

Transport properties of nonequilibrium gas mixtures

Sylviane Pascal and Raymond Brun

*Département Milieux Hors d'Equilibre, Systèmes Energétiques et Transferts Thermiques,
Université de Provence, 13397 Marseille, France*

(Received 3 December 1991; revised manuscript received 3 June 1992)

Transport properties of binary mixtures of diatomic gases in vibrational nonequilibrium are analyzed and the corresponding terms are established. In order to solve the Boltzmann equation, a generalized Chapman-Enskog method is used, valid whatever the degree of nonequilibrium, contrarily to previous analyses in which only the extreme regimes were considered, at weak or strong nonequilibrium, and generally for pure gases only. The transport coefficients, first written in terms of collision integrals, are finally expressed as functions of macroscopic quantities, known or experimentally attainable, following Mason and Monchick type approximations and with the harmonic-oscillator model. Finally, examples of calculations are given for N_2-H_2 and O_2-N_2 mixtures. Results are in good agreement with available experimental data. Comparisons with approximate formulas, extensively used in the literature, show also that, at least for the investigated mixtures, the use of these formulas seems roughly justified.

PACS number(s): 05.60.+w, 05.20.Dd

I. INTRODUCTION

Recently a renewal of research on hypersonic flows has been taking place. This new interest is of course due to the various space-flight programs, for which modeling and simulation of the reentry of hypersonic vehicles in different types of planetary atmospheres represent complex problems. In particular, the physico-chemical phenomena related to spacecraft reentry are far from being satisfactorily known: Thus velocities and temperatures are so high that the chemical composition of gas media surrounding these vehicles is strongly modified. The aim of the present paper is to analyze some transport problems for nonequilibrium gas mixtures, arising from these extreme conditions.

The theoretical analysis of the transport properties in pure or mixed gas flows in the collisional regime is usually carried out following three methods, all based on solving the Boltzmann equation: The moment method [1,2], the Gross-Jackson method [3] and the Chapman-Enskog (CE) method [4]. The first two methods may be extended to transitional regimes, but in the collisional regime, the CE method seems to be the most appropriate. In this case, the molecular velocity distribution function is expanded in a series of the smallest parameter characteristic of the problem, usually the rarefaction parameter or Knudsen number which represents the ratio between the elastic collision characteristic time and the reference flow time. In practice, the CE method has been established and used for pure monatomic gases. Results concerning the transport coefficients [4] (viscosity and conductivity) are in very good agreement with experimental data. For monatomic gas mixtures, this method gives also good results [5,6]. However, the extension of the CE method to gases having internal energy is more recent [7], first for the equilibrium case [8–10] (rotational and vibrational modes) and then for the vibrational nonequilibrium case in pure gases [11]. The aim of the present work is to ex-

tend the CE method to binary mixtures of diatomic gases in vibrational nonequilibrium.

In a first part, the general CE method is presented for this kind of mixture, and it is shown that, according to the degree of nonequilibrium, the Boltzmann equation may be solved in different ways: Thus, for a weak nonequilibrium or for a strong nonequilibrium, the split of the Boltzmann equation leads to different equation systems, and the results obtained in each case for transport properties are obviously different.

In a second part, the Boltzmann equation is solved in the case of strong vibrational nonequilibrium for which the vibrational relaxation time including translation-vibration and vibration-vibration transitions is of the order of the reference flow time. Thus a strong-nonequilibrium (SNE) method is developed and, using Mason and Monchick type approximations, the transport coefficients expressions are given in explicit form, i.e., as functions of various macroscopic quantities, in principle easy to obtain by computation or experiment.

In a third part, an alternative method of solving the Boltzmann equation, derived from the previous SNE method is presented. Since weak-nonequilibrium (WNE) and SNE methods do not match in near-equilibrium zones, it is necessary to build up a method which will be able to describe flows in a weak nonequilibrium as well as in a strong one: This is called the matching method. Calculations are similar to those of the second part. Using Mason and Monchick approximations, and the harmonic-oscillator model, the transport coefficients are also expressed in terms of macroscopic quantities.

Finally, the transport terms previously established are computed in a temperature range corresponding to the assumed validity of the starting hypotheses and for two binary diatomic gas mixtures (N_2-H_2 , N_2-O_2). The behavior of these coefficients is examined and discussed, and comparisons with other approximate formulas given by various authors [12–14] are also presented.

II. GENERAL CONSIDERATIONS ON THE BOLTZMANN EQUATION AND THE CHAPMAN-ENSKOG METHOD

The flow of a mixture of two diatomic gases (p and q), each possessing one rotational and one vibrational mode is considered. The collisions are assumed to be binary and the chemistry frozen. The quantum numbers $i = i_r, i_v$ correspond to particular rotation i_r and vibration i_v levels.

Physical considerations allow us to classify the collisions into the following two groups (I and II). Collisions I (the most probable): T - T collisions (elastic ones, translation-translation exchanges), T - R collisions (translation-rotation exchanges), and V - V_r collisions (resonant vibration-vibration collisions between two molecules of the same species: p - p and q - q); and collisions II (the less probable): T - V collisions (translation-vibration exchanges) and V - V collisions (vibration-vibration collisions between molecules of different species: p - q and q - p). The main problem in the theory of transport phenomena is the determination of the local distribution function $f_{i_p}(\mathbf{v}_{i_p}, \mathbf{r}, t)$, where i_p denotes the quantum state of the p molecules and f_{i_p} the probability density of the p molecules in the i th quantum state. The distribution function is to be determined by solving the Boltzmann equation; in the present analysis, the resolution of the Boltzmann equation is carried out by a generalized Chapman-Enskog method. \mathbf{v} is the molecular velocity, \mathbf{r} the general spatial coordinate, and t the time.

Thus the Boltzmann equation for the p component, in the absence of external forces, may be written

$$\frac{df_{i_p}}{dt} = J_p = J_{pp} + J_{pq}. \quad (2.1)$$

The rate of change of f_{i_p} is only due to collisions. Then, for a binary mixture, the collisional term J_p can be separated into two terms: the first one, J_{pp} , is the collisional term characteristic of the collisions between two molecules p ; and the second one, J_{pq} , is the collisional term characteristic of the collisions between molecules p and molecules q . With the hypothesis of the reversibility of collisions, one has

$$J_{pp} = \sum_{j,k,l} \int (f_{kp} f_{lp} - f_{ip} f_{jp}) g_{ip,jp} I_{ip,jp}^{kp,lp} d\Omega d\mathbf{c}_{jp}, \quad (2.2)$$

$$J_{pq} = J_{qp} = \sum_{j,k,l} \int (f_{kp} f_{lq} - f_{ip} f_{jq}) g_{ip,jq} I_{ip,jq}^{kp,lq} d\Omega d\mathbf{c}_{jq}, \quad (2.3)$$

where \mathbf{g} is the relative velocity, I the differential collision cross section, Ω the scattering diffusion solid angle, and \mathbf{c} the velocity ($\mathbf{v} - \mathbf{u}$). i, j are the quantum numbers before collision and h, l after.

Now, considering the previous classification of collisions, the Boltzmann equation may be written under the following nondimensional form:

$$\frac{df_{i_p}^*}{dt} = \frac{1}{\epsilon_I} J_{I_p}^* + \frac{1}{\epsilon_{II}} J_{II_p}^*, \quad (2.4)$$

where

$$J_{I_p}^* = J_{I_{pp}}^* + J_{I_{pq}}^*$$

is the collisional term of type I,

$$J_{II_p}^* = J_{II_{pp}}^* + J_{II_{pq}}^*$$

is the collisional term of type II, and

$$\epsilon_I = \frac{\tau_I}{\theta}, \quad \epsilon_{II} = \frac{\tau_{II}}{\theta},$$

where τ is a relaxation time and θ a reference flow time.

Several cases will be analyzed with regard to the relative or effective order of magnitude of the nondimensional numbers ϵ_I and ϵ_{II} . However, physical arguments will allow us to reduce the number of considered cases. (i) Type-I collisions are the most probable. Then

$$\epsilon_I \ll \epsilon_{II}.$$

(ii) In a collisional or continuum regime, because of the efficiency of type-I collisions, one has

$$\epsilon_I = \epsilon \ll 1.$$

Thus the problem is reduced to three possible distinct cases: the equilibrium case $\epsilon_I = \epsilon \ll \epsilon_{II} \ll 1$, the non-equilibrium case $\epsilon_I = \epsilon \ll \epsilon_{II} \approx 1$, and the frozen case $\epsilon_I = \epsilon \ll 1 \ll \epsilon_{II}$.

The Chapman-Enskog method consists in expanding f_{i_p} in a series of the smallest parameter. Stopping at first order, we have

$$f_{i_p}^* = f_{i_p}^{*0} + \epsilon f_{i_p}^{*1} = f_{i_p}^{*0} (1 + \epsilon \varphi_{i_p}),$$

where φ is a perturbation term.

Thus, starting from (2.4) and identifying the terms of the same order, the following systems are deduced. For the equilibrium case $df_{i_p}^*/dt = (1/\epsilon)(J_{I_p}^* + J_{II_p}^*)$,

$$J_{I_p}^0 + J_{II_p}^0 = 0, \quad \text{zeroth order} \quad \left[\frac{1}{\epsilon} \right], \quad (2.5)$$

$$\frac{df_{i_p}^0}{dt} = J_{I_p}^1 + J_{II_p}^1, \quad \text{first order}. \quad (2.6)$$

For the nonequilibrium case $df_{i_p}^*/dt = (1/\epsilon)J_{I_p}^* + J_{II_p}^*$,

$$J_{I_p}^0 = 0, \quad \text{zeroth order} \quad \left[\frac{1}{\epsilon} \right], \quad (2.7)$$

$$\frac{df_{i_p}^0}{dt} = J_{I_p}^1 + J_{II_p}^0, \quad \text{first order}. \quad (2.8)$$

For the frozen case, the influence of type-II collisions (vibrational exchanges) does not appear at the zeroth and first orders and will not be treated here, the rotational mode being in equilibrium.

The *zeroth-order* equations (2.5) and (2.7) give the zeroth-order solution $f_{i_p}^0$. In the first case (2.5), $f_{i_p}^0$ is defined at one single temperature T (translation-rotation-vibration temperature). For the second case (2.7), the vi-

brational nonequilibrium appears in the Boltzmann distribution (density of p molecules on the i_v th level). In this case, $f_{i_p}^0$ is defined with two different temperatures, i.e., the translation-rotation temperature $T = T_{tr}$, and the vibrational temperature of the p species T_{vp} . Of course this is the same for f_{jq} and for the vibrational temperature T_{vq} . The existence of this nonequilibrium (temperatures T_{vp} and T_{vq}) results from the fact that the resonant vibration-vibration collisions between two molecules p (or q) are included in type-I collisions. Thus, this taken into account, compared with the equilibrium case, gives a specific collisional invariant ϵ_{iv_p} (or ϵ_{jv_q}), the vibrational energy of p (or q) molecules on the i th (or j)th level. At this order, the macroscopic conservation equations are the Euler equations; in the second (nonequilibrium) case they are completed by two relaxation equations for the vibrational energies or vibrational temperatures T_{vp} and T_{vq} .

The first-order equations (2.6) and (2.8) allow us to obtain a formulation of the first-order solution $f_{i_p}^1$. In both cases $f_{i_p}^1$ characterizes a nonequilibrium regime which is weak, and therefore allows linearization. Thus the expressions obtained for the transport terms, which derive from a first-order calculation, correspond in the "equilibrium" case to a *weak-nonequilibrium* and in the "nonequilibrium" case to a *strong-nonequilibrium*. At this order, the conservation equations are the Navier-Stokes equations, also completed, for the SNE case, by two relaxation equations.

The WNE case has been already studied by various authors [4,5,7]. For each transport term, they give the exact expressions in the form of determinant ratios. Thus only the SNE case is developed here, for a binary mixture in vibrational nonequilibrium.

III. THE SNE CASE

As already noted, the knowledge of transport properties requires calculations at the first order. So, in a first part, the zeroth-order equation (2.7) is solved, in order to determine the zeroth-order solution $f_{i_p}^0$. Then, in a second part, using the zeroth-order result, the first-order equation (2.8) is developed and the expressions of the transport terms may be obtained. Thus the analyzed system is presented in Eqs. (2.7) and (2.8). The collision reversibility hypothesis enables one to write the collisional terms under the following form:

$$J_{I_{pq}}^0 = \sum_{j,k,l} \int (f_{kp}^0 f_{lq}^0 - f_{ip}^0 f_{jq}^0) g_{ip,jq} I_{ip}^{kp,lq}(I) d\Omega d\mathbf{c}_{jq}, \quad (3.1)$$

$$J_{II_{pq}}^0 = \sum_{j,k,l} \int (f_{kp}^0 f_{lq}^0 - f_{ip}^0 f_{jq}^0) g_{ip,jq} I_{ip}^{kp,lq}(II) d\Omega d\mathbf{c}_{jq}, \quad (3.2)$$

$$J_{I_{pq}}^1 = \sum_{j,k,l} \int (f_{kp}^0 f_{lq}^1 + f_{kp}^1 f_{lq}^0 - f_{ip}^0 f_{jq}^1 - f_{ip}^1 f_{jq}^0) \times g_{ip,jq} I_{ip}^{kp,lq}(I) d\Omega d\mathbf{c}_{jq}, \quad (3.3)$$

where $I(I)$ and $I(II)$ are, respectively, the cross sections of type I and II.

A. Zeroth-order solution

From the zeroth-order equation (2.7), $J_{I_p}^0 = 0$, it is easily shown that

$$f_{i_p}^0 = n_p \left[\frac{m_p}{2\pi kT} \right]^{3/2} \exp \left[-\frac{m_p c_{ip}^2}{2kT} \right] \times \frac{g_{ir_p} \exp \left[-\frac{\epsilon_{ir_p}}{kT} \right] \exp \left[-\frac{\epsilon_{iv_p}}{kT_{vp}} \right]}{\sum_{i,r_p} g_{ir_p} \exp \left[-\frac{\epsilon_{ir_p}}{kT} \right] \sum_{i,v_p} \exp \left[-\frac{\epsilon_{iv_p}}{kT_{vp}} \right]}, \quad (3.4)$$

where n is the molecular number density, \mathbf{u} the macroscopic velocity, m the molecular mass, k the Boltzmann constant, g the statistical weight, and ϵ the internal energy. The macroscopic quantities, n_p , T , T_{vp} , and \mathbf{u} are defined with $f_{i_p}^0$; they can be found by solving the Euler equations, to which the following vibrational relaxation equation has to be added:

$$n_p \frac{DE_{vp}}{Dt} = \sum_i \epsilon_{iv_p} \int J_{II_i}^0 d\mathbf{c}_{i_p}, \quad (3.5)$$

where E_V is the mean vibrational energy per molecule.

A Maxwell-Boltzmann distribution holds for the translational and rotational mode, respectively, at the translation-rotation temperature T . But, contrarily to the result obtained by a WNE method, a Boltzmann distribution at the vibrational temperature T_v for the considered species (T_{vp} for f_{ip} and T_{vq} for f_{jq}) appears, representing a nonequilibrium for the zeroth-order solution.

B. First-order solution—transport terms

1. The first-order solution

$f_{i_p}^1$ is obtained from the following equation:

$$\frac{df_{i_p}^0}{dt} - J_{II_p}^0 = J_{I_p}^1. \quad (2.8')$$

Because of the expansion of f_{i_p} in a series of a small parameter ϵ , linear calculation methods may be used for solving Eq. (2.8'). Thus, taking into account the form of the known terms $df_{i_p}^0/dt$ and φ_{i_p} which are deduced from $f_{i_p}^0$ (3.4), the perturbation term φ_{i_p} , which appears in the $J_{I_p}^1$ term, can be written under the form

$$\varphi_{i_p} = A_{i_p} \mathbf{c}_{i_p} \cdot \frac{\partial \ln T}{\partial \mathbf{r}} + B_{i_p} \overset{\circ}{\mathbb{C}}_{i_p} \cdot \frac{\partial \mathbf{u}}{\partial \mathbf{r}} + D_{i_p} \frac{\partial \cdot \mathbf{u}}{\partial \mathbf{r}} + F_{i_p} \mathbf{c}_{i_p} \cdot \frac{\partial \ln T_{vp}}{\partial \mathbf{r}} + G_{i_p} + H_{i_p} \mathbf{c}_{i_p} \cdot d\mathbf{p} \quad (3.6)$$

($\overset{\circ}{\mathbb{C}}$ is a nondivergent symmetrical tensor), where $X_{ip} = A_{ip}$, B_{ip} , D_{ip} , F_{ip} , G_{ip} , and H_{ip} , are unknown scalar functions of \mathbf{r} , t , \mathbf{c}_{i_p} , and ϵ_{iv_p} . In contrast to the WNE method, the

fourth and fifth terms are due to the nonequilibrium. The last term is due to the mixture,

$$d\mathbf{p} = \frac{\partial}{\partial \mathbf{r}} \left[\frac{n_p}{n} \right] - \left[\frac{n_p}{n} - \frac{n_p m_p}{nm} \right] \frac{\partial \ln P}{\partial \mathbf{r}},$$

where P is the hydrostatic pressure.

At this level, considering the gradients to which these coefficients are connected, it may be anticipated that the coefficients A_{ip} , B_{ip} , D_{ip} , F_{ip} , G_{ip} , and H_{ip} will, respectively, participate in the expressions of translational and rotational thermal conductivity, shear viscosity, bulk viscosity, vibrational thermal conductivity, pressure term (relaxation pressure), and mass-diffusion coefficient. The principle of calculation consists in developing these coefficients on the basis of the eigenfunctions of the integral operator $J_{I_p}^1$, which is generally unknown for a realistic potential interaction. However, in the case of a Maxwellian intermolecular potential these eigenfunctions may be identified: They form an orthogonal basis [15]. These functions are expressed in terms of Sonine-Laguerre polynomials for the translational mode, and by

$$J_{I_p}^1 [A_{ip} \mathbf{c}_{i_p}] = \left[\frac{m_p c_{i_p}^2}{2kT} - \frac{5}{2} + \frac{\varepsilon_{ir_p} - \bar{E}_{r_p}(T)}{kT} \right] \mathbf{c}_{i_p} f_{i_p}^0, \quad (3.7)$$

$$J_{I_p}^1 [B_{ip} \overline{\mathbf{c}_{i_p} \mathbf{c}_{i_p}}] = \left[\frac{m_p \overline{\mathbf{c}_{i_p} \mathbf{c}_{i_p}}}{kT} \right] f_{i_p}^0, \quad (3.8)$$

$$J_{I_p}^1 [D_{ip}] = - \left\{ \frac{2}{3} \left[\frac{3}{2} - \frac{m_p c_{i_p}^2}{2kT} \right] + \frac{k}{C_r} \frac{\varepsilon_{ir_p} - \bar{E}_{r_p}(T)}{kT} \right\} \frac{C_r}{C_{ir}} f_{i_p}^0, \quad (3.9)$$

$$J_{I_p}^1 [F_{ip} \mathbf{c}_{i_p}] = \frac{\varepsilon_{iv_p} - E_{v_p}(T_{v_p})}{kT_{v_p}} \mathbf{c}_{i_p} f_{i_p}^0, \quad (3.10)$$

$$J_{I_p}^1 [G_{ip}] = \left[- \frac{1}{Tn C_{tr}} \sum_p S^0(\varepsilon_{iv_p}) \left[\frac{m_p c_{i_p}^2}{2kT} - \frac{3}{2} + \frac{\varepsilon_{ir_p} - \bar{E}_{r_p}(T)}{kT} \right] + \frac{1}{T_{v_p}} \frac{\varepsilon_{iv_p} - E_{v_p}(T_{v_p})}{kT_{v_p}} \frac{S^0(\varepsilon_{iv_p})}{n_p C_{v_p}(T_{v_p})} \right] f_{i_p}^0 - J_{II_p}^0, \quad (3.11)$$

$$J_{I_p}^1 [H_{ip} \mathbf{c}_{i_p}] = \frac{n}{n_p} \mathbf{c}_{i_p} f_{i_p}^0, \quad (3.12)$$

with

$$S^0(\varepsilon_{iv_p}) = \sum_i \varepsilon_{iv} \int J_{II}^0 d\mathbf{c}_i.$$

The brackets [] represent a collisional balance,

$$\begin{aligned} J_{I_p}^1 [X_{i_p}] &= J_{I_{pp}}^1 [X_{i_p}] + J_{I_{pq}}^1 [X_{i_p}] \\ &= J_{I_{pp}}^1 (X_{k_p} + X_{l_p} - X_{i_p} - X_{j_p}) \\ &\quad + J_{I_{pq}}^1 (X_{k_p} + X_{l_q} - X_{i_p} - X_{j_q}), \end{aligned}$$

and C is the specific heat (t, r, v represent translation, rotation, and vibration, respectively).

As the macroscopic quantities are defined with the

extrapolation, in terms of Wang-Chang and Uhlenbeck polynomials for the internal modes [7]. Thus the coefficients $X_{ip} = A_{ip}, B_{ip}, D_{ip}, F_{ip}, G_{ip}$, and H_{ip} are expanded on this basis,

$$X_{i_p} = \sum_{m,n,s=0}^1 x_{pmns} \Psi_{pmns}^r,$$

where x_{pmns} do not depend on velocity ($x = a, b, d, f, g, h$). Ψ_{pmns}^r constitute a complete basis of orthogonal polynomials previously defined (translation and internal modes),

$$\Psi_{pmns}^r = S_r^m \left[\frac{m_p c_{i_p}^2}{2kT} \right] P_i^n \left[\frac{\varepsilon_{ir_p}}{kT} \right] P_i^s \left[\frac{\varepsilon_{iv_p}}{kT_{v_p}} \right],$$

where S_r^m are the Sonine-Laguerre polynomials and P_i^n the Wang-Chang and Uhlenbeck ones. Substituting $df_{i_p}^0/dt$ and φ_{i_p} (3.6) into (2.8'), the following systems, giving, respectively, the expression of $A_{ip}, B_{ip}, D_{ip}, F_{ip}, G_{ip}$, and H_{ip} , are obtained:

zeroth-order solution $f_{i_p}^0$, four conditions are imposed on the coefficients. They come from the density definition,

$$\sum_i \int f_{i_p}^0 \varphi_{i_p} d\mathbf{c}_{i_p} = 0 \implies d_{p000} = g_{p000} = 0, \quad (3.13)$$

the mass velocity definition,

$$\begin{aligned} \sum_p m_p \sum_i \int f_{i_p}^0 \varphi_{i_p} \mathbf{v}_{i_p} d\mathbf{c}_{i_p} &= 0 \\ \implies a_{p000} &= a_{q000} = f_{p000} = f_{q000} = 0 \\ \implies \sum_p m_p h_{p000} d\mathbf{p} &= 0, \end{aligned} \quad (3.14)$$

the translation-rotation temperature definition,

$$\begin{aligned}
\sum_p \sum_i \int f_{i_p}^0 \varphi_{i_p} \left(\frac{1}{2} m_p c_{i_p}^2 + \varepsilon_{i_p} \right) d\mathbf{c}_{i_p} &= \mathbf{0} \\
\Rightarrow \sum_p n_p \left\{ -\frac{3}{2} k d_{p100} + C_{r_p}(T) d_{p010} \right\} &= \mathbf{0} \\
\Rightarrow \sum_p n_p \left\{ -\frac{3}{2} k g_{p100} + C_{r_p}(T) g_{p010} \right\} &= \mathbf{0}, \quad (3.15)
\end{aligned}$$

and the vibrational temperatures definition,

$$\begin{aligned}
\sum_i \int f_{i_p}^0 \varphi_{i_p} \varepsilon_{i_p} d\mathbf{c}_{i_p} &= \mathbf{0} \Rightarrow d_{p001} = g_{p001} = \mathbf{0}, \\
\sum_i \int f_{j_q}^0 \varphi_{j_q} \varepsilon_{j_q} d\mathbf{c}_{j_q} &= \mathbf{0} \Rightarrow d_{q001} = g_{q001} = \mathbf{0}. \quad (3.16)
\end{aligned}$$

The above constraints on a , d , f , g , and h constitute only sufficient conditions.

Expanding the X_{ip} coefficients and taking into account the above conditions, the perturbation term φ_{i_p} is written as follows:

$$\begin{aligned}
\varphi_{i_p} &= \left[a_{p100} \left[\frac{5}{2} - \frac{m_p c_{i_p}^2}{2kT} \right] + a_{p010} \left[\frac{\varepsilon_{i_p} - \bar{E}_{rp}(T)}{kT} \right] + a_{p001} \left[\frac{\varepsilon_{i_p} - E_{vp}(T_{vp})}{kT_{vp}} \right] \right] \mathbf{c}_{i_p} \frac{\partial \ln T}{\partial \mathbf{r}} \overset{\circ}{b}_{p000} c_{i_p} c_{i_p} : \frac{\partial \mathbf{u}}{\partial \mathbf{r}} \\
&+ \left[d_{p100} \left[\frac{3}{2} - \frac{m_p c_{i_p}^2}{2kT} \right] + d_{p010} \left[\frac{\varepsilon_{i_p} - \bar{E}_{rp}(T)}{kT} \right] + d_{p001} \left[\frac{\varepsilon_{i_p} - E_{vp}(T_{vp})}{kT_{vp}} \right] \right] \frac{\partial \cdot \mathbf{u}}{\partial \mathbf{r}} \\
&+ \left[f_{p100} \left[\frac{5}{2} - \frac{m_p c_{i_p}^2}{2kT} \right] + f_{p010} \left[\frac{\varepsilon_{i_p} - \bar{E}_{rp}(T)}{kT} \right] + f_{p001} \left[\frac{\varepsilon_{i_p} - E_{vp}(T_{vp})}{kT_{vp}} \right] \right] \mathbf{c}_{i_p} \frac{\partial \ln T_{vp}}{\partial \mathbf{r}} \\
&+ g_{p100} \left[\frac{3}{2} - \frac{m_p c_{i_p}^2}{2kT} \right] + g_{p010} \left[\frac{\varepsilon_{i_p} - \bar{E}_{rp}(T)}{kT} \right] + g_{p001} \left[\frac{\varepsilon_{i_p} - E_{vp}(T_{vp})}{kT_{vp}} \right] \\
&+ \left[h_{p100} \left[\frac{5}{2} - \frac{m_p c_{i_p}^2}{2kT} \right] + h_{p010} \left[\frac{\varepsilon_{i_p} - \bar{E}_{rp}(T)}{kT} \right] + h_{p001} \left[\frac{\varepsilon_{i_p} - E_{vp}(T_{vp})}{kT_{vp}} \right] \right] \mathbf{c}_{i_p} d\mathbf{p}
\end{aligned}$$

where \bar{E} is the equilibrium internal energy.

2. Transport terms

In this way, through φ_{i_p} or its coefficients (a, b, f, \dots), all transport terms are expressed in terms of the collisional integrals. The stress tensor is

$$\begin{aligned}
\bar{\tau} &= nkT\bar{\bar{I}} + 2 \left[n_p m_p \left[\frac{kT}{m_p} \right]^2 b_{p000} \right. \\
&\quad \left. + n_q m_q \left[\frac{kT}{m_q} \right]^2 b_{q000} \right] \frac{\partial \mathbf{u}}{\partial \mathbf{r}} \\
&- (n_p d_{p100} + n_q d_{q100}) kT\bar{\bar{I}} \frac{\partial \cdot \mathbf{u}}{\partial \mathbf{r}} \\
&- (n_p g_{p100} + n_q g_{q100}) kT\bar{\bar{I}}, \quad (3.17)
\end{aligned}$$

where $\bar{\bar{I}}$ is the unit tensor.

In this expression, one may distinguish a term of hydrostatic pressure

$$P = nkT, \quad (3.18)$$

a term of shear viscosity, with the shear viscosity coefficient,

$$\mu = - \sum_p n_p m_p \left[\frac{kT}{m_p} \right]^2 b_{p000} \quad (3.19)$$

and a term of bulk viscosity due to the fact that, at zeroth order, the rotational mode is assumed in equilibrium. The corresponding coefficient is related to the delay that the rotational mode takes to relax, as compared to the translational mode,

$$\eta = kT \sum_p n_p d_{p100}, \quad (3.20)$$

and a term of relaxation pressure which comes also from the equilibrium assumption for the rotational mode at the zeroth order,

$$P_R = -kT \sum_p n_p g_{p100}. \quad (3.21)$$

The heat flux characterizes three types of energy diffusion: translation, rotation, and vibration. The translational heat flux is

$$\begin{aligned} \mathbf{q}_t &= \mathbf{q}_{t_p} + \mathbf{q}_{t_q} \\ &= -\frac{\zeta}{2} \sum_p n_p m_p \left(\frac{kT}{m_p} \right)^2 \left[a_{p100} \frac{\partial \ln T}{\partial \mathbf{r}} + f_{p100} \frac{\partial \ln T_{v_p}}{\partial \mathbf{r}} \right. \\ &\quad \left. + (h_{p100} - h_{p000}) d\mathbf{p} \right]. \end{aligned} \quad (3.22)$$

The rotational heat flux is

$$\begin{aligned} \mathbf{q}_r &= \mathbf{q}_{r_p} + \mathbf{q}_{r_q} \\ &= \sum_p n_p \left(\frac{kT}{m_p} \right) \left[TC_{r_p} \left[a_{p010} \frac{\partial \ln T}{\partial \mathbf{r}} + f_{p010} \frac{\partial \ln T_{v_p}}{\partial \mathbf{r}} \right. \right. \\ &\quad \left. \left. + h_{p010} d\mathbf{p} \right] \right. \\ &\quad \left. + \bar{E}_{r_p}(T) h_{p000} d\mathbf{p} \right]. \end{aligned} \quad (3.23)$$

The vibrational heat flux is

$$\mathbf{q}_v = \sum_p n_p \left(\frac{kT}{m_p} \right) \left[T_{v_p} C_{v_p}(T_{v_p}) \left[a_{p001} \frac{\partial \ln T}{\partial \mathbf{r}} + f_{p001} \frac{\partial \ln T_{v_p}}{\partial \mathbf{r}} + h_{p001} d\mathbf{p} \right] + E_{v_p}(T_{v_p}) h_{p000} d\mathbf{p} \right]. \quad (3.24)$$

The corresponding thermal conductivities are the following: For translation,

$$\begin{aligned} \lambda_{t_r} &= \frac{\zeta}{2} \sum_p n_p m_p \left(\frac{kT}{m_p} \right)^2 \left[\frac{a_{p100}}{T} \right], \\ \lambda_{t_{T_{v_p}}} &= \frac{\zeta}{2} n_p m_p \left(\frac{kT}{m_p} \right)^2 \left[\frac{f_{p100}}{T_{v_p}} \right], \\ \lambda_{t_{T_{v_q}}} &= \frac{\zeta}{2} n_q m_q \left(\frac{kT}{m_q} \right)^2 \left[\frac{f_{q100}}{T_{v_q}} \right], \end{aligned} \quad (3.25)$$

for rotation,

$$\begin{aligned} \lambda_{r_T} &= -\sum_p n_p \left(\frac{kT}{m_p} \right) [C_{r_p}(a_{p010})], \\ \lambda_{r_{T_{v_p}}} &= -n_p \left(\frac{kT}{m_p} \right) \left[TC_{r_p} \left(\frac{f_{p010}}{T_{v_p}} \right) \right], \\ \lambda_{r_{T_{v_q}}} &= -n_q \left(\frac{kT}{m_q} \right) \left[TC_{r_q} \left(\frac{f_{q010}}{T_{v_q}} \right) \right], \end{aligned} \quad (3.26)$$

and for vibration,

$$\begin{aligned} \lambda_{v_T} &= -\sum_p n_p \left(\frac{kT}{m_p} \right) \left[T_{v_p} C_{v_p}(T_{v_p}) \left(\frac{a_{p001}}{T} \right) \right], \\ \lambda_{v_{T_{v_p}}} &= -n_p \left(\frac{kT}{m_p} \right) [C_{v_p}(T_{v_p})(f_{p001})], \\ \lambda_{v_{T_{v_q}}} &= -n_q \left(\frac{kT}{m_q} \right) [C_{v_q}(T_{v_q})(f_{q001})]. \end{aligned} \quad (3.27)$$

The diffusion velocity is

$$\bar{\mathbf{c}}_{i_p} = \frac{kT}{m_p} \left[a_{p000} \frac{\partial \ln T}{\partial \mathbf{r}} + f_{p000} \frac{\partial \ln T_{v_p}}{\partial \mathbf{r}} + h_{p000} d\mathbf{p} \right]. \quad (3.28)$$

Neglecting thermal diffusion [16,17], we find

$$\bar{\mathbf{c}}_{i_p} = \frac{kT}{m_p} h_{p000} d\mathbf{p}, \quad (3.29)$$

with

$$\begin{aligned} h_{p000} &= -\frac{n^2}{\rho\rho_p} \frac{m_p^2 m_q}{kT} D_{pq}, \\ h_{q000} &= -\frac{n^2}{\rho\rho_q} \frac{m_q^2 m_p}{kT} D_{pq}, \end{aligned}$$

where D_{pq} is the mass diffusion coefficient.

All these transport terms—stress tensor, heat flux, and diffusion velocity—appear in the conservation equations of macroscopic quantities which are, actually, the Navier-Stokes equations completed by vibrational relaxation equations giving T_{v_p} and T_{v_q} (E_{v_p} and E_{v_q}). For the p species,

$$n_p \frac{DE_{v_p}}{Dt} + \frac{\partial \cdot \mathbf{q}_{v_p}}{\partial \mathbf{r}} = \sum_i \varepsilon_{i_p} \int J_{\text{II}_p}^0 d\mathbf{c}_{j_q} + \sum_i \varepsilon_{i_p} \int J_{\text{II}_p}^1 d\mathbf{c}_{i_p}. \quad (3.30)$$

Referring to previous calculations [18,19] the second term of the second member of (3.30) may be neglected.

The resolution of the system of Eqs. (3.7)–(3.12) yields expressions for the transport term coefficients, i.e., for a , b , d , f , g , and h . However, these coefficients are expressed as combinations of type-I collision integrals, except for the coefficient g which depends also on type-II collision integrals. As it is very difficult to evaluate accurately the differential collision cross sections, particularly the inelastic ones, the collision integral calculations represent a formidable task. Therefore, it may be necessary to express transport terms (or the a , b , d , f , g , and h coefficients) as functions of known or measurable macroscopic quantities, so as to make these quantities easier to use in numerical calculations. Thus, generalizing approximations of the Mason and Monchick type, which consider the inelastic contribution as a perturbation, it may be shown that the transport terms for a binary mixture, as given in the Appendix, are expressed principally as functions of shear viscosities, diffusion coefficients, and rotational relaxation times of the gases constituting the mixture.

The shear viscosity (A1) and translational thermal conductivity (A4) in binary mixtures depend on the shear viscosities of pure gases (μ_p, μ_q), the binary diffusion coefficient (D_{pq}), and the "fictitious" viscosity [21] (μ_{pq}^*). These terms are weakly influenced by the internal modes since they characterize momentum exchanges and translational energy diffusion, respectively. Thus, at this level of approximation, these coefficients are identical to their WNE expressions. Comparison with approximate formulas given by various authors [5,12,13,20] shows that, generally, these approximations give the shear viscosity and the translational thermal conductivity as functions of shear viscosities of pure gases only [12,13,20] or of shear viscosities of pure gases and binary diffusion coefficient [5]. None of them take into account the dependence on the coupling term called here the "fictitious" viscosity.

Contrary to the vibrational mode, there is no equation describing the relaxation of the rotational mode: The bulk viscosity (A2) "compensates" this absence and is typical of this particular nonequilibrium process, assumed small. That is the reason why the bulk viscosity η is connected to the different phenomenological rotational relaxation times.

The relaxation pressure P_R (A3) is due to the vibrational nonequilibrium, combined with an assumed small rotational nonequilibrium, and is added to the hydrostatic pressure P . With the harmonic-oscillator hypothesis, P_R depends on the relaxation of the two internal modes (τ_r and τ_v). Typically, for a pure gas [18], P_R is of the order of the ratio of the rotational and vibrational relaxation times: τ_r/τ_v .

The thermal conductivities for the rotational (A5) and vibrational modes (A6) and (A7) depend on the binary diffusion coefficient and on the self-diffusion coefficients. At the first order of the Mason and Monchick approximations [8], the λ_r expression is similar to that given by Mason, Monchick, and Pereira [22]. Through the vibrational temperature T_v , λ_v depends strongly on the degree of nonequilibrium.

It may be noted that results obtained by the SNE method do not tend properly to the correct near equilibrium behavior. Then, as for pure gases [23], these results cannot be applied to gas flows in weak nonequilibrium; these flows must therefore be treated by a WNE method. In order to avoid this problem, a general method valid, whatever the degree of nonequilibrium, is presented in the next part.

IV. GENERAL METHOD WNE/SNE

Hereafter, a physical deductive reasoning is used rather than a rigorous mathematical treatment. The problem comes from the cutoff of the Boltzmann equation which is different for the WNE or SNE method. Thus

	WNE method	SNE method
Zeroth order	$J_{I_p}^0 + J_{II_p}^0 = 0$	$J_{I_p}^0 = 0$
First order	$\frac{df_{I_p}^0}{dt} = J_{I_p}^1 + J_{II_p}^1$	$\frac{df_{I_p}^0}{dt} = J_{I_p}^1 + J_{II_p}^0$

At the zeroth order, the matching between both methods exists (when $T_v \rightarrow T$). At the first order, the matching between WNE and SNE methods does not exist: For the WNE case, the collision integrals or transport terms depend on collisions of type I and II. For the SNE case, except for the $J_{II_p}^0$ term, which participates only in the relaxation pressure expression, the collision integrals and therefore the transport terms depend on collisions of type I exclusively. Alexeev [24] and Kogan [25] have brought a mathematical solution to this problem. Thus, the addition of the term $J_{II_p}^1$, to the SNE first-order equation, which takes into account the relaxation of type-II collisions, is sufficient to realize the matching.

A new system is then obtained,

$$J_{I_p}^0 = 0, \quad \text{zeroth order} \quad \left[\frac{1}{\epsilon} \right], \quad (4.1)$$

$$\frac{df_{I_p}^0}{dt} = J_{I_p}^1 + J_{II_p}^0 + J_{II_p}^1, \quad \text{first order}, \quad (4.2)$$

where

$$J_{II_p}^1 = J_{II_{pp}}^1 + J_{II_{pq}}^1.$$

The SNE case is recovered when $J_{II_p}^1 \rightarrow 0$, and the WNE case when $J_{II_p}^0 \rightarrow 0$,

$$J_{II_{pp}}^1 = \sum_{j,k,l} \int (f_{k_p}^0 f_{l_p}^1 + f_{k_p}^1 f_{l_p}^0 - f_{i_p}^0 f_{j_p}^1 - f_{i_p}^1 f_{j_p}^0) \times g_{i_p j_p} J_{i_p j_p}^{k_p l_p}(\Pi) d\Omega d\mathbf{c}_{j_p}, \quad (4.3)$$

$$J_{II_{pq}}^1 = \sum_{j,k,l} \int (f_{k_p}^0 f_{l_q}^1 + f_{k_p}^1 f_{l_q}^0 - f_{i_p}^0 f_{j_q}^1 - f_{i_p}^1 f_{j_q}^0) \times g_{i_p j_q} J_{i_p j_q}^{k_p l_q}(\Pi) d\Omega d\mathbf{c}_{j_q}. \quad (4.4)$$

As in the case of a pure gas, only the self-adjoint part of the $J_{II_p}^1$ term is retained, the other part being smaller by an order of magnitude [25]. Thus

$$J_{II_p}^1 = J_{II_p}^{S(1)} + J_{II_p}^{A(1)} \\ = J_{II_{pp}}^{S(1)} + J_{II_{pq}}^{S(1)} + J_{II_{pp}}^{A(1)} + J_{II_{pq}}^{A(1)},$$

where $J_{II_p}^{A(1)}$ is the non-self-adjoint part which is of higher order [25]. $J_{II_p}^{S(1)}$ is the self-adjoint part which is to be retained at this order. Then the system becomes

$$J_{I_p}^0 = 0, \quad \text{zeroth order} \quad \left[\frac{1}{\epsilon} \right], \quad (4.5)$$

$$\frac{df_{I_p}^0}{dt} = J_{I_p}^1 + J_{II_p}^0 + J_{II_p}^{S(1)}, \quad \text{first order}, \quad (4.6)$$

with

$$J_{\text{II}_p}^{S(1)} = J_{\text{II}_{pp}}^{S(1)} + J_{\text{II}_{pq}}^{S(1)} = \frac{1}{2} \sum_{j,k,l} \int (f_{k_p}^0 f_{l_p}^0 + f_{i_p}^0 f_{j_p}^0) (\varphi_{k_p} + \varphi_{l_p} - \varphi_{j_p} - \varphi_{i_p}) g_{i_p j_p} I_{i_p j_p}^{k_p l_p}(\text{II}) d\Omega d\mathbf{c}_{j_p} \\ + \frac{1}{2} \sum_{j,k,l} \int (f_{k_p}^0 f_{l_q}^0 + f_{i_p}^0 f_{j_q}^0) (\varphi_{k_p} + \varphi_{l_q} - \varphi_{i_p} - \varphi_{j_q}) g_{i_p j_q} I_{i_p j_q}^{k_p l_q}(\text{II}) d\Omega d\mathbf{c}_{j_q}. \quad (4.7)$$

The eigenvalues of $J_{\text{II}_p}^{S(1)}$ are the collisional invariants relative to type-II collisions only, i.e., mass, momentum, and total energy.

As in the previous case (SNE), the determination of the transport terms requires us to solve successively (4.5) and (4.6). Since this general method appears like a correction to the SNE method, calculations and physical reasonings are the same as in the SNE case. However, the addition of the $J_{\text{II}_p}^I$ term brings modifications to the perturbation term φ_{i_p} or to its coefficients A_{ip} , B_{ip} , D_{ip} , F_{ip} , G_{ip} , and H_{ip} ; now, the transport terms depend on the collision integrals of type I and type II. Because of the lack of information about collision cross sections for the inelastic col-

isions, it seems necessary, like in the SNE case, to relate the collision integrals of type I and II to macroscopic quantities.

For collision integrals of type I, Mason and Monchick type approximations are similar to the previous SNE method. For collision integrals of type II, which characterize the main vibrational energy exchanges, it may be shown that the use of the harmonic-oscillator model leads to relations between type-II collision integrals and vibrational relaxation times τ^{VT} and τ^{VV} .

This may be obtained from a phenomenological equation of the Landau-Teller type for the vibrational energy, established using the harmonic-oscillator model [26],

$$\frac{DE_{v_p}(T_{v_p})}{Dt} = x_p \frac{\bar{E}_{v_p}(T) - E_{v_p}(T_{v_p})}{\tau_{pp}^{VT}} + x_q \frac{\bar{E}_{v_p}(T) - E_{v_p}(T_{v_p})}{\tau_{pq}^{VT}} \\ + \frac{x_q}{h\nu_q} \frac{E_{v_q}(T_{v_q}) [E_{v_p}(T_{v_p}) + h\nu_p] \exp\left[\frac{\Theta_{v_q} - \Theta_{v_p}}{T}\right] - E_{v_p}(T_{v_p}) [E_{v_q}(T_{v_q}) + h\nu_q]}{\tau_{pq}^{VV}}, \quad (4.8)$$

where h is the Planck constant, ν the vibration frequency, Θ_v the vibrational characteristic temperature, and x the molar fraction. τ_{pp}^{VT} is the relaxation time of translation-vibration transitions between p molecules,

$$\tau_{pp}^{VT} = \frac{1}{n \sum_j Q_{p_1 p_j}^{p_0 p_j} \left\{ 1 - \exp\left[-\frac{\Theta_{v_p}}{T}\right] \right\}}.$$

τ_{pq}^{VT} is the relaxation time of translation-vibration transitions between p and q molecules,

$$\tau_{pq}^{VT} = \frac{1}{n \sum_j Q_{p_1 q_j}^{p_0 q_j} \left\{ 1 - \exp\left[-\frac{\Theta_{v_p}}{T}\right] \right\}}.$$

$\tau_{pq}^{VV} = \tau_{qp}^{VV}$ is the relaxation time of vibration-vibration transitions between p and q molecules,

$$\tau_{pq}^{VV} = \frac{1}{n Q_{p_1 q_0}^{p_0 q_1}} = \frac{\exp\left[\frac{\Theta_{v_q} - \Theta_{v_p}}{T}\right]}{n Q_{p_0 q_1}^{p_1 q_0}}$$

(detailed balancing), where Q_{pp}^{pp} and Q_{pq}^{pq} are collision frequencies. From the vibrational relaxation equation written under the form (3.5), the following relations may be deduced by identification of the similar terms of equation (4.8):

$$\sum_{i,j,k,l} K_{i_p j_p} \int \exp(-\gamma_p^2) \gamma_p^3 I_{i_p j_p}^{i_p -1 j_p}(\text{II}) d\Omega d\gamma_p \\ + \exp\left\{ \frac{\Theta_{v_p}}{T} \left[1 - \frac{T}{T_{v_p}} \right] \right\} \sum_{i,j,k,l} K_{i_p j_p} \int \exp(-\gamma_p^2) \gamma_p^3 I_{i_p j_p}^{i_p +1 j_p}(\text{II}) d\Omega d\gamma_p \\ = \frac{1}{2n} \left[\frac{\pi m_p}{kT} \right]^{1/2} \left[\frac{kT_{v_p}}{h\nu_p} \right]^2 \frac{C_{v_p}(T_{v_p})}{k} \frac{Q_p}{Q_{v_p}} \frac{1}{\tau_{pp}^{VT}},$$

$$\begin{aligned}
& \sum_{i,j,k,l} K_{ip j_q} \int \exp(-\gamma_{pq}^2) \gamma_{pq}^3 I_{ip j_q}^{i_p-1 j_q}(\mathbf{II}) d\Omega d\gamma_{pq} \\
& + \exp \left\{ \frac{\Theta_{v_p}}{T} \left[1 - \frac{T}{T_{v_p}} \right] \right\} \sum_{i,j,k,l} K_{ip j_q} \int \exp(-\gamma_{pq}^2) \gamma_{pq}^3 I_{ip j_q}^{i_p+1 j_q}(\mathbf{II}) d\Omega d\gamma_{pq} \\
& = \frac{1}{4n} \left[\frac{2\pi m_r}{kT} \right]^{1/2} \left[\frac{kT_{v_p}}{h\nu_p} \right]^2 \frac{C_{v_p}(T_{v_p})}{k} \frac{Q_p}{Q_{v_p}} \frac{1}{\tau_{pq}^{VT}}, \\
& \sum_{i,j,k,l} K_{ip j_q} \int \exp(-\gamma_{pq}^2) \gamma_{pq}^3 I_{ip j_q}^{i_p-1 j_q+1}(\mathbf{II}) d\Omega d\gamma_{pq} \\
& + \exp \left\{ \frac{\Theta_{v_p}}{T} \left[1 - \frac{T}{T_{v_p}} \right] \right\} \exp \left\{ \frac{-\Theta_{v_q}}{T} \left[1 - \frac{T}{T_{v_q}} \right] \right\} \sum_{i,j,k,l} K_{ip j_q} \int \exp(-\gamma_{pq}^2) \gamma_{pq}^3 I_{ip j_q}^{i_p+1 j_q-1}(\mathbf{II}) d\Omega d\gamma_{pq} \\
& = \frac{1}{4n} \left[\frac{2\pi m_r}{kT} \right]^{1/2} \left[\frac{kT_{v_p}}{h\nu_p} \right]^2 \frac{C_{v_p}(T_{v_p})}{k} \frac{Q_{v_p}}{Q_{v_p}} \frac{1}{\tau_{pq}^{VV}},
\end{aligned}$$

where Q is a partition function, m_r the reduced mass, $\gamma^2 = (m/2kT)g^2$, and

$$\begin{aligned}
K_{ip j_p} &= \frac{g_{ir_p} g_{jr_p} \exp \left[\frac{-\epsilon_{ir_p} - \epsilon_{jr_p}}{kT} \right] \exp \left[\frac{-\epsilon_{iv_p} - \epsilon_{jv_p}}{kT_{v_p}} \right]}{\left[\sum_{i,r_p} g_{ir_p} \exp \left[\frac{-\epsilon_{ir_p}}{kT} \right] \right]^2 \left[\sum_{i,v_p} \exp \left[\frac{-\epsilon_{iv_p}}{kT_{v_p}} \right] \right]^2}, \\
K_{ip j_q} &= \frac{g_{ir_p} g_{jr_q} \exp \left[\frac{-\epsilon_{ir_p} - \epsilon_{jr_q}}{kT} \right] \exp \left[\frac{-\epsilon_{iv_p} - \epsilon_{jv_q}}{kT_{v_p}} - \frac{\epsilon_{jv_q}}{kT_{v_q}} \right]}{\left[\sum_{i,r_p} g_{ir_p} \exp \left[\frac{-\epsilon_{ir_p}}{kT} \right] \right] \left[\sum_{j,r_q} g_{jr_q} \exp \left[\frac{-\epsilon_{jr_q}}{kT} \right] \right] \left[\sum_{i,v_p} \exp \left[\frac{-\epsilon_{iv_p}}{kT_{v_p}} \right] \right] \left[\sum_{j,v_q} \exp \left[\frac{-\epsilon_{jv_q}}{kT_{v_q}} \right] \right]}.
\end{aligned}$$

Now, all collision integrals, or the A_{ip} , B_{ip} , D_{ip} , F_{ip} , G_{ip} , and H_{ip} coefficients, are expressed as combinations of macroscopic quantities, which are the same as in the previous SNE case, but which include also the vibrational relaxation times τ^{VT} and τ^{VV} . Thus, the expressions of the transport terms may be obtained and the nonequilibrium appears explicitly. But, as previously, if the inelastic contributions are assumed small, it may be shown that only the vibrational thermal conductivity is strongly affected by the nonequilibrium.

The shear viscosity (A1) and the translational thermal conductivity (A4) are formally the same (Appendix): In fact, the contribution of the terms depending on the type-II collisions is negligible [18], following the approximations of Mason and Monchick.

The bulk viscosity (A2) and the relaxation pressure (A3) both have an expression identical to the SNE case. This is due to the fact that, contrary to the rotational mode, the vibrational relaxation is entirely described by zeroth and first vibrational relaxation equations. Thus at

the first order it cannot be possible to find a bulk viscosity dependent on vibrational relaxation, as in the WNE case, since this process is taken into account in the vibrational relaxation equation.

The rotational thermal conductivity (A5) is not strongly influenced by the vibrational nonequilibrium. In this matching case, as for the other thermal conductivities, the "cross" thermal conductivities, i.e., $\lambda_{i_T v_p}$, $\lambda_{i_T v_q}$, $\lambda_{r_T v_p}$, $\lambda_{r_T v_q}$, and λ_{v_T} are nonzero, contrary to the SNE case. However, they remain negligible as compared to λ_{i_T} , λ_{r_T} , $\lambda_{v_T v_p}$, and $\lambda_{v_T v_q}$, respectively.

The vibrational thermal conductivity (A8) emphasizes the vibrational mode relaxation phenomenon. Its expression is given in the Appendix and presents an explicit dependence on vibrational relaxation. If the relaxation is very slow, i.e., $\tau_v \rightarrow \infty$, the vibrational thermal conductivity is identical to the SNE case. If the relaxation is

very fast, the vibrational conductivity $\lambda_{v_{T_v}}$, to be added to the "cross" vibrational conductivity λ_{v_T} , is identical to the WNE case. Thus the matching is realized.

V. APPLICATIONS

The subject of this last part is to apply the theoretical results to real mixtures and to describe the evolution of the transport coefficients in a nonequilibrium zone. Furthermore, each transport term is successively examined and compared, whenever possible, with approximations given by different authors [12–14] or with experimental data.

In a first application, a binary mixture is chosen so that the transport properties of both components are significantly different. Thus this test mixtures consists in nitrogen and hydrogen, remembering that μ_{N_2} is approximately twice greater than μ_{H_2} , and that the diffusivity of N_2 is ten times lower than that of H_2 . Results for shear viscosity and thermal conductivity are then compared with experimental data given in Ref. [5], and also with approximate formulas [12–14].

In a second application, a more classical—and more often used—mixture is analyzed, that is 79% nitrogen and 21% oxygen. For this mixture, the remaining transport terms as well as nondimensional numbers are also computed, yielding an estimation of the relative importance of these terms in the temperature range for which present results may be applied.

A. Shear viscosity and thermal conductivity for a N_2 - H_2 mixture

Computation of the transport coefficients requires the knowledge of macroscopic quantities in terms of which they have been expressed. Each macroscopic quantity depends on collision integrals which may be determined.

For the present mixture (N_2 - H_2), the Neufeld, Janzen, and Aziz [27] modeling is chosen. Starting from the numerical tables given in Ref. [5], these authors give relations for the reduced collisional integrals, and express them as functions of relations depending only on the translation-rotation temperature T since ϵ/k and σ , the parameters of the potential function [4,5], are fixed, in a temperature range, for each type of interaction. Thus the modeling of the collision integrals for the pairs N_2 - N_2 , H_2 - H_2 , and N_2 - H_2 allows the computation of macroscopic quantities and finally of the transport terms for the analyzed mixture.

1. Shear viscosity $\mu(\mu_{N_2}, \mu_{H_2}, \mu'_{N_2 H_2}, D_{N_2 H_2})$

The results for the shear viscosity determined by (A1) and by the Wilke [12] approximation are presented and compared in Table I and Fig. 1. In this case, the interaction parameters ϵ/k and σ [4,5] have been taken so that the corresponding values of viscosity for the pure gases are the closest possible to experimental values.

Thus, for more than 39.0% of H_2 , the theoretical result (A1) is closer to experimental values [5] than the Wilke

TABLE I. Shear viscosity in a N_2 - H_2 mixture (10^8 kg/m s) at 273.16 K.

H_2 (mol %)	(A1)	Wilke [12]	Expt. [5]
0	1666	1666	1688
15.9	1645	1660	1670
39.0	1587	1630	1600
65.2	1440	1520	1449
79.5	1284	1376	1285
80.3	1273	1364	1274
100	846	846	853

[12] approximation. The relative error given by Eq. (A1) does not exceed 1.5%, whereas that of the Wilke approximation reaches 7%. Calculations for a pure gas give a relative error of 1.3% and 0.8%, respectively, for nitrogen and hydrogen collision integrals; this discrepancy may be due to the modeling which has been adopted, or to possible experimental errors. If the potential function parameters ($\epsilon/k, \sigma$) are chosen to coincide with the experimental values for pure gases, the relative error becomes lower than 1% within the whole range of concentrations for Eq. (A1) and reaches 8% for the Wilke approximation.

In Fig. 1, the evolution of the shear viscosities as functions of temperature, determined by Eq. (A1), compared to the Wilke approximation for a 80% H_2 -20 mol % N_2 mixture, is represented. The relative difference between Eq. (A1) and the Wilke approximation is about 7%. Referring to Table I, it seems that, for this mixture, the Wilke formula overestimates the values of shear viscosity.

2. Thermal conductivity

$$\lambda(\mu_{N_2}, \mu_{H_2}, \mu'_{N_2 H_2}, D_{N_2 H_2}, D_{N_2 N_2}, D_{H_2 H_2}, B_{N_2 H_2}^*)$$

In order to compare the present results with experimental values, we compute the total thermal conductivity. As in VA 1, the Neufeld and al. modeling [27] for collision integrals is used but the potential parameters ϵ/k and σ derive here from a fitting of the second virial coefficients [4]. The translation thermal conductivity is calculated, first with Eq. (A4) deduced from the theoretical analysis, at the quasifrozen approximation, and then

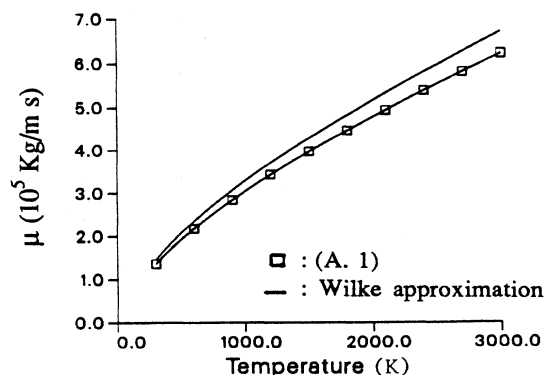


FIG. 1. Shear viscosity in a N_2 - H_2 mixture: $x_{H_2} = 0.8$.

with Wilke [14] and Yos [13] approximations. The internal (rotation-vibration) thermal conductivities, also expressed with the quasifrozen hypothesis, are then added to (A4) and to Yos relations; on the other hand, only the vibrational thermal conductivity—though its contribution is weak—is added to the Wilke approximation, since this one includes the rotational contribution through a factor called the Eucken factor [8].

The determination of the nondimensional term B_{pq}^* is carried out with an equation giving B_{pq}^* as a function of the diffusion coefficient [17,22] (or temperature): This value of B_{pq}^* is nearly equal to unity [8]. The vibrational specific heat necessary for the vibrational thermal conductivity computation is determined by the Einstein relation, in which the vibrational characteristic temperature for N_2 and H_2 is taken from Ref. [28].

In Table II the different numerical values of the total thermal conductivity are reported. The last column giving experimental results is, like the shear viscosity, taken from Ref. [5]. Thus, whatever the mixture concentration, the thermal conductivity determined with Eq. (A4) is closer to experimental values than the approximate formulas [13,14]. It may be also noted that, in spite of the simplicity of the Wilke and Yos thermal conductivity expressions, these approximate formulas give, however, a good estimation of the thermal conductivity values for a binary mixture. The maximum of the relative error is for 65.2% H_2 , i.e., for Eq. (A4), Yos and Wilke, the relative error is, respectively, 8.6%, 10.3%, and 12.9%.

In Fig. 2 the evolution of the thermal conductivity is represented as a function of temperature: It is computed with Wilke [14] and Eq. (A4) for a mixture of 65.2% H_2 . Like for the shear viscosity the relative difference between these formulas is quasiconstant and about 4%.

B. Transport terms for a N_2 - O_2 mixture

As in the previous case, the computation of the transport coefficients requires a modeling of the collision integrals. For this mixture, the Aubreton [29] modeling is chosen, at the level of the first Mason and Monchick approximation (quasifrozen approximation). The collision integrals for the pairs O_2 - O_2 , N_2 - N_2 , and O_2 - N_2 are then also expressed in terms of relations depending on the translation-rotation temperature. Thus the determination of the transport terms is possible, since the collision integrals and, consequently, the macroscopic quantities, are computable. The mixture percentage is that of simplified air: 21% of oxygen and 79% of nitrogen.

TABLE II. Thermal conductivity in a N_2 - H_2 mixture (10^5 W/m K) at 273.16 K.

H_2 (mol %)	(A4)	Yos [13]	Wilke [12]	Expt. [5]
0	2 407	2 407	2 228	2 301
15.9	3 476	3 501	3 518	3 347
39.0	5 488	5 564	5 794	5 314
65.2	8 817	8 954	9 170	8 117
79.5	11 412	11 558	11 499	10 544
80.3	11 580	11 725	11 640	10 753
100	16 849	16 849	15 553	16 903

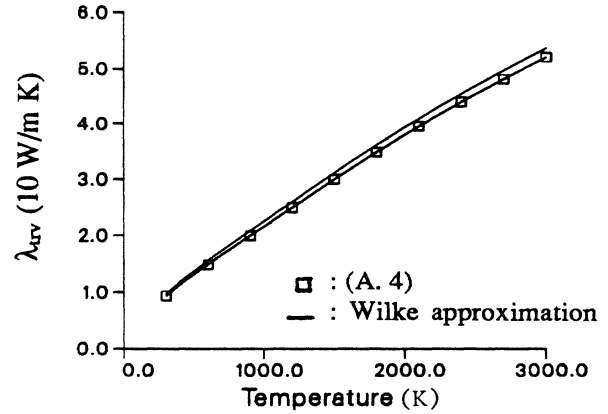


FIG. 2. Thermal conductivity in a N_2 - H_2 mixture: $x_{H_2} = 0.652$.

1. Shear viscosity $\mu(\mu_{N_2}, \mu_{O_2}, \mu'_{N_2 O_2}, D_{N_2 O_2})$

In Table III, the different shear viscosity calculations are compared. In the first two columns the shear viscosity determined with (A1) and Wilke [12] equations are given. In the last two columns, experimental results given in Refs. [30,31] are presented as well as results coming from an “exact” computation [29].

The difference between the Wilke approximation and present results (A1) for this binary air mixture, for which the properties of the two components, O_2 and N_2 , are very close, is much weaker than that noted for the mixture N_2 - H_2 . In the given temperature range and for a nonionized binary gas mixture, in which the molecular masses of the two components are close to each other, the Wilke approximation is in very good agreement with the experimental data. The greatest difference with the experimental values is for $T = 1300$ K, where one finds 3.3% and 2.5%, respectively, for Eq. (A1) and the Wilke equation. Furthermore, the relative error, compared to the “exact” calculations, is below 1% for Eq. (A1) and about 1.5% for the Wilke approximation.

2. Bulk viscosity $\eta(\tau_{r_{O_2}}, \tau_{r_{N_2}}, \tau_{r_{O_2 N_2}})$

The computation of the bulk viscosity requires the knowledge of the rotational relaxation times $\tau_{r_{O_2}}$, $\tau_{r_{N_2}}$, and $\tau_{r_{O_2 N_2}}$. Using a classical theory, Parker [8] gives a relation for a rotational collisional number Z_r , defined as

TABLE III. Shear viscosity in a N_2 - O_2 mixture (10^5 kg/m s).

T (K)	(A1)	Wilke [12]	Expt. [30,31]	Aubreton [29]
300	1.834	1.826	1.846	1.843
500	2.692	2.667	2.701	2.704
1000	4.320	4.284	4.244	4.343
1300	5.127	5.088	4.960	5.158
2000	6.793	6.755	6.900	6.840

$$Z_r = \frac{\tau_r}{\tau},$$

where τ is the elastic collision time for a rigid sphere model.

Following the authors of Refs. [20,32], the bulk viscosity for a pure gas may be expressed under the form

$$\eta = \frac{\pi\mu}{25}\tau_r.$$

But only the bulk viscosity of a pure gas may be determined by this formula [8] and its evolution for nitrogen and oxygen is presented in Fig. 3. In Figs. 4 and 5, a comparison between the bulk and shear viscosities is also presented. It is expected that the evolution of the mixture N_2 - O_2 will not be very different.

Like the shear viscosity, the bulk viscosity increases with temperature. The values of the bulk viscosity in pure gases of oxygen or nitrogen are almost equal. In the vicinity of 2500 K, oxygen has a bulk viscosity slightly greater than this of nitrogen. However, above this temperature, the results are no more significant since a non-negligible dissociation of oxygen begins for $T > 2000$ K.

From the comparison between bulk and shear viscosities of the same gas, as represented in Figs. 4 and 5, it may be seen that for $T < 1500$ K for N_2 and $T < 2100$ K for O_2 , the bulk viscosity is smaller than the shear viscosity; but, it is the contrary beyond these temperatures. It is also noted that η and μ are of the same order of magnitude, so that the Stokes approximation, which consists of neglecting the bulk viscosity, is acceptable mainly because the associated gradients are generally weaker for this viscosity.

3. Thermal conductivity

$$\lambda(\mu_{N_2}, \mu_{O_2}, \mu'_{N_2O_2}, D_{N_2O_2}, D_{N_2N_2}, D_{O_2O_2}, B_{N_2O_2}^*)$$

Like for the shear viscosity, the macroscopic quantities appearing in the expression of the translational thermal conductivity are determined with collision integrals coming from the Aubretton analysis [29]. Thus, in Table IV, the values of the translation-rotation-vibration thermal conductivity calculated for the translational thermal con-

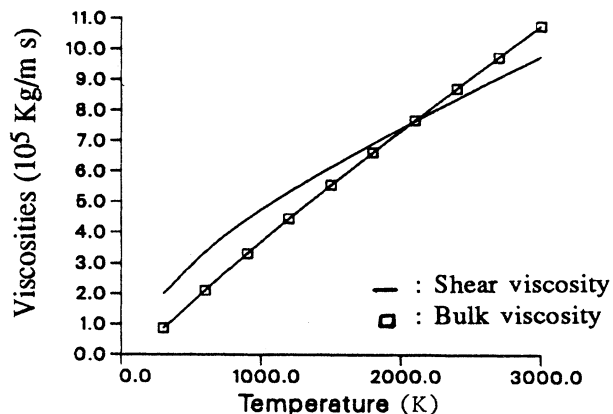


FIG. 4. Viscosities for pure oxygen.

ductivity on one hand with Eq. (A4) and on the other hand with the Wilke [12] approximation are listed. Since the rotational and vibrational thermal conductivities are computed, in both cases, with the same formulas, the difference between the two results is obviously due only to the way in which the translation thermal conductivity is computed, as previously remarked in the case of the N_2 - H_2 mixture (V A 2).

Contrary to the previous mixture N_2 - H_2 , the translational thermal conductivity computation with the Yos [13] approximation is not presented here since the numerical values for the thermal conductivity are equal to those determined by the theoretical equation (A4) (relative error below 1%). The Wilke approximation, including the Eucken correction is sometimes closer to "experimental" values [30,31] and sometimes farther than the present results, determined with Eq. (A4), which, in turn, are very close to the values given by the "exact" treatment [29]. One notices a jump of 7% of the relative error, for both relations, at $T=2000$ K: This is due to the fact that, in the present calculations, the reaction conductivity has not been considered, since the mixture composition remains constant (frozen chemistry).

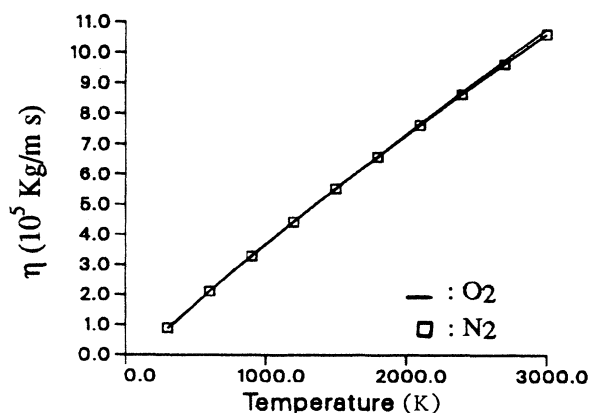


FIG. 3. Bulk viscosity.

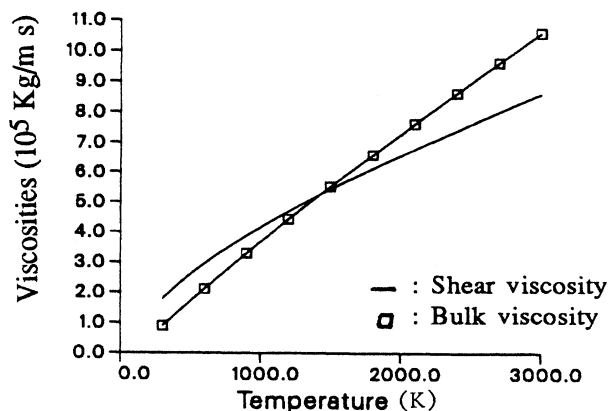


FIG. 5. Viscosities for pure nitrogen.

TABLE IV. Thermal conductivity in a N₂-O₂ mixture (10² W/m K).

T (K)	(A4)	Wilke [12]	Refs. [30,31]	Aubreton [29]
300	2.69	2.47	2.63	2.62
500	4.04	3.70	4.04	3.99
700	5.33	4.89	5.23	5.25
1000	7.15	6.59	6.81	7.01
1300	8.83	8.14	8.32	8.72
1600	1.04	9.57	1.06	1.05
2000	1.23	1.13	1.37	1.32

4. Vibrational thermal conductivity

$$\lambda_{v_{N_2}}(D_{N_2O_2}, D_{N_2N_2}), \lambda_{v_{O_2}}(D_{N_2O_2}, D_{O_2O_2})$$

Numerical values of the vibrational thermal conductivity of O₂ and N₂ have been computed for the same mixture O₂-N₂. The results for $\lambda_{v_{T_{v_{O_2}}}}$ and $\lambda_{v_{T_{v_{N_2}}}}$ are represented in Figs. 6 and 7 as functions of T , $T_{v_{O_2}}$, and $T_{v_{N_2}}$. The dotted curves correspond to the equilibrium vibrational thermal conductivity, $T = T_{v_{O_2}}$ (or $T_{v_{N_2}}$).

From this figure, it may be seen that the equilibrium vibrational conductivity values are different from the values of λ_v in nonequilibrium flows, both in expansion flows, where $T < T_{v_{O_2}}, T_{v_{N_2}}$, as well as behind shocks, where $T > T_{v_{O_2}}, T_{v_{N_2}}$. Thus, the fact of not taking into account the nonequilibrium may lead to large errors in the determination of $\lambda_{v_{T_{v_{O_2}}}}$ and $\lambda_{v_{T_{v_{N_2}}}}$ and consequently

on the values of the vibrational heat flux. The vibrational thermal conductivity (A8) determined by the matching method, has been also computed behind a shock wave at a Mach number 8, for which the dissociation processes are negligible, but the vibrational relaxation is important for O₂ and N₂.

Results obtained for vibrational relaxation times have been taken from Ref. [26]. A careful observation of the

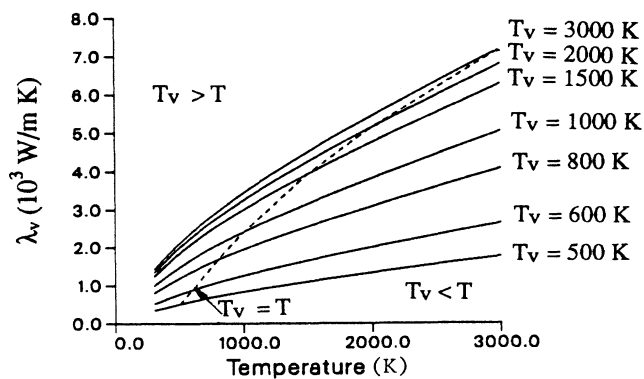


FIG. 6. Vibrational thermal conductivity for oxygen in air mixture.

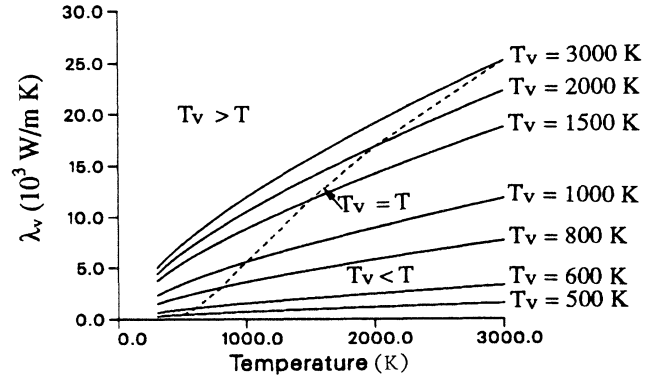


FIG. 7. Vibrational thermal conductivity for nitrogen in air mixture.

λ_v results, calculated with (A6) derived from the SNE method and with (A8) derived from the matching method, show that the difference between these two calculations is not very significant, except just behind the shock where $T_v \ll T$. In this zone, where the nonequilibrium is very strong, the Mason and Monchick approximations are invalid, due to the important effect of vibrational exchanges.

Now, from a practical point of view, it is interesting to analyze the transport properties through the nondimensional numbers, that is, the frozen Prandtl number of the mixture Pr_f , which appears in the energy equation and which may be written

$$Pr_f = \frac{\mu C_{p_f}}{\lambda_f},$$

where

$$C_{p_f} = C_{p_{tr}};$$

the frozen specific heat at constant pressure, and

$$\lambda_f = \lambda_t + \lambda_r = \lambda_{tr}.$$

The Prandtl number evolution is represented in Fig. 8, where the solid line represents the Wilke [12] expressions

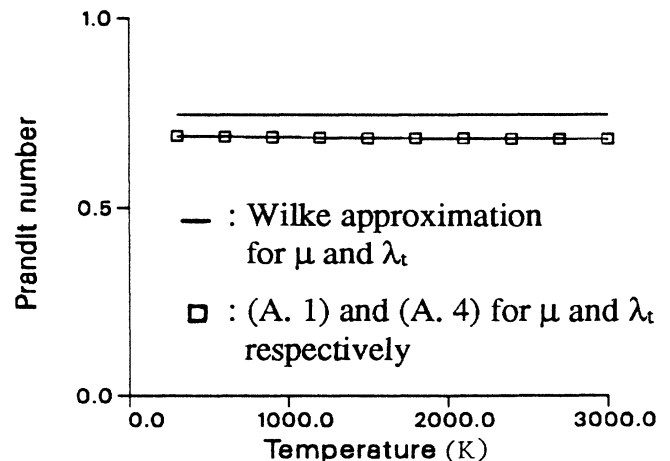


FIG. 8. Prandtl number (air).

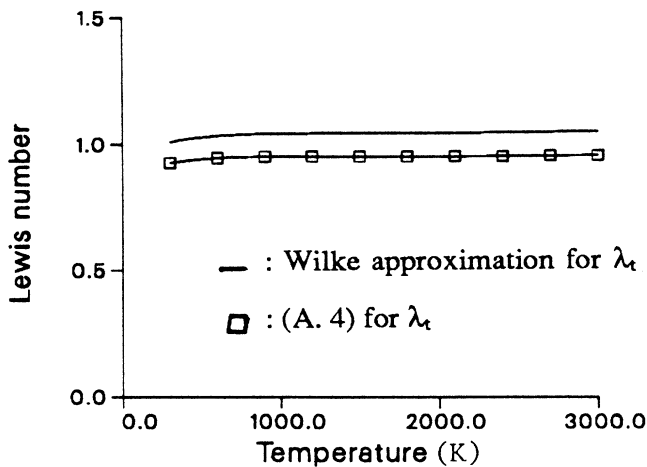


FIG. 9. Lewis number (air).

for the viscosity and translational thermal conductivity. The square-dotted line represents the result of calculation using formulas (A1) and (A4), respectively, for μ and λ_t .

For this mixture, $0.69 \leq Pr_f \leq 0.75$. The Wilke approximation for μ and λ_t leads to greater values for the Prandtl number. In both cases, Pr_f is quasi-independent of the translation-rotation temperature. The frozen Lewis number Le_f appearing in the energy equation may be written

$$Le_f = \frac{\rho D_{pq} C_{p_f}}{\lambda_f}.$$

Taking for λ_t the Wilke approximation (solid line) and Eq. (A4) (square-dotted line), it may be seen in Fig. 9, which plots the Lewis number evolution, that Le_f increases slightly with the translation-rotation temperature. Thus the conduction effects become less important than diffusive effects. The usual approximation $Le_f = 1$ is more justified in the case when the Wilke approximation for the calculation of λ_t is used.

The vibrational number F_p appears in the nondimensional vibrational relaxation equation (3.32). The ratio

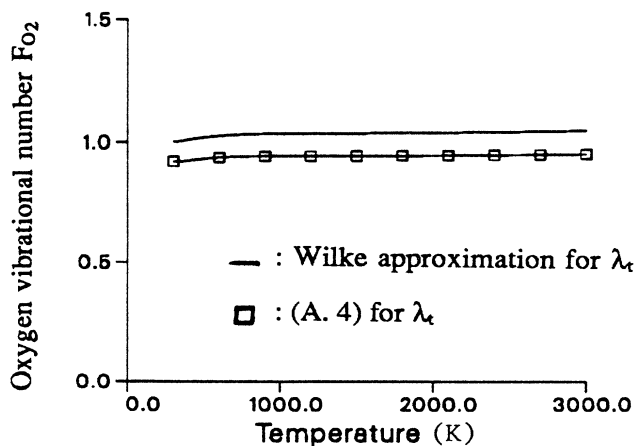


FIG. 10. Vibrational number for oxygen in air mixture.

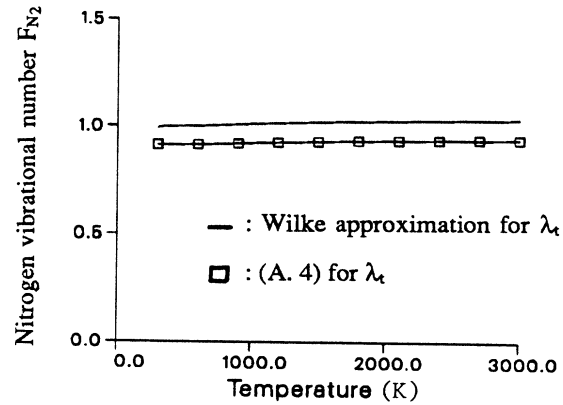


FIG. 11. Vibrational number for nitrogen in air mixture.

between this number and the Lewis number, as previously defined, may be related, always in the framework of the Mason and Monchick approximations (particularly $D_v = D$), to a vibrational Lewis number. Thus F_p may be written

$$F_p = \frac{Le_f}{Le_{v_p}} = \frac{\rho \lambda_{v_p} C_{p_f}}{\rho_p C_{v_p}(T_{v_p}) \lambda_f},$$

where ρ is the density. The vibrational number evolution is represented in Figs. 10 and 11. The solid line represents F_p values calculated with the Wilke approximation for λ_t , while the square-dotted line represents F_p values computed using Eq. (A4). For nitrogen, in both cases, this number increases slightly: $0.99 \leq F_p \leq 1.04$ when the Wilke approximation is used for the determination of λ_t , and $0.83 \leq F_p \leq 0.96$ when Eq. (A4) is used. For oxygen, the same remarks may be made: $1 \leq F_p \leq 1.05$ when the Wilke approximation is used for the determination of λ_t , and $0.92 \leq F_p \leq 0.95$ when Eq. (A4) is used. These computations show therefore, that the use of approximate formulas for the shear viscosity and translational thermal conductivity may lead to differences on the numerical values of these terms (about 10%).

VI. CONCLUSIONS

The generalized Chapman-Enskog method for the analysis of vibrational nonequilibrium regimes of gas mixtures allows us to derive expressions for the transport coefficients: shear viscosity, bulk viscosity, and thermal conductivity, for the translational, rotational, and vibrational modes. The inclusion of vibration-vibration resonant collisions in type-I collisions (the most probable) leads to nonequilibrium appearing at the zeroth order. Thus at the first order the nonequilibrium is stronger (SNE method), by opposition to the classical method (WNE) in which the zeroth order corresponds to equilibrium. All transport coefficients deduced from this method are expressed in the Appendix, and it is clear that the vibrational thermal conductivity is the most affected by the vibrational nonequilibrium.

Such a method (SNE) cannot describe a flow passing

from a strong to a weak state of nonequilibrium or vice versa; therefore, as has been developed for pure gases, a matching method, valid whatever the degree of nonequilibrium, is presented. Starting from the works of Alexeev [24] and Kogan [25], it may be shown that the addition of first-order vibration-vibration and translation-vibration collision terms allows this matching. The transport coefficients are then functions of all collisions of types I and II. The Mason and Monchick assumptions, used also in the previous SNE method, and the model of harmonic oscillator, enable one to obtain explicit expressions for the transport coefficients, as functions of macroscopic quantities. However, compared to the SNE case, only the expression of λ_v depends strongly on the vibrational relaxation. Thus, from a theoretical point of view, this analysis is an extension of the kinetic theory to the vibrational nonequilibrium for diatomic gas mixtures. From a practical point of view, the following observations may be made:

(i) *The shear viscosity* (A1) weakly influenced by the vibrational nonequilibrium is expressed as a combination of pure gas shear viscosities μ_p and μ_q , binary diffusion coefficient D_{pq} , and fictitious viscosity μ'_{pq} , characterizing the momentum transfer between both species.

(ii) *The bulk viscosity* is proportional to the relaxation time of the internal mode which is in equilibrium at the zeroth order. For the present case, this is the rotational mode and, therefore, η is expressed as a function of the rotational relaxation times τ_r , τ_{r_p} , and $\tau_{r_{pq}}$.

(iii) *The translational thermal conductivity* expression is quite complex. Like the shear viscosity, λ_t is expressed as a function of pure gas shear viscosities μ_p and μ_q , binary diffusion coefficient D_{pq} , fictitious viscosity μ'_{pq} , and a nondimensional number B_{pq}^* .

(iv) *The rotational thermal conductivity* expression is

identical to the first approximation of Mason and Monchick, i.e., it is a function of the binary diffusion D_{pq} and self-diffusion D_{pp} and D_{qq} coefficients.

(v) *The vibrational thermal conductivity* is expressed by the SNE method as a function of the binary diffusion D_{pq} and self-diffusion D_{pp} and D_{qq} coefficients. By the matching method the vibrational nonequilibrium appears explicitly, through the vibrational relaxation times τ_{pp}^{VT} , τ_{pq}^{VT} , and τ_{pq}^{VV} .

Finally, transport coefficients have been computed in the temperature range for which the validity of the present calculations may be assumed. As in the recent Makita's work [33], this computation has shown the lacunas concerning the property data of binary mixtures. In the present case good modelings for the collision integrals and for the internal relaxation times appear necessary for the transport terms computation. The values obtained are consistent and seem to give correct results. One finds also that the approximate formulas like those of Wilke and Yos for the shear viscosity and translational thermal conductivity, in spite of severe approximations, give correct results, particularly in the case when the mixture components properties are close. The study of the vibrational thermal conductivity has shown the limits of the Mason and Monchick approximations in the case of strong nonequilibrium situations.

For the future, two major directions of investigation are open: Extension of these transport coefficients to a multicomponent mixture; and inclusion of chemical reactions (and, especially, dissociation effects at high temperatures).

ACKNOWLEDGMENT

The Systèmes Energétiques et Transferts Thermiques is "Unité de recherche associée au CNRS No. 1168."

APPENDIX

The shear viscosity is given by

$$\mu = \mu_{pq} = \frac{x_p x_q \left\{ \frac{1}{\mu_p} + \frac{1}{\mu_q} \right\} + \frac{2}{nm_0} \frac{1}{D_{pq}} + \frac{2(x_p m_p - x_q m_q)^2}{m_0^2} \frac{1}{\mu'_{pq}}}{\frac{x_p x_q}{\mu_p \mu_q} + \frac{2}{nm_0} \frac{1}{D_{pq}} \left\{ \frac{x_p^2}{\mu_p} + \frac{x_q^2}{\mu_q} \right\} + \frac{2}{m_0^2} \frac{1}{\mu'_{pq}} \left\{ \frac{x_p^2 m_p^2}{\mu_p} + \frac{x_q^2 m_q^2}{\mu_q} \right\} + \frac{4x_p x_q}{nm_0} \frac{1}{D_{pq}} \frac{1}{\mu'_{pq}}}, \quad (\text{A1})$$

where μ'_{pq} is the fictitious viscosity. The bulk viscosity is

$$\eta = \eta_{pq} = \frac{C_r}{C_{tr}} nkT \frac{\frac{C_{r_p} C_{r_q}}{k} \left\{ \frac{x_q}{\tau_{r_p}} + \frac{x_p}{\tau_{r_q}} \right\} + (x_p C_{r_p} + x_q C_{r_q}) \frac{1}{\tau_{r_{pq}}}}{(C_t + x_p C_{r_p} + x_q C_{r_q}) \left\{ \frac{C_{r_p} C_{r_q}}{k^2} \frac{1}{\tau_{r_p} \tau_{r_q}} + x_p \frac{C_{r_p}}{k} \frac{1}{\tau_{r_p} \tau_{r_{pq}}} + x_q \frac{C_{r_q}}{k} \frac{1}{\tau_{r_q} \tau_{r_{pq}}} \right\}}. \quad (\text{A2})$$

The relaxation pressure is given in Eq. (A3).

$$P_R = P_{R_{pq}} = -n \frac{C_r}{C_{ir}} \frac{\frac{C_p C_{r_q}}{k} \left[\frac{S^0(\varepsilon_{jv_q})}{\tau_{r_p}} + \frac{S^0(\varepsilon_{iv_p})}{\tau_{r_q}} \right] + (x_p C_{r_p} + x_q C_{r_q}) \left[\frac{S^0(\varepsilon_{iv_p}) + S^0(\varepsilon_{jv_q})}{\tau_{r_{pq}}} \right]}{(C_i + x_p C_{r_p} + x_q C_{r_q}) \left[n \frac{C_p C_{r_q}}{k^2} \frac{1}{\tau_{r_p} \tau_{r_q}} \right] + [x_p C_i + x_p(x_p C_{r_p} + x_q C_{r_q})] \frac{C_{r_p}}{k} \frac{1}{\tau_{r_p} \tau_{r_{pq}}}} + [x_q C_i + x_q(x_p C_{r_p} + x_q C_{r_q})] \frac{C_{r_q}}{k} \frac{1}{\tau_{r_q} \tau_{r_{pq}}}. \quad (\text{A3})$$

The translational thermal conductivity is given in Eq. (A4).

$$\lambda_t = \lambda_{t_{pq}} = \frac{75}{4} k 5 x_p x_q \left[\frac{1}{m_p \mu_q} + \frac{1}{m_q \mu_p} \right] + \frac{20 m_p m_q}{m_0^3} (x_p - x_q)^2 \frac{1}{\mu'_{pq}} + 3 \frac{1}{n m_0^2} \frac{1}{D_{pq}} \left[2 x_p x_q \left(\frac{55}{4} - 3 B_{pq}^* \right) + \frac{m_p^2 x_p^2 Q_{qp}^* + m_q^2 x_q^2 Q_{pq}^*}{m_p m_q} \right] /$$

$$\frac{25 x_p x_q}{\mu_p \mu_q} + \frac{9}{n^2} \frac{m_p m_q}{m_0^4} [Q_{pq}^* Q_{qp}^* - \left(\frac{55}{4} - 3 B_{pq}^* \right)^2] \frac{x_p x_q}{D_{pq}^2} + \frac{100 m_p m_q}{m_0^3 \mu'_{pq}} \left[\frac{m_p x_p^2}{\mu_p} + \frac{m_q x_q^2}{\mu_q} \right]$$

$$+ \frac{15}{n} \left[\frac{x_p^2}{m_q} \left[\frac{m_p}{m_0} \right]^2 \frac{Q_{qp}^*}{\mu_p} + \frac{x_q^2}{m_p} \left[\frac{m_q}{m_0} \right]^2 \frac{Q_{pq}^*}{\mu_q} + \frac{4 m_p m_q}{m_0^5} [m_p^2 Q_{qp}^* + m_q^2 Q_{pq}^* - 2 m_p m_q \left(\frac{55}{4} - 3 B_{pq}^* \right)] \frac{x_p x_q}{\mu'_{pq}} \right] \frac{1}{D_{pq}}, \quad (\text{A4})$$

where B_{pq}^* is a nondimensional parameter [22]

$$m_0 = m_p + m_q$$

and

$$Q_{pq}^* = \frac{5}{4} \left[6 \left[\frac{m_p}{m_q} \right]^2 + 5 \right] - 3 B_{pq}^*,$$

$$Q_{qp}^* = \frac{5}{4} \left[6 \left[\frac{m_q}{m_p} \right]^2 + 5 \right] - 3 B_{pq}^*.$$

The rotational thermal conductivity is

$$\lambda_r = \lambda_{r_{pq}} = \frac{n x_p C_{r_p}}{\frac{x_p}{D_{pp}} + \frac{x_q}{D_{pq}}} + \frac{n x_q C_{r_q}}{\frac{x_q}{D_{qq}} + \frac{x_p}{D_{pq}}}. \quad (\text{A5})$$

The vibrational thermal conductivity is

$$\lambda_{v_p} = \frac{n_p C_{v_p}(T_{v_p})}{\frac{x_p}{D_{pp}} + \frac{x_q}{D_{pq}}}, \quad (\text{A6})$$

$$\lambda_{v_q} = \frac{n_q C_{v_q}(T_{v_q})}{\frac{x_q}{D_{qq}} + \frac{x_p}{D_{pq}}}. \quad (\text{A7})$$

The vibrational thermal conductivity (matching method) is

$$\lambda_{v_{T_{v_p}}} = \frac{n D_{pp} C_{v_p}(T_{v_p})}{1 + \frac{x_q}{x_p} \frac{D_{pp}}{D_{pq}} + \frac{1}{2} \left[\frac{m_p}{kT} \right] \frac{Q_p}{Q_{v_p}} K_{1_p} \frac{D_{pp}}{\tau_{pp}^{VT}} + \frac{x_q}{x_p} \left[\frac{m_p}{kT} \right] \left[\frac{m_p}{m_0} \right] \frac{Q_p}{Q_{v_p}} K_{1_p} \frac{D_{pp}}{\tau_{pq}^{VT}}} + \frac{x_q}{x_p} \left[\frac{m_p}{kT} \right] \left[\frac{m_p}{m_0} \right] \frac{Q_{v_q}}{Q_{v_p}} K_2 \frac{D_{pp}}{\tau_{pq}^{VT}}, \quad (\text{A8})$$

with

$$K_{1_p} = \frac{1}{2} \left[1 + \exp \left\{ -\frac{\Theta_{v_p}}{T} \left[1 - \frac{T}{T_{v_p}} \right] \right\} \right],$$

$$K_2 = \frac{1}{2} \left[1 + \exp \left\{ -\frac{\Theta_{v_p}}{T} \left[1 - \frac{T}{T_{v_p}} \right] \right\} \exp \left\{ \frac{\Theta_{v_q}}{T} \left[1 - \frac{T}{T_{v_q}} \right] \right\} \right],$$

$$Q_p = \frac{1}{1 - \exp \left\{ -\frac{h\nu_p}{kT} \right\}}, \quad Q_{v_p} = \frac{1}{1 - \exp \left\{ -\frac{h\nu_p}{kT_{v_p}} \right\}}, \quad Q_{v_q} = \frac{1}{1 - \exp \left\{ -\frac{h\nu_q}{kT_{v_q}} \right\}}.$$

-
- [1] M. N. Kogan, *Rarefied Gas Dynamics* (Plenum, New York, 1969).
- [2] R. M. Velasco and F. G. Uribe, *Physica A* **134**, 339 (1986).
- [3] E. P. Gross and E. A. Jackson, *Phys. Fluids* **2**, 4 (1959).
- [4] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Cambridge, England, 1970).
- [5] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1959).
- [6] J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases* (North-Holland, New York, 1972).
- [7] C. S. Wang Chang and G. E. Uhlenbeck, University of Michigan, Engineering Research Report No. CM 681 (1951).
- [8] E. A. Mason and L. Monchick, *J. Chem. Phys.* **36**, 6 (1962).
- [9] F. G. Hanson and T. F. Morse, *Phys. Fluids* **10**, 345 (1967).
- [10] P. C. Philippi and R. Brun, *Physica A* **105**, 147 (1981).
- [11] R. Brun and B. Zappoli, *Phys. Fluids* **20**, 9 (1977).
- [12] C. R. Wilke, *J. Chem. Phys.* **18**, 4 (1949).
- [13] J. M. Yos, Technical Memorandum, Avco Research and Advanced Development Division, Wilmington (1963) (unpublished).
- [14] G. V. Candler, Ph.D. thesis, Stanford University, 1988.
- [15] C. Cercignani, *Mathematical Methods in Kinetic Theory* (MacMillan, London, 1975).
- [16] C. Muckenfuss and C. F. Curtiss, *J. Chem. Phys.* **29**, 6 (1958).
- [17] D. Omeiri, Thèse 3ème cycle, Université de Provence, Marseille, 1984.
- [18] R. Brun, American Institute of Aeronautics and Astronautics, Washington, Paper No. 88, 2655, San Antonio (1988).
- [19] R. Brun and A. Chikhaoui, *Rarefied Gas Dynamics*, edited by R. Campagne (Commissariat à l'Energie Atomique, Paris, 1979).
- [20] L. Monchick, K. S. Yun, and E. A. Mason, *J. Chem. Phys.* **39**, 3 (1963).
- [21] B. F. Armaly and K. Sutton, American Institute of Aeronautics and Astronautics, Washington, Paper No. 81, 1965 (1980).
- [22] L. Monchick, A. N. G. Pereira, and E. A. Mason, *J. Chem. Phys.* **42**, 9 (1965).
- [23] R. Brun, M. P. Villa, and J. G. Meolans, *Rarefied Gas Dynamics*, edited by H. Oguchi (University of Tokyo Press, Tokyo, 1986).
- [24] B. V. Alexeev, *Theor. Exp. Chem. (USSR)* **5**, 4 (1969).
- [25] M. N. Kogan, V. S. Galkin, and M. F. Makashev, *Rarefied Gas Dynamics*, edited by R. Campagne (Commissariat à l'Energie Atomique, Paris, 1979).
- [26] Y. V. Stupochenko, S. A. Losev, and A. I. Osipov, *Relaxation in Shock Waves* (Springer Verlag, Berlin, 1967).
- [27] P. D. Neufeld, A. R. Janzen, and A. R. Aziz, *J. Chem. Phys.* **57**, 3 (1972).
- [28] J. D. Lambert, *Vibrational and Rotational Relaxation in Gases* (Clarendon, Oxford, 1977).
- [29] J. Aubreton (private communication).
- [30] *Encyclopédie des Gaz—L'Air Liquide*, Division Scientifique (Elsevier, New York, 1976).
- [31] N. B. Vargaftik, *Handbook of Physical Properties of Liquids and Gases—Pure Substances and Mixtures*, 2nd ed. (Hemisphere, New York, 1975).
- [32] K. Herzfeld and T. A. Litovitz, *Absorption and Dispersion of Ultrasonics Waves* (Academic, New York, 1969).
- [33] T. Makita, *Int. J. Thermophys.* **10**, 3 (1989).