

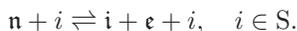
Modeling of reactive plasmas for atmospheric entry flows based on kinetic theory

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We derive a model for reactive plasmas based on kinetic theory, accounting for an ionization mechanism and dealing with a possible thermal non-equilibrium of the translational energy of the electrons and heavy particles, such as atoms and ions, given their strong disparity of mass. We conduct a dimensional analysis of the Boltzmann equation and use a multi-scale Chapman-Enskog method to derive macroscopic conservation equations and expressions for the chemical production rates. Our model satisfies the law of mass action and the first and second laws of thermodynamics.

1. Introduction

When a spacecraft enters into a planetary atmosphere at hypervelocity, the gas temperature and pressure strongly rise through a shockwave and the mixture particles dissociate and ionize in the shock layer. Return trajectory of the Orion crew exploration vehicle involves significantly higher velocities (>10 km/s) than Earth orbit re-entry experienced by the space shuttle, enhancing the ionization degree of the plasma flow. Recently, Graille *et al.* (2008) have derived from kinetic theory a unified fluid model for such multicomponent plasmas by accounting for thermal non-equilibrium between the translational energies of the electrons and heavy particles, such as atoms and ions, given their strong mass disparity. We propose to extend this model by accounting for reactive collisions in a 3-species plasma, based on the ionization mechanism comprising the reactions r_i :



Electrons, neutral particles and ions are respectively denoted by the indices \mathbf{e} , \mathbf{n} , and \mathbf{i} . The full mixture of species is denoted by the set of indices $\mathbf{S} = \{\mathbf{e}, \mathbf{n}, \mathbf{i}\}$, and the heavy particles, by the set of indices $\mathbf{H} = \{\mathbf{n}, \mathbf{i}\}$.

Appleton & Bray (1964) have derived conservation equations for reactive plasmas, accounting for the electron impact ionization reaction r_e , a chain reaction in which two electrons are produced from one. This avalanche phenomenon is limited by a chemical loss rate controlling the electron thermal energy (Park 1990). Unfortunately, their derivation is not based on the correct scaling for the mass difference between the electrons and heavy particles. Choquet & Lucquin-Desreux (2005) have studied the same reaction based on the correct scaling, but did not investigate the thermodynamics of plasmas in thermal and chemical non-equilibrium. Finally, derivation of the Saha equation, describing chemical equilibrium and modified for the case of multi-temperature plasmas, is a recurrent topic in theoretical works with the consequent debate regarding which of the forms for this equation is the correct one to apply (see Giordano & Capitelli 2001, and references cited therein). In this work, we will study both processes of ionization by electron impact, reaction r_e , and by heavy-particle impact, reactions r_n and r_i . We will also propose

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a suitable thermodynamics for plasmas and extend the Saha equation to thermal non-equilibrium for our mechanism. The derivation is based on a dimensional analysis of the Boltzmann equation. The scaling for the differential cross-sections for ionization is chosen to obtain a Maxwellian reaction regime in which the chemical production rates appear in the Euler/drift-diffusion equations.

Let us emphasize the broad field of possible applications, such as air-breathing hypersonic vehicles (control by plasma technology), spacecraft atmospheric entries (influence of precursor electrons), high-enthalpy wind tunnels (plasmatrons, arc-jet facilities and shock tubes), lightning phenomena, discharges at atmospheric pressure, laboratory nuclear fusion, and astrophysics.

2. Boltzmann equation

2.1. Assumptions

Our model for multi-component plasmas relies on the following set of assumptions:

- (1) The description is based on the kinetic theory of gases and classical mechanics.
- (2) The particle internal energy and spin are not accounted for.
- (3) The inert particle interactions are modeled as binary encounters by means of a Boltzmann collision operator.
- (4) The gas, spatially uniform, is at rest and in absence of external forces.
- (5) The ratio of the electron mass m_e^0 to a characteristic heavy-particle mass m_b^0 is such that the non-dimensional number $\varepsilon = (m_e^0/m_b^0)^{1/2}$ is small.
- (6) The macroscopic time scale t^0 is comparable with the heavy-particle kinetic time scale t_b^0 divided by ε . The macroscopic length scale $L^0 = V_b^0 t^0$ is based on the heavy-particle thermal speed V_b^0 .
- (7) The reference differential cross-section σ^0 is common to all inert collisions. The differential cross-sections for ionization are assumed to scale as σ^0 multiplied by a suitable power of ε such that a Maxwellian reaction regime be reached.

The mean free path l^0 and macroscopic length scale L^0 allow for the Knudsen number to be defined as $Kn = l^0/L^0$. This quantity is small, provided that assumptions (5)-(6) are satisfied. Therefore, a continuum description of the system is deemed to be possible.

2.2. Dimensional Boltzmann equation

Considering assumptions (1)-(4), the temporal evolution of the velocity distribution function f_i^* for the velocity \mathbf{c}_i^* of the plasma particles i is governed by the Boltzmann equation

$$\partial_{t^*} f_i^* = \mathcal{J}_i^*(f^*) + \mathcal{C}_i^*(f^*), \quad i \in S \quad (2.1)$$

(see, for instance, Giovangigli 1999). Dimensional quantities are denoted by the superscript $*$. Symbol t^* stands for time.

The non-reactive collision operator, the rate at which the velocity distribution is altered by inert collisions, is given by the expression $\mathcal{J}_i^*(f) = \sum_{j \in S} \mathcal{J}_{ij}^*(f_i^*, f_j^*)$, where the partial collision operator of particle j impacting on particle i reads

$$\mathcal{J}_{ij}^*(f_i^*, f_j^*) = \int (f_i^{*\prime} f_j^{*\prime} - f_i^* f_j^*) |\mathbf{c}_i^* - \mathbf{c}_j^*| \sigma_{ij}^* d\boldsymbol{\omega} d\mathbf{c}_j^*, \quad i, j \in S.$$

After collision, quantities are denoted by the superscript $'$. The differential cross-section for inert interaction $\sigma_{ij}^* = \sigma_{ij}^* [\mu_{ij}^* |\mathbf{c}_i^* - \mathbf{c}_j^*|^2 / (k_B T^0), \boldsymbol{\omega} \cdot \mathbf{e}]$ depends on the relative kinetic energy of the colliding particles and the cosine of the angle between the unit vectors of

relative velocities $\boldsymbol{\omega} = (\mathbf{c}_i^{*'} - \mathbf{c}_j^{*'})/|\mathbf{c}_i^{*'} - \mathbf{c}_j^{*'}|$ and $\mathbf{e} = (\mathbf{c}_i^* - \mathbf{c}_j^*)/|\mathbf{c}_i^* - \mathbf{c}_j^*|$. Quantity μ_{ij}^* is the reduced mass of the particle pair, T^0 , a reference temperature, and k_B , Boltzmann's constant. The differential cross-sections are symmetric with respect to their indices, i.e.,

$$\sigma_{ij}^* = \sigma_{ji}^*, \quad i, j \in \text{S}. \quad (2.2)$$

The chemical reactions taking place in the mixture can be written in a generic form:

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

where the set of reactions reads $R = \{r_e, r_n, r_i\}$. The indices for reactants and products are counted with their multiplicity, for instance for reaction r_e , $\mathcal{F}^{r_e} = \{n, e\}$ and $\mathcal{B}^{r_e} = \{i, e, e\}$. For reaction r , we denote by ν_{ir}^f and ν_{ir}^b the forward and the backward stoichiometric coefficients for species $i \in \text{S}$, order of multiplicity in \mathcal{F}^r and \mathcal{B}^r , respectively. Finally, we denote by \mathcal{F}_i^r a subset of \mathcal{F}^r where the index i has been removed, if possible, only once, and we use the same notation for a subset of \mathcal{B}^r , for instance, $\mathcal{B}_e^{r_e} = \{i, e\}$. The reactive collision operator, the rate at which the velocity distribution is altered by reactive collisions, is given by $\mathcal{C}_i^*(f^*) = \sum_{r \in R} \mathcal{C}_i^{r*}(f^*)$, with the partial collision operator for reaction r :

$$\begin{aligned} \mathcal{C}_i^{r*}(f^*) = & \nu_{ir}^f \int \left(\prod_{k \in \mathcal{B}^r} f_k^* \frac{\prod_{k \in \mathcal{B}^r} \beta_k^*}{\prod_{j \in \mathcal{F}^r} \beta_j^*} - \prod_{j \in \mathcal{F}^r} f_j^* \right) \mathcal{W}_{\mathcal{F}^r}^{\mathcal{B}^{r*}} \prod_{j \in \mathcal{F}_i^r} d\mathbf{c}_j^* \prod_{k \in \mathcal{B}^r} d\mathbf{c}_k^* \\ & - \nu_{ir}^b \int \left(\prod_{k \in \mathcal{B}^r} f_k^* \frac{\prod_{k \in \mathcal{B}^r} \beta_k^*}{\prod_{j \in \mathcal{F}^r} \beta_j^*} - \prod_{j \in \mathcal{F}^r} f_j^* \right) \mathcal{W}_{\mathcal{F}^r}^{\mathcal{B}^{r*}} \prod_{j \in \mathcal{F}^r} d\mathbf{c}_j^* \prod_{k \in \mathcal{B}_i^r} d\mathbf{c}_k^*, \quad i \in \text{S}, \end{aligned} \quad (2.3)$$

where quantity $\beta_i^* = (h_P/m_i^*)^3$ is the statistical weight of species i in the phase space, h_P , Planck's constant, m_i^* , the mass of particle i , and $\mathcal{W}_{\mathcal{F}^r}^{\mathcal{B}^{r*}}$, the reactive transition probability for a collision in which the reactants \mathcal{F}^r are transformed into products \mathcal{B}^r . The reciprocity relations (2.2) are generalized for the reactive transition probabilities as

$$\mathcal{W}_{\mathcal{F}^r}^{\mathcal{B}^{r*}} \prod_{k \in \mathcal{B}^r} \beta_k^* = \mathcal{W}_{\mathcal{B}^r}^{\mathcal{F}^{r*}} \prod_{j \in \mathcal{F}^r} \beta_j^*. \quad (2.4)$$

Let us illustrate Eq. (2.3) for the electron partial collision operator in reaction r_e :

$$\begin{aligned} \mathcal{C}_e^{r_e*}(f^*) = & \int \left(f_i^* f_{e_1}^* f_{e_2}^* \frac{\beta_i^* \beta_e^*}{\beta_n^*} - f_n^* f_e^* \right) \mathcal{W}_{ne}^{iee^*} d\mathbf{c}_n^* d\mathbf{c}_i^* d\mathbf{c}_{e_1}^* d\mathbf{c}_{e_2}^* \\ & - 2 \int \left(f_i^* f_e^* f_{e_2}^* \frac{\beta_i^* \beta_e^*}{\beta_n^*} - f_n^* f_{e_1}^* \right) \mathcal{W}_{ne}^{iee^*} d\mathbf{c}_n^* d\mathbf{c}_i^* d\mathbf{c}_{e_1}^* d\mathbf{c}_{e_2}^*. \end{aligned}$$

When several particles of the same species are involved in a collision, they are distinguished by adding a number to their index.

2.3. Collisional invariants

Collisional invariants of the non-reactive collision operator are microscopic quantities conserved during an inert collision between the particles $i, j \in \text{S}$, i.e., $\psi_i^* + \psi_j^* = \psi_i^{*'} + \psi_j^{*'}$.

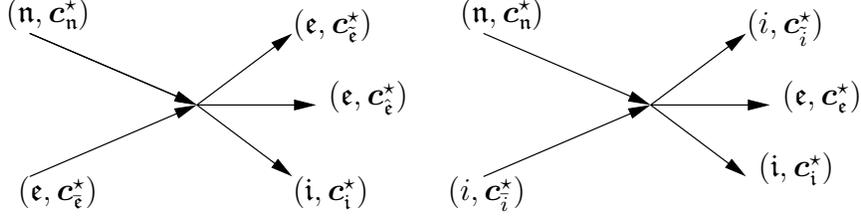


FIGURE 1. Left: ionization by electron impact; right: ionization by heavy-particle impact, where particle $i \in \mathbb{H}$ is a catalyst for the reaction.

The space of scalar collisional invariants is spanned by the following elements:

$$\begin{cases} \psi^{j^*} &= (m_i^* \delta_{ij})_{i \in \mathbb{S}}, & j \in \mathbb{S}, \\ \psi^{n^{\mathbb{S}} + \nu^*} &= (m_i^* c_{i\nu}^*)_{i \in \mathbb{S}}, & \nu \in \{1, 2, 3\}, \\ \psi^{n^{\mathbb{S}} + 4^*} &= (\frac{1}{2} m_i^* \mathbf{c}_i^* \cdot \mathbf{c}_i^* + m_i^* \mathcal{U}_i^{\text{F}^*})_{i \in \mathbb{S}}, \end{cases} \quad (2.5)$$

where symbol $n^{\mathbb{S}}$ stands for the number of species, and $\mathcal{U}_i^{\text{F}^*}$, for the formation energy of species i . At the macroscopic level of the gas, mass, momentum and energy are shown to be conserved by introducing the scalar product[†]

$$\langle\langle \xi^*, \zeta^* \rangle\rangle^* = \sum_{j \in \mathbb{S}} \int \xi_j^* \odot \zeta_j^* d\mathbf{c}_j^*, \quad (2.6)$$

for families $\xi^* = (\xi_i^*)_{i \in \mathbb{S}}$ and $\zeta^* = (\zeta_i^*)_{i \in \mathbb{S}}$, the non-reactive collision operator given in Eq. (2.1) being orthogonal to the space of collisional invariants, i.e., $\langle\langle \psi^{l^*}, \mathcal{J}^* \rangle\rangle^* = 0$, for all $l \in \{1, \dots, n^{\mathbb{S}} + 4\}$. Finally, the macroscopic properties can be expressed by means of the scalar product of the distribution functions and the collisional invariants. The partial mass density reads $\rho_i^* = \langle\langle f^*, \psi^{i^*} \rangle\rangle^*$, $i \in \mathbb{S}$, the gas is at rest $\langle\langle f^*, \psi^{n^{\mathbb{S}} + \nu^*} \rangle\rangle^* = 0$, $\nu \in \{1, 2, 3\}$, and the energy is given by $\rho^* e^{\text{T}^*} + \rho^* \mathcal{U}^{\text{F}^*} = \langle\langle f^*, \psi^{n^{\mathbb{S}} + 4^*} \rangle\rangle^*$, where quantity e^{T^*} stands for the gas thermal energy per unit mass, $\rho^* = \sum_{j \in \mathbb{S}} \rho_j^*$ is the mixture mass density, and \mathcal{U}^{F^*} , the mixture formation energy per unit mass, with $\rho^* \mathcal{U}^{\text{F}^*} = \sum_{j \in \mathbb{S}} \rho_j^* \mathcal{U}_j^{\text{F}^*}$, and $\mathcal{U}_i^{\text{F}^*}$, the species formation energy.

2.4. Parameterization of the reactive collisions

In this section, we change variables to parameterize the partial collision operator given in Eq. (2.3), for the ionization reactions sketched in Fig. 1, in terms of differential cross-sections. This step is essential for the expansion of this operator in terms of the small parameter ε . We only consider the direct reaction since expressions for the reverse reaction are obtained by means of Eq. (2.4) for the transition probabilities.

Following Alexeev *et al.* (1994), the transition probability can be related to a differential cross-section that reads, for reaction r_i ,

$$\sigma_{\text{ne}}^{\text{ie}^*} = \sigma_{\text{ne}}^{\text{ie}^*} (|\mathbf{g}_{\text{ne}}^*|, |\mathbf{g}'_{\text{ie}}^*|, \boldsymbol{\omega}_{\text{ie}}^* \cdot \mathbf{e}^*, \boldsymbol{\omega}_{\text{ee}}^* \cdot \mathbf{e}^*, \boldsymbol{\omega}_{\text{ie}}^* \cdot \boldsymbol{\omega}_{\text{ee}}^*),$$

where relative velocities are defined between the reactants $\mathbf{g}_{\text{ne}}^* = \mathbf{c}_{\text{n}}^* - \mathbf{c}_{\text{e}}^*$, and products $\mathbf{g}'_{\text{ie}}^* = \mathbf{c}_{\text{i}}^* - (\mathbf{c}_{\text{e}}^* + \mathbf{c}_{\text{e}}^*)/2$ and $\mathbf{g}'_{\text{ee}}^* = \mathbf{c}_{\text{e}}^* - \mathbf{c}_{\text{e}}^*$, and their corresponding unit vectors given by $\mathbf{e}^* = \mathbf{g}_{\text{ne}}^*/|\mathbf{g}_{\text{ne}}^*|$, $\boldsymbol{\omega}_{\text{ie}}^* = \mathbf{g}'_{\text{ie}}^*/|\mathbf{g}'_{\text{ie}}^*|$, and $\boldsymbol{\omega}_{\text{ee}}^* = \mathbf{g}'_{\text{ee}}^*/|\mathbf{g}'_{\text{ee}}^*|$. Then, the change of variables is

[†] The fully contracted product in space is denoted by symbol “ \odot ”, associated with a product ab , for two scalar a and b , and with a scalar product $\mathbf{a} \cdot \mathbf{b}$, for two vectors \mathbf{a} and \mathbf{b} .

	Electrons	Heavy particles
Mass	m_e^0	m_h^0
Thermal speed	V_e^0	V_h^0
Kinetic time scale	t_e^0	t_h^0

TABLE 1. Electron and heavy-particle reference quantities.

expressed by means of the following relation:

$$\mathcal{W}_{ne}^{iee^*} d\mathbf{c}_i^* d\mathbf{c}_e^* d\mathbf{c}_e^* = \frac{|\mathbf{g}_{ne}^*| |\mathbf{g}_{ie}^*|^2 \sigma_{ne}^{iee^*}}{\frac{16\pi^2}{3} \left(\frac{1}{2} \frac{m_n^*}{m_i^*} |\mathbf{g}_{ne}^*|^2 - \frac{m_n^* + m_e^*}{m_i^* m_e^*} \Delta\mathcal{E}^* \right)^{3/2}} d|\mathbf{g}_{ie}^*| d\omega_{ie}^* d\omega_{ee}^*, \quad (2.7)$$

where $\Delta\mathcal{E}^* = m_i^* U_i^{F^*} + m_e^* U_e^{F^*} - m_n^* U_n^{F^*}$ stands for the ionization energy. For reaction r_i , $i \in \text{H}$, the transition probability can be related to the following differential cross-section:

$$\sigma_{ni}^{ieiz^*} = \sigma_{ni}^{ieiz^*} (|\mathbf{g}_{ni}^*|, |\mathbf{g}_{he}^*|, \omega_{he}^* \cdot \mathbf{e}^*, \omega_{iz}^* \cdot \mathbf{e}^*, \omega_{he}^* \cdot \omega_{iz}^*), \quad i \in \text{H},$$

where relative velocities are defined between the reactants $\mathbf{g}_{ni}^* = \mathbf{c}_n^* - \mathbf{c}_i^*$, and products $\mathbf{g}_{he}^* = m_i^* \mathbf{c}_i^* / (m_i^* + m_e^*) + m_e^* \mathbf{c}_e^* / (m_i^* + m_e^*) - \mathbf{c}_e^*$ and $\mathbf{g}_{iz}^* = \mathbf{c}_i^* - \mathbf{c}_z^*$, and their corresponding unit vectors $\mathbf{e}^* = \mathbf{g}_{ni}^* / |\mathbf{g}_{ni}^*|$, $\omega_{he}^* = \mathbf{g}_{he}^* / |\mathbf{g}_{he}^*|$ and $\omega_{iz}^* = \mathbf{g}_{iz}^* / |\mathbf{g}_{iz}^*|$. Then, the change of variables is expressed by means of the following relation, for $i \in \text{H}$:

$$\mathcal{W}_{ni}^{ieiz^*} d\mathbf{c}_i^* d\mathbf{c}_e^* d\mathbf{c}_z^* = \frac{|\mathbf{g}_{ni}^*| |\mathbf{g}_{he}^*|^2 \sigma_{ni}^{ieiz^*}}{\frac{16\pi^2}{3} \left(\frac{m_n^* m_i^*}{m_i^* (m_i^* + m_e^*)} |\mathbf{g}_{ni}^*|^2 - \frac{2(m_n^* + m_e^*)}{m_i^* (m_i^* + m_e^*)} \Delta\mathcal{E}^* \right)^{3/2}} d|\mathbf{g}_{he}^*| d\omega_{he}^* d\omega_{iz}^*. \quad (2.8)$$

2.5. Dimensional analysis

A sound scaling of the Boltzmann equation is deduced from a dimensional analysis inspired by Petit & Darozes (1975). Reference dimensional quantities are denoted by the superscript 0 . The characteristic temperature T^0 , number density n^0 , differential cross-section for inert collisions σ^0 , mean free path l^0 , macroscopic time scale t^0 , and macroscopic length scale L^0 are assumed to be common to all species. Electron and heavy-particle reference quantities are introduced in Table 1. The non-dimensional number

$$\varepsilon = \sqrt{\frac{m_e^0}{m_h^0}} \quad (2.9)$$

quantifies the ratio of the electron mass to a reference heavy-particle mass. According to assumption (5), the value of ε is small. Consequently, electrons exhibit a larger thermal speed $V_e^0 = (k_B T^0 / m_e^0)^{1/2}$ than that of heavy particles $V_h^0 = (k_B T^0 / m_h^0)^{1/2} = \varepsilon V_e^0$. The differential cross-sections for inert collisions being of the same order of magnitude σ^0 , the characteristic mean free path $l^0 = 1/(n^0 \sigma^0)$ is found to be identical for all species. As a result, the kinetic time scale, or relaxation time of a distribution function toward its respective quasi-equilibrium state, is lower for electrons, $t_e^0 = l^0 / V_e^0$, than for heavy particles, $t_h^0 = l^0 / V_h^0 = t_e^0 / \varepsilon$. Assumption (6) states that the macroscopic time scale reads $t^0 = t_h^0 / \varepsilon$. In addition, the macroscopic temporal and spatial scales are linked by the expression $L^0 = V_h^0 t^0$. Hence, the Knudsen number $Kn = l^0 / L^0 = \varepsilon$ is small, due to our choice of macroscopic and temporal scales, leading to a continuum description.

Non-dimensional variables are based on the reference quantities. They are denoted by removing the superscript * . In particular, one uses the following expressions for the

particle velocities, $\mathbf{c}_\epsilon^* = V_\epsilon^0 \mathbf{c}_\epsilon$, and $\mathbf{c}_i^* = V_h^0 \mathbf{c}_i$, $i \in \mathbb{H}$. The non-dimensional ionization energy reads

$$\Delta \mathcal{E}^* = k_B T^0 \Delta \mathcal{E}, \quad (2.10)$$

whereas the differential cross-sections for ionization are scaled as

$$\sigma_{ne}^{ie\epsilon^*} = \varepsilon^2 \sigma^0 \sigma_{ne}^{ie\epsilon}, \quad \sigma_{ni}^{ie i^*} = \varepsilon \sigma^0 \sigma_{ni}^{ie i}, \quad i \in \mathbb{H}, \quad (2.11)$$

according to assumption (7). Using relations (2.10) and (2.11), the dimensional analysis of the transition probabilities can be deduced from Eqs. (2.7) and (2.8) in the following way:

$$\mathcal{W}_{ne}^{ie\epsilon^*} = \varepsilon^2 \frac{\sigma^0}{(V_h^0)^3 (V_\epsilon^0)^5} \mathcal{W}_{ne}^{ie\epsilon}, \quad \mathcal{W}_{ni}^{ie i^*} = \varepsilon^2 \frac{\sigma^0}{(V_h^0)^6 (V_\epsilon^0)^2} \mathcal{W}_{ni}^{ie i}, \quad i \in \mathbb{H}. \quad (2.12)$$

We investigate the system at the macroscopic time $t^* = t^0 t$, the Boltzmann Eq. (2.1) can be expressed, in non-dimensional form, for the electrons and heavy particles, as

$$\partial_t f_\epsilon = \frac{1}{\varepsilon^2} [\mathcal{J}_{e\epsilon}(f_\epsilon, f_\epsilon) + \sum_{j \in \mathbb{H}} \mathcal{J}_{e j}(f_\epsilon, f_j)] + \sum_{r \in R} \mathcal{C}_\epsilon^r(f), \quad (2.13)$$

$$\partial_t f_i = \frac{1}{\varepsilon} \left[\frac{1}{\varepsilon} \mathcal{J}_{i\epsilon}(f_i, f_\epsilon) + \sum_{j \in \mathbb{H}} \mathcal{J}_{ij}(f_i, f_j) \right] + \sum_{r \in R} \mathcal{C}_i^r(f), \quad i \in \mathbb{H}, \quad (2.14)$$

respectively. The multi-scale analysis occurs at three levels: (a) in the kinetic Eqs. (2.13) and (2.14); (b) in the collisional invariants (2.5) and thus in the conservation of the associated macroscopic quantities; (c) in the collision operators. The scaling of the reactive collision operators is investigated in the following section, the treatment of the non-reactive collision operators is given in Graille *et al.* (2008). It is important to mention that the Maxwellian reaction regime is reached, since the temporal derivative of the distribution function and the reactive collision operators of Eqs. (2.13) and (2.14) are of order ε^0 , corresponding to the macroscopic time scale t^0 at which the conservation equations are derived.

2.6. Expansion of the reactive operators \mathcal{C}_ϵ and \mathcal{C}_i , $i \in \mathbb{H}$

The study of the collision dynamics for the three-body ionization collisions yields the dependence of the velocities on the ε parameter. For reaction r_ϵ , it can be shown that these velocities can be parameterized as

$$\mathbf{c}_i = \mathbf{c}_n + \mathcal{O}(\varepsilon), \quad \mathbf{c}_{\hat{i}} = -\mathbf{g}'_{i\epsilon} - \frac{1}{2} \mathbf{g}'_{\epsilon\epsilon} + \mathcal{O}(\varepsilon), \quad \mathbf{c}_{\bar{i}} = -\mathbf{g}'_{i\epsilon} + \frac{1}{2} \mathbf{g}'_{\epsilon\epsilon} + \mathcal{O}(\varepsilon).$$

After some algebra, energy conservation is expressed by means of two decoupled equations for the electrons and heavy particles:

$$|\mathbf{c}_n|^2 = |\mathbf{c}_i|^2 + \mathcal{O}(\varepsilon), \quad |\mathbf{c}_{\bar{i}}|^2 = |\mathbf{c}_{\hat{i}}|^2 + |\mathbf{c}_{\bar{i}}|^2 + 2\Delta \mathcal{E} + \mathcal{O}(\varepsilon). \quad (2.15)$$

Due to the large mass disparity between the electrons and heavy particles, the energy required to pull an electron from a neutral particle is provided by the colliding free electron, ionization can only occur if its energy is greater than the ionization energy. After collision, two electrons are emitted with a global energy corresponding to the difference between the electron energy before interaction and the ionization energy. The ion keeps the same momentum and energy as the neutral particle before collision. For reaction r_i , $i \in \mathbb{H}$, the velocities can be parameterized as

$$\mathbf{c}_i = \mathbf{G}_0 + \frac{1}{2} \mathbf{g}'_{i i} + \mathcal{O}(\varepsilon), \quad \mathbf{c}_{\bar{i}} = \mathbf{G}_0 - \frac{1}{2} \mathbf{g}'_{i i} + \mathcal{O}(\varepsilon), \quad i \in \mathbb{H}, \quad \mathbf{c}_\epsilon = -\mathbf{g}'_{h\epsilon} + \mathcal{O}(\varepsilon),$$

where the center of mass reads $\mathbf{G}_0 = \frac{1}{2}\mathbf{c}_n + \mathbf{c}_i + \mathcal{O}(\varepsilon) = \frac{1}{2}\mathbf{c}_i + \mathbf{c}_i + \mathcal{O}(\varepsilon)$. After some algebra, energy conservation is expressed by means of one equation coupling electrons and heavy particles:

$$\frac{1}{2}m_i|\mathbf{g}_{ni}|^2 - 2\Delta\mathcal{E} = \frac{1}{2}m_i|\mathbf{g}'_{ii}|^2 + |\mathbf{g}'_{he}|^2 + \mathcal{O}(\varepsilon), \quad i \in \text{H}. \quad (2.16)$$

In order to decouple the heavy-particle energy from the electron energy, we assume that the electron pulled from the neutral particle is cold, since it is not yet thermalized at the electron temperature. Its characteristic speed has the same magnitude as the one of the heavy particles implied in the collision. Therefore, its energy is null at zero-order and we can split Eq. (2.16) into two uncoupled equations:

$$\frac{1}{2}m_i|\mathbf{g}_{ni}|^2 - 2\Delta\mathcal{E} = \frac{1}{2}m_i|\mathbf{g}'_{ii}|^2 + \mathcal{O}(\varepsilon), \quad i \in \text{H}, \quad |\mathbf{g}'_{he}|^2 = \mathcal{O}(\varepsilon). \quad (2.17)$$

Ionization can only occur if the relative kinetic energy between the neutral particle and the catalyst is greater than the ionization energy.

Let us define $Q_\varepsilon^0 = (m_\varepsilon^0 k_B T^0 / h_P^2)^{3/2}$, quantity proportional to the electron translational partition function, and the zero-order transition probability such that we have $\mathcal{W}_{ni}^{ie\varepsilon} = \mathcal{W}_{ni}^{ie\varepsilon 0} + \mathcal{O}(\varepsilon)$, $i \in \text{S}$. Then, we give, without their proof, the following theorems for the expansion of the reactive collision operators.

Theorem 2.1 *The reactive collision operator \mathcal{C}_ε can be expanded in the form*

$$\mathcal{C}_\varepsilon(f) = \mathcal{C}_\varepsilon^0(f) + \mathcal{O}(\varepsilon), \quad (2.18)$$

where $\mathcal{C}_\varepsilon^0(f) = \sum_{r \in R} \mathcal{C}_\varepsilon^{r0}(f)$, with the zero-order partial collision operators

$$\begin{aligned} \mathcal{C}_\varepsilon^{r\varepsilon 0}(f) &= \int \left(f_i f_{\varepsilon_1} f_{\varepsilon_2} \frac{n^0}{Q_\varepsilon^0} \left(\frac{m_n}{m_i} \right)^3 - f_n f_\varepsilon \right) \mathcal{W}_{ne}^{ie\varepsilon 0} d\mathbf{c}_n d\mathbf{c}_i d\mathbf{c}_{\varepsilon_1} d\mathbf{c}_{\varepsilon_2} \\ &\quad - 2 \int \left(f_i f_\varepsilon f_{\varepsilon_2} \frac{n^0}{Q_\varepsilon^0} \left(\frac{m_n}{m_i} \right)^3 - f_n f_{\varepsilon_1} \right) \mathcal{W}_{ne}^{ie\varepsilon 0} d\mathbf{c}_n d\mathbf{c}_i d\mathbf{c}_{\varepsilon_1} d\mathbf{c}_{\varepsilon_2}, \\ \mathcal{C}_\varepsilon^{r\varepsilon 0}(f) &= - \int \left(f_i f_\varepsilon f_{i_2} \frac{n^0}{Q_\varepsilon^0} \left(\frac{m_n}{m_i} \right)^3 - f_n f_{i_1} \right) \mathcal{W}_{ni}^{ie\varepsilon 0} d\mathbf{c}_n d\mathbf{c}_{i_1} d\mathbf{c}_i d\mathbf{c}_{i_2}, \quad i \in \text{H}. \end{aligned}$$

Theorem 2.2 *The reactive collision operators \mathcal{C}_i , $i \in \text{H}$, can be expanded in the form*

$$\mathcal{C}_i(f) = \mathcal{C}_i^0(f) + \mathcal{O}(\varepsilon), \quad (2.19)$$

where $\mathcal{C}_i^0(f) = \sum_{r \in R} \mathcal{C}_i^{r0}(f)$, $i \in \text{H}$, with the zero-order partial collision operators

$$\begin{aligned} \mathcal{C}_n^{r\varepsilon 0}(f) &= \int \left(f_i f_{\varepsilon_2} f_{\varepsilon_3} \frac{n^0}{Q_\varepsilon^0} \left(\frac{m_n}{m_i} \right)^3 - f_n f_{\varepsilon_1} \right) \mathcal{W}_{ne}^{ie\varepsilon 0} d\mathbf{c}_i d\mathbf{c}_{\varepsilon_1} d\mathbf{c}_{\varepsilon_2} d\mathbf{c}_{\varepsilon_3}, \\ \mathcal{C}_n^{r\varepsilon 0}(f) &= (1 + \delta_{ni}) \int \left(f_{i_1} f_\varepsilon f_i \frac{n^0}{Q_\varepsilon^0} \left(\frac{m_n}{m_i} \right)^3 - f_n f_{i_2} \right) \mathcal{W}_{ni}^{ie\varepsilon 0} d\mathbf{c}_i d\mathbf{c}_\varepsilon d\mathbf{c}_{i_1} d\mathbf{c}_{i_2} \\ &\quad - \delta_{ni} \int \left(f_i f_\varepsilon f_n \frac{n^0}{Q_\varepsilon^0} \left(\frac{m_n}{m_i} \right)^3 - f_{i_1} f_{i_2} \right) \mathcal{W}_{ni}^{ie\varepsilon 0} d\mathbf{c}_i d\mathbf{c}_\varepsilon d\mathbf{c}_{i_1} d\mathbf{c}_{i_2}, \quad i \in \text{H}, \\ \mathcal{C}_i^{r\varepsilon 0}(f) &= - \int \left(f_i f_{\varepsilon_2} f_{\varepsilon_3} \frac{n^0}{Q_\varepsilon^0} \left(\frac{m_n}{m_i} \right)^3 - f_n f_{\varepsilon_1} \right) \mathcal{W}_{ne}^{ie\varepsilon 0} d\mathbf{c}_n d\mathbf{c}_{\varepsilon_1} d\mathbf{c}_{\varepsilon_2} d\mathbf{c}_{\varepsilon_3}, \end{aligned}$$

$$\begin{aligned} \mathcal{C}_i^{n_0}(f) &= \delta_{ii} \int \left(f_{i_1} f_{\epsilon} f_{i_2} \frac{n^0}{Q_{\epsilon}^0} \left(\frac{m_n}{m_i} \right)^3 - f_n f_i \right) \mathcal{W}_{ni}^{i\epsilon i_0} d\mathbf{c}_n d\mathbf{c}_{\epsilon} d\mathbf{c}_{i_1} d\mathbf{c}_{i_2} \\ &\quad - (1 + \delta_{ii}) \int \left(f_i f_{\epsilon} f_{i_2} \frac{n^0}{Q_{\epsilon}^0} \left(\frac{m_n}{m_i} \right)^3 - f_n f_{i_1} \right) \mathcal{W}_{ni}^{i\epsilon i_0} d\mathbf{c}_n d\mathbf{c}_{\epsilon} d\mathbf{c}_{i_1} d\mathbf{c}_{i_2}, \quad i \in \mathbf{H}. \end{aligned}$$

3. Multi-scale Chapman-Enskog expansion

We employ an Enskog expansion to derive an approximate solution to the Boltzmann equation by expanding the species distribution functions in a series of the ε parameter as a perturbation of the quasi-equilibrium distribution functions f_{ϵ}^0 and f_i^0 , $i \in \mathbf{H}$,

$$f_{\epsilon} = f_{\epsilon}^0 (1 + \varepsilon \phi_{\epsilon} + \varepsilon^2 \phi_{\epsilon}^2) + \mathcal{O}(\varepsilon^3), \quad (3.1)$$

$$f_i = f_i^0 (1 + \varepsilon \phi_i) + \mathcal{O}(\varepsilon^2), \quad i \in \mathbf{H}. \quad (3.2)$$

Injecting these expressions into Eqs. (2.13) and (2.14), one obtains,

$$\partial_t f_{\epsilon} = \varepsilon^{-2} \mathcal{J}_{\epsilon}^{-2} + \varepsilon^{-1} \mathcal{J}_{\epsilon}^{-1} + \mathcal{J}_{\epsilon}^0 + \mathcal{C}_{\epsilon}^0 + \mathcal{O}(\varepsilon), \quad (3.3)$$

$$\partial_t f_i = \varepsilon^{-1} \mathcal{J}_i^{-1} + \mathcal{J}_i^0 + \mathcal{C}_i^0 + \mathcal{O}(\varepsilon), \quad i \in \mathbf{H}, \quad (3.4)$$

where the non-reactive collision operators are found in Graille *et al.* (2008).

In the Chapman-Enskog method, the plasma is described at successive orders of ε , as equivalent to as many time scales. Let us introduce some mathematical tools to derive the conservation equations. We define the electron and heavy-particle scalar products,

$$\langle\langle \xi_{\epsilon}, \zeta_{\epsilon} \rangle\rangle_{\epsilon} = \int \xi_{\epsilon} \odot \zeta_{\epsilon} d\mathbf{c}_{\epsilon}, \quad \langle\langle \xi_{\mathbf{h}}, \zeta_{\mathbf{h}} \rangle\rangle_{\mathbf{h}} = \sum_{j \in \mathbf{H}} \int \xi_j \odot \zeta_j d\mathbf{c}_j, \quad (3.5)$$

and the collisional invariants for electrons,

$$\begin{cases} \hat{\psi}_{\epsilon}^1 = 1, \\ \hat{\psi}_{\epsilon}^2 = \frac{1}{2} \mathbf{c}_{\epsilon} \cdot \mathbf{c}_{\epsilon} + \mathcal{U}_{\epsilon}^{\text{F}}, \end{cases} \quad (3.6)$$

and for heavy particles,

$$\begin{cases} \hat{\psi}_{\mathbf{h}}^l = (m_i \delta_{il})_{i \in \mathbf{H}}, & l \in \mathbf{H}, \\ \hat{\psi}_{\mathbf{h}}^{n^{\mathbf{H}} + \nu} = (m_i c_{i\nu})_{i \in \mathbf{H}}, & \nu \in \{1, 2, 3\}, \\ \hat{\psi}_{\mathbf{h}}^{n^{\mathbf{H}} + 4} = \left(\frac{1}{2} m_i \mathbf{c}_i \cdot \mathbf{c}_i + m_i \mathcal{U}_i^{\text{F}} \right)_{i \in \mathbf{H}}, \end{cases} \quad (3.7)$$

where symbol $n^{\mathbf{H}}$ denotes the number of heavy particles in the mixture. The linearized collision operators of the Boltzmann equation for electrons and heavy particles are orthogonal, with respect to the scalar product, to the space spanned by their collisional invariants. The partial mass densities read $\rho_{\epsilon} = \langle\langle f_{\epsilon}, \hat{\psi}_{\epsilon}^1 \rangle\rangle_{\epsilon}$, $\rho_i = \langle\langle f_{\mathbf{h}}, \hat{\psi}_{\mathbf{h}}^i \rangle\rangle_{\mathbf{h}}$, $i \in \mathbf{H}$; momentum vanishes, $\langle\langle f_{\mathbf{h}}, \hat{\psi}_{\mathbf{h}}^{n^{\mathbf{H}} + \nu} \rangle\rangle = 0$, $\nu \in \{1, 2, 3\}$; and the heavy-particle and electron energies are given by

$$\rho_{\epsilon} e_{\epsilon} = \rho_{\epsilon} e_{\epsilon}^{\text{T}} + \rho_{\epsilon} \mathcal{U}_{\epsilon}^{\text{F}} = \langle\langle f_{\epsilon}, \hat{\psi}_{\epsilon}^2 \rangle\rangle, \quad \rho_{\mathbf{h}} e_{\mathbf{h}} = \rho_{\mathbf{h}} e_{\mathbf{h}}^{\text{T}} + \sum_{j \in \mathbf{H}} \rho_j \mathcal{U}_j^{\text{F}} = \langle\langle f_{\mathbf{h}}, \hat{\psi}_{\mathbf{h}}^{n^{\mathbf{H}} + 4} \rangle\rangle.$$

Finally, we impose the constraints that f_ϵ^0 and f_h^0 yield the local macroscopic properties

$$\langle\langle f_\epsilon^0, \hat{\psi}_\epsilon^l \rangle\rangle_\epsilon = \langle\langle f_\epsilon, \hat{\psi}_\epsilon^l \rangle\rangle_\epsilon, \quad l \in \{1, 2\}, \quad (3.8)$$

$$\langle\langle f_h^0, \hat{\psi}_h^l \rangle\rangle_h = \langle\langle f_h, \hat{\psi}_h^l \rangle\rangle_h, \quad l \in \{1, \dots, n^H+4\}. \quad (3.9)$$

3.1. Conservation equations

When solving the electron Boltzmann Eq. (3.3) at order ε^{-2} , corresponding to the kinetic time scale t_ϵ^0 , the electron population is shown to thermalize to a quasi-equilibrium state described by a Maxwell-Boltzmann distribution function at temperature $T_\epsilon = \frac{2}{3}e_\epsilon^T$

$$f_\epsilon^0 = n_\epsilon \left(\frac{1}{2\pi T_\epsilon} \right)^{3/2} \exp \left(-\frac{1}{2T_\epsilon} \mathbf{c}_\epsilon \cdot \mathbf{c}_\epsilon \right), \quad (3.10)$$

where n_ϵ is the electron number density. In contrast, heavy particles do not exhibit any ensemble property at this order. Solving the heavy-particle Boltzmann Eqs. (3.4) at order ε^{-1} corresponding to the kinetic time scale t_h^0 , the heavy-particle population is shown to thermalize to a quasi-equilibrium state described by a Maxwell-Boltzmann distribution function at temperature $T_h = \frac{2}{3}\rho_h e_h^T / n_h$, $n_h = \sum_{i \in H} n_i$,

$$f_i^0 = n_i \left(\frac{m_i}{2\pi T_h} \right)^{3/2} \exp \left(-\frac{m_i}{2T_h} \mathbf{c}_i \cdot \mathbf{c}_i \right), \quad i \in H. \quad (3.11)$$

where n_i is the number density of species i . The quasi-equilibrium states are described by means of distinct temperatures for the electrons and heavy particles.

Macroscopic equations can be derived by means of the scalar products defined in Eq. (3.5). The projection of the Boltzmann Eq. (3.3) at order ε^{-1} on the collisional invariants $\hat{\psi}_\epsilon^l$, $l \in \{1, 2\}$, is trivial. At order ε^0 , corresponding to the macroscopic time scale t^0 , we obtain the zero-order drift-diffusion equations for the electrons and Euler equations for the heavy species in the non-homogeneous case considered in Graille *et al.* (2008). Here, we obtain as source terms for the macroscopic equations, the translational energy transferred from heavy particles to electrons, expressed as $\Delta E_h^0 = \frac{3}{2}n_\epsilon(T_\epsilon - T_h)/\tau$, where τ is the average collision time at which this energy transfer occurs, as well as zero-order chemical production rates expressed as

$$\omega_i^0 = \sum_{r \in R} \omega_i^{r0}, \quad \omega_i^{r0} = \int \mathcal{C}_i^{r0}(f^0) d\mathbf{c}_i, \quad i \in S, \quad r \in R. \quad (3.12)$$

These terms appear in the two following propositions derived by projecting Eqs. (3.3)-(3.4) on the collisional invariants.

Proposition 3.1 *If ϕ_h is a solution to Eq. (3.4) at order ε^0 , where f_ϵ^0 is given by Eq. (3.10), f_i^0 , $i \in H$, by Eq. (3.11), if $\phi_\epsilon = 0$, and if $f_h^0 \phi_h = (f_i^0 \phi_i)_{i \in H}$ satisfies the constraints*

$$\langle\langle f_h^0 \phi_h, \hat{\psi}_h^l \rangle\rangle_h = 0, \quad l \in \{1, \dots, n^H+4\},$$

then the zero-order conservation equations of heavy-particle mass and energy read

$$d_t \rho_i = m_i \omega_i^0, \quad i \in H, \quad (3.13)$$

$$d_t (\rho_h e_h^T) = \Delta E_h^0 + \Delta \mathcal{E} \omega_n^{r0} - \Delta \mathcal{E} \omega_i^{r0}. \quad (3.14)$$

Proposition 3.2 *If ϕ_ϵ^2 is a solution to Eq. (3.3) at order ε^0 , where f_ϵ^0 is given by*

Eq. (3.10), f_i^0 , $i \in \text{H}$, by Eq. (3.11), if $\phi_\epsilon = 0$, if ϕ_i , $i \in \text{H}$, is a solution of Eq. (3.4) at order ϵ^0 under the constraints $\langle\langle f_\mathfrak{h}^0 \phi_\mathfrak{h}, \hat{\psi}_\mathfrak{h}^l \rangle\rangle_\mathfrak{h} = 0$, $l \in \{1, \dots, n^{\text{H}}+4\}$, and if $f_\epsilon^0 \phi_\epsilon^2$ satisfies the constraints

$$\langle\langle f_\epsilon^0 \phi_\epsilon^2, \hat{\psi}_\epsilon^l \rangle\rangle_\epsilon = 0, \quad l \in \{1, 2\},$$

then the zero-order conservation equations of electron mass and energy read

$$d_t \rho_\epsilon = \omega_\epsilon^0, \quad (3.15)$$

$$d_t(\rho_\epsilon e_\epsilon^{\text{T}}) = -\Delta E_\mathfrak{h}^0 - \Delta \mathcal{E} \omega_\epsilon^{r_\epsilon 0}. \quad (3.16)$$

Using the property of the chemical production rates for ionization $\omega_e^{r_0} = \omega_i^{r_0} = -\omega_n^{r_0}$, $r \in R$, it can be shown that the mixture mass and energy are conserved, i.e.,

$$d_t \rho = 0, \quad d_t(\rho e^{\text{T}} + \rho \mathcal{U}^{\text{F}}) = 0.$$

The ionization energy, given by the catalyst involved in the ionization reaction, contributes to the balance of translational energy of this catalyst, our thermodynamics being globally at constant total density and total energy. Let us emphasize that we do not make any further assumption on the internal variables, defined by Woods (1986) as the mixture composition and energy distribution among the species.

3.2. Zero-order chemical production rates and microreversibility

The kinetic theory allows us to rigorously derive the expression for the zero-order chemical production rates. This is a major contribution of this work, since it provides the ingredients to obtain a new form for the second law of thermodynamics. After some lengthy algebra, these rates can be expressed in terms of the number densities as

$$\omega_\epsilon^{r_\epsilon 0} = \mathcal{K}_{r_\epsilon}^{\text{f}}(T_\epsilon) n_n n_\epsilon - \mathcal{K}_{r_\epsilon}^{\text{b}}(T_\epsilon) n_i n_\epsilon^2, \quad (3.17)$$

$$\omega_\epsilon^{r_i 0} = \mathcal{K}_{r_i}^{\text{f}}(T_\mathfrak{h}) n_n n_i - \mathcal{K}_{r_i}^{\text{b}}(T_\mathfrak{h}, T_\epsilon) n_i n_\epsilon n_i, \quad i \in \text{H}. \quad (3.18)$$

The temperature dependence for the forward and backward rate constants is strongly connected with the reaction mechanism. The ionization energy is provided by the reaction catalyst at temperature T_r , $r \in R$, defined as

$$T_{r_\epsilon} = T_\epsilon, \quad T_{r_i} = T_\mathfrak{h}, \quad i \in \text{H}.$$

The forward rate, associated with the endothermic reaction, is a function of the temperature T_r . The temperature dependence for the backward rate, associated with the exothermic reaction, is less straightforward to interpret.

The reaction rates obey the relation $\mathcal{K}_r^{\text{eq}} = \mathcal{K}_r^{\text{f}}/\mathcal{K}_r^{\text{b}}$, $r \in R$, where the quasi-equilibrium rate constant is defined as

$$\mathcal{K}_r^{\text{eq}}(T_\epsilon, T_r) = \left(\frac{m_i}{m_n}\right)^{3/2} Q_\epsilon^{\text{T}}(T_\epsilon) \exp\left(-\frac{\Delta \mathcal{E}}{T_r}\right), \quad r \in R, \quad (3.19)$$

with the electron translational partition function given by $Q_\epsilon^{\text{T}}(T_\epsilon) = (2\pi T_\epsilon)^{3/2} Q_\epsilon^0/n^0$. Such a form follows from two essential physical properties. First, Eqs. (2.15) and (2.17), for the scaled conservation of energy during reactive collisions, allow for a common symmetric reaction rate to be defined for the forward and backward reaction, such as in Giovangigli (1999). Second, the formation energies for the species involved in a given reaction, light or heavy, are taken into account into this symmetric reaction constant at the common temperature T_r . The zero-order chemical production rates are thus compatible with the law of mass action and irreversible thermodynamics. Equation (3.19) is a

generalized Saha law for a quasi-equilibrium state in which electrons and heavy particles are in chemical equilibrium and thermal non-equilibrium. We have retrieved the Morro-Romeo-van de Sanden equation for the electron-impact ionization reaction (see Giordano & Capitelli 2001) and have derived a new equation for the heavy-particle impact ionization reactions.

In addition to the thermal energy, we introduce other relevant thermodynamic functions. First, the species Gibbs free energy is defined by the relations

$$\rho_{\epsilon} g_{\epsilon} = n_{\epsilon} T_{\epsilon} \ln \left[\frac{n_{\epsilon}}{Q_{\epsilon}^{\text{T}}(T_{\epsilon})} \right] + n_{\epsilon} \mathcal{U}_{\epsilon}^{\text{F}}, \quad \rho_i g_i = n_i T_{\text{h}} \ln \left[\frac{n_i}{Q_i^{\text{T}}(T_{\text{h}})} \right] + n_i \mathcal{U}_i^{\text{F}}, \quad i \in \text{H},$$

where the translational partition functions read $Q_i^{\text{T}}(T_{\text{h}}) = (2\pi m_i T_{\text{h}})^{3/2} Q_{\text{h}}^0/n^0$, $i \in \text{H}$, with quantity $Q_{\text{h}}^0 = (m_{\text{h}}^0 k_{\text{B}} T^0 / h_{\text{p}}^2)^{3/2}$. The species enthalpy is given by $\rho_{\epsilon} h_{\epsilon} = \frac{5}{2} n_{\epsilon} T_{\epsilon} + \rho_{\epsilon} \mathcal{U}_{\epsilon}^{\text{F}}$ and $\rho_i h_i = \frac{5}{2} n_i T_{\text{h}} + \rho_i \mathcal{U}_i^{\text{F}}$, $i \in \text{H}$, and the species entropy by $s_{\epsilon} = (h_{\epsilon} - g_{\epsilon})/T_{\epsilon}$ and $s_i = (h_i - g_i)/T_{\text{h}}$, $i \in \text{H}$. The mixture entropy read $\rho s = \sum_{j \in \text{S}} \rho_j s_j$. For reactive plasmas, Gibbs relation is found to be

$$d_t(\rho s) = \frac{1}{T_{\epsilon}} d_t(\rho_{\epsilon} e_{\epsilon}) + \frac{1}{T_{\text{h}}} d_t(\rho_{\text{h}} e_{\text{h}}) - \frac{g_{\epsilon}}{T_{\epsilon}} d_t \rho_{\epsilon} - \sum_{j \in \text{H}} \frac{g_j}{T_{\text{h}}} d_t \rho_j.$$

In the present case, we note that the usual entropy produced by a chemical reaction, $-g_{\epsilon} \omega_{\epsilon}^{r0}/T_{\epsilon} - \sum_{j \in \text{H}} m_j g_j \omega_j^{r0}/T_{\text{h}}$, $r \in R$, does not have a definite sign. Thus, the Gibbs free energy does not allow the definition of a suitable chemical potential and does not include the thermal exchange in a chemical reaction between species thermalized at different temperatures. Consequently, we redefine the Gibbs free energy as

$$\rho_{\epsilon} \tilde{g}_{\epsilon}^r = \rho_{\epsilon} g_{\epsilon} + \left(\frac{T_{\epsilon}}{T_r} - 1 \right) \rho_{\epsilon} \mathcal{U}_{\epsilon}^{\text{F}}, \quad \rho_i \tilde{g}_i^r = \rho_i g_i + \left(\frac{T_{\text{h}}}{T_r} - 1 \right) \rho_i \mathcal{U}_i^{\text{F}}, \quad i \in \text{H}, \quad r \in R,$$

and distinguish two sources of entropy production, using Eqs. (3.13) and (3.15),

$$d_t(\rho s) = \Upsilon_{\text{th}} + \sum_{r \in R} \Upsilon_{\text{ch}}^r.$$

Quantity $\Upsilon_{\text{th}} = [d_t(\rho_{\epsilon} e_{\epsilon}^{\text{T}}) + \Delta \mathcal{E} \omega_{\epsilon}^{r0}]/T_{\epsilon} + [d_t(\rho_{\text{h}} e_{\text{h}}^{\text{T}}) + \Delta \mathcal{E}(\omega_i^{r0} - \omega_{\text{n}}^{r0})]/T_{\text{h}}$ stands for the entropy production rate due to thermal non-equilibrium. Using Eqs. (3.14) and (3.16), we show that this quantity is non-negative, $\Upsilon_{\text{th}} = \frac{3}{2} n_{\epsilon} (T_{\epsilon} - T_{\text{h}})^2 / (T_{\epsilon} T_{\text{h}} \tau)$. The entropy production rate is given by $\Upsilon_{\text{ch}}^r = -\tilde{g}_{\epsilon}^r \omega_{\epsilon}^{r0}/T_{\epsilon} - \sum_{j \in \text{H}} m_j \tilde{g}_j^r \omega_j^{r0}/T_{\text{h}}$, $r \in R$. After some algebra, we obtain

$$\Upsilon_{\text{ch}}^r = \mathcal{K}_{r_2}(T_{r_2}) \Omega \left(\frac{n_{\text{n}}}{Q_{\text{n}}(T_{\text{h}}, T_{r_2})} \frac{n_i}{Q_i(T_i, T_{r_2})}, \frac{n_i}{Q_i(T_{\text{h}}, T_{r_2})} \frac{n_{\epsilon}}{Q_{\epsilon}(T_{\epsilon}, T_{r_2})} \frac{n_i}{Q_i(T_i, T_{r_2})} \right), \quad i \in \text{S},$$

where $T_i = T_{\text{h}}$, $i \in \text{H}$, and $Q_i(T_{\text{h}}, T_r) = Q_i^{\text{T}}(T_{\text{h}}) \exp(-m_i \mathcal{U}_i^{\text{F}}/T_r)$, $i \in \text{H}$, $r \in R$, $Q_{\epsilon}(T_{\epsilon}, T_r) = Q_{\epsilon}^{\text{T}}(T_{\epsilon}) \exp(-\mathcal{U}_{\epsilon}^{\text{F}}/T_r)$, $r \in R$. The terms Υ_{ch}^r are non-negative, since the function $\Omega(x, y) = (x - y) \log(x/y)$ is positive. The second law of thermodynamics is satisfied.

4. Conclusion

Based on kinetic theory, we have proposed a unified description of the thermodynamic state of plasmas in thermal and chemical non-equilibrium, thus extending the

work of Woods (1986), in which the non-equilibrium effects are treated separately in terms of internal variables. The full thermodynamic equilibrium state of the system, under well-defined and natural constraints, can be studied by following the approach used in Giovangigli (1999) and Massot (2002). It can be shown that the system asymptotically converges toward a unique thermal and chemical equilibrium state. Our results are complementary of the conservation equations and transport flux expressions derived by Graille *et al.* (2008) for non-homogeneous plasmas in the presence of external forces, since we provide adequate chemical source terms to be added to the zero-order drift-diffusion/Euler set of equations or to the first-order drift-diffusion/Navier-Stokes set of equations, in particular, with a description of the Kolesnikov effect for multi-component plasmas (Kolesnikov 1974).

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