Plasma Sources Sci. Technol. **19** (2010) 034002 (6pp) doi:10.1088/0963-0252/19/3/034002

Multicomponent transport in weakly ionized mixtures

V Giovangigli[1], B Graille[2], T Magin[3,5] and M Massot[4]

[1] CMAP, CNRS, Ecole Polytechnique, 91128 Palaiseau, France
[2] Laboratoire de Mathématiques, Université Paris-Sud, 91405, Orsay, France
[3] Center for Turbulence Research, Stanford University, CA 94305, USA
[4] Laboratoire EM2C, Ecole Centrale de Paris, 92295 Châtenay-Malabry, France

E-mail: vincent.giovangigli@polytechnique.fr

Received 28 July 2009, in final form 9 October 2009
Published 21 May 2010
Online at stacks.iop.org/PSST/19/034002

Abstract
We discuss transport coefficients in weakly ionized mixtures. We investigate the situations of weak and strong magnetic fields as well as electron temperature nonequilibrium. We present in each regime the Boltzmann equations, examples of transport fluxes, the structure of transport linear systems and discuss their solution by efficient iterative techniques. Numerical simulations are presented for partially ionized high-temperature air.

1. Introduction

Ionized magnetized reactive gas mixtures have many practical applications such as laboratory plasmas, high-speed gas flows, lean flame stabilization or atmospheric phenomena. This motivates kinetic theory investigations and the derivation of macroscopic plasmas equations. We discuss in this paper the kinetic theory of partially ionized polyatomic reactive gas mixtures in weak and strong magnetic fields and the situation of electron temperature nonequilibrium. We present in each regime the scaled Boltzmann equations, the viscous tensors, the species diffusion velocities, the structure of the transport linear systems and discuss their solution by efficient iterative techniques. New asymptotic expansions are discussed for the evaluation of multicomponent diffusion matrices. Numerical simulations of transport coefficients in partially ionized high temperature air are finally presented.

2. Transport coefficients in weak magnetic fields

The kinetic theory of weakly magnetized or unmagnetized thermal plasmas has been investigated by numerous authors [11, 14, 21, 24, 31, 33, 36, 38, 39, 41–43]. In particular, the structure of the transport linear systems for polyatomic gas mixtures has been investigated as well as their solution by iterative techniques [15, 17, 24, 26].

[5] Alternative address: von Karman Institute, 72 Chausée de Waterloo, B-1640 Rhode-Saint-Genèse, Belgium

2.1. Boltzmann equations

For mixtures of polyatomic ionized reactive gases, semi-classical Boltzmann equations are typically written in the form [11, 15, 21, 24, 36, 38, 42]

$$\partial_t f_k + \boldsymbol{c}_k \cdot \boldsymbol{\nabla} f_k + \boldsymbol{b}_k \cdot \boldsymbol{\nabla}_{\boldsymbol{c}_k} f_k = \frac{1}{\epsilon} \mathcal{J}_k + \epsilon^\alpha \mathcal{R}_k, \qquad k \in \mathcal{S}, \quad (1)$$

where $\mathcal{S} = \{1, \ldots, n\}$ denotes the species indexing set, ϵ the formal parameter associated with Enskog expansion, and for $k \in \mathcal{S}$, f_k denotes the distribution function, $\boldsymbol{c}_k$ the particles velocity, $\boldsymbol{b}_k = \boldsymbol{g} + z_k(\boldsymbol{E} + \boldsymbol{c}_k \wedge \boldsymbol{B})$ the force per unit mass, $\boldsymbol{g}$ a species independent specific force, z_k the species charge per unit mass, $\boldsymbol{E}$ the electric field, $\boldsymbol{B}$ the magnetic field, and $\mathcal{J}_k$ and $\mathcal{R}_k$ the scattering and reactive collision operators [24, 38]. Application of the Chapman–Enskog method yields the fluid conservation equations, thermochemistry properties, expressions for transport fluxes and the transport linear systems [11, 15, 21, 24, 36, 38, 42].

2.2. Examples of transport fluxes

The viscous tensor derived from the kinetic theory is in the form

$$\boldsymbol{\Pi} = -\kappa(\boldsymbol{\nabla} \cdot \boldsymbol{v})\mathbb{I} - \eta(\boldsymbol{\nabla}\boldsymbol{v} + (\boldsymbol{\nabla}\boldsymbol{v})^t - \tfrac{2}{3}(\boldsymbol{\nabla} \cdot \boldsymbol{v})\mathbb{I}), \quad (2)$$

where κ is the volume viscosity, η the shear viscosity and $\boldsymbol{v}$ the average flow velocity. Note incidentally that the ratio κ/η is not small for polyatomic gases as taken for granted in most books of fluid dynamics [2]. On the other hand, the species

diffusion velocities $\mathcal{V}_k$, $k \in \mathcal{S}$, are in the form

$$\mathcal{V}_k = -\sum_{l\in\mathcal{S}} D_{kl}\boldsymbol{d}_l - \theta_k \nabla \log T, \qquad k \in \mathcal{S}, \tag{3}$$

where D_{kl} are the symmetric multicomponent diffusion coefficients introduced by Waldmann, θ_k the thermal diffusion coefficients, $\boldsymbol{d}_k = (\nabla p_k - \rho_k z_k(\boldsymbol{E} + \boldsymbol{v}\wedge\boldsymbol{B}))/p$ the diffusion driving forces, ρ_k the species mass densities and T the absolute temperature.

2.3. Transport linear systems and asymptotic expansions

The Chapman–Enskog method requires solving systems of linearized integral Boltzmann equations with constraints through a Galerkin variational procedure. Various variational approximation spaces can be used as reduced spaces [15] or spaces for a direct evaluation of the thermal conductivity and the thermal diffusion ratios [16]. The successive approximations in the Chapman–Enskog expansion of transport coefficients are still known to converge more slowly in plasmas than in neutral mixtures [3, 5, 7, 14]. The transport linear systems are also naturally obtained in their symmetric form [11, 15, 17, 21, 42, 43]. The linear system associated with any coefficient μ then takes on either a regular form or a singular form [15, 24, 26, 27]. Only the latter singular form is discussed in this paper and can be written as

$$\begin{aligned} G\alpha &= \beta, \\ \langle \alpha, \mathcal{G}\rangle &= 0, \end{aligned} \tag{4}$$

where $G \in \mathbb{R}^{\omega,\omega}$, $\alpha, \beta, \mathcal{G} \in \mathbb{R}^{\omega}$, ω is the dimension of the variational space and the coefficient is obtained with a scalar product $\mu = \langle \alpha, \beta'\rangle$ [15, 21]. The matrix G is symmetric positive semi-definite, its nullspace is one dimensional $N(G) = \mathbb{R}\mathcal{N}$, $\beta \in R(G)$ and the well-posedness condition $N(G) \oplus \mathcal{G}^{\perp} = \mathbb{R}^{\omega}$ holds [15].

The sparse transport matrix $db(G)$ is a submatrix [15] composed of diagonals of blocks of G, and $2db(G) - G$ and $db(G)$ are symmetric positive definite for $n \geqslant 3$. The solution of the transport linear system can then be obtained either from the symmetric positive definite system $(G + \mathcal{G}\otimes\mathcal{G})\alpha = \beta$ or from iterative techniques. The iterative techniques are either generalized conjugate gradients or stationary techniques associated with a splitting $G = M - W$, $M = db(G)$ and yield $\alpha = \sum_{0\leqslant j<\infty}(PT)^j PM^{-1}P^t\beta$, where $T = M^{-1}W$ and $P = I - \mathcal{N}\otimes\mathcal{G}/\langle\mathcal{N},\mathcal{G}\rangle$. The matrix $M + W = 2db(G) - G$ must be positive definite but this is a consequence from Boltzmann linearized equations. These stationary and generalized conjugate gradients methods have been found to be efficient for mixture of neutral gases [18–20] and the situation of ionized mixtures is discussed in [22, 25, 26, 28] and in section 5.

3. Transport coefficients in strong magnetic fields

The kinetic theory of gases in strong magnetic fields has been investigated by numerous authors [3, 5, 7, 11, 21, 26, 27, 32]. The main difference from the previous regime is that the magnetic force term $(\boldsymbol{c}_k - \boldsymbol{v})\wedge\boldsymbol{B}\cdot\nabla_{\boldsymbol{c}_k} f_k$ is now taken into account at the zeroth order. The natural time variation of this term is indeed the inverse of the gyrofrequency which may be of the same order as the collision time. Even though the equilibrium distributions are still Maxwellian distributions, the resulting transport fluxes are anisotropic. Many properties obtained in the isotropic case have been generalized to the situation of strong magnetic fields. New symmetry properties have recently been obtained as well as the mathematical structure of the linear systems with iterative algorithms [26, 27].

3.1. Boltzmann equations

For mixtures of polyatomic ionized reactive gases, semiclassical Boltzmann equations are typically written in the form

$$\begin{aligned} &\partial_t f_k + \boldsymbol{c}_k\cdot\nabla f_k + \tilde{\boldsymbol{b}}_k\cdot\nabla_{\boldsymbol{c}_k} f_k + \frac{1}{\epsilon}(\boldsymbol{c}_k - \boldsymbol{v})\wedge\boldsymbol{B}\cdot\nabla_{\boldsymbol{c}_k} f_k \\ &\quad = \frac{1}{\epsilon}\mathcal{J}_k + \epsilon^{\alpha}\mathcal{R}_k, \qquad k \in \mathcal{S}, \end{aligned} \tag{5}$$

where $\tilde{\boldsymbol{b}}_k = \boldsymbol{g} + z_k(\boldsymbol{E} + \boldsymbol{v}\wedge\boldsymbol{B})$. The integro-differential Boltzmann equations are solved with an Enskog expansion and the fluid macroscopic equations are obtained. The transport fluxes obtained in strong magnetic fields are then nonisotropic.

3.2. Examples of transport fluxes

The viscous tensor derived in this regime is in the form

$$\begin{aligned} \boldsymbol{\Pi} = &-\kappa\nabla\cdot\boldsymbol{v}\mathbb{I} - \eta_1\mathbf{S} - \eta_2(\boldsymbol{R}^{\mathcal{B}}\mathbf{S} - \mathbf{S}\,\boldsymbol{R}^{\mathcal{B}}) \\ &-\eta_3(-\boldsymbol{R}^{\mathcal{B}}\mathbf{S}\,\boldsymbol{R}^{\mathcal{B}} + \langle\mathbf{S}\mathcal{B},\mathcal{B}\rangle\,\mathcal{B}\otimes\mathcal{B}) \\ &-\eta_4(\mathbf{S}\,\mathcal{B}\otimes\mathcal{B} + \mathcal{B}\otimes\mathcal{B}\,\mathbf{S} - 2\langle\mathbf{S}\mathcal{B},\mathcal{B}\rangle\,\mathcal{B}\otimes\mathcal{B}) \\ &-\eta_5(\mathcal{B}\otimes\mathcal{B}\,\mathbf{S}\,\boldsymbol{R}^{\mathcal{B}} - \boldsymbol{R}^{\mathcal{B}}\,\mathbf{S}\,\mathcal{B}\otimes\mathcal{B}), \end{aligned} \tag{6}$$

where $\mathbf{S} = (\nabla\boldsymbol{v} + \nabla\boldsymbol{v}^t) - \frac{2}{3}(\nabla\cdot\boldsymbol{v})\,\mathbb{I}$ is the strain rate tensor, $\mathcal{B} = \boldsymbol{B}/\|\boldsymbol{B}\|$, $\boldsymbol{R}^{\mathcal{B}}$ the rotation matrix $\boldsymbol{R}^{\mathcal{B}}\boldsymbol{x} = \mathcal{B}\wedge\boldsymbol{x}$, κ the volume viscosity and $\eta_1, \ldots, \eta_5$ the shear viscosities. Denoting the auxiliary vectors associated with $\boldsymbol{x} \in \mathbb{R}^3$ by $\boldsymbol{x}^{\parallel} = (\mathcal{B}\cdot\boldsymbol{x})\mathcal{B}$, $\boldsymbol{x}^{\perp} = \boldsymbol{x} - \boldsymbol{x}^{\parallel}$, and $\boldsymbol{x}^{\odot} = \mathcal{B}\wedge\boldsymbol{x}$, the species diffusion velocities are in the form

$$\begin{aligned} \mathcal{V}_i = &-\sum_{j\in\mathcal{S}}(D_{ij}^{\parallel}\boldsymbol{d}_j^{\parallel} + D_{ij}^{\perp}\boldsymbol{d}_j^{\perp} + D_{ij}^{\odot}\boldsymbol{d}_j^{\odot}) \\ &-(\theta_i^{\parallel}(\nabla\log T)^{\parallel} + \theta_i^{\perp}(\nabla\log T)^{\perp} + \theta_i^{\odot}(\nabla\log T)^{\odot}). \end{aligned} \tag{7}$$

The resulting multicomponent diffusion coefficients parallel $D_{ij}^{\parallel}$, perpendicular $D_{ij}^{\perp}$ and transverse $D_{ij}^{\odot}$ to the magnetic field are symmetric and the entropy production associated with all dissipative effects has been shown to be positive [26, 27]. The perpendicular and transverse transport coefficients are conveniently evaluated in a complex framework and complex Stefan–Maxwell equations have also been obtained [11, 21, 26, 27].

3.3. Transport linear systems and asymptotic expansions

The linear systems associated with transport coefficients parallel to the magnetic field are similar to the isotropic systems already discussed in section 2. We investigate here only the linear systems associated with transport coefficients perpendicular or transverse to the magnetic field. These transport linear systems are obtained by using a Hermitian Galerkin solution of the linearized Boltzmann equations. These systems are complex since vector products with the magnetic field have been transformed into multiplication by imaginary numbers and take on either a regular or a singular form [15, 24, 26, 27]. Only the latter is addressed in this section and reads as

$$\begin{aligned} (G + \mathrm{i}G')\alpha &= \beta, \\ \langle \alpha, \mathcal{G} \rangle &= 0, \end{aligned} \tag{8}$$

where $G, G' \in \mathbb{R}^{\omega,\omega}$, $\alpha \in \mathbb{C}^{\omega}$, $\beta, \mathcal{G} \in \mathbb{R}^{\omega}$, and the corresponding transport coefficient is obtained with one scalar product $\mu^{\perp} + \mathrm{i}\mu^{\odot} = \langle \alpha, \beta' \rangle$. The matrix G and the constraint vector $\mathcal{G}$ are as in the isotropic case and $G' = Q\mathcal{D}'P$ where $\mathcal{D}'$ is diagonal, $Q = \mathbb{I} - \mathcal{G}\otimes\mathcal{N}/\langle \mathcal{G}, \mathcal{N} \rangle$ and $P = \mathbb{I} - \mathcal{N}\otimes\mathcal{G}/\langle \mathcal{G}, \mathcal{N} \rangle$. In particular $N(G + \mathrm{i}G') = \mathbb{C}\mathcal{N}$, the well-posedness property $N(G + \mathrm{i}G') \oplus \mathcal{G}^{\perp} = \mathbb{C}^{\omega}$ holds and $\beta \in R(G + \mathrm{i}G')$. The iterative techniques already available for weak magnetic fields have been extended to the anisotropic case, either of the generalized conjugate gradient type or of the stationary type [26, 27]. In particular, upon introducing the splitting $G + \mathrm{i}G' = M - W$, where $M = db(G) + \mathrm{diag}(\sigma_1, \ldots, \sigma_\omega) + \mathrm{i}G'$ is easily invertible, and the iteration matrix $\mathcal{T} = M^{-1}W$, we have $\alpha = \sum_{0 \leqslant j < \infty} (P\mathcal{T})^j P M^{-1} P^t \beta$. The advantage of these algorithms is that their convergence properties are never worse in the magnetized case $B \neq 0$.

4. Transport coefficients in a two-temperature plasma

Many authors have investigated the kinetic theory of nonequilibrium plasmas, either weakly magnetized or strongly magnetized [4, 12, 13, 35, 37, 40]. The most general thermodynamic nonequilibrium model is the state to state model where each internal state of a molecule is independent and considered as a separate species [9, 10, 33, 38, 41]. When there are partial equilibria between some of these states, species internal energy temperatures can be defined and the complexity of the model is correspondingly reduced [10, 38]. This is notably the case when vibrational temperatures are defined for each polyatomic species, aside from an electronic temperature and a translational–rotational temperature. The next reduction step then consists of equating some of the species internal temperatures or the translational temperature and it yields notably the two-temperature plasma model discussed in this section. In this framework, a multiscale second order kinetic theory derivation has recently been obtained [29].

4.1. Boltzmann equations

The Boltzmann equations in a two-temperature plasma are typically in the form [29]

$$\partial_t f_k + \boldsymbol{c}_k \cdot \boldsymbol{\nabla} f_k + \boldsymbol{b}_k \cdot \boldsymbol{\nabla}_{\boldsymbol{c}_k} f_k = \frac{1}{\epsilon}\left(\sum_{j \in \mathcal{H}} \mathcal{J}_{kj} + \frac{1}{\epsilon}\mathcal{J}_{ek} \right), \quad k \in \mathcal{H}, \tag{9}$$

$$\partial_t f_{\mathrm{e}} + \frac{1}{\epsilon}\boldsymbol{c}_{\mathrm{e}} \cdot \boldsymbol{\nabla} f_{\mathrm{e}} + \frac{1}{\epsilon}\tilde{\boldsymbol{b}}_{\mathrm{e}} \cdot \boldsymbol{\nabla}_{\boldsymbol{c}_{\mathrm{e}}} f_{\mathrm{e}} + \frac{1}{\epsilon^2}(\boldsymbol{c}_{\mathrm{e}} - \boldsymbol{v}_h) \wedge \boldsymbol{B} \cdot \boldsymbol{\nabla}_{\boldsymbol{c}_{\mathrm{e}}} f_{\mathrm{e}} = \frac{1}{\epsilon^2}\left(\sum_{j \in \mathcal{H}} \mathcal{J}_{\mathrm{e}j} + \mathcal{J}_{\mathrm{ee}} \right), \tag{10}$$

where $\mathcal{H}$ denotes the heavy species indexing set, e the electron, $\boldsymbol{b}_k = \boldsymbol{g} + z_k(\boldsymbol{E} + \boldsymbol{c}_k \wedge \boldsymbol{B})$, $k \in \mathcal{H}$ and $\tilde{\boldsymbol{b}}_{\mathrm{e}} = \boldsymbol{g} + z_{\mathrm{e}}(\boldsymbol{E} + \boldsymbol{v}_{\mathrm{h}} \wedge \boldsymbol{B})$. A multiscale Chapman–Enskog procedure is then used and requires to expand the collision operators the streaming operators and the collision invariants in powers of ϵ. The reference velocity must be that of the heavy species $\boldsymbol{v}_{\mathrm{h}}$ for a consistent theory. The macroscopic equations and the transport fluxes at $\mathcal{O}(\epsilon)$ order are then obtained with the corresponding transport linear systems [29].

4.2. Examples of transport fluxes

The heavy species viscous tensor in nonequilibrium flows is in the form

$$\boldsymbol{\Pi}_{\mathrm{h}} = -\kappa_{\mathrm{h}}(\boldsymbol{\nabla} \cdot \boldsymbol{v}_{\mathrm{h}})\mathbb{I} - \eta_{\mathrm{h}}(\boldsymbol{\nabla}\boldsymbol{v}_{\mathrm{h}} + (\boldsymbol{\nabla}\boldsymbol{v}_{\mathrm{h}})^t - \tfrac{2}{3}(\boldsymbol{\nabla} \cdot \boldsymbol{v}_{\mathrm{h}})\mathbb{I}), \tag{11}$$

where the subscript h is associated with the heavy species. The diffusion velocities of the heavy species $\boldsymbol{\mathcal{V}}_k$, $k \in \mathcal{H}$, are given by

$$\boldsymbol{\mathcal{V}}_k = -\sum_{l \in \mathcal{H}} D_{kl}\boldsymbol{d}_l - \theta_k \boldsymbol{\nabla} \log T_h, \qquad k \in \mathcal{H}, \tag{12}$$

where $\boldsymbol{d}_k = (\boldsymbol{\nabla} p_k - \rho_k z_k(\boldsymbol{E} + \boldsymbol{v}_{\mathrm{h}} \wedge \boldsymbol{B}) - \tilde{\boldsymbol{F}}_{k\mathrm{e}})/p_{\mathrm{h}}$ and $\tilde{\boldsymbol{F}}_{k\mathrm{e}}/p_{\mathrm{e}} = -\alpha^{\parallel}_{k\mathrm{e}}\boldsymbol{d}^{\parallel}_{\mathrm{e}} - \alpha^{\perp}_{k\mathrm{e}}\boldsymbol{d}^{\perp}_{\mathrm{e}} - \alpha^{\odot}_{k\mathrm{e}}\boldsymbol{d}^{\odot}_{\mathrm{e}} - \chi^{\parallel}_{k\mathrm{e}}\boldsymbol{\nabla}T^{\parallel}_{\mathrm{e}} - \chi^{\perp}_{k\mathrm{e}}\boldsymbol{\nabla}T^{\perp}_{\mathrm{e}} - \chi^{\odot}_{k\mathrm{e}}\boldsymbol{\nabla}T^{\odot}_{\mathrm{e}}$, $k \in \mathcal{H}$. In particular, there are no polarization effects for the heavy species. On the other hand, the electron viscous tensor vanishes $\boldsymbol{\Pi}_{\mathrm{e}} = 0$ and the electron diffusion velocity is in the form

$$\begin{aligned} \boldsymbol{\mathcal{V}}_{\mathrm{e}} = &-D^{\parallel}_{\mathrm{ee}}\boldsymbol{d}^{\parallel}_{\mathrm{e}} - D^{\perp}_{\mathrm{ee}}\boldsymbol{d}^{\perp}_{\mathrm{e}} - D^{\odot}_{\mathrm{ee}}\boldsymbol{d}^{\odot}_{\mathrm{e}} - \theta^{\parallel}_{\mathrm{e}}(\boldsymbol{\nabla}\log T_{\mathrm{e}})^{\parallel} \\ &-\theta^{\perp}_{\mathrm{e}}(\boldsymbol{\nabla}\log T_{\mathrm{e}})^{\perp} - \theta^{\odot}_{\mathrm{e}}(\boldsymbol{\nabla}\log T_{\mathrm{e}})^{\odot} \\ &- \sum_{i \in \mathcal{H}}(\alpha^{\parallel}_{i\mathrm{e}}\boldsymbol{d}^{2\parallel}_i + \alpha^{\perp}_{i\mathrm{e}}\boldsymbol{d}^{2\perp}_i + \alpha^{\odot}_{i\mathrm{e}}\boldsymbol{d}^{2\odot}_i), \end{aligned} \tag{13}$$

where $\boldsymbol{d}_{\mathrm{e}} = (\boldsymbol{\nabla} p_{\mathrm{e}} - \rho_{\mathrm{e}} z_{\mathrm{e}}(\boldsymbol{E} + v_{\mathrm{h}} \wedge \boldsymbol{B}))/p_{\mathrm{e}}$ and $\boldsymbol{d}^2_i = -n_i \boldsymbol{\mathcal{V}}_i$, $i \in \mathcal{H}$. The last term in (13) is a second order term required for a $\mathcal{O}(\epsilon)$ drift diffusion equation and has been termed the 'Kolesnikov effect' [29]. In the special situation $T_{\mathrm{h}} = T_{\mathrm{e}}$ these fluxes can be recovered from an equilibrium theory.

4.3. Transport linear systems and asymptotic expansions

The transport linear systems for the heavy species are identical to the isotropic systems of section 2 with $\mathcal{S}$ replaced by $\mathcal{H}$. All iterative techniques and asymptotic expansions can thus be used for nonequilibrium flows. The transport linear systems associated with electrons are small systems similar to the regular anisotropic case.

5. New algorithms

Iterative methods have led to fast and accurate evaluation of transport coefficients for nonionized mixtures [18–20]. Numerical experiments have shown that generalized conjugate gradient techniques perform as well for partially ionized mixtures, isotropic or anisotropic [25, 27, 28]. The convergence rates of stationary methods, however, deteriorate as the ionization level increases as established by García Muñoz [22, 27]. To solve this problem, new stationary algorithms have been introduced associated with *more singular* formulations of the linear systems [25]. We briefly describe in this section the more singular formulations in the situation of first order diffusion matrices D and refer to [25] for higher order diffusion matrices.

The n linear systems associated with first order diffusion are of size n and read as

$$\begin{cases} \Delta\alpha^{D_k} = \beta^{D_k}, \\ \langle \alpha^{D_k}, \mathsf{y} \rangle = 0, \end{cases} \qquad k \in \mathcal{S}, \tag{14}$$

and the diffusion coefficients are given by $D_{kl} = \langle \alpha^{D_k}, \beta^{D_l} \rangle$, $k, l \in \mathcal{S}$. The Stefan–Maxwell matrix Δ reads as $\Delta_{kk} = \sum_{l \in \mathcal{S}, l \neq k} \mathrm{X}_k \mathrm{X}_l / \mathcal{D}_{kl}$, $\Delta_{kl} = -\mathrm{X}_k \mathrm{X}_l / \mathcal{D}_{kl}$, $k, l \in \mathcal{S}$, $k \neq l$, where $\mathrm{X}_1, \ldots, \mathrm{X}_n$ are the species mole fractions and $\mathcal{D}_{kl}$, $k, l \in \mathcal{S}$, the species binary diffusion coefficients, and $\mathsf{y} = (\mathrm{Y}_1, \ldots, \mathrm{Y}_n)^t$ is the mass fractions vector [21, 23, 24]. The right-hand sides are $\beta^{D_k} = \mathsf{e}^k - \mathsf{y}$, $k \in \mathcal{S}$, where e^k, $k \in \mathcal{S}$, are the standard basis vectors of $\mathbb{R}^n$. We also have $D_{kl} = \alpha_l^{D_k} = \alpha_k^{D_l}$, $N(\Delta) = \mathbb{R}\mathsf{u}$, where $\mathsf{u} = (1, \ldots, 1)^t$, $N(D) = \mathbb{R}\mathsf{y}$ and $D = (\Delta + a\mathsf{y}\otimes\mathsf{y})^{-1} - (1/a)\mathsf{u}\otimes\mathsf{u}$ where $a > 0$ [19, 23].

Letting $\Delta = M - W$, where M is diagonal and $M_{kk} = \Delta_{kk}/(1 - \mathrm{Y}_k)$, $T = M^{-1}W$ and $P = Q^t = \mathbb{I} - \mathsf{u}\otimes\mathsf{y}$, we have $\Delta D = Q$ and the convergent asymptotic expansion

$$D = \sum_{0 \leqslant j < \infty} (PT)^j P M^{-1} P^t. \tag{15}$$

The projector P is needed in the expansion since the spectral radius of PT is strictly lower than unity whereas that of the iteration matrix T is unity [23]. The two terms expansion is especially interesting since it yields n^2 coefficients within $\mathcal{O}(n^2)$ operations [23, 24]. However, the convergence rate decreases when the ionization level increases [22, 25]. In order to improve the accuracy of the iterates (15) we define $\mathrm{Y}_c = \sum_{k \in \mathcal{I}} \mathrm{Y}_k$, where $\mathcal{I}$ denotes the set of ionized species, and the vector u_2 by $(\mathsf{u}_2)_k = 1 - \mathrm{Y}_c$ if $k \in \mathcal{I}$ and $(\mathsf{u}_2)_k = -\mathrm{Y}_c$ otherwise. Letting $\mathsf{y}_2 = \Delta\mathsf{u}_2$, $\Delta_2 = \Delta - \mathsf{y}_2\otimes\mathsf{y}_2/\langle \mathsf{u}_2, \mathsf{y}_2 \rangle$ $D_2 = D - \mathsf{u}_2\otimes\mathsf{u}_2/\langle \mathsf{u}_2, \mathsf{y}_2 \rangle$, where $Q_2 = Q - \mathsf{u}_2\otimes\mathsf{y}_2/\langle \mathsf{u}_2, \mathsf{y}_2 \rangle$, we have $\Delta_2 D_2 = Q_2$ and the nullspaces of Δ_2, D_2 and Q_2 are now two dimensional. We now set $\Delta_2 = M_2 - W_2$ where M_2 is diagonal and $(M_2)_{kk} = (\Delta_2)_{kk}/\big(1 - \mathrm{Y}_k - (\mathsf{y}_2)_k\big)$, $T_2 = M_2^{-1} W_2$, $P_2 = Q_2^t$ and we have the fast converging new expansion [25]

$$D = \frac{\mathsf{u}_2\otimes\mathsf{u}_2}{\langle \mathsf{u}_2, \mathsf{y}_2 \rangle} + \sum_{0 \leqslant j < \infty} (P_2 T_2)^j P_2 M_2^{-1} P_2^t. \tag{16}$$

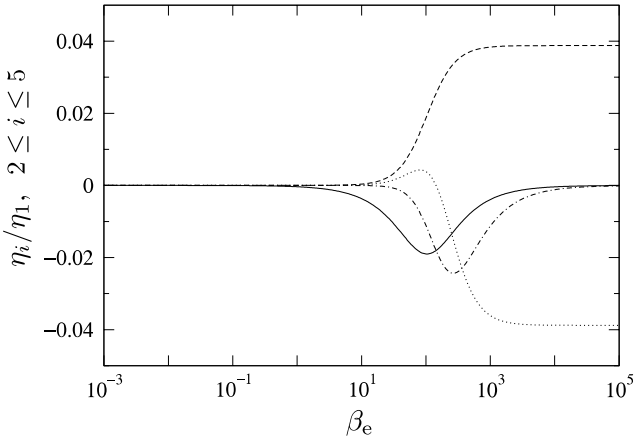

Figure 1. Reduced anisotropic viscosities η_i/η_1, $2 \leqslant i \leqslant 5$, in equilibrium air at $T = 10\,000$ K and $p = 0.1$ atm as functions of the electron Hall parameter β_e.

6. Numerical experiments

Numerical tests have been performed with equilibrium high temperature air at pressure $p = 0.1$ atm and temperature $T = 10\,000$ K. The corresponding mixture is constituted by the $n = 11$ species N_2, O_2, NO, N, O, N_2^+, O_2^+, NO^+, N^+, O^+ and e. Thermodynamic properties have been estimated from [30] and collision integrals from [44]. The rotational relaxation times for internal energy of the polyatomic ionized molecules have been approximated as the relaxation time of the corresponding neutral molecules [1].

6.1. Viscosities and electrical conductivities

The viscosities of equilibrium air are evaluated as functions of the intensity of the magnetic field B. The resulting reduced viscosities η_2/η_1, η_3/η_1, η_4/η_1 and η_5/η_1 are presented in figure 1 as functions of the electron Hall parameter $\beta_e = \omega_e\tau_e$ where ω_e denotes the electron Larmor frequency $\omega_e = eB/m_e$ and τ_e the Coulomb mean collision time $\tau_e = 3m_e/16\rho_e\Omega^{(1,1)}_{e,ion}$ [6]. The corresponding viscosity η_1 at $B = 0$ is $\eta_1 \approx 2.01 \times 10^{-3}\,\mathrm{K\,m^{-1}\,s^{-1}}$. We note that the ratios of η_i/η_1, $2 \leqslant i \leqslant 5$, are at most 0.05 and such values even require strong magnetic fields and very low pressures. This was to be expected since the heavy species Hall parameter is much smaller that the electron Hall parameter and in agreement with the two-temperature plasma model where anisotropy of the viscous tensor disappears.

In figure 2 the reduced electrical conductivities $\sigma^\perp/\sigma^\parallel$ and $\sigma^\odot/\sigma^\parallel$ are presented as functions of the electron Hall parameter β_e. The corresponding electrical conductivity parallel to the magnetic field is $\sigma^\parallel \approx 2866\,\mathrm{A\,V^{-1}\,m^{-1}}$. The electrical conductivities are evaluated from second order diffusion coefficients and the general trends in figure 2 are similar to that obtained by Bruno and co-workers for argon plasmas [6, 7]. The perpendicular and transverse coefficients change mainly when the electron Hall parameter is around unity and the electron trajectory is effectively perturbed by the magnetic field.

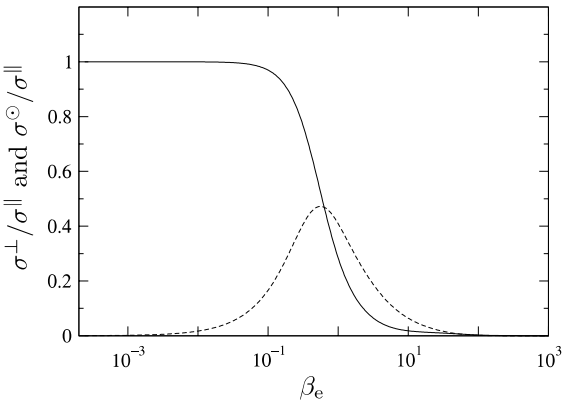

Figure 2. Reduced anisotropic electrical conductivities $\sigma^{\perp}/\sigma^{\parallel}$ and $\sigma^{\odot}/\sigma^{\parallel}$ in equilibrium air at $T = 10\,000$ K and $p = 0.1$ atm as functions of the electron Hall parameter β_e.

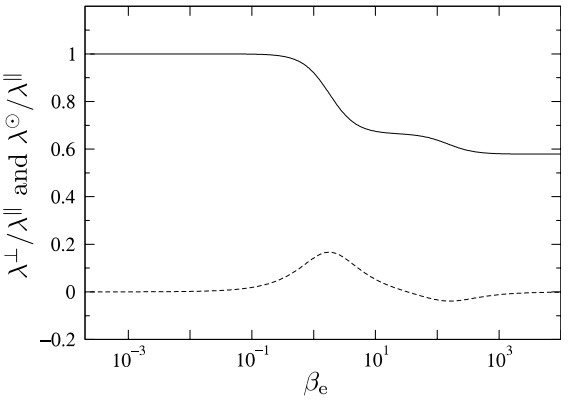

Figure 3. Reduced anisotropic thermal conductivities $\lambda^{\perp}/\lambda^{\parallel}$ and $\lambda^{\odot}/\lambda^{\parallel}$ in equilibrium air at $T = 10\,000$ K and $p = 0.1$ atm as functions of the electron Hall parameter β_e.

6.2. *Thermal conductivities*

The thermal conductivities of equilibrium air are evaluated as functions of the magnetic field B. The ratios $\lambda^{\perp}/\lambda^{\parallel}$ and $\lambda^{\odot}/\lambda^{\parallel}$ are presented in figure 3 as functions of the electron Hall parameter. The corresponding thermal conductivity parallel to the magnetic field is $\lambda^{\parallel} \approx 0.614\,\mathrm{W\,m^{-1}\,K^{-1}}$. The trends are globally similar to that of magnetized argon plasmas already investigated by Bruno *et al* [6, 7]. The transverse conductivity $\lambda^{\odot}$ reaches a positive maximum, next a negative minimum and then goes to zero as the intensity of the magnetic field increases.

We have finally considered a mixture of frozen and equilibrium air. The corresponding mole fractions are given by $X_k = (1-\delta)X_k^{\mathrm{fr}} + \delta X_k^{\mathrm{eq}}$, $k \in \mathcal{S}$, where X_k^{fr} and X_k^{eq} denote the kth species mole fraction in frozen and equilibrium air, respectively, and $0 \leqslant \delta \leqslant 1$ is the mixing ratio. The corresponding thermal conductivity λ is presented in figure 4 as a function of δ and the units are $\mathrm{W\,m^{-1}\,K^{-1}}$. We have also presented the thermal conductivity corresponding to the monoatomic approximation λ^{mon} as well as the same coefficient after application of the Euken corrective factor $\lambda^{\mathrm{euk}} = \lambda^{\mathrm{mon}}(1 + 4C^{\mathrm{int}}/15R)$, where C^{int} is the internal heat capacity per unit mole and R the perfect gas constant. This plot shows that the polyatomic effects

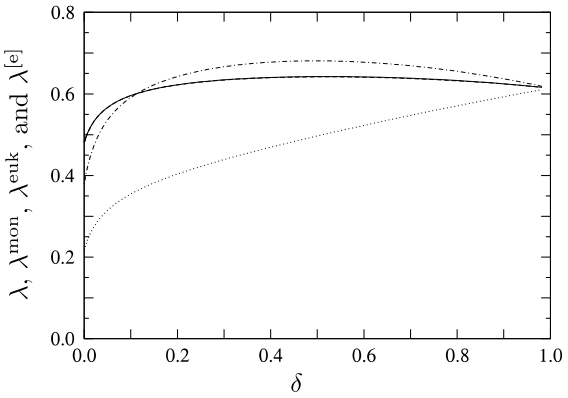

Figure 4. Thermal conductivities λ, λ^{mon}, λ^{euk} and $\lambda^{[e]}$ ($\mathrm{W\,m^{-1}\,K^{-1}}$) in a mixture of frozen and equilibrium air $T = 10\,000$ K and $p = 0.1$ atm as functions of the mixing ratio δ.

are of fundamental importance. Large errors result from the monoatomic model and even the Euken correction is not satisfactory. The only reduced model which yields a uniformly valid approximated thermal conductivity is the so-called total-energy approximation $\lambda^{[e]}$ where polynomials in the total energy are considered instead of splitting the particle energy between the kinetic and internal energy [15, 16]. The corresponding thermal conductivity is very close to λ with a relative error of the order of 10^{-3} and the two curves are nearly superposed in figure 4.

7. Conclusion and future work

Iterative methods are a powerful tool for evaluating multicomponent transport coefficients in partially ionized mixtures. Multitemperature kinetic theories should be generalized to polyatomic reactive gas mixtures taking into account electronic excited states [8, 34]. It is also of fundamental importance to obtain reliable thermodynamic, chemical and transport data over a wide temperature range for practical applications, in particular for collision integrals associated with internal energy exchange.

References

[1] Abe K, Kihara H, Uchida T and Nishida N 2002 Experimental and numerical studies of rotational relaxation behind a strong shock wave in air *Shock Waves* **11** 413–21
[2] Billet G, Giovangigli V and de Gassowski G 2008 Impact of volume viscosity on a shock/hydrogen bubble interaction *Combust. Theory Modelling* **12** 221–48
[3] Braginskii S I 1965 Transport processes in a plasma *Rev. Plasma Phys.* **1** 205–311
[4] Braginskii S I 1958 Transport phenomena in a completely ionized two-temperature plasma *Sov. Phys.—JETP* **6** 358–69
[5] Bruno D, Capitelli M and Dangola A 2003 Transport coefficients of partially ionized gases: a revisitation *AIAA Paper* AIAA-2003-4039
[6] Bruno D, Laricchiuta A, Capitelli M, Catalfamo C, Chikhaoui A, Kustova E V and Giordano D 2004 Transport properties of equilibrium argon plasma in a magnetic field *AIAA Paper* AIAA-2004-2161

[7] Bruno D, Catalfamo C, Laricchiuta A, Giordano D and Capitelli M 2006 Convergence of Chapman–Enskog calculation of transport coefficients of magnetized argon plasma *Phys. Plasmas* **13** 72307

[8] Bruno D, Laricchiuta A, Capitelli M and Catalfamo C 2006 Effect of electronic excited states on transport in magnetized hydrogen plasma *Phys. Plasmas* **13** 72307

[9] Capitelli M *et al* 2007 Non-equilibrium plasma kinetics: a state-to-state approach *Plasma Sources Sci. Technol.* **16** S30–44

[10] Colonna G, Armenise I, Bruno D and Capitelli M 2006 Reduction of state-to-state kinetics to macroscopic models in hypersonic flows *J. Thermophys. Heat Transfer* **20** 477–86

[11] Chapman S and Cowling T G 1970 *The Mathematical Theory of Non-uniform Gases* (Cambridge: Cambridge University Press)

[12] Chmieleski R M and Ferziger J H 1967 Transport properties of a nonequilibrium partially ionized gas *Phys. Fluids* **10** 364–71

[13] Daybelge U 1970 Unified transport theory of partially ionized nonisothemal plasmas *J. Appl. Phys.* **41** 2130–9

[14] Devoto R S 1966 Transport properties of ionized monatomic gases *Phys. Fluids* **9** 1230–40

[15] Ern A and Giovangigli V 1994 *Multicomponent Transport Algorithms* (*Lectures Notes in Physics, Series monographs* vol m24) (Berlin: Springer)

[16] Ern A and Giovangigli V 1995 Thermal conduction and thermal diffusion in dilute polyatomic gas mixtures *Physica* A **214** 526–46

[17] Ern A and Giovangigli V 1996 The structure of transport linear systems in dilute isotropic gas mixtures *Phys. Rev.* E **53** 485–92

[18] Ern A and Giovangigli V 1996 Optimized transport algorithms for flame codes *Combust. Sci. Technol.* **118** 387–95

[19] Ern A and Giovangigli V 1997 Projected iterative algorithms with application to multicomponent transport *Linear Algebra Appl.* **250** 289–315

[20] Ern A and Giovangigli V 1998 Thermal diffusion effects in hydrogen–air and methane–air flames *Combust. Theory Modelling* **2** 349–72

[21] Ferziger J H and Kaper H G 1972 *Mathematical Theory of Transport Processes in Gases* (Amsterdam: North-Holland)

[22] García Muñoz A 2007 Formulation of molecular diffusion in planetary atmospheres *Planet Space Sci.* **55** 1414–25

[23] Giovangigli V 1991 Convergent iterative methods for multicomponent diffusion *Impact Comput. Sci. Eng.* **3** 244–76

[24] Giovangigli V 1999 *Multicomponent Flow Modeling* (Boston, MA: Birkhäuser) erratum at http:\\cmap.polytechnique.fr\~giovangi

[25] Giovangigli V 2009 Multicomponent transport algorithms for partially ionized mixtures *Preprint 665* http://www.cmap.polytechnique.fr/preprint/

[26] Giovangigli V and Graille B 2003 Kinetic theory of partially ionized reactive gas mixtures *Physica* A **327** 313–48

[27] Giovangigli V and Graille B 2009 Kinetic theory of partially ionized reactive gas mixtures: II. *J. Phys. A: Math. Gen.* **42** 1–31

[28] Giovangigli V and Graille B 2009 Projected iterative algorithms for complex symmetric systems arising in magnetized multicomponent transport *Linear Algebra Appl.* **430** 1404–22

[29] Graille B, Magin T and Massot M 2009 Kinetic theory of plasmas: translational energy *Math. Mod. Meth. Appl. Sci.* **10** 1–2

[30] Gupta R N, Yos J M, Thomson R A and Lee K 1990 A review of reaction rates and thermodynamic and transport properties for an 11–species model for chemical and thermal nonequilibroum calculations to 30 000 K *NASA Ref. Publ.* **1232** 1–87

[31] Hirschfelder J O, Curtiss C F and Bird R B 1954 *Molecular Theory of Gases and Liquids* (New York: Wiley)

[32] Kaneko S 1960 Kinetic theory in a uniform magnetic fields *J. Phys. Soc. Japan* **15** 1685–90

[33] Kustova E V, Nagnibada E A and Chikhaoui A 2001 On the accuracy of nonequilibrium transport coefficients calculation *Chem. Phys.* **270** 459–69

[34] Kustova E V, Aliat A and Chikhaoui A 2001 Vibration-electronic and chemical kinetics of non-equilibrium radiative diatomic gas flows *Chem. Phys. Lett.* **344** 638–46

[35] Kolesnikov A F 1974 The equations of motion of a multicomponent partially ionized two-temperature mixture of gases in an electromagnetic filed with transport coeffficients in higher approximations *Technical Report* 1556, Moscow State University (in Russian)

[36] McCourt F R, Beenakker J J, Köhler W E and Kuščer I 1990 and 1991 *Non-Equilibrium Phenomena in Polyatomic Gases* vol I and II (Oxford: Clarendon)

[37] Magin T E and Degrez G 2004 Transport properties of partially ionized and unmagnetized plasmas *Phys. Rev.* E **70** 046412

[38] Nagnibeda E A and Kustova E A 2003 *Kinetic Theory of Transport and Relaxation Processes in Non-Equilibrium Reacting Flows* (Saint Petersburg: Saint Petersburg University Press) (in Russian) Engl. transl. 2009 (Berlin: Springer)

[39] Monchick L, Yun K S and Mason E A 1963 Formal kinetic theory of transport phenomena in polyatomic gas mixtures *J. Chem. Phys.* **39** 654–69

[40] Petit J P and Darrozes J S 1975 Une nouvelle formulation des équations du mouvement d'un gaz ionisé dans un régime dominé par les collisions *J. Méc.* **14** 745–59

[41] Rozhansky V A and Tsendin L D 2001 *Transport Phenomena in Partially Ionized Plasmas* (London: Taylor and Francis)

[42] Waldmann L 1958 Transporterscheinungen in Gasen von mittlerem Druck *Handbuch Phys.* **12** 295–514

[43] Waldmann L und Trübenbacher E 1962 Formale Kinetische Theorie von Gasgemischen aus Anregbaren Molekülen *Z. Naturf.* a **17** 363–76

[44] Wright M J, Bose D, Palmer G E and Levin E 2005 Recommended collision integrals for transport property computations: I. Air species *AIAA J.* **43** 2558–64