Multicomponent Transport in Polyatomic Reactive Gas Mixtures

Vincent Giovangigli

CMAP, CNRS, Ecole Polytechnique, 91128 Palaiseau cedex, France

Abstract. We investigate multicomponent reactive flow models derived from the kinetic theory of gases. We discuss in particular the conservation equations, the transport fluxes and the transport coefficients in weak and strong magnetic fields. The mathematical properties of the resulting hyperbolic-parabolic systems of partial differential equations modeling multicomponent flows are deduced from the underlying kinetic framework. The structure and solution of the transport linear systems associated with the evaluation of transport coefficients are also addressed. In particular, the convergence of iterative techniques is deduced from the properties of the linearized Boltzmann collision operator. The impact of multicomponent transport is also discussed, notably the importance of Soret effects in various flows and the impact of volume viscosity.

Keywords: Kinetic theory, Polyatomic gas mixtures, Reactive gases, Mathematical structure, Transport properties
PACS: 51.10.+y; 52.25.Fi; 47.70.Fw; 02.60.Dc

INTRODUCTION

Multicomponent reactive flows with complex chemistry and detailed transport phenomena arise in various engineering applications such as combustion [1, 2], crystal growth [3, 4], or atmospheric reentry [5, 6, 7]. This is the strong motivation for investigating the derivation and mathematical properties of the corresponding systems of partial differential equations as well as the numerical evaluation of transport coefficients and the impact of multicomponent transport.

MODELING POLYATOMIC REACTIVE GAS MIXTURES

Boltzmann equations

For mixtures of polyatomic ionized reactive gases, semiclassical Boltzmann equations are typically written in the form [7, 8, 9, 10, 11, 12, 13, 14, 15, 16]

$$\partial_t f_k + c_k \cdot \partial_x f_k + b_k \cdot \partial_{c_k} f_k = \frac{1}{\varepsilon} \mathscr{J}_k + \varepsilon^{\mathsf{a}} \mathscr{R}_k, \qquad k \in S, \tag{1}$$

where ∂_t denotes the time derivative, ∂_x the space derivative, ∂_{c_k} the derivative with repect to c_k, $S = \{1, \dots, n\}$ the species indexing set, n the number of species, ε the formal parameter associated with Enskog expansion, a the regime parameter, and for $k \in S$, f_k denotes the distribution function, c_k the particles velocity, $b_k = g + z_k(E + c_k \wedge B)$ the force per unit mass, g a species independent specific force, z_k the species charge per unit mass, E the electric field, B the magnetic field, and $\mathscr{J}_k$ and $\mathscr{R}_k$ the scattering and reactive collision operators [7, 16]. The details of the scattering and reactive terms are omitted and we refer to [7, 9, 14, 16, 17]. These collision terms $\mathscr{J}_k$ and $\mathscr{R}_k$ are conveniently written in terms of—degeneracy averaged—transition probabilities which satisfy reciprocity relations [7, 8, 9, 14, 16, 17]. Application of the Chapman-Enskog method yields the fluid conservation equations, thermochemistry properties, expressions for transport fluxes, and the transport linear systems [7, 8, 11, 12, 13, 15, 16].

We discuss in the following the transport fluxes and transport coefficients in the regimes $\mathsf{a} \in \{0, 1\}$ as well as the source terms obtained in the Maxwellian reaction regime $\mathsf{a} = 1$. The regime $\mathsf{a} = 0$ yields the same governing equations, transport fluxes and transport coefficients than for $\mathsf{a} = 1$ with the exception of a chemical pressure and perturbed source terms which are out the scope of present paper [7, 15, 16, 18]. The regime $\mathsf{a} = -1$ is the kinetic equilibrium regime [17, 19] whose equations and transport fluxes coincide with those obtained by superimposing chemical equilibrium in a nonequilibrium model but the transport coefficients differ quantitatively [17].

Conservation equations and transport fluxes

The equations for conservation of species mass, momentum and energy derived from the kinetic theory are in the form [9, 10, 15, 16]

$$\partial_t \rho_k + \partial_x \cdot (\rho_k v) + \partial_x \cdot (\rho_k \mathcal{V}_k) = m_k \omega_k, \qquad k \in S, \tag{2}$$

$$\partial_t(\rho v) + \partial_x \cdot (\rho v \otimes v + pI) + \partial_x \cdot \Pi = \sum_{k \in S} \rho_k b_k, \tag{3}$$

$$\partial_t(\mathcal{E} + \tfrac{1}{2}\rho v \cdot v) + \partial_x \cdot ((\mathcal{E} + \tfrac{1}{2}\rho v \cdot v + p)v) + \partial_x \cdot (Q + \Pi \cdot v) = \sum_{k \in S} \rho_k (v + \mathcal{V}_k) \cdot b_k, \tag{4}$$

where ρ_k denotes the mass density of the kth species, v the mass average flow velocity, $\mathcal{V}_k$ the diffusion velocity of the kth species, m_k the molar mass of the kth species, ω_k the molar production rate of the kth species, $\rho = \sum_{k \in S} \rho_k$ the total mass density, p the pressure, Π the viscous tensor, b_k the specific force acting on the kth species, $\mathcal{E}$ the internal energy per unit volume and Q the heat flux.

The transport fluxes Π, $\mathcal{V}_k$, $k \in S$, and Q due to macroscopic variable gradients can be written in the form [12, 15, 16]

$$\mathcal{V}_k = -\sum_{l \in S} D_{kl} d_l + \theta_k \partial_x \log T, \qquad k \in S, \tag{5}$$

$$\Pi = -\kappa(\partial_x \cdot v)I - \eta \left(\partial_x v + \partial_x v^t - \tfrac{2}{3}(\partial_x \cdot v)I \right), \tag{6}$$

$$Q = \sum_{k \in S} h_k \rho_k \mathcal{V}_k - \widehat{\lambda} \, \partial_x T - p \sum_{k \in S} \theta_k d_k, \tag{7}$$

where D_{kl}, $k, l \in S$, are the multicomponent diffusion coefficients, $d_k = (\partial_x p_k - \rho_k b_k)/p$, $k \in S$, the diffusion driving forces, $p_k = \rho_k R_g T / m_k$, $k \in S$, the partial pressures, κ the volume viscosity, η the shear viscosity, θ_k, $k \in S$, the thermal diffusion coefficients, $\widehat{\lambda}$ the partial thermal conductivity and ^{t} the transposition operator.

Properties of transport coefficients

The mathematical structure and properties of the transport coefficients may be obtained directly from the systems of integral equations satisfied by the perturbed distribution functions or equivalently from the transport linear systems discussed in the following [15]. The diffusion matrix is symmetric $D = D^t$, positive semi-definite, its nullspace is $N(D) = \mathbb{R}Y$ and the thermal diffusion coefficients $\theta = (\theta_1, \ldots, \theta_n)^t$, are such that $< \theta, Y > = 0$ where $Y_k = \rho_k/\rho$, $Y = (Y_1, \ldots, Y_n)^t$, and $<, >$ denotes the Euclidean scalar product. These symmetric diffusion coefficients have been introduced by Waldmann [8] and are more convenient than the non symmetric coefficients introduced by Hirschfelder, Curtiss, and Bird [20] as discussed by Van de Ree [21]. The partial thermal conductivity $\widehat{\lambda}$ and the shear viscosity η are positive, and the volume viscosity κ is nonnegative. Defining the thermal diffusion ratios $\chi = (\chi_1, \ldots, \chi_n)^t$ as the solution of the constrained system $D\chi = \theta$, $< \chi, u > = 0$, where $u = (1, \ldots, 1)^t$, and $\lambda = \widehat{\lambda} - (p/T) < D\chi, \chi >$, the thermal conductivity λ is positive. The diffusion velocities and the heat flux may conveniently be rewritten in terms of the thermal conductivity λ and the thermal diffusion ratios χ [8, 10, 12, 15] and it is also possible to introduce a variational framework for a direct evaluation of λ and χ [22].

Thermochemistry

Thermodynamics obtained from kinetic theory is valid out of equilibrium and coincides with classical thermodynamics written in terms of intensive variables. The internal energy per unit volume $\mathcal{E}$ and the pressure p are written as $\mathcal{E} = \sum_{k \in S} \rho_k e_k(T)$ and $p = \sum_{k \in S} R_g T \frac{\rho_k}{m_k}$ where T is the absolute temperature and R_g the gas constant. The internal energy e_k of the kth species is given by $e_k(T) = e_k^{\text{st}} + \int_{T^{\text{st}}}^T c_{vk}(\tau) d\tau$, $k \in S$, where e_k^{st} is the standard formation energy of the kth species at the standard temperature T^{st} and c_{vk} the constant volume specific heat of the kth species, which must be a positive function of $T \geq 0$ bounded away from zero. The (physical) entropy per unit volume $\mathcal{S}$ and the specific entropy of the kth species s_k may also be written in the form $\mathcal{S} = \sum_{k \in S} \rho_k s_k(T, \rho_k)$ with $s_k(T, \rho_k) = s_k^{\text{st}} + \int_{T^{\text{st}}}^T \frac{c_{vk}(T')}{T'} dT' - \frac{R_g}{m_k} \log\left(\frac{\rho_k}{\gamma^{\text{st}} m_k}\right)$, where s_k^{st} is the formation entropy of the kth species at the standard temperature T^{st} and standard pressure $p^{\text{st}} = p^{\text{atm}}$ and $\gamma^{\text{st}} = p^{\text{st}}/R_g T^{\text{st}}$ is the standard concentration.

A system of n^r elementary reactions involving n species may be written $\sum_{k\in S} v_{ki}^{\mathrm{d}} \mathfrak{M}_k \rightleftharpoons \sum_{k\in S} v_{ki}^{\mathrm{r}} \mathfrak{M}_k$, $i \in R$, where $\mathfrak{M}_k$ is the chemical symbol of the kth species, v_{ki}^{d} and v_{ki}^{r} the forward and backward stoichiometric coefficients of the kth species in the ith reaction, and $R = \{1,\dots,n^r\}$ the set of reaction indices. The macroscopic chemical production rates ω_k, $k \in S$, obtained in the Maxwellian reaction regime are compatible with the law of mass action and in the form

$$\omega_k = \sum_{i\in R}(v_{ki}^{\mathrm{r}} - v_{ki}^{\mathrm{d}})\tau_i, \quad k \in S, \qquad \tau_i = \mathscr{K}_i^{\mathrm{s}}\left(\exp < \mu, v_i^{\mathrm{d}} > - \exp < \mu, v_i^{\mathrm{r}} >\right), \quad i \in R,$$

where, for each reaction i, τ_i is the rate of progress, of the ith reaction, $\mathscr{K}_i^{\mathrm{s}}$ the symmetric rate constant, $v_i^{\mathrm{d}} = (v_{1i}^{\mathrm{d}},\dots,v_{ni}^{\mathrm{d}})^t$ and $v_i^{\mathrm{r}} = (v_{1i}^{\mathrm{r}},\dots,v_{ni}^{\mathrm{r}})^t$ the reaction vectors, and $\mu = (\mu_1,\dots,\mu_n)^t$, where $\mu_k = m_k g_k/R_{\mathrm{g}}T$ is the reduced molar Gibbs function of the kth species. Upon decomposing τ_i between the forward and backward contributions we have $\tau_i = \mathscr{K}_i^{\mathrm{d}}\prod_{l\in S}\left(\frac{\rho_l}{m_l}\right)^{v_{li}^{\mathrm{d}}} - \mathscr{K}_i^{\mathrm{r}}\prod_{l\in S}\left(\frac{\rho_l}{m_l}\right)^{v_{li}^{\mathrm{r}}}$ and the reaction constants $\mathscr{K}_i^{\mathrm{d}}$ and $\mathscr{K}_i^{\mathrm{r}}$ are Maxwellian averaged values of molecular chemical transition probabilities. The classical relation $\mathscr{K}_i^{\mathrm{d}}(T) = \mathscr{K}_i^{\mathrm{e}}(T)\mathscr{K}_i^{\mathrm{r}}(T)$—where $\mathscr{K}_i^{\mathrm{e}}(T)$ is the so called equilibrium constant—is thus a consequence of the reciprocity relations between reactive transition probabilities [15, 16].

From the Gibbs relation $T\,\mathbb{D}\mathscr{S} = \mathbb{D}\mathscr{E} - \sum_{k\in S}g_k\mathbb{D}\rho_k$, where $\mathbb{D}$ denotes the total derivative, one can derive a governing equation for $\rho s = \mathscr{S}$

$$\partial_t(\rho s) + \partial_x\cdot(\rho v s) + \partial_x\cdot\left(\frac{Q}{T} - \sum_{k\in S}\frac{g_k\rho_k\mathscr{V}_k}{T}\right) = \frac{\kappa}{T}(\partial_x\cdot v)^2 + \frac{\eta}{2T}\left|\partial_x v + \partial_x v^t - \frac{2}{3}(\partial_x\cdot v)I\right|^2 + \frac{\lambda}{T^2}|\partial_x T|^2$$

$$+\frac{p}{T}\sum_{k,l\in S}D_{kl}\left(d_k + \chi_k\partial_x\log T\right)\cdot\left(d_l + \chi_l\partial_x\log T\right) + \sum_{i\in R}R_{\mathrm{g}}\mathscr{K}_i^{\mathrm{s}}\left(\langle\mu,v_i^{\mathrm{d}}\rangle - \langle\mu,v_i^{\mathrm{r}}\rangle\right)\left(\exp\langle\mu,v_i^{\mathrm{d}}\rangle - \exp\langle\mu,v_i^{\mathrm{r}}\rangle\right),$$

where we have defined $|A|^2 = A : A$ for a matrix A and $|a|^2 = a\cdot a$ for a vector a. Entropy production therefore appears as a sum of nonnegative terms as for the underlying kinetic model and the fluid and kinetic entropy coincide up to second order [11, 12, 16, 23, 24, 25].

THE CAUCHY PROBLEM

The equations governing multicomponent reactive flows have local smooth solutions [26] and global solutions around constant equilibrium states [27]. A major ingredient in order to establish these results is symmetrization which results from the properties of the system coefficients extracted from the kinetic theory of gases [16, 26, 27].

Entropy and symmetrization

Denoting by U the conservative variable $U = \left(\rho_1,\dots,\rho_n, \rho v_1,\dots,\rho v_d, \mathscr{E} + \frac{1}{2}\rho v\cdot v\right)^t$ the governing equation can be recast in the compact form

$$\partial_t U + \sum_{i\in C}A_i(U)\partial_i U = \sum_{i,j\in C}\partial_i\left(B_{ij}(U)\partial_j U\right) + \Omega(U), \tag{8}$$

where ∂_i the space derivative operator in the ith direction, $C = \{1,\dots,d\}$ the set of direction indices, $d \geq 1$ the space dimension, $A_i(U) = \partial_U F_i^c$ the jacobian matrix of the convective fluxes F_i^c in the ith direction, B_{ij}, $i,j \in C$, the dissipation matrices such that $\mathscr{F}_i = -\sum_{j\in C}B_{ij}(U)\partial_j U$, $i \in C$, is the dissipative flux in the ith direction, and Ω the source term. All the system coefficients $A_i(U)$, $i \in C$, $B_{ij}(U)$, $i,j \in C$, are smooth functions of U on an open convex set $\mathscr{O}_U$. Symmetrization of second order dissipative systems generalize the classical results about hyperbolic systems and can be applied to the system of equations governing multicomponent flows [27].

We define the entropic variable by $V = -\left(\partial_U\mathscr{S}\right)^t = (1/T)\left(g_1 - \frac{1}{2}v\cdot v,\dots, g_n - \frac{1}{2}v\cdot v, v_1,\dots,v_d,-1\right)^t$ where g_k, $k \in S$, are the species Gibbs functions, and $U \to V$ is a C^∞ diffeomorphism. The corresponding governing equations can be written

$$\widetilde{A}_0(V)\partial_t V + \sum_{i\in C}\widetilde{A}_i(V)\partial_i V = \sum_{i,j\in C}\partial_i\left(\widetilde{B}_{ij}(V)\partial_j V\right) + \widetilde{\Omega}(V), \tag{9}$$

where $\widetilde{A}_0 = \partial_V U$, $\widetilde{A}_i = A_i\widetilde{A}_0$, $\widetilde{B}_{ij} = B_{ij}\widetilde{A}_0$, $\widetilde{\Omega} = \Omega$, and $\widetilde{A}_0$ is symmetric positive definite, $\widetilde{A}_i$, $i \in C$, are symmetric, we have the reciprocity relations $\widetilde{B}_{ij}^t = \widetilde{B}_{ji}$, $i,j \in C$, and $\widetilde{B} = \sum_{i,j\in C}\widetilde{B}_{ij}w_i w_j$ is symmetric positive semidefinite for w in the sphere Σ^{d-1} and $V \in \mathscr{O}_V$ [27]. The reciprocity relations $\widetilde{B}_{ij}^t = \widetilde{B}_{ji}$, $i,j \in C$, are direct consequences of symmetry properties of the transport coefficients and thus of symmetry properties of transition probabilities. Similarly, the positivity properties of $\widetilde{B}$ results from that of the linearized Boltzmann collision operator.

Normal forms and existence of solutions

The symmetrized system can next be rewritten into a normal form where hyperbolic and parabolic variables are split [27, 28, 29]. We consider the normal variable $W = \left(\rho, \log(\rho_2^{r_2}/\rho_1^{r_1}), \ldots, \log(\rho_n^{r_n}/\rho_1^{r_1}), v_1, \ldots, v_d, T \right)^t$ where $r_k = R_{\mathrm{g}}/m_k$ and $V \longmapsto W$ is a C^∞ diffeomorphism. The equations in the W variable obtained by the change of variable $V = V(W)$ and upon multiplying on the left hand side by the jacobian matrix $\partial_W V^t$ can be written

$$\overline{A}_0(W)\partial_t W + \sum_{i \in C}\overline{A}_i(W)\partial_i W = \sum_{i,j \in C}\partial_i\left(\overline{B}_{ij}(W)\partial_j W\right) + \overline{\mathscr{T}}(W,\partial_x W) + \overline{\Omega}(W), \qquad (10)$$

with $\overline{A}_0 = \partial_W V^t \widetilde{A}_0 \partial_W V$, $\overline{B}_{ij} = \partial_W V^t \widetilde{B}_{ij} \partial_W V$, $\overline{A}_i = \partial_W V^t \widetilde{A}_i \partial_W V$, $\overline{\mathscr{T}} = -\sum_{i,j \in C}\partial_i(\partial_W V^t)(\widetilde{B}_{ij}\partial_W V)\partial_j W$, and $\overline{\Omega} = \partial_W V^t \widetilde{\Omega}$. Introducing the partition $\mathit{I} = \{1\}$ and $\mathit{II} = \{2,\ldots,n+d+1\}$, we have the block structure $W_I = (\rho)$, $W_{II} = \left(\log(\rho_2^{r_2}/\rho_1^{r_1}), \ldots, \log(\rho_n^{r_n}/\rho_1^{r_1}), v_1, \ldots, v_d, T\right)^t$, $\overline{A}_0 = \begin{pmatrix} \overline{A}_0^{II} & 0 \\ 0 & \overline{A}_0^{II\!I\!I} \end{pmatrix}$, and $\overline{B}_{ij} = \begin{pmatrix} 0 & 0 \\ 0 & \overline{B}_{ij}^{II\!I\!I} \end{pmatrix}$. The matrix $\overline{B}^{II\!I\!I} = \sum_{i,j \in C}\overline{B}_{ij}^{II\!I\!I}w_i w_j$ is positive definite and we have $\overline{\mathscr{T}}(W,\partial_x W) = \left(0, \overline{\mathscr{T}}_{II}(W,\partial_x W_{II})\right)^t$. The resulting system thus appears as a composite system symmetric-hyperbolic in the W_I variable and symmetric-strongly parabolic in the W_{II} variable and it is possible to characterize all possible such normal forms [27]. Using the normal form of the system of partial differential equations, it is then possible to obtain local existence of solutions [26, 30] as well as global solutions around constant equilibrium states and asymptotic stability [27, 28].

Let us consider—as a typical example—the existence of global solutions around equilibrium states in the absence of forces acting on the species. The existence of equilibrium points is first a consequence of the Gibbsian structure of thermochemistry [16]. Typically, for $T^e > 0$ and $(\rho_1^c, \ldots, \rho_n^c)^t \in (0,\infty)^n$, there exists a unique equilibrium point U^e with $v_i^e = 0$, $i \in C$, and $(\rho_1^e - \rho_1^c, \ldots, \rho_n^e - \rho_n^c)^t \in \mathrm{Span}\{Mv_i, \ i \in R\}$ where $v_i = v_i^{\mathrm{r}} - v_i^{\mathrm{d}}$, $i \in R$, and $M = \mathrm{diag}(m_1, \ldots, m_n)$. It is then necessary to establish a number of mathematical statements—omitted for the sake of brevity—on the local dissipativity properties of the system in normal form. The linearized source term $\overline{L}(W^e) = -\partial_W\overline{\Omega}(W^e)$ at equilibrium W^e is notably symmetric positive semidefinite as a consequence of symmetry properties of reactive transition probabilities. The linearized normal form is also strictly dissipative, i.e., the eigenvalues $\lambda(\zeta,w)$ of the problem $\lambda\overline{A}_0(W^e)\phi + [\mathrm{i}\zeta\sum_{i \in C}\overline{A}_i(W^e)w_i + \zeta^2\sum_{i,j \in C}\overline{B}_{ij}(W^e)w_i w_j + \overline{L}(W^e)]\phi = 0$, for $\zeta \in \mathbb{R}\setminus\{0\}$, $\mathrm{i}^2 = -1$, and $w \in \Sigma^{d-1}$, have a negative real part. Then for $d \geq 1$, $l \geq [d/2] + 2$ and $W^0(x)$ such that $\|W^0 - W^e\|_{H^l}$ is small enough—where H^l is the lth Sobolev space—the Cauchy problem with initial conditions $W(0,x) = W^0(x)$ has a global solution such that $W_I - W_I^e \in C^0\left([0,\infty);H^l\right) \cap C^1\left([0,\infty);H^{l-1}\right)$ and $W_{II} - W_{II}^e \in C^0\left([0,\infty);H^l\right) \cap C^1\left([0,\infty);H^{l-2}\right)$, $\sup_{\mathbb{R}^d}|W(t) - W^e|$ goes to zero as $t \to \infty$, and it is also possible to establish decay estimates [27].

Similar techniques may be applied to systems of partial differential equations modeling flows in total vibrational disequilibrium [26], flows in partial chemical equilibrium [31], as well as ambipolar plasmas [32], It is also possible to investigate local in time solutions [30] as well as one dimensional traveling waves [16, 33]. More precise properties may also be required as for instance the sharp diffusion inequality $\delta\sum_{k \in S}\frac{x_k^2}{Y_k} \leq \frac{p}{T}\sum_{k,l \in S}x_k x_l D_{kl} \leq \frac{1}{\delta}\sum_{k \in S}\frac{x_k^2}{Y_k}$ valid for δ small enough and any $x \in \mathbb{R}^n$ such that $\langle x, \mathsf{u}\rangle = 0$, required in the study of deflagration waves [16], It is also possible to investigate Enskog expansion of Boltzmann entropy and to establish related entropicity properties [24, 25].

MAGNETIZED FLOWS

Boltzmann equations

The kinetic theory of gases in strong magnetic fields has been investigated by numerous authors [6, 11, 12, 34, 35, 36, 37, 38, 39]. In strong magnetic fields, semiclassical Boltzmann equations are typically written in the form

$$\partial_t f_k + c_k \cdot \partial_x f_k + \widetilde{b}_k \cdot \partial_{c_k} f_k + \frac{1}{\varepsilon}(c_k - v)\wedge B \cdot \partial_{c_k} f_k = \frac{1}{\varepsilon}\mathscr{J}_k + \varepsilon^{\mathrm{a}}\mathscr{R}_k, \qquad k \in S, \qquad (11)$$

where $\widetilde{b}_k = g + z_k(E + v\wedge B)$ and the magnetic force term $(c_k - v)\wedge B \cdot \partial_{c_k} f_k$ 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 than the collision time. Application of the Chapman-Enskog method to mixtures of magnetized polyatomic gas mixtures has been recently revisited in [38, 39]. New expansions for the perturbed distributions functions have been introduced, new symmetry properties have been established as well as simplified bracket expressions.

Conservation equations and transport fluxes

The conservation equations, completed by Maxwell's equations, are in the form

$$\partial_t \rho_i + \partial_x \cdot (\rho_i v) + \partial_x \cdot (\rho_i \mathscr{V}_i) = m_i \omega_i, \quad i \in S, \tag{12}$$

$$\partial_t (\rho v) + \partial_x \cdot (\rho v \otimes v + p \mathbb{I}) + \partial_x \cdot \Pi = \rho g + \mathscr{Q}(E + v \wedge B) + J \wedge B, \tag{13}$$

$$\partial_t \big(\rho(e + \tfrac{1}{2}v \cdot v + \tfrac{1}{2}\varepsilon_0 E^2 + \tfrac{1}{2\mu_0}B^2)\big) + \partial_x \cdot \big(\rho(h + \tfrac{1}{2}v \cdot v + \tfrac{1}{2}\varepsilon_0 E^2 + \tfrac{1}{2\mu_0}B^2)\big) + \partial_x \cdot (Q + \Pi \cdot v + \tfrac{1}{\mu_0}E \wedge B) = \rho g \cdot v, \tag{14}$$

$$\partial_t B + \partial_x \wedge E = 0, \tag{15}$$

$$\varepsilon_0 \partial_t E - \tfrac{1}{\mu_0}\partial_x \wedge B + \mathscr{Q}v + J = 0. \tag{16}$$

where E denotes the electric field, B the magnetic field, $\mathscr{Q}$ the charge per unit volume and J the diffusive current. The viscous tensor derived in this regime is in the form

$$\Pi = -\kappa \partial_x \cdot v I - \eta_1 \mathbf{S} - \eta_2 \big(R^{\mathscr{B}} \mathbf{S} - \mathbf{S} R^{\mathscr{B}}\big) - \eta_3 \big(-R^{\mathscr{B}} \mathbf{S} R^{\mathscr{B}} + \langle \mathbf{S} \mathscr{B}, \mathscr{B} \rangle \mathscr{B} \otimes \mathscr{B}\big)$$

$$-\eta_4 \big(\mathbf{S} \mathscr{B} \otimes \mathscr{B} + \mathscr{B} \otimes \mathscr{B} \mathbf{S} - 2\langle \mathbf{S} \mathscr{B}, \mathscr{B} \rangle \mathscr{B} \otimes \mathscr{B}\big) - \eta_5 \big(\mathscr{B} \otimes \mathscr{B} \mathbf{S} R^{\mathscr{B}} - R^{\mathscr{B}} \mathbf{S} \mathscr{B} \otimes \mathscr{B}\big), \tag{17}$$

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

$$\mathscr{V}_i = -\sum_{j \in S} \big(D_{ij}^{\|} d_j^{\|} + D_{ij}^{\perp} d_j^{\perp} + D_{ij}^{\odot} d_j^{\odot}\big) - \big(\theta_i^{\|}(\partial_x \log T)^{\|} + \theta_i^{\perp}(\partial_x \log T)^{\perp} + \theta_i^{\odot}(\partial_x \log T)^{\odot}\big) \tag{18}$$

$$Q = \sum_{k \in S} h_k \rho_k \mathscr{V}_k - \big(\widehat{\lambda}^{\|}(\partial_x T)^{\|} + \widehat{\lambda}^{\perp}(\partial_x T)^{\perp} + \widehat{\lambda}^{\odot}(\partial_x T)^{\odot}\big) - p \sum_{k \in S} \big(\theta_k^{\|} d_k^{\|} + \theta_k^{\perp} d_k^{\perp} + \theta_k^{\odot} d_k^{\odot}\big). \tag{19}$$

The coefficients parallel, perpendicular, and transverse to the magnetic field are denoted by the superscript $\|$, $\perp$, and $\odot$, respectively. It can be established that the transport fluxes are smooth functions of B as $B \to 0$ [38, 39].

Properties of transport coefficients

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 new iterative algorithms [38, 39, 40]. The multicomponent diffusion matrices perpendicular $D^{\perp}$ and transverse $D^{\odot}$ to the magnetic field are symmetric positive semi-definite with nullspace $\mathbb{R}Y$ and the entropy production associated with dissipative effects has been shown to be positive [38, 39]. Note that some properties of these coefficients—in particular the expansion for small magnetic fields—are not intuitive and can only be obtained from the kinetic theory [38, 39]. The perpendicular and transverse transport coefficients are conveniently evaluated in a complex framework and complex Stefan-Maxwell equations have also been obtained [11, 12, 38, 39].

The mathematical structure and properties of the resulting system of partial differential equations is more complex than in the isotropic case. A new notion of mathematical entropy has been introduced as well as partial symmetrization properties, and local existence results have been obtained [41].

ASYMPTOTIC EXPANSIONS OF TRANSPORT COEFFICIENTS

Isotropic transport coefficients

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 [22]. The successive approximations in the Chapman-Enskog expansion of transport coefficients are still known to converge more slowly in plasmas than in neutral mixtures [6, 35, 37, 42]. The transport linear systems are also naturally obtained in their symmetric form [8, 10, 11, 12, 15, 43]. The linear system associated with any coefficient μ then take on either a

regular form or a singular form [15, 16]. The singular form can be written $G\alpha = \beta$, with the constraint $\langle \alpha, \mathscr{G} \rangle = 0$, where $G \in \mathbb{R}^{\omega,\omega}$, $\alpha, \beta, \mathscr{G} \in \mathbb{R}^{\omega}$, ω is the dimension of the variational space and the coefficient is obtained with a scalar product $\mu = \langle \alpha, \beta' \rangle$ [12, 15]. The matrix G is symmetric positive semi-definite, its nullspace is one dimensional $N(G) = \mathbb{R}\mathscr{N}$, $\beta \in R(G)$, and the well posedness condition $N(G) \oplus \mathscr{G}^{\perp} = \mathbb{R}^{\omega}$ 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 $n \geq 3$. All these properties can be deduced from the properties of the Boltzmann linearized collision operator and that of the variational approximation spaces [15].

The solution of the transport linear system can then be obtained either from the symmetric positive definite system $(G + \mathscr{G} \otimes \mathscr{G})\alpha = \beta$ 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 $\alpha = \sum_{0 \leq j < \infty} (PT)^j P M^{-1} P^t \beta$, where $T = M^{-1}W$ and $P = I - \mathscr{N} \otimes \mathscr{G} / \langle \mathscr{N}, \mathscr{G} \rangle$. 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 [44, 45, 46, 47].

The situation of ionized mixtures is more complex since the convergence rate of stationary iterative techniques deteriorate as the ionization level increases as discovered by García Muñoz [48]. On the contrary, the convergence properties of generalized conjugate gradient algorithms do not depend on the ionization level. New algorithms have been thus been introduced with *more singular* versions of the transport linear systems. These algorithms have led to fast convergence rates for all ionization levels and magnetic field intensities [40].

Nonisotropic transport coefficients

The linear systems associated with transport coefficients parallel to the magnetic field are similar to the isotropic systems already discussed. On the other hand, the linear systems associated with transport coefficients perpendicular or transverse to the magnetic field are obtained by using a Hermitian Galerkin solution of the linearized Bolztmann 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 [38, 39]. The singular form can be written $(G + iG')\alpha = \beta$, with the constraint $\langle \alpha, \mathscr{G} \rangle = 0$, where $G, G' \in \mathbb{R}^{\omega,\omega}$, $\alpha \in \mathbb{C}^{\omega}$, $\beta, \mathscr{G} \in \mathbb{R}^{\omega}$, and the corresponding transport coefficient is obtained with one scalar product $\mu^{\perp} + i\mu^{\odot} = \langle \alpha, \beta' \rangle$., where $\langle, \rangle$ denotes the Hemitian scalar product. The matrix G and the constraint vector $\mathscr{G}$ are as in the isotropic case and $G' = Q\mathscr{D}'P$ where $\mathscr{D}'$ is diagonal, $Q = \mathbb{I} - \mathscr{G} \otimes \mathscr{N} / \langle \mathscr{G}, \mathscr{N} \rangle$ and $P = \mathbb{I} - \mathscr{N} \otimes \mathscr{G} / \langle \mathscr{G}, \mathscr{N} \rangle$. In particular $N(G + iG') = \mathbb{C}\mathscr{N}$, the well posedness property $N(G + iG') \oplus \mathscr{G}^{\perp} = \mathbb{C}^{\omega}$ holds and $\beta \in R(G + iG')$. 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 [38, 39]. In particular, upon introducing the splitting $G + iG' = M - W$, where $M = db(G) + \text{diag}(\sigma_1, \dots, \sigma_{\omega}) + iG'$ is easily invertible, and the iteration matrix $\mathcal{T} = M^{-1}W$, we have $\alpha = \sum_{0 \leq j < \infty} (P\mathcal{T})^j P M^{-1} P^t \beta$. The interest of these algorithms is that their convergence properties are never worse in the magnetized case $B \neq 0$.

Two temperature plasmas

Many authors have investigated the kinetic theory of nonequilibrium plasmas, either weakly magnetized or strongly magnetized, [34, 35, 49, 50, 51, 52]. 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 [7, 53, 54, 55, 56]. 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 [54, 7]. The next reduction step then consists in equating some of the species internal temperatures or the translational temperature and it yields notably two-temperature plasma models. A multiscale second order kinetic theory derivation has recently been obtained [57].

In a two temperature plasma, the transport linear systems for the heavy species turn out to be identical to the isotropic systems with the set of species S replaced by the set of heavy species. All iterative techniques and asymptotic expansions can thus be used for nonequilibrium flows [40].

IMPACT OF MULTICOMPONENT TRANSPORT

Recent numerical investigations have brought further support for the importance of accurate transport property in various multicomponent reactive flows. Thermal diffusion effects have been shown to be important in the study of vortex-flame interaction, catalytic effects near walls, interfacial phenomena, gaseous or spray diffusion flames [58], and chemical vapor deposition reactors [4]. The impact of multicomponent diffusion has also been shown to be important in multidimensional hydrogen/air and methane/air Bunsen flames [47], in freely propagating flames—especially with oxygen as pure oxydizer—as well as in direct numerical simulation of turbulent flames.

Theoretical calculations and experimental measurements have also shown that the ratio κ/η is not small for polyatomic gases. Volume viscosity also arises in dense gases and in liquids, and its absence in dilute monatomic gases is an exception rather than a rule. Despite its potential importance, volume or bulk viscosity has seldom been included in computational models of multidimensional reactive flows [59]. For small Mach number flows, however, the whole term $\partial_x \cdot \left(\kappa (\partial_x \cdot v) I \right)$ has a weak influence because of its *structure*, even though both the ratio κ/η and the dilatation $\partial_x \cdot v$ may not be small [16]. However, it has been shown that volume viscosity has an important impact during a shock/hydrogen bubble interaction [60].

REFERENCES

1. F. A. Williams, *Combustion Theory*, Second ed., The Benjamin/Cummings Pub. Co. Inc., Melo park, (1985).
2. E. Oran and J. P. Boris, *Numerical Simulation of Reactive Flows*, Cambridge university press, 2001.
3. K. F. Roenigk and K. F. Jensen, Low Pressure CVD of Silicon Nitride, *J. Electrochem. Soc.*, **134** (1987), pp. 1777–1785.
4. A. Ern, V. Giovangigli and M. Smooke, Numerical Study of a Three-Dimensional Chemical Vapor Deposition Reactor with Detailed Chemistry, *J. Comp. Phys.*, **126**, (1996) pp. 21–39.
5. J. D. Anderson, Jr., *Hypersonics and High Temperature Gas Dynamics*, McGraw-Hill Book Company, New–York, (1989).
6. D. Bruno, M. Capitelli, and A. Dangola, Transport coefficients of partially ionized gases: A revisitation, AIAA Paper, AIAA-2003-4039, (2003).
7. E. Nagnibeda and E. Kustova, *Non-equilibrium reacting gas flow* Springer Verlag, Berlin, 2009.
8. L. Waldmann, Transporterscheinungen in Gasen von mittlerem Druck, *Handbuch der Physik* **12**, (1958) pp. 295–514.
9. G. Ludwig and M. Heil, Boundary layer theory with dissociation and ionization, Advances in Applied Mathematics, Volume VI, Academic Press, New-York, (1960) pp. 39–118.
10. L. Waldmann und E. Trübenbacher, Formale Kinetische Theorie von Gasgemischen aus Anregbaren Molekülen. *Zeitschr. Naturforschg.* **17a**, (1962) pp. 363–376.
11. S. Chapman and T.G. Cowling, *The mathematical theory of non-uniform gases* Cambridge University Press, Cambridge, (1970).
12. J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases*, North Holland Pub. Co., Amsterdam, (1972).
13. F. R. McCourt, J. J. Beenakker, W. E. Köhler, and I. Kuščer, *Non equilibrium phenomena in polyatomic gases* Volumes I and II, Oxford, (1990) and (1991).
14. B.V. Alexeev, A. Chikhaoui and I.T. Grushin, Application of the generalized Chapman-Enskog method to the transport-coefficients calculation in a reacting gas mixture, *Phys. Rev. E*, **49**, (1994) pp. 2809–2825.
15. A. Ern and V. Giovangigli, *Multicomponent transport algorithms* Lectures Notes in Physics, Series monographs **m24**, Springer Verlag, Berlin, (1994).
16. V. Giovangigli, *Multicomponent flow modeling* Birkhäuser, Boston, 1999. Erratum at http://cmap.polytechnique.fr/~giovangi
17. A. Ern and V. Giovangigli, The Kinetic Equilibrium Regime, *Physica-A*, **260**, (1998) pp. 49–72.
18. B. Shizgal and M. Karplus, Nonequilibrium Contributions to the Rate of Reaction. II. Isolated Multicomponent Systems. *J. Chem. Phys.* **4**, (1971) pp. 4345–4356.
19. A. Orsini and E.V. Kustova, Elemental transport coefficients in viscous plasma flows near local thermodynamic equilibrium, *Phys. Rev. E*, **79** (2009), pp. 056309.
20. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*. Wiley, New York (1954).
21. J. Van de Ree, On the Definition of the Diffusion Coefficients in Reacting Gases, *Physica*, **36**, (1967) pp. 118–126.
22. A. Ern and V. Giovangigli, Thermal conduction and thermal diffusion in dilute polyatomic gas mixtures, *Physica-A*, **214** (1995) 526–546.
23. S.R. de Groot and P. Mazur, *Non-equilibrium thermodynamics* Dover publications, Inc. New York, (1984).
24. V. Giovangigli, Higher Order Entropies, *Arch. Rat. Mech. Anal.*, **187**, (2008) pp. 221–285.
25. V. Giovangigli, Persistence of Boltzmann Entropy in Fluid Models, *Disc. Cont. Dyn. Syst.*, **24**, (2009) pp. 95–114.
26. V. Giovangigli and M. Massot, The Local Cauchy Problem for Multicomponent Reactive Flows in Full Vibrational Nonequilibrium, *Math. Meth. Appl. Sci.*, **21**, (1998) pp. 1415–1439.
27. V. Giovangigli and M. Massot, Asymptotic Stability of Equilibrium States for Multicomponent Reactive Flows, *Mathematical Models & Methods in Applied Science*, **8**, (1998) pp. 251–297.

28. S. Kawashima, Systems of hyperbolic-parabolic composite type, with application to the equations of magnetohydrodynamics, Doctoral Thesis, Kyoto University, (1984).

29. S. Kawashima and Y. Shizuta, On the Normal Form of the Symmetric Hyperbolic-Parabolic Systems associated with the Conservation Laws, *Tôhoku Math. J.*, **40**, (1988) pp. 449-464.

30. A.I. Vol'Pert and S.I. Hudjaev, On the Cauchy Problem for composite systems of Nonlinear Differential Equations, *Math USSR Sbornik.* **16**, (1972) pp. 517–544.

31. V. Giovangigli and M. Massot, Entropic Structure of Multicomponent Reactive Flows with Partial Equilibrium Reduced Chemistry, *Math. Meth. Appl. Sci.* **27**, (2004) pp. 739–768.

32. V. Giovangigli and B. Graille, Asymptotic Stability of Equilibrium States for Ambipolar Plasmas, *Math. Mod. Meth. Appl. Sci.* **14**, (2004) pp. 1361–1399.

33. V. Giovangigli, Plane Flames with Multicomponent Transport and Complex Chemistry, *Math. Mod. Meth. Appl. Sci.* **14**, (1999) pp. 337–378.

34. S.I. Braginskii, Transport phenomena in a completely ionized two-temperature plasma *Soviet physics JETP* **6(33)**, (1958) pp. 358–369.

35. S.I. Braginskii, Transport processes in a plasma, M.A. Leontovich editor, *Rev. of plasma phys.* **1**, (1965) pp. 205–311.

36. D. Bruno, A. Laricchiuta, M. Capitelli, C. Catalfamo, A. Chikhaoui, E. V. Kustova, and D. Giordano, Transport properties of equilibrium Argon plasma in a magnetic field, AIAA Paper, AIAA-2004-2161, (2004).

37. D. Bruno, C. Catalfamo, A. Laricchiuta, D. Giordano, and M. Capitelli, Convergence of Chapman-Enskog calculation of transport coefficients of magnetized Argon plasma, *Phys. Plasmas*, **13**, (2006) 72307.

38. V. Giovangigli and B. Graille, Kinetic Theory of Partially Ionized Reactive Gas Mixtures, *Physica A*, **327**, (2003), pp. 313–348.

39. V. Giovangigli and B. Graille, Kinetic Theory of Partially Ionized Reactive Gas Mixtures II, J. Phys. A, **42**, (2009) pp. 1–31.

40. V. Giovangigli, Multicomponent Transport Algorithms for Partially Ionized Plasmas, *J. Comp. Phys.*, **229**, (2010) pp. 4117–4142.

41. Giovangigli and B. Graille, The Local Cauchy Problem for Ionized Magnetized Reactive Gas Mixtures, *Math. Meth. Appl. Sci.*, **28**, (2005) pp. 1647–1672.

42. R.S. Devoto, Transport properties of Ionized Monatomic Gases, *Phys. Fluids* **9**, (1966) pp. 1230–1240.

43. A. Ern and V. Giovangigli, The structure of transport linear systems in dilute isotropic gas mixtures, *Phys. Rev. E*, **53**, (1996) pp. 485–492.

44. A. Ern and V. Giovangigli, Fast and Accurate Multicomponent Property Evaluations, J. Comp. Physics, **120**, (1995) pp. 105–116.

45. A. Ern and V. Giovangigli, Optimized Transport Algorithms for Flame Codes, *Comb. Sci. Tech.*, **118**, (1996) pp. 387–395.

46. A. Ern and V. Giovangigli, Projected iterative algorithms with application to multicomponent transport, *Linear Algebra Appl.* **250**, (1997) pp. 289–315.

47. A. Ern and V. Giovangigli, Thermal Diffusion Effects in Hydrogen/Air and Methane/Air Flames, *Comb. Theor. Mod.*, **2**, (1998) pp. 349–372.

48. A. García Muñoz, Formulation of molecular diffusion in planetary atmospheres, *Plan. Space Sci.* **55**, (2007) pp. 1414–1425.

49. R.M. Chmieleski and J.H. Ferziger, Transport properties of a nonequilibrium partially ionized gas, *Phys. Fluids* **10**, (1967) pp. 364–371.

50. U. Daybelge, Unified transport theory of partially ionized nonisothemal plasmas, *J. App. Phys.* **41**, (1970) pp. 2130–2139.

51. T.E. Magin and G. Degrez, Transport Properties of Partially Ionized and Unmagnetized Plasmas. *Phys. Rev. E* **70**, 046412 (2004).

52. J.P. Petit and J.S. Darrozes, Une nouvelle formulation des équations du mouvement d'un gaz ionisé dans un régime dominé par les collisions, *J. Méc.* **14**, (1975) pp. 745–759.

53. M. Capitelli, I. Armenise, D. Bruno, M. Cacciatore, R. Celiberto, G. Colonna, O. de Pascale, P. Diomede, F. Esposito, C. Gorse, K. Hassouni, A. Laricchiuta, S. Longo, D. Pagano, D. Pietanza, and M. Rutigliano, Non-equilibrium Plasma Kinetics: A state-to-state approach, *Plasma Sourc. Sci. Tech.*, **16**, (2007) pp. S30–S44.

54. G. Colonna, I. Armenise, D. Bruno, and M. Capitelli, Reduction of state-to-state kinetics to macroscopic models in hypersonic flows, *J. Thermophys. Heat Transf.*, **20**, (2006) pp. 477–486.

55. E.V. Kustova, E.A. Nagnibada, and A. Chikhaoui, On the accuracy of nonequilibrium transport coefficients calculation, *Chem. Phys.* **270** I, (2001) pp. 459–469.

56. V. A. Rozhansky and L. D. Tsendin, *Transport Phenomena in Partially Ionized Plasmas*, Taylor and Francis, London, 2001.

57. B. Graille, T. Magin and M. Massot, Kinetic Theory of Plasmas: Translational Energy, *Math. Mod. Meth. App. Sci.*, **10**, (2009) pp. 1–2.

58. S. Dworkin, M. D. Smooke, and V. and Giovangigli, The Impact of Detailed Multicoponent Transport and Thermal Diffusion Effects on Soot Formation in Ethylene/Air Flames*, *Proc. Comb. Inst.*, **32**, (2009) pp. 1165–1172.*

59. G. Emanuel, Effect of bulk viscosity on a hypersonic boundary layer, *Phys. Fluids A*, **4**, (1992) pp. 491–495.

60. G. Billet, V. Giovangigli, and G. de Gassowski, Impact of Volume Viscosity on a Shock/Hydrogen Bubble interaction, *Combustion Theory and Modelling*, **12**, (2008) pp. 221–248.