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Thermo-chemical dynamics and chemical quasi-equilibrium of plasmas in thermal non-equilibrium

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1. Motivation and objective

Plasmas have a broad field of applications, such as air-breathing hypersonic vehicles (plasma control for scramjet engine), spacecraft atmospheric entries (influence of precursor electrons and prediction of blackout phenomenon), high-enthalpy wind tunnels (plasmatron, arc-jet, and shock tube facilities), lightning phenomena, discharges at atmospheric pressure, laboratory nuclear fusion and astrophysics. Graille *et al.* (2008, 2009) have derived from kinetic theory a unified fluid model for 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. The following ionization mechanism, comprising the reactions r_i, was considered:

$$\mathfrak{n} + i \rightleftharpoons \mathfrak{i} + \mathfrak{e} + i, \quad i \in \mathrm{S},$$

for a 3-species plasma. Electrons, neutral particles, and ions are, respectively, denoted by the indices $\mathfrak{e}$, $\mathfrak{n}$, and $\mathfrak{i}$. The full mixture of species is denoted by the set of indices $\mathrm{S} = \{\mathfrak{e}, \mathfrak{n}, \mathfrak{i}\}$, and the heavy particles, by the set of indices $\mathrm{H} = \{\mathfrak{n}, \mathfrak{i}\}$.

A recurrent topic in theoretical works on plasmas is the derivation of a modified Saha equation, describing systems in chemical quasi-equilibrium and thermal non-equilibrium, with the consequent debate regarding which of the forms of this equation is the correct one to apply (see Giordano & Capitelli 2001, and references cited therein). In particular, Morro & Romeo (1988) and van de Sanden *et al.* (1989) have derived an equation for the electron-impact ionization reaction based on techniques issued from thermodynamics of homogeneous systems at equilibrium. This approach is questionable for plasmas in both thermo-chemical non-equilibrium, seeing the strong coupling between chemical evolution and thermal exchange. In particular, it is not obvious to choose a suitable set of constraints associated with the optimization of the thermodynamic functions. In this work, we propose to study both processes of ionization by electron impact, reaction $r_{\mathfrak{e}}$, and by heavy-particle impact, reactions $r_{\mathfrak{n}}$ and $r_{\mathfrak{i}}$. We propose to examine systems in chemical quasi-equilibrium and thermal non-equilibrium by means of a singular perturbation analysis, as opposed to a standard thermodynamic approach, by extending the work of Massot (2002) to thermal non-equilibrium. This analysis is based on a set of differential equations derived by Graille *et al.* (2008) for the following physical scenario, in which the thermal relaxation becomes much slower than the chemical reactions. The singular perturbation analysis, consistent with the scale separation associated with this scenario, is used to study the dynamics of the system in two cases. First, electron-impact ionization is investigated. The dynamics of the system rapidly becomes close to a slow dynamics manifold

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that allows for defining a unique chemical quasi-equilibrium for two-temperature plasmas and proving that the second principle is satisfied. Then, all ionization reactions are taken into account simultaneously, leading to a surprising conclusion: when ionization through both electron and heavy-particle impact is considered, the inner layer for a short time scale (or time boundary layer) directly leads to thermal equilibrium. Thus, the global thermo-chemical equilibrium is reached within a short time scale, involving only chemical reactions, even if thermal relaxation through elastic collisions is not efficient and slow. To our knowledge, this approach sheds some completely new light on this matter and has not been used previously for such multicomponent reactive plasmas out of thermal equilibrium.

2. Conservation equations

In this section, we review the conservation equations derived from kinetic theory by Graille *et al*. (2008) for a spatially uniform plasma at rest in the absence of external forces. Then, we introduce thermodynamic functions and derive an entropy equation for the singular perturbation analysis. The derivation is based on a multicomponent Boltzmann equation with conventional elastic collision operators and reactive collision operators written in terms of transition probabilities (Giovangigli 1999). A dimensional analysis of the Boltzmann equation provides a small parameter for the scale separation, quantity $\varepsilon = (m_{\mathfrak{e}}^0/m_{\mathfrak{h}}^0)^{1/2}$, equal to the square root of the ratio of the electron mass to a reference heavy-particle mass. The Knudsen number is assumed to scale as this parameter, allowing for a continuum description of the system. The transition probabilities are linked to differential cross-sections, allowing for a parametrization of the reactive collisions and a suitable choice for the scaling leading to the Maxwellian reaction regime. In the multiscale Chapman-Enskog method, both the solution and the collision operators are expanded in a series of the ε parameter, leading to two major results. First, new expressions are derived for the reaction rate coefficients and zero-order chemical production rates for plasmas in thermal non-equilibrium. These expressions are compatible with the law of mass action. The species formation energy is associated with a temperature specific to the ionization reaction considered. Consequently, chemical reactions involving collision partners with populations distributed at distinct temperatures do not result only in changes for the mixture chemical composition, but also result in heat exchange between the electrons and heavy particles. Second, the set of derived conservation equations is compatible with the first and second laws of thermodynamics. Energy and total density are conserved and the entropy production rate for each type of ionization reaction is shown to be non-negative, involving a new definition of the Gibbs free energy for plasmas in thermal non-equilibrium.

At the electron kinetic time scale (order ε^{-2}), Graille *et al*. (2009) have shown that the electron population thermalizes to a quasi-equilibrium state described by means of a Maxwell-Boltzmann distribution function at temperature $T_{\mathfrak{e}} = \frac{2}{3} m_{\mathfrak{e}} e_{\mathfrak{e}}^{\mathrm{T}}/\mathrm{k_B}$

$$f_{\mathfrak{e}}^0 = n_{\mathfrak{e}} \left(\frac{m_{\mathfrak{e}}}{2\pi \mathrm{k_B} T_{\mathfrak{e}}} \right)^{3/2} \exp \left(-\frac{m_{\mathfrak{e}}}{2\mathrm{k_B} T_{\mathfrak{e}}} \boldsymbol{c}_{\mathfrak{e}} \cdot \boldsymbol{c}_{\mathfrak{e}} \right), \tag{2.1}$$

where quantity $m_{\mathfrak{e}}$ stands for the electron mass; $e_{\mathfrak{e}}^{\mathrm{T}}$, the electron translational energy; $n_{\mathfrak{e}}$, the electron number density; $\mathrm{k_B}$, Boltzmann's constant; and $\boldsymbol{c}_{\mathfrak{e}}$, the electron velocity. In contrast, heavy particles do not exhibit any ensemble property at this time scale. At the heavy-particle kinetic time scale (order ε^{-1}), Graille *et al*. (2009) have shown that the heavy-particle population thermalizes to a quasi-equilibrium state described by means of a Maxwell-Boltzmann distribution function at temperature $T_{\mathfrak{h}} = \frac{2}{3}\rho_{\mathfrak{h}} e_{\mathfrak{h}}^{\mathrm{T}}/(n_{\mathfrak{h}}\mathrm{k_B})$

$$f_i^0 = n_i \left(\frac{m_i}{2\pi \mathrm{k_B} T_{\mathfrak{h}}}\right)^{3/2} \exp\left(-\frac{m_i}{2\mathrm{k_B} T_{\mathfrak{h}}} \boldsymbol{c}_i \cdot \boldsymbol{c}_i\right), \quad i \in \mathrm{H}, \tag{2.2}$$

where quantity $n_i = \rho_i/m_i$ stands for the number density of species i, m_i its mass, ρ_i its mass density, $\boldsymbol{c}_i$ its velocity, $e_{\mathfrak{h}}^{\mathrm{T}}$ the heavy-particle translational energy, $\rho_{\mathfrak{h}}$ the heavy-particle mass density, and $n_{\mathfrak{h}} = \sum_{i\in\mathrm{H}} n_i$ the heavy-particle number density. The quasi-equilibrium states given in Eqs. (2.1) and (2.2) are described by means of distinct temperatures for the electrons and heavy particles. At the macroscopic time scale (order ε^0), Graille *et al.* (2008) have derived conservation equations for the mass and translational energy for the electrons and heavy particles

$$\mathrm{d}_t \rho_{\mathfrak{e}} = m_{\mathfrak{e}} \omega_{\mathfrak{e}}^0, \tag{2.3}$$

$$\mathrm{d}_t \rho_i = m_i\, \omega_i^0, \qquad i \in \mathrm{H}, \tag{2.4}$$

$$\mathrm{d}_t(\rho_{\mathfrak{e}} e_{\mathfrak{e}}^{\mathrm{T}}) = -\Delta E_{\mathfrak{h}}^0 - \Delta\mathcal{E}\, \omega_{\mathfrak{e}}^{r_{\mathfrak{e}}0}, \tag{2.5}$$

$$\mathrm{d}_t(\rho_{\mathfrak{h}} e_{\mathfrak{h}}^{\mathrm{T}}) = \Delta E_{\mathfrak{h}}^0 + \Delta\mathcal{E}\, \omega_{\mathfrak{n}}^{r_{\mathfrak{n}}0} - \Delta\mathcal{E}\, \omega_{\mathfrak{i}}^{r_{\mathfrak{i}}0}. \tag{2.6}$$

The ionization energy, $\Delta\mathcal{E} = m_{\mathfrak{i}}\mathcal{U}_{\mathfrak{i}}^{\mathrm{F}} + m_{\mathfrak{e}}\mathcal{U}_{\mathfrak{e}}^{\mathrm{F}} - m_{\mathfrak{n}}\mathcal{U}_{\mathfrak{n}}^{\mathrm{F}}$, is defined based on the formation energy $\mathcal{U}_i^{\mathrm{F}}$ for species $i \in \mathrm{S}$. The ionization energy is provided by the catalyst involved in the ionization reaction and contributes to the balance of translational energy for this catalyst, as shown in Eqs. (2.5) and (2.6). The zero-order chemical production rates comprise the contribution of the various chemical reactions

$$\omega_i^0 = \sum_{j\in\mathrm{S}} \omega_i^{r_j 0}, \quad i, j \in \mathrm{S}.$$

These rates satisfy the property $\omega_{\mathfrak{e}}^{r_i 0} = \omega_{\mathfrak{i}}^{r_i 0} = -\omega_{\mathfrak{n}}^{r_i 0}$, $i \in \mathrm{S}$ and can be expressed in terms of the number densities as

$$\omega_{\mathfrak{e}}^{r_i 0} = \mathcal{K}_{r_i}^{\mathrm{f}} n_{\mathfrak{n}} n_i - \mathcal{K}_{r_i}^{\mathrm{b}} n_{\mathfrak{i}} n_{\mathfrak{e}} n_i, \quad i \in \mathrm{S}.$$

For the reaction r_i, the direct and reverse rate coefficients are linked to a symmetric rate coefficient, $\mathcal{K}_{r_i}(T_{r_i})$, by the following relation:

$$\mathcal{K}_{r_i}^{\mathrm{f}} = \frac{\mathcal{K}_{r_i}(T_{r_i})}{Q_{\mathfrak{n}}(T_{\mathfrak{h}}, T_{r_i}) Q_i(T_i, T_{r_i})}, \quad \mathcal{K}_{r_i}^{\mathrm{b}} = \frac{\mathcal{K}_{r_i}(T_{r_i})}{Q_{\mathfrak{i}}(T_{\mathfrak{h}}, T_{r_i}) Q_{\mathfrak{e}}(T_{\mathfrak{e}}, T_{r_i}) Q_i(T_i, T_{r_i})}, \quad i \in \mathrm{S}, \tag{2.7}$$

with the global and translational partition functions

$$Q_i(T_i, T_{r_j}) = Q_i^{\mathrm{T}}(T_i) \exp\left(-\frac{m_i \mathcal{U}_i^{\mathrm{F}}}{\mathrm{k_B} T_{r_j}}\right), \quad Q_i^{\mathrm{T}}(T_i) = \left(\frac{2\pi m_i \mathrm{k_B} T_i}{\mathrm{h_P^2}}\right)^{3/2}, \quad i, j \in \mathrm{S},$$

and the heavy-particle temperature $T_i = T_{\mathfrak{h}}$, $i \in \mathrm{H}$. The temperature dependence for the direct and reverse rate coefficients is strongly connected with the reaction mechanism. The ionization energy is provided by the catalyst at a reaction temperature defined as

$$T_{r_{\mathfrak{e}}} = T_{\mathfrak{e}}, \qquad T_{r_i} = T_{\mathfrak{h}}, \quad i \in \mathrm{H}.$$

It is important to mention that the sound structure for the rate coefficients given in Eq. (2.7) results from the scaling used in Graille *et al.* (2008) for the energy conservation in the reactive collisions. The translational energy transferred from heavy particles to electrons, is expressed as

$$\Delta E_{\mathfrak{h}}^{0} = \tfrac{3}{2} n_{\mathfrak{e}} \mathrm{k_B} (T_{\mathfrak{e}} - T_{\mathfrak{h}}) \frac{1}{\tau},$$

where τ is the average collision time at which this energy transfer occurs. Defining global electron and heavy-particle particle energies

$$\mathcal{E}_{\mathfrak{e}} = \rho_{\mathfrak{e}} e_{\mathfrak{e}}^{\mathrm{T}} + \rho_{\mathfrak{e}} \mathcal{U}_{\mathfrak{e}}^{\mathrm{F}}, \quad \mathcal{E}_{\mathfrak{h}} = \rho_{\mathfrak{h}} e_{\mathfrak{h}}^{\mathrm{T}} + \sum_{j \in \mathrm{H}} \rho_j \mathcal{U}_j^{\mathrm{F}},$$

after some algebra, it is possible to write an alternative formulation for Eqs. (2.5) and (2.6) as follows,

$$\mathrm{d}_t(\mathcal{E}_{\mathfrak{e}}) = -\Delta E_{\mathfrak{h}}^{0} + \Delta_{r_{\mathfrak{e}}}^{\mathrm{F}} \omega_{\mathfrak{e}}^{r_{\mathfrak{e}}0} + \Delta_{r_{\mathfrak{i}}}^{\mathrm{F}} \omega_{\mathfrak{e}}^{r_{\mathfrak{i}}0} + \Delta_{r_{\mathfrak{n}}}^{\mathrm{F}} \omega_{\mathfrak{e}}^{r_{\mathfrak{n}}0}, \tag{2.8}$$

$$\mathrm{d}_t(\mathcal{E}_{\mathfrak{h}}) = \Delta E_{\mathfrak{h}}^{0} - \Delta_{r_{\mathfrak{e}}}^{\mathrm{F}} \omega_{\mathfrak{e}}^{r_{\mathfrak{e}}0} - \Delta_{r_{\mathfrak{i}}}^{\mathrm{F}} \omega_{\mathfrak{e}}^{r_{\mathfrak{i}}0} - \Delta_{r_{\mathfrak{n}}}^{\mathrm{F}} \omega_{\mathfrak{e}}^{r_{\mathfrak{n}}0}. \tag{2.9}$$

with the energy exchange coefficients by heavy-particle impact ionization $\Delta_{r_{\mathfrak{i}}}^{\mathrm{F}} = \Delta_{r_{\mathfrak{n}}}^{\mathrm{F}} = m_{\mathfrak{e}}\, \mathcal{U}_{\mathfrak{e}}^{\mathrm{F}}$, and by electron-impact ionization, $\Delta_{r_{\mathfrak{e}}}^{\mathrm{F}} = m_{\mathfrak{n}}\, \mathcal{U}_{\mathfrak{n}}^{\mathrm{F}} - m_{\mathfrak{i}}\, \mathcal{U}_{\mathfrak{i}}^{\mathrm{F}}$. The ionization energy is obtained from the relation $\Delta\mathcal{E} = \Delta_{r_{\mathfrak{i}}}^{\mathrm{F}} - \Delta_{r_{\mathfrak{e}}}^{\mathrm{F}}$. Using Eqs. (2.3) and (2.4), the total mass $\rho = \rho_{\mathfrak{e}} + \rho_{\mathfrak{h}}$, and the total charge, $\mathcal{Q} = q_{\mathfrak{e}}(n_{\mathfrak{e}} - n_{\mathfrak{i}})$, with the electron charge $q_{\mathfrak{e}}$, are conserved for the mixture, *i.e.*,

$$\mathrm{d}_t \rho = 0, \tag{2.10}$$

$$\mathrm{d}_t \mathcal{Q} = 0. \tag{2.11}$$

Adding Eqs. (2.8) and (2.9), the total energy $\mathcal{E} = \mathcal{E}_{\mathfrak{e}} + \mathcal{E}_{\mathfrak{h}}$, is also conserved

$$\mathrm{d}_t \mathcal{E} = 0. \tag{2.12}$$

The system evolves at constant total density, total charge and total energy. It is important to mention that no further assumption is made on the internal variables, defined by Woods (1986) as the mixture composition and energy distribution among the species.

In addition to the energy, other relevant thermodynamic functions are introduced. First, the species Gibbs free energy is defined by the relations

$$\rho_i g_i = n_i \mathrm{k_B} T_i \ln\Big(\frac{n_i}{Q_i^{\mathrm{T}}(T_i)}\Big) + \rho_i \mathcal{U}_i^{\mathrm{F}}, \quad i \in \mathrm{S}.$$

The species enthalpy is given by $\rho_i h_i = \frac{5}{2} n_i \mathrm{k_B} T_i + \rho_i \mathcal{U}_i^{\mathrm{F}}$, $i \in \mathrm{S}$, and the species entropy by $s_i = (h_i - g_i)/T_i$, $i \in \mathrm{S}$. The mixture entropy reads $\mathcal{S} = \sum_{j \in \mathrm{S}} \rho_j s_j$. For reactive plasmas, Gibbs relation is found to be

$$\mathrm{d}_t \mathcal{S} = \Upsilon_{\mathrm{th}} + \Upsilon_{\mathrm{ch}} \tag{2.13}$$

The first term of the right-hand-side of Eq. (2.13)

$$\Upsilon_{\mathrm{th}} = \frac{\mathrm{d}_t(\rho_{\mathfrak{e}} e_{\mathfrak{e}}^{\mathrm{T}}) + \Delta\mathcal{E}\, \omega_{\mathfrak{e}}^{r_{\mathfrak{e}}0}}{T_{\mathfrak{e}}} + \frac{\mathrm{d}_t(\rho_{\mathfrak{h}} e_{\mathfrak{h}}^{\mathrm{T}}) + \Delta\mathcal{E}(\omega_{\mathfrak{i}}^{r_{\mathfrak{i}}0} - \omega_{\mathfrak{n}}^{r_{\mathfrak{n}}0})}{T_{\mathfrak{h}}},$$

is the entropy production rate due to thermal non-equilibrium. Using Eqs. (2.6) and (2.5), this quantity is shown to be non-negative

$$\Upsilon_{\mathrm{th}} = \tfrac{3}{2} n_{\mathfrak{e}} (T_{\mathfrak{e}} - T_{\mathfrak{h}})^2 \frac{1}{T_{\mathfrak{e}} T_{\mathfrak{h}} \tau}. \tag{2.14}$$

The second term of the right-hand-side of Eq. (2.13)

$$\Upsilon_{\mathrm{ch}} = -\sum_{i\in \mathrm{S}} \left(\frac{m_{\mathfrak{e}} g_{\mathfrak{e}} \omega_{\mathfrak{e}}^{r_i 0}}{T_{\mathfrak{e}}} + \sum_{j\in \mathrm{H}} \frac{m_j g_j \omega_j^{r_i 0}}{T_{\mathfrak{h}}} \right),$$

is the entropy production rate due to chemical reactions. We notice that each of the usual entropy production terms associated with a chemical reaction, $-m_{\mathfrak{e}} g_{\mathfrak{e}} \omega_{\mathfrak{e}}^{r_i 0}/T_{\mathfrak{e}} - \sum_{j\in \mathrm{H}} m_j g_j \omega_j^{r_i 0}/T_{\mathfrak{h}}$, $i \in \mathrm{S}$, is not positive. Thus, the conventional expression for the Gibbs free energy does not allow for 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 propose to define a reaction dependent Gibbs free energy as

$$\rho_i \tilde{g}_i^{r_j} = \rho_i g_i + \Big(\frac{T_i}{T_{r_j}} - 1 \Big) \rho_i \mathcal{U}_i^{\mathrm{F}}, \quad i, j \in \mathrm{S},$$

and rewrite the second term of the right-hand-side of Eq. (2.13) as

$$\Upsilon_{\mathrm{ch}} = \sum_{j\in \mathrm{S}} \Upsilon_{\mathrm{ch}}^{r_j}.$$

The entropy production rate due to chemistry,

$$\Upsilon_{\mathrm{ch}}^{r_i} = -\frac{\tilde{g}_{\mathfrak{e}}^{r_i} \omega_{\mathfrak{e}}^{r_i 0}}{T_{\mathfrak{e}}} - \sum_{j\in \mathrm{H}} \frac{m_j \tilde{g}_j^{r_i} \omega_j^{r_i 0}}{T_{\mathfrak{h}}}, \quad i \in \mathrm{S},$$

can be rewritten, after some algebra as

$$\Upsilon_{\mathrm{ch}}^{r_i} = \mathcal{K}_{r_i}(T_{r_i})\, \Lambda \left(\tfrac{n_{\mathfrak{n}}}{Q_{\mathfrak{n}}(T_{r_i}, T_{\mathfrak{h}})} \tfrac{n_i}{Q_i(T_{r_i}, T_i)}, \tfrac{n_{\mathfrak{i}}}{Q_{\mathfrak{i}}(T_{r_i}, T_{\mathfrak{h}})} \tfrac{n_{\mathfrak{e}}}{Q_{\mathfrak{e}}(T_{r_i}, T_{\mathfrak{e}})} \tfrac{n_i}{Q_i(T_{r_i}, T_i)} \right), \quad i \in \mathrm{S}, \tag{2.15}$$

where the function $\Lambda(x, y) = (x - y) \log(x/y)$ is positive. The terms $\Upsilon_{\mathrm{ch}}^{r_i}$ are non-negative, and the second law of thermodynamics is thus satisfied.

3. Results

In this section, we use a singular perturbation analysis to study the dynamics of plasmas in thermo-chemical non-equilibrium.

3.1. *Second law of thermodynamics and global equilibrium*

A compact vectorial notation is introduced to study the global equilibrium of the system of Eqs. (2.3)-(2.4) and (2.8)-(2.9). The temporal evolution of the conservative variable $U = (\varrho^t, \mathcal{E}_{\mathfrak{e}}, \mathcal{E}_{\mathfrak{h}})^t$, with the mass density vector $\varrho^t = (\rho_{\mathfrak{e}}, \rho_{\mathfrak{i}}, \rho_{\mathfrak{n}})$, is described by means of the five-dimensional dynamical system

$$\mathrm{d}_t U = \Omega(U), \quad U(0) = U_0, \tag{3.1}$$

$$\Omega(U) = \Omega_{\mathrm{ch}}(U) + \Omega_{\mathrm{th}}(U), \quad \Omega_{\mathrm{ch}}(U) = \sum_{j\in \mathrm{S}} \omega_{\mathfrak{e}}^{r_j 0}(U)\, M^{*r_j} \nu^*, \quad \Omega_{\mathrm{th}} = \Delta E_{\mathfrak{e}}^0(U)\, \kappa. \tag{3.2}$$

The reaction vector in the composition space reads $\nu^t = (1, 1, -1) \in \mathbb{R}^3$, and the reaction vector in the full composition and energy space, $\nu^{*t} = (\nu^t, 1, -1) \in \mathbb{R}^5$. Mass matrices are defined in these two spaces as $M = \mathrm{diag}(m_{\mathfrak{e}},\, m_{\mathfrak{i}},\, m_{\mathfrak{n}})$ and $M^{*r_j} = \mathrm{diag}(M, \Delta_{r_j}^{\mathrm{F}}, \Delta_{r_j}^{\mathrm{F}})$. The source term associated to thermal relaxation Ω_{th} involves the vector $\kappa^t = (0, 0, 0, 1, -1)$.

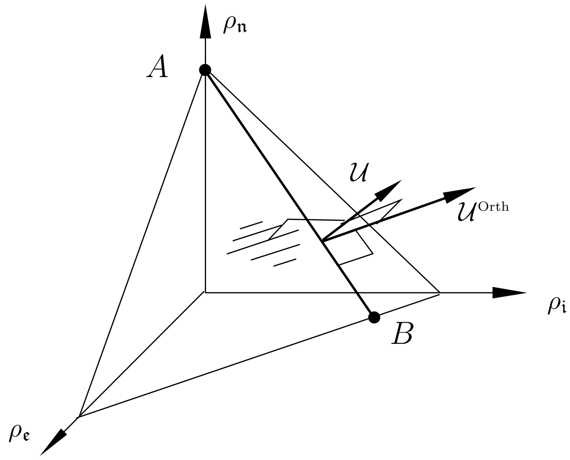

FIGURE 1. The reaction simplex is the line segment AB in the composition space $(\rho_{\mathfrak{e}}, \rho_{\mathfrak{i}}, \rho_{\mathfrak{n}})$. The total charge is assumed to be zero. Point A corresponds to a fully neutral mixture, and point B, to a fully ionized mixture. The space orthogonal to the reaction simplex is spanned by the orthogonal basis $(\mathcal{U},\mathcal{U}^{\mathrm{Orth}})$.

The total mass density reads $\rho = \langle \varrho, \mathcal{U} \rangle$, where symbol $\langle \;,\; \rangle$ denotes the euclidian scalar product, and $\mathcal{U}^t = (1,1,1)$, the unit vector in $\mathbb{R}^3$. The reaction vector space is one-dimensional, $\mathcal{R} = \mathrm{span}\{\ \nu\ \}$, and we denote the augmented vector space $\mathcal{R}^* = \mathrm{span}\{\ \nu^*\ \}$. The reaction simplex, where ϱ lives, is the one-dimensional affine subspace $\mathfrak{R} = (\varrho_0 + n_0 M \mathcal{R}) \cap (0,\infty)^3$, where quantity n_0 is a dimensional number density (see figure 1). In addition to ρ, we define $\rho^{\mathrm{Orth}} = \langle \varrho, \mathcal{U}^{\mathrm{Orth}} \rangle$, where the vector $\mathcal{U}^{\mathrm{Orth}} = (-m_{\mathfrak{i}} - m_{\mathfrak{n}}, m_{\mathfrak{n}} + m_{\mathfrak{e}}, m_{\mathfrak{i}} - m_{\mathfrak{e}})^t / m_{\mathfrak{n}}$ is orthogonal to $\mathcal{U}$ as well as orthogonal to $M\nu$ in $\mathbb{R}^3$. Then $\mathrm{d}_t \rho^{\mathrm{Orth}} = 0$ and quantity ρ^{Orth} is invariant by the dynamical system (3.1), as a result of the total mass and charge conservation Eqs. (2.10) and (2.11).

PROPOSITION 3.1. *Let us assume* $\varrho_0 \in (0,\infty)^3$, $\mathcal{E}_{\mathfrak{e}0} \in (0,\infty)$, $\mathcal{E}_{\mathfrak{h}0} \in (0,\infty)$, *and under some classical properties that can be found in Massot (2002), there exists a smooth global in time solution of the dynamical system* (3.1)*. The species densities are positive and there exists two positive temperatures,* T_1 *and* T_2*, bounding the temperatures:* $T_1 \leq T_{\mathfrak{e}}(t) \leq T_2$, $T_1 \leq T_{\mathfrak{h}}(t) \leq T_2$.

The system admits an entropic structure, i.e., it can be symmetrized through the use of the entropic variable V, $V = \partial_U \sigma^t = (\mathcal{Y}^t, -1/T_{\mathfrak{e}}, -1/T_{\mathfrak{h}})^t$, *where* $\sigma = -\mathcal{S}$ *is the mathematical entropy and* $\mathcal{Y} = (g_{\mathfrak{e}}/T_{\mathfrak{e}}, g_{\mathfrak{i}}/T_{\mathfrak{h}}, g_{\mathfrak{n}}/T_{\mathfrak{h}})^t$ *:*

$$\widetilde{A}_0(V)\ \mathrm{d}_t V = \widetilde{\Omega}(V), \qquad \widetilde{\Omega}(V) = \Omega(U),$$

where $\widetilde{A}_0(V) = \partial_V U = (\partial_{UU}\sigma)^{-1}$ *is a symmetric positive definite matrix and where* $\mathrm{d}_t \sigma = -\mathrm{d}_t \mathcal{S} = \langle V, \widetilde{\Omega}(V) \rangle$ *is non-positive; it expresses the decrease of the entropy* σ *due to chemical reactions and thermal relaxation as well as the convexity of the mathematical entropy as a function of the variable* U*.*

There exists a unique equilibrium point $U^{\mathrm{eq}} = (\varrho^{\mathrm{eq}}, \mathcal{E}_{\mathfrak{e}}^{\mathrm{eq}}, \mathcal{E}_{\mathfrak{e}}^{\mathrm{eq}}) \in \mathcal{O}_U$, *where* ϱ^{eq} *is in the reaction simplex, such that the source term vanishes* $\Omega(U^{\mathrm{eq}}) = 0$ *or equivalently* $\omega_e^{r_i 0}(U^{\mathrm{eq}}) = 0$ *for all* $i \in \mathrm{S}$ *and* $T_{\mathfrak{e}}^{\mathrm{eq}} = T_{\mathfrak{h}}^{\mathrm{eq}}$, *or equivalently* $V^{\mathrm{eq}}(U^{\mathrm{eq}}) \in (M^{*r_i} \mathcal{R}^*)^{\perp}$, *for all* $i \in \mathrm{S}$.

The equilibrium composition and energies are smooth functions of $(\rho_0, \rho_0^{\mathrm{Orth}}, \mathcal{E}_0)$, *which* *are invariant by the dynamical system* (3.1).

The linearization of the source term at U^{eq} *has non-positive eigenvalues and exactly two negative real eigenvalues. The mathematical entropy production from chemical reactions and thermal relaxation admits both zero as a strict maximum at* U^{eq}.

Proof. The arguments are similar to what can be found in Massot (2002) and are based on the previous expressions for thermal relaxation Eq. (2.14) and the entropy production from chemical reactions Eq. (2.15); these expressions directly yield the thermal equilibrium, the orthogonality relations on the entropic variables, as well as the equilibrium conditions. ☐

It is important to mention two issues in the previous results: we have provided, with the help of kinetic theory and of a multi-scale Chapman-Enkog expansion a set of ordinary differential equations which satisfies a second principle of thermodynamics and allows for defining properly global equilibrium. One of the key issues, however, is to provide a rigorous framework in order to define chemical quasi-equilibrium in thermal non-equilibrium where many possibilities and Saha law can be found in the litterature; this is the purpose of the following section.

3.2. *Chemical quasi-equilibrium for plasmas in thermal non-equilibrium*

In this section, we investigate particular flow conditions for which the thermal relaxation term Ω_{th} is assumed to be much lower that the chemical relaxation term Ω_{ch}, i.e., denoting by μ a ratio between a chemical time and a thermal relaxation time which is supposed to be small with respect to one, the system (3.1) is rewritten as:

$$\mathrm{d}_t U = \frac{\Omega_{\mathrm{ch}}(U)}{\mu} + \Omega_{\mathrm{th}}(U), \quad U(0) = U_0, \tag{3.3}$$

and a singular perturbation analysis of the dynamics of such a system is carried out in the limit $\mu \to 0$.

3.2.1. *Ionization by sole electron impact*

A simplified case, for which $\Omega = \Omega^{\mathfrak{e}} = \omega_{\mathfrak{e}}^{r_{\mathfrak{e}}0} M^{\mathfrak{e}} \nu$, is first examined. The chemical mechanism comprises ionization only by electron impact. The dynamics of the system, in the approximation of small μ parameter, can be decomposed into an inner temporal layer involving only chemical reactions and an outer temporal layer at chemical quasi-equilibrium involving only thermal relaxation toward the unique global equilibrium described in the previous section. We will first tackle the problem of the inner layer for U^{inn}, the typical time of which is denoted by $\tau = t/\mu$. It satisfies the following set of equations:

$$\mathrm{d}_\tau U^{\mathrm{inn}} = \Omega^{\mathfrak{e}}(U^{\mathrm{inn}}) = \omega_{\mathfrak{e}}^{r_{\mathfrak{e}}0}(U^{\mathrm{inn}}) M^{r_{\mathfrak{e}}\,*} \nu^*, \quad U^{\mathrm{inn}}(0) = U_0. \tag{3.4}$$

For this time scale τ, the inner layer is a regular perturbation of the dynamics of the full system at short time scales, where thermal relaxation does not play any role and fast reactions govern the evolution of the system. Let us emphasize that, within the inner layer approximation, the translation energy of the heavy particles is conserved $\mathrm{d}_\tau(\rho_{\mathfrak{h}} e_{\mathfrak{h}}^{\mathrm{T}}) = 0$, as well as the total energy, so that we also have $\mathrm{d}_\tau(\mathcal{E}_{\mathfrak{e},r_{\mathfrak{e}}}^{\mathrm{F}}) = 0$, where the augmented electron energy is given by the expression $\mathcal{E}_{\mathfrak{e},r_{\mathfrak{e}}}^{\mathrm{F}} = \rho_{\mathfrak{e}} e_{\mathfrak{e}}^{\mathrm{T}} + \sum_{i \in \mathrm{S}} \rho_i \mathfrak{U}_i^{\mathrm{F}}$. The dynamics of the full original system does not possess additional invariants, but its dynamics can be approximated, for short time scales, to the one of the inner layer.

Proposition 3.2. *Under the assumption of proposition 3.1 there exists a smooth global in time solution of the dynamical system* (3.4). *The species densities are positive and there exists two positive temperatures, T_1 and T_2, bounding the temperatures: $T_1 \leq T_{\mathfrak{e}}^{\text{inn}}(\tau) \leq T_2$, $T_1 \leq T_{\mathfrak{h}}^{\text{inn}}(\tau) \leq T_2$, for all μ.*

The system admits an entropic structure, i.e., it can be symmetrized through the use of the entropic variable V^{inn} and the system satisfies a second principle of thermodynamics, i.e. $\mathrm{d}_\tau \sigma(U^{\text{inn}})$ is non-positive; it expresses the decrease of the entropy σ purely due to the chemical reaction.

There exists a unique chemical quasi-equilibrium point $U^{\text{qe}} = (\varrho^{\text{qe}}, \mathcal{E}_{\mathfrak{e}}^{\text{qe}}, \mathcal{E}_{\mathfrak{h}}^{\text{qe}})$, where ϱ^{qe} is in the reaction simplex, such that the source term vanishes $\Omega_{\text{ch}}(U^{\text{qe}}) = 0$ or equivalently $\omega_{\mathfrak{e}}^{r_{\mathfrak{e}}\,0}(U^{\text{qe}}) = 0$, or equivalently $V^{\text{qe}}(U^{\text{qe}}) \in (M^{*r_{\mathfrak{e}}}\mathcal{R}^*)^{\perp}$.

The quasi-equilibrium composition and energies are smooth function of $(\rho_0$, ρ_0^{Orth}, $(\rho_{\mathfrak{h}} e_{\mathfrak{h}}^{\text{T}})_0$, $(\mathcal{E}_{\mathfrak{e},r_{\mathfrak{e}}}^{\text{F}})_0)$ which are invariant by the dynamical system (3.4). *The linearization of the source term at U^{qe} has non-positive eigenvalues and exactly one negative real eigenvalue. The mathematical entropy production from chemical reactions admits zero as a strict maximum at U^{qe} over the reaction simplex.*

Finally, the unique chemical quasi-equilibrium is asympotically stable and attracts the long time behavior of the dynamical system (3.4).

Proof. The approach is a direct extension of Massot (2002) to thermal non-equilibrium and we will only present a sketch of the proof. The first key issue is related to the ability to define a smooth manifold of chemical equilibrium at constant temperatures for both electrons and heavy particles, that is equilibrium of the new dynamical system $\mathrm{d}_\tau(\widetilde{U}_1^{\text{inn}}, \widetilde{U}_2^{\text{inn}}, \widetilde{U}_3^{\text{inn}})^t = \omega_{\mathfrak{e}}^{r_{\mathfrak{e}}\,0}((\widetilde{U}_1^{\text{inn}}, \widetilde{U}_2^{\text{inn}}, \widetilde{U}_3^{\text{inn}}, T_{\mathfrak{e}}, T_{\mathfrak{h}})^t) M^{r_{\mathfrak{e}}}\nu$. In order to define such equilibrium, we study the chemical dynamics at constant temperatures and use the Helmholtz free energy

$$\mathcal{H}^{r_{\mathfrak{e}}} = \sigma + \frac{\mathcal{E}_{\mathfrak{e},r_{\mathfrak{e}}}^{\text{F}}}{T_{\mathfrak{e}}} + \frac{\rho_{\mathfrak{h}} e_{\mathfrak{h}}^{\text{T}}}{T_{\mathfrak{h}}};$$

we heavily rely on the fact the $\mathcal{E}_{\mathfrak{e},r_{\mathfrak{e}}}^{\text{F}}$ and $\rho_{\mathfrak{h}} e_{\mathfrak{h}}^{\text{T}}$ are invariant by the original dynamical system (3.3). It allows for defining a smooth two-dimensional manifold $\widetilde{U}^{\text{eq}}(T_{\mathfrak{e}}, T_{\mathfrak{h}}, \rho_0, \rho_0^{\text{Orth}})$ for all $(T_{\mathfrak{e}}, T_{\mathfrak{h}}) \in [T_1, T_2]$. Then, for a fixed $T_{\mathfrak{e}} \in [T_1, T_2]$, it can be shown that $\rho_{\mathfrak{h}} e_{\mathfrak{h}}^{\text{T}}$ is a monotone function of $T_{\mathfrak{h}}$ so that there exists a unique $T_{\mathfrak{h}}^{\text{eq}}$ such that $\rho_{\mathfrak{h}} e_{\mathfrak{h}}^{\text{T}} = (\rho_{\mathfrak{h}} e_{\mathfrak{h}}^{\text{T}})_0$. This defines a smooth one-dimensional manifold $\widetilde{U}^{\text{eq}}(T_{\mathfrak{e}}, T_{\mathfrak{h}}^{\text{eq}}((\rho_{\mathfrak{h}} e_{\mathfrak{h}}^{\text{T}})_0), \rho_0, \rho_0^{\text{Orth}})$ of chemical equilibrium at constant electron temperature. The last step consists in showing that $\mathcal{E}_{\mathfrak{e},r_{\mathfrak{e}}}^{\text{F}}(\widetilde{U}^{\text{eq}})$ is a smooth monotone function of $T_{\mathfrak{e}}$ so that there exists a unique $T_{\mathfrak{e}}^{\text{eq}}$ such that $\mathcal{E}_{\mathfrak{e},r_{\mathfrak{e}}}^{\text{F}} = (\mathcal{E}_{\mathfrak{e},r_{\mathfrak{e}}}^{\text{F}})_0$. The obtained equilibrium can be shown to be the global chemical equilibrium that satisfies all the properties in the proposition. It is in particular straightforward to prove that this equilibrium is the global maximizer of the mathematical entropy production under the original constraints. We further can use the estimate on the entropy production used in Massot (2002) in order to prove that this equilibrium is asymptotically stable and attracts the full dynamics of the inner layer. □

Following Massot (2002), the fast chemical dynamics which leads to chemical quasi-equilibrium provides us with the ability of partitioning the system (3.3) into fast and slow variables. The fast variable U^{Fast} is simply defined as a projection; let us denote $U^{\text{Fast}} = (\Pi^{\text{Fast}})^t\, U$, where $\Pi^{\text{Fast}} = M^{*r_{\mathfrak{e}}}\nu$ is the projection matrix, up to a metric, onto the reaction vector space. In fact, in our particular simple case, it is easy to describe the basis of $(M^{*r_{\mathfrak{e}}}\mathcal{R}^*)^{\perp}$ since it corresponds to the four invariant variables of our dynamical system: $a_1 = (\mathcal{U}^t, 0, 0)^t$ for the conservation of mass, $a_2 = (0, 0, 0, 1, 1)^t$ for the conservation of total energy, $a_3 = (\mathcal{U}^{\text{Orth},t}, 0, 0)^t$ for the conservation of ρ^{Orth} and $a_4 = (0, \mathfrak{U}_i^{\text{F}}, \mathfrak{U}_n^{\text{F}}, 1, 0)^t$ for the conservation of augmented electron energy. These vectors form a basis which was denoted $\Pi^{\perp} = [a_1, a_2, a_3, a_4]$ in Massot (2002).

Following Massot (2002) the orthogonality relations satisfied at chemical quasi-equilibrium by the entropic variable defines, once a basis of $(M^{*r_{\mathfrak{e}}}\mathcal{R}^*)^{\perp}$ is chosen, the slows variable which is denoted by $U^{\perp} = (\Pi^{\perp})^t\, U$. We will then naturally have

$$\mathbb{R}^5 = M^{*r_{\mathfrak{e}}}\mathcal{R}^* \overset{\perp}{\oplus} \text{span}\{\ a_i,\ i \in [1, 4]\ \}.$$

From there, the outer layer can easily be defined:

$$\mathrm{d}_t U^{\perp,\text{out}} = (\Pi^{\perp})^t \Omega_{\text{th}}(U^{\text{qe}}(U^{\perp,\text{out}})), \tag{3.5}$$

which can also be rewritten :

$$\mathrm{d}_t \rho = 0, \tag{3.6}$$

$$\mathrm{d}_t \mathcal{E} = 0, \tag{3.7}$$

$$\mathrm{d}_t \rho^{\text{Orth}} = 0, \tag{3.8}$$

$$\mathrm{d}_t \mathcal{E}^{\text{F}}_{\mathfrak{e},r_{\mathfrak{e}}} = -\Delta E^0_{\mathfrak{h}} \Big(U^{\text{qe}}\big(\rho_0, \rho_0^{\text{Orth}}, (\rho_{\mathfrak{h}} e^{\text{T}}_{\mathfrak{h}})_0, \mathcal{E}^{\text{F}}_{\mathfrak{e},r_{\mathfrak{e}}}\big)\Big), \tag{3.9}$$

with the help of the slow variable $\mathcal{E}^{\text{F},\text{qe}}_{\mathfrak{e},r_{\mathfrak{e}}}$ left invariant by the fast chemical reaction. This last equation describes rather straightforwardly the fact that the chemical quasi-equilibrium will evolve owing to heat exchange and converge toward the unique global equilibrium point.

PROPOSITION 3.3. *The outer layer follows a second principle of thermodynamics, that is,* $\mathrm{d}_\tau \sigma^{\text{out}} \leq 0$*, where* $\sigma^{\text{out}} = \sigma(U^{\text{out}})$*. In addition, the global equilibrium point defined in the previous section is asymptotically stable and the dynamics of the outer layer converges toward this point.*

Proof. The entropy $\sigma^{\perp}(U^{\perp,\text{out}}) = \sigma\big(U(U^{\perp,\text{out}})\big)$ is a smooth convex function of $U^{\perp,\text{out}}$; the corresponding entropic variable on the chemical quasi-equilibrium manifold is such that, since $V = \Pi^{\perp} V^{\perp,\text{out}}$:

$$V^{\perp,\text{out}} = \partial_{U^{\perp,\text{out}}} \sigma^{\perp}, V \in \big((M^{r_{\mathfrak{e}}\,*}\mathcal{R}^{\text{Fast}\,*})\big)^{\perp}.$$

Differentiating $(\Pi^{\text{Fast}})^t\, V = 0$ with respect to $U^{\perp}$, and using $\partial^2_{U^{\perp,\text{out}}\,U^{\perp,\text{out}}} \sigma^{\perp} = \partial_{U^{\perp}} V^{\perp,\text{out}}$, we finally get :

$$\partial^2_{U^{\perp,\text{out}}\,U^{\perp,\text{out}}} \sigma = \big(\Pi^{\perp} J^{\perp} + \Pi^{\text{Fast}} J^{\text{Fast}} \partial_{U^{\perp,\text{out}}} U^{\text{Fast qe}}\big)^t \partial^2_{U\,U} \sigma \big(\Pi^{\perp} J^{\perp} + \Pi^{\text{Fast}} J^{\text{Fast}} \partial_{U^{\perp,\text{out}}} U^{\text{Fast qe}}\big),$$

where J^{Fast} and $J^{\perp}$ are metric matrices related to the projections Π^{Fast} and $\Pi^{\perp}$, so that $\sigma^{\perp}$ is a convex function of $U^{\perp,\text{out}}$ at quasi-equilibrium ($\partial^2_{U\,U}\sigma$ is symmetric positive definite), which allows this conclusion. The chemical entropy production at quasi-equilibrium reads $\partial_t \sigma^{\perp} = \langle V^{\perp,\text{out}}, (\Pi^{\perp})^t \Omega_{\text{th}} \rangle = \langle V, \Omega_{\text{th}} \rangle$, so that it is non-positive. The end of the proof is then classical and we refer to Massot (2002). $\square$

Thus, we can completely characterize through a singular perturbation analysis the dynamical behavior of the system in the limit of small μ. We do not provide the details of the proof omitted here for two reasons. First the principle of such an analysis was already provided in Massot (2002); second, it is not the scope of the present contribution to focus on mathematical background, but rather to focus on the physics of the considered phenomena.

It can then be proved that the dynamics of (3.3) can be approximated in the following way:

$$\begin{aligned} U^{\perp} &= U^{\perp,\mathrm{out}} + \mathcal{O}(\mu), \\ U^{\mathrm{Fast}} &= U^{\mathrm{Fast\ qe}}(U^{\perp,\mathrm{out}}) + \mathcal{O}(\exp(-\delta\, t/\mu)) + \mathcal{O}(\mu), \end{aligned}$$

where both the inner layer where $U^{\perp \mathrm{inn}} = U_0^{\perp}$ and $U^{\mathrm{Fast\ inn}}$ converge toward $U^{\mathrm{Fast\ qe}}$ and the outer layer $U^{\perp,\mathrm{out}}$ with $U^{\mathrm{Fast\ qe}}(U^{\perp,\mathrm{out}})$ satisfy a second principle of thermodynamics. Such an expansion provides a very precise sense to the notion of chemical quasi-equilibrium in the framework of thermal non-equilibrium because it describes the outer layer, that is the slow dynamics, of (3.3) through thermal relaxation, whereas the reaction operates in temporal boundary layers associated to the time ratio μ. Let us emphasize that the same study can be conducted in the framework of the ionization by the sole heavy particles, leading to the same type of results. As a conclusion, for this case of a single ionization reaction through electron impact, we have been able to identify and characterize the two-temperature chemical quasi-equilibrium. The purpose of the following subsection is to conduct the same kind of analysis in the framework of the whole set of three ionization reactions.

3.2.2. *Ionization by electron and heavy-particle impact*

In this section, we only have to tackle the problem of the inner layer. Starting from the same initial conditions as the full system, it satisfies the following set of equations :

$$\mathrm{d}_\tau U^{\mathrm{inn}} = \Omega(U^{\mathrm{inn}}), \quad U^{\mathrm{inn}}(0) \,=\, U_0, \tag{3.10}$$

where the chemical source term is defined by (3.2). Once again, it represents the dynamics at short time scales where thermal relaxation does not play any role, but where the three fast reactions govern the evolution of the system. It is important to mention that for this configuration, we do not have the conservation of translation energy of heavy species $\mathrm{d}_\tau(\rho_{\mathfrak{h}} e_{\mathfrak{h}}^{\mathrm{T}}) \neq 0$, but we still have the conservation of total energy.

Proposition 3.4. *Under the assumption of proposition 3.1 there exists a smooth global in time solution of the dynamical system* (3.4). *The species densities are positive and there exists two positive temperatures, T_1 and T_2, bounding the temperatures: $T_1 \leq T_{\mathfrak{e}}^{\mathrm{inn}}(\tau) \leq T_2$, $T_1 \leq T_{\mathfrak{h}}^{\mathrm{inn}}(\tau) \leq T_2$.*

The system admits an entropic structure, i.e., it can be symmetrized through the use of the entropic variable V^{inn} and the system satisfies a second principle of thermodynamics, i.e. $\mathrm{d}_\tau \sigma(U^{\mathrm{inn}})$ is non-positive; it expresses the decrease of the entropy σ purely due to the chemical reaction.

There exists a unique chemical equilibrium point $U^{\mathrm{eq}} = (\varrho^{\mathrm{eq}}, \mathcal{E}_{\mathfrak{e}}^{\mathrm{eq}}, \mathcal{E}_{\mathfrak{h}}^{\mathrm{eq}})$, where ϱ^{eq} is in the reaction simplex, such that the source term vanishes $\Omega_{\mathrm{ch}}(U^{\mathrm{eq}}) = 0$ or equivalently $\omega_{\mathfrak{e}}^{r_i 0}(U^{\mathrm{eq}}) = 0$, for all $i \in \mathrm{S}$, or equivalently $V^{\mathrm{eq}}(U^{\mathrm{eq}}) \in (M^{*r_i}\mathcal{R}^*)^{\perp}$, for all $i \in \mathrm{S}$.

However, this chemical equilibrium satisfies the extra property : $T_{\mathfrak{e}}^{\mathrm{eq}} = T_{\mathfrak{h}}^{\mathrm{eq}}$, i.e., ionization by electron and heavy-particle impact with different temperatures leads to fast temperature relaxtion and the global chemical and thermal equilibrium is reached within the inner layer.

Thus the equilibrium composition and energies are smooth functions of $(\rho_0, \rho_0^{\mathrm{Orth}}, \mathcal{E}_0)$

which are invariant by the dynamical system (3.4)*. The mathematical entropy production from chemical reactions admits zero as a strict maximum at* U^{qe} *over the reaction simplex.*

Finally, the unique chemical quasi-equilibrium is asympotically stable and attracts the long time behavior of the dynamical system (3.4)*.*

Proof. Most of the material has already been given either in the previous parts or in Massot (2002) and we focus on the key issues. It is not no longer possible in this context to define chemical equilibrium at constant electron and heavy species temperature, because the only invariant quantity by the dynamical system in terms of energy is the only global energy $\mathcal{E}$. The second point, related to the first, is a direct interpretation of the orthogonality relations in terms of entropic variables $V^{\mathrm{eq}}(U^{\mathrm{eq}}) \in (M^{*r_i}\mathcal{R}^*)^{\perp}$, for all $i \in \mathrm{S}$, that is a direct equivalent formulation of a zero entropy production rate. This constraint directly implies the following relation:

$$\Delta\mathcal{E}\left(\frac{1}{T_{\mathfrak{e}}^{\mathrm{eq}}} - \frac{1}{T_{\mathfrak{h}}^{\mathrm{eq}}}\right) = 0,$$

so that the two types of chemical reactions systematically yield thermal equilibrium. ☐

Let us emphasize that when ionization through both electron and heavy-particle impact is considered, the inner layer for short time scale directly leads to thermal equilibrium. Thus, the global thermo-chemical equilibrium is reached within a short time scale, involving only chemical reactions, even if thermal relaxation through elastic collisions is not efficient and slow. To our knowledge, this approach sheds some completely new light on this matter and has not been used previously for such multicomponent reactive plasmas out of thermal equilibrium.

4. Future plans

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). Our results are complementary to the conservation equations and transport flux expressions derived by Graille *et al.* (2009) for non-homogeneous plasmas in the presence of external forces, because 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).

From a numerical point of view, it can be difficult to simulate plasmas flows with fast chemical reactions; however, using operator splitting such as in Descombes & Massot (2004); Descombes *et. al* (2003), it is not necessary to reduce the numerical stiffness induced by fast reactions and work within the framework of chemical quasi-equilibrium but it is possible to treat the full chemical system. This will have a strong impact on the numerical simulation for such flows.

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