JOURNAL OF THERMOPHYSICS AND HEAT TRANSFER
Vol. 15, No. 1, January–March 2001

Calculation of Transport Coefficients with Vibrational Nonequilibrium

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An extended Enskog asymptotic expansion method is used to find approximate solutions of the Boltzmann equation in the cases of strong thermal nonequilibrium. The formalism to determine thermal conductivities in the expanding flow of a binary mixture of a diatomic and its parent atoms through a supersonic nozzle is applied. Results show that the diffusion of highly excited vibrational levels, which become overpopulated during the expansion, substantially contributes to the transport of energy. This effect cannot be represented by simplified theories such as the multitemperature model.

Nomenclature

b = impact parameter in collision
D_{cidk} = diffusion coefficients
D_{mol} = self-diffusion coefficient of molecules
D_{Tci} = thermal diffusion coefficients
$\boldsymbol{d}_{ci}$ = diffusion driving forces of species c in the vibrational level i
$f_{cij}(\boldsymbol{r}, \boldsymbol{u}, t)$ = distribution function for particles of species c in the vibrational level i and rotational level j over the velocities $\boldsymbol{u}$, the spatial and temporal coordinates
g = relative speed in collision
h_{ci} = molar enthalpy for species c in the vibrational level i
m_c = mass of species c
m_{cd} = reduced mass for a c-species/d-species pair
n = total number density
n_{ci} = number density of species c in the vibrational level i
$\boldsymbol{P}^{(k)}$ = pressure tensor, kth-order approximation
p = hydrostatic pressure
$Q^{(l)}_{cidk}$ = kinetic cross section
$\boldsymbol{q}^{(k)}$ = heat flux vector, kth-order approximation
$\boldsymbol{q}^{\mathrm{mol}}_{\mathrm{vib}}$ = convection term contribution to the heat flux due to molecules
T = temperature
$\boldsymbol{V}^{(k)}_{ci}$ = diffusion velocity of species c in the vibrational level i, kth-order approximation
$\boldsymbol{V}_{\mathrm{eff}}$ = effective diffusion velocity of molecules
$\bar{\boldsymbol{v}}$ = hydrodynamic velocity
ε^c = formation energy for species c
ε^c_i = vibrational energy for species c in the vibrational level i
$\langle \varepsilon^{ci}_j \rangle_{\mathrm{rot}}$ = average rotational energy for species c in the vibrational level i
λ' = thermal conductivity
ρ = total mass density
ρ_{ci} = mass density of species c in the vibrational level i
$\chi_{cidk(b,g)}$ = scattering angle for a collision between (c, i) and (d, k) particles
$\Omega^{(l,r)}_{cidk}$ = elastic omega integral

Introduction

TRANSPORT properties of polyatomic gas mixtures are of interest in many fields. In particular, in reacting mixtures, the coupling between chemical and vibrational kinetics produces strong nonequilibrium vibrational distributions. In this work we try to assess the role of these nonequilibrium internal energy distributions in the transport properties of the system. To this end we make use of a generalized formulation of the Enskog expansion extended to treat nonequilibrium conditions.[1]

The model assumes that the relaxation times for the chemical and vibrational modes are much longer than the relaxation times for the translational and rotational ones. Therefore, the chemical composition of the system and the populations of the vibrational levels for molecules are treated as given parameters that vary on the same timescale as temperature and velocity. The transport coefficients derived in this way are a function of these thermodynamic state variables. The method allows explicit inclusion of the nonequilibrium conditions in the calculation.

We have applied this formulation to the calculation of the thermal conductivity and heat flux in a supersonic nozzle flow of a binary mixture of nitrogen (N_2–N) and oxygen (O_2–O). We have compared these calculations with results derived from two-temperature models that consider a Boltzmann distribution for the vibrational level populations. The discrepancy in the calculated heat flux can be as high as 5%, thus showing that the state-to-state model is needed for accurate evaluation of this quantity.

State-to-State Transport Model

The transport properties of dilute gases are evaluated through the asymptotic expansion of the Boltzmann equation, using the density as an expansion parameter. This is now a standard procedure, for example, see Ref. 2. The extension of the method to treat strong nonequilibrium follows the same steps although giving different weight to different collision processes. The elastic collisions and collisions involving a change in rotational state only (rotation–translation energy exchange collisions) are considered to have small relaxation times τ_{el} and τ_r, respectively, as compared with the macroscopic time of the flow, θ. However, collisions involving a

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Received 5 October 1999; revision received 12 June 2000; accepted for publication 17 July 2000.

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change in vibrational level [vibration–vibration energy exchange (VV) and vibration–translation energy exchange (VT) collisions], τ_{vib}, or a change in chemical species, τ_{chem}, that is chemical reactions, are treated separately as slow processes. The nonequilibrium condition can be characterized by a relaxation time hierarchy as follows:

$$\tau_{\text{el}} < \tau_r \ll \tau_{\text{vib}} < \tau_{\text{chem}} \sim \theta \tag{1}$$

This implies that vibrational excitation, chemical changes, and fluid motion all evolve on the same timescale. Experimental data[3] show that this relation holds in many cases of practical interest. With this assumption, the so-called level approach in nonequilibrium gasdynamics is developed,[1] a model important for the study of vibrational–chemical coupling in the boundary layer, in the short relaxation zone behind a shock wave, where steady-state vibrational distributions do not establish, and in nozzle flows with a high vibrational energy content. When the vibrational energy content is not high compared to the gas temperature, a different hierarchy can be assumed for the relaxation times, thus leading to multitemperature approaches.[4] Starting from Eq. (1), we expand the Boltzmann equations with $\varepsilon = \tau_{\text{fast}}/\tau_{\text{slow}}$ as the small parameter:

$$\frac{\partial f_{cij}}{\partial t} + \boldsymbol{u}_c \frac{\partial f_{cij}}{\partial \boldsymbol{r}} = \frac{1}{\varepsilon} \boldsymbol{J}^{\text{fast}}_{cij} + \boldsymbol{J}^{\text{slow}}_{cij} \tag{2}$$

where $\boldsymbol{J}^{\text{fast}}_{cij} = \boldsymbol{J}^{\text{el}}_{cij} + \boldsymbol{J}^{r}_{cij}$ and $\boldsymbol{J}^{\text{slow}}_{cij} = \boldsymbol{J}^{\text{vib}}_{cij} + \boldsymbol{J}^{\text{chem}}_{cij}$ are collision integrals over collisions of the fast and slow type, respectively.

A consequence of this approach is that mass conservation equations can be written for each vibrational level and each chemical species as

$$\frac{\mathrm{d}n_{ci}}{\mathrm{d}t} + n_{ci} \nabla \cdot \boldsymbol{v} + \nabla \cdot (n_{ci} \boldsymbol{V}_{ci}) = R_{ci}$$
$$c = 1, \ldots, L \qquad i = 0, 1, \ldots, L_c \tag{3}$$

Here, $\boldsymbol{V}_{ci}$ is the diffusion velocity corresponding to n_{ci}, and R_{ci} is a source term that represents, to each order of approximation, the rate of change of the vibrational and chemical state. This is the so-called level approach in nonequilibrium gasdynamics.[1]

To the lowest-order approximation, the kinetic equation for the distribution function $f_{cij}(\boldsymbol{r}, \boldsymbol{u}, t)$ contains the collision integrals over collisions of the rapid type only. Therefore, the distribution function describes the equilibrium Maxwell–Boltzmann distribution over velocities and rotational energy and nonequilibrium distribution over vibrational energy and chemical species in the form

$$f^{(0)}_{cij} = \left(\frac{m_c}{2\pi kT}\right)^{\frac{3}{2}} s^{ci}_j \frac{n_{ci}}{Z^{\text{rot}}_{ci}(T)} \exp\left(-\frac{m_c u_c^2}{2kT} - \frac{E^{ci}_j}{kT}\right) \tag{4}$$

where T is the gas temperature, m_c is the mass of species c, s^{ci}_j is the statistical weight of the rotational level of energy E^{ci}_j, and $Z^{\text{rot}}_{ci}(T)$ is the rotational partition function.

To this order of approximation, the equations for the macroscopic parameters n_{ci}, $\bar{\boldsymbol{v}}$, and T are the inviscid Euler equations, and the flux vectors take the form

$$\boldsymbol{V}^{(0)}_{ci} = 0, \qquad \boldsymbol{P}^{(0)} = p\boldsymbol{I}, \qquad \boldsymbol{q}^{(0)} = 0 \tag{5}$$

where $\boldsymbol{V}^{(0)}_{ci}$ is the diffusion velocity, $\boldsymbol{P}^{(0)}$ the pressure tensor, and $\boldsymbol{q}^{(0)}$ the heat flux. The subscripts c and i refer to the chemical species and the vibrational level. The transport terms appear in the first-order approximation. The correction to the distribution functions is a linear function of the gradients of the macroscopic parameters whose coefficients can be written in terms of transport coefficients and known functions of the particle velocities $\boldsymbol{u}$ and the macroscopic parameters $n_{ci}(\boldsymbol{r}, t)$, $\boldsymbol{v}(\boldsymbol{r}, t)$, and $T(\boldsymbol{r}, t)$. The integro–differential equation for $f^{(1)}_{cij}(\boldsymbol{r}, \boldsymbol{u}, t)$ is thus reduced to a system of algebraic equations for the transport coefficients that depends on the macroscopic parameters and on the so-called bracket integrals. Bracket integrals are integrals of functions of the particle velocities over all collisions of the rapid type.[1] They are reduced by a standard procedure[5] to a linear combination of elastic Ω integrals:

$$\Omega^{(l,r)}_{cidk} = \left(\frac{kT}{2\pi m_{cd}}\right)^{\frac{1}{2}} \int_0^\infty \exp(-g^2) g^{2r+3} Q^{(l)}_{cidk}\, \mathrm{d}g$$
$$Q^{(l)}_{cidk} = 2\pi \int \left(1 - \cos^l \chi_{cidk(b,g)}\right) b\, \mathrm{d}b \tag{6}$$

It is seen that these standard integrals depend on the gas temperature and on the interaction model used to describe particle–particle collisions.[5]

Evaluating the fluxes with these distribution functions, we obtain

$$\boldsymbol{V}^{(1)}_{ci} = -\sum_{dk} D_{cidk} \boldsymbol{d}_{dk} - D_{Tci} \nabla \ln T \tag{7}$$

$$\boldsymbol{q}^{(1)} = -\lambda' \nabla T - p \sum_{ci} D_{Tci} \boldsymbol{d}_{ci}$$
$$+ \sum_{ci} \left(\frac{5}{2}kT + \left\langle \varepsilon^{ci}_j \right\rangle_{\text{rot}} + \varepsilon^c_i + \varepsilon^c\right) n_{ci} \boldsymbol{V}^{(1)}_{ci} \tag{8}$$

where now

$$\boldsymbol{d}_{ci} = \nabla\left(\frac{n_{ci}}{n}\right) + \left(\frac{n_{ci}}{n} - \frac{\rho_{ci}}{\rho}\right) \nabla \ln p \tag{9}$$

involves the gradients of the vibrational level populations. In this case, the system of transport coefficients is enlarged to include diffusion coefficients for every vibrational level.

If we suppose that the bracket integrals do not depend on the vibrational level of the particles, the system of transport coefficients is further simplified; thus, we obtain D_{cici} for every vibrational level i; $D_{cc} = D_{cick}$, $i \neq k$; $D_{cd} = D_{cidk}$, $c \neq d$; and D_{Tc} for every chemical species c.

For a binary mixture consisting of one molecular species and its parent atoms, taking into account that the diffusion driving forces satisfy (where 1 refers to molecules and 2 to atoms)

$$\sum_i \boldsymbol{d}_{1i} + \boldsymbol{d}_2 = \boldsymbol{d}_1 + \boldsymbol{d}_2 = 0 \tag{10}$$

we obtain the following final expression for the diffusion velocities and the heat flux:

$$\boldsymbol{V}^{(1)}_{1i} = -D_{1i1i} \boldsymbol{d}_{1i} - D_{11} \sum_{k \neq i} \boldsymbol{d}_{1k} - D_{12} \boldsymbol{d}_2 - D_{T1} \nabla \log p$$
$$= (D_{11} - D_{1i1i}) \boldsymbol{d}_{1i} + (D_{11} - D_{12}) \boldsymbol{d}_2 - D_{T1} \nabla \log p$$

$$\boldsymbol{V}^{(1)}_2 = -D_{22} \boldsymbol{d}_2 - D_{12} \boldsymbol{d}_1 - D_{T2} \nabla \log p \tag{11}$$

$$\boldsymbol{q}^{(1)} = -\lambda' \nabla T - p \sum_c D_{Tc} \boldsymbol{d}_c$$
$$+ \sum_{ci} \left(\frac{5}{2}kT + \left\langle E^{ci}_j \right\rangle_r + E^c_i + E_c\right) n_{ci} \boldsymbol{V}^{(1)}_{ci} \tag{12}$$

Assuming that thermal diffusion has only a small effect, we can distinguish two contributions to the heat flux. The flux due to conduction, the first term on the right-hand side of Eq. (12), or Fourier term, describes the transport of energy due to the collisions of the rapid type. Because of our assumptions on the dependence of these collisions on vibrational level, this term does not depend on the particular vibrational distribution of the molecules but only on the chemical composition of the gas mixture. The second term describes the convection contribution, due to the diffusion of atoms and molecules. The convection term due to molecules is the term that depends on the vibrational distribution function (VDF) and its relaxation [through n_{ci} and $\nabla(n_{ci})$]. To show this, we take expression (12) for the heat flux and single out the terms that depend on the shape of the VDF, neglecting those that depend on the gas temperature or composition alone:

$$\boldsymbol{q}^{\text{mol}}_{\text{vib}} = \sum_{\text{mol}} h_{ci} n_{ci} \boldsymbol{V}_{ci} = -D_{\text{mol}} \sum_{\text{mol}} h_{ci} \nabla(n_{ci}) + \boldsymbol{V}_{\text{eff}} \sum_{\text{mol}} h_{ci} n_{ci} \tag{13}$$

Here, the sum runs over all molecular levels and the following relations between the diffusion coefficients have been taken into account:

$$m_1 n_1 D_{12} + m_2 n_2 D_{22} = 0$$

$$m_1 n_{1k}(D_{1k1k} - D_{11}) + n_2(m_2 D_{12} - m_1 D_{11}) + n m_1 D_{11} = 0 \tag{14}$$

We have defined a self-diffusion coefficient:

$$D_{\text{mol}} = n_{10}(D_{1010} - D_{11})/n = n_{1i}(D_{1i1i} - D_{11})/n \tag{15}$$

and an effective diffusion velocity of molecules:

$$\begin{aligned} \boldsymbol{V}_{\text{eff}} = {} & \nabla \ell n T \left[\frac{n_2}{n} \left(1 - \frac{m_2}{m_1} \right) D_{12} - D_{11} - D_{T1} \right] \\ & - \nabla \ell n p \left[\frac{n_2 m_2 - n_1 m_1}{n \bar{m}} (D_{11} - D_{12}) - D_{12} \right] \\ & + \nabla \ell n n_2 \left[\frac{n_2 (D_{11} - D_{12})}{n} \right] \end{aligned} \tag{16}$$

We note that they do not depend on the shape of the VDF, but only on gas temperature and chemical composition. Thus, we see that the diffusion of vibrationally excited molecules contributes to the transport of energy. The second term in Eq. (13) is dominant when the atomic fraction is significant: It is proportional to the total vibrational energy content. The first term is more sensitive to the details of the relaxation. As we will see, the transport of energy due to the diffusion of molecules is strongly modified by the vibrational nonequilibrium and cannot be described by an internal thermal conductivity coefficient as in the usual Eucken description of polyatomic gases.

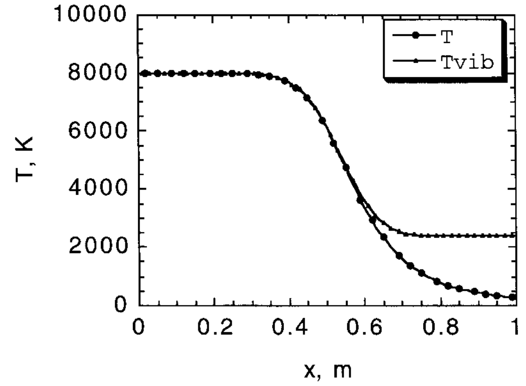
Calculations and Results

We have applied the method to the calculation of the transport properties in a model nozzle flow. We studied three cases with different reservoir conditions: nitrogen mixture, pressure $p = 1$ bar, temperature $T = 8000$ K; nitrogen mixture, pressure $p = 100$ bar, temperature $T = 8000$ K; and oxygen mixture, pressure $p = 1$ bar, temperature $T = 6000$ K.

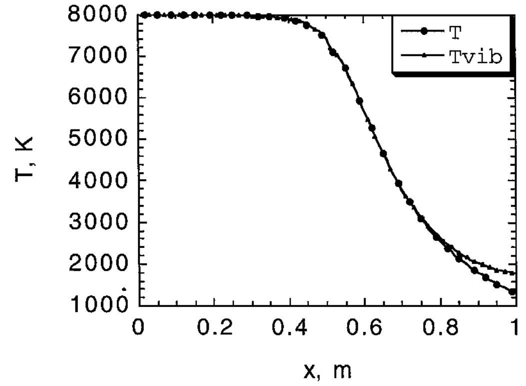
The nozzle flow calculations were performed by Colonna et al.[6] for 1-m-long, parabolic nozzle having cylindrical symmetry and the axis radius dependence:

$$r(x) = 3.5x^2 - 3.5x + 1 \tag{17}$$

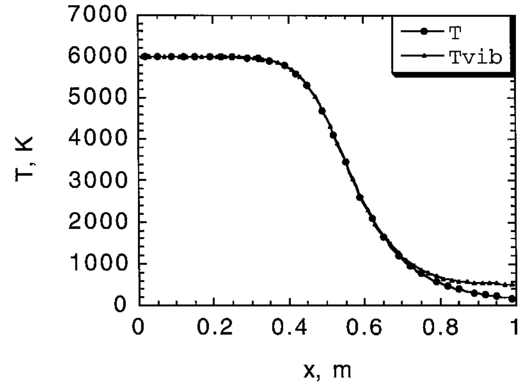
with x in meters ($x_{\text{throat}} = 0.5$ m). The nozzle flow equations were solved in a quasi-one-dimensional approximation, with no consideration of viscous effects. In addition to the simplified modeling of the fluid dynamics, the model included a detailed description of the state-to-state vibrational kinetics.[6]



a) N_2-N, $p = 1$ bar, and $T = 8000$ K



b) N_2-N, $p = 100$ bar, and $T = 8000$ K

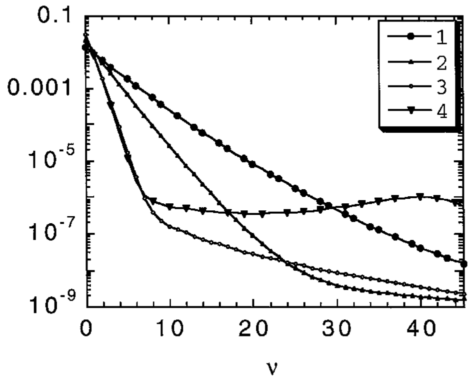


c) O_2-O, $p = 1$ bar, and $T = 6000$ K

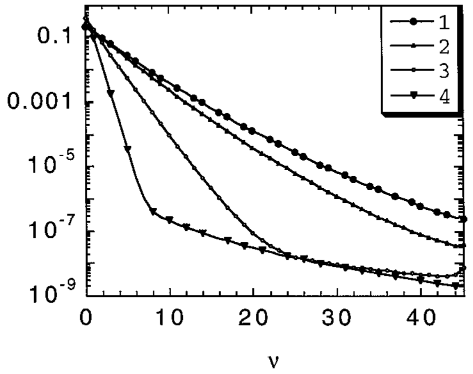
Fig. 1 Evolution of gas temperature and vibrational temperature along the flow.

In Figs. 1a–1c, we show the behavior of the temperatures T_{gas} and T_{vib} along the nozzle in the three cases: We see that the gas temperature suddenly drops to low values after the throat of the nozzle, due to the rapid expansion into the vacuum; however, the vibrational temperature lags behind because the relaxation of the vibrational modes is much slower. During relaxation, recombination of atomic species pumps vibrational quanta on the top of the vibrational ladder. These quanta are redistributed (especially at low translational temperatures) by VV and VT energy transfer processes, leading to the strong nonequilibrium vibrational distributions. This can be seen in Figs. 2a–2c.

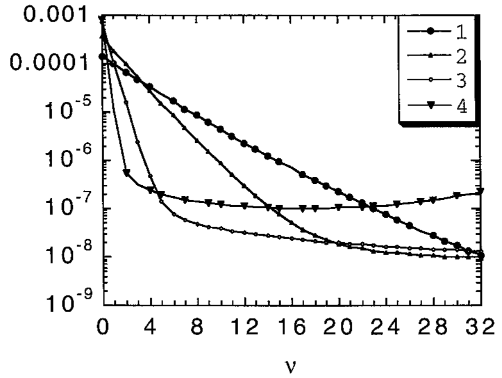
In Figs. 3a–3c, we show the evolution of the system composition for the cases discussed, as compared to the composition of a system in chemical equilibrium at the same temperature. Before the expansion, the gas has a high degree of dissociation. After the expansion, due to the low gas temperature, the atoms slowly recombine through the upper vibrational level; however, the pressure after the nozzle throat ($x = 0.5$ m) is very low, and the global recombination is very inefficient. In all cases, we see that the chemical reactions are



a) N_2-N, $p = 1$ bar, and $T = 8000$ K

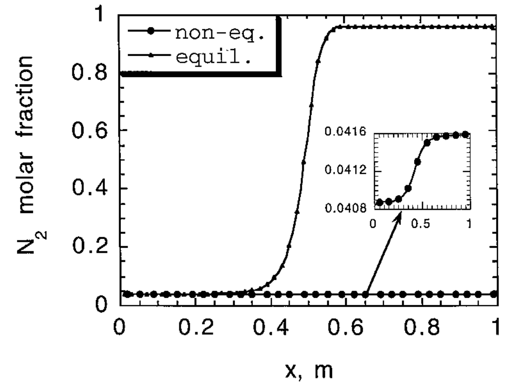


b) N_2-N, $p = 100$ bar, and $T = 8000$ K

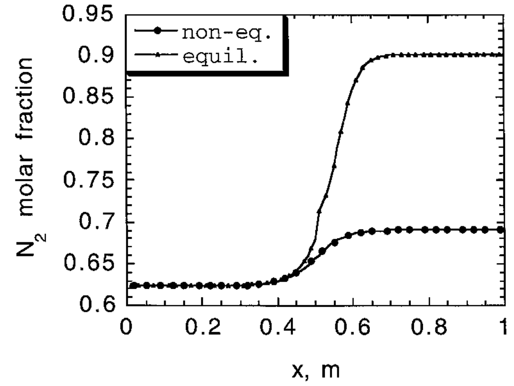


c) O_2-O, $p = 1$ bar, and $T = 6000$ K

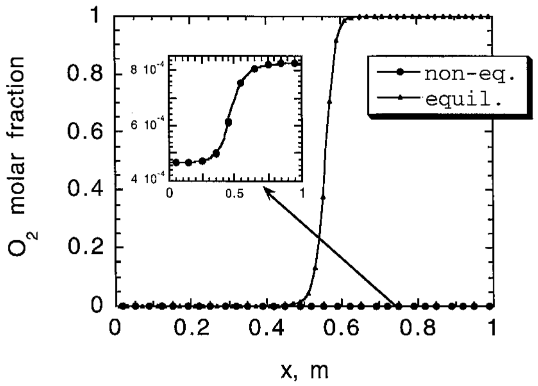
Fig. 2 Evolution of the VDF at different points along the flow: 1, $x = 0$ m; 2, $x = 0.55$ m; 3, $x = 0.7$ m; 4, $x = 1.0$ m.



a) N_2-N, $p = 1$ bar, and $T = 8000$ K



b) N_2-N, $p = 100$ bar, and $T = 8000$ K



c) O_2-O, $p = 1$ bar, and $T = 6000$ K

Fig. 3 Evolution of the system chemical composition.

nearly frozen shortly after the nozzle throat. We note, however, that the small recombination is sufficient to create the nonequilibrium vibrational distributions reported in Figs. 2.

These data are used as input for a calculation of the heat flux in the flow. We report the different contributions to the total heat flux as they appear in Eq. (12). We thus distinguish a conduction, or Fourier part, due to the energy exchanges during rapid collisions; a term due to the thermal diffusion; and a convection term due to particle diffusion. The latter can be further split into the sum over molecules plus the term concerning the diffusion of atoms.

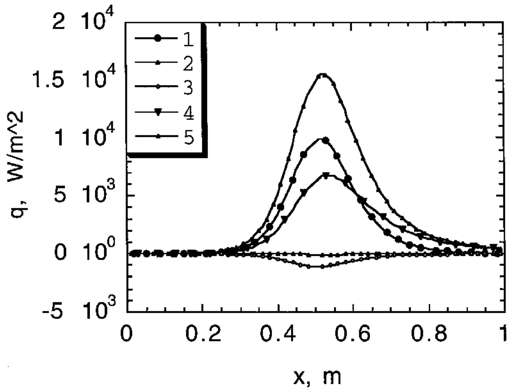
Figures 4a–4c show that the flux is composed of two main components, the Fourier part and the diffusion of the atomic component that brings the formation energy of the atoms. Thus, we see that the molecular diffusion term has little impact on the total heat flux. We shall see, however, that this is the term directly influenced by vibrational nonequilibrium.

In Fig. 5, we compare the heat flux due to molecular diffusion obtained from the calculations with the value obtained by assuming Boltzmann distribution at the vibrational temperature T_{vib}. We see that the two models give essentially the same results within a few percent.

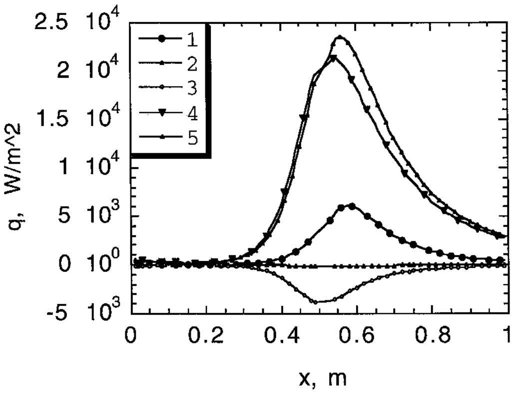
Finally, we want to analyze in detail the role of the VDF in modifying the convection heat flux. As we noted earlier, in Eq. (13), the coefficients D_{mol} and V_{eff} do not depend on the shape of the VDF, but only on gas temperature and chemical composition: They are equal for the two cases of nonequilibrium, in which the calculated VDF are used, or internal equilibrium, in which Boltzmann vibrational distributions are used at T_{vib}. For the case where the atomic fraction is relevant, the second term in Eq. (13) accounts for the largest contribution. Therefore, the heat flux depends on the shape of the VDF through the term

$$\sum_{\mathrm{mol}} h_{ci} n_{ci}$$

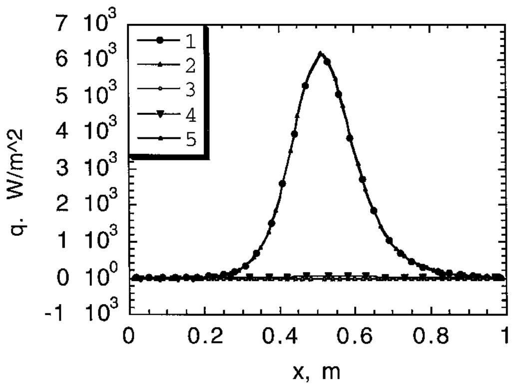
which is sensitive to the details of the distribution only for the first few levels. The high lying levels contribute little to the flux so that a Boltzmann distribution at T_{vib} can describe the transport properties fairly well, within a few percent accuracy.



a) N_2-N, $p = 1$ bar, and $T = 8000$ K



b) N_2-N, $p = 100$ bar, and $T = 8000$ K



c) O_2-O, $p = 1$ bar, and $T = 6000$ K

Fig. 4 Different contributions to the total heat flux: 1, Fourier term; 2, thermal diffusion; 3, molecular diffusion; 4, atomic diffusion; 5, total heat flux.

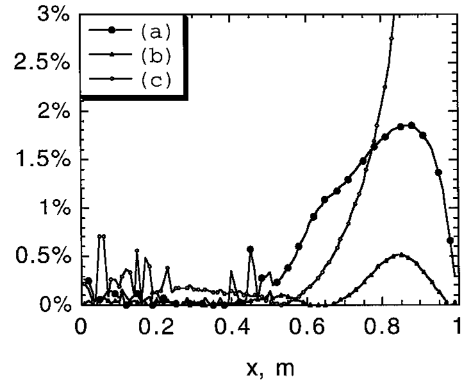


Fig. 5 Convection contribution to the heat flux, due to molecules; percentage difference between nonequilibrium and T_{vib} models: a) N_2-N, $p = 1$ bar, and $T = 8000$ K; b) N_2-N, $p = 100$ bar, and $T = 8000$ K; and c) O_2-O, $p = 1$ bar, and $T = 6000$ K.

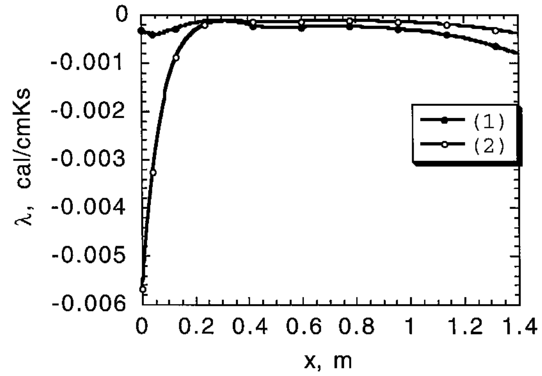


Fig. 6 Convective contribution to the thermal conductivity due to molecules where 1 is the level approach and 2 is the two-temperature model.

These conclusions apply to the present flow conditions characterized by large concentration of atomic species and small concentration of molecular species. The approach being quite general, other conditions can be envisaged in which a reversed situation occurs, that is, the concentration of molecular species exceeds that of the atomic species. In this case, the contribution of molecular diffusion to the total heat flux increases, and a state-to-state approach becomes necessary for an accurate evaluation of the heat flux. The present approach has been applied to the calculation of the transport properties in nonequilibrium nozzle flows,[7] in the boundary layer near a reentry body,[8] or in a cooling flow.[9] In this last case, nitrogen was mostly in molecular form, the vibrational distribution corresponds to $T_{vib} = 8000$ K, the gas temperature is $T_{gas} = 1000$ K, the gas is in steady flow at $v = 10^5$ cm/s, and the relaxation was simulated by a direct simulation Monte Carlo (DSMC) method.[10] In Fig. 6 we show the thermal conductivity due to molecular diffusion, as given by

$$q_{vib}^{mol} = -\lambda \nabla T \tag{18}$$

Figure 6 shows the comparison between the values calculated with the state-to-state approach and the values obtained by a two-temperature model that assumes Boltzmann vibrational distributions at T_{vib}. Differences up to one order of magnitude have been found in this case.

Conclusions

In this work, by using the approach developed by Kustova and Nagnibeda,[1] we have shown a case in which the state-to-state vibrational kinetics has a large impact on the transport coefficients of a N_2/N mixture. Downstream of a supersonic nozzle expansion, the vibrational distribution function of the molecules is very far from a Boltzmann distribution so that the transport of vibrational energy due to diffusion of high lying vibrational states cannot be described by a multitemperature formalism. The contribution of this molecular diffusion to the total heat flux can become predominant as long as the molecular fraction increases.

In conclusion, we can say that a state-to-state approach seems necessary for kinetic and transport studies of systems far from equilibrium conditions. Future progress in this direction should consider the role of inelastic processes in affecting the results.

Acknowledgment

This work has been partially supported by Agenzia Spaziale Italiana.

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