PHYSICAL REVIEW E **80**, 046407 (2009)

Transport coefficients in nonequilibrium gas-mixture flows with electronic excitation

E. V. Kustova* and L. A. Puzyreva†
Department of Mathematics and Mechanics, Saint Petersburg State University, 28 Universitetsky Pr., 198504 Saint Petersburg, Russia

(Received 12 June 2009; published 28 October 2009)

In the present paper, a one-temperature model of transport properties in chemically nonequilibrium neutral gas-mixture flows with electronic excitation is developed. The closed set of governing equations for the macroscopic parameters taking into account electronic degrees of freedom of both molecules and atoms is derived using the generalized Chapman-Enskog method. The transport algorithms for the calculation of the thermal-conductivity, diffusion, and viscosity coefficients are proposed. The developed theoretical model is applied for the calculation of the transport coefficients in the electronically excited N/N_2 mixture. The specific heats and transport coefficients are calculated in the temperature range 50–50 000 K. Two sets of data for the collision integrals are applied for the calculations. An important contribution of the excited electronic states to the heat transfer is shown. The Prandtl number of atomic species is found to be substantially nonconstant.

DOI: 10.1103/PhysRevE.80.046407 PACS number(s): 52.25.Fi, 05.60.−k, 51.10.+y, 47.70.Fw

I. INTRODUCTION

The modeling of nonequilibrium kinetics and transport properties in high-temperature gases is needed for the development of the aerospace industry. When a space vehicle enters into the Earth atmosphere, it undergoes very strong heating, up to several thousands and tens of thousands Kelvins. Under such conditions, along with the excitation of the rotational and vibrational degrees of freedom and chemical reactions, the electronic excitation and ionization take place.

The transport properties of nonequilibrium flows are widely studied in the literature, starting from the famous book of Chapman and Cowling [1], who assumed gas mixtures to be composed of structureless particles. In Refs. [2,3], the transport theory of gas mixtures under conditions of weak deviations from equilibrium was further developed. Internal degrees of freedom were introduced to the kinetic transport theory in Refs. [4–8] and other works in 50–60ies. During the last decades, the main attention was focused on the transport properties of strongly nonequilibrium flows (see Refs. [9–13] for strong vibrational nonequilibrium and Refs. [13–16] for chemically nonequilibrium flows) as well as on the transport phenomena in ionized gases (see Refs. [3,17–24]). However, the impact of the electronic degrees of freedom of atoms and molecules on the transport coefficients is not sufficiently understood up to the present time. We cannot say that the electronic excitation was completely neglected in the recent studies. Indeed, during the last years, a chemically equilibrium atomic hydrogen plasma with electronically excited states is actively studied by the scientific group of Bari (see Refs. [25–29]). In these references, the effect of electronic degrees of freedom of atoms is found to be important; the molecular species are not considered in these works. On the other hand, some aspects of the electronic excitation of molecules are briefly discussed in Refs. [30,31]. In these papers, the contribution of the electronic states to the heat transfer is found to be negligible. Therefore, the role of the electronic excitation in the transport processes is still not completely clear.

The objective of the present paper is to study the transport coefficients in a mixture of electronically excited molecules and atoms. We consider chemically nonequilibrium neutral gas-mixture flows taking into account the electronic degrees of freedom of both atoms and molecules. Using the kinetic theory methods proposed earlier in Refs. [11,13,14], we develop a one-temperature model of a reacting gas-mixture flow, estimate the influence of the number of the excited electronic levels on the internal specific heats, and calculate the transport coefficients in the N/N_2 mixture with electronic excitation. In this study, we do not consider ionization since our objective is to understand the pure effect of electronic excitation on the transport properties. Ionization will be taken into account in the future work.

II. MACROSCOPIC PARAMETERS AND GOVERNING EQUATIONS

We consider a nonequilibrium flow assuming that the rate of the internal energy relaxation substantially exceeds that of chemical reactions

$$\tau_{tr} < \tau_{rot} < \tau_{vibr} < \tau_{el} \ll \tau_{react} \sim \theta. \tag{1}$$

Here τ_{tr}, τ_{rot}, τ_{vibr}, τ_{el}, and τ_{react} are the characteristic times for translational, rotational, vibrational and electronic relaxations, and chemical reactions; θ is the mean time of the variation in gas-dynamic parameters. Under this relation, on the time scale of the order θ, chemical reactions can be considered on the basis of the maintaining Boltzmann distributions over the velocity and internal energy levels.

Under the condition (1), the kinetic equations for the distribution functions $f_{cl}(\mathbf{r},\mathbf{u},t)$ in the absence of external forces have the following form:

$$\frac{\partial f_{cl}}{\partial t} + \mathbf{u}_c \cdot \nabla f_{cl} = \frac{1}{\epsilon} J_{cl}^{rap} + J_{cl}^{sl},$$

$$\epsilon = \frac{\tau_{int}}{\tau_{react}} \sim \frac{\tau_{int}}{\theta} \ll 1, \tag{2}$$

where c is the chemical species, l is a set of the quantum numbers: for molecules $l=\{nij\}$, for atoms $l=n$ (n, i, j are,

---

*elena_kustova@mail.ru
†larisa.puzyreva@gmail.com

respectively, the electronic, vibrational, and rotational levels), $\mathbf{r}$, $\mathbf{u}$, and t are the coordinates, particle velocities, and time; ϵ is the small parameter, τ_{int} is the characteristic time for the relaxation of all internal degrees of freedom, and J_{cl}^{rap}, J_{cl}^{sl} are the integral operators of rapid and slow processes

$$J_{cl}^{rap} = J_{cl}^{tr} + J_{cl}^{rot} + J_{cl}^{vibr} + J_{cl}^{el}, \quad J_{cl}^{sl} = J_{cl}^{react}. \tag{3}$$

An important problem is to determine the macroscopic flow parameters, for which a closed system of equations of the nonequilibrium hydrodynamics can be derived. According to the generalized Chapman-Enskog method for nonequilibrium gas flows with rapid and slow processes (see Refs. [13,14]), the macroscopic parameters are introduced by averaging the invariants of the most frequent collisions. In our case, the set of collision invariants includes the mass, momentum, total energy, and additional invariants, which are conserved only in the rapid process, namely, a_c are any quantities, arbitrarily depending on the chemical species c and independent of the velocity and internal state,

$$\psi_{cl}^{(1,2,3)} = m_c u_{cx}, m_c u_{cy}, m_c u_{cz},$$

$$\psi_{cl}^{(4)} = \frac{m_c u_c^2}{2} + \varepsilon_l^c + \varepsilon_c,$$

$$\psi_{cl}^{(\lambda+4)} = a_c, \quad \lambda = 1, \ldots, L. \tag{4}$$

Here m_c is the mass of a particle of c species, ε_l^c is the internal energy of molecules and atoms of the species c, ε_c is the energy of formation, and L is number of chemical species.

The internal energy of molecules and atoms is modeled as follows:

$$\varepsilon_l^c = \begin{cases} \varepsilon_{nij}^{mol} = \varepsilon_{el}(n) + \varepsilon_{vibr}(n,i) + \varepsilon_{rot}(n,i,j) \\ \varepsilon_n^{at} = \varepsilon_{el}(n), \end{cases} \tag{5}$$

where ε_{el}, ε_{vibr}, and ε_{rot} are, respectively, the internal energies of the electronic, vibrational, and rotational degrees of freedom. For the calculation of the internal energy of molecules, we use the spectroscopic data from [32]; the electronic states of atoms are provided in Ref. [33]. The electronic energy is taken from the tables of the spectroscopic data, the vibrational energy for each electronic state is calculated on the basis of the Morse potential for anharmonic oscillators, and the rotational energy is simulated taking into account its dependence on the electronic and vibrational levels [33].

The system of collision invariants (4) provides the following set of the macroscopic parameters: the number densities of species $n_c(\mathbf{r},t)$, the gas velocity $\mathbf{v}(\mathbf{r},t)$, and the total energy per unit mass $u(\mathbf{r},t)$ [or, which is essentially the same, the gas temperature $T(\mathbf{r},t)$].

Governing equations for the macroscopic parameters are obtained in the following form:

$$\frac{dn_c}{dt} + n_c \nabla \cdot \mathbf{v} + \nabla \cdot (n_c \mathbf{V}_c) = R_c^{react}, \quad c = 1, \ldots, L, \tag{6}$$

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \boldsymbol{P} = 0, \tag{7}$$

$$\rho \frac{du}{dt} + \nabla \cdot \mathbf{q} + \boldsymbol{P} : \nabla \mathbf{v} = 0, \tag{8}$$

here $\mathbf{V}_c$ is the diffusion velocity, R_c^{react} is the production term due to chemical reactions, ρ is the mixture density, $\boldsymbol{P}$ is the pressure tensor, and $\mathbf{q}$ is the heat flux.

The set of governing Eqs. (6)–(8) is formally similar to that given in Refs. [13,16] for thermally weak nonequilibrium and chemically strong nonequilibrium flows. However, in the present study, the internal energy per unit mass includes those for the rotational, vibrational, and electronic degrees of freedom.

III. ZERO-ORDER APPROACH

In the zero-order approximation of the modified Chapman-Enskog method, the distribution functions are obtained in the form,

$$f_{cl}^{(0)} = \left(\frac{m_c}{2\pi kT}\right)^{3/2} \frac{n_c s_{cl}}{Z_c^{int}(T)} \exp\left(-\frac{m_c c_c^2}{2kT} - \frac{\varepsilon_l^c}{kT}\right), \tag{9}$$

where k is the Boltzmann constant, s_{cl} is the statistical weight for the internal state l, $\mathbf{c}_c$ is the peculiar velocity, and $Z_c^{int}(T)$ is the equilibrium internal partition function,

$$Z_c^{int}(T) = \sum_l s_{cl} \exp\left(-\frac{\varepsilon_l^c}{kT}\right).$$

The distribution functions [Eq. (9)] represent the local equilibrium Maxwell-Boltzmann distributions of molecules and atoms over the velocity and internal energy and nonequilibrium distribution over chemical species. A substantial difference from the models developed earlier is that for atoms, we obtain not only the Maxwell velocity distribution but also the Boltzmann distribution over the electronic energy levels.

The Chapman-Enskog method makes it possible to express, in each approximation, the transport terms as functions of the main macroscopic parameters and their spatial derivatives. In the zero-order approximation, the pressure tensor takes a diagonal form $\boldsymbol{P} = p\boldsymbol{I}$ (p is the hydrostatic pressure, $\boldsymbol{I}$ is the unit tensor), whereas the remaining transport terms are equal to zero: $\mathbf{V}_c = \mathbf{q} = 0$. The production term $R_c^{react(0)}$ is specified by the zero-order reaction-rate coefficients $k_{f,r}^{(0)}$, $k_{b,r}^{(0)}$, which are related through the law of mass action.

IV. SPECIFIC HEATS

Thermodynamic properties of molecules and atoms are required for the calculation of the transport coefficients and numerical solution of the governing equations. In this section, we consider in detail the specific heats. The specific heat at constant volume is given by the expression

$$c_V = \left(\frac{\partial u}{\partial T}\right)_V = \left(\frac{\partial E_{tr}}{\partial T}\right)_V + \left(\frac{\partial E_{int}}{\partial T}\right)_V = c_{tr} + c_{int}, \tag{10}$$

where E_{tr}, E_{int} are the translational and internal energies per unit mass; c_{tr} and c_{int} are the components of the specific heat corresponding to the translational and internal degrees of freedom. Since the mixture composition in the above expression is assumed to be fixed, the specific heats introduced by Eq. (10) can be treated as "frozen." In the case of strongly nonequilibrium chemical reactions, the frozen specific heats are used for the calculation of the transport coefficients.

In order to estimate the contribution of electronic levels to the specific heats, we calculate the internal energy per unit mass using two ways:

(a) Taking into account all internal modes, namely, the electronic, rotational, and vibrational degrees of freedom

$$E_{int,c}(T)=\frac{1}{m_c Z_c^{int}(T)}\sum_l s_{cl}\varepsilon_l^c \exp\left(-\frac{\varepsilon_l^c}{kT}\right), \quad l=\{nij\}. \tag{11}$$

(b) Neglecting electronic excitation, i.e., taking into account only the rotational and vibrational levels of the ground electronic state

$$E_{rv,c}(T)=\frac{1}{m_c Z_c^{rv}(T)}\sum_{ij} s_{cij}\varepsilon_{ij}^c \exp\left(-\frac{\varepsilon_{ij}^c}{kT}\right). \tag{12}$$

In the last formula,

$$Z_{rv,c}(T)=\sum_{ij} s_{cij}\exp\left(-\frac{\varepsilon_{ij}^c}{kT}\right).$$

Thus, for the model (a), the specific heats of the internal degrees of freedom of molecules and atoms have the following form:

$$c_{int,mol}=\left(\frac{\partial E_{int}}{\partial T}\right)_V, \quad c_{int,at}=\left(\frac{\partial E_{el}}{\partial T}\right)_V. \tag{13}$$

For the model (b), we obtain

$$c_{int,mol}=c_{rv,mol}=\left(\frac{\partial E_{rv}}{\partial T}\right)_V, \quad c_{int,at}=0. \tag{14}$$

On the basis of the formulas (10), (13), and (14), the specific heats of N_2 and N were calculated in the temperature range 50–50 000 K. Figure 1 presents the nondimensional specific heats $c_{V,c}$ as functions of T. We can see that the specific heat for atoms $c_{V,N}$ reaches rather high values, exceeding substantially that for molecules in the interval T=15 000–30 000 K. Thus, the common assumption that $c_{V,at}=c_{tr,at}$ is violated, which can affect essentially the accuracy of the solution of the governing equations. The total specific heat of nitrogen molecules $c_{V,\mathrm{N}_2}=c_{tr,\mathrm{N}_2}+c_{int,\mathrm{N}_2}$ taking into account the electronic, rotational, and vibrational excitations exceeds significantly the specific heat $c_{V,\mathrm{N}_2}=c_{tr,\mathrm{N}_2}+c_{rv,\mathrm{N}_2}$ calculated neglecting electronic states in the range T=9000–42 000 K. Then, with the temperature rise, the specific heat c_{V,N_2} taking into account all the internal degrees of freedom becomes slightly smaller than c_{V,N_2} including only the rotational and vibrational modes.

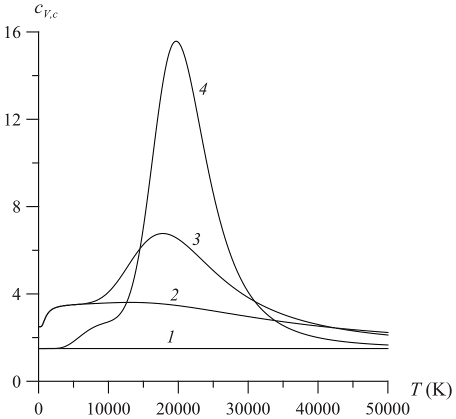

FIG. 1. The nondimensional specific heats $c_{V,c}$ as functions of T. Curves 1: $c_{tr,\mathrm{N}_2}=c_{tr,\mathrm{N}}$, 2: $c_{tr,\mathrm{N}_2}+c_{rv,\mathrm{N}_2}$, 3: $c_{tr,\mathrm{N}_2}+c_{int,\mathrm{N}_2}$, and 4: $c_{tr,\mathrm{N}}+c_{int,\mathrm{N}}$.

This last effect may look surprising since the specific heat is basically considered as a sum of separate contributions of various energy modes: rotational, vibrational, and electronic. However, in our case all kinds of energy are strongly coupled. The vibrational energy depends on the electronic state, whereas the rotational energy depends on both electronic and vibrational levels. Therefore, the total internal specific heat cannot be represented as a sum of independent terms corresponding to various energy modes. Moreover, in order to understand this effect, let us consider the different contributions to the specific energy. Figure 2 presents the specific translational, internal, and rovibrational energies of the ground electronic state of N_2 (E_{tr,N_2}, E_{int,N_2}, and E_{rv,N_2}, respectively) as functions of temperature. Up to $T\approx 9000$ K, the contribution of the electronic states to the internal energy of molecules is rather weak. Then the rapid excitation of the electronic states starts, and the specific internal energy increases sharply up to $T\approx 40\,000$ K. This region corresponds to the high values of the internal specific heat, and the location of its maximum at $T\approx 17\,000$ K obviously coincides with the point of inflexion of the internal energy. Further, at $T>40\,000$ K, the rate of increasing of the internal energy drops sharply and so do the specific heat. The rovibrational specific energy E_{rv,N_2} increases almost linearly in the region 5000–20 000 K, which provides the values of c_{rv,N_2} close to constant. Then the rate of increasing of E_{rv,N_2} becomes lower and, consequently, the corresponding

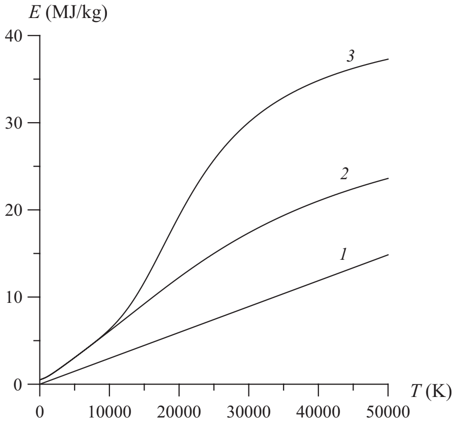

FIG. 2. The energy per unit mass E, MJ/kg as a function of T. Curves 1: E_{tr,N_2}, 2: E_{rv,N_2}, and 3: E_{int,N_2}.

specific heat decreases. In the temperature range about 50 000 K, the rate of increasing of the total internal energy E_{int,N_2} is lower than that of the rovibrational energy E_{rv,N_2}. Therefore, c_{int,N_2} becomes smaller than c_{rv,N_2}. Thus, the fact that $c_{int,\mathrm{N}_2} < c_{rv,\mathrm{N}_2}$ is not contradictory.

Let us discuss now the number of electronic levels, which contribute to the atomic internal specific heat. It is known that for atoms, the internal partition functions diverge due to the high values of the statistical weight. Therefore, some cut-off criterion should be chosen in order to obtain reliable values of the partition functions and specific heats. In the present study, we apply the cut-off criterion proposed in Ref. [34] and efficiently used in Ref. [33] for the calculation of the thermodynamic properties of many species of practical interest. This cut-off criterion is obtained introducing the parameter ΔE_i, which characterizes the lowering of the ionization potential as a result of the presence of other components. The parameter ΔE_i depends on the temperature and number densities of charged particles. In Ref. [33], this parameter was set to 250, 500, and 1000 cm^{-1}. For most of our calculations, we set $\Delta E_i = 500\ \mathrm{cm}^{-1}$.

Figure 3 presents the internal specific heat of nitrogen atoms calculated for $\Delta E_i = 500\ \mathrm{cm}^{-1}$ (a) and $\Delta E_i = 250\ \mathrm{cm}^{-1}$ (b), taking into account different numbers of the excited electronic levels. We can see that for $\Delta E_i = 500\ \mathrm{cm}^{-1}$, taking into account 300 excited levels provides a good accuracy: the specific heat calculated using 600 levels coincides with that obtained for 300 levels. For $\Delta E_i = 250\ \mathrm{cm}^{-1}$, 300 levels is not sufficient, and we need about 480 electronic levels to obtain a satisfactory accuracy. Note that $c_{int,\mathrm{N}}$ calculated for $\Delta E_i = 250\ \mathrm{cm}^{-1}$ is greater than that for $\Delta E_i = 500\ \mathrm{cm}^{-1}$. We also compared our results with those given in Ref. [33], and a very close agreement was obtained within the whole temperature range: the discrepancy does not exceed 1%.

V. FIRST-ORDER APPROACH

In the first-order approximation of the modified Chapman-Enskog method, the distribution function is obtained in the following form:

$$f_{cl}^{(1)} = f_{cl}^{(0)}\left(-\frac{1}{n}\mathbf{A}_{cl}\cdot\nabla \ln T - \frac{1}{n}\sum_{d}\mathbf{D}_{cl}^{d}\cdot\mathbf{d}_{d} - \frac{1}{n}\boldsymbol{B}_{cl}:\nabla\mathbf{v} - \frac{1}{n}F_{cl}\nabla\cdot\mathbf{v} - \frac{1}{n}G_{cl}\right). \qquad (15)$$

The first-order correction depends on the gradients of all macroscopic parameters and contains the unknown functions $\mathbf{A}_{cl}$, $\mathbf{D}_{cl}$, $\boldsymbol{B}_{cl}$, F_{cl}, and G_{cl}, which are found from the linear integral equations similar to those given in Ref. [13].

Using the procedure of the modified Chapman-Enskog method, we derive the expressions for the pressure tensor, diffusion velocity, and energy flux,

$$\boldsymbol{P} = (p - p_{rel})\boldsymbol{I} - 2\eta\boldsymbol{S} - \zeta\nabla\cdot\mathbf{v}\boldsymbol{I}, \qquad (16)$$

$$\mathbf{V}_c = -\sum_{d} D_{cd}\mathbf{d}_c - D_{Tc}\nabla\ln T, \qquad (17)$$

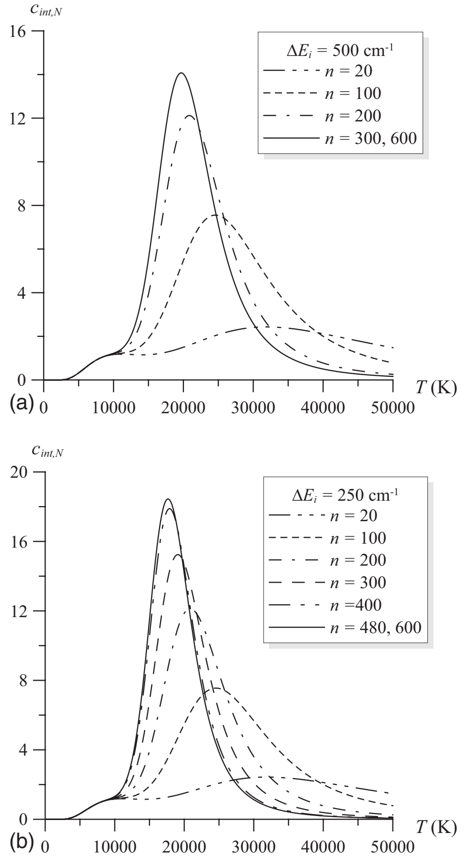

FIG. 3. The nondimensional specific heat $c_{int,\mathrm{N}}$ as a function of T for (a) $\Delta E_i = 500\ \mathrm{cm}^{-1}$ and (b) $\Delta E_i = 250\ \mathrm{cm}^{-1}$.

$$\mathbf{q} = -\lambda'\nabla T - p\sum_{c} D_{T_c}\mathbf{d}_c + \sum_{c}\rho_c h_c\mathbf{V}_c. \qquad (18)$$

Here $\boldsymbol{S}$ is the deformation rate tensor, $\mathbf{d}_c$ is the diffusive driving force, and h_c is the specific enthalpy of species c.

In Eqs. (16)–(18), η, ζ are the shear and bulk viscosity coefficients, p_{rel} is the relaxation pressure, D_{cd}, D_{Tc} are the diffusion and thermal diffusion coefficients, and $\lambda' = \lambda_{tr} + \lambda_{int}$ is the partial thermal-conductivity coefficient, including contributions of the translational and internal degrees of freedom. Note that the normal mean stress in this case includes the terms $\zeta\nabla\cdot\mathbf{v}$ and p_{rel} associated, respectively, to the flow compressibility and to the contribution of nonequilibrium chemical reactions.

The rate coefficients of chemical reactions in the first-order approximation include the correction terms $k_{f,r}^{(1)}$, $k_{b,r}^{(1)}$ specified by the scalar functions F_{cl} and G_{cl} and depending on the temperature, mixture composition, and on the velocity divergence. These first-order corrections are related to the flow compressibility and deviations from the Maxwell-Boltzmann distributions; they are similar to those discussed in Ref. [35] for the case of a one-temperature flow without electronic excitation. The perturbed rate coefficients $k_{f,r}^{(1)}$, $k_{b,r}^{(1)}$ were also discussed before in Refs. [13–15,36] for various flow conditions. Note that due to the first-order terms in the reaction rates, the law of mass action is violated in the viscous flow approximation. Moreover, the cross effects between the normal mean stress and the chemical reaction rate can be demonstrated for the present case, similarly to the conditions considered in Ref. [35].

VI. TRANSPORT COEFFICIENTS

In order to calculate the transport coefficients, we make the following steps:

(1) The unknown functions are expanded into the series of the Sonine and Waldmann-Trübenbacher polynomials; the trial functions for the polynomials are introduced according to the right-hand sides of the integral equations for the first-order correction to the distribution function,

$$\mathbf{A}_{cl} = -\frac{m_c\mathbf{c}_c}{2kT}\sum_{rp} a_{c,rp}S^{(r)}_{3/2}\left(\frac{m_c c_c^2}{2kT}\right)P^{(p)}_l\left(\frac{\varepsilon^c_l}{kT}\right), \tag{19}$$

$$\mathbf{D}^d_{cl} = \frac{m_c\mathbf{c}_c}{2kT}\sum_{r} d^d_{c,r}S^{(r)}_{3/2}\left(\frac{m_c c_c^2}{2kT}\right), \tag{20}$$

$$\boldsymbol{B}_{cl} = \frac{m_c}{2kT}\left(\mathbf{c}_c\mathbf{c}_c - \frac{1}{3}c_c^2\boldsymbol{I}\right)\sum_{r} b_{c,r}S^{(r)}_{5/2}\left(\frac{m_c c_c^2}{2kT}\right), \tag{21}$$

$$F_{cl} = \sum_{rp} f_{c,rp}S^{(r)}_{1/2}\left(\frac{m_c c_c^2}{2kT}\right)P^{(p)}_l\left(\frac{\varepsilon^c_l}{kT}\right), \tag{22}$$

$$G_{cl} = \sum_{rp} g_{c,rp}S^{(r)}_{1/2}\left(\frac{m_c c_c^2}{2kT}\right)P^{(p)}_l\left(\frac{\varepsilon^c_l}{kT}\right). \tag{23}$$

Here $S^{(r)}_\nu$ are the Sonine polynomials in the reduced peculiar velocity, $P^{(p)}_l$ are the Waldmann-Trübenbacher polynomials in the internal energy, and $a_{c,rp}$, $d^d_{c,r}$, $b_{c,r}$, $f_{c,rp}$, and $g_{c,rp}$ are the expansion coefficients.

Note that for atomic species, the functions $\mathbf{A}_{cl}$, F_{cl}, and G_{cl} are usually expanded into the series of the Sonine polynomials only. In the present case, we use the double polynomial systems for atomic species since they possess the internal (electronic) energy.

(2) The transport coefficients are expressed in terms of the expansion coefficients,

$$\lambda' = \sum_c \frac{5}{4}k\frac{n_c}{n}a_{c,10} + \sum_c \frac{m_c}{2}\frac{n_c}{n}c_{int,c}a_{c,01}, \tag{24}$$

$$D_{cd} = \frac{1}{2n}d^d_{c,0}, \tag{25}$$

$$D_{Tc} = -\frac{1}{2n}a_{c,00}, \tag{26}$$

$$\eta = \frac{kT}{2}\sum_c \frac{n_c}{n}b_{c,0}, \tag{27}$$

$$\zeta = -kT\sum_c \frac{n_c}{n}f_{c,10}, \tag{28}$$

$$p_{rel} = kT\sum_c \frac{n_c}{n}g_{c,10}. \tag{29}$$

(3) The integral equations are reduced to the transport linear systems of algebraic equations involving the bracket integrals as coefficients. For example, the system for the expansion coefficients specifying the thermal-conductivity and thermal diffusion coefficients is obtained in the form

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

and should be solved together with the additional constraint providing the uniqueness of the solution

$$\sum_c \frac{\rho_c}{\rho}a_{c,00} = 0.$$

Here the coefficients $\Lambda^{cd}_{rr'pp'}$ are the bracket integrals containing the cross sections of the rapid processes, i.e., all elastic and inelastic collisions, which do not result in chemical reactions.

(4) The bracket integrals are simplified applying the commonly used assumptions proposed by Mason and Monchick (see Refs. [3,7,8]). Finally, they are expressed in terms of the collision integrals $\Omega^{(l,r)}_{cd}$ and the relaxation times for the internal energy. The $\Omega^{(l,r)}_{cd}$ integrals are calculated for the particular models of intermolecular interaction potentials. In the present study, we use the repulsive Born-Meyer potential and the approximate formulas for the collision integrals obtained in Refs. [37,38].

(5) The transport coefficients are then calculated numerically as the solutions of the transport linear systems using the Gauss method. For a binary mixture, this method provides a satisfactory efficiency. For complex multicomponent mixtures, the iterative algorithms proposed in Ref. [16] are more appropriate.

VII. RESULTS AND DISCUSSIONS

The transport coefficients were calculated for the N/N_2 mixture in the temperature range 50–50 000 K using the approach developed above.

The impact of the electronic excitation on the coefficients of diffusion, thermal diffusion, and shear viscosity is found to be negligible. In contrast to this conclusion, the influence of the electronic states on the thermal-conductivity coefficients is significant.

The coefficients of thermal conductivity $\lambda_{tr,c}$, $\lambda_{int,c}$, $\lambda_{rv,c}$ of the components of the N/N_2 mixture are given in Fig. 4 as functions of T. The excitation of the electronic degrees of freedom influences substantially the internal thermal conductivity. Thus, neglecting the electronic states results in the significant underestimation of the molecular internal thermal conductivity: for T about 20 000 K, the coefficient λ_{int,N_2} is almost twice larger than the coefficient λ_{rv,N_2} calculated neglecting the electronic states. The contribution of the electronic states to the thermal conductivity of atomic species in the temperature range 12 000–30 000 K is even higher; for

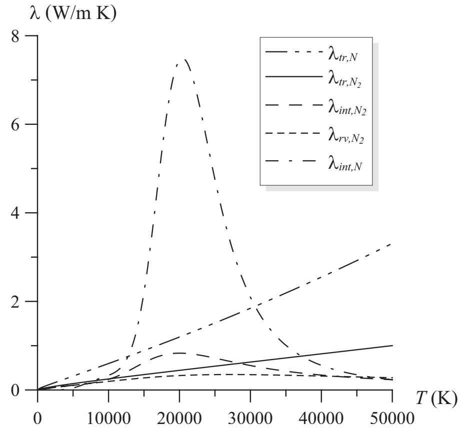

FIG. 4. The thermal-conductivity coefficients $\lambda_{tr,c}$, $\lambda_{int,c}$, and $\lambda_{rv,c}$ of atomic N and molecular N_2 species as functions of T.

$T \approx 20\,000$ K, the coefficient of internal thermal conductivity for atoms $\lambda_{int,\mathrm{N}}$ is six to seven times larger than the corresponding translational thermal-conductivity coefficient $\lambda_{tr,N}$.

Figure 5 presents the total coefficient of thermal conductivity λ' as well as that for the internal degrees of freedom λ_{int} calculated in the mixture N/N_2 as functions of the N_2 molar fraction for $T = 10\,000 - 50\,000$ K. We can see that the thermal-conductivity coefficients take the maximum values for the lowest concentrations of molecules (except the only case of λ_{int} at $T = 50\,000$ K, for which the values of the internal specific heats become rather low). Thus, we can conclude that the most significant contribution to the thermal-conductivity coefficients is given by atoms, and, in the temperature range $15\,000 - 35\,000$ K, the main role belongs to the atomic electronic states. With the rise of the N_2 concentration in a mixture, the thermal-conductivity coefficients decrease noticeably.

Although the contribution of atomic electronic states to the thermal conductivity is found to be maximum, the impact of the molecular electronic states for $T = 10\,000 - 40\,000$ K is not negligible as well. This can be seen from Table I, where the contribution of different degrees of freedom to the total thermal conductivity of atoms and molecules is given. We see that for the temperatures under 5000 K, the internal thermal conductivity of molecules is completely determined by the rotational-vibrational modes of the ground electronic state. Then the contribution of the electronically excited states to the molecular internal thermal conductivity becomes essential (it gives about 10% for $T = 10\,000$ K and 40% for $T = 20\,000$ K). With the further temperature rise, for $T > 20\,000$ K, the role of the electronic levels decreases becoming negligible for $T > 40\,000$ K. Note that for $T > 40\,000$ K, the internal thermal-conductivity coefficient of molecules calculated taking into account only the ground electronic state $\lambda_{rv,\mathrm{N}_2}$ becomes larger than the coefficient $\lambda_{int,\mathrm{N}_2}$ obtained including the electronically excited states. It is explained by the similar behavior of the internal specific heat discussed above. For atoms, the contribution of the electronic states is negligible for low temperatures $T < 2000$ K; at $T \approx 20\,000$ K, it achieves the maximum of about 86% and then decreases with the temperature.

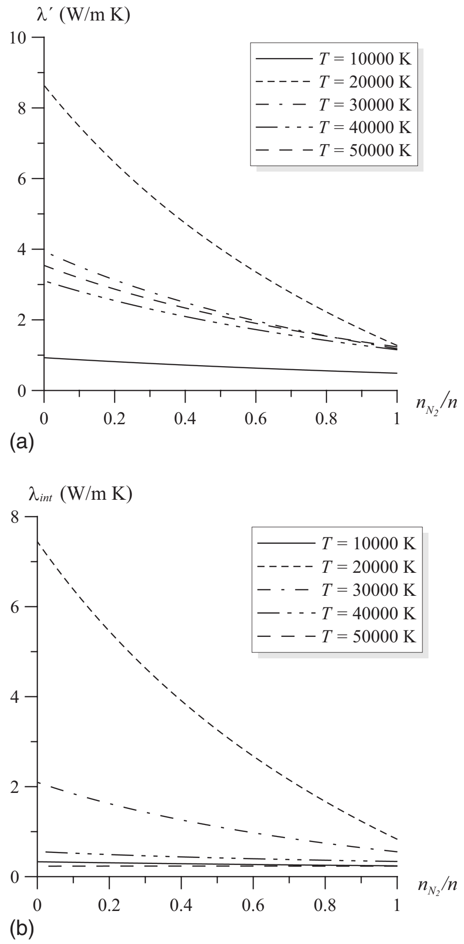

FIG. 5. The thermal-conductivity coefficients (a) λ' and (b) λ_{int} of the N/N_2 mixture as functions of the N_2 molar fraction n_{N_2}/n.

The results obtained above for atomic species agree qualitatively with those presented in Refs. [25–29] for a hydrogen plasma. On the other hand, in Ref. [30], the role of the electronic excitation in the heat transfer near the surface of a body re-entering the Earth's atmosphere with a high velocity (up to 13 km/s) was found to be rather weak. This is explained by the fact that although the temperature behind the shock wave is very high (about 50 000 K), the temperature near the surface drops sharply and becomes lower than 10 000 K. Therefore, in this case, the wall heat flux is not affected by the electronic excitation. However, for a different flow situation, the temperature near the wall may occur higher (for instance, for the Jupiter re-entry conditions), and the contribution of the electronic states to the heat flux should be much more important. Moreover, for the case of a thermally nonequilibrium gas, when the populations of the highly excited internal states occur larger, the influence of the electronic modes on the heat transfer is expected to be significant.

The above calculations were carried out using the set of data on the collision integrals proposed in Ref. [38]. These approximate formulas provide a rather good accuracy of the transport coefficients in the moderate temperature range. However, the limits of the validity of the collision integrals given in Ref. [38] are not discussed by the authors. In the

TABLE I. Contribution of the translational and internal modes to the total thermal conductivity of species (%).

T (K)	N		N_2		
	$\lambda_{tr,\mathrm{N}}$ (%)	$\lambda_{int,\mathrm{N}}$ (%)	$\lambda_{tr,\mathrm{N}_2}$ (%)	$\lambda_{rv,\mathrm{N}_2}$ (%)	$\lambda_{int,\mathrm{N}_2}$ (%)
500	100	0	72.6	27.4	27.4
1000	100	0	66.2	33.8	33.8
5000	87.2	12.8	57.4	42.5	42.6
10000	64.4	35.6	50.9	39.6	49.1
15000	28.7	71.3	36.0	28.3	64.0
20000	13.8	86.2	34.8	25.6	65.2
25000	24.2	75.8	42.8	27.6	57.2
30000	46.8	53.2	53.3	29.3	46.7
35000	68.5	31.5	63.0	29.0	37.0
40000	82.1	17.9	70.8	27.3	29.2
45000	89.5	10.5	76.7	24.9	23.3
50000	93.5	6.5	81.1	22.4	18.9

next figures, we compare the transport coefficients calculated using the data from Ref. [38] with those obtained with the collision integrals proposed by Capitelli *et al.* in Ref. [37]. The approximate expressions given in the latter paper are valid up to 100 000 K. Figure 6 presents the thermal-conductivity coefficients calculated using the two data sets. We can see that the coefficients obtained for the collision integrals from Ref. [38] are larger than those calculated using the data from Ref. [37]. While for the molecular species the maximum discrepancy does not exceed 15%, for atoms it occurs within 30–40 %. Thus, the maximum discrepancy for different coefficients varies as follows: for $\lambda_{int,\mathrm{N}_2}$, 2.5% at 20 000 K; for $\lambda_{tr,\mathrm{N}_2}$, 14% at 50 000 K; for λ'_{N_2}, 13% at 50 000 K; for $\lambda_{int,\mathrm{N}}$, 33% at 20 450 K; for $\lambda_{tr,\mathrm{N}}$, 37% at 50 000 K; and for λ'_{N}, 30.5% at 20 450 K. For the thermal conductivity of the translational degrees of freedom, the difference increases with the temperature, whereas for that of the internal modes, the maximum difference is achieved at $T \approx 20\,000$ K. We can conclude that the correct choice of the model for the collision integrals is of great importance for the accurate calculation of the transport properties in a high-temperature gas.

In Fig. 7, the Prandtl number

$$\mathrm{Pr} = \frac{c_p \eta}{\lambda'} \tag{30}$$

for different species is presented as a function of T. It is seen that the two models for the collision integrals provide the opposite behavior of the Prandtl number for atoms and molecules. Thus, the Prandtl number for atoms calculated using the data from Ref. [37] is larger than 0.67 and achieves the maximum at $T \approx 20\,000$ K. In contrast, the atomic Prandtl number obtained on the basis of the data from Ref. [38] is less than 0.67 and has the minimum at the similar temperature. For molecules, the discrepancy is less but still there is the difference. In any case, the Prandtl number is far from being constant, especially for atoms. This conclusion is of importance for the computational fluid dynamics, where the Prandtl number for atoms is commonly assumed to be constant Pr=0.67.

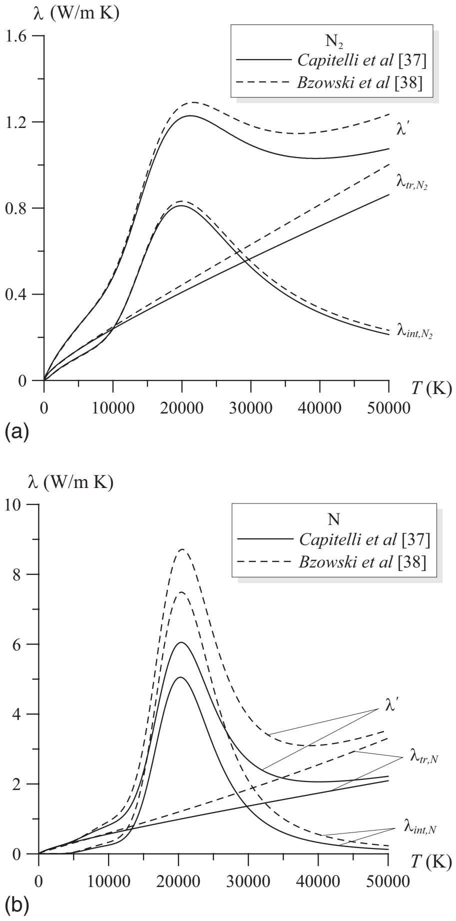

FIG. 6. The thermal-conductivity coefficients $\lambda_{tr,c}$, $\lambda_{int,c}$, and λ' of molecules (a) N_2 and atoms (b) N calculated as functions of T using the collision integrals from Refs. [37,38].

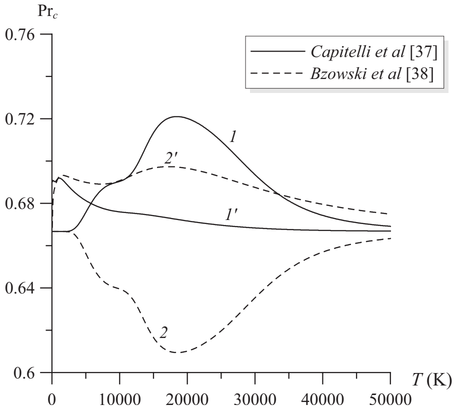

FIG. 7. The Prandtl number of species calculated as a function of T using the collision integrals from Refs. [37,38]. Curves: 1, 2—Pr_N; 1′, 2′—$\mathrm{Pr}_{\mathrm{N}_2}$.

VIII. GENERAL CONSIDERATIONS

In the present study, we calculate the transport coefficients using the arbitrarily fixed mixture composition. This approach can be used only for chemically nonequilibrium conditions. In the case of thermal-chemical equilibrium, the species number densities cannot be chosen arbitrarily since they are found from the equations of chemical equilibrium. In an inviscid flow, the equilibrium chemical composition is found from the set of algebraic equations, which express the conservation of mass and of the number of elements. In this case, the equilibrium mixture composition (EMC) is specified only by the pressure, temperature, and molar fractions of elements. In the majority of studies on chemically equilibrium flows, the EMC calculated on the basis of the equations of chemical equilibrium is used in both inviscid and viscous gas approximations. Such a technique is commonly used also for the calculation of the transport coefficients in chemically equilibrium flows (see Refs. [25–30,39,40] and many others). For instance, Butler and Brokaw [39,40] introduced the reactive thermal-conductivity coefficient on the basis of the diffusion coefficients and the EMC specified only by the pressure and temperature. The generalization of the Butler and Brokaw formulation for ionized mixtures is suggested in Ref. [41].

For the calculation of the transport terms, this method is correct since the transport coefficients involve the linearized collision operator and therefore depend on the zero-order species number densities. On the other hand, such an approach is not self-consistent for the calculation of the mixture composition in a viscous flow. Indeed, by definition,

$$n_c = \sum_l \int f_{cl} d\mathbf{u}_c. \tag{31}$$

In the case of chemical nonequilibrium [under the condition (1)], the species number density n_c is one of the main macroscopic parameters associated to the collision invariants of rapid processes (4). Therefore, according to the Chapman-Enskog formalism, it is totally specified by the zero-order distribution function,

$$n_c = n_c^{(0)} = \sum_l \int f_{cl}^{(0)} d\mathbf{u}_c. \tag{32}$$

In the case of thermal-chemical equilibrium, the set of collision invariants is different (see, for instance, Refs. [14,42]), and the corresponding set of macroscopic parameters includes the number densities of elements n_α instead of n_c; the number of elements is less than the number of species. The normalizing conditions of the Chapman-Enskog method are applicable in this case to n_α rather than to n_c,

$$n_\alpha = n_\alpha^{(0)} = \sum_{cl} \sigma_{\alpha c} \int f_{cl}^{(0)} d^3\mathbf{u}_c, \tag{33}$$

where $\sigma_{\alpha c}$ is the number of elements α in the component c. Now, if we calculate the number densities of species n_c, in the zero-order approximation we obtain

$$n_c^{(0)} = \sum_l \int f_{cl}^{(0)} d\mathbf{u}_c. \tag{34}$$

The number densities $n_c^{(0)} = n_c^{(0)}(p, T, n_\alpha/n)$ are equal to those found using the equations of chemical equilibrium.

In the first-order (viscous) approximation,

$$n_c = \sum_l \int f_{cl}^{(0)} (1 + \phi_{cl}^{(1)}) d\mathbf{u}_c, \tag{35}$$

$\phi_{cl}^{(1)}$ is the first-order correction to the distribution function, which, in the case of thermal-chemical equilibrium, is found in the form (see Ref. [14] and also the paper by Ern and Giovangigli [42])

$$\phi_{cl}^{(1)} = -\frac{1}{n}\mathbf{A}_{cl} \cdot \nabla \ln T - \frac{1}{n}\sum_\alpha \mathbf{D}_{cl}^\alpha \cdot \nabla \ln n_\alpha - \frac{1}{n}\boldsymbol{B}_{cl}:\nabla \mathbf{v} - \frac{1}{n} F_{cl} \nabla \cdot \mathbf{v}. \tag{36}$$

The functions $\mathbf{A}_{cl}$, $\mathbf{D}_{cl}^\alpha$, $\boldsymbol{B}_{cl}$, and F_{cl} are found from the appropriate linear integral equations.

If we substitute Eq. (36) into Eq. (35), all the vector and tensor terms vanish as integrals of odd functions over a symmetric interval. The only term making contribution to n_c in the first-order approximation is the scalar term associated to $\nabla \cdot \mathbf{v}$. Therefore,

$$n_c = n_c^{(0)} - \frac{\nabla \cdot \mathbf{v}}{n} \sum_l \int f_{cl}^{(0)} F_{cl} d\mathbf{u}_c, \tag{37}$$

and the species number densities (as well as their molar and mass fractions) in a viscous gas flow depend on the velocity divergence. The same function F_{cl} specifies the bulk viscosity coefficient in a weakly thermally chemically nonequilibrium flow.

Thus, we can conclude that calculating the species molar fractions from the equations of chemical equilibrium in a viscous gas is correct only in incompressible flows or in a nonmoving gas (with $\nabla \cdot \mathbf{v} = 0$). Moreover, in a viscous flow, evaluating the specific enthalpy on the basis of $n_c^{(0)}$ is not rigorous from the point of view of the kinetic theory. We suggest first to estimate the first-order corrections to the equilibrium mixture composition and then to conclude whether they are negligible or not.

IX. CONCLUSION

A closed description of a one-temperature mixture flow taking into account electronic excitation is proposed on the basis of the kinetic theory methods. The macroscopic equations and transport terms are derived, and the algorithms for the calculation of the transport coefficients are developed. The transport coefficients of the N/N_2 mixture are calculated in the temperature range 50–50 000 K. The influence of the electronic excitation on the specific heats and transport coefficients is estimated. In the temperature range

10 000–40 000 K, the contribution of the electronic modes to the thermal conductivity of species is found to be essential. The model of the collision integrals is very important for the correct prediction of the transport properties. The Prandtl number of atomic species is substantially nonconstant. The limits of the validity of the commonly used technique for the calculation of the transport properties in thermally and chemically equilibrium gas mixtures are shown. As the next step of this study, we plan to include the ionized species into consideration.

ACKNOWLEDGMENTS

The authors are grateful to Dr. D. Giordano for providing the tables of the atomic electronic states. We also thank Dr. M. Fertig for a useful discussion.

---

[1] S. Chapman and T. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 3rd ed. (Cambridge University Press, Cambridge, 1970).
[2] J. Hirschfelder, C. Curtiss, and R. Bird, *The Molecular Theory of Gases and Liquids* (John Wiley and Sons, New York, 1954).
[3] J. Ferziger and H. Kaper, *Mathematical Theory of Transport Processes in Gases* (North-Holland, Amsterdam, 1972).
[4] C. Wang Chang and G. Uhlenbeck, Transport Phenomena in Polyatomic Gases, University of Michigan Research Report No. CM-681, Project M604–6, July 10, 1951 (unpublished).
[5] L. Waldmann, Z. Naturforsch. A **12**, 660 (1957).
[6] R. Snider, J. Chem. Phys. **32**, 1051 (1960).
[7] E. Mason and L. Monchick, J. Chem. Phys. **36**, 1622 (1962).
[8] L. Monchick, K. Yun, and E. Mason, J. Chem. Phys. **39**, 654 (1963).
[9] S. Pascal and R. Brun, Phys. Rev. E **47**, 3251 (1993).
[10] E. Kustova and E. Nagnibeda, Chem. Phys. **208**, 313 (1996).
[11] A. Chikhaoui, J. Dudon, E. Kustova, and E. Nagnibeda, Physica A **247**, 526 (1997).
[12] E. Kustova and E. Nagnibeda, Chem. Phys. **233**, 57 (1998).
[13] E. Nagnibeda and E. Kustova, *Kinetic Theory of Transport and Relaxation Processes in Nonequilibrium Reacting Gas Flows* (Saint Petersburg University Press, Saint Petersburg, 2003).
[14] S. Vallander, E. Nagnibeda, and M. 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.
[15] B. Alexeev, *Mathematical Kinetics of Reacting Gases* (Nauka, Moscow, 1982).
[16] A. Ern and V. Giovangigli, *Multicomponent Transport Algorithms*, Lecture Notes in Physics, Series Monographs, M24 (Springer-Verlag, Berlin, 1994).
[17] R. Devoto, Phys. Fluids **9**, 1230 (1966).
[18] R. Devoto, Phys. Fluids **10**, 354 (1967).
[19] V. Zhdanov, *Transport Phenomena in Multicomponent Plasmas* (Energoizdat, Moscow, 1982).
[20] A. Kolesnikov and G. Tirskyi, Fluid Dyn. **19**, 643 (1984).
[21] S. Vasil'evsky, I. Sokolova, and G. Tirskyi, J. Appl. Mech. Tech. Phys. **27**, 61 (1986).
[22] A. Murphy and C. Arundell, Plasma Chem. Plasma Process. **14**, 451 (1994).
[23] A. Kolesnikov, 31st AIAA Plasmadynamics and Lasers Conference (AIAA 2000–2570, Denver, CO) (American Institute of Aeronautics and Astronautics, Denver, CO, 2000).
[24] T. E. B. Magin and G. Degrez, Phys. Rev. E **70**, 046412 (2004).
[25] M. Capitelli, R. Celiberto, C. Gorse, A. Laricchiuta, P. Minelli, and D. Pagano, Phys. Rev. E **66**, 016403 (2002).
[26] M. Capitelli, R. Celiberto, C. Gorse, A. Laricchiuta, D. Pagano, and P. Traversa, Phys. Rev. E **69**, 026412 (2004).
[27] D. Bruno, A. Laricchiuta, M. Capitelli, and C. Catalfamo, Phys. Plasmas **14**, 022303 (2007).
[28] D. Bruno, M. Capitelli, C. Catalfamo, and A. Laricchiuta, Phys. Plasmas **14**, 072308 (2007).
[29] D. Bruno, M. Capitelli, C. Catalfamo, and A. Laricchiuta, Phys. Plasmas **15**, 112306 (2008).
[30] M. Fertig, A. Dohr, and H.-H. Frühauf, J. Thermophys. Heat Transfer **15**, 148 (2001).
[31] B. Bottin, D. V. Abeele, T. Magin, and P. Rini, Prog. Aerosp. Sci. **42**, 38 (2006).
[32] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).
[33] M. Capitelli, G. Colonna, D. Giordano, L. Marraffa, A. Casavola, P. Minelli, D. Pagano, L. Pietanza, and F. Taccogna, *ESA STR-246* (ESA Publications Division, ESTEC, Noordwijk, The Netherlands, 2005).
[34] H. Griem, Phys. Rev. **128**, 997 (1962).
[35] E. Kustova, E. Nagnibeda, and D. Giordano, *ESA STR-255* (ESA Communication Production Office, ESTEC, Noordwijk, The Netherlands, 2008).
[36] V. Giovangigli, *Multicomponent Flow Modeling* (Birkhauser, Boston, 1999).
[37] M. Capitelli, C. Gorse, S. Longo, and D. Giordano, J. Thermophys. Heat Transfer **14**, 259 (2000).
[38] J. Bzowski, J. Kestin, E. Mason, and F. Uribe, J. Phys. Chem. Ref. Data **19**, 1179 (1990).
[39] J. Butler and R. Brokaw, J. Chem. Phys. **26**, 1636 (1957).
[40] R. Brokaw, J. Chem. Phys. **32**, 1005 (1960).
[41] A. Orsini and E. V. Kustova, Phys. Rev. E **79**, 056309 (2009).
[42] A. Ern and V. Giovangigli, Physica A **260**, 49 (1998).