_c^{vibr} = Z_c^{vibr}(T) = \sum_i s_i^c \exp\left(-\frac{\epsilon_i^c}{kT}\right).$$

4.2. First order distribution functions and transport terms

The equations for the first order solution coincides with Eq. (38). Using the zeroth order macroscopic equations we represent $df_{cij}^{(0)}/dt$ as following:

$$\begin{aligned} \frac{df_{cij}^{(0)}}{dt} = f_{cij}^{(0)} & \left\{ \left(\frac{m_c c_c^2}{2kT} - \frac{5}{2} + \left[\frac{\varepsilon_{ij}^c}{kT} \right]' \right) \mathbf{c}_c \cdot \nabla \ln T \right. \\ & + \frac{n}{n_c} \mathbf{c}_c \cdot \mathbf{d}_c + \frac{m_c}{kT} (\mathbf{c}_c \mathbf{c}_c - \frac{1}{3} c_c^2 \mathbf{I}) : \nabla \mathbf{v} \\ & + \left(\frac{m_c c_c^2}{3kT} - 1 - \frac{p}{\rho T c_u} \left(\frac{m_c c_c^2}{2kT} - \frac{3}{2} + \left[\frac{\varepsilon_{ij}^c}{kT} \right]' \right) \right) \nabla \cdot \mathbf{v} + \frac{R_c^{(0)}}{n_c} \\ & \left. - \frac{\sum_c R_c^{(0)} \left(\frac{3}{2} kT + \langle \varepsilon_{ij}^c \rangle + \varepsilon^c \right)}{\rho T c_u} \left(\frac{m_c c_c^2}{2kT} - \frac{3}{2} + \left[\frac{\varepsilon_{ij}^c}{kT} \right]' \right) \right\}; \end{aligned} \quad (74)$$

here $\varepsilon_{ij}^c = \varepsilon_j^c + \varepsilon_i^c$, $[\zeta_{ij}]' = \zeta_{ij} - \langle \zeta_{ij} \rangle$, the averaging over the internal energy is defined in the following way:

$$\langle \zeta_{ij} \rangle = \frac{\sum_{ij} s_{ij}^c \zeta_{ij} \exp(-(\varepsilon_{ij}^c/kT))}{\sum_{ij} s_{ij}^c \exp(-(\varepsilon_{ij}^c/kT))}. \quad (75)$$

Proceeding from expression (74) we can write the first-order distribution functions in the form:

$$\begin{aligned} f_{cij}^{(1)} = f_{cij}^{(0)} & \left(-\frac{1}{n} \mathbf{A}_{cij} \cdot \nabla \ln T - \frac{1}{n} \sum_d \mathbf{D}_{cij}^d \cdot \mathbf{d}_d - \frac{1}{n} \mathbf{B}_{cij} : \nabla \mathbf{v} \right. \\ & \left. - \frac{1}{n} F_{cij} \nabla \cdot \mathbf{v} - \frac{1}{n} G_{cij} \right), \end{aligned} \quad (76)$$

and traditionally obtain the equations for the coefficients of the gradients. In this case they contain the operators of rotational and all vibrational inelastic transfers. Additional normalization conditions are given by Eqs. (44)–(49) and (52).

The pressure tensor is defined by Eq. (24), with the linear integral equations for functions \mathbf{B}_{cij} , F_{cij} and G_{cij} determined by Eq. (74), the appropriate kinetic coefficients can be found from Eq. (25) with bracket integrals determined by expression (53) containing not only the cross sections of the VV_1 exchange but also all the inelastic energy transfers.

The relaxation pressure and vibrational bulk viscosity coefficient also depend on the cross sections of all energy exchanges.

The diffusion velocity is written as

$$\mathbf{V}_c = - \sum_d D_{cd} \mathbf{d}_d - D_{Tc} \nabla \ln T \quad (77)$$

with the following definition of the diffusion and thermal diffusion coefficients:

$$D_{cd} = \frac{1}{3n} [\mathbf{D}^c, \mathbf{D}^d], \quad D_{Tc} = \frac{1}{3n} [\mathbf{D}^c, \mathbf{A}]. \quad (78)$$

For the total heat flux we have

$$\mathbf{q} = -\lambda' \nabla T - p \sum_c D_{Tc} \mathbf{d}_c + \sum_c \left(\frac{5}{2} kT + \langle \varepsilon_{ij}^c \rangle + \varepsilon^c \right) n_c \mathbf{V}_c, \quad (79)$$

$$\lambda' = \frac{k}{3} [\mathbf{A}, \mathbf{A}].$$

The heat conductivity coefficient λ' cannot be measured experimentally because of the thermal diffusion presence. It is convenient to define the thermal diffusion rates k_{Tc} [28,17]:

$$\sum_d D_{cd} k_{Td} = D_{Tc}, \quad c = 1, \dots, L.$$

Then the heat flux can be expressed as follows:

$$\mathbf{q} = -\lambda \nabla T + p \sum_c \left(k_{Tc} + \left(\frac{5}{2} + \left\langle \frac{\varepsilon_{ij}^c}{kT} \right\rangle + \frac{\varepsilon^c}{kT} \right) \frac{n_c}{n} \right) \mathbf{V}_c; \quad (80)$$

here λ is the heat conductivity coefficient for a mixture,

$$\lambda = \lambda' - nk \sum_c k_{Tc} D_{Tc}. \quad (81)$$

The coefficient λ may be determined experimentally in a steady-state mixture.

4.2.1. Thermal conductivity, diffusion and thermal diffusion coefficients

Now, the expressions for transport coefficients in the one-temperature approach are considered. The integral equations for the functions \mathbf{D}_{cij}^d has the same form as in the multi-temperature case and are given by Eq. (62). Therefore, we expand these functions into the same series of Sonine polynomials, Eq. (65). Functions \mathbf{A}_{cij} are found from the following equations:

$$\sum_d \frac{n_c n_d}{n^2} I_{cd}(\mathbf{A}) = \frac{1}{n} f_{cij}^{(0)} \left(\frac{m_c c_c^2}{2kT} - \frac{5}{2} + \left[\frac{\varepsilon_{ij}^c}{kT} \right]' \right) \mathbf{c}_c. \quad (82)$$

In order to solve these equations one can expand the functions \mathbf{A}_{cij} into double series of orthogonal polynomials

$$\mathbf{A}_{cij} = \frac{m_c \mathbf{c}_c}{2kT} \sum_{rp} a_{c,rp} S_{3/2}^{(r)} \left(\frac{m_c c_c^2}{2kT} \right) P_j^{(p)} \left(\frac{\varepsilon_{ij}^c}{kT} \right). \quad (83)$$

The equations for coefficients $a_{c,rp}$ are given in Appendix B. The thermal conductivity coefficient becomes

$$\lambda' = \sum_c \frac{5}{4} k \frac{n_c}{n} a_{c,10} + \sum_c \frac{k}{2} \frac{n_c}{n} c_{int,c} a_{c,01} = \lambda'_t + \lambda'_{int}, \quad (84)$$

where

$$c_{int,c} = \frac{\partial E_{int}^c}{\partial T}, \quad \rho_c E_{int}^c = \sum_{ij} \int (\varepsilon_j^{ci} + \varepsilon_i^c) f_{cij} d\mathbf{u}_c.$$

In the case where the rotational and vibrational spectra can be separated the thermal conductivity coefficient λ'_{int} may be written as the sum of two terms connected with the transfer of rotational and vibrational energy: $\lambda'_{int} = \lambda'_r + \lambda'_v$.

The diffusion and thermal diffusion coefficients are defined, respectively, by Eqs. (69) and (70). The coefficients $d_{c,r}^d$ can be found from the same system as in multi-temperature approach, i.e. (A.7) and (A.9).

It can be noted that using the different polynomial expansions for functions \mathbf{A}_{cij} , \mathbf{D}_{cij}^d , etc., seems to be reasonable and provides a good convergence for all transport coefficients.

5. Conclusions

The expressions of transport terms are derived, respectively, in (i) level approach, (ii) generalized multi-temperature approach and (iii) one-temperature approach. The level approach is valid in a wide range of conditions of the rapid exchange of translational and rotational energy. In this case, the system of macroscopic equations contains the equations for the populations of vibrational levels of every chemical species n_{ci} and the conservation equations of momentum and total energy. This model gives the detailed description of nonequilibrium reacting mixtures, however, it is complicated due to the large number of macroparameters and transport coefficients. This approach should be used, for example, in a short zone behind a shock wave. The number of macroparameters is reduced when the exchange of vibrational quanta within every mode occurs more frequently than the vibrational energy exchange between modes and chemical reactions. Such a condition takes place, for example, in the zone of vibrational nonequilibrium behind a shock wave when the steady-state distributions over vibrational levels already exist and the multi-temperature approach is valid. It is particularly important in expanding streams, nozzle flows or high-enthalpy facilities. The anharmonism of molecular vibrations and the different rates of the various vibrational energy-exchanges lead to the non-Boltzmann distribution functions and to the appearance of additional thermal conductivity and thermal diffusion coefficients. The equations of the level vibrational and chemical kinetics are reduced in this case to the equations for number densities of chemical species n_c and for the “effective” vibrational temperatures of the first level of every component T_1^c . For the harmonic-oscillator model the “effective” temperatures coincide with the vibrational temperatures of components and the relaxation equations for the number of vibrational quanta are replaced by the relaxation equations for the vibrational energy. The one-temperature approach is valid in the conditions of thermal equilibrium in chemically nonequilibrium reacting gas mixtures. In this regime the

number of macroparameters is further reduced, all vibrational temperatures are equal to the gas temperature and macroscopic equations are the equations for n_c , \mathbf{v} and T .

The influence of chemical reactions on transport coefficients is defined by their dependence on the number densities of chemical species n_c which are governed by the equations of the detailed chemical–vibrational kinetics, multi- or one-temperature chemical kinetics.

In conclusion, it should be added that the choice of one of the three models considered in this study is determined by the hierarchy of the relaxation times. It is obvious that the distribution function in the zeroth-order approximation can be easily reduced going from the most detailed model to the others. Nevertheless, this is not valid for the transport terms because they depend on the different inelastic cross sections and are defined in terms of macroparameters which are found from different macroscopic equations.

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Appendix A

To derive the equations for the coefficients $a_{c,rpq}$ in multi-temperature approach one should substitute the series (63)–(65) into integral Eqs. (60)–(62) and multiply them by the velocity. After integration over the velocities and summation over rotational, vibrational quantum numbers and chemical species the following system of linear algebraic equations is obtained:

$$\sum_d \sum_{r'p'q'} \Lambda_{rr'pp'qq'}^{cd} a_{d,r'p'q'} = \frac{15}{2} \frac{kT}{m_c} \frac{n_c}{n} \delta_{r1} \delta_{p0} \delta_{q0} + \frac{3kT}{m_c} \frac{n_c}{n} c_{r,c} \delta_{r0} \delta_{p1} \delta_{q0} + \frac{3kT}{m_c} \frac{n_c}{n} c_{a,c}^\top \delta_{r0} \delta_{p0} \delta_{q1}, \quad c = 1, \dots, L, \quad r, p, q = 0, 1, \dots \tag{A.1}$$

Here the following notation is introduced:

$$\Lambda_{rr'pp'qq'}^{cd} = \delta_{cd} \sum_b \frac{n_c n_b}{n^2} [Q^{rpq}, Q^{r'p'q'}]_{cb}' + \frac{n_c n_d}{n^2} [Q^{rpq}, Q^{r'p'q'}]_{cd}'' \tag{A.2}$$

where

$$Q^{rpq} = \sqrt{\frac{m_c}{2kT}} \mathbf{c}_c S_{3/2}^{(r)} \left(\frac{m_c \mathbf{c}_c^2}{2kT} \right) P_j^{(p)} \left(\frac{\varepsilon_j^c}{kT} \right) P_i^{(q)} \left(\frac{\varepsilon_i^c - i\tilde{\varepsilon}_i^c}{kT} \right).$$

One can see that the coefficients of the linear algebraic equations (A.1) are expressed in terms of partial bracket integrals of the most rapid processes which were defined in

Section 3.4. In the multi-temperature approach they depend on the cross sections of the elastic collisions, collisions with the rotational energy exchange and with the transfer of the vibrational quanta inside every mode.

Eq. (A.1) occur not to be linear independent in the case $r = p = q = 0$. It follows from the momentum conservation and the symmetry of the bracket integrals. Taking into account the normalizing conditions (44) one can derive the additional equation for the coefficients $a_{c,rpq}$

$$\sum_c \frac{\rho_c}{\rho} a_{c,000} = 0. \tag{A.3}$$

The system (A.1) completed by Eq. (A.3) has a unique solution.

The equations for coefficients $a_{c,r}^{d(1)}$ are written as follows:

$$\sum_d \sum_{r'} \alpha_{rr'}^{cd} a_{d,r'}^{b(1)} = \frac{3kT}{m_c} \frac{n_c}{n} c_{w,c}^{T_i} \delta_{r1}, \quad b, c = 1, \dots, L, \quad r = 0, 1, \dots, \tag{A.4}$$

where

$$\alpha_{rr'}^{cd} = \delta_{cd} \sum_b \frac{n_c n_b}{n^2} [Q^r, Q^{r'}]_{cb}' + \frac{n_c n_d}{n^2} [Q^r, Q^{r'}]_{cd}'' \tag{A.5}$$

and

$$Q^r = \sqrt{\frac{m_c}{2kT}} \mathbf{c} P_i^{(r)} \left(\frac{i \tilde{\epsilon}_1^c}{kT} \right).$$

Adding to the Eq. (A.4) the condition following from the constraint, Eq. (43)

$$\sum_c \frac{\rho_c}{\rho} a_{c,0}^{d(1)} = 0, \quad d = 1, \dots, L \tag{A.6}$$

one can obtain the system of equations for $a_{c,r}^{d(1)}$ which are linear independent.

Similarly, the equations for the coefficients $d_{c,r}^d$ can be written as

$$\sum_d \sum_{r'} \gamma_{rr'}^{cd} d_{d,r'}^b = 3kT \left(\delta_{cb} - \frac{\rho_c}{\rho} \right) \delta_{r0}, \quad b, c = 1, \dots, L, \quad r = 0, 1, \dots, \tag{A.7}$$

where

$$\gamma_{rr'}^{cd} = \sqrt{m_c m_d} \left(\delta_{cd} \sum_b \frac{n_c n_b}{n^2} [Q^r, Q^{r'}]_{cb}' + \frac{n_c n_d}{n^2} [Q^r, Q^{r'}]_{cd}'' \right), \tag{A.8}$$

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

The linear-independent system can be derived taking into account constraints, Eq. (45), which have the next form in terms of coefficients $d_{c,r}^d$:

$$\sum_c \frac{\rho_c}{\rho} d_{c,0}^d = 0, \quad d = 1, \dots, L. \tag{A.9}$$

Appendix B

The linear algebraic equations for the coefficients $a_{c,rp}$ in the one-temperature approach are given here as follows:

$$\sum_d \sum_{r'p'} A_{rr'pp'}^{cd} a_{d,r'p'} = \frac{15}{2} \frac{kT}{m_c} \frac{n_c}{n} \delta_{r1} \delta_{p0} + \frac{3kT}{m_c} \frac{n_c}{n} c_{int,c} \delta_{r0} \delta_{p1},$$

$$c = 1, \dots, L, \quad r, p = 0, 1, \dots. \quad (\text{B.1})$$

Here

$$A_{rr'pp'}^{cd} = \delta_{cd} \sum_b \frac{n_c n_b}{n^2} [Q^{rp}, Q^{r'p'}]_{cb}' + \frac{n_c n_d}{n^2} [Q^{rp}, Q^{r'p'}]_{cd}'' \quad (\text{B.2})$$

and

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

In the one-temperature approach, partial-bracket integrals contain the cross-sections of the collisions with all elastic and inelastic energy exchanges.

The additional equation for $a_{c,rpq}$ follows from Eq. (44) and coincides with Eq. (A.3). The system (B.1) and (A.3) has a unique solution.

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