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Kinetic theory of partially ionized reactive gas mixtures

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Abstract

We investigate partially ionized reactive gas mixtures in the presence of electric and magnetic fields. Our starting point is a generalized Boltzmann equation with a chemical source term valid for arbitrary reaction mechanism. We study the Enskog expansion and obtain macroscopic equations in the zeroth- and first-order regimes, together with transport fluxes and transport coefficients. New bracket expressions are obtained for perpendicular/transverse diffusion, thermal diffusion and thermal conductivity coefficients as well as shear viscosity coefficients. A new definition of thermal diffusion ratios—consistent with the zero magnetic fields limit—is introduced. Positivity properties of multicomponent diffusion matrices are investigated and macroscopic entropy production is shown to be positive. The mathematical structure of the transport linear systems that are to be solved in order to evaluate transport coefficients is discussed. In particular, all transport coefficients are expressed as convergent series. These series yield by truncation accurate approximated coefficients relevant to computational models.

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1. Introduction

Extensive interest in the kinetic theory of ionized gas mixtures with chemical reactions has grown significantly over the past years. The subject is indeed related to a

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wide range of practical applications including laboratory plasmas, high-speed gas flows and atmospheric phenomena.

Application of the Chapman–Enskog method to partially ionized gases is feasible for low temperature high density plasmas [1,2]. The effects of electrical and magnetic fields are then split into two different contributions. The interactions between particles at distances greater than the Debye length are considered to be mediated by the electric and magnetic fields while those at shorter distance are considered to be true collisions [1]. Additionally, the number of particles in a Debye sphere must be large, the cyclotron radius and the wavelength of any electromagnetic wave must be larger than the Debye length. For partially ionized gases, the proper operator to be used is the Boltzmann collision operator with shielded potentials [3]. In the particular situation of fully ionized gases, the Fokker–Planck operator can also be used, but yields identical results within a few percent [1]. The Fokker–Planck operator can indeed be obtained from the Boltzmann operator in the limit of grazing collisions and, for most particles, multiple collisions involving weak forces are statistically equivalent to successions of numerous small angle binary collisions [4].

Application of the Chapman–Enskog theory to ionized mixtures was first discussed by Chapman and Cowling for monatomic binary mixtures [5]. Higher order evaluations of transport coefficients were performed by Kaneko and coworkers for binary neutral mixtures in uniform magnetic fields in a simplified steady kinetic framework [6–8]. The case of multicomponent mixtures of monatomic gases was comprehensively investigated by Ferziger and Kaper [1]. In this paper we consider the general case of reactive polyatomic gas mixtures. The mixture of polyatomic species is described in a semi-classical framework by using Wang Chang–Uhlenbeck–de Boer equations. These equations preaverage the collision cross sections over degeneracies [9,10]. The chemical source terms appearing in the Boltzmann equations are taken essentially from Ludwig and Heil [11], Alexeev et al. [12], Ern and Giovangigli [13] and Grunfeld [14]. These chemical source terms are valid for arbitrary chemical mechanisms. We also assume that the distribution functions do not depend on any of the angular momentum [15].

We consider a regime where there is only one temperature in the mixture, assuming that the electric field is not intense [1]. This situation arises in various laboratory or atmospheric plasmas as for instance positive columns of high pressure arcs, inductively coupled plasma torches, microwaves plasmatrons or continuous optical discharges [1,9]. The generalization to mixture at thermodynamic nonequilibrium with multitemperature transport and chemistry—arising from small electron/ion mass ratio asymptotics—is beyond the scope of the present paper. We also assume that there is only one velocity in the mixture and discard multifluid models where each species has its own velocities [16]. We note, incidentally, that macroscopic multifluid conservation equations lead to very serious mathematical pathologies [17].

We study the Enskog expansion and obtain macroscopic equations in the zeroth- and first-order regimes, together with transport fluxes and transport coefficients. Our bracket expressions for transport coefficients perpendicular and transverse to the magnetic field include quadratic terms overlooked in [1]. We also express the shear viscosities as bracket products for the first time. A new definition of thermal diffusion ratios is introduced which reduces to the usual definition in the absence of magnetic field. We further investigate the positivity properties of the resulting multicomponent diffusion matrices parallel, perpendicular and transverse to the magnetic field. These properties, established here for the exact matrices arising from the kinetic theory of gases, are a key point in numerical approximations of multicomponent diffusion, where these properties must be enforced by the computational algorithms used to evaluate the transport coefficients. From these positivity properties, we next establish that macroscopic entropy production is positive. To the author's knowledge, it is the first time that such an analysis is made and this result is important from a thermodynamical, mathematical and numerical points of view [18]. As a tool, we generalize the use of complex quantities introduced in Refs. [1,5] which reduce vector products to scalar multiplication by imaginary numbers.

Upon using matrix approximations of the collision operator, the transport coefficients can finally be evaluated by solving large linear systems. We address the question of the mathematical structure of the resulting transport linear systems. Although direct inversion of these linear systems is feasible, it is prohibitively expensive for most practical applications involving multidimensional multicomponent flows. With an eye toward the development of efficient numerical models, there is thus a strong motivation for deriving cost effective approximations of transport coefficients in a manner consistent with the underlying kinetic theory rather than by simply using empirical mixture-averaged expressions which are often less accurate. To this aim, we investigate well posedness of the transport linear systems and establish the convergence of iterative technique. As a consequence, we express the transport coefficients as convergent series which yield by truncation sequences of approximations of increasing accuracy as in the nonionized case [19,20].

Our paper is organized as follows. In Section 2, we present the generalized equation for chemically reactive mixtures. In Section 3 we investigate the zeroth-order Enskog expansion. Sections 4 and 5 are concerned with the molecular and the macroscopic equations in the first-order expansion. In Section 6, we investigate the structure of the corresponding transport linear systems. Finally, in Section 7 we briefly address the weak magnetic field regime.

2. Theoretical framework

In this section, we describe a theoretical framework for polyatomic reactive gas mixtures in the presence of electric and magnetic fields. We first present a generalized Boltzmann equation valid for an arbitrary reaction mechanism. We then show that both nonreactive and reactive source terms are compatible with the positivity of kinetic entropy production. We next present the collisional invariants and investigate Enskog expansion.

2.1. Generalized Boltzmann equation

We consider a dilute reactive gas mixture composed of n^s chemical species having internal degrees of freedom. The starting point is the Boltzmann equation for polyatomic gas mixtures derived from Ref. [2] in a semiclassical framework. It preaverages the collision cross sections over the degeneracies and can be derived from the Waldmann–Snider quantum mechanical Boltzmann equation [2]. This equation is then generalized to reactive partially ionized gas mixtures with chemical source terms taken from Refs. [11–14].

The state of the mixture is described by the species distribution functions denoted by $f_i(t, \boldsymbol{x}, \boldsymbol{c}_i, \mathrm{I})$, where i is the index of the species, t the time, $\boldsymbol{x}$ the three-dimensional spatial coordinate, $\boldsymbol{c}_i$ the velocity and I the index for the internal energy state. We denote by S the species indexing set $\mathrm{S} = \{1, \dots, n^s\}$, by m_i, e_i, and $z_i = e_i/m_i$ the molecular mass, charge, and charge per unit mass of the ith species, and finally by $\mathscr{E}_{i\mathrm{I}}$ the internal energy of the ith species in the Ith state. For a family of functions ξ_i, $i \in \mathrm{S}$, we introduce the compact notation $\xi = (\xi_i)_{i\in\mathrm{S}}$.

The family of species distribution functions $f = (f_i)_{i\in\mathrm{S}}$ is the solution of the following generalized Boltzmann equation

$$\mathscr{D}_i(f_i) = \mathscr{S}_i(f) + \mathscr{C}_i(f), \quad i \in \mathrm{S}, \tag{2.1}$$

where $\mathscr{D}_i$ is the usual differential operator and $\mathscr{S}_i(f)$ and $\mathscr{C}_i(f)$ are respectively the nonreactive and the reactive source terms. The streaming operator $\mathscr{D}_i$ can be written

$$\mathscr{D}_i(f_i) = \partial_t f_i + \boldsymbol{c}_i \cdot \partial_{\boldsymbol{x}} f_i + \boldsymbol{b}_i \cdot \partial_{\boldsymbol{c}_i} f_i, \tag{2.2}$$

where $\boldsymbol{b}_i$ is the force acting on the ith species. In our model, $\boldsymbol{b}_i$ is in the form $\boldsymbol{b}_i = \boldsymbol{g} + z_i(\boldsymbol{E} + \boldsymbol{c}_i \wedge \boldsymbol{B})$, where $\boldsymbol{g}$ is a species independent external force, $\boldsymbol{E}$ the electric field and $\boldsymbol{B}$ the magnetic field.

The nonreactive source term can be written in the form

$$\mathscr{S}_i(f) = \sum_j \sum_{\mathrm{I'JJ'}} \int \left(f_i' f_j' \frac{\alpha_{i\mathrm{I}}\alpha_{j\mathrm{J}}}{\alpha_{i\mathrm{I'}}\alpha_{j\mathrm{J'}}} - f_i f_j \right) \mathtt{W}_{ij}^{\mathrm{IJI'J'}} \,\mathrm{d}\boldsymbol{c}_j \,\mathrm{d}\boldsymbol{c}_i' \,\mathrm{d}\boldsymbol{c}_j', \tag{2.3}$$

where $\alpha_{i\mathrm{I}}$ is the degeneracy of the Ith quantum state and $\mathtt{W}_{ij}^{\mathrm{IJI'J'}}$ the transition probability for nonreactive collisions. Note that we work with transition probabilities rather than collision cross sections since reactive collision terms are then much easier to write [11,12,18]. The following reciprocity relations hold for transition probabilities [2]:

$$\alpha_{i\mathrm{I}}\alpha_{j\mathrm{J}}\mathtt{W}_{ij}^{\mathrm{IJI'J'}} = \alpha_{i\mathrm{I'}}\alpha_{j\mathrm{J'}}\mathtt{W}_{ij}^{\mathrm{I'J'IJ}}. \tag{2.4}$$

The reactive source term $\mathscr{C}_i(f)$ results from chemical reactions between species in the mixture. We consider an arbitrary reaction mechanism, including, in particular, bimolecular and trimolecular chemical reactions. Indeed, although triple nonreactive collisions have been neglected in the nonreactive source term $\mathscr{S}_i(f)$, triple reactive collisions are retained since recombination reactions cannot often proceed otherwise [11,12]. Triple reactive collisions can also be viewed as a sequence of two bimolecular reactions proceeding extremely fast [12]. The chemical reactions taking place in the mixture are indexed by $r \in \mathfrak{R}$ and can be written in the form [13]

$$\sum_{i\in\mathscr{F}^r} \mathfrak{M}_i \rightleftharpoons \sum_{k\in\mathscr{B}^r} \mathfrak{M}_k, \quad r \in \mathfrak{R},$$

where $\mathscr{F}^r$ and $\mathscr{B}^r$ are the indices for reactants and products, counted with their multiplicity. We denote by ν_{ir}^{f} and ν_{ir}^{b} the forward and the backward stoichiometric coefficients of the ith species for the rth reaction, that is, the order of multiplicity of species i in $\mathscr{F}^r$ and $\mathscr{B}^r$, respectively. We denote by F^r and B^r the indices of the quantum states for reactants and products, respectively. Lastly, we denote by $\mathscr{F}_i^r$ a subset of $\mathscr{F}^r$ where the index i has been removed only once. We introduce similar notations for $\mathscr{B}_k^r$, F_I^r and B_K^r. The reactive source term for the ith species then reads [13]

$$\mathscr{C}_i(f) = \sum_{r \in \mathfrak{R}} \mathscr{C}_i^r(f)\,, \tag{2.5}$$

where $\mathscr{C}_i^r(f)$ represents the reactive source term due to the rth reaction. The source term $\mathscr{C}_i^r(f)$ is given by

$$\begin{aligned} \mathscr{C}_i^r(f) = {} & \nu_{ir}^{\mathrm{f}} \sum_{\mathrm{F}_\mathrm{I}^r, \mathrm{B}^r} \int \left(\prod_{k \in \mathscr{B}^r} f_k \, \frac{\prod_{k \in \mathscr{B}^r} \beta_{k\mathrm{K}}}{\prod_{j \in \mathscr{F}^r} \beta_{j\mathrm{J}}} - \prod_{j \in \mathscr{F}^r} f_j \right) \mathscr{W}_{\mathscr{F}^r \mathscr{B}^r}^{\mathrm{F}^r \mathrm{B}^r} \prod_{j \in \mathscr{F}_i^r} \mathrm{d}\boldsymbol{c}_j \prod_{k \in \mathscr{B}^r} \mathrm{d}\boldsymbol{c}_k \\ & - \nu_{ir}^{\mathrm{b}} \sum_{\mathrm{F}^r, \mathrm{B}_\mathrm{I}^r} \int \left(\prod_{k \in \mathscr{B}^r} f_k \, \frac{\prod_{k \in \mathscr{B}^r} \beta_{k\mathrm{K}}}{\prod_{j \in \mathscr{F}^r} \beta_{j\mathrm{J}}} - \prod_{j \in \mathscr{F}^r} f_j \right) \mathscr{W}_{\mathscr{F}^r \mathscr{B}^r}^{\mathrm{F}^r \mathrm{B}^r} \prod_{j \in \mathscr{F}^r} \mathrm{d}\boldsymbol{c}_j \prod_{k \in \mathscr{B}_i^r} \mathrm{d}\boldsymbol{c}_k\,, \end{aligned} \tag{2.6}$$

where $\beta_{i\mathrm{I}} = \mathrm{h}_\mathrm{P}^3/(\alpha_{i\mathrm{I}} m_i^3)$ and h_P is the Planck constant. The quantity $\mathscr{W}_{\mathscr{F}^r \mathscr{B}^r}^{\mathrm{F}^r \mathrm{B}^r}$ is the transition probability for a reactive collision in which the reactants $\mathscr{F}^r$ with energy states F^r are transformed into products $\mathscr{B}^r$ with energy states B^r. The summation over F^r in (2.6) represents the sum over all quantum states J for all $j \in \mathrm{F}^r$ with similar conventions for F_I^r, B^r, and B_I^r. Finally, the following reciprocity relations hold for the reactive transition probabilities [11–13]:

$$\mathscr{W}_{\mathscr{F}^r \mathscr{B}^r}^{\mathrm{F}^r \mathrm{B}^r} \prod_{k \in \mathscr{B}^r} \beta_{k\mathrm{K}} = \mathscr{W}_{\mathscr{B}^r \mathscr{F}^r}^{\mathrm{B}^r \mathrm{F}^r} \prod_{j \in \mathscr{F}^r} \beta_{j\mathrm{J}}\,. \tag{2.7}$$

2.2. Kinetic entropy

The nonreactive source term (2.3) and the reactive source term (2.5) are both compatible with the H-theorem [13]. In other words, they yield a positive kinetic entropy production. We introduce to this purpose the kinetic entropy per unit volume

$$\mathscr{S}^{\mathrm{kin}} = -\mathrm{k}_\mathrm{B} \sum_{i,\mathrm{I}} \int f_i(\log(\beta_{i\mathrm{I}} f_i) - 1)\, \mathrm{d}\boldsymbol{c}_i\,, \tag{2.8}$$

where k_B is the Boltzmann constant. Multiplying the Boltzmann equation (2.1) by $\log(\beta_{i\mathrm{I}} f_i)$, integrating over $\mathrm{d}\boldsymbol{c}_i$ and summing over $i \in \mathrm{S}$ and I yields the entropy conservation equation in the form

$$\partial_t \mathscr{S}^{\mathrm{kin}} + \partial_{\boldsymbol{x}} \cdot (\mathscr{S}^{\mathrm{kin}} \boldsymbol{v}) + \partial_{\boldsymbol{x}} \cdot \mathscr{J}^{\mathrm{kin}} = \mathfrak{v}^{\mathrm{kin}}\,, \tag{2.9}$$

where $\mathscr{J}^{\mathrm{kin}}$ is the entropy diffusive flux given by

$$\mathscr{J}^{\mathrm{kin}} = -\mathrm{k}_\mathrm{B} \sum_{i,\mathrm{I}} \int f_i(\boldsymbol{c}_i - \boldsymbol{v})(\log(\beta_{i\mathrm{I}} f_i) - 1)\, \mathrm{d}\boldsymbol{c}_i\,, \tag{2.10}$$

and $\mathfrak{b}^{\mathrm{kin}}$ the kinetic entropy source term. After a little algebra, we obtain

$$\mathfrak{b}^{\mathrm{kin}} = \mathfrak{b}^{\mathscr{S}} + \mathfrak{b}^{\mathscr{C}} , \tag{2.11}$$

where the nonreactive and reactive contributions are

$$\mathfrak{b}^{\mathscr{S}} = \frac{\mathrm{k_B}}{4} \sum_{i,j\in\mathrm{S}} \sum_{\mathrm{II'JJ'}} \int \Omega\left(\frac{f_i' f_j'}{\alpha_{i\mathrm{I'}}\alpha_{j\mathrm{J'}}}, \frac{f_i f_j}{\alpha_{i\mathrm{I}}\alpha_{j\mathrm{J}}}\right) \mathrm{W}_{ij}^{\mathrm{IJI'J'}} \alpha_{i\mathrm{I}}\alpha_{j\mathrm{J}} \,\mathrm{d}\boldsymbol{c}_i \,\mathrm{d}\boldsymbol{c}_j \,\mathrm{d}\boldsymbol{c}_i' \,\mathrm{d}\boldsymbol{c}_j' ,$$

$$\mathfrak{b}^{\mathscr{C}} = \frac{\mathrm{k_B}}{4} \sum_{r\in\mathfrak{R}} \sum_{\mathrm{F}^r,\mathrm{B}^r} \int \Omega\left(\prod_{k\in\mathscr{B}^r} \beta_{k\mathrm{K}} f_k, \prod_{j\in\mathscr{F}^r} \beta_{j\mathrm{J}} f_j\right) \frac{\mathscr{W}_{\mathscr{F}^r\mathscr{B}^r}^{\mathrm{F}^r\mathrm{B}^r}}{\prod_{j\in\mathscr{F}^r} \beta_{j\mathrm{J}}} \prod_{j\in\mathscr{F}^r} \mathrm{d}\boldsymbol{c}_j \prod_{k\in\mathscr{B}^r} \mathrm{d}\boldsymbol{c}_k ,$$

and where $\Omega(x,y) = (x-y)\log(x/y)$ is a positive function. We observe that both $\mathfrak{b}^{\mathscr{S}}$ and $\mathfrak{b}^{\mathscr{C}}$ are a sum of positive terms. In other words, all the collisions, nonreactive or reactive, yield a positive contribution to the kinetic entropy production. The generalized Boltzmann equation is thus compatible with the H-theorem and yields a dissipative structure. This property is particularly important in the modeling of reactive gas mixtures where special care should be taken so that all the terms arising in the macroscopic entropy production yield a positive—or zero—contribution.

2.3. Invariants of the nonreactive collision operator

The scalar collisional invariants of the nonreactive collision operator form a linear space spanned by $\psi^l, l \in \{1,\ldots,n^s+4\}$, with

$$\psi^l = \begin{cases} (\delta_{li})_{i\in\mathrm{S}}, & l\in\mathrm{S} , \\ (m_i c_{i\nu})_{i\in\mathrm{S}}, & l = n^s+\nu , \qquad \nu\in\{1,2,3\} , \\ (\frac{1}{2}\, m_i \boldsymbol{c}_i\cdot\boldsymbol{c}_i + \mathscr{E}_{i\mathrm{I}})_{i\in\mathrm{S}}, & l = n^s+4 , \end{cases}$$

where $c_{i\nu}$ is the component of $\boldsymbol{c}_i$ in the νth spatial coordinate. On the other hand the collisional invariant of the complete collision operator are constituted by the momentum and energy invariants together with the element invariants. These later invariants are associated with the conservation of elements in chemical reactions [13].

For two families $\xi = (\xi_i)_{i\in\mathrm{S}}$ and $\zeta = (\zeta_i)_{i\in\mathrm{S}}$, we introduce the scalar product

$$\langle\langle \xi, \zeta \rangle\rangle = \sum_{i,\mathrm{I}} \int \xi_i \odot \bar{\zeta}_i \,\mathrm{d}\boldsymbol{c}_i ,$$

where $\xi_i \odot \bar{\zeta}_i$ denotes the maximum contracted product between the tensor ξ_i and the complex conjugate tensor ζ_i. The scalar product is defined for families of complex tensors as such quantities will naturally arise in the solution of Boltzmann linearized equations in the presence of magnetic fields. The macroscopic properties are then conveniently written in the form

$$\langle\langle f, \psi^l \rangle\rangle = \begin{cases} n_l, & l\in\mathrm{S} , \\ \rho v_\nu, & l = n^s+\nu , \qquad \nu\in\{1,2,3\} , \\ \frac{1}{2}\,\rho\boldsymbol{v}\cdot\boldsymbol{v} + \mathscr{E}, & l = n^s+4 , \end{cases}$$

where n_l is the number density of the lth species, $\rho = \sum_{l \in \mathrm{S}} m_l n_l$ the mixture mass density, v_ν the component of the mixture velocity $\boldsymbol{v}$ in the νth spatial coordinate, and $\mathscr{E}$ the internal energy per unit volume.

2.4. Enskog expansion

An approximate solution to the Boltzmann equation (2.1) is now obtained using an Enskog expansion. We assume that the chemistry characteristic times are larger than the characteristic times of internal energy relaxation and the characteristic times of free flight. Furthermore, we distinguish two models according to the intensity of the magnetic field [16]. More specifically, when the magnetic field is strong enough, we have to assume that $\boldsymbol{E} + \boldsymbol{v} \wedge \boldsymbol{B}$ is much smaller than $(\boldsymbol{c}_i - \boldsymbol{v}) \wedge \boldsymbol{B}$. Accordingly, we rewrite Boltzmann equation (2.1) in the form

$$\tilde{\mathscr{D}}_i(f_i) + \frac{1}{\varepsilon^b} \hat{\mathscr{D}}_i(f_i) = \frac{1}{\varepsilon} \mathscr{S}_i(f) + \varepsilon^a \mathscr{C}_i(f), \quad i \in \mathrm{S}, \tag{2.12}$$

where $\tilde{\mathscr{D}}_i$ is the streaming operator

$$\tilde{\mathscr{D}}_i(f_i) = \partial_t f_i + \boldsymbol{c}_i \cdot \partial_{\boldsymbol{x}} f_i + \tilde{\boldsymbol{b}}_i \cdot \partial_{\boldsymbol{c}_i} f_i, \tag{2.13}$$

associated with the reduced force $\tilde{\boldsymbol{b}}_i$

$$\tilde{\boldsymbol{b}}_i = \boldsymbol{g} + z_i(\boldsymbol{E} + \boldsymbol{v} \wedge \boldsymbol{B}), \tag{2.14}$$

and $\hat{\mathscr{D}}_i$ is the remaining term

$$\hat{\mathscr{D}}_i(f_i) = z_i((\boldsymbol{c}_i - \boldsymbol{v}) \wedge \boldsymbol{B}) \cdot \partial_{\boldsymbol{c}_i} f_i. \tag{2.15}$$

In these equations, ε is the usual formal parameter associated with Enskog expansion, and a and b are positive integers which depends on the regime under consideration. In this paper, we will consider both the strong magnetic field regime $b = 1$, and the simpler weak magnetic field regime $b = 0$. On the other hand, the different regimes associated with the parameter a are discussed, in particular, in Refs. [13,18]. We will consider the Maxwellian reaction regime $a = 1$ and briefly discuss the strong reaction regime $a = 0$, the kinetic equilibrium regime $a = -1$ being out of the scope of the present work [13]. Finally, we expand the species distribution functions as

$$f_i = f_i^0(1 + \varepsilon\phi_i + \mathcal{O}(\varepsilon^2)), \quad i \in \mathrm{S}, \tag{2.16}$$

and we impose that f^0 yields the local macroscopic properties

$$\langle\langle f^0, \psi^l \rangle\rangle = \langle\langle f, \psi^l \rangle\rangle, \quad l \in \{1, \ldots, n^s + 4\}. \tag{2.17}$$

For convenience we also introduce the notation $\mathscr{D}(\xi) = (\mathscr{D}_i(\xi_i))_{i \in \mathrm{S}}$, $\tilde{\mathscr{D}}(\xi) = (\tilde{\mathscr{D}}_i(\xi_i))_{i \in \mathrm{S}}$, $\hat{\mathscr{D}}(\xi) = (\hat{\mathscr{D}}_i(\xi_i))_{i \in \mathrm{S}}$, $\mathscr{S}(\xi) = (\mathscr{S}_i(\xi))_{i \in \mathrm{S}}$, and $\mathscr{C}(\xi) = (\mathscr{C}_i(\xi))_{i \in \mathrm{S}}$, where $\xi = (\xi_i)_{i \in \mathrm{S}}$ is any family of functionals ξ_i depending on $(\boldsymbol{c}_i, \mathrm{I})$.

3. Zeroth-order approximation

In this section, we obtain the expression of f_i^0, $i \in \mathrm{S}$, and we present the corresponding macroscopic equations for polyatomic gas mixtures resulting from the Euler zeroth-order approximation in both regimes $b=0$ and $b=1$.

3.1. Generalized Maxwellian distribution functions

The family of zeroth-order species distribution functions $f^0 = (f_i^0)_{i \in \mathrm{S}}$ is the solution of

$$\mathscr{S}_i(f^0) = \delta_{1b} \hat{\mathscr{D}}_i(f_i^0), \quad i \in \mathrm{S}, \tag{3.1}$$

where $\delta_{\alpha\beta}$ denotes the usual Kronecker symbol. Multiplying Eq. (3.1) by $\log(\beta_{i\mathrm{I}} f_i^0)$, integrating over $\mathrm{d}\boldsymbol{c}_i$ and summing over $i \in \mathrm{S}$ and I yields

$$\sum_{i,\mathrm{I}} \int \log(\beta_{i\mathrm{I}} f_i^0) \mathscr{S}_i(f^0)\, \mathrm{d}\boldsymbol{c}_i = \delta_{1b} \sum_{i,\mathrm{I}} \int \log(\beta_{i\mathrm{I}} f_i^0) \hat{\mathscr{D}}_i(f^0)\, \mathrm{d}\boldsymbol{c}_i .$$

Using relation (2.15) expressing $\hat{\mathscr{D}}_i(f_i^0)$ and integrating by parts, we obtain that the right member of the latter equation vanishes. As a consequence $(\log(\beta_{i\mathrm{I}} f_i^0))_{i \in \mathrm{S}}$ is a collisional invariant so that

$$\log(\beta_{i\mathrm{I}} f_i^0) = \alpha_i - \boldsymbol{\beta} \cdot m_i \boldsymbol{c}_i - \gamma(\tfrac{1}{2} m_i \boldsymbol{c}_i \cdot \boldsymbol{c}_i + \mathscr{E}_{i\mathrm{I}}), \quad i \in \mathrm{S},$$

where $\alpha_i \in \mathbb{R}$, $\boldsymbol{\beta} \in \mathbb{R}^3$ and $\gamma \in \mathbb{R}$, and these parameters are determined from the macroscopic constraints (2.17). After some algebra, we obtain

$$f_i^0 = \frac{n_i}{\beta_{i\mathrm{I}} Q_i} \exp\left(-\frac{m_i}{2\mathrm{k_B} T} \boldsymbol{C}_i \cdot \boldsymbol{C}_i - \frac{\mathscr{E}_{i\mathrm{I}}}{\mathrm{k_B} T} \right), \quad i \in \mathrm{S}, \tag{3.2}$$

where $\boldsymbol{C}_i = \boldsymbol{c}_i - \boldsymbol{v}$ is the relative velocity of the ith species, T the temperature and Q_i the full partition function per unit volume of the ith species

$$Q_i = Q_i^{\mathrm{int}} Q_i^{\mathrm{tr}},$$

with Q_i^{int} the partition function for internal energy and Q_i^{tr} the translational partition function per unit volume of the ith species

$$Q_i^{\mathrm{int}} = \sum_{\mathrm{I}} \alpha_{i\mathrm{I}} \exp\left(-\frac{\mathscr{E}_{i\mathrm{I}}}{\mathrm{k_B} T} \right), \quad Q_i^{\mathrm{tr}} = \left(\frac{2\pi m_i \mathrm{k_B} T}{\mathrm{h_P^2}} \right)^{3/2} .$$

3.2. Zeroth-order macroscopic equations

The macroscopic conservation equations are obtained by taking the scalar product of Boltzmann equation by collisional invariants. At zeroth-order, only the terms that are

$\mathscr{O}(\varepsilon^0)$ are kept, and we obtain

$$\langle\langle \tilde{\mathscr{D}}(f^0), \psi^l \rangle\rangle + \delta_{1b} \langle\langle \hat{\mathscr{D}}(f^0 \phi), \psi^l \rangle\rangle = \delta_{a0} \langle\langle \mathscr{C}(f^0), \psi^l \rangle\rangle \,, \tag{3.3}$$

for $l \in \{1, \ldots, n^s + 4\}$. After some algebra, we obtain, for $l = 1, \ldots, n^s$, the equations expressing the conservation of species mass

$$\partial_t \rho_i + \partial_{\boldsymbol{x}} \cdot (\rho_i \boldsymbol{v}) = \delta_{a0} m_i \bar{\omega}_i^0, \quad i \in \mathrm{S} \,, \tag{3.4}$$

where $\rho_i = m_i n_i$ is the mass density of the ith species and $\bar{\omega}_i^0$ the zeroth-order chemical source term

$$\bar{\omega}_i^0 = \langle\langle \psi^i, \mathscr{C}(f^0) \rangle\rangle = \sum_{\mathrm{I}} \int \mathscr{C}_i(f^0)\, \mathrm{d}\boldsymbol{c}_i, \quad i \in \mathrm{S} \,.$$

This source term can be written in the form [14]

$$\bar{\omega}_i^0 = \sum_{r \in \mathfrak{R}} (\nu_{ir}^{\mathrm{b}} - \nu_{ir}^{\mathrm{f}}) \bar{\tau}_r, \quad i \in \mathrm{S} \,, \tag{3.5}$$

where $\bar{\tau}_r$ is the zeroth-order macroscopic rate of progress of the rth reaction

$$\bar{\tau}_r = \mathscr{K}_{\mathrm{r}} \left[\prod_{j \in \mathrm{S}} \left(\frac{n_j}{Q_j} \right)^{\nu_{jr}^{\mathrm{f}}} - \prod_{j \in \mathrm{S}} \left(\frac{n_j}{Q_j} \right)^{\nu_{jr}^{\mathrm{b}}} \right], \quad r \in \mathfrak{R} \,, \tag{3.6}$$

and $\mathscr{K}_{\mathrm{r}}$ is the rate constant of the rth reaction. This quantity can be written

$$\mathscr{K}_{\mathrm{r}} = \sum_{\mathrm{F}^r, \mathrm{B}^r} \int \mathfrak{D}_r \prod_{\mathscr{F}^r} \mathrm{d}\boldsymbol{c}_j \prod_{\mathscr{B}^r} \mathrm{d}\boldsymbol{c}_k \,, \tag{3.7}$$

where $\mathfrak{D}_r$ can be expressed in terms of reaction transition probabilities [13]

$$\mathfrak{D}_r = \prod_{j \in \mathscr{F}^r} \exp\left[-\frac{m_j}{2 \mathrm{k_B} T} \boldsymbol{C}_j \cdot \boldsymbol{C}_j - \frac{\mathscr{E}_{j\mathrm{J}}}{\mathrm{k_B} T} \right] \frac{\mathscr{W}_{\mathscr{F}^r \mathscr{B}^r}^{\mathrm{F}^r \mathrm{B}^r}}{\prod_{j \in \mathscr{F}^r} \beta_{j\mathrm{J}}} \,. \tag{3.8}$$

These zeroth-order chemistry production terms are compatible with the law of mass action and classical thermochemistry.

The momentum conservation equation, obtained for $l = n^s + 1, \ldots, n^s + 3$, can be written in the form

$$\partial_t (\rho \boldsymbol{v}) + \partial_{\boldsymbol{x}} \cdot (\rho \boldsymbol{v} \otimes \boldsymbol{v} + p \mathbb{I}) = \rho \boldsymbol{g} + \mathscr{Q}(\boldsymbol{E} + \boldsymbol{v} \wedge \boldsymbol{B}) + \delta_{1b} \boldsymbol{j} \wedge \boldsymbol{B} \,, \tag{3.9}$$

where $\mathbb{I}$ is the unit tensor, $p = n \mathrm{k_B} T$ the pressure and $\mathscr{Q} = \sum_{i \in \mathrm{S}} n_i e_i$ the mixture charge per unit volume. The current density $\boldsymbol{j}$, measured with an observer moving with the gas, depends on the first-order species distribution functions

$$\boldsymbol{j} = \sum_{i,\mathrm{I}} \int f_i^0 \phi_i e_i \boldsymbol{C}_i \, \mathrm{d}\boldsymbol{c}_i \,. \tag{3.10}$$

Finally, the last equation, obtained for $l = n^s + 4$, expresses the conservation of total energy

$$\begin{aligned} &\partial_t (\tfrac{1}{2} \rho \boldsymbol{v} \cdot \boldsymbol{v} + \mathscr{E}) + \partial_{\boldsymbol{x}} \cdot ((\tfrac{1}{2} \rho \boldsymbol{v} \cdot \boldsymbol{v} + \mathscr{E} + p) \boldsymbol{v}) \\ &\quad = (\rho \boldsymbol{g} + \mathscr{Q}(\boldsymbol{E} + \boldsymbol{v} \wedge \boldsymbol{B})) \cdot \boldsymbol{v} + \delta_{1b} (\boldsymbol{j} \wedge \boldsymbol{B}) \cdot \boldsymbol{v} \,. \end{aligned} \tag{3.11}$$

The zeroth-order macroscopic equations thus appear as the reactive compressible Euler equations for polyatomic gas mixtures with new terms expressing the effect of the Lorentz force on the gas as a whole. In the regime $b=1$, provided the conduction current $\boldsymbol{j}$ is expressed in terms of the natural unknowns, these equations, together with Maxwell's equations, form the magnetogasdynamic equations. Eventhough the molecular equations at zeroth-order can be solved for f^0, and yield Maxwellian distributions, the zeroth-order macroscopic equations still contain terms involving the first-order perturbation ϕ when $b=1$. The origin of the difficulty is that the term $\hat{\mathscr{D}}(f^0\phi)$ is not orthogonal to collisional invariants—with respect to the scalar product $\langle\langle f^0\cdot,\cdot\rangle\rangle$. In magnetogasdynamics, the conduction current is usually expressed by using Ohm's law $\boldsymbol{j}=\boldsymbol{\sigma}(\boldsymbol{E}+\boldsymbol{v}\wedge\boldsymbol{B})$ where $\boldsymbol{\sigma}$ is a tensorial electrical conductivity. We will see in the next sections that, at first-order, the kinetic theory yields more complex expressions for the conduction current $\boldsymbol{j}$.

3.3. Temperature governing equation

A governing equation for temperature is easily recovered from the energy conservation equation. We first express the internal energy $\mathscr{E}$ in the form

$$\mathscr{E}=\sum_{i\in \mathrm{S}} n_i(\tfrac{3}{2}\,\mathrm{k_B}T+\bar{\mathscr{E}}_i)\ ,$$

where $\bar{\mathscr{E}}_i$ is the averaged internal energy of the ith species defined by

$$\bar{\mathscr{E}}_i=\frac{1}{Q_i^{\mathrm{int}}}\sum_{\mathrm{I}}\alpha_{i\mathrm{I}}\mathscr{E}_{i\mathrm{I}}\exp\left(-\frac{\mathscr{E}_{i\mathrm{I}}}{\mathrm{k_B}T}\right),\qquad i\in \mathrm{S}\ .$$

For convenience, we also introduce the internal specific heat per molecule for the ith species $\mathfrak{c}_i^{\mathrm{int}}$, the mixture internal specific heat $\mathfrak{c}^{\mathrm{int}}$, the translational constant volume specific heat $\mathfrak{c}_v^{\mathrm{tr}}$ and the mixture constant volume specific heat $\mathfrak{c}_v$ given by

$$\mathfrak{c}_i^{\mathrm{int}}=\frac{\mathrm{d}\bar{\mathscr{E}}_i}{\mathrm{d}T}=\frac{1}{\mathrm{k_B}T^2Q_i^{\mathrm{int}}}\sum_{\mathrm{I}}\alpha_{i\mathrm{I}}(\mathscr{E}_{i\mathrm{I}}-\bar{\mathscr{E}}_i)^2\exp\left(-\frac{\mathscr{E}_{i\mathrm{I}}}{\mathrm{k_B}T}\right),\qquad \mathrm{i}\in \mathrm{S}\ ,$$

$$\mathfrak{c}^{\mathrm{int}}=\sum_{i\in \mathrm{S}}\frac{n_i}{n}\,\mathfrak{c}_i^{\mathrm{int}},\qquad \mathfrak{c}_v^{\mathrm{tr}}=\tfrac{3}{2}\,\mathrm{k_B},\qquad \mathfrak{c}_v=\mathfrak{c}_v^{\mathrm{tr}}+\mathfrak{c}^{\mathrm{int}}\ .$$

After some algebra, we obtain the temperature zeroth-order governing equation

$$n\mathfrak{c}_v(\partial_t T+\boldsymbol{v}\cdot\partial_{\boldsymbol{x}}T)=-p\partial_{\boldsymbol{x}}\cdot\boldsymbol{v}-\delta_{a0}\sum_{i\in \mathrm{S}}(\tfrac{3}{2}\,\mathrm{k_B}T+\bar{\mathscr{E}}_i)\bar{\omega}_i^0\ . \tag{3.12}$$

4. First-order molecular equations

In this section, we discuss the first-order molecular equations for polyatomic gas mixtures in the regime $b=1$, that is, when the magnetic field is strong enough. In Section 5, we will derive the corresponding macroscopic equations.

4.1. Linearized Boltzmann operator

The linearized Boltzmann operator, $\mathscr{F}^{\mathscr{S}} = (\mathscr{F}_i^{\mathscr{S}})_{i\in \mathrm{S}}$, is defined by

$$\mathscr{F}_i^{\mathscr{S}}(\phi) = \sum_{j\in\mathrm{S}} \sum_{1'\mathrm{JJ}'} \int f_j^0(\phi_i + \phi_j - \phi_i' - \phi_j')\mathtt{W}_{ij}^{\mathrm{IJI'J'}}\, \mathrm{d}\boldsymbol{c}_j\, \mathrm{d}\boldsymbol{c}_i'\, \mathrm{d}\boldsymbol{c}_j', \quad i \in \mathrm{S} .$$

An important property is that the linearized Boltzmann operator is isotropic, i.e., it converts a tensor constructed from $(\boldsymbol{c}_i)_{i\in\mathrm{S}}$ into another tensor of the same type as in the monatomic case [1].

We further introduce the associated bracket operator $[\![\xi,\zeta]\!] = \langle\langle f^0\xi, \mathscr{F}^{\mathscr{S}}(\zeta)\rangle\rangle$, where $\xi = (\xi_i)_{i\in\mathrm{S}}$, $\zeta = (\zeta_i)_{i\in\mathrm{S}}$, and where ξ_i and ζ_i depend on $\boldsymbol{c}_i$ and I. The bracket operator is hermitian $[\![\xi,\zeta]\!] = \overline{[\![\zeta,\xi]\!]}$, it is positive semi-definite $[\![\xi,\xi]\!] \geqslant 0$, and its kernel is spanned by the collisional invariants, that is, $[\![\xi,\xi]\!] = 0$ implies that ξ is a (tensorial) collisional invariants, or in other words, that all its tensorial components are scalar collisional invariants.

4.2. Linearized Boltzmann equations

The first-order integro-differential equations governing $\phi = (\phi_i)_{i\in\mathrm{S}}$ are easily obtained from (2.12) and can be written

$$\mathscr{F}_i^{\mathscr{S}}(\phi) = -z_i(\boldsymbol{C}_i \wedge \boldsymbol{B})\cdot \partial_{\boldsymbol{c}_i}\phi_i + \Psi_i, \quad i \in \mathrm{S} , \tag{4.1}$$

where

$$\Psi_i = -\tilde{\mathscr{D}}_i(\log f_i^0) + \delta_{a0}\,\frac{\mathscr{C}_i(f^0)}{f_i^0} .$$

Moreover, relations (2.17) yield the scalar constraints

$$\langle\langle f^0\phi, \psi^l\rangle\rangle = 0, \quad l \in \{1, \ldots, n^s + 4\} . \tag{4.2}$$

The right member $\tilde{\mathscr{D}}_i(\log f_i^0)$ may be evaluated by using the zeroth-order macroscopic conservation equations. After lengthy calculations, we obtain

$$\mathscr{F}_i^{\mathscr{S}}(\phi) + z_i(\boldsymbol{C}_i \wedge \boldsymbol{B})\cdot\partial_{\boldsymbol{c}_i}\phi_i + \sum_{j,\mathrm{J}} \frac{m_i e_j}{\rho \mathrm{k_B} T}\,\boldsymbol{C}_j \cdot \int f_j^0 \phi_j \boldsymbol{C}_j \wedge \boldsymbol{B}\, \mathrm{d}\boldsymbol{c}_j$$

$$= \Psi_i^{\mathscr{S}} + \delta_{a0}\Psi_i^{\mathscr{C}}, \quad i \in \mathrm{S} , \tag{4.3}$$

where

$$\Psi_i^{\mathscr{S}} = -\boldsymbol{\Psi}_i^{\eta} : \partial_{\boldsymbol{x}}\boldsymbol{v} - \tfrac{1}{3}\,\Psi_i^{\kappa}\partial_{\boldsymbol{x}}\cdot\boldsymbol{v} - \sum_{j\in\mathrm{S}} p\boldsymbol{\Psi}_i^{D_j}\cdot\boldsymbol{d}_j - \boldsymbol{\Psi}_i^{\hat{\lambda}}\cdot\partial_{\boldsymbol{x}}\left(\frac{1}{\mathrm{k_B}T}\right) ,$$

$$\Psi_i^{\mathscr{C}} = \frac{\mathscr{C}_i(f^0)}{f_i^0} - \frac{\bar{\omega}_i^0}{n_i} - \frac{1}{p\mathfrak{c}_v T}\left[\frac{3}{2}\,\mathrm{k_B}T - \frac{m_i}{2}\,\boldsymbol{C}_i\cdot\boldsymbol{C}_i + \bar{\mathscr{E}}_i - \mathscr{E}_{i\mathrm{I}}\right]$$

$$\times\sum_{j\in\mathrm{S}}\left(\frac{3}{2}\,\mathrm{k_B}T + \bar{\mathscr{E}}_j\right)\bar{\omega}_j^0 ,$$

and where $p_i = n_i \mathrm{k_B} T$ is the partial pressure and $\boldsymbol{d}_i = (\partial_{\boldsymbol{x}} p_i - \rho_i \tilde{\boldsymbol{b}}_i)/p$ is the diffusion driving forces of the ith species. In these expressions, we have

$$\boldsymbol{\Psi}_i^{\eta} = \frac{m_i}{\mathrm{k_B} T} \left(\boldsymbol{C}_i \otimes \boldsymbol{C}_i - \tfrac{1}{3}\, \boldsymbol{C}_i \cdot \boldsymbol{C}_i \mathbb{I}\right), \tag{4.4}$$

$$\Psi_i^{\kappa} = \frac{2\mathfrak{c}^{\mathrm{int}}}{\mathfrak{c}_v \mathrm{k_B} T}\left(\tfrac{1}{2}\, m_i \boldsymbol{C}_i \cdot \boldsymbol{C}_i - \tfrac{3}{2} \mathrm{k_B} T\right) + \frac{2\mathfrak{c}_v^{\mathrm{tr}}}{\mathfrak{c}_v \mathrm{k_B} T} \left(\bar{\mathscr{E}}_i - \mathscr{E}_{i\mathrm{I}}\right), \tag{4.5}$$

$$\boldsymbol{\Psi}_i^{D_j} = \frac{1}{p_i} \left(\delta_{ij} - \frac{\rho_i}{\rho}\right) \boldsymbol{C}_i\,, \tag{4.6}$$

$$\boldsymbol{\Psi}_i^{\hat{\lambda}} = \left(\tfrac{5}{2}\, \mathrm{k_B} T - \tfrac{1}{2} m_i \boldsymbol{C}_i \cdot \boldsymbol{C}_i + \bar{\mathscr{E}}_i - \mathscr{E}_{i\mathrm{I}}\right) \boldsymbol{C}_i\,. \tag{4.7}$$

In order to expand $\Psi_i^{\mathscr{C}}$, we now write that

$$\Psi_i^{\mathscr{C}} = \sum_{r \in \mathfrak{R}} \Psi_i^r \bar{\tau}_r, \quad i \in \mathrm{S}\,,$$

where $\bar{\tau}_r$ is the zeroth-order macroscopic rate of progress of the rth reaction (3.6) and where Ψ_i^r is given by

$$\begin{aligned} \Psi_i^r = \frac{1}{f_i^0 \mathscr{K}_{\mathrm{r}}} &\left(v_{ir}^{\mathrm{b}} \sum_{\mathrm{F}^r, \mathrm{B}_{\mathrm{I}}^r} \int \mathfrak{D}_r \prod_{\mathscr{F}^r} \mathrm{d}\boldsymbol{c}_j \prod_{\mathscr{B}_i^r} \mathrm{d}\boldsymbol{c}_k - v_{ir}^{\mathrm{f}} \sum_{\mathrm{F}_I^r, \mathrm{B}^r} \int \mathfrak{D}_r \prod_{\mathscr{F}_i^r} \mathrm{d}\boldsymbol{c}_j \prod_{\mathscr{B}^r} \mathrm{d}\boldsymbol{c}_k \right) \\ &- \frac{v_{ir}^{\mathrm{b}} - v_{ir}^{\mathrm{f}}}{n_i} - \frac{1}{p \mathfrak{c}_v T} \left(\sum_{j \in \mathrm{S}} \left(\tfrac{3}{2} \mathrm{k_B} T + \bar{\mathscr{E}}_j\right)\left(v_{jr}^{\mathrm{b}} - v_{jr}^{\mathrm{f}}\right) \right) \\ &\times \left(\frac{3}{2} \mathrm{k_B} T - \frac{m_i}{2}\, \boldsymbol{C}_i \cdot \boldsymbol{C}_i + \bar{\mathscr{E}}_i - \mathscr{E}_{i\mathrm{I}} \right)\,. \end{aligned}$$

By linearity and isotropy of the linearized Boltzmann operator $\mathscr{F}^{\mathscr{S}}$, the solution $\phi = (\phi_i)_{i \in \mathrm{S}}$ of (4.3) is expanded in a similar form

$$\phi_i = \phi_i^{\mathscr{S}} + \delta_{a0} \phi_i^{\mathscr{C}}\,, \tag{4.8}$$

where

$$\phi_i^{\mathscr{S}} = -\boldsymbol{\phi}_i^{\eta} : \partial_{\boldsymbol{x}} \boldsymbol{v} - \tfrac{1}{3} \phi_i^{\kappa} \partial_x \cdot \boldsymbol{v} - \sum_{j \in \mathrm{S}} \boldsymbol{\phi}_i^{D_j} \cdot (\partial_{\boldsymbol{x}} p_j - \rho_j \tilde{\boldsymbol{b}}_j) - \boldsymbol{\phi}_i^{\hat{\lambda}} \cdot \partial_{\boldsymbol{x}} \left(\frac{1}{\mathrm{k_B} T}\right)\,, \tag{4.9}$$

$$\phi_i^{\mathscr{C}} = \sum_{r \in \mathfrak{R}} \phi_i^r \bar{\tau}_r\,. \tag{4.10}$$

The functions ϕ^{μ}, for $\mu \in \{\eta, \kappa, (D_j)_{j \in \mathrm{S}}, \hat{\lambda}, r \in \mathfrak{R}\}$, are now tensorial and satisfy the integro-differential equations

$$\begin{aligned} &\mathscr{F}_i^{\mathscr{S}}(\phi^{\mu}) + z_i (\boldsymbol{C}_i \wedge \boldsymbol{B}) \cdot \partial_{\boldsymbol{c}_i} \phi_i^{\mu} + \sum_{j,\mathrm{J}} \frac{m_i e_j}{\rho \mathrm{k_B} T}\, \boldsymbol{C}_i \cdot \int f_j^0 \boldsymbol{C}_j \wedge \boldsymbol{B} \phi_j^{\mu}\, \mathrm{d}\boldsymbol{c}_j \\ &\quad = \Psi_i^{\mu}, \quad i \in \mathrm{S}\,, \end{aligned} \tag{4.11}$$

and the scalar constraints

$$\langle\langle f^0\phi^\mu, \psi^l \rangle\rangle = 0, \quad l \in \{1,\ldots,n^s+4\} . \tag{4.12}$$

4.3. Equations associated with $\boldsymbol{\phi}^{\hat{\lambda}}$ and $\boldsymbol{\phi}^{D_j}$

We look for a solution $\boldsymbol{\phi}^{\hat{\lambda}} = (\boldsymbol{\phi}_i^{\hat{\lambda}})_{i\in \mathrm{S}}$ in the form

$$\boldsymbol{\phi}_i^{\hat{\lambda}} = \boldsymbol{\phi}_i^{\hat{\lambda}(1)} \boldsymbol{C}_i + \boldsymbol{\phi}_i^{\hat{\lambda}(2)} \boldsymbol{C}_i \wedge \boldsymbol{B} + \boldsymbol{\phi}_i^{\hat{\lambda}(3)} \boldsymbol{C}_i \cdot \boldsymbol{B}\boldsymbol{B} ,$$

where $\boldsymbol{\phi}_i^{\hat{\lambda}(1)}$, $\boldsymbol{\phi}_i^{\hat{\lambda}(2)}$ and $\boldsymbol{\phi}_i^{\hat{\lambda}(3)}$ are scalar functions of $\boldsymbol{C}_i \cdot \boldsymbol{C}_i, (\boldsymbol{C}_i \cdot \boldsymbol{B})^2$ and $\boldsymbol{B} \cdot \boldsymbol{B}$, since $\boldsymbol{\phi}^{\hat{\lambda}}$ must be invariant under a change of coordinates. Substituting this expansion into (4.11) for $\mu = \hat{\lambda}$ and using isotropy, this equation splits into the three separate coupled equations

$$\mathscr{F}_i^{\mathscr{S}}(\phi^{\hat{\lambda}(1)}\boldsymbol{C}) + \sum_{j,\mathrm{J}} \frac{m_i e_j}{3\rho \mathrm{k_B} T} B^2 \boldsymbol{C}_i \int f_j^0 \phi_j^{\hat{\lambda}(2)} \boldsymbol{C}_j \cdot \boldsymbol{C}_j \,\mathrm{d}\boldsymbol{c}_j$$
$$- z_i B^2 \phi_i^{\hat{\lambda}(2)} \boldsymbol{C}_i = \boldsymbol{\Psi}_i^{\hat{\lambda}}, \quad i \in \mathrm{S} , \tag{4.13}$$

$$\mathscr{F}_i^{\mathscr{S}}(\phi^{\hat{\lambda}(2)}\boldsymbol{C} \wedge \boldsymbol{B}) - \sum_{j,\mathrm{J}} \frac{m_i e_j}{3\rho \mathrm{k_B} T} \boldsymbol{C}_i \wedge \boldsymbol{B} \int f_j^0 \phi_j^{\hat{\lambda}(1)} \boldsymbol{C}_j \cdot \boldsymbol{C}_j \,\mathrm{d}\boldsymbol{c}_j$$
$$+ z_i \phi_i^{\hat{\lambda}(1)} \boldsymbol{C}_i \wedge \boldsymbol{B} = 0, \quad i \in \mathrm{S} , \tag{4.14}$$

$$\mathscr{F}_i^{\mathscr{S}}(\phi^{\hat{\lambda}(3)}\boldsymbol{C} \cdot \boldsymbol{B}\boldsymbol{B}) - \sum_{j,\mathrm{J}} \frac{z_j m_i m_j}{3\rho \mathrm{k_B} T} \boldsymbol{C}_i \cdot \boldsymbol{B}\boldsymbol{B} \int f_j^0 \phi_j^{\hat{\lambda}(2)} \boldsymbol{C}_j \cdot \boldsymbol{C}_j \,\mathrm{d}\boldsymbol{c}_j$$
$$+ z_i \phi_i^{\hat{\lambda}(2)} \boldsymbol{C}_i \cdot \boldsymbol{B}\boldsymbol{B} = 0, \quad i \in \mathrm{S} , \tag{4.15}$$

where $B^2 = \boldsymbol{B} \cdot \boldsymbol{B}$, $\phi^{\hat{\lambda}(1)}\boldsymbol{C} = (\phi_i^{\hat{\lambda}(1)}\boldsymbol{C}_i)_{i\in\mathrm{S}}$, $\phi^{\hat{\lambda}(2)}\boldsymbol{C} \wedge \boldsymbol{B} = (\phi_i^{\hat{\lambda}(1)}\boldsymbol{C}_i \wedge \boldsymbol{B})_{i\in\mathrm{S}}$ and $\phi^{\hat{\lambda}(3)}\boldsymbol{C} \cdot \boldsymbol{B}\boldsymbol{B} = (\phi_i^{\hat{\lambda}(3)}\boldsymbol{C}_i \cdot \boldsymbol{B}\boldsymbol{B})_{i\in\mathrm{S}}$. At this step, the integro-differential equations associated with $\boldsymbol{\phi}^{\hat{\lambda}}$ have been reduced to integral equations. Further simplification is now obtained if, for each species i, instead of three real quantities $\phi_i^{\hat{\lambda}(1)}$, $\phi_i^{\hat{\lambda}(2)}$ and $\phi_i^{\hat{\lambda}(3)}$, we introduce one real and one complex unknowns defined by

$$\varphi_i^{\hat{\lambda}(1)} = \phi_i^{\hat{\lambda}(1)} + B^2 \phi_i^{\hat{\lambda}(3)}, \quad \varphi_i^{\hat{\lambda}(2)} = \phi_i^{\hat{\lambda}(1)} + \mathrm{i} B \phi_i^{\hat{\lambda}(2)}, \quad i \in \mathrm{S} ,$$

where of course $\mathrm{i}^2 = -1$. Summing Eqs. (4.13) and (4.15), and taking the scalar product with $\boldsymbol{B}$ yields the equation satisfied by $\varphi^{\hat{\lambda}(1)}$

$$\mathscr{F}_i^{\mathscr{S}}(\varphi^{\hat{\lambda}(1)}\boldsymbol{C}) = \boldsymbol{\Psi}_i^{\hat{\lambda}}, \quad i \in \mathrm{S} . \tag{4.16}$$

The equation for $\varphi^{\hat{\lambda}(2)}$ is obtained by taking the vector product of Eq. (4.13) with $\boldsymbol{B}$, multiplying Eq. (4.14) by iB and adding the two resulting equations

$$\mathscr{F}_i^{\mathscr{S}}(\varphi^{\hat{\lambda}(2)}\boldsymbol{C}) - \mathrm{i}B\sum_{j,\mathrm{J}} \frac{m_i e_j}{3\rho k_{\mathrm{B}}T}\,\boldsymbol{C}_i \int f_j^0 \varphi_j^{\hat{\lambda}(2)} \boldsymbol{C}_j\cdot\boldsymbol{C}_j\,\mathrm{d}\boldsymbol{c}_j$$

$$+\,\mathrm{i}Bz_i\varphi_i^{\hat{\lambda}(2)}\boldsymbol{C}_i = \boldsymbol{\Psi}_i^{\hat{\lambda}}, \quad i\in \mathrm{S}\,. \tag{4.17}$$

Upon introducing $\boldsymbol{\varphi}^{\hat{\lambda}(1)} = (\varphi_i^{\hat{\lambda}(1)}\boldsymbol{C}_i)_{i\in\mathrm{S}}$, $\boldsymbol{\varphi}^{\hat{\lambda}(2)} = (\varphi_i^{\hat{\lambda}(2)}\boldsymbol{C}_i)_{i\in\mathrm{S}}$, and the operator $\mathscr{F}^{\mathscr{B},v} = (\mathscr{F}_i^{\mathscr{B},v})_{i\in\mathrm{S}}$ defined for $\mathbf{u} = (\mathbf{u}_i)_{i\in\mathrm{S}}$ by

$$\mathscr{F}_i^{\mathscr{B},v}(\mathbf{u}) = -Bm_i\boldsymbol{C}_i\sum_{j,\mathrm{J}}\frac{e_j}{3\rho k_{\mathrm{B}}T}\int f_j^0\mathbf{u}_j\cdot\boldsymbol{C}_j\,\mathrm{d}\boldsymbol{C}_j + Bz_i\mathbf{u}_i, \quad i\in\mathrm{S}\,,$$

where $\mathbf{u}_i$ is the product of $\boldsymbol{C}_i$ by a (complex) scalar function of $\boldsymbol{C}_i\cdot\boldsymbol{C}_i$, $(\boldsymbol{C}_i\cdot\boldsymbol{B})^2$ and $\boldsymbol{B}\cdot\boldsymbol{B}$, Eqs. (4.16) and (4.17) are conveniently rewritten in the form

$$\mathscr{F}^{\mathscr{S}}(\boldsymbol{\varphi}^{\hat{\lambda}(1)}) = \boldsymbol{\Psi}^{\hat{\lambda}}\,, \tag{4.18}$$

$$(\mathscr{F}^{\mathscr{S}} + \mathrm{i}\mathscr{F}^{\mathscr{B},v})(\boldsymbol{\varphi}^{\hat{\lambda}(2)}) = \boldsymbol{\Psi}^{\hat{\lambda}}\,. \tag{4.19}$$

Furthermore, the constraint equations (4.12) are easily rewritten in the form

$$\langle\langle f^0\boldsymbol{\varphi}^{\hat{\lambda}(1)}, \psi^l\rangle\rangle = 0, \quad l\in\{1,\ldots,n^s+4\}\,, \tag{4.20}$$

$$\langle\langle f^0\boldsymbol{\varphi}^{\hat{\lambda}(2)}, \psi^l\rangle\rangle = 0, \quad l\in\{1,\ldots,n^s+4\}\,. \tag{4.21}$$

The structure of the integral equation (4.18) is classical and the structure of Eq. (4.19) is similar in a complex framework. More specifically, the operator $\mathscr{F}^{\mathscr{S}} + \mathrm{i}\mathscr{F}^{\mathscr{B},v}$ and the associated bilinear form $\mathsf{a}(\mathbf{u},\mathbf{v}) = (\mathbf{u},(\mathscr{F}^{\mathscr{S}} + \mathrm{i}\mathscr{F}^{\mathscr{B},v})\mathbf{v})$, defined on the proper Hilbert space of complex isotropic squared integrable functions, are such that $|\mathsf{a}(\mathbf{u},\mathbf{u})| \geqslant [\mathbf{u},\mathbf{u}]$ which yields existence and uniqueness thanks to the constraints. Moreover, from the isotropy of the operator $\mathscr{F}^{\mathscr{S}}$, the functions $\varphi^{\hat{\lambda}(1)}$ and $\varphi^{\hat{\lambda}(2)}$ cannot be functions of $(\boldsymbol{C}\cdot\boldsymbol{B})^2$ [1].

In order to conveniently express $\boldsymbol{\phi}^{\hat{\lambda}}$ in terms of $\varphi^{\hat{\lambda}(1)}$ and $\varphi^{\hat{\lambda}(2)}$, we introduce some extra notation. We define the unitary vector $\mathscr{B}$ by $\mathscr{B} = \mathbf{B}/B$ and for any vector $\mathbf{X}$, we introduce the associated vectors

$$\mathbf{X}^{\parallel} = (\mathscr{B}\cdot\mathbf{X})\mathscr{B}, \quad \mathbf{X}^{\perp} = \mathbf{X} - \mathbf{X}^{\parallel} \quad \text{and} \quad \mathbf{X}^{t} = \mathscr{B}\wedge\mathbf{X}\,.$$

For any vector $\mathbf{X}$, the vectors $\mathbf{X}^{\parallel}$, $\mathbf{X}^{\perp}$ and $\mathbf{X}^{t}$ are mutually orthogonal. In addition, for any vectors $\mathbf{X}$ and $\mathbf{Y}$, we have $\mathbf{X}^{\perp}\cdot\mathbf{Y}^{\parallel} = 0$, $\mathbf{X}^{t}\cdot\mathbf{Y}^{\parallel} = 0$, $\mathbf{X}^{\perp}\cdot\mathbf{Y}^{t} + \mathbf{Y}^{\perp}\cdot\mathbf{X}^{t} = 0$, and $\mathbf{X}^{\perp}\cdot\mathbf{Y}^{\perp} = \mathbf{X}^{t}\cdot\mathbf{Y}^{t}$. Finally $\mathbf{X}^{\parallel}$, $\mathbf{X}^{\perp}$ and $\mathbf{X}^{t}$ are obtained from $\mathbf{X}$ by applying the linear operators $p^{\parallel} = \mathscr{B}\otimes\mathscr{B}$, $p^{\perp} = \mathbb{I} - \mathscr{B}\otimes\mathscr{B}$ and $p^{t} = \boldsymbol{M}^{\mathscr{B}}$, that is

$$p^{\parallel}\mathbf{X} = \mathbf{X}^{\parallel}, \quad p^{\perp}\mathbf{X} = \mathbf{X}^{\perp}, \quad p^{t}\mathbf{X} = \mathbf{X}^{t}\,,$$

where $\boldsymbol{M}^{\mathscr{B}}$ is the matrix defined by

$$\boldsymbol{M}^{\mathscr{B}} = \begin{pmatrix} 0 & -\mathscr{B}_3 & \mathscr{B}_2 \\ \mathscr{B}_3 & 0 & -\mathscr{B}_1 \\ -\mathscr{B}_2 & \mathscr{B}_1 & 0 \end{pmatrix}.$$

It is then straightforward to obtain that

$$\boldsymbol{\phi}^{\hat{\lambda}} = (\varphi^{\hat{\lambda}(1)}\mathscr{B}\otimes\mathscr{B} + \Re(\varphi^{\hat{\lambda}(2)})(\mathbb{I} - \mathscr{B}\otimes\mathscr{B}) - \Im(\varphi^{\hat{\lambda}(2)})\mathbf{M}^{\mathscr{B}})\boldsymbol{C}_i \,, \tag{4.22}$$

or equivalently

$$\boldsymbol{\phi}^{\hat{\lambda}} = \Re(\varphi^{\hat{\lambda}(1)}\boldsymbol{C}_i^{\|} + \varphi^{\hat{\lambda}(2)}(\boldsymbol{C}_i^{\perp} + \mathrm{i}\boldsymbol{C}_i^{t})) \,, \tag{4.23}$$

where $\Re(z)$ and $\Im(z)$ denote the real and imaginary part of a complex quantity $z = \Re(z) + \mathrm{i}\Im(z)$.

The success of the complex framework can be understood upon introducing a complex representation $\mathbf{X}^c = \mathbf{X}^{\|} + \mathbf{X}^{\perp} - \mathbf{i}\mathbf{X}^t$ associated with any real vector $\mathbf{X} = \mathbf{X}^{\|} + \mathbf{X}^{\perp}$. Indeed, in this complex framework, applying $\boldsymbol{M}^{\mathscr{B}}$ is then equivalent to a multiplication by i in the plane orthogonal to $\mathscr{B}$, that is, we have $\mathscr{B}\wedge(\mathbf{X}^{\perp} - \mathrm{i}\mathbf{X}^t) = \mathbf{X}^t + \mathrm{i}\mathbf{X}^{\perp} = \mathrm{i}(\mathbf{X}^{\perp} - \mathrm{i}\mathbf{X}^t)$.

The above development can be followed through for $\boldsymbol{\phi}^{D_j}$, $j \in \mathrm{S}$, as well. More specifically, the perturbed distribution functions $\boldsymbol{\phi}^{D_j}$ are expanded in the form

$$\boldsymbol{\phi}_i^{D_j} = \phi_i^{D_j(1)}\boldsymbol{C}_i + \phi_i^{D_j(2)}\boldsymbol{C}_i \wedge \boldsymbol{B} + \phi_i^{D_j(3)}\boldsymbol{C}_i \cdot \boldsymbol{BB} \,,$$

and defining

$$\varphi_i^{D_j(1)} = \phi_i^{D_j(1)} + B^2\phi_i^{D_j(3)}, \qquad \varphi_i^{D_j(2)} = \phi_i^{D_j(1)} + \mathrm{i}B\phi_i^{D_j(2)}, \qquad i,j \in \mathrm{S} \,,$$

and $\boldsymbol{\varphi}^{D_j(1)} = (\varphi_i^{D_j(1)}\boldsymbol{C}_i)_{i\in\mathrm{S}}$, $\boldsymbol{\varphi}^{D_j(2)} = (\varphi_i^{D_j(2)}\boldsymbol{C}_i)_{i\in\mathrm{S}}$, $j \in \mathrm{S}$, we obtain

$$\mathscr{F}^{\mathscr{S}}(\boldsymbol{\varphi}^{D_j(1)}) = \boldsymbol{\Psi}^{D_j} \,, \tag{4.24}$$

$$(\mathscr{F}^{\mathscr{S}} + \mathrm{i}\mathscr{F}^{\mathscr{B},v})(\boldsymbol{\varphi}^{D_j(2)}) = \boldsymbol{\Psi}^{D_j} \,, \tag{4.25}$$

together with the constraints

$$\langle\langle f^0\boldsymbol{\varphi}^{D_j(1)}, \psi^l \rangle\rangle = 0, \qquad l \in \{1,\dots,n^s+4\} \,, \tag{4.26}$$

$$\langle\langle f^0\boldsymbol{\varphi}^{D_j(2)}, \psi^l \rangle\rangle = 0, \qquad l \in \{1,\dots,n^s+4\} \,, \tag{4.27}$$

for all $j \in \mathrm{S}$. An important property of the right members $\boldsymbol{\Psi}^{D_j}$ is then that $\sum_{j\in\mathrm{S}} \rho_j \boldsymbol{\Psi}^{D_j} = 0$, which in turns implies by linearity that $\sum_{j\in\mathrm{S}} \rho_j \boldsymbol{\phi}^{D_j} = 0$ so that

$$\sum_{j\in\mathrm{S}} \rho_j \boldsymbol{\varphi}^{D_j(1)} = 0, \qquad \sum_{j\in\mathrm{S}} \rho_j \boldsymbol{\varphi}^{D_j(2)} = 0 \,. \tag{4.28}$$

We can also write that

$$\boldsymbol{\phi}^{D_j} = (\varphi^{D_j(1)}\mathscr{B}\otimes\mathscr{B} + \Re(\boldsymbol{\varphi}^{D_j(2)})(\mathbb{I} - \mathscr{B}\otimes\mathscr{B}) - \Im(\varphi^{D_j(2)})\boldsymbol{M}^{\mathscr{B}})\boldsymbol{C}_i \,, \tag{4.29}$$

or equivalently

$$\boldsymbol{\phi}^{D_j} = \Re(\varphi^{D_j(1)}\boldsymbol{C}_i^{\|} + \varphi^{D_j(2)}(\boldsymbol{C}_i^{\perp} + \mathrm{i}\boldsymbol{C}_i^{t})) \,. \tag{4.30}$$

Finally, it is also established that the linear rank of $\varphi^{\hat{\lambda}(1)}, \varphi^{D_1(1)}, \dots, \varphi^{D_{n^s}(1)}$ and $\varphi^{\hat{\lambda}(2)}$, $\varphi^{D_1(2)}, \dots, \varphi^{D_{n^s}(2)}$ is exactly n^s, because it is the rank of the corresponding right members $\boldsymbol{\Psi}^{\hat{\lambda}}.\boldsymbol{\Psi}^{D_1}, \dots, \boldsymbol{\Psi}^{D_{n^s}}$.

4.4. Equations associated with $\boldsymbol{\phi}^\eta$

For the sake of simplicity, we introduce the following renormalized velocities:

$$\mathscr{C}_i = \sqrt{\frac{m_i}{2\mathrm{k_B}T}}\,\boldsymbol{C}_i, \quad i \in \mathrm{S}\ .$$

We look for a solution $\boldsymbol{\phi}^\eta = (\boldsymbol{\phi}_i^\eta)_{i\in\mathrm{S}}$ such that $\boldsymbol{\phi}_i^\eta$ is composed from all the symmetric, traceless second-order tensors that can be created from the vector $\mathscr{C}_i$ and the pseudo-vector $\boldsymbol{B}$. As the dimension of this space is five, it would be sufficient to consider five independent tensors. However, it is more elegant [1] to consider the six tensors $\mathbf{T}_i^{(1)},\dots,\mathbf{T}_i^{(6)}$, defined by

$$\mathbf{T}_i^{(1)} = \mathscr{C}_i \otimes \mathscr{C}_i - \tfrac{1}{3}\,\mathscr{C}_i \cdot \mathscr{C}_i \mathbb{I}\ ,$$

$$\mathbf{T}_i^{(2)} = \tfrac{1}{2}[\mathscr{C}_i \otimes (\mathscr{C}_i \wedge \boldsymbol{B}) + (\mathscr{C}_i \wedge \boldsymbol{B}) \otimes \mathscr{C}_i]\ ,$$

$$\mathbf{T}_i^{(3)} = (\mathscr{C}_i \wedge \boldsymbol{B}) \otimes (\mathscr{C}_i \wedge \boldsymbol{B}) - \tfrac{1}{3}[\mathscr{C}_i \cdot \mathscr{C}_i \boldsymbol{B} \cdot \boldsymbol{B} - (\mathscr{C}_i \cdot \boldsymbol{B})^2]\mathbb{I}\ ,$$

$$\mathbf{T}_i^{(4)} = \tfrac{1}{2}\mathscr{C}_i \cdot \boldsymbol{B}[\mathscr{C}_i \otimes \boldsymbol{B} + \boldsymbol{B} \otimes \mathscr{C}_i] - \tfrac{1}{3}(\mathscr{C}_i \cdot \boldsymbol{B})^2 \mathbb{I}\ ,$$

$$\mathbf{T}_i^{(5)} = \tfrac{1}{2}\mathscr{C}_i \cdot \boldsymbol{B}[\boldsymbol{B} \otimes (\mathscr{C}_i \wedge \boldsymbol{B}) + (\mathscr{C}_i \wedge \mathbf{B}) \otimes \boldsymbol{B}]\ ,$$

$$\mathbf{T}_i^{(6)} = (\mathscr{C}_i \cdot \boldsymbol{B})^2[\boldsymbol{B} \otimes \boldsymbol{B} - \tfrac{1}{3}\,\boldsymbol{B} \cdot \boldsymbol{B}\mathbb{I}]\ ,$$

which span the same space, and the following linear relation:

$$\mathscr{C}_i \cdot \mathscr{C}_i \mathbf{T}_i^{(6)} + (\mathscr{C}_i \cdot \boldsymbol{B})^2[\mathbf{T}_i^{(3)} + \boldsymbol{B} \cdot \boldsymbol{B}\mathbf{T}_i^{(1)} - 2\mathbf{T}_i^{(4)}] = 0\ .$$

We then expand the tensor $\boldsymbol{\phi}_i^\eta$ as

$$\boldsymbol{\phi}_i^\eta = \sum_{n=1}^{6} \phi_i^{\eta(n)} \mathbf{T}_i^{(n)}\ , \tag{4.31}$$

where $\phi_i^{\eta(n)}$ are scalar functions of $\mathscr{C}_i \cdot \mathscr{C}_i$, $(\mathscr{C}_i \cdot \boldsymbol{B})^2$ and $\boldsymbol{B} \cdot \boldsymbol{B}$, for $i \in \mathrm{S}$. Substituting this expansion into Eq. (4.11) for $\mu = \eta$ and equating the corresponding terms yields six equations, each one involving one tensor $\mathbf{T}_i^{(n)}$ for $n = 1,\dots,6$. Using the property that all the tensors $\mathbf{T}_i^{(n)}$ for $n = 1,\dots,6$ are simple transformations of the tensor $\mathbf{T}_i^{(1)}$, and thanks to the isotropy of the Boltzmann linearized operator $\mathscr{F}^{\mathscr{S}}$, we then obtain six coupled equations between the family of tensors $\boldsymbol{\phi}^{\eta(n)} = (\boldsymbol{\phi}_i^{\eta(n)})_{i\in\mathrm{S}}$ defined by

$$\boldsymbol{\phi}_i^{\eta(n)} = \phi_i^{\eta(n)}(\mathscr{C}_i \otimes \mathscr{C}_i - \tfrac{1}{3}\,\mathscr{C}_i \cdot \mathscr{C}_i \mathbb{I})\ .$$

The resulting equations are in the form

$$\mathscr{F}_i^{\mathscr{S}}(\boldsymbol{\phi}^{\eta(1)}) - z_i B^2 \boldsymbol{\phi}_i^{\eta(2)} = \boldsymbol{\Psi}_i^\eta, \quad i \in \mathrm{S}\ , \tag{4.32}$$

$$\mathscr{F}_i^{\mathscr{S}}(\boldsymbol{\phi}^{\eta(2)}) + 2z_i(\boldsymbol{\phi}_i^{\eta(1)} - B^2 \boldsymbol{\phi}_i^{\eta(3)}) = 0, \quad i \in \mathrm{S}\ , \tag{4.33}$$

$$\mathscr{F}_i^{\mathscr{S}}(\boldsymbol{\phi}^{\eta(3)}) + z_i \boldsymbol{\phi}_i^{\eta(2)} = 0, \quad i \in \mathrm{S}\ , \tag{4.34}$$

$$\mathscr{F}_i^{\mathscr{S}}(\boldsymbol{\phi}^{\eta(4)}) + z_i(\boldsymbol{\phi}_i^{\eta(2)} - B^2\boldsymbol{\phi}_i^{\eta(5)}) = 0, \quad i \in \mathrm{S}\,, \tag{4.35}$$

$$\mathscr{F}_i^{\mathscr{S}}(\boldsymbol{\phi}^{\eta(5)}) + z_i(2\boldsymbol{\phi}_i^{\eta(3)} + \boldsymbol{\phi}_i^{\eta(4)}) = 0, \quad i \in \mathrm{S}\,, \tag{4.36}$$

$$\mathscr{F}_i^{\mathscr{S}}(\boldsymbol{\phi}^{\eta(6)}) + z_i\boldsymbol{\phi}_i^{\eta(5)} = 0, \quad i \in \mathrm{S}\,. \tag{4.37}$$

As $\mathscr{F}^{\mathscr{S}}$ is a linear operator and $\boldsymbol{\phi}^{\eta(n)}$, $n \in \{1,\dots,6\}$, are orthogonal to collisional invariants, adding (4.34) minus (4.35) minus B^2 (4.37) yields

$$B^2\boldsymbol{\phi}_i^{\eta(6)} = \boldsymbol{\phi}_i^{\eta(3)} - \boldsymbol{\phi}_i^{\eta(4)}, \quad i \in \mathrm{S}\,. \tag{4.38}$$

Therefore, we may solve Eqs. (4.32)–(4.36) and subsequently obtain $\boldsymbol{\phi}_i^{\eta(6)}$ from Eq. (4.38). We again introduce auxiliary complex quantities

$$\begin{aligned}
\boldsymbol{\varphi}_i^{\eta(1)} &= \boldsymbol{\phi}_i^{\eta(1)} + B^2\boldsymbol{\phi}_i^{\eta(3)}\,,\\
\boldsymbol{\varphi}_i^{\eta(2)} &= \boldsymbol{\phi}_i^{\eta(1)} + \mathrm{i}B\boldsymbol{\phi}_i^{\eta(2)} - B^2\boldsymbol{\phi}_i^{\eta(3)}\,,\\
\boldsymbol{\varphi}_i^{\eta(3)} &= \boldsymbol{\phi}_i^{\eta(1)} + \tfrac{1}{2}\,\mathrm{i}B\boldsymbol{\phi}_i^{\eta(2)} + \tfrac{1}{2}\,B^2\boldsymbol{\phi}_i^{\eta(4)} + \tfrac{1}{2}\,\mathrm{i}B^3\boldsymbol{\phi}_i^{\eta(5)}\,,
\end{aligned}$$

defined for each species $i \in \mathrm{S}$. After a little algebra, the corresponding families $\boldsymbol{\varphi}^{\eta(1)}$, $\boldsymbol{\varphi}^{\eta(2)}$, and $\boldsymbol{\varphi}^{\eta(3)}$ are found to satisfy the following uncoupled equations

$$\mathscr{F}_i^{\mathscr{S}}(\boldsymbol{\varphi}^{\eta(1)}) = 2\boldsymbol{\mathsf{T}}_i^{(1)}, \quad i \in \mathrm{S}\,, \tag{4.39}$$

$$\mathscr{F}_i^{\mathscr{S}}(\boldsymbol{\varphi}^{\eta(2)}) + 2\mathrm{i}Bz_i\boldsymbol{\varphi}_i^{\eta(2)} = 2\boldsymbol{\mathsf{T}}_i^{(1)}, \quad i \in \mathrm{S}\,, \tag{4.40}$$

$$\mathscr{F}_i^{\mathscr{S}}(\boldsymbol{\varphi}^{\eta(3)}) + \mathrm{i}Bz_i\boldsymbol{\varphi}_i^{\eta(3)} = 2\boldsymbol{\mathsf{T}}_i^{(1)}, \quad i \in \mathrm{S}\,. \tag{4.41}$$

We introduce the operator $\mathscr{F}^{\mathscr{B},m} = (\mathscr{F}_i^{\mathscr{B},m})_{i\in\mathrm{S}}$ defined for $\boldsymbol{\mathsf{u}} = (\boldsymbol{\mathsf{u}}_i)_{i\in\mathrm{S}}$ by

$$\mathscr{F}_i^{\mathscr{B},m}(\boldsymbol{\mathsf{u}}) = Bz_i\boldsymbol{\mathsf{u}}_i, \quad i \in \mathrm{S}\,,$$

where $\boldsymbol{\mathsf{u}}_i$ is the product of $\mathscr{C}_i \otimes \mathscr{C}_i - \frac{1}{3}\mathscr{C}_i \cdot \mathscr{C}_i\mathbb{I}$ by a (complex) scalar function of $\boldsymbol{C}_i \cdot \boldsymbol{C}_i$ $(\boldsymbol{C}_i \cdot \boldsymbol{B})^2$ and $\boldsymbol{B} \cdot \boldsymbol{B}$. Eqs. (4.39)–(4.41) are then conveniently rewritten in the form

$$\mathscr{F}^{\mathscr{S}}(\boldsymbol{\varphi}^{\eta(1)}) = \boldsymbol{\Psi}^{\eta}, \tag{4.42}$$

$$(\mathscr{F}^{\mathscr{S}} + 2\mathrm{i}\mathscr{F}^{\mathscr{B},m})(\boldsymbol{\varphi}^{\eta(2)}) = \boldsymbol{\Psi}^{\eta}\,. \tag{4.43}$$

$$(\mathscr{F}^{\mathscr{S}} + \mathrm{i}\mathscr{F}^{\mathscr{B},m})(\boldsymbol{\varphi}^{\eta(3)}) = \boldsymbol{\Psi}^{\eta}\,. \tag{4.44}$$

These systems are shown to be well posed and imply that the (complex) scalar function $\varphi_i^{\eta(n)}$ such that $\boldsymbol{\varphi}_i^{\eta(n)} = \varphi_i^{\eta(n)}(\mathscr{C}_i \otimes \mathscr{C}_i - \frac{1}{3}\mathscr{C}_i \cdot \mathscr{C}_i\mathbb{I})$ only depends on $\boldsymbol{C}_i \cdot \boldsymbol{C}_i$ and $\boldsymbol{B} \cdot \boldsymbol{B}$ [1], for $n = 1, 2, 3$. It is also possible to express ϕ^{η} in terms of $\boldsymbol{\varphi}^{\eta(n)}$, $n = 1, 2, 3$, but the corresponding relation is intricate.

4.5. Equations associated with ϕ_i^κ and ϕ_i^r

For $\mu = \kappa$, Eqs. (4.11) become

$$\mathscr{F}_i^{\mathscr{S}}(\phi^\kappa) + z_i(\boldsymbol{C}_i \wedge \boldsymbol{B}) \cdot \partial_{\boldsymbol{c}_i}\phi_i^\kappa + \sum_{j,\mathrm{J}} \frac{m_i e_j}{\rho \mathrm{k}_B T} \boldsymbol{C}_i \cdot \int f_j^0 C_j \wedge \boldsymbol{B}\phi_j^\kappa \, \mathrm{d}\boldsymbol{c}_j$$

$$= \boldsymbol{\Psi}_i^\kappa, \quad i \in \mathrm{S} . \tag{4.45}$$

We look for scalar functions ϕ_i^κ of $\boldsymbol{C}_i \cdot \boldsymbol{C}_i$, $(\boldsymbol{C}_i \cdot \boldsymbol{B})^2$ and $\boldsymbol{B} \cdot \boldsymbol{B}$. As $f_i^0 \boldsymbol{C}_i \wedge \boldsymbol{B}\phi_i^\kappa$ is an odd function of $\boldsymbol{C}_i$, all the integrals $\int f_j^0 \boldsymbol{C}_j \wedge \boldsymbol{B}\phi_j^\kappa \, \mathrm{d}\boldsymbol{c}_j$ vanish. Moreover, the vector $\partial_{\boldsymbol{c}_i}\phi_i^\kappa$ is in the plane spanned by $\boldsymbol{C}_i$ and $\boldsymbol{B}$ so that $(\boldsymbol{C}_i \wedge \boldsymbol{B}) \cdot \partial_{\boldsymbol{c}_i}\phi_i^\kappa = 0$ for $i \in \mathrm{S}$. Eq. (4.45) then becomes

$$\mathscr{F}^{\mathscr{S}}(\phi^\kappa) = \Psi^\kappa , \tag{4.46}$$

which are to be completed with the constraints (4.12)

$$\langle\langle f^0\phi^\kappa, \psi^l \rangle\rangle = 0, \quad l \in \{1, \ldots, n^s + 4\} . \tag{4.47}$$

This problem falls then into the common framework without electric and magnetic fields [1,21]. As a consequence, we obtain that there exist only one scalar function of $\boldsymbol{C}_i \cdot \boldsymbol{C}_i$ which satisfies Eqs. (4.46) and (4.47).

Similar results are obtained for $\mu = r$, $r \in \mathfrak{R}$, and Eqs. (4.11) are easily reduced to

$$\mathscr{F}^{\mathscr{S}}(\phi^r) = \Psi^r, \quad r \in \mathfrak{R} , \tag{4.48}$$

$$\langle\langle f^0\phi^r, \psi^l \rangle\rangle = 0, \quad l \in \{1, \ldots, n^s + 4\} . \tag{4.49}$$

5. First-order macroscopic equations

In this section we investigate the macroscopic first-order equations for polyatomic gas mixtures in the regime $b = 1$. More specifically, we investigate the conservation equations, the transport fluxes and the transport coefficients. We also investigate the structure and properties of the resulting multicomponent diffusion matrices and multicomponent heat–mass transport matrices. These properties are fundamental in order to investigate macroscopic entropy production. These properties, established here for exact matrices arising from the kinetic theory of gases, are a key point in numerical approximations of multicomponent diffusion. In this situation, the coefficients arising from theoretical physics are replaced by ordinary numerical parameters, so that these properties have to be guaranteed by the computational algorithms used to evaluate the transport coefficients. We finally investigate the macroscopic entropy conversation equation and establish that macroscopic entropy production is positive.

5.1. First-order conservative equations

The macroscopic conservation equations at first-order are obtained by taking the scalar product of Boltzmann equation by collisional invariants and by keeping the terms that are $\mathcal{O}(\varepsilon^0)$ or $\mathcal{O}(\varepsilon^1)$. More specifically, in the regime $b=1$, these equations are obtained from

$$\langle\langle \tilde{\mathscr{D}}(f^0 + f^0\phi), \psi^l\rangle\rangle + \langle\langle \hat{\mathscr{D}}(f^0\phi), \psi^l\rangle\rangle = \langle\langle \mathscr{C}(f^0), \psi^l\rangle\rangle + \delta_{a0}\langle\langle \partial_f \mathscr{C}(f^0) f^0\phi, \psi^l\rangle\rangle \;, \tag{5.1}$$

for $l \in \{1,\dots,n^s+4\}$, where we have defined $\partial_f \mathscr{C}_i(f^0) f^0\phi = (\partial_f \mathscr{C}_i(f^0) f^0\phi)_{i\in \mathrm{S}}$. After some algebra, the species mass conservation equations, obtained for $l=1,\dots,n^s$, are found in the form

$$\partial_t \rho_i + \partial_{\boldsymbol{x}} \cdot (\rho_i \boldsymbol{v}) + \partial_{\boldsymbol{x}} \cdot (\rho_i \boldsymbol{V}_i) = m_i \bar{\omega}_i, \quad i \in \mathrm{S} \;, \tag{5.2}$$

where $\boldsymbol{V}_i$ is the diffusion velocities and $\bar{\omega}_i$ the first-order chemical source term of the ith species. The diffusion velocities are defined by

$$\boldsymbol{V}_i = \frac{1}{n_i} \sum_{\mathrm{I}} \int \boldsymbol{C}_i f_i^0 \phi_i \, \mathrm{d}\boldsymbol{c}_i, \quad i \in \mathrm{S} \;, \tag{5.3}$$

and the source term by

$$\bar{\omega}_i = \sum_{\mathrm{I}} \int (\mathscr{C}_i(f^0) + \delta_{ao} \partial_f \mathscr{C}_i(f^0) f^0\phi) \, \mathrm{d}\boldsymbol{c}_i, \quad i \in \mathrm{S} \;. \tag{5.4}$$

The momentum conservation equation, obtained for $l = n^s+1,\ n^s+2,\ n^s+3$, reads

$$\partial_t(\rho\boldsymbol{v}) + \partial_{\boldsymbol{x}} \cdot (\rho \boldsymbol{v} \otimes \boldsymbol{v} + p\mathbb{I}) + \partial_{\boldsymbol{x}} \cdot \boldsymbol{\Pi} = \rho \boldsymbol{g} + \mathscr{Q}(\boldsymbol{E} + \boldsymbol{v} \wedge \boldsymbol{B}) + \boldsymbol{j} \wedge \boldsymbol{B} \;, \tag{5.5}$$

where $\boldsymbol{j}$ is the electric current density (3.10), which can also be written in the form $\boldsymbol{j} = \sum_{i\in \mathrm{S}} n_i e_i \boldsymbol{V}_i$, and $\boldsymbol{\Pi}$ is the viscous stress tensor

$$\boldsymbol{\Pi} = \sum_{i,\mathrm{I}} \int m_i \boldsymbol{C}_i \otimes \boldsymbol{C}_i f_i^0 \phi_i \, \mathrm{d}\boldsymbol{c}_i \;. \tag{5.6}$$

The energy conservation equation, obtained for $l = n^s+4$, finally reads

$$\begin{aligned} &\partial_t(\tfrac{1}{2}\rho \boldsymbol{v}\cdot\boldsymbol{v} + \mathscr{E}) + \partial_{\boldsymbol{x}} \cdot ((\tfrac{1}{2}\rho \boldsymbol{v}\cdot\boldsymbol{v} + \mathscr{E} + p)\boldsymbol{v}) \\ &\quad + \partial_{\boldsymbol{x}} \cdot (\boldsymbol{q} + \boldsymbol{\Pi}\cdot\boldsymbol{v}) = (\rho\boldsymbol{g} + \mathscr{Q}(\boldsymbol{E} + \boldsymbol{v}\wedge\boldsymbol{B}))\cdot\boldsymbol{v} + \boldsymbol{j}\cdot\boldsymbol{E} \;, \end{aligned} \tag{5.7}$$

where $\boldsymbol{q}$ is the heat flux vector

$$\boldsymbol{q} = \sum_{i,\mathrm{I}} \int (\tfrac{1}{2} m_i \boldsymbol{C}_i \cdot \boldsymbol{C}_i + \mathscr{E}_{i\mathrm{I}}) \boldsymbol{c}_i f_i^0 \phi_i \, \mathrm{d}\boldsymbol{c}_i \;. \tag{5.8}$$

Note that there should be an extra term in the left member of (5.1). This extra term reads $\langle\langle \hat{\mathscr{D}}(f^0\phi^{(2)}), \psi^l\rangle\rangle$—where $\phi^{(2)}$ is the second order contribution in the Enskog expansion of f—and seems to be usually neglected without notice. It yields contributions in the form $\boldsymbol{j}^{(2)} \wedge \boldsymbol{B}$ in the right member of the momentum conservation equation and $(\boldsymbol{B}\wedge\boldsymbol{v})\cdot\boldsymbol{j}^{(2)}$ in the right member of the energy conservation equation, where $\boldsymbol{j}^{(2)}$ is the second order current [4]. Since the charge usually goes to zero rapidly in globally neutral ionized reactive flows, this second order current is likely to be neglected.

5.2. Expressions of the diffusion velocities $\boldsymbol{V}_i$

Using definition (5.3) of $\boldsymbol{V}_i$ and expression (4.6) of $\boldsymbol{\Psi}_i^{D_j}$ yields [10]

$$\boldsymbol{V}_i = \mathrm{k_B} T \langle\langle \boldsymbol{\Psi}^{D_i}, f^0 \phi \rangle\rangle, \quad i \in \mathrm{S} .$$

Substituting expansion (4.8), (4.9) into the latter equation, only the terms in $\boldsymbol{\phi}^{D_j}$, $j \in \mathrm{S}$, and $\boldsymbol{\phi}^{\hat{\lambda}}$, yield non-null contributions, so that

$$\boldsymbol{V}_i = -\mathrm{k_B} T \sum_{j\in \mathrm{S}} \langle\langle \boldsymbol{\Psi}^{D_i}, f^0 \boldsymbol{\phi}^{D_j} \cdot (\partial_{\mathbf{x}} p_j - \rho_j \tilde{\mathbf{b}}_j) \rangle\rangle$$
$$- \mathrm{k_B} T \left\langle\left\langle \boldsymbol{\Psi}^{D_i}, f^0 \phi^{\hat{\lambda}} \cdot \partial_{\boldsymbol{x}} \left(\frac{1}{\mathrm{k_B} T} \right) \right\rangle\right\rangle .$$

Further expanding $\boldsymbol{\phi}^{D_j}$, $j \in \mathrm{S}$, and $\boldsymbol{\phi}^{\hat{\lambda}}$, with (4.22) and (4.29), using isotropy and keeping in mind that $\boldsymbol{d}_j = (\partial_{\boldsymbol{x}} p_j - \rho_j \tilde{\mathbf{b}}_j)/p$, we obtain

$$\boldsymbol{V}_i = -\sum_{j\in \mathrm{S}} (D_{ij}^{\|} \boldsymbol{d}_j^{\|} + D_{ij}^{\perp} \boldsymbol{d}_j^{\perp} + D_{ij}^{t} \boldsymbol{d}_j^{t})$$
$$- (\theta_i^{\|} (\partial_{\boldsymbol{x}} \log T)^{\|} + \theta_i^{\perp} (\partial_{\boldsymbol{x}} \log T)^{\perp} + \theta_i^{t} (\partial_{\boldsymbol{x}} \log T)^{t}) , \tag{5.9}$$

where the transport coefficients are defined by $D_{ij}^{\|} = (p\mathrm{k_B}T/3)\langle\langle \boldsymbol{\Psi}^{D_i}, \boldsymbol{\varphi}^{D_j(1)} \rangle\rangle$, $D_{ij}^{\perp} + \mathrm{i}D_{ij}^{t} = (p\mathrm{k_B}T/3)\langle\langle \boldsymbol{\Psi}^{D_i}, \boldsymbol{\varphi}^{D_j(2)} \rangle\rangle$, $\theta_i^{\|} = -(1/3)\langle\langle \boldsymbol{\Psi}^{D_i}, \boldsymbol{\varphi}^{\hat{\lambda}(1)} \rangle\rangle$, $\theta_i^{\perp} + \mathrm{i}\theta_i^{t} = -(1/3)\langle\langle \boldsymbol{\Psi}^{D_i}, \boldsymbol{\varphi}^{\hat{\lambda}(2)} \rangle\rangle$. These coefficients are easily rewritten in the symmetrized form

$$D_{ij}^{\|} = \tfrac{1}{3} p\mathrm{k_B} T [\![\boldsymbol{\varphi}^{D_i(1)}, \boldsymbol{\varphi}^{D_j(1)}]\!] , \tag{5.10}$$

$$D_{ij}^{\perp} + \mathrm{i}D_{ij}^{t} = \tfrac{1}{3} p\mathrm{k_B} T \left([\![\boldsymbol{\varphi}^{D_i(2)}, \boldsymbol{\varphi}^{D_j(2)}]\!] + \mathrm{i}((\boldsymbol{\varphi}^{D_i(2)}, \boldsymbol{\varphi}^{D_j(2)})) \right) , \tag{5.11}$$

and

$$\theta_i^{\|} = -\tfrac{1}{3} [\![\boldsymbol{\varphi}^{D_i(1)}, \boldsymbol{\varphi}^{\hat{\lambda}(1)}]\!] , \tag{5.12}$$

$$\theta_i^{\perp} + \mathrm{i}\theta_i^{t} = -\tfrac{1}{3} \left([\![\boldsymbol{\varphi}^{D_i(2)}, \boldsymbol{\varphi}^{\hat{\lambda}(2)}]\!] + \mathrm{i}((\boldsymbol{\varphi}^{D_i(2)}, \boldsymbol{\varphi}^{\hat{\lambda}(2)})) \right) , \tag{5.13}$$

where we have defined the scalar product

$$((\xi, \zeta)) = \sum_{k,\mathrm{K}} z_k B \int f_k^0 \xi_k \odot \bar{\zeta}_k \, \mathrm{d}\boldsymbol{c}_k . \tag{5.14}$$

Note that the contributions involving the scalar product $((\cdot,\cdot))$ in $D^{\perp}$ D^{t}, $\theta^{\perp}$, and θ^{t} have been overlooked in Ref. [1].

It is also possible to rewrite (5.9) in the compact form

$$\boldsymbol{V}_i = -\sum_{j\in \mathrm{S}} \boldsymbol{D}_{ij} \boldsymbol{d}_j - \boldsymbol{\theta}_i \partial_{\boldsymbol{x}} \log T , \tag{5.15}$$

where we have defined the tensorial coefficients

$$\boldsymbol{D}_{ij} = D_{ij}^{\|}\boldsymbol{\mathscr{B}} \otimes \boldsymbol{\mathscr{B}} + D_{ij}^{\perp}(\mathbb{I} - \boldsymbol{\mathscr{B}} \otimes \boldsymbol{\mathscr{B}}) + D_{ij}^{t}\boldsymbol{M}^{\boldsymbol{\mathscr{B}}}, \quad i,j \in \mathrm{S}\,, \tag{5.16}$$

$$\boldsymbol{\theta}_{i} = \theta_{i}^{\|}\boldsymbol{\mathscr{B}} \otimes \boldsymbol{\mathscr{B}} + \theta_{i}^{\perp}(\mathbb{I} - \boldsymbol{\mathscr{B}} \otimes \boldsymbol{\mathscr{B}}) + \theta_{i}^{t}\boldsymbol{M}^{\boldsymbol{\mathscr{B}}}, \quad i \in \mathrm{S}\,. \tag{5.17}$$

We now investigate the properties of the multicomponent diffusion matrices $D^{\|} = (D_{ij}^{\|})_{i,j\in\mathrm{S}}$, $D^{\perp} = (D_{ij}^{\perp})_{i,j\in\mathrm{S}}$, and $D^{t} = (D_{ij}^{t})_{i,j\in\mathrm{S}}$. These properties are fundamental in order to establish that macroscopic entropy production is positive and for efficient computational evaluation of transport coefficient in multicomponent numerical simulations. We will denote by $\langle x, y\rangle$ the euclidean scalar product between two real vectors x and y, or equivalently the hermitian scalar products between two complex vectors x and y, and we introduce the mass fraction vector $Y = (Y_i)_{i\in\mathrm{S}}$ where $Y_i = \rho_i/\rho$, $i \in \mathrm{S}$. From the properties of the bracket operator, the linear constraint (4.28) among the $\boldsymbol{\varphi}^{D_j(1)}$, $j \in \mathrm{S}$, and the identity

$$\langle D^{\|}x, x\rangle = \tfrac{1}{3}\, pk_{\mathrm{B}}T \left[\!\!\left[\sum_{i\in\mathrm{S}} \boldsymbol{\varphi}^{D_i(1)}x_i,\ \sum_{i\in\mathrm{S}} \boldsymbol{\varphi}^{D_i(1)}x_i \right]\!\!\right],$$

valid for $x \in \mathbb{R}^{n^s}$, it is easily established—as in the nonionized case [10]—that $D^{\|}$ is real symmetric positive semi-definite and that its nullspace is spanned by the vector Y in $\mathbb{R}^{n^s}$. On the other hand, the matrices $D^{\perp}$ and D^{t} have a more complex structure since

$$D_{ij}^{\perp} = \tfrac{1}{3}\, pk_{\mathrm{B}}T \left(\Re\llbracket \boldsymbol{\varphi}^{D_i(2)}, \boldsymbol{\varphi}^{D_j(2)} \rrbracket - \Im\left((\!(\boldsymbol{\varphi}^{D_i(2)}, \boldsymbol{\varphi}^{D_j(2)})\!) \right) \right),$$

$$D_{ij}^{t} = \tfrac{1}{3}\, pk_{\mathrm{B}}T \left(\Im\llbracket \boldsymbol{\varphi}^{D_i(2)}, \boldsymbol{\varphi}^{D_j(2)} \rrbracket + \Re\left((\!(\boldsymbol{\varphi}^{D_i(2)}, \boldsymbol{\varphi}^{D_j(2)})\!) \right) \right),$$

so that the symmetric part of $D^{\perp}$ is associated with $\Re\llbracket\cdot,\cdot\rrbracket$ and its antisymmetric part with $\Im((\cdot,\cdot))$, whereas the symmetric part of D^{t} is associated with $\Re((\cdot,\cdot))$ and its antisymmetric part with $\Im\llbracket\cdot,\cdot\rrbracket$. For these matrices, one can first establish that for $x \in \mathbb{R}^{n^s}$ and $y \in \mathbb{R}^{n^s}$

$$\begin{aligned}
&\langle D^{\perp}x, x\rangle + \langle D^{\perp}y, y\rangle + \langle D^{t}x, y\rangle - \langle x, D^{t}y\rangle \\
&\quad = \Re\langle (D^{\perp} + \mathrm{i}D^{t})(x - \mathrm{i}y),\ x + \mathrm{i}y\rangle\,, \\
&\quad = \tfrac{1}{3}\, pk_{\mathrm{B}}T \left[\!\!\left[\sum_{i\in\mathrm{S}} \boldsymbol{\varphi}^{D_i(2)}(x_i - \mathrm{i}y_i), \sum_{i\in\mathrm{S}} \boldsymbol{\varphi}^{D_i(2)}(x_i - \mathrm{i}y_i) \right]\!\!\right]
\end{aligned}$$

so that this quantity is nonnegative, and it is zero if and only if both vectors x and y are proportional to Y. Note, in particular, that only the symmetric part of $D^{\perp}$ and the antisymmetric part of D^{t} are associated with this nonnegativity property, needed to establish that the entropy production term associated with $D^{\perp}$ and D^{t} is nonnegative. In addition, proceeding essentially as in Ref. [10], one can also establish that the nullspace of the complex matrix $D^{\perp} + \mathrm{i}D^{t}$ is spanned by Y in $\mathbb{C}^{n^s}$ and that its range is the (hermitian) orthogonal complement of Y in $\mathbb{C}^{n^s}$. Similarly, the nullspace of the real matrix $D^{\perp}$ is spanned by Y in $\mathbb{R}^{n^s}$ and that its range is the (euclidean) orthogonal complement of Y in $\mathbb{R}^{n^s}$ eventhough $D^{\perp}$ is not symmetric. Finally, still using the linear constraint (4.28) and the definition of thermal diffusion coefficients we easily obtain that $\langle \theta^{\parallel}, Y\rangle = 0$, $\langle \theta^{\perp}, Y\rangle = 0$, and $\langle \theta^{t}, Y\rangle = 0$.

We now define the thermal diffusion ratios $\chi^{\parallel}=(\chi_i^{\parallel})_{i\in \mathrm{S}}$, $\chi^{\perp}=(\chi_i^{\perp})_{i\in \mathrm{S}}$, and $\chi^{t}=(\chi_i^{t})_{i\in S}$, from the linear systems

$$\begin{cases} D^{\parallel}\chi^{\parallel} = \theta^{\parallel}\,, \\ \langle \chi^{\parallel}, U\rangle = 0\,, \end{cases} \qquad \begin{cases} (D^{\perp} + \mathrm{i}D^{t})(\chi^{\perp} + \mathrm{i}\chi^{t}) = \theta^{\perp} + \mathrm{i}\theta^{t}\,, \\ \langle \chi^{\perp} + \mathrm{i}\chi^{t}, U\rangle = 0\,, \end{cases} \tag{5.18}$$

where U is the vector of length n^s with unity component $U = (1)_{i\in\mathrm{S}}$. From these definitions, after some algebra, we obtain an alternative expression for the diffusion velocities $\boldsymbol{V}_i$

$$\begin{aligned} \boldsymbol{V}_i = &-\sum_{j\in\mathrm{S}} D_{ij}^{\parallel}(\boldsymbol{d}_j^{\parallel} + \chi_j^{\parallel}(\partial_{\boldsymbol{x}} \log T)^{\parallel}) - \sum_{j\in\mathrm{S}} D_{ij}^{\perp}(\boldsymbol{d}_j^{\perp} + \chi_j^{\perp}(\partial_{\boldsymbol{x}} \log T)^{\perp} \\ &+ \chi_j^{t}(\partial_{\boldsymbol{x}} \log T)^{t}) - \sum_{j\in\mathrm{S}} D_{ij}^{t}(\boldsymbol{d}_j^{t} + \chi_j^{\perp}(\partial_{\boldsymbol{x}} \log T)^{t} - \chi_j^{t}(\partial_{\boldsymbol{x}} \log T)^{\perp})\,. \end{aligned} \tag{5.19}$$

Another definition of the thermal diffusion ratios $\chi^{\perp}$ and χ^{t} has been given by Ferziger and Kaper. This definition is in the form $D^{\perp}\chi^{\perp} = \theta^{\perp}$, $\langle \chi^{\perp}, U\rangle = 0$, and $D^{t}\chi^{t} = \theta^{t}$, $\langle \chi^{t}, U\rangle = 0$. However, there are several difficulties associated with this definition. First, the linear system $D^{t}x = \theta^{t}$, $\langle x, U\rangle = 0$ is not always well posed. In particular, in the limit of zero magnetic fields, the matrix D^{t} is the zero matrix and the constraint $\langle \chi^{t}, U\rangle = 0$ is insufficient to determine that $\chi^{t} = 0$. In addition, the projections of $\boldsymbol{d}_i$ and $\partial_{\boldsymbol{x}} \log T$ that are denoted by $\boldsymbol{d}_i^{\perp}$ and $(\partial_{\boldsymbol{x}} \log T)^{\perp}$ are not necessarily in the same direction and it is somewhat artificial to try to regroup these projections under the same coefficients. On the other hand, we note that system (5.18) is always well posed since $\theta^{\perp} + \mathrm{i}\theta^{t}$ is in the range of $D^{\perp} + \mathrm{i}D^{t}$ and U is complementary to the nullspace of $D^{\perp} + \mathrm{i}D^{t}$ in $\mathbb{C}^{n^s}$. In particular, in the limit of zero magnetic field $\boldsymbol{B} = 0$, it is easily checked that $\Im(\boldsymbol{\varphi}^{\hat{\lambda}(2)}) = 0$ and $\Im(\boldsymbol{\varphi}^{D_i(2)}) = 0$, so that $\theta^{t} = 0$ and $D^{t} = 0$, which implies directly $D^{\perp}\chi^{t} = 0$ and finally $\chi^{t} = 0$ thanks to $\langle \chi^{t}, U\rangle = 0$.

Finally, from the expressions of the diffusion velocities, we can readily express the first-order conduction current $\boldsymbol{j}$ in terms of the macroscopic variable gradients, the electric field and the magnetic field. After some algebra, we obtain that

$$\begin{aligned} \boldsymbol{j} = &-\sum_{j\in\mathrm{S}} (\sigma_j^{\parallel}\boldsymbol{d}_j'^{\parallel} + \sigma_j^{\perp}\boldsymbol{d}_j'^{\perp} + \sigma_j^{t}\boldsymbol{d}_j'^{t}) \\ &+ (\sigma^{\parallel}\boldsymbol{E}^{\parallel} + \sigma^{\perp}(\boldsymbol{E}^{\perp} + \boldsymbol{v}\wedge\boldsymbol{B}) + \sigma^{t}(\boldsymbol{E} + \boldsymbol{v}\wedge\boldsymbol{B})^{t})\,, \\ &- (\sigma_T^{\parallel}(\partial_{\boldsymbol{x}} \log T)^{\parallel} + \sigma_T^{\perp}(\partial_{\boldsymbol{x}} \log T)^{\perp} + \sigma_T^{t}(\partial_{\boldsymbol{x}} \log T)^{t})\,, \end{aligned} \tag{5.20}$$

where $\boldsymbol{d}_j' = (\partial_{\boldsymbol{x}} p_j - \rho_j \boldsymbol{g})/p$ and where the electrical conductivities $\sigma^{\parallel}, \sigma^{\perp}, \sigma^{t}$ are defined by

$$\sigma^{\parallel} = \sum_{i,j\in\mathrm{S}} D_{ij}^{\parallel} n_i e_i n_j e_j, \qquad \sigma^{\perp} = \sum_{i,j\in\mathrm{S}} D_{ij}^{\perp} n_i e_i n_j e_j, \qquad \sigma^{t} = \sum_{i,j\in\mathrm{S}} D_{ij}^{t} n_i e_i n_j e_j\,,$$

the electro-thermal coefficients $\sigma_T^{\|}, \sigma_T^{\perp}, \sigma_T^{t}$ are defined by

$$\sigma_T^{\|} = \sum_{i\in S} \theta_i^{\|} n_i e_i, \quad \sigma_T^{\perp} = \sum_{i\in S} \theta_i^{\perp} n_i e_i, \quad \sigma_T^{t} = \sum_{i\in S} \theta_i^{t} n_i e_i \ ,$$

and the electro-diffusion coefficients $\sigma_j^{\|}, \sigma_T^{\perp}, \sigma_j^{t}$ are given by

$$\sigma_j^{\|} = \sum_{i\in S} D_{ij}^{\|} n_i e_i, \quad \sigma_j^{\perp} = \sum_{i\in S} D_{ij}^{\perp} n_i e_i, \quad \sigma_j^{t} = \sum_{i\in S} D_{ij}^{t} n_i e_i \ .$$

5.3. Expressions of the heat flux $\boldsymbol{q}$

Using definition (5.8) of $\boldsymbol{q}$ and expression (4.7) of $\boldsymbol{\Psi}_{\boldsymbol{i}}^{\hat{\lambda}}$ yields [10]

$$\boldsymbol{q} = -\langle\langle \boldsymbol{\Psi}^{\hat{\lambda}}, f^0 \phi \rangle\rangle + \sum_{i\in S} (\tfrac{5}{2} \mathrm{k_B} T + \bar{\mathscr{E}}_i) n_i \boldsymbol{V}_i \ .$$

Using expansions (4.8), (4.9), (4.22), and (4.29) we further obtain that

$$\begin{aligned} \boldsymbol{q} = & -(\hat{\lambda}^{\|} (\partial_{\boldsymbol{x}} T)^{\|} + \hat{\lambda}^{\perp} (\partial_{\boldsymbol{x}} T)^{\perp} + \hat{\lambda}^{t} (\partial_{\boldsymbol{x}} T)^{t}) \\ & - p \sum_{i\in S} (\hat{\theta}_i^{\|} \boldsymbol{d}_i^{\|} + \hat{\theta}_i^{\perp} \boldsymbol{d}_i^{\perp} + \hat{\theta}_i^{t} \boldsymbol{d}_i^{t}) + \sum_{i\in S} (\tfrac{5}{2} \mathrm{k_B} T + \bar{\mathscr{E}}_i) n_i \boldsymbol{V}_i \ , \end{aligned} \tag{5.21}$$

where the transport coefficients are defined by $\hat{\lambda}^{\|} = (1/3\mathrm{k_B} T^2) \langle\langle \boldsymbol{\Psi}^{\hat{\lambda}}, \boldsymbol{\varphi}^{\hat{\lambda}(1)} \rangle\rangle$, $\hat{\lambda}^{\perp} + \mathrm{i}\hat{\lambda}^{t} = (1/3\mathrm{k_B} T^2) \langle\langle \boldsymbol{\Psi}^{\hat{\lambda}}, \boldsymbol{\varphi}^{\hat{\lambda}(2)} \rangle\rangle$, $\hat{\theta}_i^{\|} = -(1/3) \langle\langle \boldsymbol{\Psi}^{\hat{\lambda}}, \boldsymbol{\varphi}^{D_i(1)} \rangle\rangle$, and $\hat{\theta}_i^{\perp} + \mathrm{i}\hat{\theta}_i^{t} = -(1/3) \langle\langle \boldsymbol{\Psi}^{\hat{\lambda}}, \boldsymbol{\varphi}^{D_i(2)} \rangle\rangle$. These coefficients can be easily rewritten in the symmetrized form

$$\hat{\lambda}^{\|} = \frac{1}{3\mathrm{k_B} T^2} [\![\boldsymbol{\varphi}^{\hat{\lambda}(1)}, \boldsymbol{\varphi}^{\hat{\lambda}(1)}]\!] \ ,$$

$$\hat{\lambda}^{\perp} + \mathrm{i}\hat{\lambda}^{t} = \frac{1}{3\mathrm{k_B} T^2} \left([\![\boldsymbol{\varphi}^{\hat{\lambda}(2)}, \boldsymbol{\varphi}^{\hat{\lambda}(2)}]\!], \ + \mathrm{i}((\boldsymbol{\varphi}^{\hat{\lambda}(2)}, \boldsymbol{\varphi}^{\hat{\lambda}(2)})) \right) \ ,$$

and

$$\hat{\theta}_i^{\|} = -\tfrac{1}{3} [\![\boldsymbol{\varphi}^{\hat{\lambda}(1)}, \boldsymbol{\varphi}^{D_i(1)}]\!] \ ,$$

$$\hat{\theta}_i^{\perp} + \mathrm{i}\hat{\theta}_i^{t} = -\tfrac{1}{3} \left([\![\boldsymbol{\varphi}^{\hat{\lambda}(2)}, \boldsymbol{\varphi}^{D_i(2)}]\!] + \mathrm{i}((\boldsymbol{\varphi}^{\hat{\lambda}(2)}, \boldsymbol{\varphi}^{D_i(2)})) \right) \ .$$

Note that the contributions involving the scalar product $((\cdot,\cdot))$ in $\hat{\lambda}^{\perp}$, $\hat{\lambda}^{t}$, $\hat{\lambda}^{t}$, $\hat{\theta}^{\,\perp}$, and $\hat{\theta}^{\,t}$ have been overlooked in Ref. [1]. It is easily established that $\hat{\theta}_i^{\|} = \theta_i^{\|}$ and that $\hat{\theta}_i^{\perp}(\boldsymbol{B}) = \theta_i^{\perp}(-\boldsymbol{B})$ and $\hat{\theta}_i^{t}(\boldsymbol{B}) = \theta_i^{t}(-\boldsymbol{B})$ where only the dependence on the magnetic field is explicited. These relations will be investigated in more details in the section concerning Onsager relations.

Relation (5.21) can also be written in the compact form

$$\boldsymbol{q} = -\hat{\boldsymbol{\lambda}} \partial_{\boldsymbol{x}} T - p \sum_{i\in S} \hat{\boldsymbol{\theta}}_i \boldsymbol{d}_i + \sum_{i\in S} (\tfrac{5}{2} \, \mathrm{k_B} T + \bar{\mathscr{E}}_i) n_i \boldsymbol{V}_i \ ,$$

where we have defined the tensorial coefficients

$$\hat{\boldsymbol{\lambda}} = \hat{\lambda}^{\|}\mathscr{B}\otimes\mathscr{B} + \hat{\lambda}^{\perp}(\mathbb{I} - \mathscr{B}\otimes\mathscr{B}) + \hat{\lambda}^{t}\boldsymbol{M}^{\mathscr{B}} , \tag{5.22}$$

$$\hat{\boldsymbol{\theta}}_i = \hat{\theta}_i^{\|}\mathscr{B}\otimes\mathscr{B} + \hat{\theta}_i^{\perp}(\mathbb{I} - \mathscr{B}\otimes\mathscr{B}) + \hat{\theta}_i^{t}\boldsymbol{M}^{\mathscr{B}}, \quad i\in\mathrm{S} . \tag{5.23}$$

The positivity properties associated with the heat flux and the diffusion velocities can be written with the help of the heat–mass transport matrices

$$A^{\|} = \begin{pmatrix} \frac{T}{p}\hat{\lambda}^{\|} & \hat{\theta}^{\,\|\mathrm{T}} \\ \theta^{\,\|} & D^{\|} \end{pmatrix}, \quad A^{\perp} + \mathrm{i}A^{t} = \begin{pmatrix} \frac{T}{p}\hat{\lambda}^{\perp} & \hat{\theta}^{\,\perp\mathrm{T}} \\ \theta^{\,\perp} & D^{\perp} \end{pmatrix} + \mathrm{i}\begin{pmatrix} \frac{T}{p}\hat{\lambda}^{t} & \hat{\theta}^{\,t\mathrm{T}} \\ \theta^{\,t} & D^{t} \end{pmatrix} ,$$

where the superscript `T` indicates a transposition. Proceeding as for the multicomponent matrices, and using

$$\langle A^{\|}x', x'\rangle = \tfrac{1}{3}\, p\mathrm{k_B}T[\![\Phi,\Phi]\!] ,$$

where $\Phi = \sum_{i\in\mathrm{S}} x_i\boldsymbol{\varphi}^{D_i(1)} - x_0\boldsymbol{\varphi}^{\hat{\lambda}(1)}/(p\mathrm{k_B}T)$ and $x' = (x_0, x)\in\mathbb{R}^{n^s+1}$, one can establish that the matrix $A^{\|}$ is real symmetric positive semi-definite and that its nullspace is one dimensional and spanned by $(0, Y)$. Similarly, one can also establish that for $x' = (x_0, x)$ and $y' = (y_0, y)$, $x', y'\in\mathbb{R}^{n^s+1}$, $x, y\in\mathbb{R}^{n^s}$

$$\langle A^{\perp}x', x'\rangle + \langle A^{\perp}y', y'\rangle + \langle A^{t}x', y'\rangle - \langle x', A^{t}y'\rangle = \tfrac{1}{3}\, p\mathrm{k_B}T[\![\Phi,\Phi]\!] ,$$

where $\Phi = \sum_{i\in\mathrm{S}}(x_i + \mathrm{i}y_i)\boldsymbol{\varphi}^{D_i(2)} - (x_0 + \mathrm{i}y_0)\boldsymbol{\varphi}^{\hat{\lambda}(2)}/(p\mathrm{k_B}T)$. In particular, the latter quantity is nonnegative and is zero if and only if $x_0 = y_0 = 0$ and both vectors x and y are proportional to Y. Once again, only the terms involving the bracket product, that is, only the symmetric part of $A^{\perp}$ and the antisymmetric part of A^{t}, are associated with nonnegativity properties. In addition, one can establish that the nullspace of $A^{\perp} + \mathrm{i}A^{t}$ is spanned by $(0, Y)$ in $\mathbb{C}^{n^s+1}$ whereas its range is the (hermitian) orthogonal to $(0, Y)$ in $\mathbb{C}^{n^s+1}$. Similarly, the nullspace of $A^{\perp}$ is spanned by $(0, Y)$ in $\mathbb{R}^{n^s+1}$ and its range is the (euclidean) orthogonal to $(0, Y)$ in $\mathbb{R}^{n^s+1}$.

We next define the modified thermal diffusion ratios $\hat{\chi}^{\|} = (\hat{\chi}_i^{\|})_{i\in\mathrm{S}}$, $\hat{\chi}^{\perp} = (\hat{\chi}_i^{\perp})_{i\in\mathrm{S}}$ and $\hat{\chi}^{t} = (\hat{\chi}_i^{t})_{i\in\mathrm{S}}$ from the linear systems

$$\begin{cases} D^{\|}\hat{\chi}^{\|} = \hat{\theta}^{\,\|} , \\ \langle\hat{\chi}^{\|}, U\rangle = 0 , \end{cases} \begin{cases} (\hat{\chi}^{\perp} + \mathrm{i}\hat{\chi}^{t})^{\mathrm{T}}(D^{\perp} + \mathrm{i}D^{t}) = (\hat{\theta}^{\,\perp} + \mathrm{i}\hat{\theta}^{\,t})^{\mathrm{T}} , \\ \langle\hat{\chi}^{\perp} + \mathrm{i}\hat{\chi}^{t}, U\rangle = 0 . \end{cases}$$

One can then obtain the following alternative expression of the heat flux

$$\begin{aligned} \boldsymbol{q} = {} & -\lambda^{\|}(\partial_{\boldsymbol{x}}T)^{\|} - \lambda^{\perp}(\partial_{\boldsymbol{x}}T)^{\perp} - \lambda^{t}(\partial_{\boldsymbol{x}}T)^{t} \\ & + p\sum_{i\in\mathrm{S}}(\hat{\chi}_i^{\|}\boldsymbol{V}_i^{\|} + \hat{\chi}_i^{\perp}\boldsymbol{V}_i^{\perp} + \hat{\chi}_i^{t}\boldsymbol{V}_i^{t}) + \sum_{i\in\mathrm{S}}(\tfrac{5}{2}\,\mathrm{k_B}T + \bar{\mathscr{E}}_i)n_i\boldsymbol{V}_i , \end{aligned} \tag{5.24}$$

where we have introduced

$$\lambda^{\|} = \hat{\lambda}^{\|} - (p/T)\sum_{i,j\in\mathrm{S}} D_{ji}^{\|}\hat{\chi}_j^{\|}\chi_i^{\|} ,$$

$$\lambda^{\perp} + \mathrm{i}\lambda^{t} = \hat{\lambda}^{\perp} + \mathrm{i}\hat{\lambda}^{t} - (p/T)\sum_{i,j\in\mathrm{S}}(D_{ji}^{\perp} + \mathrm{i}D_{ji}^{t})(\hat{\chi}_j^{\perp} + \mathrm{i}\hat{\chi}_j^{\perp})(\chi_i^{\perp} + \mathrm{i}\chi_i^{t}) .$$

Note that there is no term involving $(\frac{5}{2}\mathrm{k_B}T + \bar{\mathscr{E}}_i)n_i \boldsymbol{V}_i^t$ in the heat flux [1] since $\boldsymbol{V}_i = \boldsymbol{V}_i^{\|} + \boldsymbol{V}_i^{\perp}$. The positivity properties can also be explicitly written in terms of $\lambda^{\perp} + \mathrm{i}\lambda^t$ with the help of the hermitian part $A^h = (A + \bar{A}^{\mathrm{T}})/2$ of $A = A^{\perp} + \mathrm{i}A^t$ and the (generalized) Schur complement of its lower right block D^h. More specifically, we have $D_{ij}^h = (p\mathrm{k_B}T/3)[\![\boldsymbol{\varphi}^{D_i(2)}, \boldsymbol{\varphi}^{D_j(2)}]\!]$, $\theta_i^h = -(1/3)[\![\boldsymbol{\varphi}^{\hat{\lambda}(2)}, \boldsymbol{\varphi}^{D_i(2)}]\!]$, $\hat{\lambda}^h = \hat{\lambda}^{\perp}$ and defining χ^h from $D^h\chi^h = \theta^h$ and $\langle \chi^h, U\rangle = 0$, the Schur complement $\lambda^h = \hat{\lambda}^h - (p/T)\langle D^h\chi^h, \bar{\chi}^h\rangle$ must be positive.

5.4. *Expressions of the viscous stress tensor* $\boldsymbol{\Pi}$

Using expressions (4.4) and (4.5) and Eq. (5.6) yields the following relation for the viscous stress tensor $\boldsymbol{\Pi}$

$$\boldsymbol{\Pi} = \mathrm{k_B}T\langle\langle \boldsymbol{\Psi}^{\eta}, f^0\phi\rangle\rangle + \tfrac{1}{3}\mathrm{k_B}T\langle\langle \Psi^{\kappa}, f^0\phi\rangle\rangle \mathbb{I} \ .$$

The term $\langle\langle \Psi^{\kappa}, f^0\phi\rangle\rangle$ is easily evaluated in the form

$$\langle\langle \Psi^{\kappa}, f^0\phi\rangle\rangle = -\tfrac{1}{3}\mathrm{k_B}T\langle\langle \Psi^{\kappa}, f^0\phi^{\kappa}\rangle\rangle + \delta_{a0}\sum_{r\in\mathfrak{R}}\langle\langle \Psi^{\kappa}, f^0\phi^r\rangle\rangle\bar{\tau}_r \ .$$

Defining the volume viscosity κ by

$$\kappa = \tfrac{1}{9}\mathrm{k_B}T[\![\phi^{\kappa}, \phi^{\kappa}]\!] \ , \tag{5.25}$$

and the reactive pressure by

$$p^{\mathrm{reac}} = \sum_{r\in\mathfrak{R}}[\![\Psi^{\kappa}, \phi^r]\!]\bar{\tau}_r \ ,$$

we obtain that

$$\boldsymbol{\Pi} = \hat{\boldsymbol{\Pi}} - \kappa\partial_{\boldsymbol{x}}\cdot\boldsymbol{v}\mathbb{I} + \delta_{a0}\,p^{\mathrm{reac}}\mathbb{I} \ ,$$

where $\hat{\boldsymbol{\Pi}} = \mathrm{k_B}T\langle\langle \boldsymbol{\Psi}^{\eta}, f^0\phi\rangle\rangle$. In order to evaluate

$$\hat{\boldsymbol{\Pi}} = \mathrm{k_B}T\langle\langle \boldsymbol{\Psi}^{\eta}, f^0\phi\rangle\rangle = -\mathrm{k_B}T\langle\langle \boldsymbol{\Psi}^{\eta}, f^0\boldsymbol{\phi}^{\eta}\colon\, \partial_{\boldsymbol{x}}\boldsymbol{v}\rangle\rangle \ ,$$

we substitute expansion (4.31), we use the relations expressing the tensors $\mathsf{T}_i^{(n)}$ for $n = 1,\ldots,6$ as simple transformations of the tensor $\mathsf{T}_i^{(1)}$, and the isotropy of the Boltzmann linearized operator $\mathscr{F}^{\mathscr{S}}$. Defining the five shear viscosities $\eta_1,\ldots,\eta_5$ by

$$\eta_1 = \tfrac{1}{20}\mathrm{k_B}T([\![\boldsymbol{\varphi}^{\eta(1)}, \boldsymbol{\varphi}^{\eta(1)}]\!] + [\![\boldsymbol{\varphi}^{\eta(2)}, \boldsymbol{\varphi}^{\eta(2)}]\!]), \tag{5.26}$$

$$\eta_2 = -\tfrac{1}{10}\mathrm{k_B}T((\boldsymbol{\varphi}^{\eta(2)}, \boldsymbol{\varphi}^{\eta(2)})) \ , \tag{5.27}$$

$$\eta_3 = \tfrac{1}{20}\mathrm{k_B}T([\![\boldsymbol{\varphi}^{\eta(1)}, \boldsymbol{\varphi}^{\eta(1)}]\!] - [\![\boldsymbol{\varphi}^{\eta(2)}, \boldsymbol{\varphi}^{\eta(2)}]\!]) \ , \tag{5.28}$$

$$\eta_4 = \tfrac{1}{10}\mathrm{k_B}T([\![\boldsymbol{\varphi}^{\eta(3)}, \boldsymbol{\varphi}^{\eta(3)}]\!] - \tfrac{1}{2}[\![\boldsymbol{\varphi}^{\eta(1)}, \boldsymbol{\varphi}^{\eta(1)}]\!] - \tfrac{1}{2}[\![\boldsymbol{\varphi}^{\eta(2)}, \boldsymbol{\varphi}^{\eta(2)}]\!]) \ , \tag{5.29}$$

$$\eta_5 = \tfrac{1}{10}\mathrm{k_B}T\,\Big(\,((\boldsymbol{\varphi}^{\eta(2)}, \boldsymbol{\varphi}^{\eta(2)})) - ((\boldsymbol{\varphi}^{\eta(3)}, \boldsymbol{\varphi}^{\eta(3)}))\,\Big) \ , \tag{5.30}$$

we obtain after lengthy algebra the following expression for $\hat{\boldsymbol{\Pi}}$

$$\begin{aligned}-\hat{\boldsymbol{\Pi}} = {}& \eta_1 \mathsf{S} + \eta_2(M^{\mathscr{B}}\mathsf{S} - \mathsf{S}M^{\mathscr{B}}) + \eta_3(-M^{\mathscr{B}}\mathsf{S}M^{\mathscr{B}} + \mathscr{B}^{\mathrm{T}}\mathsf{S}\mathscr{B}\mathscr{B}\otimes\mathscr{B}) \\ & + \eta_4(\mathsf{S}\mathscr{B}\otimes\mathscr{B} + \mathscr{B}\otimes\mathscr{B}\mathsf{S} - 2\mathscr{B}^{\mathrm{T}}\mathsf{S}\mathscr{B}\mathscr{B}\otimes\mathscr{B}) \\ & + \eta_5(\mathscr{B}\otimes\mathscr{B}\mathsf{S}M^{\mathscr{B}} - M^{\mathscr{B}}\mathsf{S}\mathscr{B}\otimes\mathscr{B})\,,\end{aligned}$$

where S is given by

$$\mathsf{S} = (\partial_{\boldsymbol{x}}\boldsymbol{v} + \partial_{\boldsymbol{x}}\boldsymbol{v}^{\mathrm{T}}) - \tfrac{2}{3}\,(\partial_{\boldsymbol{x}}\cdot\boldsymbol{v})\mathbb{I}\ .$$

To the best of our knowledge, the bracket expressions (5.26)–(5.30) expressing the five shear vicosities in terms of the solutions $\boldsymbol{\varphi}^{\eta(1)}, \boldsymbol{\varphi}^{\eta(2)}$, and $\boldsymbol{\varphi}^{\eta(3)}$ are new.

5.5. Expression of the chemical source term $\bar{\omega}_i$

Eq. (5.4) can be rewritten in the form

$$\bar{\omega}_i = \bar{\omega}_i^0 + \mathfrak{w}_i, \qquad i\in\mathrm{S}\,,$$

with

$$\mathfrak{w}_i = \delta_{a0}\sum_{\mathrm{I}}\int \partial_f\mathscr{C}_i(f^0)f^0\phi\,\mathrm{d}\boldsymbol{c}_i, \qquad i\in\mathrm{S}\ .$$

The structure of the perturbed chemical source terms $\mathfrak{w}_i$ are investigated in [18] for nonionized gas mixtures but the same formalism apply. In particular, the perturbed source term is a quadratics in the zeroth-order forward and backward reaction rates of progress plus a linear combination of the same quantities multiplied by $\partial_{\boldsymbol{x}}\cdot\boldsymbol{v}$. Some estimates of the perturbed terms $\mathfrak{w}_i$ have been given in the literature and they are believed to be small as well as the chemical pressure and we refer to [10] for more details. Finally, upon neglecting both the chemical pressure p^{reac} and the perturbed source terms $\mathfrak{w}_i$, $i\in\mathrm{S}$, the governing equations for both regimes $a=0$ and $a=1$ coincide.

5.6. Macroscopic entropy

Expanding (2.8) up to first-order terms yields that $\mathscr{S}^{\mathrm{kin}} = \mathscr{S} + \mathcal{O}(\varepsilon^2)$ where $\mathscr{S}$ is the zeroth-order macroscopic entropy per unit volume, easily evaluated in the form

$$\mathscr{S} = -\mathrm{k_B}\sum_{i,\mathrm{I}}\int f_i^0(\log(\beta_{i\mathrm{I}}f_i^0)-1)\,\mathrm{d}\boldsymbol{c}_i = \sum_{i\in\mathrm{S}}\rho_i\left(\frac{5}{2}\,\frac{\mathrm{k_B}}{m_i} + \frac{\bar{\mathscr{E}}_i}{Tm_i} - \frac{\mathrm{k_B}}{m_i}\log\left(\frac{n_i}{Q_i}\right)\right).$$

From the explicit expression of $\mathscr{S}$ we can obtain the macroscopic entropy conservation equation

$$\partial_t\mathscr{S} + \partial_{\boldsymbol{x}}\cdot(\mathscr{S}\boldsymbol{v}) + \partial_{\boldsymbol{x}}\cdot\left(\frac{\boldsymbol{q}}{T} - \sum_{i\in\mathrm{S}}\frac{g_i}{T}\rho_i\boldsymbol{V}_i\right) = \Upsilon, \tag{5.31}$$

where Υ is the entropy production term given by

$$\Upsilon = -\sum_{i\in\mathrm{S}} \frac{g_i m_i \bar{\omega}_i}{T} - \frac{\mathbf{\Pi} : \partial_{\boldsymbol{x}}\boldsymbol{v}}{T} - \left(\boldsymbol{q} - \sum_{i\in\mathrm{S}} \rho_i h_i \boldsymbol{V}_i\right) \cdot \frac{\partial_{\boldsymbol{x}} T}{T^2} - \sum_{i\in\mathrm{S}} \frac{p}{T} \boldsymbol{V}_i \cdot \boldsymbol{d}_i . \qquad (5.32)$$

5.7. Positivity of entropy production

In this section, we show that the entropy production term Υ splits into a sum of nonnegative terms. This property is important from several points of view. First, from a thermodynamical point of view, it shows that the macroscopic model satisfies the second principle, inherited from the kinetic model. From a mathematical point of view, entropy plays a central role in establishing well posedness of the resulting system of partial differential equations and in the definition of shock waves. It can also be used to derive symmetrized form of the system of conservation laws. These symmetric forms can be used for theoretical purposes as well as finite element numerical simulations [18]. In order to establish that the entropy production term splits into a sum of nonnegative terms, we use in particular the structure properties that have been established for the heat-mass transport matrices.

We first investigate entropy production in the Maxwellian reaction regime where $a = 1$. When $a = 1$, using Eqs. (3.5), (3.6), entropy production due to chemistry is easily rewritten in the form

$$-\frac{1}{T}\sum_{i\in\mathrm{S}} g_i m_i \bar{\omega}_i = \mathrm{k_B} \sum_{r\in\mathfrak{R}} \mathscr{K}_{\mathrm{r}} \Omega \left(\prod_{i\in\mathrm{S}} \left(\frac{n_i}{Q_i}\right)^{v_{ir}^{\mathrm{f}}}, \prod_{i\in\mathrm{S}} \left(\frac{n_i}{Q_i}\right)^{v_{ir}^{\mathrm{b}}} \right) ,$$

where $\Omega(x, y) = (x - y)\log(x/y)$ is a nonnegative function. In other words, when $a = 1$, the chemistry terms arising from the Maxwellian distributions are compatible with classical thermo-chemistry.

Furthermore, when $a = 1$, the entropy production due to viscous effects reads

$$-\frac{\mathbf{\Pi} : \partial_{\boldsymbol{x}}\boldsymbol{v}}{T} = \frac{\kappa}{T}(\partial_{\boldsymbol{x}} \cdot \boldsymbol{v})^2 - \frac{\hat{\mathbf{\Pi}} : \mathsf{S}}{T} ,$$

so that, κ being nonnegative—and positive if there is at least one polyatomic species in the mixture—it is sufficient to show that $-\hat{\mathbf{\Pi}} : \mathsf{S}$ is positive. To this aim, we first rewrite $\hat{\mathbf{\Pi}} : \mathsf{S}$ into an intrinsic form, i.e., which is basis independent. Denoting by $p^{\parallel}$ the orthogonal projection with range spanned by the vector $\boldsymbol{B}$ and $p^{\perp} = \mathbb{I} - p^{\parallel}$ the orthogonal projection with kernel spanned by the vector $\boldsymbol{B}$, one can establish after lengthy calculations that

$$\begin{aligned} -\hat{\mathbf{\Pi}} : \mathsf{S} = {} & 2(\eta_1 + \eta_4)\mathrm{Tr}(p^{\parallel}\mathsf{S}p^{\perp}p^{\perp}\mathsf{S}p^{\parallel}) \\ & +(\eta_1 + \eta_3)[(\mathrm{Tr}(p^{\parallel}\mathsf{S}p^{\parallel}))^2 + \tfrac{1}{2}(\mathrm{Tr}(p^{\perp}\mathsf{S}p^{\perp}))^2] \\ & +(\eta_1 - \eta_3)[\mathrm{Tr}(p^{\perp}\mathsf{S}p^{\perp}p^{\perp}\mathsf{S}p^{\perp}) - \tfrac{1}{2}(\mathrm{Tr}(p^{\perp}\mathsf{S}p^{\perp}))^2] , \end{aligned}$$

where $\mathrm{Tr}(A)$ denotes the trace of a tensor A. However, according to bracket expressions (5.26)–(5.30) of the five shear viscosities, we have the following relations

$$\eta_1 + \eta_4 > 0, \quad \eta_1 + \eta_3 > 0, \quad \eta_1 - \eta_3 > 0 .$$

It is therefore sufficient to show that

$$\mathrm{Tr}(p^{\|}\mathsf{S}p^{\perp}p^{\perp}\mathsf{S}p^{\|})\,,$$

$$(\mathrm{Tr}(p^{\|}\mathsf{S}p^{\|}))^2+\tfrac{1}{2}(\mathrm{Tr}(p^{\perp}\mathsf{S}p^{\perp}))^2$$

and

$$\mathrm{Tr}(p^{\perp}\mathsf{S}p^{\perp}p^{\perp}\mathsf{S}p^{\perp})-\tfrac{1}{2}(\mathrm{Tr}(p^{\perp}\mathsf{S}p^{\perp}))^2$$

are nonnegative. As these expressions are invariant under a change of coordinates, we choose an orthonormal basis $(\mathbf{e}_1,\mathbf{e}_2,\mathbf{e}_3)$ such as $\mathbf{e}_1$ is proportional to the vector $\boldsymbol{B}$. In this situation, we then obtain

$$\mathrm{Tr}(p^{\|}\mathsf{S}p^{\perp}p^{\perp}\mathsf{S}p^{\|})=\mathsf{S}_{12}^2+\mathsf{S}_{13}^2\,,$$

$$(\mathrm{Tr}(p^{\|}\mathsf{S}p^{\|}))^2+\tfrac{1}{2}(\mathrm{Tr}(p^{\perp}\mathsf{S}p^{\perp}))^2=\mathsf{S}_{11}^2+\tfrac{1}{2}(\mathsf{S}_{22}+\mathsf{S}_{33})^2$$

and

$$\mathrm{Tr}(p^{\perp}\mathsf{S}p^{\perp}p^{\perp}\mathsf{S}p^{\perp})-\tfrac{1}{2}(\mathrm{Tr}(p^{\perp}\mathsf{S}p^{\perp}))^2=2\mathsf{S}_{23}^2+\tfrac{1}{2}(\mathsf{S}_{22}-\mathsf{S}_{33})^2\,,$$

so that $-\hat{\boldsymbol{\Pi}}:\mathsf{S}$ is nonnegative and $-\hat{\boldsymbol{\Pi}}:\mathsf{S}$ is zero if and only if S is zero.

We finally show that the entropy production term involving the heat flux and the diffusion velocities

$$\Upsilon_v=-\left(\boldsymbol{q}-\sum_{i\in\mathrm{S}}\rho_i h_i\boldsymbol{V}_i\right)\cdot\frac{\partial_{\boldsymbol{x}}T}{T^2}-\sum_{i\in\mathrm{S}}\frac{p}{T}\,\boldsymbol{V}_i\cdot\boldsymbol{d}_i, \tag{5.33}$$

is nonnegative. By using expressions (5.19) and (5.24) of $\boldsymbol{V}_i$ and $\boldsymbol{q}$, we can write

$$\begin{aligned}\Upsilon_v={}&\frac{1}{T^2}\,\hat{\lambda}^{\|}(\partial_{\boldsymbol{x}}T)^{\|}\cdot(\partial_xT)^{\|}+\frac{p}{T}\sum_{i,j\in\mathrm{S}}D_{ij}^{\|}\boldsymbol{d}_j^{\|}\cdot\boldsymbol{d}_i^{\|}+\frac{p}{T^2}\sum_{i\in\mathrm{S}}\hat{\theta}_i^{\|}\boldsymbol{d}_i^{\|}\cdot(\partial_xT)^{\|}\\&+\frac{p}{T^2}\sum_{i\in\mathrm{S}}\theta_i^{\|}(\partial_xT)^{\|}\cdot\boldsymbol{d}_i^{\|}+\frac{1}{T^2}\hat{\lambda}^{\perp}(\partial_xT)^{\perp}\cdot(\partial_xT)^{\perp}+\frac{p}{T^2}\sum_{i\in\mathrm{S}}\hat{\theta}_i^{\perp}\boldsymbol{d}_i^{\perp}\cdot(\partial_xT)^{\perp}\\&+\frac{p}{T^2}\sum_{i\in\mathrm{S}}\theta_i^{\perp}(\partial_xT)^{\perp}\cdot\boldsymbol{d}_i^{\perp}+\frac{p}{T}\sum_{i,j\in\mathrm{S}}D_{ij}^{\perp}\boldsymbol{d}_j^{\perp}\cdot\boldsymbol{d}_i^{\perp}+\frac{p}{T^2}\sum_{i\in\mathrm{S}}\hat{\theta}_i^{t}\boldsymbol{d}_i^{t}\cdot(\partial_xT)^{\perp}\\&+\frac{p}{T^2}\sum_{i\in\mathrm{S}}\theta_i^{t}(\partial_xT)^{t}\cdot\boldsymbol{d}_i^{\perp}+\frac{p}{T}\sum_{i,j\in\mathrm{S}}D_{ij}^{t}\boldsymbol{d}_i^{\perp}\cdot\boldsymbol{d}_j^{\perp}\,.\end{aligned}$$

We claim that this expression is nonnegative from the positivity properties established for the matrices $A^{\|}$ and $A^{\perp}+\mathrm{i}A^{t}$. Indeed, we can readily rewrite the four first terms of Υ_v into a sum of terms $\langle A^{\|}x^{\|},x^{\|}\rangle$ with $x_0^{\|}=(\partial_\alpha T)^{\|}$ and $x_i^{\|}=(\boldsymbol{d}_{\alpha i})^{\|}$ for $\alpha=1,2,3$. Similarly, using $\mathbf{X}^{\perp}\cdot\mathbf{Y}^{\perp}=\mathbf{X}^{t}\cdot\mathbf{Y}^{t}$ and $\mathbf{X}^{\perp}\cdot\mathbf{Y}^{t}=-\mathbf{X}^{t}\cdot\mathbf{Y}^{\perp}$ for any vectors $\mathbf{X}$ and $\mathbf{Y}$, we can rewrite the seven remaining terms of Υ_v into a sum of terms $\langle A^{\perp}x^{\perp},x^{\perp}\rangle+\langle A^{\perp}x^{t},x^{t}\rangle+\langle A^{\perp}x^{\perp},x^{t}\rangle-\langle A^{t}x^{t},x^{\perp}\rangle$, with $x_0=(\partial_\alpha T)^{\perp}$, $x_i=(\boldsymbol{d}_{\alpha i})^{\perp}$, $y_0=(\partial_\alpha T)^{t}$, $x_i=(\boldsymbol{d}_{\alpha i})^{t}$, for $\alpha = 1, 2, 3$. This shows that Υ_v is a sum of positive contributions, and after a little algebra, we also obtain that

$$\Upsilon_v = \mathrm{k_B}[\![\boldsymbol{\varphi}_v^{\|}, \boldsymbol{\varphi}_v^{\|}]\!] + \tfrac{1}{2}\,\mathrm{k_B}[\![\boldsymbol{\varphi}_v^{\perp} - \mathrm{i}\boldsymbol{\varphi}_v^{t}, \boldsymbol{\varphi}_v^{\perp} - \mathrm{i}\boldsymbol{\varphi}_v^{t}]\!]\,,$$

where

$$\boldsymbol{\varphi}_v^{\|} = -\sum_{i \in \mathrm{S}} \boldsymbol{\varphi}^{D_i(1)} \cdot p\boldsymbol{d}_i^{\|} - \boldsymbol{\varphi}^{\hat{\lambda}(1)} \cdot \partial_{\boldsymbol{x}} \left(\frac{1}{\mathrm{k_B}T} \right)^{\|}\,,$$

and

$$\boldsymbol{\varphi}_v^{\perp} - \mathrm{i}\boldsymbol{\varphi}_v^{t} = -\sum_{i \in \mathrm{S}} \boldsymbol{\varphi}^{D_i(2)} \cdot p(\boldsymbol{d}_i^{\perp} - \mathrm{i}\boldsymbol{d}_i^{t}) - \boldsymbol{\varphi}^{\hat{\lambda}}(2) \cdot \left(\partial_{\boldsymbol{x}} \left(\frac{1}{\mathrm{k_B}T} \right)^{\perp} - \mathrm{i}\partial_{x} \left(\frac{1}{\mathrm{k_B}T} \right)^{t} \right)\,.$$

We now briefly discuss the strong reaction regime where $a = 0$. In this situation, the calculations are more complex and one can show that the extra entropy production is [18]

$$d\,\Upsilon = \frac{p^{\mathrm{reac}}}{T}\,\partial_{\boldsymbol{x}} \cdot \boldsymbol{v} - \frac{1}{T} \sum_{i \in \mathrm{S}} g_i m_i \mathfrak{w}_i\,.$$

A close examination reveals that, in this regime $a = 0$, entropy production arising solely from reactive collisions is not necessarily nonnegative, at variance with the kinetic underlying framework [18]. This shows that, in the regime $a = 0$, the macroscopic governing equations are somewhat ill-posed. However, neglecting the two contributions p^{reac} and $\mathfrak{w}_i$, $i \in \mathrm{S}$, the governing equations in both regimes $a = 0$ and $a = 1$ coincide and yields a positive entropy production as the underlying kinetic framework.

5.8. Onsager's reciprocal relations

The Onsager relations are symmetry constraints which must hold between the transport coefficients. In the case of gases, these symmetry properties can directly be deduced from the kinetic theory of gases [22].

The tensorial relations expressing the transport fluxes in terms of the macroscopic gradients have been given in the preceding sections. From these relations, the Onsager's reciprocal relations read

$$\boldsymbol{D}_{ij}(-\boldsymbol{B}) = \boldsymbol{D}_{ji}(\boldsymbol{B})^{\mathrm{T}}, \quad \boldsymbol{\theta}_i(-\boldsymbol{B}) = \hat{\boldsymbol{\theta}}_i(\boldsymbol{B})^{\mathrm{T}}, \quad \hat{\boldsymbol{\lambda}}(-\boldsymbol{B}) = \hat{\boldsymbol{\lambda}}(\boldsymbol{B})^{\mathrm{T}}, \quad i, j \in \mathrm{S}\,.$$

Since $p^{\|} = \mathscr{B} \otimes \mathscr{B}$ and $p^{\perp} = \mathbb{I} - \mathscr{B} \otimes \mathscr{B}$ are symmetric matrices and odd functions of $\boldsymbol{B}$, and $\boldsymbol{M}^{\mathscr{B}}$ is antisymmetric matrix and even function of $\boldsymbol{B}$, these relations can be written as follow

$$D_{ij}^{\|}(-\boldsymbol{B}) = D_{ji}^{\|}(\boldsymbol{B}), \quad D_{ij}^{\perp}(-\boldsymbol{B}) = D_{ji}^{\perp}(\boldsymbol{B}), \quad D_{ij}^{t}(-\boldsymbol{B}) = D_{ji}^{t}(\boldsymbol{B})\,,$$

$$\theta_i^{\|}(-\boldsymbol{B}) = \hat{\theta}_i^{\|}(\boldsymbol{B}), \quad \theta_i^{\perp}(-\boldsymbol{B}) = \hat{\theta}_i^{\perp}(\boldsymbol{B}), \quad \theta_i^{t}(-\boldsymbol{B}) = \hat{\theta}_i^{t}(\boldsymbol{B})\,,$$

$$\hat{\lambda}^{\|}(-\boldsymbol{B}) = \hat{\lambda}^{\|}(\boldsymbol{B}), \quad \hat{\lambda}^{\perp}(-\boldsymbol{B}) = \hat{\lambda}^{\perp}(\boldsymbol{B}), \quad \hat{\lambda}^{t}(-\boldsymbol{B}) = \hat{\lambda}^{t}(\boldsymbol{B})\,.$$

It is easy, however, to check that

$$\varphi_i^{\hat{\lambda}(1)}(-\boldsymbol{B}) = \varphi_i^{\hat{\lambda}(1)}(\boldsymbol{B}), \quad \varphi_i^{\hat{\lambda}(2)}(-\boldsymbol{B}) = \overline{\varphi_i^{\hat{\lambda}(2)}(\boldsymbol{B})},$$

$$\varphi_i^{D_j(1)}(-\boldsymbol{B}) = \varphi_i^{D_j(1)}(\boldsymbol{B}), \quad \varphi_i^{D_j(2)}(-\boldsymbol{B}) = \overline{\varphi_i^{D_j(2)}(\boldsymbol{B})},$$

and these properties directly imply the above relations.

6. Structure of transport linear systems

In order to evaluate the transport coefficients, in practice, the linearized Boltzmann integral equations are solved approximatively by using a variational procedure. The transport coefficients in multicomponent mixtures can then be evaluated by solving large linear systems [10]. Although direct inversion of these systems is feasible, it is prohibitively expensive for most practical applications involving multidimensional multicomponent flows [19]. Following previous work on nonionized mixtures [10,18–20] we investigate here the mathematical structure of the transport linear systems resulting from the kinetic framework described in the preceding sections. We establish, in particular, that the transport coefficients can be expanded as convergent series which yield approximate expressions by truncation.

6.1. Variational formulation

For each transport coefficient μ to be evaluated, we have to solve linear integral equations that can be written in the form

$$(\mathscr{F}^{\mathscr{S}} + \mathrm{i}\mathscr{F}^{\mathscr{B}})(\varphi^\mu) = \psi^\mu, \tag{6.1}$$

where $\mathscr{F}^{\mathscr{B}}$ denotes either the null operator in the scalar case, or the operator $\mathscr{F}^{\mathscr{B},v}$ in the vector case, or the operator $\mathscr{F}^{\mathscr{B},m}$ in the traceless matrix case. This (complex) integral equations must be completed with the constraints

$$\langle\langle f^0\varphi^\mu, \psi^l\rangle\rangle = 0, \quad l \in \{1,\ldots,n^s+4\}. \tag{6.2}$$

The transport coefficient μ is then generally obtained from scalar products in the form $\mu = \langle\langle f^0\varphi^\mu, \psi^\mu\rangle\rangle$. The linear integral equations (6.1), (6.2) associated with the transport coefficients are solved approximately by using a variational procedure. A finite dimensional space is first selected

$$\mathscr{A} = \mathrm{span}\{\xi^{rk}, (r,k) \in \mathscr{B}\},$$

where $\xi^{rk}, (r,k) \in \mathscr{B}$, are basis functions and where $\mathscr{B}$ is a set of basis function indices. The set of basis function indices is such that $\mathscr{B} \subset \mathscr{F} \times \mathrm{S}$ where $\mathscr{F}$ denotes a function type indexing set and we denote by ω the dimension of the functional space $\mathscr{A}$.

The species perturbed distribution functions ϕ^μ are next expanded in the form

$$\varphi^\mu = \sum_{(r,k)\in\mathscr{B}} \alpha_k^r \xi^{rk}, \tag{6.3}$$

where the α_k^r are scalars. A (hermitian) Galerkin approach is used by requiring the difference between the approximated $(\mathscr{F}^{\mathscr{S}} + \mathrm{i}\mathscr{F}^{\mathscr{B}})(\varphi^\mu)$ and Ψ^μ to be orthogonal to the space $\mathscr{A}$. The components with respect to the basis $\xi^{rk}, (r,k) \in \mathscr{B}$, of any function $\xi = \sum_{(r,k)\in\mathscr{B}} x_k^r \xi^{rk}$ of $\mathscr{A}$ now form a vector of $\mathbb{C}^\omega$ denoted by $x = (x_k^r)_{(r,k)\in\mathscr{B}}$ and the set $\mathscr{B}$ can be used as a natural indexing set. For $x, y \in \mathbb{C}^\omega$, the scalar product $\langle x, y\rangle$ is given by $\langle x, y\rangle = \sum_{(r,k)\in\mathscr{B}} x_k^r \bar{y}_k^r$. For $A \in \mathbb{C}^{\omega,\omega}$, we write $A = (A_{kl}^{rs})_{(r,k),(s,l)\in\mathscr{B}}$ the coefficients of the matrix A. Making use of this notation, the expansion coefficients $\alpha_k^r, (r,k)\in\mathscr{B}$, form a vector $\alpha = (\alpha_k^r)_{(r,k)\in\mathscr{B}} \in \mathbb{C}^\omega$ which is easily shown to be the solution of a constrained linear system in the form

$$(G + \mathrm{i}\tilde{G}^B)\alpha = \beta,$$

$$\alpha \in \mathscr{C}\ , \tag{6.4}$$

where we have defined

$$G_{kl}^{rs} = \langle\langle f^0 \mathscr{F}^{\mathscr{S}}(\xi^{sl}), \xi^{rk}\rangle\rangle = [\![\xi^{sl}, \xi^{rk}]\!]\ ,$$

$$(\tilde{G}^B)_{kl}^{rs} = \langle\langle f^0 \mathscr{F}^{\mathscr{B}}(\xi^{sl}), \xi^{rk}\rangle\rangle\ ,$$

$$\beta_k^r = \langle\langle \psi^\mu, \xi^{rk}\rangle\rangle\ .$$

In addition, we have introduced the constraint space $\mathscr{C}$ given by

$$\mathscr{C} = (\operatorname{span}\{\mathscr{G}^{l\nu}, l \in \{1,\ldots,n^s+4\},\ \nu \in \{1,\ldots,n^\tau\}\})^\perp\ ,$$

where the constraint vectors have components given by

$$\mathscr{G}_k^{rl\nu} = \langle\langle \xi^{rk}, \mathscr{T}_\nu \psi^l\rangle\rangle, \quad l \in \{1,\ldots,n^s+4\},\ \nu \in \{1,\ldots,n^\tau\}\ .$$

Here ψ^l, $l \in \{1,\ldots,n^s+4\}$ are the scalar collisional invariants whereas $\mathscr{T}_\nu$, $\nu \in \{1,\ldots,n^\tau\}$, is the canonical basis of tensors of the same type than φ^μ, and n^τ is the dimension of the corresponding tensor space, that is, $n^\tau = 1$ in the scalar case, $n^\tau = 3$ in the vector case, and $n^\tau = 9$ in the matrix case. Note that, thanks to isotropy, the constraint space is usually at most one dimensional [10]. Finally, the transport coefficients are evaluated from simple scalar products in the form

$$\mu = \langle \alpha, \beta' \rangle\ ,$$

where β' denotes a vector of $\mathbb{C}^\omega$.

It is then of fundamental interest to select as basis functions the usual real expansion polynomials. In this situation, the matrix G is the same as in the zero magnetic field case and $\tilde{G}^B$ is a real matrix although without a simple structure. In particular, the whole formalism developed in Refs. [10,20] can be used for the matrix G so that G is symmetric positive semi-definite and $\beta \in R(G) = N(G)^\perp$. The well posedness property $N(G) \oplus \mathscr{C} = \mathbb{R}^\omega$ (associated with the system where $\tilde{G}^B = 0$) also holds provided that the Galerkin variational approximation space $\mathscr{A}$ is perpendicular to the linear space of collisional invariants $\mathscr{I}$ that are of the same tensorial rank [10,20], that is, provided that

$$\mathscr{I} = \mathscr{I} \cap \mathscr{A} \oplus \mathscr{I} \cap \mathscr{A}^\perp\ ,$$

where $\mathscr{I} \cap \mathscr{A}^{\perp}$ denotes the elements of $\mathscr{I}$ that are orthogonal to $\mathscr{A}$ with respect to the bilinear form $\langle\langle f^0 \cdot, \cdot \rangle\rangle$.

A careful analysis then reveals that the system in its initial form (6.4) is not properly structured. In particular, the nullspace $N(G + \mathrm{i}\tilde{G}^B)$ is not known explicitly, there are no simple positivity properties associated with $G + \mathrm{i}\tilde{G}^B$, and iterative techniques are not guaranteed to be convergent. As a consequence, we rewrite this system into a new form which is shown to have a much better mathematical structure and whose unique solution is still α. To this aim, we introduce the matrix

$$G^B = \tilde{G}^B P_{\mathscr{C},N(G)} ,$$

where for two supplementary subspaces $A \oplus B = \mathbb{C}^{\omega}$ we denote by $P_{A,B}$ the projector onto A along B. The corresponding modified system then reads

$$\begin{aligned} &(G + \mathrm{i}G^B)\alpha = \beta , \\ &\alpha \in \mathscr{C} , \end{aligned} \qquad (6.5)$$

and is strictly equivalent to (6.4) since $\alpha = P_{\mathscr{C},N(G)}\alpha$. The structure of the matrix $G + \mathrm{i}G^B$ can then be investigated by using essentially the same techniques as those used for G in the nonionized case [10]. Among the important properties are the symmetry of $G^B = (G^B)^{\mathrm{T}}$, that $N(G) \subset N(G^B)$ and that $R(G^B) \subset N(G)^{\perp}$. One can then show that the nullspace $N(G + \mathrm{i}G^B)$ is spanned in $\mathbb{C}^{\omega}$ by the same real vectors spanning $N(G)$ in $\mathbb{R}^{\omega}$, and that $R(G + \mathrm{i}G^B)$ is the (hermitian) orthogonal of $N(G + \mathrm{i}G^B)$ eventhough $G + \mathrm{i}G^B$ is not hermitian. In addition, the well posedness property

$$N(G + \mathrm{i}G^B) \oplus \mathscr{C} = \mathbb{C}^{\omega} ,$$

is a direct consequence of the similar result in $\mathbb{R}^{\omega}$ for G and we also have $\beta \in R(G + \mathrm{i}G^B)$ so that the linear system (6.5) is well posed.

6.2. *Iterative techniques*

We introduce the sparse transport matrix $db(G) \in \mathbb{R}^{\omega,\omega}$ associated with the unperturbed part of the transport linear system [10]

$$db(G)^{rs}_{kl} = G^{rs}_{kl}\delta_{kl}, \quad (r,k),(s,l) \in \mathscr{B} .$$

The matrix $db(G)$ plays a fundamental role in the asymptotic expansion of the transport coefficients [10]. One can establish that the matrix $2db(G) - G$ is symmetric positive semi-definite for $n^s \geqslant 1$ and positive definite for $n^s \geqslant 3$. The nullspace of $2db(G) - G$ is easily identified is the special cases $n^s \leqslant 2$. The structure of the matrix $2db(G) - G$ shows incidentally that the general case for mixtures is $n^s \geqslant 3$ and that binary mixtures are a degenerate case inadequate for a general theory [10]. In order to obtain asymptotic expansions for the transport coefficients, we now use the theory of projective iterative methods for constrained singular linear systems. Several mathematical results have been derived in the framework of multicomponent transport [10].

We introduce a matrix decomposition $G + \mathrm{i}G^B = M - Z$ and the corresponding iteration matrix $T = M^{-1}Z = I - M^{-1}(G + \mathrm{i}G^B)$. Let $P = P_{\mathscr{C},N(G)}$ be the oblique projector onto the subspace $\mathscr{C}$ along $N(G+\mathrm{i}G^B)$, let also $\beta \in R(G+\mathrm{i}G^B)$, $x_0 \in \mathbb{C}^\omega$, $y_0 = Px_0$, and consider for $i \geqslant 0$ the iterates $x_{i+1} = Tx_i + M^{-1}\beta$, $i \geqslant 1$, and $y_{i+1} = PTy_i + PM^{-1}\beta$, $i \geqslant 1$. The projector matrix P ensures that at each iteration the approximation to the species perturbed distribution functions satisfies the physical constraints. Our aim is to chose M in such a way that the powers of the matrix T are convergent [10]. In this situation, the product PT has a spectral radius strictly lower than unity, the iterates x_i, $i \geqslant 1$, and y_i, $i \geqslant 1$, are convergent and

$$\lim_{i\to\infty} y_i = P\left(\lim_{i\to\infty} x_i\right) = \alpha\ ,$$

where α is the unique solution of the transport linear system (6.5). Upon defining the approximate transport coefficients

$$\mu_{[i]} = \left\langle \sum_{j=0}^{i} (PT)^j PM^{-1}P^t\beta, \beta' \right\rangle\ ,$$

we then have

$$\lim_{i\to\infty} \mu_{[i]} = \left\langle \sum_{j=0}^{\infty} (PT)^j PM^{-1}P^t\beta, \beta' \right\rangle = \mu\ ,$$

and all transport coefficient are written as convergent series.

A first appropriate choice for the splitting matrix M is $M = db(G)$ in the general case $n^s \geqslant 3$, whereas in the particular cases $n^s = 1$ or 2, the main diagonal of $db(G)$ needs to be weighted by some positive coefficients. Indeed, when $M = db(G)$, has been established that the spectral radius of $PM^{-1}(M-G)$ is strictly lower that unity since $2M - G$ is then positive definite [10]. As a consequence, since $PT = PM^{-1}(M-G) - PM^{-1}G^B$, the spectral radius of PT is strictly lower than unity whenever G^B is small enough, that is, provided the magnetic field is small enough.

In order to obtain convergent algorithms in the general case, is necessary to include the matrix $\mathrm{i}G^B$ in the matrix M. More specifically, we consider the choice $M = db(G) + \mathrm{i}G^B$ in the general case $n^s \geqslant 3$ with the above diagonal modifications of $db(G)$ for $n^s \leqslant 2$. This matrix $M = db(G) + \mathrm{i}G^B$ is still simple to invert in practice since the complex part $\mathrm{i}G^B$ is either diagonal or is a rank-one perturbation of a diagonal matrix [1]. The convergence proof can then be directly established following the zero magnetic investigations—mutatis mutandis—and using that for any $x \in \mathbb{C}^\omega \langle db(G)x, x\rangle < |\langle Mx, x\rangle|$ thanks to the symmetry of G^B [23]. The choice $M = db(G) + \mathrm{i}G^B$ thus leads to convergent asymptotic expansions of the transport coefficients for any magnetic field strength, generalizing previous results obtained for nonionized mixtures [10,19,20].

7. First-order approximation in the regime $b = 0$

In this section, we are interested in the weak magnetic field regime where $b = 0$. This case is simpler than the previous since $b = 1$ since we do not have anymore to distinguish between the parallel, perpendicular and transverse components. We do not detail the calculations since they are identical to those without electromagnetic fields [18].

7.1. First-order macroscopic equations

In this regime $b=0$ we obtain the following first-order macroscopic equations

$$\partial_t\rho_i + \partial_{\boldsymbol{x}}\cdot(\rho_i\boldsymbol{v}) + \partial_{\boldsymbol{x}}\cdot(\rho_i\boldsymbol{V}_i) = m_i\bar{\omega}_i, \quad i\in \mathrm{S}\,, \tag{7.1}$$

$$\partial_t(\rho\boldsymbol{v}) + \partial_{\boldsymbol{x}}\cdot(\rho\boldsymbol{v}\otimes\boldsymbol{v} + p\mathbb{I}) + \partial_{\boldsymbol{x}}\cdot\boldsymbol{\Pi} = \rho\boldsymbol{g} + \mathcal{Q}(\boldsymbol{E}+\boldsymbol{v}\wedge\boldsymbol{B}) + \boldsymbol{j}\wedge\boldsymbol{B}\,, \tag{7.2}$$

$$\begin{aligned}&\partial_t(\tfrac{1}{2}\,\rho\boldsymbol{v}\cdot\boldsymbol{v}+\mathscr{E}) + \partial_{\boldsymbol{x}}\cdot[(\tfrac{1}{2}\rho\boldsymbol{v}\cdot\boldsymbol{v}+\mathscr{E}+p)\boldsymbol{v}] + \partial_{\boldsymbol{x}}\cdot(\boldsymbol{q}+\boldsymbol{\Pi}\cdot\boldsymbol{v})\\ &\quad=(\rho\boldsymbol{g}+\mathcal{Q}(\boldsymbol{E}+\boldsymbol{v}\wedge\boldsymbol{B}))\cdot\boldsymbol{v} + \boldsymbol{j}\cdot\boldsymbol{E}\,.\end{aligned} \tag{7.3}$$

These first-order macroscopic equations appear as the Navier–Stokes reactive compressible equations with terms expressing the effect of the Lorentz force on the gas as a whole and the Ohmic heating.

7.2. Flux and transport coefficients

In this regime, the species diffusion velocities $\boldsymbol{V}_i$, $i\in\mathrm{S}$, read

$$\boldsymbol{V}_i = -\theta_i\partial_{\boldsymbol{x}}\log T - \sum_{j\in\mathrm{S}} D_{ij}\boldsymbol{d}_j, \quad i\in\mathrm{S}\,, \tag{7.4}$$

with

$$D_{ij} = \tfrac{1}{3}\,p\mathrm{k_B}T[\![\boldsymbol{\phi}^{D_i},\boldsymbol{\phi}^{D_j}]\!], \quad \theta_i = -\tfrac{1}{3}[\![\boldsymbol{\phi}^{D_i},\boldsymbol{\phi}^{\hat{\lambda}}]\!]\,.$$

We can then define the thermal diffusion ratios $\chi=(\chi_i)_{i\in\mathrm{S}}$, from the linear system

$$D\chi=\theta\,, \quad \langle\chi,U\rangle=0\,,$$

and we obtain an alternative expression for the species diffusion velocities

$$\boldsymbol{V}_i = -\sum_{j\in\mathrm{S}} D_{ij}(\boldsymbol{d}_j+\chi_j\partial_{\boldsymbol{x}}\log T), \quad i\in\mathrm{S}\,. \tag{7.5}$$

On the other hand, the heat flux $\boldsymbol{q}$ is given by

$$\boldsymbol{q} = -\hat{\lambda}\partial_{\boldsymbol{x}}T - p\sum_{i\in\mathrm{S}}\theta_i\,\boldsymbol{d}_i + \sum_{i\in\mathrm{S}}(\tfrac{5}{2}\,\mathrm{k_B}T+\bar{\mathscr{E}}_i)n_i\boldsymbol{V}_i\,, \tag{7.6}$$

with

$$\hat{\lambda} = \frac{1}{3\mathrm{k_B}T^2}[\![\boldsymbol{\phi}^{\hat{\lambda}},\boldsymbol{\phi}^{\hat{\lambda}}]\!]\,.$$

By introducing the new coefficient

$$\lambda = \hat{\lambda} - n\mathrm{k_B}\sum_{i,j\in\mathrm{S}} D_{ij}\chi_i\chi_j\,,$$

we obtain another expression of the heat flux

$$\boldsymbol{q} = -\lambda \partial_{\boldsymbol{x}} T + p \sum_{i \in \mathrm{S}} \chi_i \boldsymbol{V}_i + \sum_{i \in \mathrm{S}} \left(\tfrac{5}{2} \mathrm{k_B} T + \bar{\mathscr{E}}_i \right) n_i \boldsymbol{V}_i \ . \tag{7.7}$$

In addition, in the regime $a = 1$, we obtain the following expression for the viscous stress tensor

$$\boldsymbol{\Pi} = -\kappa \partial_{\mathbf{x}} \cdot \boldsymbol{v} \mathbb{I} - \eta \mathsf{S} \ , \tag{7.8}$$

with

$$\kappa = \tfrac{1}{9} \mathrm{k_B} T [\![\phi^{\kappa}, \phi^{\kappa}]\!], \qquad \eta = \tfrac{1}{10} \mathrm{k_B} T [\![\boldsymbol{\phi}^{\eta}, \boldsymbol{\phi}^{\eta}]\!] \ .$$

Finally, the mathematical structure of the corresponding transport linear systems that are to be solved in order to evaluate the transport coefficients has already been investigated in Ref. [10].

7.3. Entropy production

The entropy conservation equation is similar to Eq. (5.31) but the source term is changed into

$$\begin{aligned} \Upsilon = {} & \kappa (\partial_{\boldsymbol{x}} \cdot \boldsymbol{v})^2 + \eta \mathbf{S} : \mathbf{S} + \frac{\lambda}{T^2} \partial_{\boldsymbol{x}} T \cdot \partial_{\boldsymbol{x}} T \\ & + \frac{p}{T} \sum_{i,j \in \mathrm{S}} D_{ij} (\boldsymbol{d_i} + \chi_i \partial_{\boldsymbol{x}} \log T) \cdot (\boldsymbol{d}_j + \chi_j \partial_{\boldsymbol{x}} \log T) \ , \end{aligned} \tag{7.9}$$

so that entropy production is easily shown to be positive.

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