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# Multitemperature kinetic model for heat transfer in reacting gas mixture flows

A. Chikhaoui, J. P. Dudon, and S. Genieys

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Heat transfer in a high temperature reacting gas flow is investigated taking into account the influence of strong vibrational and chemical nonequilibrium. Rapid and slow vibrational energy exchanges in a mixture of molecular gases with realistic molecular spectra are taken into account and the deviation from the Boltzmann distribution over vibrational levels is studied. A kinetic theory approach is developed for the modeling of transport properties of a reacting mixture of polyatomic gases and a generalized multitemperature model is given. This theoretical model is applied for the analysis of the heat transfer and diffusion behind a strong shock wave propagating in air. The heat conductivity, diffusion coefficients, and heat flux are calculated on the basis of this model and compared to the one-temperature approach. The influence of anharmonicity of molecular vibrations is evaluated. © 2000 American Institute of Physics. [S1070-6631(99)00807-7]

## I. INTRODUCTION

The investigation of high temperature reacting gas flows like those around space vehicles requires adequate models for transport properties such as thermal conductivity, diffusion, and viscosity. The excitation of internal degrees of freedom and nonequilibrium chemical reactions should be taken into account in the modeling of mass and heat transfer in real gas flows. The kinetic theory approach gives theoretical models for dissipative processes under different nonequilibrium conditions. Starting from Refs. 1 and 2 the kinetic theory of molecular gases was developed by many authors; a bibliography can be found in Refs. 3–5. Most results concerning transport properties of reacting mixtures were obtained under the condition of weak vibrational nonequilibrium. Such models are based on the assumption that the distribution over internal energies deviates weakly from the Boltzmann one, and it is supposed that all exchanges of internal energy have comparable rates which are much larger than the chemical reaction rates. But at high temperature it is important to take into account different rates of various energy exchanges because some of them become comparable with the rates of chemical reactions. Under such conditions the chemical–vibrational coupling can influence significantly the gas flow parameters.<sup>6–9</sup> Kinetic models of transport properties of reacting gas flows taking into account different rates of various vibrational energy exchanges are given in Refs. 10 and 11 and in Ref. 12 where some applications are also presented. In the present paper heat transfer in a high temperature reacting flow behind a shock wave is studied using the method given in Ref. 11.

We consider the following relation between the characteristic times of different processes in a reacting mixture:

$$\tau_{el} < \tau_r < \tau_{VV_1} \ll \tau_{VV_2} < \tau_{VRT} < \tau_{react} \sim \theta. \quad (1)$$

Here  $\tau_{el}$ ,  $\tau_r$ , and  $\tau_{react}$  are, respectively, the mean times between collisions with translational, rotational energy transfer and those with chemical reactions,  $\theta$  is the macroscopic relaxation time,  $\tau_{VV_1}$  is the mean time between the collisions with an exchange of vibrational quanta between molecules of the same chemical species,  $\tau_{VV_2}$  is that for the vibrational energy exchanges between different species,  $\tau_{VRT}$  is the time between collisions with inelastic translational–rotational–vibrational transfer. The condition (1) corresponds to rapid translational and rotational relaxation and rapid vibrational energy exchange between molecules of the same chemical species. From many experimental data<sup>6</sup> such a relation is known to be valid in vibrationally excited gases at high temperature and also in nozzle streams and expanding flows. With increasing the gas temperature, the characteristic time of  $VT$  relaxation becomes comparable to  $\tau_{VV_1}$  and  $\tau_{VV_2}$ , especially for the reactions with a high threshold or for slow reactions, so that the condition is modified as follows:

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

In this case the one-temperature approach follows from the kinetic equations. This model is widely used in chemical kinetics but it does not allow one to study the vibrational–chemical coupling in the vibrational nonequilibrium zone. In the present paper the kinetic theory treatment of transport properties of reacting mixture of polyatomic gases is performed for condition (1). The generalized multitemperature model based on non-Boltzmann distributions and taking into account realistic molecular spectra is given. This theoretical model is applied for the investigation of heat transfer and

diffusion in a nonequilibrium five component reacting mixture behind a plane shock wave propagating in air. The results are compared with the ones obtained for the harmonic oscillator model and also in the one-temperature approach under condition (2).

## II. MULTITEMPERATURE APPROACH

### A. Kinetic equations

We consider the kinetic equations for distribution functions  $f_{cij}(\mathbf{r}, \mathbf{u}, t)$  for every chemical species  $c$ , vibrational  $i$ , and rotational energy levels  $j$  over the velocity  $\mathbf{u}$ , and spatial coordinates:<sup>13</sup>

$$\frac{\partial f_{cij}}{\partial t} + \mathbf{u} \cdot \frac{\partial f_{cij}}{\partial \mathbf{r}} = \frac{1}{\varepsilon} J_{cij}^{\text{rap}} + J_{cij}^{\text{sl}}. \quad (3)$$

Here  $J_{cij}^{\text{rap}}$  and  $J_{cij}^{\text{sl}}$  are the collision integrals of rapid and slow processes, and  $\varepsilon = \tau_{\text{rap}}/\tau_{\text{sl}}$  is the small parameter, with  $\tau_{\text{rap}}$ ,  $\tau_{\text{sl}}$  the average times between the frequent and rare collisions, respectively. Under condition (1) the operator  $J_{cij}^{\text{rap}}$  may be written in the form

$$J_{cij}^{\text{rap}} = J_{cij}^{\text{el}} + J_{cij}^r + J_{cij}^{\text{VV}_1}. \quad (4)$$

Here  $J_{cij}^{\text{el}}$ ,  $J_{cij}^r$ ,  $J_{cij}^{\text{VV}_1}$  are the collision integrals corresponding, respectively, to elastic collisions, collisions with rotational energy change, and collisions with the exchange of vibrational quanta between molecules of the same chemical species.

The operator  $J_{cij}^{\text{sl}}$  has the form

$$J_{cij}^{\text{sl}} = J_{cij}^{\text{VV}_2} + J_{cij}^{\text{TRV}} + J_{cij}^{\text{react}}. \quad (5)$$

Here the collision integrals  $J_{cij}^{\text{VV}_2}$  and  $J_{cij}^{\text{TRV}}$  describe the  $\text{VV}_2$  exchanges of vibrational energy between different species and translational, rotational, and vibrational energy exchanges. The integral  $J_{cij}^{\text{react}}$  may be split into parts corresponding to collisions with chemical exchange reactions and to collisions with dissociation and recombination:

$$J_{cij}^{\text{react}} = J_{cij}^{\text{react}(2 \leftrightarrow 2)} + J_{cij}^{\text{react}(2 \leftrightarrow 3)}. \quad (6)$$

Expressions for the latter collision operators can be found in Refs. 13–16,4. The general formula for the inelastic collision integral  $J_{cij}^{\text{inel}}$  for a mixture has the form

$$J_{cij}^{\text{inel}} = \sum_{dki'l'j'k'l'} \int \left( f_{ci'l'j'k'l'} \frac{s_{ij}^c s_{kl}^d}{s_{i'l'}^c s_{k'l'}^d} - f_{cij} f_{dkl} \right) \times g \sigma_{cd,ijkl}^{i'l'j'k'l'} d^2 \Omega d\mathbf{u}_1, \quad (7)$$

where  $s_{ij}^c$  and  $s_{kl}^d$  are statistical weight factors and  $\sigma_{cd,ijkl}^{i'l'j'k'l'}$  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 labels of the energy levels after collision;  $\mathbf{g} = \mathbf{u} - \mathbf{u}_1$  is the relative velocity, and  $d^2 \Omega$  is the solid angle referring to the relative velocity after collision. The expressions for  $J_{cij}^{\text{VV}_1}$ ,  $J_{cij}^{\text{VV}_2}$ ,  $J_{cij}^{\text{TRV}}$ ,  $J_{cij}^r$ ,  $J_{cij}^{\text{el}}$  can be written in such manner using the cross sections for corresponding collisions.

The collision operator  $J_{cij}^{\text{react}(2 \leftrightarrow 2)}$  has the form

$$J_{cij}^{\text{react}(2 \leftrightarrow 2)} = \sum_{dc'd'kli'j'k'l'} \int \left( f_{c'i'j'k'l'} f_{d'k'l'} \frac{s_{ij}^c s_{kl}^d}{s_{i'l'}^c s_{k'l'}^d} - f_{cij} f_{dkl} \right) \times \left( \frac{m_c m_d}{m_c' m_{d'}} \right)^3 \times g \sigma_{cd,ijkl}^{c'd',i'l'j'k'l'} d^2 \Omega d\mathbf{u}_1, \quad (8)$$

where  $\sigma_{cd,ijkl}^{c'd',i'l'j'k'l'}$  is the cross section of the chemically active collision. The expression for  $J_{cij}^{\text{react}(2 \leftrightarrow 3)}$  in a mixture of diatomic molecules and atoms can be written in the form

$$J_{cij}^{\text{react}(2 \leftrightarrow 3)} = \sum_{dklk'l'} \int \left( f_{c'} f_{f'} f_{dk'l'} \hbar^3 \frac{s_{ij}^c s_{kl}^d}{s_{k'l'}^d} - f_{cij} f_{dkl} \right) \times \left( \frac{m_c}{m_c' m_{f'}} \right)^3 \times g \sigma_{cd,ijkl}^{c'f'd',k'l'} d\mathbf{u}_1 d\mathbf{u}' d\mathbf{u}_1' d\mathbf{u}_2', \quad (9)$$

where  $\sigma_{cd,ijkl}^{c'f'd',k'l'}$  is the cross section for dissociation of the molecule of  $c$ th species at the  $i$ th and  $j$ th vibrational and rotational levels in a collision with the molecule  $d$ th species at  $k$ th and  $l$ th vibrational and rotational levels;  $c'$ ,  $f'$  are the atomic species product of dissociation,  $k'$  and  $l'$  are the vibrational and rotational levels of the partner after the collision (usually it can be supposed that  $k' = k$ ,  $l' = l$ );  $\mathbf{u}$ ,  $\mathbf{u}_1$  and  $\mathbf{u}'$ ,  $\mathbf{u}_1'$ ,  $\mathbf{u}_2'$  are the velocities of particles before and after collision, respectively.

### B. Zero-order distribution functions and macroscopic equations

Using the generalized Chapman–Enskog method given in Ref. 11 for the solution of Eq. (3), the zero-order distribution functions may be approximated in the following form:

$$f_{cij}^{(0)} = \frac{n_c}{Z_c} s_{ij}^c \exp \left( - \frac{m_c c^2}{2k_B T} - \frac{\varepsilon_j^{ci}}{k_B T} - \frac{\varepsilon_i^c}{k_B T} - \vartheta_c i \right). \quad (10)$$

Here  $n_c$  is the number density of molecules of species  $c$ ,  $k_B$  the Boltzmann constant,  $T$  the gas temperature, and  $\mathbf{c} = \mathbf{u} - \mathbf{v}(\mathbf{r}, t)$ , with  $\mathbf{v}$  the macroscopic gas velocity;  $\varepsilon_j^{ci}$  is the rotational energy of a molecule of species  $c$  at the  $i$ th vibrational level,  $\varepsilon_i^c$  is the vibrational energy of a molecule of species  $c$  and  $Z_c$  is the total partition function for species  $c$ . The parameters  $\vartheta_c$  can be expressed in terms of the average number of vibrational quanta  $W_c$  carried by the  $c$ th component:

$$\rho_c W_c = \sum_{ij} i \int f_{cij}^{(0)} d\mathbf{u}. \quad (11)$$

The distribution function (10) is based on the system of the collision invariants of the most frequent collisions described by the operator  $J_{cij}^{\text{rap}}$  (4) and reflects the conservation of momentum, total energy, and the number of vibrational quanta for each molecular species. Similarly as for a one-component gas,<sup>17</sup> it is possible to introduce the temperature  $T_1^c$  of the first vibrational level of species  $c$  as follows:

$$\vartheta_c = \frac{\varepsilon_1^c}{k_B} \left( \frac{1}{T_1^c} - \frac{1}{T} \right).$$

Since vibrational and rotational energy spectra are simulated, respectively, in terms of an anharmonic oscillator and a rigid rotator,<sup>18</sup> we have  $Z_c = Z_c^r Z_c^v Z_c^e$ , with the vibrational partition functions

$$Z_c^v = Z_c^v(T, T_1^c) = \sum_i s_i^c \exp \left( - \frac{\varepsilon_i^c - i\varepsilon_1^c}{k_B T} - \frac{i\varepsilon_1^c}{k_B T_1^c} \right).$$

The distribution functions are normalized in terms of the macroscopic parameters  $n_c(\mathbf{r}, t)$ ,  $\mathbf{v}(\mathbf{r}, t)$ ,  $T(\mathbf{r}, t)$ ,  $T_1^c(\mathbf{r}, t)$ :

$$\begin{aligned} \sum_{ij} \int f_{cij} d\mathbf{u} &= \sum_{ij} \int f_{cij}^{(0)} d\mathbf{u} = n_c, \quad c=1, 2, \dots, L, \\ \sum_{cij} m_c \int \mathbf{u} f_{cij} d\mathbf{u} &= \sum_{cij} m_c \int \mathbf{u} f_{cij}^{(0)} d\mathbf{u} = \rho \mathbf{v}, \\ \sum_{cij} \int \left( \frac{m_c c^2}{2} + \varepsilon_i^c + \varepsilon_j^c \right) f_{cij} d\mathbf{u} & \\ = \sum_{cij} \int \left( \frac{m_c c^2}{2} + \varepsilon_i^c + \varepsilon_j^c \right) f_{cij}^{(0)} d\mathbf{u} &= \frac{3}{2} n k_B T + \rho E_r + \rho E_v, \\ \sum_{ij} i \int f_{cij} d\mathbf{u} &= \sum_{ij} i \int f_{cij}^{(0)} d\mathbf{u} = \rho_c W_c(T, T_1^c), \\ & c=1, 2, \dots, L_{\text{mol}}. \end{aligned} \quad (12)$$

Here  $n = \sum_c n_c$  is the total number density of particles,  $\rho = \sum_c m_c n_c$  the gas density,  $\rho_c = m_c n_c$ ,  $L$  the total (molecular and atomic) number of chemical species, and  $L_{\text{mol}}$  the number of molecular species,  $E_r$  and  $E_v$  are the rotational and vibrational energy per unit mass, respectively:

$$\begin{aligned} \rho E_r(T) &= \sum_{cij} \int \varepsilon_j^c f_{cij} d\mathbf{u}, \quad \rho E_v = \sum_c \rho_c E_v^c, \\ \rho_c E_v^c(T, T_1^c) &= \sum_i \varepsilon_i^c n_{ci}, \quad n_{ci} = \sum_j \int f_{cij} d\mathbf{u}. \end{aligned} \quad (13)$$

The expression for the level populations  $n_{ci}$  follows from Eq. (10):

$$n_{ci} = \frac{n_c}{Z_c^{\text{vibr}}(T, T_1^c)} s_i^c \exp \left( - \frac{\varepsilon_i^c - i\varepsilon_1^c}{k_B T} - \frac{i\varepsilon_1^c}{k_B T_1^c} \right). \quad (14)$$

Equation (14) may be considered as the generalized Treanor distribution<sup>17</sup> for a multicomponent mixture.

If anharmonic effects are negligible, distribution (14) reduces to the multitemperature Boltzmann distribution,

$$n_{ci} = \frac{n_c}{Z_c^{\text{vibr}}} s_i^c \exp \left( - \frac{\varepsilon_i^c}{k_B T_v^c} \right), \quad T_v^c = T_1^c. \quad (15)$$

In equilibrium ( $T_1^c = T$ ) Eq. (14) reduces to the one-temperature Boltzmann distribution.

The important feature of the distribution (14) is its dependence on two temperatures  $T$  and  $T_1^c$  in comparison to distributions for harmonic oscillators and the equilibrium

distributions which depend only on one temperature,  $T_v^c$  and  $T$ , respectively. The distinction is due to the fact that the rapid vibrational energy  $VV_1$  exchange inside every mode is nonresonant in case of a realistic molecular spectrum, and thus the vibrational energy of each species is not conserved in such collisions.

In Ref. 11 it is shown that distribution (14) is adequate for real vibrational level populations when the storage of vibrational energy of the species is not very high:  $T_1^c/T \ll 1$ . Such conditions, typical for shock waves, are considered in the present paper. In the case of the high storage of vibrational energy like in expanding flows ( $T_1^c/T \gg 1$ ) the model developed in Ref. 19 can be used, and Eq. (14) then describes the populations of only the low levels.

The nonequilibrium distribution functions (10) are specified in terms of the macroscopic parameters:  $n_c(\mathbf{r}, t)$ ,  $\mathbf{v}(\mathbf{r}, t)$ ,  $T(\mathbf{r}, t)$ ,  $T_1^c(\mathbf{r}, t)$ . The differential equations for these parameters are obtained from Eq. (3) using the classical procedure of kinetic theory and can be expressed in the following form:<sup>11</sup>

$$\frac{dn_c}{dt} + n_c \nabla \cdot \mathbf{v} + \nabla \cdot (n_c \mathbf{V}_c) = R_c^{\text{react}}, \quad c=1, \dots, L, \quad (16)$$

$$\begin{aligned} \rho_c \frac{dW_c}{dt} + \nabla \cdot \mathbf{q}_w^c &= R_c^w - W_c m_c R_c^{\text{react}} + W_c \nabla \cdot (\rho_c \mathbf{V}_c), \\ & c=1, \dots, L_{\text{mol}}, \end{aligned} \quad (17)$$

$$\rho \frac{d\mathbf{v}}{dt} + \nabla \cdot \mathbf{P} = 0, \quad (18)$$

$$\rho \frac{dU}{dt} + \nabla \cdot \mathbf{q} + \mathbf{P} : \nabla \mathbf{v} = 0. \quad (19)$$

Here  $U$  is the total internal energy per unit mass:

$$\rho U = \frac{3}{2} n k_B T + \rho E_r + \rho E_v + \rho E_f, \quad (20)$$

with  $\rho E_f = \sum_c \varepsilon^c n_c$ ,  $\varepsilon^c = -D_c$ ,  $D_c$  is defined by the energy of dissociation.

The diffusion velocity  $\mathbf{V}_c$  of component  $c$  is obtained from

$$n_c \mathbf{V}_c = \sum_{ij} \int \mathbf{c} f_{cij} d\mathbf{u}. \quad (21)$$

Next,  $\mathbf{P}$  is the pressure tensor,

$$\mathbf{P} = \sum_{cij} \int m_c \mathbf{c} \mathbf{c} f_{cij} d\mathbf{u}, \quad (22)$$

$\mathbf{q}$  the heat flux,

$$\mathbf{q} = \sum_{cij} \int \left( \frac{m_c c^2}{2} + \varepsilon_j^{ci} + \varepsilon_i^c + \varepsilon^c \right) \mathbf{c} f_{cij} d\mathbf{u} \quad (23)$$

and  $\mathbf{q}_w^c$  the flux of vibrational quanta

$$\mathbf{q}_w^c = \sum_{ij} i \int \mathbf{c} f_{cij} d\mathbf{u}. \quad (24)$$

The expressions for  $R_c^{\text{react}}$  and  $R_c^w$  on the right-hand sides of the equations for  $n_c$  and  $W_c$  are

$$R_c^{\text{react}} = \sum_{ij} \int J_{cij}^{\text{react}} d\mathbf{u}, \quad (25)$$

$$R_c^w = \sum_{ij} \int iJ_{cij}^{\text{sl}} d\mathbf{u}, \quad (26)$$

Equations (16) are the equations for number densities of chemical species, Eqs. (18) and (19) the momentum and energy conservation equations, and Eq. (17) the relaxation equations for the number of vibrational quanta for each component. Equation (17) appears due to strong vibrational and chemical nonequilibrium and rapid  $VV_1$  exchange. It may be noticed that under condition (2) when all vibrational energy exchanges occur more often than chemical reactions, the system of macroscopic equations includes only Eqs. (16), (18), and (19).

The transport terms (21)–(24) and production terms (25), (26) in Eqs. (16)–(19) are found proceeding from the distribution functions. In the zero-order approximation (10),  $\mathbf{q}^{(0)} = 0$ ,  $\mathbf{q}_w^{(0)} = 0$ ,  $\mathbf{V}_c^{(0)} = 0$ ,  $\mathbf{P}^{(0)} = p\mathbf{I}$ ,

$$R_c^{w(0)} = \sum_{ij} \int iJ_{cij}^{\text{sl}(0)} d\mathbf{u}, \quad (27)$$

$$R_c^{\text{react}(0)} = \sum_{ij} \int J_{cij}^{\text{react}(0)} d\mathbf{u}. \quad (28)$$

The expressions for  $R_c^{\text{react}(0)}$  and  $R_c^{w(0)}$  are obtained after substitution of the distributions (10) into the collision integrals (6):

$$R_c^{\text{react}(0)} = R_c^{2 \leftrightarrow 2(0)} + R_c^{2 \leftrightarrow 3(0)}, \quad (29)$$

$$R_c^{2 \leftrightarrow 2(0)} = \sum_{dc'd'} (n_c n_d k_{cd}^{c'd'} - n_c n_d k_{cd}^{c'd'}),$$

$$R_c^{2 \leftrightarrow 3(0)} = \sum_d n_d (n_c n_f k_{rec,d}^c - n_c k_{cd}^{\text{diss}}), \quad (30)$$

where  $k_{c'd'}^{cd}(T, T_1^c, T_1^d)$ ,  $k_{cd}^{\text{diss}}(T, T_1^c, T_1^d)$ ,  $k_{rec,d}^c(T, T_1^c, T_1^d)$  are the nonequilibrium rate coefficients for exchange reactions, dissociation, and recombination, respectively. The constraints connecting the rate constants of the forward and backward reactions follow from the detailed balance principle

$$\frac{k_{c'd'}^{cd}}{k_{cd}^{c'd'}} = \frac{Z_c Z_d}{Z_{c'} Z_{d'}}, \quad \frac{k_{rec,d}^c}{k_{cd}^{\text{diss}}} = \frac{Z_c}{Z_{c'} Z_{f'}}, \quad (31)$$

$$Z_c = Z_c^{\text{tr}}(T) Z_c^{\text{r}}(T) Z_c^{\text{v}}(T, T_1^c).$$

The nonequilibrium rate coefficients may be written in the form

$$k_{cd}^{c'd'} = \frac{1}{Z_c^{\text{v}} Z_d^{\text{v}}} \sum_{iki'k'} s_i^c s_k^d \times \exp\left(-\frac{\varepsilon_i^c + \varepsilon_k^d - i\varepsilon_1^c - k\varepsilon_1^d}{k_B T} - \frac{i\varepsilon_1^c}{k_B T_1^c} - \frac{k\varepsilon_1^d}{k_B T_1^d}\right) \times P_{cdik}^{c'd'i'k'}(T), \quad (32)$$

$$k_{cd}^{\text{diss}} = \frac{1}{Z_c^{\text{v}} Z_d^{\text{v}}} \sum_{ikk'} s_i^c s_k^d \times \exp\left(-\frac{\varepsilon_i^c + \varepsilon_k^d - i\varepsilon_1^c - k\varepsilon_1^d}{k_B T} - \frac{i\varepsilon_1^c}{k_B T_1^c} - \frac{k\varepsilon_1^d}{k_B T_1^d}\right) \times P_{cdik}^{\text{diss},dk'}(T), \quad (33)$$

where the state-to-state rate coefficients  $P_{cdik}^{c'd'i'k'}(T)$ ,  $P_{cdik}^{\text{diss},dk'}(T)$  are obtained after averaging the inelastic cross sections of reactive collisions over velocities and rotational energies.<sup>16</sup> Usually in Eq. (33) it is supposed that  $k' = k$  and therefore  $P_{cdik}^{\text{diss},dk'} = P_{cdik}^{\text{diss}}$ . The rate coefficients  $k_{cd}^{c'd'}$ ,  $k_{cd}^{c'd}$ , and  $k_{rec,d}^{\text{diss}}$  have a dimension  $\text{m}^3 \text{s}^{-1}$ , and the dimension of  $k_{rec,d}^c$  is  $\text{m}^6 \text{s}^{-1}$ .

### C. First-order solution and transport terms

The first-order distribution functions are derived in Ref. 11 using the generalized Chapman–Enskog method for Eq. (3):

$$f_{cij}^{(1)} = f_{cij}^{(0)} \left( -\frac{1}{n} \mathbf{A}_{cij} \cdot \nabla \ln T - \frac{1}{n} \sum_d \mathbf{A}_{cij}^{d(1)} \cdot \nabla \ln T_1^d - \frac{1}{n} \sum_d \mathbf{D}_{cij}^d \cdot \mathbf{d}_d - \frac{1}{n} \mathbf{B}_{cij} : \nabla \mathbf{v} - \frac{1}{n} F_{cij} \nabla \cdot \mathbf{v} - \frac{1}{n} G_{cij} \right). \quad (34)$$

The functions  $\mathbf{A}_{cij}$ ,  $\mathbf{A}_{cij}^{d(1)}$ ,  $\mathbf{B}_{cij}$ ,  $\mathbf{D}_{cij}^d$ ,  $F_{cij}$  and  $G_{cij}$  are found from linear integral equations and additional constraints following from the normalizing conditions.<sup>11</sup>

The first-order distribution functions in the multitemperature approximation contain gradients of the gas temperature  $T$ , of the temperatures of the first vibrational levels  $T_1^c$  of the different chemical species, and of the corresponding number densities. These distribution functions describe the strong vibrational and chemical nonequilibrium and differ from the weak nonequilibrium solution.<sup>2</sup> In the latter case  $T_1^c = T$ , so that  $f_{cij}^{(1)}$  contains the gradient of the gas temperature  $\nabla T$  only and does not contain  $G_{cij}$ .

Now the pressure tensor, diffusion velocities, the flux of total energy, and the fluxes of vibrational quanta for each molecular species in the first-order approximation will be derived. The distribution functions (34) provide the following expressions for the pressure tensor:

$$\mathbf{P} = (p - p_{\text{rel}}) \mathbf{I} - 2\mu \mathbf{S} - \eta \nabla \cdot \mathbf{V}. \quad (35)$$

Here  $\mu$ ,  $\eta$  are the shear and bulk viscosity coefficients,  $p_{\text{rel}}$  is the relaxation pressure:

$$\mu = \frac{k_B T}{10} [\mathbf{B}, \mathbf{B}], \quad \eta = k_B T [F, F], \quad p_{\text{rel}} = k_B T [F, G]. \quad (36)$$

The bracket integrals  $[A, B]$  are introduced in Ref. 11 in the form

$$[A, B] = \sum_{cd} \frac{n_c n_d}{n^2} ([A, B]_{cd}' + [A, B]_{cd}''), \quad (37)$$

where

$$[A, B]'_{cd} = \frac{1}{2n_c n_d} \sum_{ijkli'j'k'l'} \int f_{cij}^{(0)} f_{dkl}^{(0)} (B_{cij} - B_{ci'j'}) \times (A_{cij} - A_{ci'j'}) g \sigma_{cd, ijkl}^{i'j'k'l'} d^2\Omega d\mathbf{u} d\mathbf{u}_1,$$

$$[A, B]''_{cd} = \frac{1}{2n_c n_d} \sum_{ijkli'j'k'l'} \int f_{cij}^{(0)} f_{dkl}^{(0)} (B_{cij} - B_{ci'j'}) \times (A_{dkl} - A_{dk'l'}) g \sigma_{cd, ijkl}^{i'j'k'l'} d^2\Omega d\mathbf{u} d\mathbf{u}_1.$$

The bracket integrals contain the cross sections of the most frequent collisions.

The additional terms in the pressure tensor such as the relaxation pressure  $p_{\text{rel}}$  and bulk viscosity  $\eta$  appear in this case due to the inelastic translational-rotational  $TR$  energy transfers and  $VV_1$  vibrational exchanges in the collisions between molecules of the same chemical species. They are expressed as a sum of two terms:

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

which are related to the inelastic  $TR$  and nonresonant  $VV_1$  energy exchanges inside every mode. The bulk viscosity phenomenon is widely discussed in the literature.<sup>20,13,21-25</sup> The transport kinetic theory shows that the appearance of bulk viscosity in the diagonal elements of the pressure tensor is connected with weakly nonequilibrium inelastic processes.<sup>2,23,13,21,26</sup> The distribution functions (10) correspond to a weak deviation from the Maxwell-Boltzmann equilibrium distribution over translational and rotational energy and to a strong vibrational and chemical nonequilibrium. In this case bulk viscosity describes the equilibration only due to rapid inelastic processes (translational-rotational energy exchange and nonresonant  $VV_1$  exchange of vibrational quanta inside each mode).<sup>26</sup> The equations for  $f_{cij}^{(1)}$  contain the operator of only rapid processes. Strong vibrational and chemical nonequilibrium leads to additional relaxation equations for the number densities of species and for the numbers of vibrational quanta (or for the fictitious vibrational temperature  $T_1^c$ ) of each molecular species and also to the appearance of relaxation pressure. The modeling of non-equilibrium processes only in the frame of bulk viscosity without additional relaxation equations is possible only in the case when all inelastic processes are weakly nonequilibrium and have the characteristic times much shorter than the mean time of change of macroscopic parameters.<sup>1,2</sup> On the contrary, if all inelastic processes can be considered as the slow ones, the bulk viscosity does not appear, and relaxation processes in all internal modes should be described by the equations for the populations of internal states.

The diffusion velocity in the first-order approximation takes the following form:

$$\mathbf{V}_c = - \sum_d D_{cd} \mathbf{d}_d - D_{T_c} \nabla \ln T - \sum_d D_{T_c}^{d(1)} \nabla \ln T_1^d, \quad (38)$$

where

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

is the diffusive driving force for each chemical species. The diffusion and thermal diffusion coefficients  $D_{cd}$  and  $D_{T_c}$  are:

$$D_{cd} = \frac{1}{3n} [\mathbf{D}^c, \mathbf{D}^d], \quad D_{T_c} = \frac{1}{3n} [\mathbf{D}^c, \mathbf{A}]. \quad (39)$$

Additional thermal diffusion coefficients  $D_{T_c}^{d(1)}$  at the gradients of  $T_1^c$  are found to be zero under the assumption of uncorrelated translational and internal motions:

$$D_{T_c}^{d(1)} = \frac{1}{3n} [\mathbf{D}^c, \mathbf{A}^{d(1)}] = 0. \quad (40)$$

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 the gradients of  $n_c$  involved in  $\mathbf{d}_c$ :<sup>11</sup>

$$\mathbf{q} = -\lambda'_{irv} \nabla T - \sum_c \lambda_v^c \nabla T_1^c - p \sum_c D_{T_c} \mathbf{d}_c + \sum_c \left( \frac{5}{2} k_B T + \langle \varepsilon_j \rangle_r + \langle \varepsilon_i \rangle_v + \varepsilon^c \right) n_c \mathbf{V}_c, \quad (41)$$

and

$$\varepsilon_1^c \mathbf{q}_w^c = -\lambda_{vi}^c \nabla T - \lambda_{vv}^c \nabla T_1^d. \quad (42)$$

Here  $\langle \varepsilon_j \rangle_r$  and  $\langle \varepsilon_i \rangle_v$  are the averaged rotational and vibrational energies. The thermal conductivity coefficients are defined as follows:

$$\lambda' = \frac{k_B}{3} [\mathbf{A}, \mathbf{A}], \quad \lambda_{vi}^c = \frac{k_B T_1^c}{3T} [\mathbf{A}^{c(1)}, \mathbf{A}], \quad (43)$$

$$\lambda_{iv}^c = \frac{k_B T}{3T_1^c} [\mathbf{A}, \mathbf{A}^{c(1)}], \quad \lambda_{vv}^c = \frac{k_B}{3} [\mathbf{A}^{c(1)}, \mathbf{A}^{c(1)}],$$

$$\lambda'_{irv} = \lambda' + \sum_c \lambda_{vi}^c, \quad \lambda_v^c = \lambda_{iv}^c + \lambda_{vv}^c. \quad (44)$$

The coefficient  $\lambda'$  determines the transport of the translational and rotational energy and a small part of vibrational energy which transfers to the translational one in the rapid process due to the nonresonant character of  $VV_1$  exchange in all vibrational modes:  $\lambda' = \lambda_{ir} + \lambda_r + \lambda_a$ . The coefficients  $\lambda_{vv}^c$  correspond to the transport of the total number of vibrational quanta  $W_c$  of each molecular species. The remaining coefficients  $\lambda_{vi}^c$ ,  $\lambda_{iv}^c$  are determined by the transport of vibrational quanta as well as by the loss or gain of vibrational energy in nonresonant  $VV_1$  exchange in species  $c$ . For harmonic oscillators  $\lambda_{vi}^c = \lambda_{iv}^c = \lambda_a = 0$ , and vibrational bulk viscosity and vibrational relaxation pressure vanish too, because rapid  $VV_1$  exchange is resonant and does not contribute to these transport coefficients.

#### D. Thermal conductivity, diffusion, and thermal diffusion coefficients

In order to calculate the thermal conductivity and diffusion coefficients, the linear integral equations for the functions  $\mathbf{A}_{cij}$ ,  $\mathbf{A}_{cij}^{d(1)}$ , and  $\mathbf{D}_{cij}^d$  following from Eq. (3) have to be

solved. Approximate solutions are found using finite expansions in Sonine and Waldmann-Trübenbacher orthogonal polynomials:

$$\mathbf{A}_{cij} = \frac{m_c \mathbf{c}}{2k_B T} \sum_{rpq} a_{c,rpq} S_{3/2}^{(r)} \left( \frac{m_c c^2}{2k_B T} \right) \times P_j^{(p)} \left( \frac{\varepsilon_j^c}{k_B T} \right) P_i^{(q)} \left( \frac{\varepsilon_i^c - i\varepsilon_1^c}{k_B T} \right), \quad (45)$$

$$\mathbf{A}_{cij}^{d(1)} = \frac{m_c \mathbf{c}}{2k_B T} \sum_r a_{c,r}^{d(1)} P_i^{(r)} \left( \frac{i\varepsilon_1^c}{k_B T} \right), \quad (46)$$

$$\mathbf{D}_{cij}^d = \frac{m_c \mathbf{c}}{2k_B T} \sum_r a_{c,r}^d S_{3/2}^{(r)} \left( \frac{m_c c^2}{2k_B T} \right). \quad (47)$$

The ensuing systems of linear algebraic equations for the expansion coefficients  $a_{c,rpq}$ ,  $a_{c,r}^{d(1)}$ ,  $d_{c,r}^d$  are given in Ref. 11.

Substituting the expansions (45)–(47) into Eqs. (39) and (43) and using the normalizing conditions for the polynomials, one can express the diffusion, thermal diffusion, and thermal conductivity coefficients in terms of the expansion coefficients. The lowest-order approximations are

$$D_{cd} = \frac{1}{2n} d_{d,0}^c, \quad (48)$$

$$D_{Tc} = -\frac{1}{2n} a_{c,000}, \quad (49)$$

$$\lambda'_{trv} = \sum_c \frac{n_c}{n} \left( \frac{5k_B}{4} a_{c,100} + \frac{k_B^2 C_{r,c}}{m_c} a_{c,010} + \frac{k_B^2 C_{v,c}^T}{m_c} a_{c,001} \right), \quad (50)$$

$$\lambda_{v^c}^c = \frac{n_c}{n} \frac{k_B^2 C_{v,c}^{T_1}}{m_c} a_{c,1}^{c(1)}, \quad \lambda_{v^c}^c = \frac{n_c}{n} \frac{k_B^2 C_{w,c}^T}{m_c} a_{c,001}, \quad (51)$$

$$\lambda_{vv^c}^c = \frac{n_c}{n} \frac{k_B^2 C_{w,c}^{T_1}}{m_c} a_{c,1}^{c(1)}.$$

Here modified specific heats at constant volume are introduced as follows:

$$C_{r,c} = \frac{\partial}{\partial T} E_r^c, \quad C_{v,c}^T = \frac{\partial}{\partial T} E_v^c(T, T_1^c),$$

$$C_{v,c}^{T_1} = \frac{\partial}{\partial T_1^c} E_v^c(T, T_1^c),$$

$$C_{w,c}^T = \frac{\partial}{\partial T} (\varepsilon_1^c W_c(T, T_1^c)), \quad C_{w,c}^{T_1} = \frac{\partial}{\partial T_1^c} (\varepsilon_1^c W_c(T, T_1^c)),$$

$$C_{a,c}^T = C_{v,c}^T - C_{w,c}^T, \quad C_{a,c}^{T_1} = C_{v,c}^{T_1} - C_{w,c}^{T_1}.$$

In this way all transport coefficients are expressed in terms of macroscopic parameters, elastic and inelastic colli-

sion integrals of the most frequent collisions, and nonequilibrium specific heats (52) determined by the nonequilibrium distribution (14). The macroscopic parameters should be found from the macroscopic equations (16)–(19). Similarly as in Ref. 19, the calculation shows that the contribution of the inelastic collision integrals to the thermal conductivity and diffusion coefficients is rather small and does not exceed 2%. The main information about the nonequilibrium vibrational distributions is contained in the specific heats.

It should be pointed out that simplified formulas for the evaluation of transport properties in reacting gas mixtures based on the various assumptions were obtained by several authors. One can find a review of the models in Refs. 27–29. In Ref. 27 the approximate expressions for transport coefficients are given in the cases of thermal equilibrium, frozen and nonequilibrium mixtures of dissociating and ionized gases. In the nonequilibrium case the vibrational modes are supposed to be completely excited and the single vibrational temperature is introduced for a mixture. The assumption about the same vibrational temperature for all species is questionable and is not always adequate for realistic nonequilibrium conditions.

The one-temperature weakly nonequilibrium regime in mixtures of ionized and neutral gases is considered in Ref. 28. Simplified useful formulas for transport properties are obtained on the basis of the Hirschfelder approximation<sup>30</sup> and using chemical equilibrium distributions.

In paper<sup>29</sup> numerous results concerning the transport coefficients of dissociating gases of Earth and Martian atmospheres are reported. The transport properties have been calculated in the frame of the one-temperature Chapman–Enskog approximation for the chemical equilibrium mixture composition. Empirical approximate expressions for the transport coefficients are also analyzed.

All these papers do not take into account the different rates of  $VV$  and  $TRV$  energy exchange and the non-Boltzmann vibrational distributions. It is supposed that the distributions over vibrational energy and chemical species deviate only slightly from thermal equilibrium. In the present study we calculate the transport coefficients using expressions obtained in the case of strong vibrational and chemical nonequilibrium in mixtures of neutral particles.

### III. THE ONE-TEMPERATURE APPROACH

The results obtained above in the generalized multitemperature approach can be compared with the ones obtained on the basis of the one-temperature model which is appropriate under condition (2). In this case the zero-order solution  $f_{cij}^{(0)}$  has the form of thermal equilibrium Maxwell–Boltzmann distribution with the gas temperature  $T$  and is determined by the macroscopic parameters  $n_c(\mathbf{r}, t)$ ,  $\mathbf{v}(\mathbf{r}, t)$ ,  $T(\mathbf{r}, t)$ . These macroscopic parameters are found from the equations of nonequilibrium one-temperature chemical kinetics.

The first-order distribution functions are obtained in the form:

$$f_{cij}^{(1)} = f_{cij}^{(0)} \left( -\frac{1}{n} \mathbf{A}_{cij} \cdot \nabla \ln T - \frac{1}{n} \sum_d \mathbf{D}_{cij}^d \cdot \mathbf{d}_d - \frac{1}{n} \mathbf{B}_{cij} : \nabla \mathbf{v} - \frac{1}{n} F_{cij} \nabla \cdot \mathbf{v} - \frac{1}{n} G_{cij} \right). \quad (53)$$

These distribution functions describe strong chemical non-equilibrium under the condition of weak vibrational-rotational nonequilibrium. They contain only the gradient of the gas temperature  $T$  and do not depend on the vibrational temperature gradients as in the multitemperature approach.

In this case the equations for the coefficients of the gradients contain the operators of rotational and all vibrational inelastic transfers. The pressure tensor is defined by Eq. (35), the appropriate kinetic coefficients can be found from Eq. (36) with bracket integrals containing not only the cross sections of the  $VV_1$  exchange but all inelastic energy transfers. Consequently the relaxation pressure and vibrational bulk viscosity coefficient also depend on the cross sections of all energy exchanges.

The diffusion velocity and the total heat flux contain the gradients of  $n_c$  and gas temperature and have the form:

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

$$\mathbf{q} = -\lambda' \nabla T - p \sum_c D_{Tc} \mathbf{d}_c + \sum_c \left( \frac{5}{2} k_B T + \langle \varepsilon_{ij}^c \rangle + \varepsilon^c \right) n_c \mathbf{V}_c. \quad (55)$$

Here the diffusion, thermal diffusion, and thermal conductivity coefficients are expressed by Eq. (39) and the first expression in (43) but the functions  $\mathbf{A}_{cij}$  are found from the integral equations different from the ones in the multitemperature case. In order to solve integral equations for the functions  $\mathbf{A}_{cij}$  one can expand them into double series of the Sonine and Waldmann-Trübenbacher polynomials over the dimensionless translational and internal energies. The equations for the coefficients  $a_{c,rp}$  of these expansions are given in Ref. 11. The thermal conductivity coefficient becomes:

$$\lambda' = \sum_c \frac{n_c}{n} \left( \frac{5}{4} k_B a_{c,10} + \frac{k_B^2 C_{\text{int},c}}{m_c} a_{c,01} \right) = \lambda'_t + \lambda'_{\text{int}}, \quad (56)$$

where

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

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

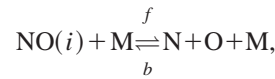
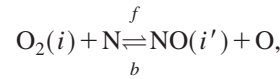
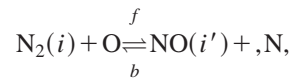
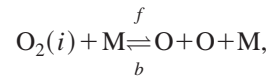
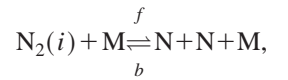
The diffusion and thermal diffusion coefficients are defined, respectively, by Eqs. (48) and (49). The coefficients  $d_{c,r}^d$  can be found from the same system as in the multitemperature approach.

One should mention here that the one-temperature approximation for reacting mixtures was studied in Ref. 4,

where the tempered reaction regime is considered when the chemical characteristic times are greater by an order of magnitude than the mean free time. Expressions of transport properties in this regime are derived and the mathematical aspects of the linear equations for coefficients and computational algorithms are discussed.

#### IV. APPLICATION TO THE FLOW BEHIND A PLANE SHOCK WAVE

In this section the nonequilibrium kinetics and transport properties in a five-component reacting air mixture behind a plane shock wave is studied using the multitemperature approach developed in Sec. II. The reaction system is the following:



where M is any molecule. Since the vibrational relaxation time of NO is rather short compared to those of  $\text{N}_2$  and  $\text{O}_2$ ,<sup>6</sup> the NO molecules are close to thermal equilibrium with the gas temperature.

#### A. Governing equations

The system of macroscopic equations (16)–(19) will now be solved in the zero-order approximation. The one-dimensional stationary version of the system is considered. This gives an approximation of the macroscopic parameters of the mixture which are used in order to compute the transport coefficients. The numerical resolution of the complete system (16)–(19) with dissipative terms (35), (38), (41) and (42) requires the calculation of transport coefficients at each step of the gas dynamic code and will be considered in a future work.

In the zero-order approximation, the one-dimensional stationary version of the system (16)–(19) for a multicomponent mixture can be rewritten as

$$\frac{d}{dx} (\rho Y_c v) = m_c R_c^{\text{react}}, \quad c = 1, \dots, L, \quad (57)$$

$$\frac{d}{dx} (\rho Y_c W_c v) = R_c^w, \quad c = 1, \dots, \tilde{L}_{\text{mol}}, \quad (58)$$

$$\frac{d}{dx} (\rho v^2 + p) = 0, \quad (59)$$



$$\frac{d}{dx}((\rho U + p)v) = 0. \quad (60)$$

where  $Y_c = \rho_c/\rho$  is the mass fraction of the species  $c$ , and  $\tilde{L}_{\text{mol}}$  is the number of those species that require the introduction of a distinct first-level vibrational temperature  $T_1^c$ .

The numerical code used to compute the solution of system (57)–(60) is the extension to real molecular spectrum of the code<sup>31</sup> based on the Boltzmann distribution and valid for the harmonic oscillator model. The vector of unknowns is

$$X = \begin{pmatrix} v \\ T \\ Y_c, \quad c = 1, \dots, L \\ Y_c W_c, \quad c = 1, \dots, \tilde{L}_{\text{mol}} \end{pmatrix}.$$

In order to express  $dU/dx$  in terms of  $dX/dx$ , we use Eqs. (20) and (13) and notice that

$$\frac{dE_v^c}{dx} = \begin{pmatrix} C_{v,c}^T \\ C_{w,c}^{T_1} \end{pmatrix} \cdot \left( J_{(T,T_1^c)}^{-1}(T, W_c) \frac{d}{dx} \begin{pmatrix} T \\ W_c \end{pmatrix} \right),$$

where  $J_{(T,T_1^c)}(T, W_c)$  denotes the Jacobian matrix of  $(T, W_c)$  with respect to  $(T, T_1^c)$ . The modified specific heats  $C_{v,c}^T$  and  $C_{w,c}^{T_1}$ , as well as  $C_{v,c}^T$  and  $C_{w,c}^{T_1}$  are defined by Eq. (52). A simple computation shows that  $C_{w,c}^{T_1}$  is nonnegative, which ensures the invertibility of  $J_{(T,T_1^c)}(T, W_c)$ . Hence,

$$\frac{dE_v^c}{dx} = \begin{cases} \left( C_{v,c}^T - C_{v,c}^{T_1} \frac{C_{w,c}^T}{C_{w,c}^{T_1}} \right) \frac{dT}{dx} + \frac{C_{v,c}^{T_1}}{C_{w,c}^{T_1}} \frac{dW_c}{dx} & \text{vibrational nonequilibrium} \\ (C_{v,c}^T + C_{v,c}^{T_1}) \frac{dT}{dx} & \text{vibrational equilibrium.} \end{cases}$$

The production terms (27)–(28) are expressed as functions of  $(T, T_1^c)$  and not as functions of  $(T, W_c)$ . In the present computation,  $T_1^c$  is computed starting from the calculated value of  $W_c$  for  $T$  fixed by a Newton procedure, using the nonnegativeness of  $C_{w,c}^{T_1}$ .

## B. Production terms

In this section we consider the zero-order production terms (27) and (28) in Eqs. (57)–(60) [hereafter we will omit the index (0) at the production terms]. Using (27) and (5) the vibrational production term  $R_c^w$  splits into three parts:

$$R_c^w = R_c^{w, VV_2} + R_c^{w, TRV} + R_c^{w, \text{react}},$$

where  $R_c^{w, VV_2}$  and  $R_c^{w, TRV}$  express the change of vibrational quanta of molecules of  $c$  species due to slow  $VV_2$  and  $TRV$  vibrational energy exchange,  $R_c^{w, \text{react}}$  describes the change of vibrational quanta of molecules  $c$  species due to chemical reactions.

In our calculations we suppose that the probability of the simultaneous translation–rotation–vibration transition is low

compared to the probability of  $VT$  vibrational energy exchange, and therefore the production term  $R_c^{w, TRV}$  reduces to  $R_c^{w, VT}$ . One can introduce the relaxation time of  $VT$  process in molecular species  $c$  in the following way:

$$\begin{aligned} \tau_{\text{vibr},c} &= \frac{\sum_{ij} i! j! J_{cij}^{VT} d\mathbf{u}}{\rho_c (W_c(T, T) - W_c(T, T_1^c))} \\ &= \frac{R_c^{w, VT}}{\rho_c (W_c(T, T) - W_c(T, T_1^c))} \end{aligned} \quad (61)$$

and thus connect the production term  $R_c^{w, VT}$  due to  $VT$  relaxation with some empirical data on the vibrational relaxation time. We use for the computation of  $\tau_{\text{vibr},c}$  the empirical expression of Millikan and White<sup>32</sup> corrected by Park.<sup>33</sup> The production term  $R_c^{w, VV_2}$  is simulated using the method described in Ref. 6.

The chemical production term  $R_c^{\text{react}}$  may be written in the form:

$$R_c^{\text{react}} = \mathcal{N} \sum_r (\nu''_{c,r} - \nu'_{c,r}) \left( k_{f,r} \prod_s \xi_s^{\nu'_{s,r}} - k_{b,r} \prod_s \xi_s^{\nu''_{s,r}} \right), \quad (62)$$

where  $\mathcal{N}$  is the Avogadro number. The summation is taken over all the reactions  $r$  ( $r = 1, \dots, R$ ), and the products are taken over all the species  $s$ . Furthermore  $\nu'_{c,r}$  and  $\nu''_{c,r}$  denote the stoichiometric coefficients of the reaction  $r$ , respectively, associated to the reagents and to the products of the forward reaction, and  $\xi_c = n_c/\mathcal{N}$  denotes the molar concentration of species  $c$ .

The forward and backward rate constants  $k_{f,r}$  and  $k_{b,r}$  are connected to the nonequilibrium rate coefficients  $k_{c'd'}^{cd}$ ,  $k_{cd}^{\text{diss}}$ ,  $k_{\text{rec},d}^c$  given in Eqs. (32), (33) by the following relations:

$$k_{f,r} = \frac{\mathcal{N}}{\nu''_{c,r} - \nu'_{c,r}} k_{c'd'}^{cd}, \quad k_{b,r} = \frac{\mathcal{N}}{\nu''_{c,r} - \nu'_{c,r}} k_{c'd'}^{cd},$$

for exchange reactions, (63)

$$k_{f,r} = \frac{\mathcal{N}}{\nu''_{c,r} - \nu'_{c,r}} k_{cd}^{\text{diss}}, \quad k_{b,r} = \frac{\mathcal{N}^2}{\nu''_{c,r} - \nu'_{c,r}} k_{\text{rec},d}^c,$$

for dissociation, recombination. (64)

The dimensions of the rate constants  $k_{f,r}$  and  $k_{b,r}$  are  $\text{mol}^{-1} \text{m}^3 \text{s}^{-1}$  for exchange reactions and dissociation, and  $\text{mol}^{-2} \text{m}^6 \text{s}^{-1}$  for recombination.

The vibrational production term corresponding to

chemistry–vibration exchanges,  $R_c^{w,\text{react}}$ , reads:

$$\begin{aligned}
 R_c^{w,\text{react}} = & \mathcal{N} \sum_{r, v''_{c,r} > v'_{c,r}} (v''_{c,r} - v'_{c,r}) \\
 & \times \left( k_{f,r} \prod_s \xi_s^{v'_{s,r}} G_{\text{app},f,r,c} - k_{b,r} \prod_s \xi_s^{v''_{s,r}} G_{\text{va},b,r,c} \right) \\
 & + \mathcal{N} \sum_{r, v''_{c,r} < v'_{c,r}} (v''_{c,r} - v'_{c,r}) \\
 & \times \left( k_{f,r} \prod_s \xi_s^{v'_{s,r}} G_{\text{va},f,r,c} - k_{b,r} \prod_s \xi_s^{v''_{s,r}} G_{\text{app},b,r,c} \right),
 \end{aligned} \tag{65}$$

where  $G_{\text{app},c}$  and  $G_{\text{va},c}$  are the numbers of vibrational quanta gained or lost when the molecule  $c$  is created or destroyed. The subscripts  $f,r$  and  $b,r$  indicate, respectively, that the energy exchanges happen during the forward and backward reaction  $r$ .

We will write the rate constants as

$$k_{f,r} = Z_{f,r} k_{f,r}^{\text{eq}}, \tag{66}$$

where  $Z_{f,r}$  is the nonequilibrium factor,  $k_{f,r}^{\text{eq}}$  is the rate constant of a forward reaction calculated under assumption of thermal equilibrium. For the computation of the nonequilibrium factor  $Z_{f,r}$  the state-specific rate constants are defined by

$$k_{f,r} = \frac{1}{n_c} \sum_i n_{ci} k_{f,r,ci}.$$

Then, following Treanor and Marrone<sup>34</sup> we introduce a dimensionless coefficient  $P_{f,r,ci}$  which may be considered as a probability of the fact that a molecule  $c$  involved in forward reaction  $r$  was at the  $i$ th vibrational level:

$$P_{f,r,ci} = \frac{n_{ci} k_{f,r,ci}}{n_c k_{f,r}}.$$

The state-specific rate constants  $k_{f,r,ci}$  do not depend on the distribution over vibrational levels  $i$  of molecular species  $c$ . This yields

$$\frac{P_{f,r,ci}^{\text{eq}} k_{f,r}^{\text{eq}}}{n_{ci}^{\text{eq}}} = \frac{P_{f,r,ci} k_{f,r}}{n_{ci}},$$

where the superscript “eq” refers to thermal equilibrium with  $T_1^c = T$ . From the last expression it follows that for each vibrational level  $i$  we can write:

$$\frac{n_{ci} P_{f,r,ci}^{\text{eq}}}{n_{ci}^{\text{eq}} P_{f,r,ci}} = \frac{k_{f,r}}{k_{f,r}^{\text{eq}}} = Z_{f,r} \tag{67}$$

For the calculation  $P_{f,r,ci}$  we use the Treanor–Marrone model<sup>34</sup> for dissociation and its extension to exchange reactions given in Ref. 31. It is supposed that reactions occur with equal probability in any collision that has sufficient translational energy and that they occur preferentially from the high vibrational levels. In Ref. 31 the probability  $P_{f,r,ci}$  for exchange reaction is given in the form:

$$P_{f,r,ci} = C_r n_{ci} M(A_r - \varepsilon_i^c) F_{r,ci}. \tag{68}$$

Here  $A_r$  is the activation energy of the reaction  $r$ ,  $M(A_r - \varepsilon_i^c)$  is the fractional number of collisions with line-of-center relative energy exceeding  $(A_r - \varepsilon_i^c)$ , and  $F_{r,ci}$  is the probability that the molecule  $c$  is at the  $i$ th vibrational level, when colliding in a sufficiently energetic collision, will react in the reaction  $r$ . The coefficient  $C_r$  is found from the normalizing condition:

$$\sum_i P_{f,r,ci} = 1,$$

The probability  $F_{r,ci}$  in (68) reads:

$$F_{r,ci} = \begin{cases} C_1 \exp(-(A_r - \varepsilon_i^c)/k_B U_r) & \text{for } \varepsilon_i^c \leq A_r \\ C_1 & \text{for } \varepsilon_i^c > A_r, \end{cases} \tag{69}$$

where  $U_r$  is an additional parameter with a dimension of temperature and  $C_1$  is a constant independent of  $i$ . In the present computation,  $U_r$  is taken equal to  $A_r/3k_B$ .

For a Maxwell distribution over velocities, the function  $M$  has the form

$$M(A_r - \varepsilon_i^c) = \begin{cases} C_2 \exp(-(A_r - \varepsilon_i^c)/k_B T) & \text{for } \varepsilon_i^c \leq A_r \\ C_2 & \text{for } \varepsilon_i^c > A_r, \end{cases} \tag{70}$$

where  $C_2$  is the constant independent of  $i$ .

Taking into account Eqs. (70), (68) and the nonequilibrium Treanor distribution (14) we compute the nonequilibrium factors. For exchange reactions,

$$Z_{f,r}(T, T_1^c) = \frac{S_c(T, T_1^c) Z_c^{\text{vibr}}(T, T)}{S_c(T, T) Z_c^{\text{vibr}}(T, T_1^c)}, \tag{71}$$

where

$$\begin{aligned}
 S_c(T, T_1^c) = & \sum_{i, \varepsilon_i^c \leq A_r} s_i^c \exp\left(-i\varepsilon_1^c \left(\frac{1}{k_B T_1^c} - \frac{1}{k_B T}\right)\right) \\
 & + \frac{\varepsilon_i^c}{k_B U_r} - A_r \left(\frac{1}{k_B T} + \frac{1}{k_B U_r}\right) + \sum_{i, \varepsilon_i^c > A_r} s_i^c \\
 & \times \exp\left(-i\varepsilon_1^c \left(\frac{1}{k_B T_1^c} - \frac{1}{k_B T}\right) - \frac{\varepsilon_i^c}{k_B T}\right).
 \end{aligned} \tag{72}$$

The summation is taken over all the vibrational levels.

The backward reaction rate constant is written similarly to (66), the nonequilibrium factor  $Z_{b,r}$  for exchange reaction

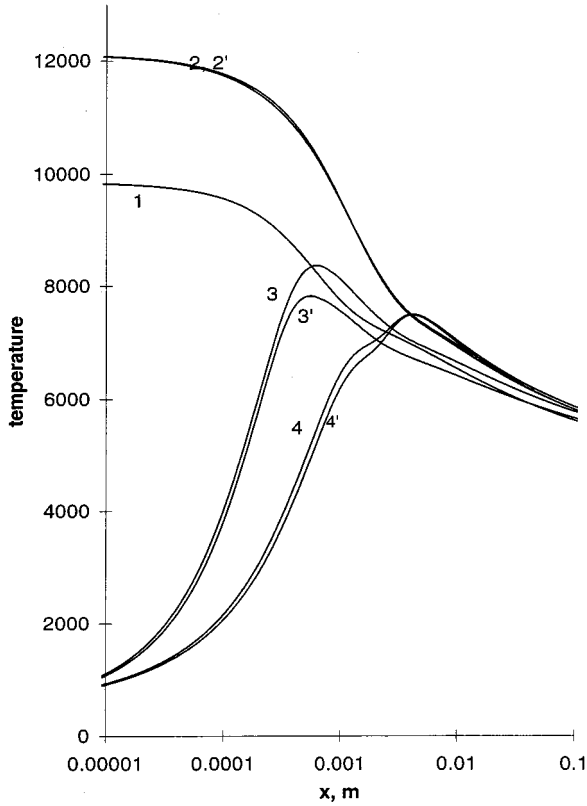


FIG. 1. Translational and vibrational temperatures  $T, T_1^{(c)}$ , K, as functions of distance  $x$ . Curve 1— $T$ , one-temperature approach; 2, 2'— $T$ , multitemperature approach, anharmonic and harmonic oscillator; 3— $T_1^{O_2}$ , 3'— $T_1^{O_2}$ , 4— $T_1^{N_2}$ , 4'— $T_1^{N_2}$ .

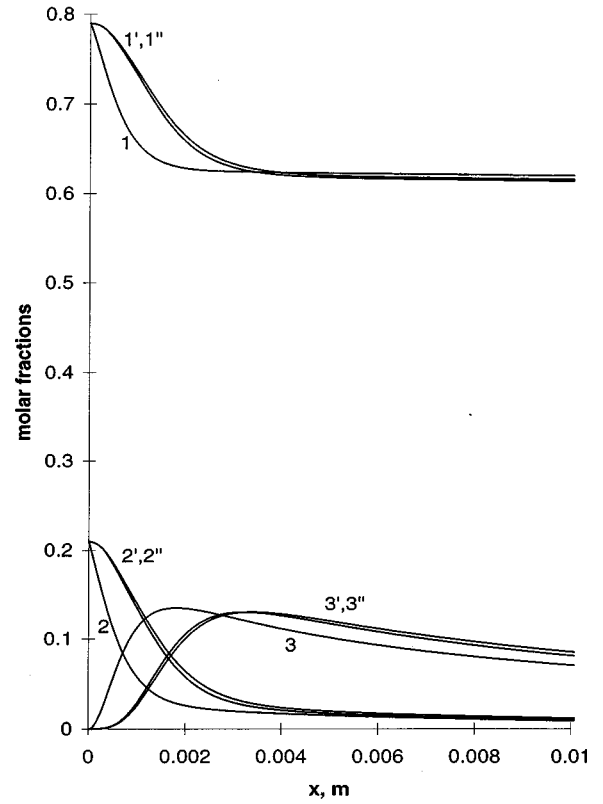


FIG. 2. Molar fractions of molecules as functions of distance  $x$ . Curves 1, 1'— $n_{N_2}/n$ , 2, 2'— $n_{O_2}/n$ , 3, 3'— $n_{NO}/n$ . 1, 2, 3—one-temperature approach; 1', 2', 3'—multitemperature approach, anharmonic oscillator; 1'', 2'', 3''—multitemperature approach, harmonic oscillator.

is given by expression (71) where  $A_r=0$  and  $T_1^c$  is the temperature of the first level of a molecule being destroyed in the backward reaction.

For dissociation  $Z_{f,r}$  is given by expressions (71) and (72) where  $A_r$  is adjusted to the dissociation energy of a molecule. Note that in this case the second sum in Eq. (72) vanishes. The nonequilibrium factor for recombination is  $Z_{b,r}=1$ .

The number of vibrational quanta lost when the molecule  $c$  is destroyed in reaction  $r$  is  $\sum_i iP_{f,r,ci}$ , where the summation is taken over all the vibrational levels. This yields the following expressions for exchange reactions,

$$G_{va,f,r,c}(T, T_1^c) = \frac{V_c(T, T_1^c)}{S_c(T, T_1^c)}, \quad (73)$$

where

$$\begin{aligned} V_c(T, T_1^c) = & \sum_{i, \varepsilon_i^c \leq A_r} i s_i^c \exp\left(-i\varepsilon_1^c \left(\frac{1}{k_B T_1^c} - \frac{1}{k_B T}\right)\right) \\ & + \frac{\varepsilon_i^c}{k_B U_r} - A_r \left(\frac{1}{k_B T} + \frac{1}{k_B U_r}\right) + \sum_{i, \varepsilon_i^c > A_r} i s_i^c \\ & \times \exp\left(-i\varepsilon_1^c \left(\frac{1}{k_B T_1^c} - \frac{1}{k_B T}\right) - \frac{\varepsilon_i^c}{k_B T}\right). \end{aligned} \quad (74)$$

By aid of the detailed balance principle it can be shown that  $G_{app,b,r,c}$  is function of only the gas temperature  $T$ . In ther-

mal equilibrium  $R_c^{w,react}=0$  and from Eq. (65) it follows that  $G_{app,b,r,c}(T) = G_{va,f,r,c}(T, T)$ . The backward terms are deduced from the forward terms by substituting  $A_r=0$ . For dissociation,  $G_{app,f,r,c} = G_{va,b,r,c} = 0$ ; finally  $G_{va,f,r,c}$  is obtained by adjusting  $A_r$  to the dissociation energy of a molecule in expression (73).

It is to be noted that when the anharmonism of vibrations is neglected, the expressions for  $Z_f, Z_b, G_{app}$  and  $G_{va}$  presented here reduce to the ones obtained in Ref. 31 for harmonic oscillators.

The thermal equilibrium rate constants  $k_{f,r}^{eq}$  are supposed to follow an Arrhenius law,

$$k_{f,r}^{eq} = C_r T^{n_r} \exp(-A_r/k_B T),$$

with the coefficients taken from Ref. 35. In particular, the rate constants of dissociation are the ones given in Ref. 36. The rate constants of exchange reactions are taken from Refs. 37 and 38.

The backward rate constant at vibrational equilibrium are computed from the forward ones using the chemical equilibrium constant  $K_{r,c}$ :

$$k_{b,r}^{eq} = k_{f,r}^{eq} / K_r,$$

and

$$K_r = \left(\frac{P_*}{RT}\right)^{\nu_r} \exp(\gamma_{r*}/RT),$$

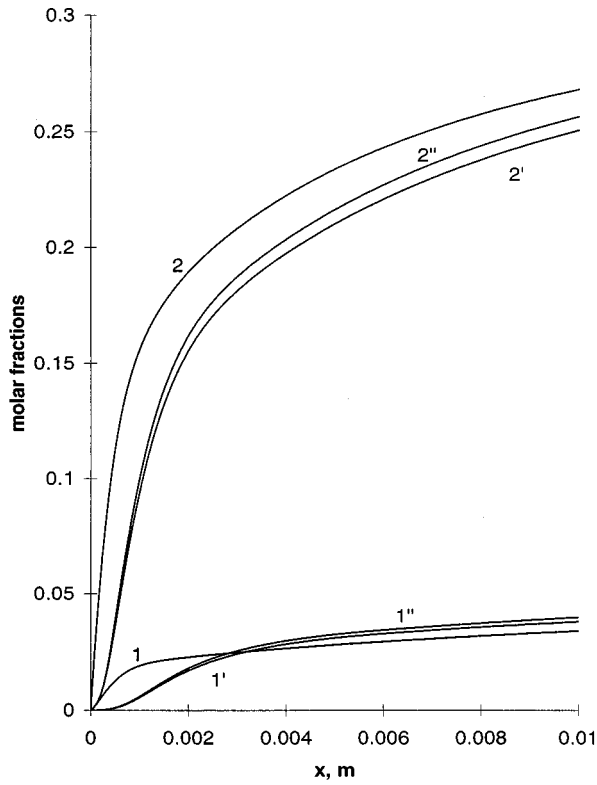


FIG. 3. Molar fractions of atoms as functions of distance  $x$ . Curves 1, 1', 1''— $n_N/n$ , 2, 2', 2''— $n_O/n$ . 1, 2—one-temperature approach; 1', 2'—multitemperature approach, anharmonic oscillator; 1'', 2''—multitemperature approach, harmonic oscillator.

where  $p_*$  is the standard pressure,  $\nu_r = \sum_s (\nu''_{s,r} - \nu'_{s,r})$ ,  $\mathcal{R}$  is the universal gas constant, and  $\gamma_{r*}$  the affinity of the reaction at standard pressure.

### C. Results and discussion

The system (57)–(60) of one-dimensional ordinary differential equations is solved using the LSODE package,<sup>39</sup> and thus all macroscopic parameters are computed in the relaxation zone behind a strong shock wave propagating in air mixture. Using these macroscopic parameters the heat conductivity, diffusion, and thermal diffusion coefficients and the total heat flux are calculated for the same conditions. The results are obtained on the basis of three models:

- (1) Multitemperature model, anharmonic oscillator,
- (2) multitemperature model, harmonic oscillator,
- (3) one-temperature model.

The results are presented in Figs. 1–6. In Fig. 1 the gas temperature and the vibrational temperatures of  $N_2$  and  $O_2$  computed in the three approaches are given as a function of the distance  $x$  from the shock front. The conditions in the free stream are the following, respectively, for the Mach number, temperature, pressure, and molar fractions:  $M_0 = 15$ ,  $T_0 = 271$  K,  $p_0 = 100$  Pa,  $n_{N_2} = 0.79$ ,  $n_{O_2} = 0.21$ . One can notice that the one-temperature model underestimates the gas temperature in the beginning of the relaxation zone. It is due to the fact that this model does not take into account the process of excitation of the vibrational modes. In this ap-

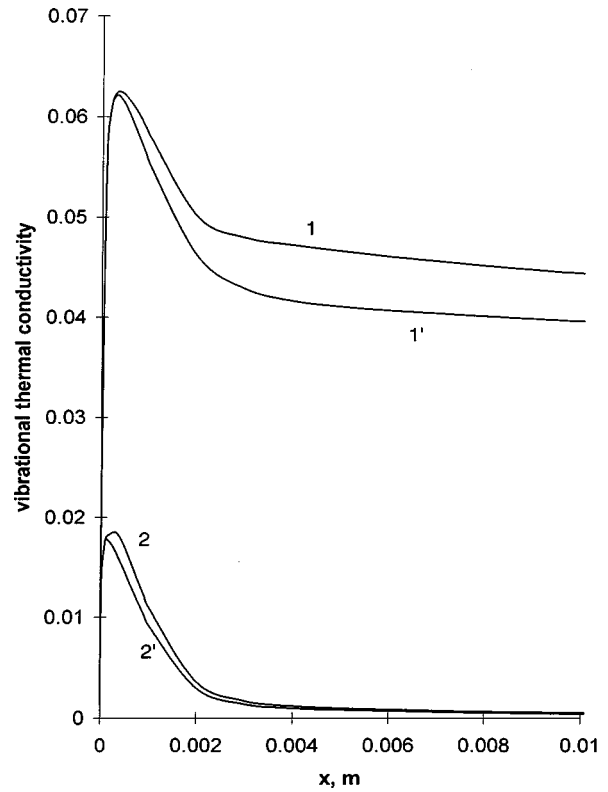


FIG. 4. Vibrational thermal conductivity coefficients  $\lambda_v^c$  in W/m K, as functions of distance  $x$ . Curves 1, 1'— $\lambda_v^{N_2}$ , 2, 2'— $\lambda_v^{O_2}$ . 1, 2—multitemperature approach, anharmonic oscillator; 1', 2'—multitemperature approach, harmonic oscillator.

proach it is assumed that just behind the shock front, the distribution over the vibrational levels of molecular species is of the one-temperature Boltzmann type. The difference between the one-temperature and multitemperature models decreases with the distance from the shock. The influence of anharmonism on the temperature is small, the maximum deviation does not exceed 5% on  $T_v^{O_2}$ . The behavior of  $T_v^{N_2}$ ,  $T_v^{N_2}$  and  $T_v^{O_2}$ ,  $T_v^{O_2}$  reflects the relation between relaxation times of  $N_2$  and  $O_2$ . In the region close to the front where vibrational excitation plays a more important role compared to chemical reactions,  $T_v^{O_2}$  and  $T_v^{O_2}$  are much higher than  $T_v^{N_2}$  and  $T_v^{N_2}$  due to rapid vibrational excitation of  $O_2$  ( $\tau_{\text{vibr}, O_2} \ll \tau_{\text{vibr}, N_2}$ ,<sup>32</sup>). Then the effects of chemical reactions and vibrational relaxation become comparable. A similar behavior of  $T_v^{O_2}$  and  $T_v^{N_2}$  in air mixtures is shown in Refs. 7 and 31. With rising  $x$  the gas temperature and vibrational temperatures converge to the equilibrium value:  $T_v^{O_2, \text{eq}} = T_v^{O_2, \text{eq}} = T_v^{N_2, \text{eq}} = T_v^{N_2, \text{eq}} = T^{\text{eq}}$ . The results obtained in the one-temperature approach correspond to the ones given in Ref. 6.

Figs. 2 and 3 give the molar fractions of molecular and atomic species, respectively. The one-temperature model does not describe the delay of dissociation, this effect may be seen only in the frame of the multitemperature approach. It is seen that dissociation of  $O_2$  is more rapid, whereas that of  $N_2$  is delayed. One can also see the maximum of NO concentration in the beginning of the relaxation zone. The influence of anharmonism on the concentration of  $N_2$  is negligible (about

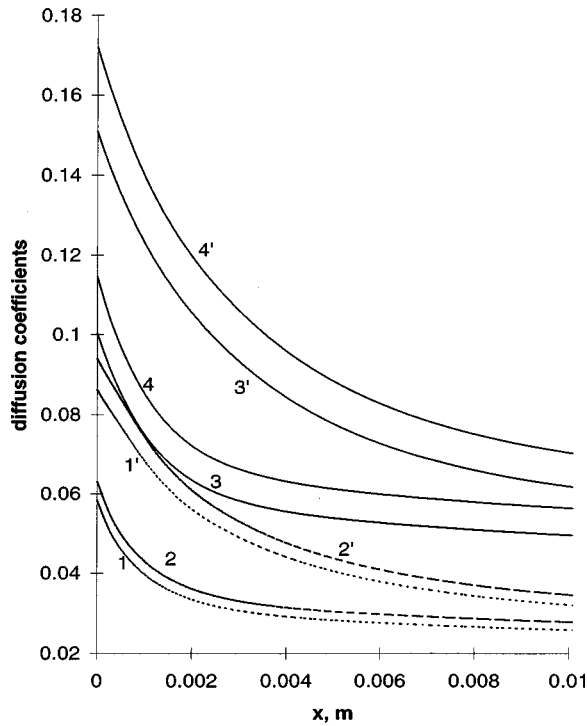


FIG. 5. Multicomponent diffusion coefficients,  $D_{cd}$  in  $m^2/s$ , as functions of distance  $x$ . Curves 1, 1'— $D_{N_2-O_2}$ , 2, 2'— $D_{N_2-NO}$ , 3, 3'— $D_{N_2-O}$ , 4, 4'— $D_{N_2-N}$ . 1–4—one-temperature approach; 1'–4'—multitemperature approach, anharmonic oscillator.

2%), whereas it becomes much more significant for the remaining species (up to 25% for  $O_2$  and  $O$  and up to 36% for  $NO$  and 34% for  $N$ ). In the case of harmonic oscillators the results given in Figs. 1–3 coincide with the ones obtained in Ref. 31.

The vibrational heat conductivity coefficients in thermal nonequilibrium are plotted in Fig. 4 for the harmonic and anharmonic oscillator models. It is seen that  $\lambda_v^{O_2}, \lambda_v^{N_2}$  grow rapidly in the beginning of the relaxation zone due to vibrational excitation (with  $T_v^c$  and  $T_1^c$  rising). Then  $\lambda_v^{O_2}, \lambda_v^{N_2}$  decrease with  $x$  due to the decrease in the molecular molar fractions through dissociation. These coefficients are smaller for harmonic oscillators than for anharmonic ones, the difference being about 10%–12% for  $\lambda_v^{N_2}$  and 18% for  $\lambda_v^{O_2}$ . In translational and rotational heat conductivities anharmonicity is negligible, these coefficients decrease with  $x$  toward the equilibrium values.

The multicomponent diffusion coefficients of  $N_2$  for one-temperature and multitemperature models are presented in Fig. 5. One can see the noticeable discrepancy between the two models (up to 40%). The diffusion coefficients calculated in the multitemperature regime exceed the ones computed in the one-temperature approximation due to the higher value of the gas temperature obtained in the former case. Near equilibrium the diffusion coefficients calculated for the different models approach each other. It has been shown in Ref. 12 that the diffusion and thermal diffusion coefficients depend on the gas temperature and molar fractions of species, and do not depend on the vibrational tem-

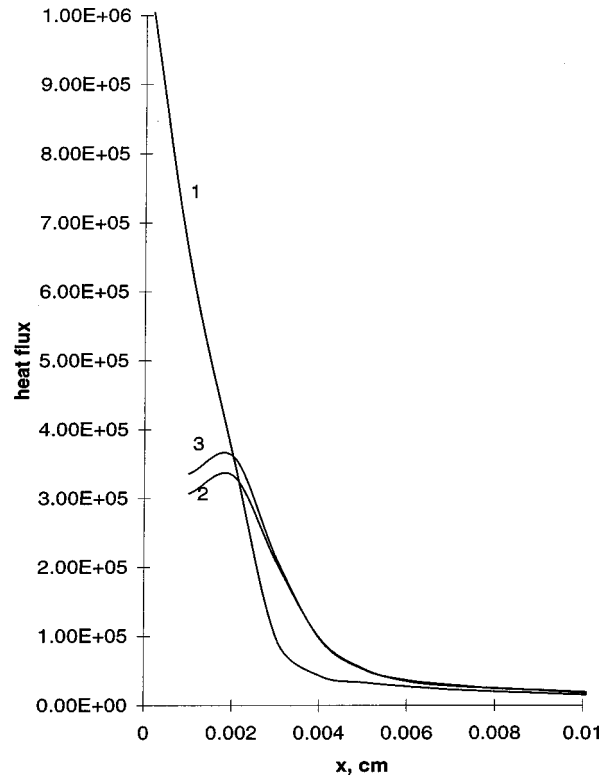


FIG. 6. Total heat flux,  $q$  in  $W/m^2$ , as a function of distance  $x$ . Curve 1—one-temperature approach; 2—multitemperature approach, anharmonic oscillator; 3—multitemperature approach, harmonic oscillator.

peratures, the deviation of the vibrational distribution from the Boltzmann one does not influence these coefficients. Strong vibrational nonequilibrium influences the diffusion and thermal diffusion coefficients only through the macroscopic parameters  $T$  and  $n_c$ . The anharmonic effects on these coefficients are rather small (not more than 5%).

In Fig. 6 the total heat flux calculated for the three models is given. It is seen that the one-temperature approach leads to an overestimation of the heat flux in the beginning of the relaxation zone because this model does not describe the initial process of vibrational excitation and gives a very steep drop of the gas temperature. The difference between the values of the heat flux decreases with distance from the shock front and at  $x > 0.5\text{--}0.7$  cm the gas flow may be described by the simpler one-temperature model. In the multitemperature regime with the anharmonic oscillator model the heat flux appears to be less than in the other cases because this model gives a more exact description of vibrational excitation especially in the beginning of the relaxation zone where the anharmonic effect reaches 25%.

With increasing the Mach number in the free stream the length of the initial nonequilibrium zone, where the role of the multitemperature model is particularly important, decreases due to rapid vibrational excitation at high temperature.

### V. CONCLUSIONS

The multitemperature kinetic model of heat transfer in reacting gas mixtures is developed and applied for the con-

ditions in the relaxation zone behind a strong shock wave. The macroscopic gas parameters (gas temperature, vibrational temperatures of the first levels of the molecular species, molar fractions of species), heat conductivity, diffusion coefficients, and heat flux are examined on the basis of this model. The computations have been performed for the five-component reacting air mixture with dissociation, recombination, and exchange reactions taken into account. A comparison is made with the results obtained in the one-temperature approach. A significant difference is found in the beginning of the relaxation zone just after the shock front. The one-temperature model gives an underestimation of the gas temperature because it does not take into account the initial process of vibrational excitation. It leads to a large deviation in the computed heat flux. Hence, in the beginning of the relaxation zone the multitemperature model should be used. With increasing the distance from the shock front the results deduced in the frame of the two approaches become close to each other and the one-temperature model may be applied.

The anharmonic effects on the macroscopic parameters, transport coefficients, and heat flux are estimated in the relaxation zone behind a shock wave. The maximum influence of anharmonism on the heat flux is found to be about 25% within a very short initial zone. The anharmonic effect on the diffusion, thermal diffusion, and translational-rotational heat conductivity coefficients is negligible. Such a small influence of anharmonism behind a shock wave may be explained by the dominant role of  $TV$  vibrational excitation. In the case of  $VT$  deactivation (for example, in an expanding flow) one can expect more significant anharmonic effects.

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