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Thermal conduction and thermal diffusion in dilute polyatomic gas mixtures

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Abstract

A novel theoretical basis for the evaluation of the thermal conductivity and the thermal diffusion ratios of dilute polyatomic gas mixtures is derived within the semi-classical isotropic kinetic theory. New expressions for species diffusion coefficients, thermal diffusion coefficients, and thermal diffusion ratios are also obtained by using an expansion vector based upon the total energy of the molecules. Finally, practical and accurate expressions for the thermal conductivity and the thermal diffusion ratios are derived by using the recent theory of iterative transport algorithms, as developed by the authors. The resulting expressions can be used in either theoretical calculations or computational models of multicomponent flows.

1. Introduction

Fundamental scientific interest as well as a wide range of practical applications have motivated extensive interest in the study of transport properties in dilute polyatomic gas mixtures. The purpose of this paper is to provide a new theoretical basis and also practical expressions for the evaluation of two transport coefficients in dilute polyatomic gas mixtures: the thermal conductivity and the thermal diffusion ratios. As discussed later, these two coefficients arise in the kinetic theory expression of the species diffusion velocities and the heat flux vector.

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In this paper transport properties of dilute polyatomic gases are treated semi-classically [1] rather than quantum mechanically [2]. Indeed we will not consider the effects of applied magnetic or electric fields on transport properties, e.g., polarization of angular momentum, for which a quantum mechanical theory is needed. Furthermore, the quantum mechanical theory yields the same formal results as the semi-classical approach for the isotropic approximation valid in the absence of polarization effects [2–4]. We consider here the semi-classical theory as extended to dilute polyatomic gas mixtures in [5]. The corresponding Boltzmann equation preaverages the cross-sections over all the magnetic quantum numbers and can be derived from the Waldmann-Snyder [6,7] quantum mechanical Boltzmann equation. This form of the Boltzmann equation is also equivalent to the Wang Chang and Uhlenbeck type equation considered in [8].

In the next section we introduce some useful notation and briefly restate some classical kinetic theory results. We then derive, for the first time, a variational framework for evaluating the thermal conductivity and the thermal diffusion ratios directly. This allows the derivation of linear systems with which to evaluate these transport coefficients without cumbersome algebraic manipulations. Furthermore, we introduce new expressions for the species diffusion coefficients, the thermal diffusion coefficients, and the thermal diffusion ratios by generalizing the total-energy approach derived in [9,10] for the thermal conductivity of pure gases and in [11] for the partial thermal conductivity of binary mixtures. When some species concentrations become arbitrarily small, it is worthwhile to note that artificial singularities arise in the linear systems presented in Section 2. These numerical difficulties can be overcome by introducing rescaled linear systems [12] and will not be discussed further in this paper. Finally, in Section 3 we apply the general theory of iterative transport algorithms [12] to the evaluation of the thermal conductivity and the thermal diffusion ratios. Iterative methods provide indeed a particularly cost-effective approach to obtain accurate approximate solutions to the linear systems described in Section 2. Practical expressions for the thermal conductivity and the thermal diffusion ratios are then obtained by truncation. These expressions can be used at a low computational cost in numerical models of multicomponent flows such as flames [25–27] or chemical vapor deposition reactors. Numerical simulation of these flows indeed requires the evaluation of transport properties at each computational cell in space and time, since temperature, pressure and concentration distributions are generally not uniform. These simplified expressions are also directly related to the linear system coefficients written in terms of collision integrals.

2. Theory

2.1. Preliminaries

We consider a multicomponent gas mixture with n species and we denote by $\mathcal{S} = [1, n]$ the set of species indices. For a family of functions ξ_k , $k \in \mathcal{S}$, where $\xi_k = \xi_k(c_k, \kappa)$ depends on the particle velocity c_k and the κ^{th} energy state $E_{k\kappa}$, we introduce

the compact notation $\xi = (\xi_k)_{k \in \mathcal{S}}$. Denoting by \mathcal{E}_k the set of quantum energy shells of the k^{th} species, we then introduce the scalar product

$$\langle\langle \xi, \zeta \rangle\rangle = \sum_{\substack{k \in \mathcal{S} \\ \kappa \in \mathcal{E}_k}} \int (\xi_k \zeta_k) f_k^0 dc_k, \tag{1}$$

where f_k^0 is the Maxwellian equilibrium distribution function of the k^{th} species. Following [13], we next define the integral bracket operator $[\xi, \zeta] = \langle\langle \xi, \text{Im}(\zeta) \rangle\rangle$, where Im is the linearized Boltzmann collision operator.

In the Enskog-Chapman procedure, the species distribution functions are written as a linear perturbation of the equilibrium Maxwellian distribution functions [5,11,13]. In the first-order expansion, the species diffusion velocities may be expressed as

$$V_k = - \sum_{l \in \mathcal{S}} D_{kl} d_l - \theta_k \nabla \log T, \quad k \in \mathcal{S}, \tag{2}$$

and the heat flux vector as

$$q = \sum_{k \in \mathcal{S}} \rho h_k Y_k V_k - \lambda' \nabla T - \bar{p} \sum_{k \in \mathcal{S}} \theta_k d_k, \tag{3}$$

where d_k is diffusion driving force acting on the k^{th} species given by

$$d_k = \nabla X_k + (X_k - Y_k) \frac{\nabla \bar{p}}{\bar{p}} + \frac{\rho}{\bar{p}} \sum_{l \in \mathcal{S}} Y_k Y_l (b_l - b_k), \quad k \in \mathcal{S}, \tag{4}$$

and where X_k is the mole fraction of the k^{th} species, Y_k its mass fraction, \bar{p} the pressure, ρ the density, b_k the external force on the k^{th} species, T the temperature, and h_k the specific enthalpy of the k^{th} species. Furthermore, several transport coefficients arise in (2) and (3): the diffusion matrix $D = (D_{kl})_{k,l \in \mathcal{S}}$ formed by the species diffusion coefficients, the thermal diffusion vector $\theta = (\theta_k)_{k \in \mathcal{S}}$ formed by the thermal diffusion coefficients, and the partial thermal conductivity λ' . These transport coefficients can be written in the form [5,11,13]

$$\begin{cases} D_{kl} = \frac{\bar{p} k_b T}{3} [\phi^{D_k}, \phi^{D_l}], & k, l \in \mathcal{S}, \\ \theta_k = -\frac{1}{3} [\phi^{D_k}, \phi^{\lambda'}], & k \in \mathcal{S}, \\ \lambda' = \frac{1}{3 k_b T^2} [\phi^{\lambda'}, \phi^{\lambda'}]. \end{cases} \tag{5}$$

Here, k_b denotes the Boltzmann constant and we have also introduced $n + 1$ families of functions $\phi^\mu = (\phi_k^\mu)_{k \in \mathcal{S}}$, where μ stands for $D_l, l \in \mathcal{S}$, and λ' .

The auxiliary functions ϕ^μ are three-dimensional vector functions that are the solution of the following linearized Boltzmann equations

$$\begin{cases} \text{Im}(\phi^\mu) = \Psi^\mu, \\ \langle\langle \phi^\mu, \widehat{\psi}^k \rangle\rangle = 0, & k \in [1, n+4], \end{cases} \tag{6}$$

where $\hat{\psi}^k$ are the $n+4$ collisional invariants of the mixture. Furthermore, the right-hand sides in (6) have components given by [5]

$$\begin{cases} \Psi_k^{Dl} = (1/(X_k \bar{p})) (\delta_{kl} - Y_k) (c_k - v), & l \in \mathcal{S}, \\ \Psi_k^{\Lambda'} = k_B T (\frac{5}{2} - w_k \cdot w_k + \bar{\epsilon}_k - \epsilon_{kk}) (c_k - v), \end{cases} \quad (7)$$

where δ_{kl} is the Kronecker symbol and v the mass averaged flow velocity. The reduced velocity w_k , the reduced internal energy ϵ_{kk} , and the averaged reduced internal energy $\bar{\epsilon}_k$ of the k^{th} species are given by

$$w_k = \left(\frac{m_k}{2k_B T} \right)^{1/2} (c_k - v), \quad \epsilon_{kk} = \frac{E_{kk}}{k_B T}, \quad \bar{\epsilon}_k = \sum_{\kappa \in \mathcal{E}_k} a_{k\kappa} \epsilon_{k\kappa} \exp(-\epsilon_{k\kappa}) / Q_k, \quad (8)$$

where m_k is the mass of the molecules of the k^{th} species, $a_{k\kappa}$ the degeneracy of the κ^{th} quantum energy shell of the k^{th} species, and $Q_k = \sum_{\kappa \in \mathcal{E}_k} a_{k\kappa} \exp(-\epsilon_{k\kappa})$ the partition function.

2.2. Polynomial expansions

The linearized Boltzmann Eqs. (6) are solved approximately with a variational procedure using polynomial expansions [5]. More specifically, a finite dimensional functional space $\mathcal{A} = \text{span}\{ \xi^{rk}, (r, k) \in \mathcal{B} \}$ is first selected, where ξ^{rk} are orthogonal basis functions for the scalar product (1) and where \mathcal{B} is a set of basis function indices. The basis functions ξ^{rk} are generally chosen as simple linear combinations of the vector functions ϕ^{10cdk} defined by

$$\phi^{10cdk} = \left(S_{3/2}^c(w_k \cdot w_k) W_k^d(\epsilon_{kk}) w_k \delta_{kl} \right)_{l \in \mathcal{S}}, \quad (9)$$

where $S_{3/2}^c$ is the Laguerre and Sonine polynomial of order c with parameter $3/2$, and W_k^d the Wang Chang and Uhlenbeck polynomial of order d for the k^{th} species. The notation in (9) is similar to the one in [11], but the basis functions (9) are not normalized since it would lead to artificial notational complexities and introduce concentration dependent functions. In particular, the following vector basis functions will be used to expand the auxiliary functions ϕ^μ

$$\begin{cases} \phi^{1000k} = (w_k \delta_{kl})_{l \in \mathcal{S}}, & k \in \mathcal{S}, \\ \phi^{1010k} = \left((\frac{5}{2} - w_k \cdot w_k) w_k \delta_{kl} \right)_{l \in \mathcal{S}}, & k \in \mathcal{S}, \\ \phi^{1001k} = \left((\bar{\epsilon}_k - \epsilon_{kk}) w_k \delta_{kl} \right)_{l \in \mathcal{S}}, & k \in \mathcal{P}. \end{cases} \quad (10)$$

Here, \mathcal{P} denotes the set of species that have at least two different energy levels. This set is generally taken to be the set of polyatomic species, and we denote by p the number of such species in the mixture.

Since the basis functions ϕ^{10cdk} involve the polynomials W_k^d in the internal energy ϵ_{kk} of the molecules, all the internal modes of the molecules, e.g., rotation and vibration, are forced to have the same internal temperature [14]. However, it is possible to consider polynomials in the energies of the various internal modes, which leads to larger variational approximation spaces for the species perturbed distribution functions [14,15]. This would only complicate the final expressions for the transport coefficients, but the general theory that is presented would equally apply. In addition, considering polynomials in the internal energy of the molecules only may sometimes lead to a faster convergence of the orthogonal polynomial expansions of the perturbed distribution functions. In particular, it has been observed experimentally in [16] that, for iodine at room temperature, in the presence of a temperature gradient, the perturbed distribution function $\phi^{\lambda'}$ is linear in the total internal energy, but not in the different internal energy modes, i.e., rotation and vibration, for which the quadratic terms become significant in the orthogonal polynomial expansions.

Expanding the auxiliary functions ϕ^μ in terms of the basis functions ξ^{rk} yields linear systems in the form

$$\sum_{(s,l) \in \mathcal{B}} L_{kl}^{rs} \alpha_l^{s\mu} = \beta_k^{r\mu}, \quad (r, k) \in \mathcal{B}, \quad (11)$$

completed with the appropriate constraints, where

$$\begin{cases} L_{kl}^{rs} = \frac{2\sqrt{m_k m_l}}{3\bar{p}} [\xi^{rk}, \xi^{sl}], \\ \beta_k^{rD_l} = \frac{\sqrt{2m_k k_B T}}{3} \langle\langle \xi^{rk}, \Psi^{D_l} \rangle\rangle, \quad \beta_k^{r\lambda'} = \frac{\sqrt{2m_k}}{3\bar{p}\sqrt{k_B T}} \langle\langle \xi^{rk}, \Psi^{\lambda'} \rangle\rangle. \end{cases} \quad (12)$$

The scaling factors appearing in (12) have been chosen for convenience. Furthermore, since we use the same functional space to expand ϕ^{D_l} and $\phi^{\lambda'}$, the same matrix L is obtained in (11) for $\mu = D_l$ and $\mu = \lambda'$. Finally, it is straightforward to relate the cross-sections appearing in the elements of the matrix L to those defined in [11].

2.3. Evaluation of D , λ' , and θ

We now assume that the functions ϕ^{1000k} are in the functional space \mathcal{A} . This assumption is natural since the suppression of these functions in the polynomial expansions of $\phi^{\lambda'}$ would yield $\theta = 0$. The set $\{00\} \times \mathcal{S}$ is then included in the indexing set \mathcal{B} . Hence, we obtain the following partitioning

$$\mathcal{B} = \{00\} \times \mathcal{S} \cup \mathcal{B}^\lambda, \quad (13)$$

and we denote by ω and $\omega^\lambda = \omega - n$ the number of elements of \mathcal{B} and \mathcal{B}^λ , respectively.

One may then easily verify that the partitioning (13) yields the following block structure for the linear system (11)

$$\begin{bmatrix} L^{0000} & L^{00\lambda} \\ L^{\lambda 00} & L^{\lambda\lambda} \end{bmatrix} \begin{bmatrix} \alpha^{00\mu} \\ \alpha^{\lambda\mu} \end{bmatrix} = \begin{bmatrix} \beta^{00\mu} \\ \beta^{\lambda\mu} \end{bmatrix}. \quad (14)$$

Here, L^{0000} is a $n \times n$ matrix, $L^{00\lambda}$ is a $n \times \omega^\lambda$ matrix, $L^{\lambda 00}$ is a $\omega^\lambda \times n$ matrix, and $L^{\lambda\lambda}$ is a $\omega^\lambda \times \omega^\lambda$ matrix. Similarly, $\alpha^{00\mu}$ and $\beta^{00\mu}$ are n vectors and $\alpha^{\lambda\mu}$ and $\beta^{\lambda\mu}$ are ω^λ vectors. The linear system (14) must be completed by the constraint

$$\sum_{k \in S} Y_k \alpha_k^{00\mu} = 0. \tag{15}$$

Furthermore, one can show [12] that the matrix L is symmetric positive semi-definite, and that the submatrix $L^{\lambda\lambda}$ is symmetric positive definite. In addition, the kernel of the matrix L is spanned by the vector $U = (U^{00}, U^\lambda)$ such that $U_k^{00} = 1, k \in S$, and $U^\lambda = 0$, and the vectors β^μ are in the range of the matrix L since $\sum_{k \in S} \beta_k^{00\mu} = 0$, for $\mu = D_l$ and $\mu = \lambda'$. As a consequence, the constrained singular system (14) and (15) is well posed and admits, therefore, a unique solution.

Finally, the diffusion matrix, the thermal diffusion vector, and the partial thermal conductivity are given by

$$D_{kl} = \alpha_k^{00D_l} = \alpha_l^{00D_k}, \quad \theta_k = -\alpha_k^{00\lambda'}, \quad \lambda' = \frac{\bar{p}}{T} \sum_{(r,k) \in B} \alpha_k^{r\lambda'} \beta_k^{r\lambda'}. \tag{16}$$

2.4. The thermal conductivity and the thermal diffusion ratios

The partial thermal conductivity coefficient λ' , appearing in the expression for the heat flux vector (3), is not accessible to direct experimental measurement. Indeed, in a mixture of gases, a temperature gradient induces thermal diffusion and thus concentration gradients, so that the term $\sum_{k \in S} \theta_k d_k$ is nonzero. It may then be convenient to introduce the thermal diffusion ratios $\chi = (\chi_k)_{k \in S}$ defined by the relations [5,17]

$$\begin{cases} D\chi = \theta, \\ \sum_{k \in S} \chi_k = 0. \end{cases} \tag{17}$$

The above system is well posed and, therefore, defines uniquely the thermal diffusion ratios [12,13]. Defining next the thermal conductivity λ as [5]

$$\lambda = \lambda' - (\bar{p}/T) \sum_{k \in S} \theta_k \chi_k, \tag{18}$$

the species diffusion velocities and the heat flux vector may be expressed as

$$V_k = - \sum_{l \in S} D_{kl} (d_l + \chi_l \nabla \log T), \quad k \in S, \tag{19}$$

$$q = \sum_{k \in S} \rho h_k Y_k V_k - \lambda \nabla T + \bar{p} \sum_{k \in S} \chi_k V_k. \tag{20}$$

The thermal conductivity coefficient λ is accessible to direct experimental measurement. Indeed, in a gas mixture with an external temperature gradient, the species diffusion velocities vanish at equilibrium so that the relation $q = -\lambda \nabla T$ is then recovered.

The thermal conductivity and the thermal diffusion ratios can be expressed in terms of the solution of a linear system which is simply a subsystem of (14). Indeed, denote $A = L^{\lambda\lambda}$ and $\beta^\lambda = \beta^{\lambda\lambda}$. Keeping in mind that the matrix A is symmetric positive definite, the linear system

$$A\alpha^\lambda = \beta^\lambda, \quad (21)$$

admits a unique solution α^λ . Moreover, after some algebra, one can deduce from (17) and (18) that the thermal conductivity and the thermal diffusion ratios are given by

$$\lambda = \frac{\bar{p}}{T} \sum_{(r,k) \in \mathcal{B}^\lambda} \alpha_k^{r\lambda} \beta_k^{r\lambda}, \quad (22)$$

$$\chi = L^{00\lambda} \alpha^\lambda. \quad (23)$$

Expression (22) for the thermal conductivity has been derived in [18] also. On the other hand, the expression (23) for the thermal diffusion ratios generalizes the one given in [13], which is a first-order approximation valid for monatomic mixtures.

2.5. New definition of the thermal conductivity and the thermal diffusion ratios

We now show, for the first time, that the thermal conductivity and the thermal diffusion ratios can also be defined within the variational procedure described in Section 2.2. We first note that it is possible to express these transport coefficients in terms of bracket products. Indeed, let ϕ^λ and Ψ^λ be given by

$$\begin{cases} \phi^\lambda = \phi^{\lambda'} + \bar{p} k_B T \sum_{l \in \mathcal{S}} \chi_l \phi^{D_l}, \\ \Psi^\lambda = \Psi^{\lambda'} + \bar{p} k_B T \sum_{l \in \mathcal{S}} \chi_l \Psi^{D_l}. \end{cases} \quad (24)$$

By linearity, ϕ^λ then satisfies the linearized Boltzmann Eq. (6) for $\mu = \lambda$. Furthermore, the function ϕ^λ has necessarily to be orthogonal to the basis functions ϕ^{1000l} , $l \in \mathcal{S}$. Indeed, making use of (5), (17), and (18), we first have the relations $[\phi^{D_l}, \phi^\lambda] = 0$ which imply that $\langle \Psi^{D_l}, \phi^\lambda \rangle = 0$ for $l \in \mathcal{S}$. On the other hand, it is straightforward to check that ϕ^{1000l} is a linear combination of Ψ^{D_l} and of the vector collisional invariant $\sum_{k \in \mathcal{S}} \sqrt{m_k} \phi^{1000k}$ to which ϕ^λ must also be orthogonal. Hence, we conclude that we must have $\langle \phi^{1000l}, \phi^\lambda \rangle = 0$ for $l \in \mathcal{S}$. Finally, after some algebra, one may establish from (5), (17), and (18) that

$$\begin{cases} \lambda = \frac{1}{3k_B T^2} [\phi^\lambda, \phi^\lambda], \\ \chi_k = \frac{m_k}{3\bar{p} k_B T} [C^k, \phi^\lambda], \quad k \in \mathcal{S}, \end{cases} \quad (25)$$

where the family C^k is defined by $C^k = ((c_k - v) \delta_{kl})_{l \in \mathcal{S}}$. The above expression for λ is classical, but the one for χ is, to the authors' knowledge, new.

Assume now that a functional space \mathcal{A} has been selected to approximate ϕ^{D_l} and $\phi^{\lambda'}$ in such a way that the partitioning (13) holds. Such a partitioning yields the following decomposition for the functional space \mathcal{A}

$$\mathcal{A} = \text{span}\{ \phi^{1000k}, k \in \mathcal{S} \} \oplus \mathcal{A}^\lambda, \tag{26}$$

where $\mathcal{A}^\lambda = \text{span}\{ \xi^{rk}, (r, k) \in \mathcal{B}^\lambda \}$. Since ϕ^λ is orthogonal to the basis functions $\phi^{1000l}, l \in \mathcal{S}$, the natural functional space for expanding ϕ^λ is the space \mathcal{A}^λ . The resulting matrix $A_{kl}^{rs} = (2\sqrt{m_k m_l} / 3\bar{p}) [\xi^{rk}, \xi^{sl}], (r, k), (s, l) \in \mathcal{B}^\lambda$, is clearly a submatrix of L in such a way that $A = L^{\lambda\lambda}$. Furthermore, consider the vector $\beta_k^{\lambda'} = (\sqrt{2m_k} / 3\bar{p}\sqrt{k_0 T}) \langle \xi^{rk}, \Psi^\lambda \rangle, (r, k) \in \mathcal{B}^\lambda$. Since the basis functions ξ^{rk} in \mathcal{A}^λ are necessarily orthogonal to the functions $\Psi^{D_l}, l \in \mathcal{S}$, we deduce from (24) that we have $\langle \xi^{rk}, \Psi^\lambda \rangle = \langle \xi^{rk}, \Psi^{\lambda'} \rangle$. Hence, the thermal diffusion ratios are eliminated from the computation of β^λ which simply becomes the subvector of $\beta^{\lambda'}$ such that $\beta^\lambda = \beta^{\lambda\lambda'}$.

Conversely, assume that the thermal conductivity and the thermal diffusion ratios are defined by (25) and that the space \mathcal{A}^λ is used to approximate ϕ^λ . Consider then the functional space \mathcal{A} such that the decomposition (26) holds and the resulting diffusion matrix, thermal diffusion vector, and partial thermal conductivity. We now prove that the classical relations (17) and (18) are recovered.

Let indeed \mathcal{A}^\dagger be the functional space

$$\mathcal{A}^\dagger = \{ \xi \in \mathcal{A}, \langle \xi, \sum_{k \in \mathcal{S}} \sqrt{m_k} \phi^{1000k} \rangle = 0 \}, \tag{27}$$

and consider, for $\xi \in \mathcal{A}$, the functional $\mathcal{F}(\xi) = \frac{1}{2} \langle \xi, \text{Im}(\xi) \rangle - \langle \Psi^{\lambda'}, \xi \rangle$. We note that $\phi^{\lambda'}$ minimizes \mathcal{F} on \mathcal{A}^\dagger whereas ϕ^λ minimizes \mathcal{F} on \mathcal{A}^λ . Furthermore, it is straightforward to check that

$$\mathcal{A}^\lambda = \{ \xi \in \mathcal{A}^\dagger, \langle \xi, \Psi^{D_l} \rangle = 0, 1 \leq l \leq n-1 \}, \tag{28}$$

keeping in mind that $\sum_{l \in \mathcal{S}} Y_l \Psi^{D_l} = 0$ and that $\phi^{1000l}, l \in \mathcal{S}$, is a linear combination of Ψ^{D_l} and of the collisional invariant $\sum_{k \in \mathcal{S}} \sqrt{m_k} \phi^{1000k}$. As a consequence, there exist Lagrange multipliers $\eta_1, \dots, \eta_{n-1}$ such that $\text{Im}(\phi^\lambda) = \Psi^{\lambda'} + \sum_{1 \leq l \leq n-1} \eta_l \Psi^{D_l}$. Letting now $\eta_n = 0$ and $(\bar{p} k_0 T) \omega_l = (\eta_l - Y_l \sum_{k \in \mathcal{S}} \eta_k), l \in \mathcal{S}$, we deduce that

$$\text{Im}(\phi^\lambda) = \Psi^{\lambda'} + \bar{p} k_0 T \sum_{l \in \mathcal{S}} \omega_l \Psi^{D_l}, \tag{29}$$

where $\sum_{l \in \mathcal{S}} \omega_l = 0$ since $\sum_{l \in \mathcal{S}} Y_l \Psi^{D_l} = 0$. By linearity we obtain that

$$\phi^\lambda = \phi^{\lambda'} + \bar{p} k_0 T \sum_{l \in \mathcal{S}} \omega_l \phi^{D_l}, \tag{30}$$

and from (25) we then deduce that $\omega_l = \chi_l, l \in \mathcal{S}$. Hence, the relations (24) are recovered, and it is then straightforward to obtain the classical relations (17) and (18).

2.6. Translational-and-internal-energy approach

Noticing that the right-hand side $\Psi^{\lambda'}$ can be written in the form

$$\Psi^{\lambda'} = \sum_{k \in \mathcal{S}} \sqrt{2(k_b T)^3 / m_k} \phi^{1010k} + \sum_{k \in \mathcal{P}} \sqrt{2(k_b T)^3 / m_k} \phi^{1001k}, \tag{31}$$

a first natural approximation space \mathcal{A} for ϕ^{D_l} , $l \in \mathcal{S}$, and $\phi^{\lambda'}$ is then

$$\mathcal{A} = \text{span}\{ \phi^{1000k}, k \in \mathcal{S}, \quad \phi^{1010k}, k \in \mathcal{S}, \quad \phi^{1001k}, k \in \mathcal{P} \}, \tag{32}$$

with the indexing set $\mathcal{B} = \{00, 10\} \times \mathcal{S} \cup \{01\} \times \mathcal{P}$. We refer to this approach as the translational–and–internal–energy approach. Since it has been used traditionally to evaluate the diffusion matrix, the thermal diffusion vector, and the partial thermal conductivity, the resulting transport coefficients will still be denoted by D , θ , and λ' , respectively. The system matrix is still denoted by L and is given in the Appendix in terms of collision integrals. The matrix L is given in its naturally symmetric singular form which is preferable for a cost-effective implementation of iterative transport algorithms and which also yields simpler analytic expressions [12]. On the other hand, the matrix L given in [8] is not symmetric and also contains one misprint. For $\mu = D_l$, the right member may be written

$$\beta_k^{00D_l} = \delta_{kl} - Y_k, \quad \beta_k^{10D_l} = 0, \quad \beta_k^{01D_l} = 0, \tag{33}$$

and for $\mu = \lambda'$ the right member becomes

$$\beta_k^{00\lambda'} = 0, \quad \beta_k^{10\lambda'} = \frac{5}{2} X_k, \quad \beta_k^{01\lambda'} = \frac{5}{2} r_k X_k. \tag{34}$$

For convenience, we have introduced the ratio $r_k = 2c_k^{\text{int}} / (5k_b)$ where c_k^{int} denotes the internal heat capacity of the molecules of the k^{th} species. The explicit expressions for D , θ , and λ' are directly obtained from the ones derived in Section 2.3 and are omitted for brevity.

We now turn to the thermal conductivity and the thermal diffusion ratios. In the translational-and-internal-energy approach, the approximation space is given by $\mathcal{A}^\lambda = \text{span}\{ \phi^{1010k}, k \in \mathcal{S}, \quad \phi^{1001k}, k \in \mathcal{P} \}$ with the indexing set $\mathcal{B}^\lambda = \{10\} \times \mathcal{S} \cup \{01\} \times \mathcal{P}$. Hence, the resulting linear system is of size $n+p$ and admits the block structure

$$\begin{bmatrix} A^{1010} & A^{1001} \\ A^{0110} & A^{0101} \end{bmatrix} \begin{bmatrix} \alpha^{10\lambda} \\ \alpha^{01\lambda} \end{bmatrix} = \begin{bmatrix} \beta^{10\lambda} \\ \beta^{01\lambda} \end{bmatrix}. \tag{35}$$

Here, A^{1010} is a $n \times n$ matrix, A^{1001} is a $n \times p$ matrix, A^{0110} is a $p \times n$ matrix, and A^{0101} is a $p \times p$ matrix. Similarly, $\alpha^{10\lambda}$ and $\beta^{10\lambda}$ are n vectors and $\alpha^{01\lambda}$ and $\beta^{01\lambda}$ are p vectors. The matrix A is simply a submatrix of the larger matrix L given in the Appendix, and the right-hand side β^λ is a subvector of the vector $\beta^{\lambda'}$ given by (34). The thermal conductivity and the thermal diffusion ratios are then given by

$$\lambda = \frac{5\bar{p}}{2T} \left(\sum_{k \in \mathcal{S}} X_k \alpha_k^{10\lambda} + \sum_{k \in \mathcal{P}} X_k r_k \alpha_k^{01\lambda} \right), \tag{36}$$

$$\chi = L^{0010} \alpha^{10\lambda} + L^{0001} \alpha^{01\lambda}, \tag{37}$$

where L^{0010} and L^{0001} are subblocks of the matrix L given in the Appendix. A result equivalent to (36) is presented for the thermal conductivity in [18]. Finally, as a result of Section 2.5, the relations (17) and (18) are automatically recovered.

2.7. Total-energy approach

Upon introducing the functions $\phi^{10ek} = \phi^{1010k} + \delta_{\mathcal{P}}(k) \phi^{1001k}$, where for $k \in \mathcal{S}$ we have defined $\delta_{\mathcal{P}}(k) = 1$ if $k \in \mathcal{P}$ and $\delta_{\mathcal{P}}(k) = 0$ otherwise, the right member $\Psi^{\lambda'}$ can be written in the form

$$\Psi^{\lambda'} = \sum_{k \in \mathcal{S}} \sqrt{2(k_{\text{B}}T)^3/m_k} \phi^{10ek}. \tag{38}$$

The superscript e is used here because ϕ^{10ek} is associated with the total energy of the molecules, i.e., the sum of the translational and internal energy. The expression (38) then suggests the use of the approximation space

$$\mathcal{A}_{[e]} = \text{span}\{ \phi^{1000k}, k \in \mathcal{S}, \phi^{10ek}, k \in \mathcal{S} \}, \tag{39}$$

with the corresponding indexing set $\mathcal{B}_{[e]} = \{00, e\} \times \mathcal{S}$. This approach extends the ideas of [9,10] for the thermal conductivity of pure mixtures and [11] for the partial thermal conductivity of binary mixtures. The accuracy of the thermal conductivity in this approach has been verified in [4] for polyatomic gases and in [19] for atom–diatom gas mixtures.

Using the approximation space $\mathcal{A}_{[e]}$, we obtain linear systems denoted by $L_{[e]} \alpha_{[e]}^{\mu} = \beta_{[e]}^{\mu}$, with the block structure

$$\begin{bmatrix} L_{[e]}^{0000} & L_{[e]}^{00e} \\ L_{[e]}^{e00} & L_{[e]}^{ee} \end{bmatrix} \begin{bmatrix} \alpha_{[e]}^{00\mu} \\ \alpha_{[e]}^{e\mu} \end{bmatrix} = \begin{bmatrix} \beta_{[e]}^{00\mu} \\ \beta_{[e]}^{e\mu} \end{bmatrix}, \tag{40}$$

and which must be completed by the constraint

$$\sum_{k \in \mathcal{S}} Y_k \alpha_{[e]k}^{00\mu} = 0. \tag{41}$$

Here, $L_{[e]}^{0000}$, $L_{[e]}^{00e}$, $L_{[e]}^{e00}$, and $L_{[e]}^{ee}$ are $n \times n$ matrices. Similarly, $\alpha_{[e]}^{00\mu}$, $\alpha_{[e]}^{e\mu}$, $\beta_{[e]}^{00\mu}$, and $\beta_{[e]}^{e\mu}$ are n vectors. The matrix $L_{[e]}$ is explicitly given in the Appendix. For $\mu = D_l$, the right member may be written

$$\beta_{[e]k}^{00D_l} = \delta_{kl} - Y_k, \quad \beta_{[e]k}^{eD_l} = 0, \tag{42}$$

and for $\mu = \lambda'$ the right member becomes

$$\beta_{[e]k}^{00\lambda'} = 0, \quad \beta_{[e]k}^{e\lambda'} = \frac{5}{2}(1 + r_k) X_k. \tag{43}$$

Applying the results of Section 2.3, we deduce that the matrix $L_{[e]}$ is symmetric positive semi-definite, and that the submatrix $L_{[e]}^{ee}$ is symmetric positive definite. In

addition, the kernel of the matrix $L_{[e]}$ is spanned by the vector $U_{[e]} = (U_{[e]}^{00}, U_{[e]}^e)$ such that $U_{[e]}^{00k} = 1$, $k \in \mathcal{S}$, and $U_{[e]}^ek = 0$, $k \in \mathcal{S}$, and the vectors $\beta_{[e]}^\mu$ are in the range of the matrix $L_{[e]}$ since $\sum_{k \in \mathcal{S}} \beta_{[e]}^{00\mu} = 0$, for $\mu = D_l$ and $\mu = \lambda'$. As a consequence, the constrained singular system (40) and (41) is well posed and admits, therefore, a unique solution.

The total-energy approach yields new expressions for the diffusion matrix, the thermal diffusion vector, and the partial thermal conductivity. These transport coefficients are denoted by $D_{[e]}$, $\theta_{[e]}$, and $\lambda'_{[e]}$, respectively, and are given by

$$D_{[e]kl} = \alpha_{[e]k}^{00D_l} = \alpha_{[e]l}^{00D_k}, \quad \theta_{[e]k} = -\alpha_{[e]k}^{00\lambda'}, \quad \lambda'_{[e]} = \frac{5\bar{p}}{2T} \sum_{k \in \mathcal{S}} X_k (1 + r_k) \alpha_{[e]k}^{e\lambda'}. \quad (44)$$

In the total-energy approach, the thermal conductivity and the thermal diffusion ratios are denoted by $\lambda_{[e]}$ and $\chi_{[e]}$, respectively. Using the approximation space $\mathcal{A}_{[e]}^\lambda = \text{span}\{\phi^{10ek}, k \in \mathcal{S}\}$ with the indexing set $\mathcal{B}_{[e]}^\lambda = \{e\} \times \mathcal{S}$ yields the linear system

$$A_{[e]} \alpha_{[e]}^\lambda = \beta_{[e]}^\lambda. \quad (45)$$

Here, $A_{[e]}$ is a $n \times n$ matrix given by $A_{[e]} = L_{[e]}^{ee}$, and $\beta_{[e]}^\lambda$ is a n vector given by $\beta_{[e]}^\lambda = \beta_{[e]}^{e\lambda}$. The system (45) is of size n and admits a unique solution $\alpha_{[e]}^\lambda$, since the matrix $A_{[e]}$ is symmetric positive definite. Finally, the thermal conductivity and the thermal diffusion ratios are given by

$$\lambda_{[e]} = \frac{5\bar{p}}{2T} \sum_{k \in \mathcal{S}} X_k (1 + r_k) \alpha_{[e]k}^{e\lambda}, \quad (46)$$

$$\chi_{[e]} = L_{[e]}^{00e} \alpha_{[e]}^\lambda. \quad (47)$$

The expression (47) is, to the authors' knowledge, new, whereas an expression equivalent to (46) has been derived in [18].

As a result of Section 2.5, we immediately obtain, without further algebraic manipulations, that the thermal diffusion ratios $\chi_{[e]}$ are also the unique solution of the linear system

$$\begin{cases} D_{[e]} \chi_{[e]} = \theta_{[e]}, \\ \sum_{k \in \mathcal{S}} \chi_{[e]k} = 0, \end{cases} \quad (48)$$

and that the thermal conductivity $\lambda_{[e]}$ is also given by

$$\lambda_{[e]} = \lambda'_{[e]} - (\bar{p}/T) \sum_{k \in \mathcal{S}} \theta_{[e]k} \chi_{[e]k}. \quad (49)$$

3. Practical, approximate expressions

3.1. Iterative methods

In Section 2 we have expressed the thermal conductivity and the thermal diffusion ratios of dilute polyatomic gas mixtures in terms of the solution of various linear systems. These linear systems relate the transport coefficients to a series of collision cross-sections describing the dynamical interaction between polyatomic molecules. However, solving these linear systems by direct methods (such as Gaussian elimination) presents two serious drawbacks. First, it does not provide expressions for the transport coefficients that can be written explicitly in a tractable manner for an arbitrary number of species in the mixture. Second, this approach is extremely expensive in computational models of multicomponent flows since the size of the linear systems can be relatively large and since transport properties have to be evaluated at each computational cell in space and time. Numerical algorithms devoted to solve the nonlinear discretized equations governing these flows may also proceed by iteration, such as Newton's method for instance, and this even increases the number of transport properties evaluations. In this context, iterative methods offer an interesting alternative since they provide a rigorous way to define approximate transport coefficients by truncating convergent series.

Iterative methods have been considered implicitly in [20,21] when deriving approximate formulas for the thermal conductivity of monatomic gas mixtures. A general theory of iterative methods for evaluating transport coefficients in dilute polyatomic gas mixtures has been developed in [12]. Convergence theorems were presented in a rigorous mathematical framework that was extracted from the Boltzmann equation and from the variational procedure used to expand the species perturbed distribution functions. Two categories of iterative methods were considered: standard iterative methods and conjugate gradient methods. These two methods are now briefly described and we refer to [12,22–24] for a more mathematical description of these algorithms.

Consider a linear system in the form

$$G\alpha = \beta, \quad (50)$$

where, in our applications, the matrix G stands for A or $A_{[e]}$ and is, therefore, symmetric positive definite. Standard iterative methods are based on a splitting of the form

$$G = M - Z, \quad (51)$$

where the matrix M is assumed to be symmetric positive definite. Consider the iteration matrix $S = M^{-1}Z$, the initialization $x_0 = 0$, and for $i \geq 0$ the iterative scheme

$$x_{i+1} = Sx_i + M^{-1}\beta. \quad (52)$$

Then the iterates x_i converge towards the unique solution of (50) if and only if the matrix $2M - G$ is positive definite. On the other hand, the conjugate gradient method is particularly cost-effective for solving symmetric positive definite systems. Let $\langle \cdot, \cdot \rangle$

denote the scalar product between vectors and consider the initialization $x_0 = 0$, $r_0 = \beta$, $p_0 = 0$, and $t_0 = 0$, and for $i \geq 0$ the iterates

$$\begin{cases} p_{i+1} = M^{-1}r_i + t_i p_i, \\ s_{i+1} = \langle r_i, M^{-1}r_i \rangle / \langle p_{i+1}, Gp_{i+1} \rangle, \\ x_{i+1} = x_i + s_{i+1} p_{i+1}, \\ r_{i+1} = r_i - s_{i+1} Gp_{i+1}, \\ t_{i+1} = \langle r_{i+1}, M^{-1}r_{i+1} \rangle / \langle r_i, M^{-1}r_i \rangle. \end{cases} \quad (53)$$

Then the iterates x_i converge towards the solution of (50) in at most ω steps, where ω is the size of the matrix G . The matrix M in (53) is termed the preconditioner. It is clear from the above discussion that an efficient implementation of both iterative methods requires a matrix M such that the action of M^{-1} on a given vector can be written explicitly in a simple form. Examples of such matrices are presented in the next section.

3.2. The matrices $db(\Lambda)$ and $db(\Lambda_{[e]})$

A fundamental matrix in the theory of iterative transport algorithms is the matrix $db(G)$ formed by the diagonal of the blocks of the matrix G [12]. In the translational- and-internal-energy approach, the system matrix Λ is composed of four blocks, as discussed in Section 2.6. The matrix $db(\Lambda)$ is then given by

$$db(\Lambda) = \begin{bmatrix} \text{diag}(\Lambda^{1010}) & \text{diag}(\Lambda^{1001}) \\ \text{diag}(\Lambda^{0110}) & \text{diag}(\Lambda^{0101}) \end{bmatrix}, \quad (54)$$

and it is straightforward to write the matrix $db(\Lambda)^{-1}$ explicitly in terms of the inverse of the 2×2 subblocks

$$\begin{bmatrix} \Lambda_{kk}^{1010} & \Lambda_{kk}^{1001} \\ \Lambda_{kk}^{0110} & \Lambda_{kk}^{0101} \end{bmatrix}. \quad (55)$$

Furthermore, one can show that the matrices $db(\Lambda)$ and $2db(\Lambda) - \Lambda$ are symmetric positive definite [12].

In the total-energy approach, the system matrix $\Lambda_{[e]}$ is composed of one block, as discussed in Section 2.7. The matrix $db(\Lambda_{[e]})$ is simply given by

$$db(\Lambda_{[e]}) = \text{diag}(\Lambda_{[e]}^{ee}), \quad (56)$$

and one can show that the matrices $db(\Lambda_{[e]})$ and $2db(\Lambda_{[e]}) - \Lambda_{[e]}$ are symmetric positive definite [12]. The total-energy approach is particularly attractive since the diagonal matrix $db(\Lambda_{[e]})$ is trivially inverted.

3.3. Truncated convergent series

Using standard iterative methods, the thermal conductivity and the thermal diffusion ratios can be expressed as convergent series [12]. Truncating these series then provides explicit, approximate expressions for the thermal conductivity and the thermal diffusion ratios. In the translational-and-internal-energy approach, we obtain

$$\begin{cases} \lambda^{[i]} = \frac{\bar{p}}{T} \left\langle \sum_{j=0}^i S^j db(\Lambda)^{-1} \beta^\lambda, \beta^\lambda \right\rangle, \\ \chi^{[i]} = [L^{0010}, L^{0001}] \sum_{j=0}^i S^j db(\Lambda)^{-1} \beta^\lambda, \end{cases} \quad (57)$$

where $S = I - db(\Lambda)^{-1}\Lambda$, I is the identity matrix, and $[L^{0010}, L^{0001}]$ is a $n \times (n + p)$ matrix formed by the blocks L^{0010} and L^{0001} . Similar expressions are easily derived in the total-energy approach [12].

Explicit approximate expressions for the thermal conductivity and the thermal diffusion ratios can also be obtained by truncating the conjugate gradient method. In the translational-and-internal-energy approach, this yields sequences of iterates in the form

$$\begin{cases} \lambda^{[i]} = \frac{\bar{p}}{T} \sum_{j=1}^i \frac{\langle \beta^\lambda, p_j \rangle^2}{\langle p_j, \Lambda p_j \rangle}, \\ \chi^{[i]} = [L^{0010}, L^{0001}] \sum_{j=1}^i \frac{\langle \beta^\lambda, p_j \rangle}{\langle p_j, \Lambda p_j \rangle} p_j, \end{cases} \quad (58)$$

where the vectors p_j are given by the iterative scheme (53). Similar expressions are easily derived in the total-energy approach [12].

The explicit expressions (57) and (58) are relatively straightforward to implement on a computer and the evaluation of the first few terms in the series requires significantly less computational effort than if Gaussian elimination were employed on the original linear system. Furthermore, these expressions are directly related to the matrix elements of the original systems, as detailed in Section 3.1. Thus, they can be written explicitly in terms of collision integrals.

3.4. Numerical experiments

In this section we verify the accuracy of all the transport coefficients obtained in the total-energy approach. We also consider iterative methods for the evaluation of the thermal conductivity and the thermal diffusion ratios. The numerical experiments are performed on four gas mixtures. Mixture 1 is air, i.e., a binary mixture consisting of oxygen and nitrogen with mole fractions $X_{O_2} = 0.21$ and $X_{N_2} = 0.79$. Mixture 2 is a typical ternary mixture often considered in crystal growth applications [25]; it is formed by hydrogen, arsine, and trimethylgallium with mole fractions $X_{H_2} = 0.9895$, $X_{AsH_3} = 0.01$,

Table 1
Reduced errors for the transport coefficients in the total-energy approach

	Mixture 1	Mixture 2	Mixture 3	Mixture 4
$e_{\lambda_{[e]}}$	1.90E-3	2.66E-3	8.15E-4	1.56E-3
$e_{\lambda'_{[e]}}$	1.90E-3	2.68E-3	7.22E-4	1.51E-3
$e_{\chi_{[e]}}$	2.13E-2	3.26E-2	1.68E-2	4.66E-2
$e_{\theta_{[e]}}$	2.18E-2	3.28E-2	4.03E-3	9.11E-3
$e_{D_{[e]}}$	5.07E-4	6.09E-6	5.48E-3	6.29E-3

and $X_{\text{Ga}(\text{CH}_3)_3} = 0.005$, respectively. Mixtures 3 and 4 contain more chemical species and are typical mixtures considered in hydrogen and methane combustion applications [25–27]. Mixture 3 is an equimolar hydrogen mixture composed of the $n = 9$ species H_2 , O_2 , N_2 , H_2O , H , O , OH , HO_2 , and H_2O_2 . Mixture 4 is an equimolar methane mixture composed of the $n = 26$ species CH_4 , CH_3 , CH_2 , CH , N_2 , H_2 , O_2 , H_2O , H , O , OH , HO_2 , H_2O_2 , C_2H_6 , C_2H_5 , C_2H_4 , C_2H_3 , C_2H_2 , C_2H , CHO , CH_2O , CH_3O , CH_2CO , CO_2 , CO , and C_2HO . Finally, mixtures 1 and 2 are considered at pressure $\bar{p} = 1$ atm and temperature $T = 300$ K, and mixtures 3 and 4 at pressure $\bar{p} = 1$ atm and temperature $T = 1500$ K.

In the present numerical experiments, the linear system coefficients given in the Appendix are evaluated using approximate collision integrals [12,28–30]. The convergence of the iterative algorithms in the framework of these approximations has been proven in [12]. The validity of some of these approximations is sometimes questioned [4], but we point out that the general theory presented in this paper does not rely upon these approximations since convergence theorems are valid for the exact systems also.

In Table 1 we first present the reduced errors associated with all the transport coefficients obtained in the total-energy approach. More specifically, we evaluate

$$e_{\lambda_{[e]}} = \frac{|\lambda - \lambda_{[e]}|}{\lambda}, \quad e_{\lambda'_{[e]}} = \frac{|\lambda' - \lambda'_{[e]}|}{\lambda'}, \quad (59)$$

$$e_{\chi_{[e]}} = \frac{\|\chi - \chi_{[e]}\|_{\infty}}{\|\chi\|_{\infty}}, \quad e_{\theta_{[e]}} = \frac{\|\theta - \theta_{[e]}\|_{\infty}}{\|\theta\|_{\infty}}, \quad e_{D_{[e]}} = \frac{\|D - D_{[e]}\|_{\infty}}{\|D\|_{\infty}}, \quad (60)$$

where we have defined $\|v\|_{\infty} = \max_{k \in S} |v_k|$ and $\|A\|_{\infty} = \max_{k, l \in S} |A_{kl}|$ for a vector v and a matrix A , respectively. For the four test mixtures, the thermal conductivity $\lambda_{[e]}$ and the partial thermal conductivity $\lambda'_{[e]}$ are within 2×10^{-3} accuracy, the diffusion matrix $D_{[e]}$ is within 6×10^{-3} accuracy, and the thermal diffusion vector $\theta_{[e]}$ and the thermal diffusion ratios $\chi_{[e]}$ are within 4×10^{-2} accuracy. The transport coefficients $\theta_{[e]}$, $\chi_{[e]}$, and $D_{[e]}$ provide, therefore, a new and accurate means of evaluating thermal and species diffusion coefficients in polyatomic gas mixtures.

We now consider iterative methods in both the translational-and-internal-energy and the total-energy approaches. Only the numerical experiments obtained with conjugate gradient methods are discussed here, and we refer to [12] for those related to standard

Table 2

Conjugate gradient method. Reduced errors for $\lambda_{[e]}^{[i]}$

i	Mixture 1	Mixture 2	Mixture 3	Mixture 4
1	1.07E-2	7.78E-5	8.60E-3	4.48E-3
2	–	2.41E-11	5.23E-6	3.01E-7
3	–	2.00E-16	1.28E-10	5.09E-12
4	–	–	7.26E-15	2.01E-16

Table 3

Conjugate gradient method. Reduced errors for $\chi_{[e]}^{[i]}$

i	Mixture 1	Mixture 2	Mixture 3	Mixture 4
1	1.20E+0	9.00E-4	9.87E-2	1.11E-1
2	8.24E-16	3.34E-7	2.27E-3	9.74E-4
3	–	1.93E-16	1.13E-5	3.39E-6
4	–	–	1.19E-7	2.24E-8

iterative methods. We first apply the conjugate gradient method to the system $A_{[e]} \alpha_{[e]}^\lambda = \beta_{[e]}^\lambda$ preconditioned by the matrix $db(A_{[e]})$ defined in Section 3.2. The reduced errors

$$e_{\lambda_{[e]}}^{[i]} = \frac{|\lambda_{[e]} - \lambda_{[e]}^{[i]}|}{\lambda_{[e]}}, \quad e_{\chi_{[e]}}^{[i]} = \frac{\|\chi_{[e]} - \chi_{[e]}^{[i]}\|_\infty}{\|\chi_{[e]}\|_\infty}, \quad i = 1, 2, 3, 4, \quad (61)$$

are presented in Tables 2 and 3 for the four test mixtures. For the thermal conductivity, the first iterate, $\lambda_{[e]}^{[1]}$, is within 10^{-2} accuracy of $\lambda_{[e]}$ and may be expressed as

$$\lambda_{[e]}^{[1]} = \frac{\bar{p}}{T} \frac{\langle \beta_{[e]}^\lambda, db(A_{[e]})^{-1} \beta_{[e]}^\lambda \rangle^2}{\langle db(A_{[e]})^{-1} \beta_{[e]}^\lambda, A_{[e]} db(A_{[e]})^{-1} \beta_{[e]}^\lambda \rangle} = \frac{\bar{p}}{T} \frac{(\sum_{k \in S} A_{[e]kk}^{ee} \mathcal{V}_k^2)^2}{\sum_{k,l \in S} A_{[e]kl}^{ee} \mathcal{V}_k \mathcal{V}_l}, \quad (62)$$

where $\mathcal{V}_k = \beta_{[e]k}^\lambda / A_{[e]kk}^{ee}$. An additional iteration yields the approximate expression

$$\lambda_{[e]}^{[2]} = \lambda_{[e]}^{[1]} + \frac{\bar{p}}{T} \frac{\langle \beta_{[e]}^\lambda, p_2 \rangle^2}{\langle p_2, A_{[e]} p_2 \rangle}, \quad (63)$$

with p_2 given by (53). We deduce from Table 2 that $\lambda_{[e]}^{[2]}$ is within 5×10^{-6} accuracy of $\lambda_{[e]}$ for the present test mixtures. For the thermal diffusion ratios, two iterates yield the approximate expression

$$\chi_{[e]}^{[2]} = L_{[e]}^{00e} \left(\frac{\langle \beta_{[e]}^\lambda, p_1 \rangle}{\langle p_1, A_{[e]} p_1 \rangle} p_1 + \frac{\langle \beta_{[e]}^\lambda, p_2 \rangle}{\langle p_2, A_{[e]} p_2 \rangle} p_2 \right), \quad (64)$$

which is within 2×10^{-3} accuracy of $\chi_{[e]}$.

Similar results are obtained in the translational-and-internal-energy approach for the system $\Lambda \alpha^\lambda = \beta^\lambda$ preconditioned by the matrix $db(\Lambda)$ defined in Section 3.2. One iteration yields the expression

$$\lambda^{[1]} = \frac{\bar{p}}{T} \frac{\langle \beta^\lambda, db(\Lambda)^{-1} \beta^\lambda \rangle^2}{\langle db(\Lambda)^{-1} \beta^\lambda, \Lambda db(\Lambda)^{-1} \beta^\lambda \rangle}, \quad (65)$$

which is within 2×10^{-2} accuracy of λ . Instead of the matrix $db(\Lambda)$, one can also consider the simpler preconditioner $\text{diag}(\Lambda)$ which can be trivially inverted. The expression for the thermal conductivity, after one conjugate gradient iteration, is given by

$$\lambda^{[1]} = \frac{\bar{p}}{T} \frac{\left(\sum_{(r,k) \in \mathcal{B}} A_{kk}^{rr} (\mathcal{W}_k^r)^2 \right)^2}{\sum_{(r,k),(s,l) \in \mathcal{B}} A_{kl}^{rs} \mathcal{W}_k^r \mathcal{W}_l^s}, \quad (66)$$

where $\mathcal{W}_k^r = \beta_k^{r\lambda} / A_{kk}^{rr}$. Finally, for the thermal diffusion ratios, the approximate expression

$$\chi^{[2]} = [L^{0010}, L^{0001}] \left(\frac{\langle \beta^\lambda, p_1 \rangle}{\langle p_1, \Lambda p_1 \rangle} p_1 + \frac{\langle \beta^\lambda, p_2 \rangle}{\langle p_2, \Lambda p_2 \rangle} p_2 \right), \quad (67)$$

obtained after two conjugate gradient iterations, is within 3×10^{-3} accuracy of χ for the mixtures considered in this paper.

4. Conclusion

In this paper we have derived, for the first time, a variational framework with which to evaluate directly the thermal conductivity and the thermal diffusion ratios of dilute polyatomic gas mixtures. By considering basis functions in the variational space based on the total energy of the molecules, we have also introduced new expressions for the diffusion matrix, the thermal diffusion vector, and the thermal diffusion ratios. Finally, we have obtained practical, approximate expressions for the thermal conductivity and the thermal diffusion ratios of dilute polyatomic gas mixtures. These expressions are associated with a low computational cost and are directly related to the collision integrals appearing in the linear system coefficients. Hence, they are particularly appealing to use in numerical calculations of multicomponent flows – such as flames or chemical vapor deposition reactors – and may also provide further incentive to compute collision cross-sections of polyatomic gases.

Appendix

In this appendix we restate the explicit expression of the system matrix L in its naturally symmetric singular form [12]. We also present, for the first time, the explicit expression of the system matrix $L_{[e]}$. The subblock $L_{[e]}^{ee}$ has already been written in [19] for a monatomic–diatomic binary mixture. The present expression is more general since it is valid for arbitrary polyatomic gas mixtures. There are no approximations in it beyond those involved in the semi-classical isotropic kinetic theory and the total–energy approach.

The notation used in this appendix follows that in [13]. For a species pair (k, l) , we denote by \mathcal{D}_{kl} the binary diffusion coefficient and by $\mathcal{D}_{k\text{int},l}$ the binary diffusion coefficient for internal energy. Furthermore, we introduce the quantities $\Delta\epsilon_{kl} = \Delta\epsilon_k + \tilde{\Delta}\epsilon_l$, where $\Delta\epsilon_k = \epsilon_{kk'} - \epsilon_{kk}$ and $\tilde{\Delta}\epsilon_l = \epsilon_{ll'} - \epsilon_{ll}$. The primes denote values after the binary collision in which a molecule of the k^{th} species in energy state κ interacts with a molecule of the l^{th} species in energy state L . The superscript \sim is used to distinguish one of the collisions partners from the other, in the case where k and l are the same. We denote by g the modulus of the relative velocity $c_k - \tilde{c}_l$ of the colliding particles before collision, and by χ and φ the polar and azimuthal angles which describe the orientation of $c'_k - \tilde{c}'_l$ with respect to $c_k - \tilde{c}_l$.

We consider the averaging operator $[[\]]_{kl}$ defined in [12] and equivalent to the one introduced in [8], and we define the following classical collision integrals $\Omega_{kl}^{(1,1)} = [\gamma^2 - \gamma\gamma' \cos\chi]_{kl}$, $\Omega_{kl}^{(2,2)} = [\gamma^4 - \gamma^2\gamma'^2 \cos^2\chi - \frac{1}{6}(\Delta\epsilon_{kl})^2]_{kl}$, $\Omega_{kl}^{(1,2)} = [\gamma^4 - \gamma^3\gamma' \cos\chi]_{kl}$, and $\Omega_{kl}^{(1,3)} = [\gamma^6 - \gamma^3\gamma'^3 \cos\chi]_{kl}$, where $\gamma = g(m_{kl}/2k_B T)^{1/2}$, $\gamma' = g'(m_{kl}/2k_B T)^{1/2}$, and $m_{kl} = m_k m_l / (m_k + m_l)$. The quantities \bar{a}_{kl} , \bar{b}_{kl} , and \bar{c}_{kl} are classical ratios of collision integrals given by

$$\bar{a}_{kl} = \frac{1}{2} \frac{\Omega_{kl}^{(2,2)}}{\Omega_{kl}^{(1,1)}}, \quad \bar{b}_{kl} = \frac{1}{3} \frac{5\Omega_{kl}^{(1,2)} - \Omega_{kl}^{(1,3)}}{\Omega_{kl}^{(1,1)}}, \quad \bar{c}_{kl} = \frac{1}{3} \frac{\Omega_{kl}^{(1,2)}}{\Omega_{kl}^{(1,1)}}. \tag{A.1}$$

We also introduce

$$\left\{ \begin{aligned} \bar{E}_{kl} &= \frac{[\epsilon_{kk}^0 (\gamma^2 - \gamma\gamma' \cos\chi)]_{kl}}{\Omega_{kl}^{(1,1)}}, \\ \bar{F}_{kl} &= \frac{5}{2} \bar{E}_{kl} - \frac{[\epsilon_{kk}^0 (\gamma^4 - \gamma\gamma'^3 \cos\chi)]_{kl}}{\Omega_{kl}^{(1,1)}}, \\ \bar{G}_{kl} &= \frac{[\epsilon_{kk}^0 (\epsilon_{ll}^0 \gamma^2 - \epsilon_{ll'}^0 \gamma\gamma' \cos\chi)]_{kl}}{\Omega_{kl}^{(1,1)}}, \end{aligned} \right. \tag{A.2}$$

where $\epsilon_{kk}^0 = \epsilon_{kk} - \bar{\epsilon}_k$ is a shifted reduced internal energy. Finally, the pure species thermal conductivity $\lambda_{|e|k}$ is defined as

$$\frac{1}{\lambda_{|e|k}} = \frac{8}{25} \frac{T}{\bar{p}} \frac{\bar{a}_{kk}}{\mathcal{D}_{kk}} \frac{1}{(1+r_k)^2} \left[1 + \frac{5}{4} \frac{1}{\bar{a}_{kk}} r_k \frac{\mathcal{D}_{kk}}{\mathcal{D}_{k\text{int},k}} + \frac{1}{6} \frac{[(\Delta\epsilon_{kk})^2]_{kk}}{\Omega_{kk}^{(2,2)}} \right]. \tag{A.3}$$

The matrix L may then be expressed as

$$L_{kk}^{0000} = \sum_{\substack{l \in S \\ l \neq k}} \frac{X_k X_l}{\mathcal{D}_{kl}}, \quad k \in S, \tag{A.4}$$

$$L_{kl}^{0000} = -\frac{X_k X_l}{\mathcal{D}_{kl}}, \quad k, l \in S, \quad k \neq l, \tag{A.5}$$

$$L_{kk}^{0010} = -\sum_{\substack{l \in S \\ l \neq k}} \frac{X_k X_l}{2\mathcal{D}_{kl}} \frac{m_l}{m_k + m_l} (6\bar{c}_{kl} - 5), \quad k \in S, \tag{A.6}$$

$$L_{kl}^{0010} = \frac{X_k X_l}{2\mathcal{D}_{kl}} \frac{m_k}{m_k + m_l} (6\bar{c}_{kl} - 5), \quad k, l \in \mathcal{S}, \quad k \neq l, \quad (\text{A.7})$$

$$L_{kk}^{0001} = - \sum_{\substack{l \in \mathcal{S} \\ l \neq k}} \frac{X_k X_l}{\mathcal{D}_{kl}} \bar{E}_{kl}, \quad k \in \mathcal{P}, \quad (\text{A.8})$$

$$L_{kl}^{0001} = \frac{X_k X_l}{\mathcal{D}_{kl}} \bar{E}_{lk}, \quad k \in \mathcal{S}, \quad l \in \mathcal{P}, \quad k \neq l, \quad (\text{A.9})$$

$$L_{kk}^{1010} = \sum_{\substack{l \in \mathcal{S} \\ l \neq k}} \frac{X_k X_l}{\mathcal{D}_{kl}} \frac{m_k m_l}{(m_k + m_l)^2} \left[\frac{15}{2} \frac{m_k}{m_l} + \frac{25}{4} \frac{m_l}{m_k} - 3 \frac{m_l}{m_k} \bar{B}_{kl} + 4 \bar{A}_{kl} \right. \\ \left. + \frac{25}{12} \frac{[(\Delta\epsilon_{kl})^2]_{kl}}{\Omega_{kl}^{(1,1)}} \right] + \frac{X_k^2}{2\mathcal{D}_{kk}} \left[4\bar{A}_{kk} + \frac{25}{12} \frac{[(\Delta\epsilon_{kk})^2]_{kk}}{\Omega_{kk}^{(1,1)}} \right], \quad k \in \mathcal{S}, \quad (\text{A.10})$$

$$L_{kl}^{1010} = - \frac{X_k X_l}{\mathcal{D}_{kl}} \frac{m_k m_l}{(m_k + m_l)^2} \left[\frac{55}{4} - 3\bar{B}_{kl} - 4\bar{A}_{kl} \right. \\ \left. - \frac{25}{12} \frac{[(\Delta\epsilon_{kl})^2]_{kl}}{\Omega_{kl}^{(1,1)}} \right], \quad k, l \in \mathcal{S}, \quad k \neq l, \quad (\text{A.11})$$

$$L_{kk}^{1001} = - \sum_{\substack{l \in \mathcal{S} \\ l \neq k}} \frac{X_k X_l}{\mathcal{D}_{kl}} \frac{m_k}{m_k + m_l} \left[\frac{5}{4} \frac{[\Delta\epsilon_k \Delta\epsilon_{kl}]_{kl}}{\Omega_{kl}^{(1,1)}} + \frac{m_l}{m_k} \bar{F}_{kl} \right] \\ - \frac{5}{8} \frac{X_k^2}{\mathcal{D}_{kk}} \frac{[(\Delta\epsilon_{kk})^2]_{kk}}{\Omega_{kk}^{(1,1)}}, \quad k \in \mathcal{P}, \quad (\text{A.12})$$

$$L_{kl}^{1001} = \frac{X_k X_l}{\mathcal{D}_{kl}} \frac{m_l}{m_k + m_l} \left[- \frac{5}{4} \frac{[\tilde{\Delta}\epsilon_l \Delta\epsilon_{kl}]_{kl}}{\Omega_{kl}^{(1,1)}} + \bar{F}_{lk} \right], \quad k \in \mathcal{S}, \quad l \in \mathcal{P}, \quad k \neq l, \quad (\text{A.13})$$

$$L_{kk}^{0101} = \sum_{\substack{l \in \mathcal{S} \\ l \neq k}} \frac{X_k X_l}{\mathcal{D}_{kl}} \left[\frac{5}{2} r_k \frac{\mathcal{D}_{kl}}{\mathcal{D}_{\text{int},l}} + \frac{3}{4} \frac{m_k}{m_l} \frac{[(\Delta\epsilon_k)^2]_{kl}}{\Omega_{kl}^{(1,1)}} \right] \\ + \frac{X_k^2}{\mathcal{D}_{kk}} \left[\frac{5}{2} r_k \frac{\mathcal{D}_{kk}}{\mathcal{D}_{\text{int},k}} + \frac{3}{8} \frac{[(\Delta\epsilon_{kk})^2]_{kk}}{\Omega_{kk}^{(1,1)}} \right], \quad k \in \mathcal{P}, \quad (\text{A.14})$$

$$L_{kl}^{0101} = - \frac{X_k X_l}{\mathcal{D}_{kl}} \left[\bar{G}_{kl} - \frac{3}{4} \frac{[\Delta\epsilon_k \tilde{\Delta}\epsilon_l]_{kl}}{\Omega_{kl}^{(1,1)}} \right], \quad k, l \in \mathcal{P}, \quad k \neq l, \quad (\text{A.15})$$

and the matrix $L_{[e]}$ as

$$L_{[e]kk}^{0000} = \sum_{\substack{l \in \mathcal{S} \\ l \neq k}} \frac{X_k X_l}{\mathcal{D}_{kl}}, \quad k \in \mathcal{S}, \quad (\text{A.16})$$

$$L_{[e]kl}^{0000} = - \frac{X_k X_l}{\mathcal{D}_{kl}}, \quad k, l \in \mathcal{S}, \quad k \neq l, \quad (\text{A.17})$$

$$L_{[e]kk}^{00e} = - \sum_{\substack{l \in S \\ l \neq k}} \frac{X_k X_l}{2\mathcal{D}_{kl}} \left[\frac{m_l}{m_k + m_l} (6\bar{C}_{kl} - 5) + 2\bar{E}_{kl} \right], \quad k \in S, \quad (\text{A.18})$$

$$L_{[e]kl}^{00e} = \frac{X_k X_l}{2\mathcal{D}_{kl}} \left[\frac{m_k}{m_k + m_l} (6\bar{C}_{kl} - 5) + 2\bar{E}_{lk} \right], \quad k, l \in S, \quad k \neq l, \quad (\text{A.19})$$

$$\begin{aligned} L_{[e]kk}^{ee} = & \sum_{\substack{l \in S \\ l \neq k}} \frac{X_k X_l}{\mathcal{D}_{kl}} \left[\frac{1}{(m_k + m_l)^2} \left(\frac{15}{2} m_k^2 + \left(\frac{25}{4} - 3\bar{B}_{kl} \right) m_l^2 + 4m_k m_l \bar{A}_{kl} \right) \right. \\ & \left. + \frac{5}{2} r_k \frac{\mathcal{D}_{kl}}{\mathcal{D}_{\text{int},l}} - 2 \frac{m_l}{m_k + m_l} \bar{F}_{kl} + \frac{3}{4} \frac{m_k}{m_l} \left[\frac{(\Delta\epsilon_k - \frac{5}{3} \frac{m_l}{m_k + m_l} \Delta\epsilon_{kl})^2}{\Omega_{kl}^{(1,1)}} \right]_{kl} \right] \\ & + \frac{25}{4} \frac{\bar{p}}{T} (1 + r_k)^2 \frac{X_k^2}{\lambda_{[e]k}}, \quad k \in S, \end{aligned} \quad (\text{A.20})$$

$$\begin{aligned} L_{[e]kl}^{ee} = & - \frac{X_k X_l}{\mathcal{D}_{kl}} \left[\left(\frac{55}{4} - 3\bar{B}_{kl} - 4\bar{A}_{kl} \right) \frac{m_k m_l}{(m_k + m_l)^2} - \frac{1}{m_k + m_l} (m_k \bar{F}_{kl} + m_l \bar{F}_{lk}) \right. \\ & \left. + \bar{G}_{kl} + \frac{5}{12} \frac{m_k (3m_k - 2m_l)}{(m_k + m_l)^2} \left[\frac{(\Delta\epsilon_k)^2}{\Omega_{kl}^{(1,1)}} \right]_{kl} + \frac{5}{12} \frac{m_l (3m_l - 2m_k)}{(m_k + m_l)^2} \left[\frac{(\Delta\epsilon_l)^2}{\Omega_{kl}^{(1,1)}} \right]_{kl} \right. \\ & \left. + \frac{1}{2} \left(1 - \frac{25}{3} \frac{m_k m_l}{(m_k + m_l)^2} \right) \left[\frac{\Delta\epsilon_k \tilde{\Delta\epsilon}_l}{\Omega_{kl}^{(1,1)}} \right]_{kl} \right], \quad k, l \in S, \quad k \neq l. \end{aligned} \quad (\text{A.21})$$

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