Transport properties of partially ionized and unmagnetized plasmas

Thierry E. Magin* and Gérard Degrez†
von Karman Institute for Fluid Dynamics, Department of Aeronautics and Aerospace, 72 Chaussée de Waterloo, B-1640 Rhode-Saint-Genèse, Belgium

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This work is a comprehensive and theoretical study of transport phenomena in partially ionized and unmagnetized plasmas by means of kinetic theory. The pros and cons of different models encountered in the literature are presented. A dimensional analysis of the Boltzmann equation deals with the disparity of mass between electrons and heavy particles and yields the epochal relaxation concept. First, electrons and heavy particles exhibit distinct kinetic time scales and may have different translational temperatures. The hydrodynamic velocity is assumed to be identical for both types of species. Second, at the hydrodynamic time scale the energy exchanged between electrons and heavy particles tends to equalize both temperatures. Global and species macroscopic fluid conservation equations are given. New constrained integral equations are derived from a modified Chapman-Enskog perturbative method. Adequate bracket integrals are introduced to treat thermal nonequilibrium. A symmetric mathematical formalism is preferred for physical and numerical standpoints. A Laguerre-Sonine polynomial expansion allows for systems of transport to be derived. Momentum, mass, and energy fluxes are associated to shear viscosity, diffusion coefficients, thermal diffusion coefficients, and thermal conductivities. A Goldstein expansion of the perturbation function provides explicit expressions of the thermal diffusion ratios and measurable thermal conductivities. Thermal diffusion terms already found in the Russian literature ensure the exact mass conservation. A generalized Stefan-Maxwell equation is derived following the method of Kolesnikov and Tirskiy. The bracket integral reduction in terms of transport collision integrals is presented in Appendix for the thermal nonequilibrium case. A simple Eucken correction is proposed to deal with the internal degrees of freedom of atoms and polyatomic molecules, neglecting inelastic collisions. The authors believe that the final expressions are readily usable for practical applications in fluid dynamics.

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I. INTRODUCTION

In a uniform mixture of gases at equilibrium, the velocities of the different species follow a Maxwellian distribution. Boltzmann has derived an integrodifferential equation to describe the evolution of the species velocity distribution functions in space and time and justified Maxwell's statement in his *H* Theorem for dilute gases [1,2]. The solution of the Boltzmann equation for dilute gases neglecting the internal energy contribution is known since the works of Chapman and Enskog [3]. It allows for the transport fluxes to be computed. This result of kinetic theory is described in the book of Chapman and Cowling [4]. Hirschfelder, Curtiss, and Bird [5] and later Ferziger and Kaper [6] have collected the latest developments in that field of research and greatly contributed to spread kinetic theory in the scientific community.

On the other hand, the description of mixtures composed of species of disparate masses is not well established. Partially ionized plasmas, composed of electrons and molecules, belong to this category. The first model describing a binary mixture composed of light and heavy species dates from the beginning of kinetic theory and is due to Lorentz. This model applies to weakly ionized plasmas when the number density of the light components is smaller than that of the heavy components. Hence, collisions among light particles are neglected with respect to collisions among heavy particles and between unlike particles. This assumption ceases to be valid when the number density of the light species increases. Delcroix and Bers [7] distinguish an intermediate category of plasmas characterized by all collisional contributions. Eventually, at higher ionization degree, collective effects of the charges have to be incorporated in the plasma description. To that end, various kinetic equations are found in the literature [8]. The present work deals with partially ionized plasmas and makes use of a collision operator of Boltzmann with a screening of the Coulomb potential. Furthermore, this research is restricted to unmagnetized plasmas. The flow around a space vehicle entering a planetary atmosphere at hypersonic speed represents one possible example of unmagnetized plasma.

In the 1960s, significant progress was made in the kinetic description of partially ionized plasmas. The interaction between electrons was incorporated to Lorentz's description. Various results emanate from the Stanford group. Devoto [9,10] has simplified the expressions given by Hirschfelder *et al.* [5] for the transport properties, accounting for the small mass of electrons in ionized mixtures. Kruger and Mitchner [11], Kruger *et al.* [12], and Daybelge [13] have applied similar simplifications to ionized gases in thermal nonequilibrium in the presence of a magnetic field. Chmieleski and Ferziger [14] have presented an elegant formalism to derive the transport properties of ionized gases assuming that heavy particles have an infinite mass in collisions with electron

*Email address: magin@vki.ac.be; URL: http://www.vki.ac.be/
†Email address: degrez@vki.ac.be. Also at Université Libre de Bruxelles, Service de Mécanique des fluides, 50 Avenue F.D. Roosevelt, B-1050 Bruxelles, Belgium.

partners; they also investigated the magnetic field influence [15]. All the models mentioned above assume no transfer of energy in the electron-heavy collisions. This assumption is necessary to decouple the thermal bath of heavy particles from that of electrons, and thus, define an intermediate state of the system where the electron temperature can be different from that of heavy particles. This state corresponds to the zero order solution of the Chapman-Enskog perturbative method. Nevertheless, if the energy decoupling hypothesis is conserved deriving a perturbative solution, thermal diffusion is not correctly treated and diffusion velocities do not rigorously respect mass conservation. The first model for two-temperature plasmas in the presence of magnetic field, self-consistent with respect to diffusion phenomenon and based upon kinetic theory, was published in the 1970s by Kolesnikov [16]. Some transfer of energy is considered in the perturbation function for the electron-heavy collisions. However, some steps and approximations in the development remain debatable. The final results of this work have been subsequently published in English [17,18]. Concerning the mathematical aspect of partially ionized plasmas, Petit and Darrozes [19] have stressed that the Chapman-Enskog perturbative method must be revisited. A dimensional analysis of the Boltzmann equation shows that electrons and heavy particles have different relaxation times. In the 1990s, Ramshaw [20], Ramshaw and Chang [21] have deduced a pragmatic model for diffusion from a less cumbersome hydrodynamic theory. At the same time, Degond and Lucquin-Desreux [22–25] have followed the dimensional analysis of Petit and Darrozes to introduce an epochal relaxation treatment. Electrons and heavy particles exhibit distinct kinetic time scales and may have different translational temperatures. At the hydrodynamic time scale, the energy exchanged between electrons and heavy particles tends to equalize both temperatures. Moreover, a suitable Knudsen number is proved to be proportional to the square root of the electron heavy-particle mass ratio. Rat *et al.* [26] have recently proposed an alternate derivation of the transport properties in a two-temperature plasma. Unfortunately, the Chapman-Enskog method employed rests on an incorrect scaling of the Boltzmann equation, in contrast with the dimensional analysis used in Refs. [19,22,23]. Nevertheless, at thermal equilibrium, their results are consistent with those obtained in Ref. [5]. Finally, the moment method of Grad to obtain a solution of the Boltzmann equation is an alternative to the Chapman-Enskog method. The expressions of the transport fluxes of multicomponent plasmas derived by the higher approximations of the moment method turn out to be equivalent to the results given by the Chapman-Enskog method, as demonstrated by Zhdanov [27].

In the present work, various ideas, some of which not widespread, are combined together to obtain a new kinetic treatment of the transport fluxes for two-temperature plasmas. According to Ramshaw and Chang, theories generalizing the Chapman-Enskog solution procedure to the case where electrons and heavy particles have different temperatures are “so intricate that is by no means trivial even to identify and extract the final results” (see Ref. [28]). The authors aim to provide here final expressions of the transport fluxes readily usable by readers interested in practical applications. In addition, the remaining problems mentioned above in the derivation of these expressions are eliminated. Our results are consistent with respect to diffusion. The epochal relaxation introduced in Ref. [22] gives a sound interpretation to a modified Chapman-Enskog perturbative method. A symmetric formalism for the transport systems and coefficients, analogous to that of Ferziger and Kaper [6], is preferred for physical considerations to the approach of Hirschfelder *et al.* [5]. Moreover, the formalism retained is advantageous from a numerical standpoint and allows for the transport algorithms developed by Ern and Giovangigli [29] to be employed in applications. It is regrettable that the nonsymmetric formalism introduced in Ref. [5] is still used today despite its disadvantages (see for instance Ref. [26]), albeit Curtiss had eventually abandoned this approach in favor of symmetric transport coefficients [30]. A generalized Stefan-Maxwell equation in any order of approximation is derived following a method proposed by Kolesnikov and Tirskiy [31]. If possible, final expressions of the transport fluxes are compared to the various models and commented.

II. BOLTZMANN EQUATION AND CONSERVATION EQUATIONS

A. General remarks

The plasma is assumed to fulfill the following assumptions:

$\Lambda \gg 1$. The plasma parameter Λ is defined as the ratio of the Debye length to the mean impact parameter for 90° scattering. This nondimensional number is also proportional to the number of electrons in a sphere of radius equal to the Debye length. If the plasma parameter is sufficiently large, charged particle interactions can be treated as binary collisions with Debye-Hückel screening of the Coulomb potential using a collision operator of Boltzmann [7].

$K_n \ll 1$. The Knudsen number K_n being small, the plasma is collision dominated.

$\varepsilon = \sqrt{m_e/m_h} \ll 1$. Our gas mixture is composed of N species referred to the set of indices $\mathcal{S}=\{1,\ldots,N\}=\mathcal{H}\cup\{e\}$, where heavy particles are distinguished from electrons. The electron mass reads m_e. A characteristic mass for heavy particles is given by m_h.

$|T_e - T_h| \ll T_e \sim T_h$. Due to the small electron heavy-particle mass ratio, small departures from thermal equilibrium are envisaged. The electron and heavy-particle temperatures, respectively, read T_e and T_h.

$\beta_e \ll K_n$. The Hall parameter of electrons β_e is assumed to be smaller than the Knudsen number. Thus, the magnetic field influence on transport properties remains negligible, the plasma is unmagnetized. The approach followed here can be generalized to derive transport properties sensitive to a magnetic field.

$\lambda_D \ll L^0$. The Debye length λ_D being smaller than a reference length L^0 in the flow, quasineutrality of the plasma is prescribed.

No chemical reactions. Ern and Giovangigli [29] have shown that chemical reactions do not influence the transport properties if the characteristic time for chemistry is larger than that for collisions implied in transport phenomena.

No internal energy. The internal energy is not taken into account in the present derivation. The influence of the internal degrees of freedom on transport phenomena is addressed in various specialized publications cited in general Refs. [6,27,29,32]. Indeed, a rigorous treatment including the internal energy leads to transport collision integrals difficult to estimate with accuracy in high-temperature applications. Capitelli *et al.* [33] have recently assessed the role of electronically excited states on the viscosity for a hydrogen plasma in the temperature range 10 000–25 000 K by computing the adequate resonant charge and excitation transfer cross sections. In this contribution, a simple correction due to Eucken [4–6] has been retained instead.

Classical description. Quantum mechanical effects on transport phenomena in a gas are caused by the wave nature of molecules (diffraction) and their statistics (symmetry). Diffraction effects become important when the de Broglie wavelength is about as large as the dimension of molecules, whereas symmetry effects depend on the gas density and appear when the de Broglie wavelength is of the order of magnitude of the average distance between the gas molecules. In this work, transport properties are derived from classical mechanics. Nevertheless, Hirschfelder *et al.* [5] have shown that diffraction and some symmetry effects are correctly described by classical expressions of the transport properties provided that the transport collision integrals are computed from quantum mechanics.

Concerning notation of spatial quantities, *light-face* type stands for scalars, **bold-face** type for vectors, and sans serif type for tensors. Indices i,j,k,l allow for the species in the mixture to be distinguished. Indices p,q,r correspond to the Laguerre-Sonine polynomial order. When indices are omitted for quantities associated to either the species or polynomial order, those quantities are implicitly considered to be vectors or tensors.

B. Boltzmann equation

The velocity distribution function f_i for the species $i \in \mathcal{S}$ is solution of the Boltzmann equation

$$\mathcal{D}_i(f_i) = J_i. \tag{1}$$

The streaming operator is defined by

$$\mathcal{D}_i(f_i) = \frac{\partial}{\partial t} f_i + \mathbf{c}_i \cdot \boldsymbol{\nabla} f_i + \frac{\mathbf{F}_i}{m_i} \cdot \boldsymbol{\nabla}_{\mathbf{c}_i} f_i, \tag{2}$$

where $\mathbf{c}_i$ and m_i are the velocity and mass of particle. The only external force considered acting on the particle is an electric force $\mathbf{F}_i = q_i(\mathbf{E} + \mathbf{c}_i \times \mathbf{B})$, with the electric field $\mathbf{E}$, magnetic field $\mathbf{B}$, and species charge q_i. The scattering collision operator is given by

$$J_i = \sum_{j \in \mathcal{S}} J_{ij}(f_i, f_j), \tag{3a}$$

$$J_{ij}(f_i, f_j) = \int (f_i' f_j' - f_i f_j) g\sigma \, d\boldsymbol{\Omega} \, d\mathbf{c}_j, \tag{3b}$$

where g is the relative velocity, σ the differential cross section, and $\boldsymbol{\Omega}$ a solid angle. The primes denote values after collision. The species number density $n_i = \int f_i d\mathbf{c}_i$ and mass density $\rho_i = n_i m_i$ allow for the mixture number density $n = \Sigma_{j \in \mathcal{S}} n_j$, mass density $\rho = \Sigma_{j \in \mathcal{S}} \rho_j$, and hydrodynamic velocity

$$\rho \mathbf{v} = \sum_{j \in \mathcal{S}} \int m_j \mathbf{c}_j f_j d\mathbf{c}_j, \tag{4}$$

to be defined. Hence, the peculiar diffusion velocity reads

$$\mathbf{C}_i = \mathbf{c}_i - \mathbf{v}. \tag{5}$$

The streaming operator (2) is written in terms of the variables $\mathbf{r}$, $\mathbf{C}_i$, and t

$$\mathcal{D}_i(f_i) = \frac{\partial}{\partial t} f_i + (\mathbf{v} + \mathbf{C}_i) \cdot \boldsymbol{\nabla} f_i + \left(\frac{\mathbf{F}_i}{m_i} - \frac{d\mathbf{v}}{dt} \right) \cdot \boldsymbol{\nabla}_{\mathbf{C}_i} f_i - (\boldsymbol{\nabla}_{\mathbf{C}_i} f_i \otimes \mathbf{C}_i) : \boldsymbol{\nabla} \mathbf{v}, \tag{6}$$

where $d/dt = \partial/\partial t + \mathbf{v} \cdot \boldsymbol{\nabla}$ is the material derivative.

Collisional invariants expressed into axes moving with the gas are introduced

$$\Psi^j = m_j (\delta_{ij})_{i \in \mathcal{S}}, \quad j \in \mathcal{S}, \tag{7a}$$

$$\Psi^{N+\nu} = (m_i C_{\nu i})_{i \in \mathcal{S}}, \quad \nu \in \{1,2,3\}, \tag{7b}$$

$$\Psi^{N+4} = \left(\tfrac{1}{2} m_i C_i^2 \right)_{i \in \mathcal{S}}. \tag{7c}$$

A scalar product is defined

$$\langle\langle \xi, \zeta \rangle\rangle = \sum_{j \in \mathcal{S}} \int \xi_j \odot \zeta_j d\mathbf{c}_j, \tag{8}$$

where $\xi_j \odot \zeta_j$ is the maximum contracted product in space between the tensors ξ_j and ζ_j. Employing Liouville's law for elastic collisions, it is shown that the average rate of change for the entire gas of the molecular property $\Psi^m, m \in \{1, \ldots, N+4\}$ vanishes

$$\frac{1}{n} \langle\langle \Psi^m, J \rangle\rangle = \frac{1}{4n} \sum_{i,j \in \mathcal{S}} \int (\Psi_i^m + \Psi_j^m - \Psi_i^{m'} - \Psi_j^{m'}) \times (f_i' f_j' - f_i f_j) g\sigma \, d\boldsymbol{\Omega} \, d\mathbf{c}_i d\mathbf{c}_j = 0, \tag{9}$$

by conservation of mass, momentum, and energy in elastic collisions. The following scalar products are also introduced for later convenience

$$\langle\langle \xi, \zeta \rangle\rangle_h = \sum_{j \in \mathcal{H}} \int \xi_j \odot \zeta_j d\mathbf{c}_j, \tag{10a}$$

$$\langle\langle \xi, \zeta \rangle\rangle_e = \int \xi_e \odot \zeta_e d\mathbf{c}_e. \tag{10b}$$

The Boltzmann H Theorem (see Refs. [4–6]) induces that the equilibrium solution of Eq. (1) is a Maxwellian distribution function

$$f_i^M = n_i\left(\frac{m_i}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m_i C_i^2}{2k_B T}\right), \quad i \in \mathcal{S}, \tag{11}$$

where the gas equilibrium temperature T is defined proportional to the average of the particle kinetic energy

$$\frac{3}{2} n k_B T = \sum_{j\in\mathcal{S}} \int \frac{1}{2} m_j C_j^2 f_j d\mathbf{c}_j. \tag{12}$$

Symbol k_B stands for Boltzmann's constant. There exist situations where one species may attain a temperature different from that of the other species. For instance the temperature of electrons can be higher than that of heavy particles in inductively coupled plasma wind tunnels at low pressures. In these facilities, the energy is brought into the plasma by electromagnetic coupling between mainly the electrons and a coil driven by a radio frequency current. Electrons exchange some energy with heavy particles through collisions. This energy exchange is not efficient because of the large difference of mass between both partners. This exchange becomes weaker when pressure decreases as described in Sec. III B. Consequently, electrons may remain hotter than heavy particles. Therefore, the heavy-particle translational temperature (for all $i \in \mathcal{H}, T_i = T_h$) is distinguished from the electron temperature T_e

$$\frac{3}{2} n_i k_B T_h = \int \frac{1}{2} m_i C_i^2 f_i d\mathbf{c}_i, \quad i \in \mathcal{H}, \tag{13a}$$

$$\frac{3}{2} n_e k_B T_e = \int \frac{1}{2} m_e C_e^2 f_e d\mathbf{c}_e. \tag{13b}$$

This is not in contradiction with the H Theorem. After a relaxation time, both temperatures tend to equalize if no external forces are applied to the system.

C. Conservation equations

Multiplication of the Boltzmann equation (1) by the collisional invariants given in Eq. (7) and integration over velocity yields species conservation equations

$$\int \Psi_i^m \mathcal{D}_i(f_i) d\mathbf{c}_i = \int \Psi_i^m J_i(f_i) d\mathbf{c}_i,$$

$$m \in \{1, \ldots, N+4\}, \quad i \in \mathcal{S}. \tag{14}$$

Summing up over the species and using the property of the collisional invariants [see Eq. (9)], global conservation equations read

$$\langle\langle \Psi^m, \mathcal{D} \rangle\rangle = 0, \quad m \in \{1, \ldots, N+4\}. \tag{15}$$

A detailed derivation can be found in the book of Mitchner and Kruger [34].

(i) Species continuity

$$\frac{\partial}{\partial t}\rho_i + \nabla \cdot (\rho_i \mathbf{v}) + \nabla \cdot (\rho_i \mathbf{V}_i) = 0, \quad i \in \mathcal{S} \tag{16}$$

with the species diffusion velocity

$$\mathbf{V}_i = \frac{1}{n_i} \int \mathbf{C}_i f_i d\mathbf{c}_i. \tag{17}$$

Remark, the diffusion velocities are not linearly independent and a mass conservation constraint is obtained employing Eqs. (4) and (5):

$$\sum_{j\in\mathcal{S}} \rho_j \mathbf{V}_j = 0. \tag{18}$$

(ii) Global continuity

$$\frac{\partial}{\partial t}\rho + \nabla \cdot (\rho \mathbf{v}) = 0. \tag{19}$$

(iii) Momentum

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) + \nabla \cdot \mathsf{P} - nq\mathbf{E}' - \mathbf{j} \times \mathbf{B} = 0 \tag{20}$$

with the stress tensor

$$\mathsf{P} = \sum_{j\in\mathcal{S}} \mathsf{P}_j, \quad \text{and} \quad \mathsf{P}_i = \int m_i \mathbf{C}_i \otimes \mathbf{C}_i\, f_i d\mathbf{c}_i, \tag{21}$$

mixture charge $q = \sum_{j\in\mathcal{S}} x_j q_j$ (x_i is the mole fraction), species conduction current $\mathbf{j}_i = n_i q_i \mathbf{V}_i$, and mixture conduction current $\mathbf{j} = \sum_{j\in\mathcal{S}} \mathbf{j}_j$. The electric field in the hydrodynamic velocity frame reads $\mathbf{E}' = \mathbf{E} + \mathbf{v} \times \mathbf{B}$.

(iv) Species energy

$$\frac{\partial}{\partial t}(\rho_i e_i) + \nabla \cdot (\rho_i e_i \mathbf{v}) + \nabla \cdot (\mathbf{q}_i) - \mathbf{j}_i \cdot \mathbf{E}' + \rho_i \mathbf{V}_i \cdot \frac{d}{dt}\mathbf{v} + \mathsf{P}_i : \nabla \mathbf{v} = \Delta E_i, \quad i \in \mathcal{S} \tag{22}$$

with the species energy $\rho_i e_i = \frac{3}{2} n_i k_B T_i = \int \frac{1}{2} m_i C_i^2 f_i d\mathbf{c}_i$. The species heat flux reads

$$\mathbf{q}_i = \int \frac{1}{2} m_i C_i^2 \mathbf{C}_i f_i d\mathbf{c}_i, \tag{23}$$

and the energy exchange term is given by

$$\Delta E_i = \int \frac{1}{2} m_i C_i^2 J_i d\mathbf{c}_i. \tag{24}$$

(v) Global energy

$$\frac{\partial}{\partial t}(\rho e) + \nabla \cdot (\rho e \mathbf{v}) + \nabla \cdot (\mathbf{q}) - \mathbf{j} \cdot \mathbf{E}' + \mathsf{P} : \nabla \mathbf{v} = 0, \tag{25}$$

with the mixture energy $\rho e = \sum_{j\in\mathcal{S}} \rho_j e_j$ and heat fluxes $\mathbf{q} = \mathbf{q}_h + \mathbf{q}_e$, $\mathbf{q}_h = \sum_{j\in\mathcal{H}} \mathbf{q}_j$. Two-temperature plasmas are described by the global conservation equations (19), (20), and (25), supplied with the species continuity equations (16) for all species and the electron energy equation [i.e., Eq. (22) with index $i = e$]. The quasineutrality hypothesis eliminates the term $nq\mathbf{E}'$ in Eq. (20). Equations for the electromagnetic field are not presented in this work.

III. CHAPMAN-ENSKOG PERTURBATIVE METHOD

A. Dimensional analysis

A dimensional analysis was proposed by Petit and Darrozes [19] to adequately scale the Boltzmann equation. This idea was further exploited by Degond and Lucquin-Desreux [22,23] in their epochal relaxation concept. A small parameter is introduced to deal with mass disparity between the mixture species. It is defined as the square root of the electron heavy-particle mass ratio $\varepsilon=\sqrt{m_e/m_h}$. Reference quantities are now presented. Electrons and heavy particles exhibit distinct thermal speeds employed as reference peculiar diffusion velocities

$$V_e^0=\sqrt{\frac{k_BT^0}{m_e}}, \tag{26a}$$

$$V_h^0=\sqrt{\frac{k_BT^0}{m_h}}=\varepsilon V_e^0, \tag{26b}$$

where T^0 is a common reference temperature. Two collision time scales coexist

$$t_e=\frac{1}{n^0\sigma^0V_e^0}, \tag{27a}$$

$$t_h=\frac{1}{n^0\sigma^0V_h^0}=\frac{t_e}{\varepsilon}, \tag{27b}$$

where n^0 and σ^0 are, respectively, a reference density and differential cross section. The mean free path is identical for both types of species $l^0=1/(n^0\sigma^0)=t_eV_e^0=t_hV_h^0$. A reference hydrodynamic velocity is given by v^0. The length scale reads $L^0=t^0v^0$; the time scale t^0 employed as reference time will be explicited later. The Knudsen number is given by $K_n=l^0/L^0$. A reference electric field E^0 is assumed to verify $q^0E^0L^0=k_BT^0$, such that any change in the characteristic length requires a simultaneous change of the force scale, q^0 being a reference species charge. This assumption ensures that the space gradient and velocity gradient terms of the streaming operator are of the same order of magnitude [23]. Hall numbers are introduced for electrons and heavy particles

$$\beta_e=\frac{q^0B^0}{m_e}t_e, \tag{28a}$$

$$\beta_h=\frac{q^0B^0}{m_h}t_h=\varepsilon\beta_e, \tag{28b}$$

where B^0 is a reference magnetic field. The Boltzmann equation (1) is written in nondimensional form as

$$\tilde{\mathbf{C}}_i\cdot\tilde{\boldsymbol{\nabla}}\tilde{f}_i+\frac{\tilde{q}_i}{\tilde{m}_i}\tilde{\mathbf{E}}\cdot\tilde{\boldsymbol{\nabla}}_{\tilde{\mathbf{C}}_i}\tilde{f}_i+\frac{\beta_h}{K_n}\frac{\tilde{q}_i}{\tilde{m}_i}[(M_h\tilde{\mathbf{v}}+\tilde{\mathbf{C}}_i)\times\tilde{\mathbf{B}}]\cdot\tilde{\boldsymbol{\nabla}}_{\tilde{\mathbf{C}}_i}\tilde{f}_i+M_h\left[\frac{\partial}{\partial\tilde{t}}\tilde{f}_i+\tilde{\mathbf{v}}\cdot\tilde{\boldsymbol{\nabla}}\tilde{f}_i-(\tilde{\boldsymbol{\nabla}}_{\tilde{\mathbf{C}}_i}\tilde{f}_i\otimes\tilde{\mathbf{C}}_i):\tilde{\boldsymbol{\nabla}}\tilde{\mathbf{v}}\right]-(M_h)^2\frac{d\tilde{\mathbf{v}}}{d\tilde{t}}\cdot\tilde{\boldsymbol{\nabla}}_{\tilde{\mathbf{C}}_i}\tilde{f}_i=\frac{1}{K_n}\tilde{J}_i,\quad i\in\mathcal{H}, \tag{29a}$$

$$\frac{1}{\varepsilon}\left\{\tilde{\mathbf{C}}_e\cdot\tilde{\boldsymbol{\nabla}}\tilde{f}_e+\tilde{q}_e\tilde{\mathbf{E}}\cdot\tilde{\boldsymbol{\nabla}}_{\tilde{\mathbf{C}}_e}\tilde{f}_e+\frac{\beta_e}{K_n}\tilde{q}_e[(\varepsilon M_h\tilde{\mathbf{v}}+\tilde{\mathbf{C}}_e)\times\tilde{\mathbf{B}}]\cdot\tilde{\boldsymbol{\nabla}}_{\tilde{\mathbf{C}}_e}\tilde{f}_e\right\}+M_h\left[\frac{\partial}{\partial\tilde{t}}\tilde{f}_e+\tilde{\mathbf{v}}\cdot\tilde{\boldsymbol{\nabla}}\tilde{f}_e-(\tilde{\boldsymbol{\nabla}}_{\tilde{\mathbf{C}}_e}\tilde{f}_e\otimes\tilde{\mathbf{C}}_e):\tilde{\boldsymbol{\nabla}}\tilde{\mathbf{v}}\right]-\varepsilon(M_h)^2\frac{d\tilde{\mathbf{v}}}{d\tilde{t}}\cdot\tilde{\boldsymbol{\nabla}}_{\tilde{\mathbf{C}}_e}\tilde{f}_e=\frac{1}{\varepsilon K_n}\tilde{J}_e, \tag{29b}$$

where $M_h=v^0/V_h^0$ is the Mach number associated to heavy species. Degond and Lucquin-Desreux [22,23] distinguish three different time scales and demonstrate an epochal relaxation. The fastest time scale t_e rules the evolution of the electrons, the intermediate time scale t_h corresponds to the heavy species and the slowest time scale $t^0=t_h/\varepsilon$ governs the relaxation of temperatures. In consequence of the choice of t^0, the Knudsen number scales as $K_n=\varepsilon/M_h$. The classical Chapman-Enskog perturbative method postulates only two time scales: the microscopic or kinetic scale and the macroscopic or hydrodynamic scale. Furthermore, in this classical approach, the parameter ε does not appear in the left-hand side of Eq. (29b).

The magnetic field is assumed to be sufficiently low such that $\beta_e\ll K_n$. It has no influence on the transport phenomena, the plasma is considered to be unmagnetized. Due to the choice of scale for the electric field, the magnetic Reynolds number $R_m=B^0v^0/E^0$ is related to the Hall numbers

$$R_m=\beta_e=\frac{\beta_h}{\varepsilon}. \tag{30}$$

Then, the condition $\beta_e\ll K_n=\varepsilon/M_h$ is automatically satisfied if the magnetic Reynolds number verifies $R_m\ll\varepsilon$. The distribution functions are expanded as usual upon the Knudsen number, or equivalently the parameter ε:

$$f_i\simeq f_i^0(1+\varepsilon\phi_i),\quad i\in\mathcal{S}. \tag{31}$$

Following Chmieleski and Ferziger [14,15], in the limit as m_h becomes infinite, the zero order distribution function of heavy species is assumed to satisfy the limit

$$\lim_{m_i\to\infty}f_i^0=n_i\delta(\mathbf{C}_i),\quad i\in\mathcal{H}, \tag{32}$$

where $\delta(\mathbf{x})$ is the Dirac distribution. For the interactions between electrons and heavy particles, we propose to write the distribution function of heavy species as

$$f_i\simeq n_i\delta(\mathbf{C}_i)(1+\varepsilon\phi_i),\quad i\in\mathcal{H}. \tag{33}$$

B. Zero order solution

Injecting the expressions given in Eqs. (31) and (33) into the Eq. (29) and equating the coefficients of like powers of ε, the zero order distribution system reads in dimensional form

$$\sum_{j\in\mathcal{H}}J_{ij}(f_i^0,f_j^0)+J_{ie}[n_i\delta(\mathbf{C}_i),f_e^0]=0,\quad i\in\mathcal{H}, \tag{34}$$

$$\sum_{j\in\mathcal{H}}J_{ej}[f_e^0,n_j\delta(\mathbf{C}_j)]+J_{ee}(f_e^0,f_e^0)=0. \tag{34b}$$

A H Theorem *at the kinetic time scale of electrons or heavy particles* is derived in absence of external forces and for a spatially uniform gas in thermal nonequilibrium. The Boltzmann equation reads in this special case as

$$\frac{\partial}{\partial t} f_i = \sum_{j \in \mathcal{H}} J_{ij}(f_i, f_j) + J_{ie}(f_i, f_e), \quad i \in \mathcal{H}, \tag{35a}$$

$$\frac{\partial}{\partial t} f_e = \sum_{j \in \mathcal{H}} J_{ej}(f_e, f_j) + J_{ee}(f_e, f_e). \tag{35b}$$

Defining a function $H = -\Sigma_{j \in \mathcal{S}} \int f_j \ln f_j d\mathbf{c}_j$, employing the Boltzmann equation (35) and Liouville's law for elastic collisions, the derivative of H with respect to time is given by

$$\begin{aligned}\frac{dH}{dt} &= \frac{1}{4} \sum_{i,j \in \mathcal{H}} \int [\ln(f_i' f_j') - \ln(f_i f_j)](f_i' f_j' - f_i f_j) g\sigma \, d\mathbf{\Omega} \, d\mathbf{c}_i \, d\mathbf{c}_j \\ &\quad + \frac{1}{2} \sum_{j \in \mathcal{H}} \int [\ln(f_e' f_j') - \ln(f_e f_j)](f_e' f_j' \\ &\quad - f_e f_j) g\sigma \, d\mathbf{\Omega} \, d\mathbf{c}_e \, d\mathbf{c}_j + \frac{1}{4} \int [\ln(f_e' \overline{f_e'}) - \ln(f_e \overline{f_e})](f_e' \overline{f_e'} \\ &\quad - f_e \overline{f_e}) g\sigma \, d\mathbf{\Omega} \, d\mathbf{c}_e \, d\overline{\mathbf{c}_e} \\ &\geqslant 0,\end{aligned} \tag{36}$$

where the bar is used to distinguish collision partner indices. Examining the sign of the expression $(x-y)(\ln x - \ln y)$, the H function cannot decrease in time. When the zero order solution of the Boltzmann equation is reached, the coupling term between heavy particles and electrons vanishes

$$\frac{1}{2} \sum_{j \in \mathcal{H}} \int n_j \delta(\mathbf{C}_j) [\ln(f_e^{0\prime}) - \ln(f_e^0)](f_e^{0\prime} - f_e^0) g\sigma \, d\mathbf{\Omega} \, d\mathbf{c}_e \, d\mathbf{c}_j = 0. \tag{37}$$

It was assumed in Eq. (37) that momentum and kinetic energy of heavy particles are unaltered in collisions with electrons. Kinetic energy of electrons does not change either, only their momentum is modified due to a change of trajectory. Heavy particles act as random diffusers opposed to any organized movement of electrons (see Ref. [7]). Thanks to this approximation, the zero order solution of the Eq. (34) is a set of Maxwellian distribution functions at different temperatures

$$f_i^0 = n_i \left(\frac{m_i}{2\pi k_B T_h} \right)^{3/2} \exp\left(-\frac{m_i C_i^2}{2 k_B T_h} \right), \quad i \in \mathcal{H}, \tag{38a}$$

$$f_e^0 = n_e \left(\frac{m_e}{2\pi k_B T_e} \right)^{3/2} \exp\left(-\frac{m_e C_e^2}{2 k_B T_e} \right). \tag{38b}$$

The transport fluxes vanish and the zero order conservation equations reduce to the Euler equations.

In plasmas at equilibrium, the electron and heavy-particle velocities follow Maxwellian distributions at the same temperature [see Eq. (11)]. Particles exchange some momentum and energy during encounters, but there is no net exchange between two populations. A two-temperature intermediate state was defined with the electron and heavy-particle velocities distributed according to Maxwellian functions, respectively, at the electron and heavy-particle temperatures [see Eq. (38)]. In spite of thermal disparity, there is no net energy exchanged between the electron and heavy-particle populations if the mass of heavy particles is assumed to be infinite in collisions with electrons. Thus, electrons are preferentially thermalized through electron-electron collisions. However, the net energy exchanged in electron-electron interactions is zero. Even though the energy transfer between electrons and heavy particles is not efficient, it plays an important role and tends to equalize both temperatures after a sufficient relaxation time, previously defined as t^0. The energy exchange term must then be computed assuming a finite-heavy-particle mass. Consequently, the two-temperature intermediate state disappears if not artificially sustained and the system tends to an equilibrium state at one single temperature.

Following similar arguments, an intermediate state can be defined with distinct hydrodynamic velocities for electrons and heavy particles. However, Morse [35] has shown that momentum is exchanged more efficiently than energy for hard sphere and Coulomb interactions between electrons and heavy particles. The relaxation time to equalize the hydrodynamic velocities of both populations is of the order of ε^2 compared to the relaxation time to equalize their translational temperatures. A Coulomb force law with exponential Debye-Hückel shielding is well suited to model electron-ion interactions. Electron-neutral interactions are better described by quantum mechanics than classical hard sphere interaction potentials [36]. It is nevertheless assumed that Morse's argument remains qualitatively valid and electrons are considered to share the same hydrodynamic velocity as heavy particles. Desloge [37] has derived a general expression for the energy exchanged between two Maxwellian gases with different temperatures and the same hydrodynamic velocity

$$\Delta E_e^0 = 16 n_e k_B (T_h - T_e) \sum_{j \in \mathcal{H}} n_j \frac{m_e}{m_j} \Omega_{ej}^{(1,1)}. \tag{39}$$

The momentum cross-sections $\Omega_{ej}^{(1,1)}$ are defined in Appendix B. The energy exchange term goes to zero when the mass of heavy particles tends to infinity in Eq. (39). Furthermore, this term is proportional to the number density to the square and thus rapidly drops with pressure.

C. First-order solution

Injecting the expressions given in Eqs. (31) and (33) into the Eq. (29) and equating the coefficients of like powers of ε, the perturbation function defined in Eq. (31) is solution of the equations

$$\begin{aligned}&\sum_{j \in \mathcal{H}} [J_{ij}(f_i^0 \phi_i, f_j^0) + J_{ij}(f_i^0, f_j^0 \phi_j)] + J_{ie}[n_i \delta(\mathbf{C}_i) \phi_i, f_e^0] \\ &\quad + J_{ie}[n_i \delta(\mathbf{C}_i), f_e^0 \phi_e] \\ &\quad = \frac{\partial}{\partial t} f_i^0 + (\mathbf{v} + \mathbf{C}_i) \cdot \nabla f_i^0 + \left(\frac{q_i}{m_i} \mathbf{E} - \frac{d\mathbf{v}}{dt} \right)\end{aligned}$$

$$\cdot \nabla_{\mathbf{C}_i} f_i^0 - (\nabla_{\mathbf{C}_i} f_i^0 \otimes \mathbf{C}_i) : \nabla \mathbf{v}, \quad i \in \mathcal{H}, \tag{40a}$$

$$\sum_{j \in \mathcal{H}} \{J_{ej}[f_e^0 \phi_e, n_j \delta(\mathbf{C}_j)] + J_{ej}[f_e^0, n_j \delta(\mathbf{C}_j)\phi_j]\} + J_{ee}(f_e^0 \phi_e, f_e^0) + J_{ee}(f_e^0, f_e^0 \phi_e) = \mathbf{C}_e \cdot \nabla f_e^0 + \left(\frac{q_e}{m_e}\mathbf{E} - \frac{d\mathbf{v}}{dt}\right) \cdot \nabla_{\mathbf{C}_e} f_e^0. \tag{40b}$$

The lower order term $d\mathbf{v}/dt \cdot \nabla_{\mathbf{C}_e} f_e^0$ is kept in Eq. (40b) for later convenience. A linearized scattering collision operator is introduced

$$I_i(\phi) = \sum_{j \in \mathcal{S}} \frac{n_i n_j}{n^2} I_{ij}(\phi), \quad i \in \mathcal{S}. \tag{41}$$

The partial linearized collision operators I_{ij} are defined in Appendix A. Making use of the conservation equations (16), (20), and (22) with the zero order distribution functions [see Eq. (38)], the following constrained integral equations appear after lengthy calculations

$$n^2 I_i(\phi) = -f_i^0 \left[\frac{n}{n_i}\Theta_i \mathbf{C}_i \cdot \mathbf{d}_i + \left(\mathcal{C}_i^2 - \frac{5}{2}\right)\mathbf{C}_i \cdot \nabla \ln T_i + 2(1-\delta_{ie})\left(\boldsymbol{\mathcal{C}}_i \otimes \boldsymbol{\mathcal{C}}_i - \frac{\mathcal{C}_i^2}{3}\mathsf{I}\right) : \nabla \mathbf{v}\right], \quad i \in \mathcal{S}, \tag{42}$$

where I is the identity tensor. The contribution of the energy exchange term is not taken into account providing that $|T_e - T_h| \ll T^0$. Constraints

$$\langle\langle \Psi^m, f^0 \phi \rangle\rangle = 0, \quad m \in \{1, \ldots, N+4\}, \tag{43}$$

assure uniqueness of the solution of Eq. (42). A thermal nonequilibrium parameter is defined as $\Theta_i = T_h/T_i$. Driving forces read

$$\mathbf{d}_i = \frac{\nabla p_i}{n k_B T_h} - \frac{y_i p}{n k_B T_h} \nabla \ln p + (y_i q - x_i q_i)\frac{\mathbf{E}}{k_B T_h}, \tag{44}$$

where y_i is the mass fraction. The driving forces are not linearly independent. The relation

$$\sum_{j \in \mathcal{S}} \mathbf{d}_j = 0 \tag{45}$$

is exactly satisfied thanks to the lower order term kept in the right-hand side of Eq. (40b). The partial pressure reads $p_i = n_i k_B T_i$. The pressure of the mixture is defined by $p = \sum_{j \in \mathcal{S}} p_j$. Nondimensional velocities are given by

$$\boldsymbol{\mathcal{C}}_i = \left(\frac{m_i}{2 k_B T_i}\right)^{1/2} \mathbf{C}_i. \tag{46}$$

Bracket integral operators are introduced as

$$[F,G] = \langle\langle G, I(F) \rangle\rangle = [F,G]_h + [F,G]_e, \tag{47a}$$

$$[F,G]_h = \langle\langle G, I(F) \rangle\rangle_h, \tag{47b}$$

$$[F,G]_e = \langle\langle G, I(F) \rangle\rangle_e. \tag{47c}$$

Their explicit expressions are found in Appendix A. The total bracket integral [,] is symmetric $[F,G]=[G,F]$, positive semidefinite $[F,F] \geqslant 0$, and its kernel is spanned by the collisional invariants. Consequently, the homogeneous solution of Eq. (42) is spanned by the collisional invariants. The general first-order solution takes the form

$$\phi_i = -\frac{1}{n}\mathbf{A}_i^h \cdot \nabla \ln T_h - \frac{1}{n}\mathbf{A}_i^e \cdot \nabla \ln T_e - \frac{1}{n} B_i : \nabla \mathbf{v} - \frac{1}{n}\sum_{j \in \mathcal{S}} \mathbf{D}_i^j \cdot \mathbf{d}_j + \psi_i, \tag{48}$$

where ψ_i is a solution of the associated homogeneous equation $I_i(\psi) = 0$. Seeing that there exists some energy exchanged in the collisions between electrons and heavy particles in the first order expansion, new terms will appear in the final expressions of the diffusion velocities ensuring the exact mass conservation [see Eq. (18)]. Moreover, both the heavy particle and electron temperature gradients are present in the expression of the perturbation ϕ_i, whatever the species type. The coefficients of ϕ_i must take the form

$$\mathbf{A}_i^h = A_i^h(C_i)\mathbf{C}_i, \tag{49a}$$

$$\mathbf{A}_i^e = A_i^e(C_i)\mathbf{C}_i, \tag{49b}$$

$$\mathsf{B}_i = B_i(C_i)\left(\mathbf{C}_i \otimes \mathbf{C}_i - \frac{C_i^2}{3}\mathsf{I}\right), \tag{49c}$$

$$\mathbf{D}_i^j = D_i^j(C_i)\mathbf{C}_i, \tag{49d}$$

and are solution of the integral equations

$$I_i(\mathbf{D}^k) = \frac{1}{n_i} f_i^0 (\delta_{ik} - y_i)\Theta_i \mathbf{C}_i, \quad k \in \mathcal{S}, \tag{50a}$$

$$I_i(\mathbf{A}^h) = \frac{1}{n} f_i^0 (1-\delta_{ie})\left(\mathcal{C}_i^2 - \frac{5}{2}\right)\mathbf{C}_i, \tag{50b}$$

$$I_i(\mathbf{A}^e) = \frac{1}{n} f_i^0 \delta_{ie}\left(\mathcal{C}_i^2 - \frac{5}{2}\right)\mathbf{C}_i, \tag{50c}$$

$$I_i(\mathsf{B}) = \frac{2}{n} f_i^0 (1-\delta_{ie})\left(\boldsymbol{\mathcal{C}}_i \otimes \boldsymbol{\mathcal{C}}_i - \frac{\mathcal{C}_i^2}{3}\mathsf{I}\right), \tag{50d}$$

with the constraints

$$\sum_{j \in \mathcal{S}} m_j \int f_j^0 C_j^2 A_j^h d\mathbf{c}_j = 0, \tag{51a}$$

$$\sum_{j \in \mathcal{S}} m_j \int f_j^0 C_j^2 A_j^e d\mathbf{c}_j = 0, \tag{51b}$$

$$\sum_{j\in\mathcal{S}} m_j \int f_j^0 C_j^2 D_j^k d\mathbf{c}_j = 0. \tag{51c}$$

Similar integral equations are found in the Russian literature, however without a sound and rigorous justification (see Ref. [16]). The vectors $\mathbf{D}^k$ are not linearly independent and a symmetric formalism [4,6] is chosen,

$$\sum_{k\in\mathcal{S}} y_k \mathbf{D}^k = 0, \tag{52}$$

to derive symmetric expressions in agreement with Onsager's reciprocity relations. Symbol ψ_i in Eq. (48) corresponding to the collisional invariants does not contribute to the diffusion velocities, heat fluxes, and stress tensor and is omitted in our analysis.

D. Transport fluxes and coefficients

An additional bracket integral operator is introduced to deal with thermal nonequilibrium

$$[F,G]^\Theta = \langle\langle G, I^\Theta(F)\rangle\rangle = [F,G]_h + \frac{1}{\Theta_e}[F,G]_e, \tag{53}$$

with $I_i^\Theta = I_i/\Theta_i$ ($i \in \mathcal{S}$). This operator is symmetric $[F,G]^\Theta = [G,F]^\Theta$. Some useful bracket integrals to derive the expressions of the transport fluxes are now presented

$$[\mathbf{D}^k,\mathbf{d}]^\Theta = \frac{1}{n_k}\int f_k^0 \mathbf{d}_k \cdot \mathbf{C}_k d\mathbf{c}_k - \frac{1}{\rho}\sum_{j\in S} m_j \int f_j^0 \mathbf{d}_j \cdot \mathbf{C}_j d\mathbf{c}_j, \tag{54a}$$

$$[\mathbf{A}^h,\mathbf{a}] = [\mathbf{A}^h,\mathbf{a}]_h = \frac{1}{n}\sum_{j\in\mathcal{H}} \int f_j^0\left(\mathcal{C}_j^2 - \frac{5}{2}\right)\mathbf{a}_j \cdot \mathbf{C}_j d\mathbf{c}_j, \tag{54b}$$

$$[\mathbf{A}^e,\mathbf{a}] = [\mathbf{A}^e,\mathbf{a}]_e = \frac{1}{n}\int f_e^0\left(\mathcal{C}_e^2 - \frac{5}{2}\right)\mathbf{a}_e \cdot \mathbf{C}_e d\mathbf{c}_e, \tag{54c}$$

$$[\mathsf{B},\mathsf{b}] = [\mathsf{B},\mathsf{b}]_h = \frac{2}{n}\sum_{j\in\mathcal{H}} \int f_j^0\left(\boldsymbol{\mathcal{C}}_j \otimes \boldsymbol{\mathcal{C}}_j - \frac{\mathcal{C}_j^2}{3}\mathsf{I}\right):\mathsf{b}_j\, d\mathbf{c}_j. \tag{54d}$$

Giving the transport fluxes definitions [see Eqs. (17), (21), and (23)], perturbation function [see Eq. (48)], constraints [see Eq. (51)], and bracket integrals [see Eq. (54)], the expressions of the transport fluxes are calculated.

1. Diffusion velocity

$$\mathbf{V}_i = \frac{1}{n_i}\int \mathbf{C}_i f_i^0 \phi_i d\mathbf{c}_i$$
$$= -\sum_{j\in\mathcal{S}} D_{ij}\mathbf{d}_j - D_{Ti}^h \boldsymbol{\nabla} \ln T_h - D_{Ti}^e \boldsymbol{\nabla} \ln T_e, \quad i \in \mathcal{S}, \tag{55}$$

with the multicomponent diffusion coefficients and multicomponent thermal diffusion coefficients

$$D_{ij} = \frac{1}{3n}[\mathbf{D}^i,\mathbf{D}^j]^\Theta, \tag{56a}$$

$$D_{Ti}^h = \frac{1}{3n}[\mathbf{D}^i,\mathbf{A}^h]^\Theta, \tag{56b}$$

$$D_{Ti}^e = \frac{1}{3n}[\mathbf{D}^i,\mathbf{A}^e]^\Theta, \tag{56c}$$

$i,j \in \mathcal{S}$. D_{ij} is symmetric and $D_{ii} > 0$. Furthermore D_{ij}, D_{Ti}^h, and D_{Ti}^e are not linearly independent:

$$\sum_{j\in\mathcal{S}} y_j D_{ji} = 0, \tag{57a}$$

$$\sum_{j\in\mathcal{S}} y_j D_{Tj}^h = 0, \tag{57b}$$

$$\sum_{j\in\mathcal{S}} y_j D_{Tj}^e = 0. \tag{57c}$$

Thermal diffusion ratios are introduced

$$\sum_{j\in\mathcal{S}} D_{ij} k_{Tj}^h = D_{Ti}^h, \tag{58a}$$

$$\sum_{j\in\mathcal{S}} D_{ij} k_{Tj}^e = D_{Ti}^e, \tag{58b}$$

$$\sum_{j\in\mathcal{H}} k_{Tj}^h + \frac{T_e}{T_h} k_{Te}^h = 0, \tag{58c}$$

$$\sum_{j\in\mathcal{H}} k_{Tj}^e + \frac{T_e}{T_h} k_{Te}^e = 0. \tag{58d}$$

Hence the diffusion velocities are alternately expressed by the relations

$$\mathbf{V}_i = -\sum_{j\in\mathcal{S}} D_{ij}(\mathbf{d}_j + k_{Tj}^h \boldsymbol{\nabla} \ln T_h + k_{Tj}^e \boldsymbol{\nabla} \ln T_e). \tag{59}$$

As found by Kolesnikov [16], thermal diffusion through the electron temperature gradient influences the heavy-particle diffusion velocities. The mass conservation constraint given in Eq. (18) is exactly satisfied with the expression of the diffusion velocity presented in Eq. (59). This result is fundamental from a numerical standpoint because it ensures the compatibility of the Stefan-Maxwell equation system presented in Sec. III F.

2. Shear stress

$$\mathsf{P} = \sum_{j\in\mathcal{S}} \int m_j \mathbf{C}_j \otimes \mathbf{C}_j f_j^0 (1+\phi_j) d\mathbf{c}_j$$

$$= p\mathsf{I} - \eta[\boldsymbol{\nabla}\mathbf{v} + (\boldsymbol{\nabla}\mathbf{v})^T] + \frac{2}{3}\eta \boldsymbol{\nabla} \cdot \mathbf{v}\mathsf{I}, \tag{60a}$$

$$\mathsf{P}_e = \int m_e \mathbf{C}_e \otimes \mathbf{C}_e f_e^0 (1 + \phi_e) d\mathbf{c}_e = n_e k_B T_e \mathsf{I} \tag{60b}$$

with the shear viscosity

$$\eta = \tfrac{1}{10} k_B T_h [\mathsf{B},\mathsf{B}]_h. \tag{61}$$

Due to the scaling of the Boltzmann equation, electrons do not contribute the viscous shear stress, as mentioned by Degond and Lucquin-Desreux [23].

3. Heat flux

$$\mathbf{q}_h = \sum_{j\in\mathcal{H}} \int \frac{1}{2} m_j C_j^2 \mathbf{C}_j f_j^0 \phi_j d\mathbf{c}_j$$

$$= \sum_{j\in\mathcal{H}} \rho_j h_j \mathbf{V}_j - \lambda_h' \nabla T_h - n k_B T_h \sum_{j\in\mathcal{S}} D_{Tj}^h \mathbf{d}_j, \tag{62a}$$

$$\mathbf{q}_e = \int \frac{1}{2} m_e C_e^2 \mathbf{C}_e f_e^0 \phi_e d\mathbf{c}_e$$

$$= \rho_e h_e \mathbf{V}_e - \lambda_e' \nabla T_e - n k_B T_h \sum_{j\in\mathcal{S}} D_{Tj}^e \mathbf{d}_j, \tag{62b}$$

with the partial thermal conductivities

$$\lambda_h' = \frac{k_B}{3} [\mathbf{A}^h, \mathbf{A}^h]_h, \tag{63a}$$

$$\lambda_e' = \frac{k_B}{3} [\mathbf{A}^e, \mathbf{A}^e]_e, \tag{63b}$$

and the species translational enthalpies $h_i = h_{Ti} = \frac{5}{2} k_B T_i / m_i$. No cross contributions due to temperature gradients are found, i.e., the heavy-particle heat flux does not depend on the electron temperature gradient and vice versa. This is due to the exact cancellation of the bracket integrals $[\mathbf{A}^h, \mathbf{A}^h]_e$ and $[\mathbf{A}^e, \mathbf{A}^e]_h$. The heat flux expressions derived by Kolesnikov [16] include some cross contributions of temperature gradients probably generated by polluting small order terms present in the approximations. In terms of measurable quantities, the heat fluxes read

$$\mathbf{q}_h = \sum_{j\in\mathcal{H}} \rho_j h_j \mathbf{V}_j + n k_B T_h \sum_{j\in\mathcal{S}} k_{Tj}^h \mathbf{V}_j - \lambda_h \nabla T_h - \lambda_{he} \nabla T_e, \tag{64a}$$

$$\mathbf{q}_e = \rho_e h_e \mathbf{V}_e + n k_B T_h \sum_{j\in\mathcal{S}} k_{Tj}^e \mathbf{V}_j - \lambda_{eh} \nabla T_h - \lambda_e \nabla T_e, \tag{64b}$$

with the thermal conductivities

$$\lambda_h = \lambda_h' - n k_B \sum_{j\in\mathcal{S}} k_{Tj}^h D_{Tj}^h, \tag{65a}$$

$$\lambda_{he} = - n k_B \frac{T_h}{T_e} \sum_{j\in\mathcal{S}} k_{Tj}^h D_{Tj}^e, \tag{65b}$$

$$\lambda_{eh} = - n k_B \sum_{j\in\mathcal{S}} k_{Tj}^e D_{Tj}^h, \tag{65c}$$

$$\lambda_e = \lambda_e' - n_B \frac{T_h}{T_e} \sum_{j\in\mathcal{S}} k_{Tj}^e D_{Tj}^e. \tag{65d}$$

Seeing the transport flux expressions, the first order conservation equations are identified as the Navier-Stokes equations. It will be shown further that the cross contributions due to temperature gradients [see Eqs. (65b) and (65c)] vanish as well in the case of measurable quantities in the hypothesis of weak thermal nonequilibrium.

E. Laguerre-Sonine polynomial expansion

The integral equations (50) are solved by a spectral Galerkin method. The coefficients of the perturbation function defined in Eq. (49) are expanded in a truncated series of Laguerre-Sonine polynomials

$$\mathbf{A}_i^h = - \sqrt{\frac{m_i}{2k_B T_i}} \sum_{p\in\mathcal{P}} a_{i,p}^h(\xi) S_{\frac{3}{2}}^{(p)}(\mathcal{C}_i^2) \boldsymbol{\mathcal{C}}_i, \tag{66a}$$

$$\mathbf{A}_i^e = - \sqrt{\frac{m_i}{2k_B T_i}} \sum_{p\in\mathcal{P}} a_{i,p}^e(\xi) S_{\frac{3}{2}}^{(p)}(\mathcal{C}_i^2 \boldsymbol{\mathcal{C}}_i), \tag{66b}$$

$$\mathsf{B}_i = \sum_{p\in\mathcal{P}} b_{i,p}(\xi) S_{\frac{5}{2}}^{(p)}(\mathcal{C}_i^2) \left(\boldsymbol{\mathcal{C}}_i \otimes \boldsymbol{\mathcal{C}}_i - \frac{\mathcal{C}_i^2}{3} \mathsf{I} \right), \tag{66c}$$

$$\mathbf{D}_i^k = \sqrt{\frac{m_i}{2k_B T_i}} \sum_{p\in\mathcal{P}} d_{i,p}^k(\xi) S_{\frac{3}{2}}^{(p)}(\mathcal{C}_i^2) \boldsymbol{\mathcal{C}}_i, \quad k \in \mathcal{S}, \tag{66d}$$

$i \in \mathcal{S}$, and where $\mathcal{P} = \{0, \dots, \xi - 1\}$ is the set of polynomial indices. Substituting Eq. (66d) into the integral equation (50a), Eq. (66a) into the integral equation (50b), and Eq. (66b) into the integral equation (50c), multiplying by the vector $S_{3/2}^{(p)}(\mathcal{C}_i^2)\boldsymbol{\mathcal{C}}_i$, and integrating over $\mathbf{c}_i$, the transport systems for mass and heat transfer are readily obtained

$$\sum_{j\in\mathcal{H}} \sum_{q\in\mathcal{P}} \Lambda_{ij}^{pq} d_{j,q}^k + \sum_{q\in\mathcal{P}} \Lambda_{ie}^{0q} d_{e,q}^k \delta_{p0}$$

$$= \frac{8}{25 k_B} (\delta_{ik} - y_i) \delta_{p0}, \quad i \in \mathcal{H}, \tag{67a}$$

$$\sum_{j\in\mathcal{H}} \Lambda_{ej}^{p0} d_{j,0}^k + \sum_{q\in\mathcal{P}} \Lambda_{ee}^{pq} d_{e,q}^k = \frac{8}{25 k_B} (\delta_{ek} - y_e) \frac{T_h}{T_e} \delta_{p0}, \tag{67b}$$

$$\sum_{j\in\mathcal{H}} \sum_{q\in\mathcal{P}} \Lambda_{ij}^{pq} a_{j,q}^h + \sum_{q\in\mathcal{P}} \Lambda_{ie}^{0q} a_{e,q}^h \delta_{p0} = \frac{4}{5 k_B} \frac{n_i}{n} \delta_{p1}, \quad i \in \mathcal{H}, \tag{67c}$$

$$\sum_{j\in\mathcal{H}} \Lambda_{ej}^{p0} a_{j,0}^h + \sum_{q\in\mathcal{P}} \Lambda_{ee}^{pq} a_{e,q}^h = 0, \tag{67d}$$

$$\sum_{j\in\mathcal{H}}\sum_{q\in\mathcal{P}}\Lambda_{ij}^{pq}a_{j,q}^{e}+\sum_{q\in\mathcal{P}}\Lambda_{ie}^{0q}a_{e,q}^{e}\delta_{p0}=0,\quad i\in\mathcal{H},\tag{67e}$$

$$\sum_{j\in\mathcal{H}}\Lambda_{ej}^{p0}a_{j,0}^{e}+\sum_{q\in\mathcal{P}}\Lambda_{ee}^{pq}a_{e,q}^{e}=\frac{4}{5k_B}\frac{n_e}{n}\delta_{p1},\tag{67f}$$

$k\in\mathcal{S},p\in\mathcal{P}$. Likewise, substituting Eq. (66c) into the integral equation (50d), multiplying by the tensor $S_{5/2}^{(p)}(\mathcal{C}_i^2)(\boldsymbol{\mathcal{C}}_i\otimes\boldsymbol{\mathcal{C}}_i-\mathcal{C}_i^2\mathsf{I}/3)$ and integrating over $\mathbf{c}_i$, the transport system for momentum transfer is given by

$$\sum_{j\in\mathcal{H}}\sum_{q\in\mathcal{P}}H_{ij}^{pq}b_{j,q}=\frac{2}{k_B}\frac{n_i}{n}\delta_{p0},\quad i\in\mathcal{H},\tag{68a}$$

$$\sum_{q\in\mathcal{P}}H_{ee}^{pq}b_{e,q}=0,\tag{68b}$$

$p\in\mathcal{P}$. The bracket integral reduction is found in Appendix A. Transport collision integrals are introduced in Appendix B. Transport matrices Λ_{ij}^{pq} and H_{ij}^{pq}, $i,j\in\mathcal{S},p,q\in\mathcal{P}$ are presented in terms of the transport collision integrals in Appendix C. The transport matrices are symmetric

$$\Lambda_{ij}^{pq}=\Lambda_{ji}^{qp},\tag{69a}$$

$$H_{ij}^{pq}=H_{ji}^{qp},\tag{69b}$$

and satisfy the relations

$$\sum_{j\in\mathcal{H}}\Lambda_{ji}^{0p}+\frac{T_e}{T_h}\Lambda_{ei}^{0p}=0,\quad i\in\mathcal{S}.\tag{70}$$

In order to keep a symmetric form in thermal nonequilibrium, temperatures do not explicitly appear in the momentum transport system given in Eq. (68) contrary to the expression derived by Ferziger and Kaper [6]. Substituting Eqs. (66a), (66b), and (66d) into Eq. (51), a new set of constraints is obtained

$$\sum_{j\in\mathcal{S}}y_j a_{j,0}^{h}=0,\tag{71a}$$

$$\sum_{j\in\mathcal{S}}y_j a_{j,0}^{e}=0,\tag{71b}$$

$$\sum_{j\in\mathcal{S}}y_j d_{j,0}^{i}=0,\quad i\in\mathcal{S}.\tag{71c}$$

Substituting Eq. (66) into Eqs. (56), (61), and (63), transport coefficients for mass and heat transfer read in the approximation order ξ:

$$D_{ij}(\xi)=\frac{1}{2n}d_{i,0}^{j},\quad i,j\in\mathcal{S},\tag{72a}$$

$$D_{Ti}^{h}(\xi)=-\frac{1}{2n}a_{i,0}^{h},\quad i\in\mathcal{S},\tag{72b}$$

$$D_{Ti}^{e}(\xi)=-\frac{1}{2n}a_{i,0}^{e},\quad i\in\mathcal{S},\tag{72c}$$

$$\lambda_h'(\xi)=\frac{5k_B}{4}\sum_{j\in\mathcal{H}}\frac{n_j}{n}a_{j,1}^{h},\tag{72d}$$

$$\lambda_e'(\xi)=\frac{5k_B}{4}\frac{n_e}{n}a_{e,1}^{e}.\tag{72e}$$

Thermal diffusion coefficients are alternately given by

$$D_{Ti}^{h}(\xi)=-\frac{5}{4n}\sum_{j\in\mathcal{H}}\frac{n_j}{n}d_{j,1}^{i},\tag{73a}$$

$$D_{Ti}^{e}(\xi)=-\frac{5}{4n}\frac{n_e}{n}\frac{T_e}{T_h}d_{e,1}^{i}.\tag{73b}$$

The shear viscosity coefficient reads

$$\eta(\xi)=\frac{k_BT_h}{2}\sum_{j\in\mathcal{H}}\frac{n_j}{n}b_{j,0}.\tag{74}$$

The system for the heavy-particle shear viscosity given in Eq. (68a) does not depend on electrons.

F. Goldstein expansion

Expressions of thermal diffusion ratios [see Eq. (58)] and thermal conductivities [see Eq. (65)] are elegantly derived expanding the perturbation function in Laguerre-Sonine polynomials as proposed by Goldstein [38]

$$\begin{aligned}\theta_i&=\phi_i+\frac{1}{n}\mathsf{B}_i:\boldsymbol{\nabla}\mathbf{v}-\psi_i\\&=\sqrt{\frac{m_i}{2k_BT_i}}\boldsymbol{\mathcal{C}}_i\cdot\sum_{p\in\mathcal{P}}\boldsymbol{\omega}_i^pS_{\frac{3}{2}}^{(p)}(\mathcal{C}_i^2),\quad i\in\mathcal{S},\end{aligned}\tag{75}$$

with the vectors

$$\boldsymbol{\omega}_i^p=\frac{1}{n}a_{i,p}^{h}\boldsymbol{\nabla}\ln T_h+\frac{1}{n}a_{i,p}^{e}\boldsymbol{\nabla}\ln T_e-\frac{1}{n}\sum_{j\in\mathcal{S}}d_{i,p}^{j}\mathbf{d}_j^{*}.\tag{76}$$

Only the contribution to the heat transfer and diffusion phenomena has been retained in the perturbation function given in Eq. (75). The vectors $\mathbf{d}_i^*$ are linearly independent. Their projections onto the driving force constraint hyperplane [see Eq. (45)] along the mass fraction vector are the driving forces $\mathbf{d}_i=\mathbf{d}_i^*-y_i\sum_{k\in\mathcal{S}}\mathbf{d}_k^*$. Generalizing Kolesnikov and Tirskiy's argument [31] to thermal nonequilibrium, if $\boldsymbol{\nabla}\ln T_h$, $\boldsymbol{\nabla}\ln T_e$ and $\mathbf{d}_i^*$ are treated as a set of basis vectors, then the projections of $\boldsymbol{\omega}_i^p$ in this basis satisfy Eq. (67). The vectors $\boldsymbol{\omega}_i^p$ are solutions of the system

$$\begin{aligned}&\sum_{j\in\mathcal{H}}\sum_{q\in\mathcal{P}}\Lambda_{ij}^{pq}\boldsymbol{\omega}_j^q+\sum_{q\in\mathcal{P}}\Lambda_{ie}^{0q}\boldsymbol{\omega}_e^q\delta_{p0}\\&\quad=\frac{4}{5nk_B}\frac{n_i}{n}\boldsymbol{\nabla}\ln T_h\delta_{p1}-\frac{8}{25nk_B}\mathbf{d}_i\delta_{p0},\quad i\in\mathcal{H},\end{aligned}\tag{77a}$$

$$\sum_{j\in\mathcal{H}} \Lambda_{ej}^{p0}\boldsymbol{\omega}_j^0 + \sum_{q\in\mathcal{P}} \Lambda_{ee}^{pq}\boldsymbol{\omega}_e^q = \frac{4}{5nk_B}\frac{n_e}{n}\boldsymbol{\nabla}\ln T_e\delta_{p1} - \frac{8}{25nk_B}\frac{T_h}{T_e}\mathbf{d}_e\delta_{p0}, \tag{77b}$$

with the constraints derived from Eq. (71)

$$\sum_{j\in\mathcal{S}} y_j\boldsymbol{\omega}_j^0 = 0. \tag{78}$$

The first moments of the distribution function lead to a physical interpretation of the vectors $\boldsymbol{\omega}_i^0$ and $\boldsymbol{\omega}_i^1$. Employing Eq. (75) and the properties of the Laguerre-Sonine polynomials, one obtains

$$\mathbf{M}_i^1 = \int f_i^0\phi_i\mathbf{C}_i d\mathbf{c}_i = \frac{n_i}{2}\boldsymbol{\omega}_i^0, \tag{79a}$$

$$\mathbf{M}_i^3 = \int C_i^2 f_i^0\phi_i\mathbf{C}_i d\mathbf{c}_i = \frac{5}{2}\frac{n_ik_BT_i}{m_i}(\boldsymbol{\omega}_i^0 - \boldsymbol{\omega}_i^1). \tag{79b}$$

Hence the diffusion velocities and the heat fluxes are related to the vectors $\boldsymbol{\omega}_i^0$ and $\boldsymbol{\omega}_i^1$

$$[\mathbf{V}_i]_\xi = \frac{1}{n_i}\mathbf{M}_i^1 = \frac{1}{2}\boldsymbol{\omega}_i^0, \quad i\in\mathcal{S}, \tag{80a}$$

$$[\mathbf{q}_h]_\xi = \sum_{j\in\mathcal{H}}\frac{m_j}{2}\mathbf{M}_j^3 = \frac{5}{4}k_BT_h\sum_{j\in\mathcal{H}} n_j(\boldsymbol{\omega}_j^0 - \boldsymbol{\omega}_j^1), \tag{80b}$$

$$[\mathbf{q}_e]_\xi = \frac{m_e}{2}\mathbf{M}_e^3 = \frac{5}{4}k_BT_en_e(\boldsymbol{\omega}_e^0 - \boldsymbol{\omega}_e^1). \tag{80c}$$

Kolesnikov [18] has derived the expressions of the thermal diffusion ratios, thermal conductivities, and generalized Stefan-Maxwell equation. The same approach is followed here with the formalism of Ferziger and Kaper and a more numerically adequate presentation where systems are preferred to determinants. Using Eq. (80a), the system given in Eq. (77) can be written for any approximation order $\xi > 1$

$$\sum_{j\in\mathcal{H}}\sum_{q\in\mathcal{P}_1} \Lambda_{ij}^{pq}\boldsymbol{\omega}_j^q = \frac{4}{5nk_B}\frac{n_i}{n}\boldsymbol{\nabla}\ln T_h\delta_{p1} - 2\sum_{j\in\mathcal{H}}\Lambda_{ij}^{p0}[\mathbf{V}_j]_\xi, \quad i\in\mathcal{H}, \tag{81a}$$

$$\sum_{q\in\mathcal{P}_1} \Lambda_{ee}^{pq}\boldsymbol{\omega}_e^q = \frac{4}{5nk_B}\frac{n_e}{n}\boldsymbol{\nabla}\ln T_e\delta_{p1} - 2\sum_{j\in\mathcal{S}}\Lambda_{ej}^{p0}[\mathbf{V}_j]_\xi, \tag{81b}$$

$p\in\mathcal{P}_1=\{1,\ldots,\xi-1\}$. After inversion of the nonsingular system given in Eq. (81), the vectors $\boldsymbol{\omega}_i^p$ read

$$\boldsymbol{\omega}_i^p = \alpha_{i,p}^h\boldsymbol{\nabla}\ln T_h + \alpha_{i,p}^e\boldsymbol{\nabla}\ln T_e + \sum_{j\in\mathcal{S}}\beta_{ij,p}[\mathbf{V}_j]_\xi, \quad i\in\mathcal{S}, \quad p\in\mathcal{P}_1. \tag{82}$$

The coefficients in Eq. (82) are solutions of the transport systems

$$\sum_{j\in\mathcal{H}}\sum_{q\in\mathcal{P}_1}\Lambda_{ij}^{pq}\alpha_{j,q}^h = \frac{4}{5nk_B}\frac{n_i}{n}\delta_{p1}, \quad i\in\mathcal{H}, \tag{83a}$$

$$\sum_{q\in\mathcal{P}_1}\Lambda_{ee}^{pq}\alpha_{e,q}^h = 0, \tag{83b}$$

$$\sum_{j\in\mathcal{H}}\sum_{q\in\mathcal{P}_1}\Lambda_{ij}^{pq}\alpha_{j,q}^e = 0, \quad i\in\mathcal{H}, \tag{83c}$$

$$\sum_{q\in\mathcal{P}_1}\Lambda_{ee}^{pq}\alpha_{e,q}^e = \frac{4}{5nk_B}\frac{n_e}{n}\delta_{p1}, \tag{83d}$$

$$\sum_{j\in\mathcal{H}}\sum_{q\in\mathcal{P}_1}\Lambda_{ij}^{pq}\beta_{jk,q} = -2\Lambda_{ik}^{p0}, \quad i,k\in\mathcal{H}, \tag{83e}$$

$$\sum_{j\in\mathcal{H}}\sum_{q\in\mathcal{P}_1}\Lambda_{ij}^{pq}\beta_{je,q} = 0, \quad i\in\mathcal{H}, \tag{83f}$$

$$\sum_{q\in\mathcal{P}_1}\Lambda_{ee}^{pq}\beta_{ek,q} = -2\Lambda_{ek}^{p0}, \quad k\in\mathcal{S}, \tag{83g}$$

$p\in\mathcal{P}_1$. The heat flux can be obtained injecting Eq. (82) into Eqs. (80b) and (80c). The thermal conductivities and thermal diffusion ratios are identified as

$$\lambda_h(\xi) = \frac{5}{4}k_B\sum_{j\in\mathcal{H}} n_j\alpha_{j,1}^h, \tag{84a}$$

$$\lambda_{he}(\xi) = 0, \tag{84b}$$

$$\lambda_{eh}(\xi) = 0, \tag{84c}$$

$$\lambda_e(\xi) = \tfrac{5}{4}k_Bn_e\alpha_{e,1}^e, \tag{84d}$$

$$k_{Ti}^h(\xi) = -\frac{5}{4}\sum_{j\in\mathcal{H}}\frac{n_j}{n}\beta_{ji,1}, \quad i\in\mathcal{H}, \tag{84e}$$

$$k_{Te}^h(\xi) = 0, \tag{84f}$$

$$k_{Ti}^e(\xi) = -\frac{5}{4}\frac{T_e}{T_h}\frac{n_e}{n}\beta_{ei,1}, \quad i\in\mathcal{S}. \tag{84g}$$

It turns out that the cross contributions due to temperature gradients given in Eqs. (84b) and (84c) vanish as well when heat fluxes are written in terms of measurable quantities. Furthermore, both systems for heavy particle [see Eq. (83a)] and electron [see Eq. (83d)] thermal conductivities are decoupled. Different orders of approximation can be employed in the Laguerre-Sonine expansion for each contribution. Regarding the systems given in Eqs. (83e) and (83g), the same argument can be applied to the thermal diffusion ratios. The expressions of λ_h and λ_e agree with the results of Devoto [10]. Thermal diffusion ratios correspond to the expressions derived by Kolesnikov [18].

The first order Stefan-Maxwell equation for the diffusion velocities is readily obtained writing Eq. (77) for $\xi=1$ and using Eq. (80a)

$$\sum_{\substack{j\in\mathcal{H}\\ j\neq i}}\frac{x_ix_j}{\mathcal{D}_{ij}}([\mathbf{V}_j]_1-[\mathbf{V}_i]_1)+\frac{T_e}{T_h}\frac{x_ix_e}{\mathcal{D}_{ie}}\left([\mathbf{V}_e]_1-\frac{T_e}{T_h}[\mathbf{V}_i]_1\right)=\mathbf{d}_i,\quad i\in\mathcal{H}, \tag{85a}$$

$$\sum_{j\in\mathcal{H}}\frac{x_ex_j}{\mathcal{D}_{ej}}\left(\frac{T_e}{T_h}[\mathbf{V}_j]_1-[\mathbf{V}_e]_1\right)=\frac{T_h}{T_e}\mathbf{d}_e. \tag{85b}$$

with the mass conservation given in Eq. (78)

$$\sum_{j\in\mathcal{S}}y_j[\mathbf{V}_j]_1=0. \tag{86}$$

Binary diffusion coefficients $\mathcal{D}_{ij}$ are defined in Appendix B. The Stefan-Maxwell equation for any higher approximation order is derived from Eq. (77) written for $p=0$ and $\xi>1$

$$\sum_{j\in\mathcal{S}}\Lambda_{ij}^{00}[\mathbf{V}_j]_\xi+\frac{1}{2}\sum_{j\in\mathcal{S}}\sum_{q\in\mathcal{P}_1}\Lambda_{ij}^{0q}\boldsymbol{\omega}_j^q=-\frac{4}{25nk_B}\mathbf{d}_i,\quad i\in\mathcal{H}, \tag{87a}$$

$$\sum_{j\in\mathcal{S}}\Lambda_{ej}^{00}[\mathbf{V}_j]_\xi+\frac{1}{2}\sum_{q\in\mathcal{P}_1}\Lambda_{ee}^{0q}\boldsymbol{\omega}_e^q=-\frac{4}{25nk_B}\frac{T_h}{T_e}\mathbf{d}_e. \tag{87b}$$

The second term in the left-hand side of Eq. (87) can be transformed by means of Eq. (82). After some algebra, the final result reads

$$\sum_{\substack{j\in\mathcal{H}\\ j\neq i}}\frac{x_ix_j}{\mathcal{D}_{ij}}[1+\varphi_{ij}(\xi)]([\mathbf{V}_j]_\xi-[\mathbf{V}_i]_\xi)+\frac{T_e}{T_h}\frac{x_ix_e}{\mathcal{D}_{ie}}[1+\varphi_{ie}(\xi)]\times\left([\mathbf{V}_e]_\xi-\frac{T_e}{T_h}[\mathbf{V}_i]_\xi\right)=\mathbf{d}_i+k_{Ti}^h(\xi)\,\boldsymbol{\nabla}\ln T_h+k_{Ti}^e(\xi)\frac{T_h}{T_e}\,\boldsymbol{\nabla}\ln T_e,\quad i\in\mathcal{H}, \tag{88a}$$

$$\sum_{j\in\mathcal{H}}\frac{x_ex_j}{\mathcal{D}_{ej}}[1+\varphi_{ej}(\xi)]\left(\frac{T_e}{T_h}[\mathbf{V}_j]_\xi-[\mathbf{V}_e]_\xi\right)=\frac{T_h}{T_e}[\mathbf{d}_e+k_{Te}^e(\xi)\,\boldsymbol{\nabla}\ln T_e]. \tag{88b}$$

with the mass conservation obtained from Eq. (78),

$$\sum_{j\in\mathcal{S}}y_j[\mathbf{V}_j]_\xi=0. \tag{89}$$

The correction function $\varphi_{ij}(\xi)$ defined for $\xi>1$ by the equations

$$\frac{16}{25nk_B}\frac{x_ix_j}{\mathcal{D}_{ij}}\varphi_{ij}(\xi)=\sum_{q,r\in\mathcal{P}_1}\sum_{k,l\in\mathcal{H}}\Lambda_{kl}^{qr}\beta_{li,r}\beta_{kj,q}+\sum_{q,r\in\mathcal{P}_1}\Lambda_{ee}^{qr}\beta_{ei,r}\beta_{ej,q},\quad i,j\in\mathcal{H}, \tag{90a}$$

$$\frac{16}{25nk_B}\frac{x_ix_e}{\mathcal{D}_{ie}}\frac{T_e}{T_h}\varphi_{ie}(\xi)=\sum_{q,r\in\mathcal{P}_1}\Lambda_{ee}^{qr}\beta_{ee,r}\beta_{ei,q},\quad i\in\mathcal{H}, \tag{90b}$$

$$\frac{16}{25nk_B}\frac{x_e^2}{\mathcal{D}_{ee}}\varphi_{ee}(\xi)=\sum_{q,r\in\mathcal{P}_1}\Lambda_{ee}^{qr}\beta_{ee,r}\beta_{ee,q} \tag{90c}$$

is symmetric and verifies the relations

$$\sum_{j\in\mathcal{H}}\frac{x_ix_j}{\mathcal{D}_{ij}}\varphi_{ij}(\xi)+\frac{x_ix_e}{\mathcal{D}_{ie}}\left(\frac{T_e}{T_h}\right)^2\varphi_{ie}(\xi)=0,\quad i\in\mathcal{H}, \tag{91a}$$

$$\sum_{j\in\mathcal{H}}\frac{x_ex_j}{\mathcal{D}_{ej}}\varphi_{ej}(\xi)+\frac{x_e^2}{\mathcal{D}_{ee}}\varphi_{ee}(\xi)=0. \tag{91b}$$

Let us write $\varphi_{ij}(1)\equiv 0$ to encompass the first order Stefan-Maxwell equation (85) in Eq. (88). Remark, once again, it is possible to use different orders of Laguerre-Sonine approximation to evaluate the first contribution in Eq. (90a) on the one hand, and the second contribution in the same equation together with Eqs. (90b) and (90c) on the other hand.

G. Simplifications of the Stefan-Maxwell equation

To emphasize the electric field driving forces, the Stefan-Maxwell equation (88) is changed accordingly

$$\sum_{\substack{j\in\mathcal{H}\\ j\neq i}}\frac{x_ix_j}{\mathcal{D}_{ij}}[1+\varphi_{ij}(\xi)]([\mathbf{V}_j]_\xi-[\mathbf{V}_i]_\xi)+\frac{T_e}{T_h}\frac{x_ix_e}{\mathcal{D}_{ie}}[1+\varphi_{ie}(\xi)]\times\left([\mathbf{V}_e]_\xi-\frac{T_e}{T_h}[\mathbf{V}_i]_\xi\right)+\kappa_i\mathbf{E}=\mathbf{d}_i',\quad i\in\mathcal{H}, \tag{92a}$$

$$\sum_{j\in\mathcal{H}}\frac{x_ex_j}{\mathcal{D}_{ej}}[1+\varphi_{ej}(\xi)]\left(\frac{T_e}{T_h}[\mathbf{V}_j]_\xi-[\mathbf{V}_e]_\xi\right)+\kappa_e\frac{T_h}{T_e}\mathbf{E}=\frac{T_h}{T_e}\mathbf{d}_e'. \tag{92b}$$

The driving forces are modified to incorporate thermal diffusion and exclude the electric field

$$\mathbf{d}_i'=\frac{\boldsymbol{\nabla}p_i}{nk_BT_h}-\frac{y_ip}{nk_BT_h}\,\boldsymbol{\nabla}\ln p+k_{Ti}^h(\xi)\,\boldsymbol{\nabla}\ln T_h+k_{Ti}^e(\xi)\frac{T_i}{T_e}\,\boldsymbol{\nabla}\ln T_e, \tag{93a}$$

$$\kappa_i=\frac{1}{k_BT_h}(x_iq_i-y_iq). \tag{93b}$$

The modified driving forces and electric field factors are not linearly independent

$$\sum_{j\in\mathcal{S}}\mathbf{d}_j'=0, \tag{94a}$$

$$\sum_{j\in\mathcal{S}}\kappa_j=0. \tag{94b}$$

The electric field remains unknown and can be determined from the ambipolar assumption stating that there is no net conduction current

$$\sum_{j\in\mathcal{S}}x_jq_j[\mathbf{V}_j]_\xi=0. \tag{95}$$

Combining both mass [see Eq. (89)] and ambipolar [see Eq. (95)] constraints, a new constraint appears

$$\sum_{j\in\mathcal{S}}\kappa_j[\mathbf{V}_j]_\xi=0. \tag{96}$$

To close the system given in Eq. (92), Eq. (96) is preferred to Eq. (95) for symmetry reason. If charge neutrality is verified in the plasma, Eqs. (95) and (96) are equivalent. The mass conservation constraint given in Eq. (89) complements the set of equations.

Existing models from the literature [18,28] are shown to be approximations of the present complete description. Assuming that for all $i\in\mathcal{H}$, there exists $j\in\mathcal{H}, j\neq i$, such that $x_e/\mathcal{D}_{ie}\ll x_j/\mathcal{D}_{ij}$, an approximate form of the Stefan-Maxwell equation (92a) is found for heavy particles

$$\sum_{\substack{j\in\mathcal{H}\\ j\neq i}}\frac{x_ix_j}{\mathcal{D}_{ij}}[1+\varphi_{ij}(\xi)]([\mathbf{V}_j]_\xi-[\mathbf{V}_i]_\xi)+\frac{x_ix_e}{\mathcal{D}_{ie}}[1+\varphi_{ie}(\xi)]\frac{T_e}{T_h}[\mathbf{V}_e]_\xi + \kappa_i\mathbf{E}=\mathbf{d}'_i,\quad i\in\mathcal{H}. \tag{97}$$

Equation for electrons is obtained consistently to ensure compatibility of the system

$$-\sum_{j\in\mathcal{H}}\frac{x_ex_j}{\mathcal{D}_{ej}}[1+\varphi_{ej}(\xi)][\mathbf{V}_e]_\xi+\kappa_e\frac{T_h}{T_e}\mathbf{E}=\frac{T_h}{T_e}\mathbf{d}'_e. \tag{98}$$

The mass and ambipolar constraints Eqs. (89) and (96) are still applicable. Equations (97) and (98) correspond to Kolesnikov's model [18].

Assuming further that for all $i\in\mathcal{H}$, there exists $j\in\mathcal{H}, j\neq i$, such that $x_eV_e/\mathcal{D}_{ie}\ll x_jV_j/\mathcal{D}_{ij}$ or such that $x_eV_e/\mathcal{D}_{ie}\ll x_jV_i/\mathcal{D}_{ij}$, the Stefan-Maxwell equation for heavy particles (92a) simplifies

$$\sum_{\substack{j\in\mathcal{H}\\ j\neq i}}\frac{x_ix_j}{\mathcal{D}_{ij}}[1+\varphi_{ij}(\xi)]([\mathbf{V}_j]_\xi-[\mathbf{V}_i]_\xi)+\kappa_i\mathbf{E}=\mathbf{d}'_i,\quad i\in\mathcal{H}. \tag{99}$$

Summing up Eq. (99) over heavy species and using Eq. (94), the electric field is given by $\mathbf{E}=\mathbf{d}'_e/\kappa_e$. Equation (99) is rewritten

$$\sum_{\substack{j\in\mathcal{H}\\ j\neq i}}\frac{x_ix_j}{\mathcal{D}_{ij}}[1+\varphi_{ij}(\xi)]([\mathbf{V}_j]_\xi-[\mathbf{V}_i]_\xi)=\mathbf{d}'_i-\frac{\kappa_i}{\kappa_e}\mathbf{d}'_e,\quad i\in\mathcal{H}. \tag{100}$$

To get a closed form, the electron diffusion velocity is eliminated between the constraints presented in Eqs. (89) and (96). Thus, the system given in Eq. (100) is supplied with the equation $\Sigma_{j\in\mathcal{H}}[y_j-y_ex_jq_j/(x_eq_e)][\mathbf{V}_j]_\xi=0$. Quasineutrality of the plasma provides the simplified equation

$$\sum_{j\in\mathcal{H}}y_j[\mathbf{V}_j]_\xi=0. \tag{101}$$

From Eq. (95), the electron diffusion velocity reads $[\mathbf{V}_e]_\xi=-\Sigma_{j\in\mathcal{H}}\,x_jq_j[\mathbf{V}_j]_\xi/(x_eq_e)$. Equation (100) generalizes Ramshaw and Chang's diffusion model [20] to any higher order of approximation for the Laguerre-Sonine polynomials, including the thermal diffusion effect.

H. Internal energy and chemistry

Internal energy of atoms and polyatomic molecules has been entirely neglected in this derivation. In elastic collisions, the internal degrees of freedom of molecules do not change and the macroscopic result is a passive transport of internal energy. In inelastic collisions, the internal degrees of freedom vary. Diffusion and heat transfer phenomena are affected. As mentioned earlier, kinetic theory has been generalized to incorporate both contributions [6,27,29,32]. A rigorous treatment of internal energy is not the object of the present research and inelastic collisions were therefore not accounted for. However, simple Eucken corrections are now considered in order to provide some pragmatic treatment of the internal degrees of freedom. These expressions are useful in situations where it is difficult to estimate with high accuracy the contribution of inelastic collisions. Only the thermal equilibrium case is addressed in this section. Thermal nonequilibrium requires additional energy conservation equations with specific relaxation models. The heat flux expressions given in Eq. (64) are modified

$$\mathbf{q}_h=\sum_{j\in\mathcal{H}}\rho_jh_j\mathbf{V}_j+nk_BT\sum_{j\in\mathcal{S}}k^h_{Tj}\mathbf{V}_j-(\lambda_h+\lambda_R+\lambda_V+\lambda_E)\,\boldsymbol{\nabla}\,T, \tag{102a}$$

$$\mathbf{q}_e=\rho_eh_e\mathbf{V}_e+nk_BT\sum_{j\in\mathcal{S}}k^e_{Tj}\mathbf{V}_j-\lambda_e\,\boldsymbol{\nabla}\,T. \tag{102b}$$

Species enthalpies used in the heat flux expressions [see Eq. (102)] are now given by

$$h_i=h_{Ti}+h_{Ei}+h_{Fi},\quad i\in\mathcal{H}_a, \tag{103a}$$

$$h_i=h_{Ti}+h_{Ri}+h_{Vi}+h_{Ei}+h_{Fi},\quad i\in\mathcal{H}_p, \tag{103b}$$

$$h_e=h_{Te}+h_{Fe}, \tag{103c}$$

where $\mathcal{H}_a$ and $\mathcal{H}_p$ stand for the sets of indices of atoms and polyatomic molecules. Expressions h_{Ri}, h_{Vi}, and h_{Ei} correspond, respectively, to the rotational, vibrational, and electronic species enthalpies. The chemical reaction contribution is included by means of the formation enthalpy h_{Fi}. Rotational, vibrational, and electronic thermal conductivities, λ_R, λ_V, and λ_E, are derived on a rigorous basis considering all the collisions to be elastic in the transport systems given by Ern and Giovangigli [29]. After some trivial algebra, one obtains

$$\lambda_R = n \sum_{i \in \mathcal{H}_p} \frac{x_i C_i^R}{\sum_{j \in \mathcal{H}} x_j/\mathcal{D}_{ij}}, \tag{104a}$$

$$\lambda_V = n \sum_{i \in \mathcal{H}_p} \frac{x_i C_i^V}{\sum_{j \in \mathcal{H}} x_j/\mathcal{D}_{ij}}, \tag{104b}$$

$$\lambda_E = n \sum_{i \in \mathcal{H}} \frac{x_i C_i^E}{\sum_{j \in \mathcal{H}} x_j/\mathcal{D}_{ij}}, \tag{104c}$$

where C_i^R, C_i^V, and C_i^E are the rotational, vibrational, and electronic species specific heats per particle. Remark, even though less frequent, inelastic collisions play a role in the establishment of local equilibrium (see Ref. [6]).

IV. CONCLUSIONS

In this contribution, the modeling of transport phenomena was addressed for partially ionized and unmagnetized plasmas in thermal nonequilibrium. Different models found in the literature were reviewed. Most of the expressions derived from kinetic theory are inconsistent with respect to mass conservation. Moreover, it is difficult to extract the final results for real applications. Kolesnikov [16] has established a self-consistent model from a nonsymmetric kinetic approach. Petit and Darrozes [19] and Degond and Lucquin-Desreux [22,23] have derived the correct scaling of the Boltzmann equation from a dimensional analysis. Ramshaw and Chang [20,21] have proposed a pragmatic diffusion model from hydrodynamic theory. Rat *et al.* [26] have envisaged the possibility of a strong thermal nonequilibrium in two-temperature plasmas. Their scaling of the Boltzmann equation is in contrast with Refs. [19,22,23] and a nonsymmetric formalism has been used in the derivation.

We have presented a kinetic approach to compute the transport properties. Following Petit and Darrozes [19], a dimensional analysis of the Boltzmann equation deals with the disparity of mass between electrons and heavy particles. This analysis yields the epochal relaxation concept worked out by Degond and Lucquin-Desreux [22,23]. We assumed a translational temperature of electrons distinct from that of heavy particles and a common hydrodynamic velocity. The plasma was described by macroscopic fluid conservation equations. The expressions of the transport fluxes and coefficients were derived from kinetic theory together with a high-order Stefan-Maxwell equation. These expressions remain valid in thermal equilibrium situations. The mathematical treatment includes a modified first-order Chapman-Enskog perturbative method and Laguerre-Sonine polynomial and Goldstein expansions. New bracket integrals were introduced to deal with thermal nonequilibrium. We retrieved the expressions of viscosity and thermal conductivities found by Devoto [10] and the thermal diffusion terms computed by Kolesnikov [16]. Our results for diffusion generalize the models presented by Kolesnikov and Ramshaw and Chang. Thus, kinetic theory can be employed to provide general, rigorous, and readily applicable expressions of the transport fluxes and coefficients in thermal nonequilibrium.

Thanks to the symmetric formalism retained, the numerical methods introduced by Ern and Giovangigli [29] can be employed. In another publication [39], the validity of the models developed is verified in physicochemical applications and the numerical advantages of the symmetric formalism is demonstrated. An extension of our theory to strong thermal nonequilibrium would allow for a comparison to the results of Rat *et al.* [26].

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APPENDIX A: BRACKET INTEGRALS

1. Linearized collision operator

The linearized scattering collision operator is defined by

$$I_i(\phi) = \sum_{j \in \mathcal{S}} \frac{n_i n_j}{n^2} I_{ij}(\phi), \quad i \in \mathcal{S}. \tag{A1}$$

The partial linearized scattering collision operators read

$$I_{ij}(\phi) = -\frac{1}{n_i n_j}[J_{ij}(f_i^0 \phi_i, f_j^0) + J_{ij}(f_i^0, f_j^0 \phi_j)]$$
$$= \frac{1}{n_i n_j} \int f_i^0 f_j^0 (\phi_i + \phi_j - \phi_i' - \phi_j') g \sigma d\mathbf{\Omega} d\mathbf{c}_j, \quad i,j \in \mathcal{H}, \tag{A2a}$$

$$I_{ie}(\phi) = -\frac{1}{n_i n_e}\{J_{ie}[n_i \delta(\mathbf{C}_i)\phi_i, f_e^0] + J_{ie}[n_i \delta(\mathbf{C}_i), f_e^0 \phi_e]\}$$
$$= \frac{1}{n_e} \int \delta(\mathbf{C}_i) f_e^0 (\phi_e + \phi_i - \phi_e' - \phi_i') g \sigma d\mathbf{\Omega} d\mathbf{c}_e, \quad i \in \mathcal{H}, \tag{A2b}$$

$$I_{ei}(\phi) = -\frac{1}{n_i n_e}\{J_{ei}[f_e^0 \phi_e, n_i \delta(\mathbf{C}_i)] + J_{ei}[f_e^0, n_i \delta(\mathbf{C}_i)\phi_i]\}$$
$$= \frac{1}{n_e} \int \delta(\mathbf{C}_i) f_e^0 (\phi_e + \phi_i - \phi_e' - \phi_i')$$
$$\times g \sigma d\mathbf{\Omega} d\mathbf{c}_i, \quad i \in \mathcal{H}, \tag{A2c}$$

$$I_{ee}(\phi) = -\frac{1}{n_e^2}[J_{ee}(f_e^0 \phi_e, f_e^0) + J_{ee}(f_e^0, f_e^0 \phi_e)]$$
$$= \frac{1}{n_e^2} \int f_e^0 \overline{f}_e^0 (\phi_e + \overline{\phi}_e - \phi_e' - \overline{\phi}_e') g \sigma d\mathbf{\Omega} d\overline{\mathbf{c}}_e, \tag{A2d}$$

where the bar is used to distinguish collision partner indices.

2. Bracket integral definition

The total bracket integral operator is defined by

$$[F,G]=\langle\langle G,I(F)\rangle\rangle \tag{A3}$$

and can be expressed under the form

$$\begin{aligned}[F,G]=&\frac{1}{4n^2}\sum_{i,j\in\mathcal{H}}\int f_i^0 f_j^0(F_i+F_j-F_i'-F_j')\odot(G_i+G_j-G_i'\\&-G_j')g\sigma d\boldsymbol{\Omega}d\mathbf{c}_i d\mathbf{c}_j+\frac{1}{2n^2}\sum_{j\in\mathcal{H}}n_j\int\delta(\mathbf{C}_j)f_e^0(F_e+F_j\\&-F_e'-F_j')\odot(G_e+G_j-G_e'-G_j')g\sigma d\boldsymbol{\Omega}d\mathbf{c}_e d\mathbf{c}_j\\&+\frac{1}{4n^2}\int f_e^0\overline{f}_e^0(F_e+\overline{F}_e-F_e'-\overline{F}_e')\odot(G_e+\overline{G}_e-G_e'\\&-\overline{G}_e')g\sigma d\boldsymbol{\Omega}d\mathbf{c}_e d\overline{\mathbf{c}}_e.\end{aligned} \tag{A4}$$

From Eq. (A4), we deduce that the bracket integral operator is symmetric $[F,G]=[G,F]$, positive semidefinite $[F,F]\geqslant 0$ and its kernel is spanned by the collisional invariants given in Eq. (7). The total bracket integral is decomposed in terms of both the electron and heavy-particle contributions

$$[F,G]_h=\langle\langle G,I(F)\rangle\rangle_h, \tag{A5a}$$

$$[F,G]_e=\langle\langle G,I(F)\rangle\rangle_e, \tag{A5b}$$

$$[F,G]=[F,G]_h+[F,G]_e. \tag{A5c}$$

The bracket integrals are expressed in terms of partial bracket integrals

$$[F,G]_h=\sum_{i,j\in\mathcal{H}}\frac{n_in_j}{n^2}([F,G]_{ij}'+[F,G]_{ij}'')+\sum_{j\in\mathcal{H}}\frac{n_en_j}{n^2}([F,G]_{je}'+[F,G]_{je}''), \tag{A6a}$$

$$[F,G]_e=\sum_{j\in\mathcal{H}}\frac{n_en_j}{n^2}([F,G]_{ej}'+[F,G]_{ej}'')+\frac{n_e^2}{n^2}([F,G]_{ee}'+[F,G]_{ee}''), \tag{A6b}$$

defined by the following expressions:

(i) Heavy-heavy and electron-electron partial bracket integrals, $(i,j)\in\mathcal{H}\times\mathcal{H}\cup\{(e,e)\}$

$$[F,G]_{ij}'=\frac{1}{n_in_j}\int f_i^0f_j^0(F_i-F_i')\odot G_ig\sigma d\boldsymbol{\Omega}d\mathbf{c}_id\mathbf{c}_j, \tag{A7a}$$

$$[F,G]_{ij}''=\frac{1}{n_in_j}\int f_i^0f_j^0(F_j-F_j')\odot G_ig\sigma d\boldsymbol{\Omega}d\mathbf{c}_id\mathbf{c}_j, \tag{A7b}$$

(ii) Electron-heavy partial bracket integrals, $i\in\mathcal{H}$

$$[F,G]_{ie}'=\frac{1}{n_e}\int f_e^0\delta(\mathbf{C}_i)(F_i-F_i')\odot G_ig\sigma d\boldsymbol{\Omega}d\mathbf{c}_id\mathbf{c}_e, \tag{A8a}$$

$$[F,G]_{ie}''=\frac{1}{n_e}\int f_e^0\delta(\mathbf{C}_i)(F_e-F_e')\odot G_ig\sigma d\boldsymbol{\Omega}d\mathbf{c}_id\mathbf{c}_e, \tag{A8b}$$

$$[F,G]_{ei}'=\frac{1}{n_e}\int f_e^0\delta(\mathbf{C}_i)(F_e-F_e')\odot G_eg\sigma d\boldsymbol{\Omega}d\mathbf{c}_id\mathbf{c}_e, \tag{A8c}$$

$$[F,G]_{ei}''=\frac{1}{n_e}\int f_e^0\delta(\mathbf{C}_i)(F_i-F_i')\odot G_eg\sigma d\boldsymbol{\Omega}d\mathbf{c}_id\mathbf{c}_e. \tag{A8d}$$

3. Bracket integral reduction

Reduction of the bracket integrals in terms of collision integrals generalizes Ferziger and Kaper's treatment for unlike particles to weak thermal nonequilibrium. Results for heavy-heavy or electron-electron interactions are directly applicable providing that the adequate translational temperature is selected. The major steps in the derivation for electron-heavy interactions are outlined. The reader is referred to the original work for further details [6]. For instance, the partial bracket $[S_{3/2}^{(p)}(\mathcal{C}^2)\boldsymbol{\mathcal{C}},S_{3/2}^{(q)}(\mathcal{C}^2)\boldsymbol{\mathcal{C}}]_{ie}''$ is given by

$$\lim_{m_i\to\infty}\frac{1}{n_in_e}\int f_i^0f_e^0[S_{3/2}^{(p)}(\mathcal{C}_e^2)\boldsymbol{\mathcal{C}}_e-S_{3/2}^{(q)}(\mathcal{C}_e'^2)\boldsymbol{\mathcal{C}}_e']\cdot S_{3/2}^{(p)}(\mathcal{C}_i^2)\boldsymbol{\mathcal{C}}_ig\sigma d\boldsymbol{\Omega}d\mathbf{c}_id\mathbf{c}_e,\quad i\in\mathcal{H}. \tag{A9}$$

To simplify the calculation, the Dirac distribution is replaced by f_i^0/n_i and the infinite mass hypothesis of species i is assumed at the end of the derivation. Notice the misprint in Eq. (A9) in Ref. [6], where the arguments of the bracket are inverted. To perform such an integration, a new set of variables is preferred to the nondimensional velocities. The center of mass and relative velocities are introduced for electron-heavy collisions

$$(m_e+m_i)\mathbf{G}=m_e\mathbf{c}_e+m_i\mathbf{c}_i, \tag{A10a}$$

$$\mathbf{g}=\mathbf{c}_i-\mathbf{c}_e. \tag{A10b}$$

The center of mass relative to the moving gas stream is given by $\mathbf{G}_0=\mathbf{G}-\mathbf{v}$. In elastic collisions, the center of mass velocity and the module of the relative velocity are identical after collision for physical considerations ($\mathbf{G}=\mathbf{G}'$ and $g=g'$). Hence, it is verified that $\mathbf{g}\cdot\mathbf{g}'=g^2\cos\chi$, where χ is the deflection angle. Following Devoto [40], nondimensional center of mass and relative velocities are introduced for the thermal nonequilibrium case:

$$\boldsymbol{\mathcal{G}}_0=\sqrt{\frac{1}{2k_B}\left(\frac{m_e}{T_e}+\frac{m_i}{T_h}\right)}\mathbf{G}_0, \tag{A11a}$$

$$\boldsymbol{\mathcal{g}}=\sqrt{\frac{1}{2k_B}\frac{m_em_i}{(m_e+m_i)^2}\left(\frac{m_e}{T_h}+\frac{m_i}{T_e}\right)}\mathbf{g}. \tag{A11b}$$

Nondimensional velocities defined in Eq. (46) are expressed in terms of the vector quantities given in Eq. (A11),

$$\boldsymbol{\mathcal{C}}_e = \sqrt{\frac{m_e T_h}{m_e T_h + m_i T_e}}\boldsymbol{\mathcal{G}}_0 - \sqrt{\frac{m_i T_h}{m_e T_e + m_i T_h}}\boldsymbol{\mathscr{g}}, \quad (A12a)$$

$$\boldsymbol{\mathcal{C}}_i = \sqrt{\frac{m_i T_e}{m_e T_h + m_i T_e}}\boldsymbol{\mathcal{G}}_0 + \sqrt{\frac{m_e T_e}{m_e T_e + m_i T_h}}\boldsymbol{\mathscr{g}}. \quad (A12b)$$

The determinant of the Jacobian of the transformation reads

$$\left|\frac{\partial(\boldsymbol{\mathcal{G}}_0,\boldsymbol{\mathscr{g}})}{\partial(\boldsymbol{\mathcal{C}}_e,\boldsymbol{\mathcal{C}}_i)}\right| = \frac{1}{m_e + m_i}\sqrt{\frac{(m_e T_h + m_i T_e)(m_e T_e + m_i T_h)}{T_e T_h}} \quad (A13)$$

and

$$\mathcal{C}_e^2 + \mathcal{C}_i^2 = \mathcal{G}_0^2 + \mathscr{g}^2 + 2\boldsymbol{\mathcal{G}}_0 \cdot \mathbf{g}(T_e - T_h) \times \sqrt{\frac{m_e m_i}{(m_e T_h + m_i T_e) + (m_e T_e + m_i T_h)}}. \quad (A14)$$

Providing that

$$\max\left(\frac{T_e}{T_h}, \frac{T_h}{T_e}\right) \ll \frac{m_i}{m_e}, \quad (A15)$$

the previous expressions simplify as

$$\boldsymbol{\mathscr{g}} \approx \sqrt{\frac{m_e}{2k_B T_e}}\mathbf{g}, \quad (A16a)$$

$$\boldsymbol{\mathcal{C}}_e \approx \sqrt{\mu_e}\sqrt{\frac{T_h}{T_e}}\boldsymbol{\mathcal{G}}_0 - \sqrt{\mu_i}\boldsymbol{\mathscr{g}}, \quad (A16b)$$

$$\boldsymbol{\mathcal{C}}_i \approx \sqrt{\mu_i}\boldsymbol{\mathcal{G}}_0 + \sqrt{\mu_e}\sqrt{\frac{T_e}{T_h}}\boldsymbol{\mathscr{g}}, \quad (A16c)$$

$$\mathcal{C}_e^2 + \mathcal{C}_i^2 \approx \mathcal{G}_0^2 + \mathrm{g}^2, \quad (A16d)$$

$$\left|\frac{\partial(\boldsymbol{\mathcal{G}}_0,\boldsymbol{\mathscr{g}})}{\partial(\boldsymbol{\mathcal{C}}_e,\boldsymbol{\mathcal{C}}_i)}\right| \approx 1, \quad (A16e)$$

where $\mu_e = m_e/m_i$ and $\mu_i = 1$. The explicit calculation of the partial bracket integrals such as given in Eq. (A9) presents no difficulties and is not detailed here. The approximation made in Eq. (A16) is justified under conditions of weak thermal nonequilibrium. As pointed out by Devoto [40], under extreme nonequipartition of energy, as might be obtained in a strong electric field, this method of solving the Boltzmann equation is certainly not valid.

APPENDIX B: COLLISION INTEGRALS AND BINARY DIFFUSION COEFFICIENTS

In classical mechanics, the deflection angle is related to the interaction potential $\varphi(r)$ by the relation

$$\chi = \pi - 2b\int_{r_m}^{\infty} \frac{dr/r^2}{\sqrt{1 - b^2/r^2 - \varphi(r)/\left(\frac{1}{2}\frac{m_i m_j}{m_i + m_j}g^2\right)}}, \quad (B1)$$

where b is the impact parameter, r the distance between colliding particles, and r_m the distance of closest approach. Cross sections are given in terms of the deflection angle

$$Q_{ij}^{(l)} = 2\pi\int_0^{\infty} (1 - \cos^l\chi) b\, db. \quad (B2)$$

Collision integrals and binary diffusion coefficients in thermal nonequilibrium are now introduced as follows:

(i) Heavy-heavy interactions, $i, j \in \mathcal{H}$

$$\Omega_{ij}^{(l,s)} = \sqrt{\frac{k_B T_h}{2\pi}\frac{m_i + m_j}{m_i m_j}}\int_0^{\infty} \exp(-\mathscr{g}^2)\mathscr{g}^{2s+3}Q_{ij}^{(l)}d\mathscr{g} = \frac{1}{2\sqrt{\pi}}\left(\frac{1}{2k_B T_h}\frac{m_i m_j}{m_i + m_j}\right)^{s+3/2}\int_0^{\infty} \exp\left(-\frac{1}{2k_B T_h} \times \frac{m_i m_j}{m_i + m_j}g^2\right)g^{2s+3}Q_{ij}^{(l)}dg, \quad (B3a)$$

$$\mathcal{D}_{ij} = \frac{3}{16n}\frac{m_i + m_j}{m_i m_j}\frac{k_B T_h}{\Omega_{ij}^{(1,1)}}, \quad (B3b)$$

where $\mathscr{g} = \{m_i m_j/[(m_i + m_j)2k_B T_h]\}^{1/2}g$.

(ii) Heavy-electron interactions, $i \in \mathcal{H}$

$$\Omega_{ie}^{(l,s)} = \sqrt{\frac{k_B T_e}{2\pi m_e}}\int_0^{\infty} \exp(-\mathscr{g}^2)\mathscr{g}^{2s+3}Q_{ie}^{(l)}d\mathscr{g} = \frac{1}{2\sqrt{\pi}}\left(\frac{m_e}{2k_B T_e}\right)^{s+3/2}\int_0^{\infty} \exp\left(-\frac{m_e}{2k_B T_e}g^2\right)g^{2s+3}Q_{ie}^{(l)}dg, \quad (B4a)$$

$$\mathcal{D}_{ie} = \frac{3}{16nm_e}\frac{k_B T_e}{\Omega_{ie}^{(1,1)}}, \quad (B4b)$$

where $\mathscr{g} = [m_e/(2k_B T_e)]^{1/2}g$.

(iii) Electron-electron interactions

$$\Omega_{ee}^{(l,s)} = \sqrt{\frac{k_B T_e}{\pi m_e}}\int_0^{\infty} \exp(-\mathscr{g}^2)\mathscr{g}^{2s+3}Q_{ee}^{(l)}d\mathscr{g} = \frac{1}{2\sqrt{\pi}}\left(\frac{m_e}{4k_B T_e}\right)^{s+3/2}\int_0^{\infty} \exp\left(-\frac{m_e}{4k_B T_e}g^2\right)g^{2s+3}Q_{ee}^{(l)}dg, \quad (B5a)$$

$$\mathcal{D}_{ee} = \frac{3}{8nm_e}\frac{k_B T_e}{\Omega_{ee}^{(1,1)}}, \quad (B5b)$$

where $\mathscr{g} = [m_e/(4k_B T_e)]^{1/2}g$.

The collision integrals and binary diffusion coefficients are symmetric in the species.

APPENDIX C. TRANSPORT SYSTEMS

The transport matrices Λ_{ij}^{pq} and H_{ij}^{pq}, $i,j \in \mathcal{S}, p,q \in \mathcal{P}$, are defined by the expressions

$$\Lambda_{ij}^{pq} = \frac{8}{75k_B^2}\sqrt{\frac{m_i m_j}{T_i T_j}}\Big\{\delta_{ij}\sum_{k\in\mathcal{S}} x_i x_k [S_{3/2}^{(p)}(\mathcal{C}^2)\boldsymbol{\mathcal{C}}, S_{3/2}^{(q)}(\mathcal{C}^2)\boldsymbol{\mathcal{C}}]'_{ik} + x_i x_j [S_{3/2}^{(p)}(\mathcal{C}^2)\boldsymbol{\mathcal{C}}, S_{3/2}^{(q)}(\mathcal{C}^2)\boldsymbol{\mathcal{C}}]''_{ji}\Big\}, \tag{C1}$$

and

$$H_{ij}^{pq} = \frac{2}{5k_B}\Big\{\delta_{ij}\sum_{k\in\mathcal{S}} x_i x_k [S_{5/2}^{(p)}(\mathcal{C}^2)(\boldsymbol{\mathcal{C}}\otimes\boldsymbol{\mathcal{C}} - \mathcal{C}^2\mathbb{I}/3), S_{5/2}^{(q)}(\mathcal{C}^2)(\boldsymbol{\mathcal{C}}\otimes\boldsymbol{\mathcal{C}} - \mathcal{C}^2\mathbb{I}/3)]'_{ik} + x_i x_j [S_{5/2}^{(p)}(\mathcal{C}^2)(\boldsymbol{\mathcal{C}}\otimes\boldsymbol{\mathcal{C}} - \mathcal{C}^2\mathbb{I}/3), S_{5/2}^{(q)}(\mathcal{C}^2)(\boldsymbol{\mathcal{C}}\otimes\boldsymbol{\mathcal{C}} - \mathcal{C}^2\mathbb{I}/3)]''_{ji}\Big\}. \tag{C2}$$

Note the misprint in the indices of the partial bracket $[,]''_{ji}$ in Ref. [6]. This misprint compensates the error indicated before in Eq. (A9).

(i) Heavy-particle subsystem, $i,j \in \mathcal{H}$

The transport matrices are detailed up to order 2 for Λ and order 1 for H.

$$\Lambda_{ij}^{00} = \Lambda_{ji}^{00} = -\frac{64}{75k_B^2 T_h} x_i x_j \frac{m_i m_j}{m_i + m_j}\Omega_{ij}^{(1,1)}, \quad i \neq j, \tag{C3a}$$

$$\Lambda_{ii}^{00} = \frac{64}{75k_B^2 T_h}\sum_{\substack{j\in\mathcal{H}\\ j\neq i}} x_i x_j \frac{m_i m_j}{m_i + m_j}\Omega_{ij}^{(1,1)} + \frac{64}{75k_B^2 T_e}\left(\frac{T_e}{T_h}\right)^2 x_i x_e m_e \Omega_{ie}^{(1,1)}, \tag{C3b}$$

$$\Lambda_{ij}^{01} = \Lambda_{ji}^{10} = -\frac{64}{75k_B^2 T_h} x_i x_j \frac{m_i^2 m_j}{(m_i + m_j)^2}\times\left(\frac{5}{2}\Omega_{ij}^{(1,1)} - \Omega_{ij}^{(1,2)}\right), \quad i \neq j, \tag{C3c}$$

$$\Lambda_{ii}^{01} = \Lambda_{ii}^{10} = \frac{64}{75k_B^2 T_h}\sum_{\substack{j\in\mathcal{H}\\ j\neq i}} x_i x_j \frac{m_i m_j^2}{(m_i + m_j)^2}\left(\frac{5}{2}\Omega_{ij}^{(1,1)} - \Omega_{ij}^{(1,2)}\right), \tag{C3d}$$

$$\Lambda_{ij}^{11} = \Lambda_{ji}^{11} = -\frac{64}{75k_B^2 T_h} x_i x_j \frac{m_i^2 m_j^2}{(m_i + m_j)^3}\left(\frac{55}{4}\Omega_{ij}^{(1,1)} - 5\Omega_{ij}^{(1,2)} + \Omega_{ij}^{(1,3)} - 2\Omega_{ij}^{(2,2)}\right), \quad i \neq j, \tag{C3e}$$

$$\Lambda_{ii}^{11} = \frac{64}{75k_B^2 T_h}\sum_{\substack{j\in\mathcal{H}\\ j\neq i}} x_i x_j \frac{m_i m_j}{(m_i + m_j)^3}\left(\frac{5}{4}(6m_i^2 + 5m_j^2)\Omega_{ij}^{(1,1)} - 5m_j^2\Omega_{ij}^{(1,2)} + m_j^2\Omega_{ij}^{(1,3)} + 2m_i m_j \Omega_{ij}^{(2,2)}\right) + \frac{64}{75k_B^2 T_h} x_i^2 \frac{m_i}{2}\Omega_{ii}^{(2,2)}, \tag{C3f}$$

$$H_{ij}^{00} = H_{ji}^{00} = -\frac{32}{15k_B} x_i x_j \frac{m_i m_j}{(m_i + m_j)^2}\times\left(5\Omega_{ij}^{(1,1)} - \frac{3}{2}\Omega_{ij}^{(2,2)}\right), \quad i \neq j, \tag{C3g}$$

$$H_{ii}^{00} = \frac{32}{15k_B}\sum_{\substack{j\in\mathcal{H}\\ j\neq i}} x_i x_j \frac{m_j}{(m_i + m_j)^2}\left(5m_i\Omega_{ij}^{(1,1)} + \frac{3}{2}m_j\Omega_{ij}^{(2,2)}\right) + \frac{32}{15k_B}x_i^2\frac{3}{4}\Omega_{ii}^{(2,2)}. \tag{C3h}$$

(ii) Heavy-particle-electron subsystem, $i \in \mathcal{H}$

The transport matrices are detailed up to order 3 for Λ and order 1 for H.

$$\Lambda_{ie}^{00} = \Lambda_{ei}^{00} = -\frac{64 m_e}{75k_B^2 T_e}\frac{T_e}{T_h} x_i x_e \Omega_{ie}^{(1,1)}, \tag{C4a}$$

$$\Lambda_{ie}^{01} = \Lambda_{ei}^{10} = -\frac{64 m_e}{75k_B^2 T_e}\frac{T_e}{T_h} x_i x_e\left(\frac{5}{2}\Omega_{ie}^{(1,1)} - \Omega_{ie}^{(1,2)}\right), \tag{C4b}$$

$$\Lambda_{ei}^{01} = \Lambda_{ie}^{10} = 0, \tag{C4c}$$

$$\Lambda_{ie}^{11} = \Lambda_{ei}^{11} = 0, \tag{C4d}$$

$$\Lambda_{ie}^{02} = \Lambda_{ei}^{20} = -\frac{64 m_e}{75k_B^2 T_e}\frac{T_e}{T_h} x_i x_e\left(\frac{35}{8}\Omega_{ie}^{(1,1)} - \frac{7}{2}\Omega_{ie}^{(1,2)} + \frac{1}{2}\Omega_{ie}^{(1,3)}\right), \tag{C4e}$$

$$\Lambda_{ei}^{02} = \Lambda_{ie}^{20} = 0, \tag{C4f}$$

$$\Lambda_{ei}^{12} = \Lambda_{ie}^{21} = \Lambda_{ie}^{12} = \Lambda_{ei}^{21} = 0, \tag{C4g}$$

$$\Lambda_{ei}^{22} = \Lambda_{ie}^{22} = 0, \tag{C4h}$$

$$H_{ie}^{00} = H_{ei}^{00} = 0. \tag{C4i}$$

(iii) Electron subsystem

The transport matrices are detailed up to order 3 for Λ and order 1 for H.

$$\Lambda_{ee}^{00} = \frac{64m_e}{75k_B^2T_e}\sum_{j\in\mathcal{H}} x_e x_j \Omega_{ej}^{(1,1)}, \tag{C5a}$$

$$\Lambda_{ee}^{01} = \Lambda_{ee}^{10} = \frac{64m_e}{75k_B^2T_e}\sum_{j\in\mathcal{H}} x_e x_j\left(\frac{5}{2}\Omega_{ej}^{(1,1)} - \Omega_{ej}^{(1,2)}\right), \tag{C5b}$$

$$\Lambda_{ee}^{11} = \frac{64m_e}{75k_B^2T_e}\sum_{j\in\mathcal{H}} x_e x_j\left(\frac{25}{4}\Omega_{ej}^{(1,1)} - 5\Omega_{ej}^{(1,2)} + \Omega_{ej}^{(1,3)}\right) + \frac{64m_e}{75k_B^2T_e}x_e^2\frac{1}{2}\Omega_{ee}^{(2,2)}, \tag{C5c}$$

$$\Lambda_{ee}^{02} = \Lambda_{ee}^{20} = \frac{64m_e}{75k_B^2T_e}\sum_{j\in\mathcal{H}} x_e x_j\left(\frac{35}{8}\Omega_{ej}^{(1,1)} - \frac{7}{2}\Omega_{ej}^{(1,2)} + \frac{1}{2}\Omega_{ej}^{(1,3)}\right), \tag{C5d}$$

$$\Lambda_{ee}^{12} = \Lambda_{ee}^{21} = \frac{64m_e}{75k_B^2T_e}\sum_{j\in\mathcal{H}} x_e x_j\left(\frac{175}{16}\Omega_{ej}^{(1,1)} - \frac{105}{8}\Omega_{ej}^{(1,2)} + \frac{19}{4}\Omega_{ej}^{(1,3)} - \frac{1}{2}\Omega_{ej}^{(1,4)}\right) + \frac{64m_e}{75k_B^2T_e}x_e^2\left(\frac{7}{8}\Omega_{ee}^{(2,2)} - \frac{1}{4}\Omega_{ee}^{(2,3)}\right), \tag{C5e}$$

$$\Lambda_{ee}^{22} = \frac{64m_e}{75k_B^2T_e}\sum_{j\in\mathcal{H}} x_e x_j\left(\frac{1225}{64}\Omega_{ej}^{(1,1)} - \frac{245}{8}\Omega_{ej}^{(1,2)} + \frac{133}{8}\Omega_{ej}^{(1,3)} - \frac{7}{2}\Omega_{ej}^{(1,4)} + \frac{1}{4}\Omega_{ej}^{(1,5)}\right) + \frac{64m_e}{75k_B^2T_e}x_e^2\left(\frac{77}{32}\Omega_{ee}^{(2,2)} - \frac{7}{8}\Omega_{ee}^{(2,3)} + \frac{1}{8}\Omega_{ee}^{(2,4)}\right), \tag{C5f}$$

$$H_{ee}^{00} = \frac{32}{15k_B}\sum_{j\in\mathcal{H}} x_e x_j \frac{3}{2}\Omega_{ej}^{(2,2)} + \frac{32}{15k_B}x_e^2\frac{3}{4}\Omega_{ee}^{(2,2)}. \tag{C5g}$$

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