The Kinetic Chemical Equilibrium Regime *

Alexandre ERN[1,2] and Vincent GIOVANGIGLI[2]

[1]CERMICS, ENPC, 6 et 8 av. Blaise Pascal, Cité Descartes, 77455 Marne la Vallée cedex 2, France
[2]CMAP, CNRS, Ecole Polytechnique, 91128 Palaiseau cedex, France

Abstract. We investigate reactive gas mixtures in the kinetic chemical equilibrium regime. Our starting point is a generalized Boltzmann equation with a chemical source term valid for arbitrary reaction mechanisms and yielding a positive entropy production. We first study the Enskog expansion in the kinetic chemical equilibrium regime. We derive a new set of macroscopic equations in the zeroth and first order regimes, expressing conservation of element densities, momentum and energy. The transport fluxes arising in the Navier-Stokes equilibrium regime are the element diffusion velocities, the heat flux vector and the pressure tensor and are written in terms of transport coefficients. Upon introducing species diffusion velocities, the kinetic equilibrium regime appears to be formally equivalent to the one obtained for gas mixtures in chemical nonequilibrium and then letting the chemical reactions approach equilibrium. The actual values of the transport coefficients are, however, different. Finally, we derive the entropy conservation equation in the Navier-Stokes equilibrium regime and show that the source term is positive and that it is compatible with Onsager's reciprocal relations.

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Corresponding Author
Alexandre ERN
CERMICS, ENPC (see above address)
fax: 33 1 64 15 35 86
ern@cermics.enpc.fr

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1 Introduction

Extensive interest in the kinetic theory of gas mixtures with chemical reactions has grown significantly over the past few years. The subject is indeed related to a wide range of practical applications, including spacecraft flights, plasma physics, combustion processes and chemical reactors. An attractive approach for modeling gas mixtures with chemical reactions relies upon a generalized Boltzmann equation with chemical source term and the Enskog expansion. With this approach, the collision term in the Boltzmann equation is split into fast and slow processes, thus giving rise to a formal expansion of the species distribution functions and the kinetic equations. Most applications are concerned with the zeroth and first order terms in the expansion.

In this context, several kinetic regimes may arise for chemically reactive gas mixtures [1,2]. When the chemistry times are much larger than the relaxation times for translational and internal energy exchange, the chemical source term in the Boltzmann equation accounts for slow processes while the nonreactive source term results from fast processes. This regime has been studied extensively in the past and gives rise, in particular, to the tempered and slow reaction regimes, for which expressions of transport coefficients have been given [1,3–6]. On the other hand, when the chemical characteristic times are of the same order of magnitude as the relaxation times of translational and internal energy, a kinetic chemical equilibirum regime arises. This regime has been introduced formally by Ludwig and Heil [6] for dissociation and ionization of gas mixtures, but these authors did not introduce the appropriate collisional invariants associated with the chemical elements. The main goal of this work is now to derive a general theoretical framework for gas mixtures in the kinetic chemical equilibrium regime.

Our paper is organized as follows. In the next section we present the generalized Boltzmann equation for chemically reactive mixtures in a semi-classical framework. Our analysis is concerned with dilute, isotropic mixtures with fast relaxation of all the internal energy modes, thus excluding cases such as external magnetic and electric

fields or strong vibrational desequilibrium [7]. We discuss the form of the chemical source term for arbitrary chemical reaction mechanisms and show that all nonreactive and reactive collisions arising at the microscopic level yield a positive contribution to the entropy production. We then introduce the collisional invariants associated with chemical elements, momentum and energy and study the Enskog expansion in the kinetic chemical equilibrium regime.

In Section 3 we investigate the Euler regime corresponding to the zeroth order Enskog expansion. In this regime, the species distribution functions are given by local Maxwellian distribution functions, but the species number densities are constrained by the chemical equilibrium conditions. We present the macroscopic equations expressing conservation of element densities, momentum and energy.

Finally, in Section 4 we investigate the Navier-Stokes regime corresponding to the first order Enskog expansion. The macroscopic equations for element densities, momentum and energy involve several transport fluxes: the element diffusion velocities, the pressure tensor and the heat flux vector. We express these fluxes in terms of various transport coefficients including, in particular, the element diffusion matrix. Upon introducing the species diffusion velocities, we show that the first order kinetic equilibrium regime is formally equivalent to the one obtained from a first order expansion with nonequilibrium chemistry and then letting the chemical reactions approach equilibrium. The actual values of the transport coefficients are, however, different. Finally, we derive the conservation equation for the entropy and show that the source term is positive and that it is compatible with Onsager's reciprocal relations.

2 Theoretical framework

In this section we derive a theoretical framework for the kinetic chemical equilibrium regime. We first derive a generalized Boltzmann equation for chemically reactive mixtures and present explicitly the form of the chemical source term for an arbitrary reaction mechanism. We then show that both nonreactive and reactive source terms are compatible with the positivity of entropy production. We next present the collisional invariants for reactive mixtures at equilibrium, accounting for element, momentum and energy conservation. Finally, we investigate the Enskog expansion in the kinetic chemical equilibrium regime.

2.1 Generalized Boltzmann equation

We consider a dilute reactive mixture consisting of n chemical species having internal degrees of freedom. We are concerned here with isotropic gas mixtures, thus excluding the case of external magnetic or electric fields. The starting point of our analysis is the Boltzmann equation derived in [8] for polyatomic gas mixtures without chemical reactions. This equation has been obtained in a semiclassical framework, i.e., the translational motion of the particules is treated classically and the internal degrees of freedom are treated quantum mechanically. It preaverages the collision cross-sections over all the magnetic quantum numbers and can be derived from the Waldmann-Snider quantum mechanical Boltzmann equation [9,10].

The state of the mixture is described by the species distribution functions denoted by $f_i(t, \boldsymbol{x}, \boldsymbol{c}_i, \imath)$, where t is the time, $\boldsymbol{x}$ the three-dimensional spatial coordinate, $\boldsymbol{c}_i$ the velocity of the i^{th} species and $\imath$ the index for the internal energy state. For brevity, the dependence on $(t, \boldsymbol{x})$ is made implicit. For a family of functions ξ_i, $i \in \mathcal{S}$, where ξ_i depends on $\boldsymbol{c}_i$ and $\imath$, we introduce the compact notation $\xi = (\xi_i)_{i\in\mathcal{S}}$. The family of species distribution functions $f = (f_i)_{i\in\mathcal{S}}$ is the solution of a generalized Boltzmann equation written in the form

$$\mathcal{D}_i(f_i) = \mathcal{B}_i(f) + \mathcal{C}_i(f), \qquad i \in \mathcal{S}, \tag{2.1}$$

where $\mathcal{S} = [1, n]$ is the set of species indices. In the above equation, $\mathcal{D}_i$ is the usual differential operator

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

where $\boldsymbol{b}_i$ is the external force acting on the i^{th} species, and $\mathcal{B}_i(f)$ and $\mathcal{C}_i(f)$ are, respectively, the nonreactive and reactive source terms. The nonreactive source term is given by [1,8]

$$\mathcal{B}_i(f) = \sum_{j\in\mathcal{S}} \sum_{\imath,\imath',\jmath'} \int \Big(f_i' f_j' \frac{a_{i\imath} a_{j\jmath}}{a_{i\imath'} a_{j\jmath'}} - f_i f_j\Big) W_{ij}^{\imath\jmath\imath'\jmath'} d\boldsymbol{c}_j d\boldsymbol{c}_i' d\boldsymbol{c}_j', \tag{2.3}$$

where $\imath$ and $\jmath$ are the indices for the quantum energy states of the i^{th} and j^{th} species before collision, $\imath'$ and $\jmath'$ the corresponding numbers after collision, $a_{i\imath}$ the degeneracy of the $\imath^{\text{th}}$ quantum energy shell of the i^{th} species and $W_{ij}^{\imath\jmath\imath'\jmath'}$ the transition probability for the nonreactive collision. Note that the transition probabilities have been preaveraged over all the magnetic quantum numbers and satisfy the reciprocity relations [8]

$$W_{ij}^{\imath\jmath\imath'\jmath'} a_{i\imath} a_{j\jmath} = W_{ij}^{\imath'\jmath'\imath\jmath} a_{i\imath'} a_{j\jmath'}. \tag{2.4}$$

It is also possible to consider a formalism based on collision cross-sections rather than transition probabilities, but the present formalism is more convenient for reactive collisions [2,6].

The reactive source term $\mathcal{C}_i(f)$ results from chemical reactions between species in the mixture. We consider both bimolecular and trimolecular chemical reactions. In particular, although triple nonreactive collisions have been neglected in the nonreactive source term (2.3), triple reactive collisions are retained since recombination reactions cannot often proceed otherwise [6,11]. Triple reactive collisions can also be viewed as a sequence of two bimolecular reactions proceeding extremely fast [2].

Before giving the general form of the reactive source term, we present some examples. Consider first a bimolecular reaction of the form

$$\chi_i + \chi_j \rightleftharpoons \chi_k + \chi_l, \tag{2.5}$$

with species indices i, j, k, l assumed to be distinct and with χ_i denoting the chemical symbol for the i^{th} species. Let I, J, K, L denote the indices for the internal energy states of the species. The reactive source term then reads [1,2,6,11]

$$\mathcal{C}_i(f) = \sum_{J,K,L} \int \Big(f_k f_l \frac{\beta_{kK}\beta_{lL}}{\beta_{iI}\beta_{jJ}} - f_i f_j \Big) \mathcal{W}_{ijkl}^{IJKL} d\boldsymbol{c}_j d\boldsymbol{c}_k d\boldsymbol{c}_l, \tag{2.6}$$

where the statistical weight β_{iI} is given by

$$\beta_{iI} = \frac{h_{\text{P}}^3}{a_{iI} m_i^3}, \tag{2.7}$$

and where h_{P} is the Planck constant, m_i the mass of the particules of the i^{th} species and $\mathcal{W}_{ijkl}^{IJKL}$ the transition probability for the forward reaction in (2.5). In (2.6), we have used the reciprocity relation between the forward and reverse transition probabilities which reads [1,2,6,11]

$$\frac{\mathcal{W}_{ijkl}^{IJKL}}{\beta_{iI}\beta_{jJ}} = \frac{\mathcal{W}_{klij}^{KLIJ}}{\beta_{kK}\beta_{lL}}. \tag{2.8}$$

In the case where i and j are the same in reaction (2.5), i.e.,

$$\chi_i + \chi_i \rightleftharpoons \chi_k + \chi_l, \tag{2.9}$$

the forward and reverse reaction delete or produce, respectively, two molecules of the i^{th} species so that the reactive source term becomes [2,6,11]

$$\mathcal{C}_i(f) = 2 \sum_{\tilde{I},K,L} \int \Big(f_k f_l \frac{\beta_{kK}\beta_{lL}}{\beta_{iI}\beta_{i\tilde{I}}} - f_i \tilde{f}_i \Big) \mathcal{W}_{iikl}^{I\tilde{I}KL} d\tilde{\boldsymbol{c}}_i d\boldsymbol{c}_k d\boldsymbol{c}_l, \tag{2.10}$$

with $\tilde{f}_i$ denoting $\tilde{f}_i(t, \boldsymbol{x}, \tilde{\boldsymbol{c}}_i, \tilde{\imath})$. In the case of a chemical reaction involving three products, as in

$$\chi_i + \chi_j \rightleftharpoons \chi_k + \chi_l + \chi_m, \tag{2.11}$$

with all the indices assumed to be distinct, the reactive source term reads [2,6,11]

$$\mathcal{C}_i(f) = \sum_{J,K,L,M} \int \Big(f_k f_l f_m \frac{\beta_{kK}\beta_{lL}\beta_{mM}}{\beta_{iI}\beta_{jJ}} - f_i f_j \Big) \mathcal{W}_{ijklm}^{IJKLM} d\boldsymbol{c}_j d\boldsymbol{c}_k d\boldsymbol{c}_l d\boldsymbol{c}_m, \tag{2.12}$$

with obvious notation. Note that the Planck constant does no longer cancel out in (2.12). Finally, in the case where the i^{th} species is present as reactant and product in reaction (2.5), i.e.,

$$\chi_i + \chi_j \rightleftharpoons \chi_i + \chi_l, \tag{2.13}$$

the forward and reverse reactions do not account for the same statistical event regarding species i so that the source term reads [2,6,11]

$$\begin{aligned} \mathcal{C}_i(f) = & \sum_{J,\tilde{I},L} \int \Big(\tilde{f}_i f_l \frac{\beta_{i\tilde{I}}\beta_{lL}}{\beta_{iI}\beta_{jJ}} - f_i f_j \Big) \mathcal{W}_{ijil}^{IJ\tilde{I}L} d\boldsymbol{c}_j d\tilde{\boldsymbol{c}}_i d\boldsymbol{c}_l \\ & + \sum_{L,\tilde{I},J} \int \Big(\tilde{f}_i f_j - \frac{\beta_{iI}\beta_{lL}}{\beta_{i\tilde{I}}\beta_{jJ}} f_i f_l \Big) \mathcal{W}_{ijil}^{\tilde{I}JIL} d\tilde{\boldsymbol{c}}_i d\boldsymbol{c}_j d\boldsymbol{c}_l. \end{aligned} \tag{2.14}$$

Our goal is now to generalize the above expressions into a single formalism valid for arbitrary reaction mechanisms. The reactive source term for the i^{th} species reads

$$\mathcal{C}_i(f) = \sum_{(r)} \mathcal{C}_i^{(r)}(f). \tag{2.15}$$

Here, $\mathcal{C}_i^{(r)}(f)$ is the source term for the r^{th} elementary reaction written in the form

$$\sum_{j \in \mathcal{R}^{(r)}} \chi_j \rightleftharpoons \sum_{k \in \mathcal{P}^{(r)}} \chi_k, \tag{2.16}$$

where $\mathcal{R}^{(r)}$ and $\mathcal{P}^{(r)}$ are, respectively, the indices for reactants and products. For instance, for reaction (2.5), we have $\mathcal{R}^{(r)} = \{ i, j \}$ and $\mathcal{P}^{(r)} = \{ k, l \}$, whereas for reaction (2.9), we have $\mathcal{R}^{(r)} = \{ i, i \}$ and $\mathcal{P}^{(r)} = \{ k, l \}$. We denote by $\nu_i^{\mathcal{R}^{(r)}}$ and $\nu_i^{\mathcal{P}^{(r)}}$ the stoichiometric coefficients of the i^{th} species among reactants and products, respectively, and we also denote by R and P the indices of internal energy states for reactants and products, respectively. For a given species $i \in \mathcal{S}$, we denote by $\mathcal{R}_i^{(r)}$ the set of reactant indices where the index i has been removed only once. For example, for

reaction (2.5), we have $\mathcal{R}_i^{(r)} = \{\, j \,\}$ and for reaction (2.9) we have $\mathcal{R}_i^{(r)} = \{\, i \,\}$. Finally, we introduce a similar notation for $\mathcal{P}_i^{(r)}$, $_{R_I}$ and $_{P_I}$. With this notation, the source term for the r^{th} elementary reaction reads

$$\begin{aligned}\mathcal{C}_i^{(r)}(f) = \nu_i^{\mathcal{R}^{(r)}} \sum_{R_I,P} \int \Big(\prod_{\mathcal{P}^{(r)}} f_k \frac{\prod_{\mathcal{P}^{(r)}} \beta_{kK}}{\prod_{\mathcal{R}^{(r)}} \beta_{jJ}} - \prod_{\mathcal{R}^{(r)}} f_j\Big) \mathcal{W}^{RP}_{\mathcal{R}^{(r)}\mathcal{P}^{(r)}} \prod_{\mathcal{R}_i^{(r)},\mathcal{P}^{(r)}} d\boldsymbol{c}_j d\boldsymbol{c}_k \\ + \nu_i^{\mathcal{P}^{(r)}} \sum_{R,P_I} \int \Big(\prod_{\mathcal{R}^{(r)}} f_j - \frac{\prod_{\mathcal{P}^{(r)}} \beta_{kK}}{\prod_{\mathcal{R}^{(r)}} \beta_{jJ}} \prod_{\mathcal{P}^{(r)}} f_k\Big) \mathcal{W}^{RP}_{\mathcal{R}^{(r)}\mathcal{P}^{(r)}} \prod_{\mathcal{R}^{(r)},\mathcal{P}_i^{(r)}} d\boldsymbol{c}_j d\boldsymbol{c}_k,\end{aligned} \tag{2.17}$$

with, for instance, $\prod_{\mathcal{R}^{(r)},\mathcal{P}_i^{(r)}} d\boldsymbol{c}_j d\boldsymbol{c}_k$ standing for $\prod_{\mathcal{R}^{(r)}} d\boldsymbol{c}_j \prod_{\mathcal{P}_i^{(r)}} d\boldsymbol{c}_k$. In addition, $\mathcal{W}^{RP}_{\mathcal{R}^{(r)}\mathcal{P}^{(r)}}$ is the transition probability for a reactive collision in which the reactants $\mathcal{R}^{(r)}$ with internal energy states $_R$ are transformed into products $\mathcal{P}^{(r)}$ with internal energy states $_P$. Note that the following reciprocity relation holds for the transition probabilities [2]

$$\frac{\mathcal{W}^{RP}_{\mathcal{R}^{(r)}\mathcal{P}^{(r)}}}{\prod_{\mathcal{R}^{(r)}} \beta_{jJ}} = \frac{\mathcal{W}^{PR}_{\mathcal{P}^{(r)}\mathcal{R}^{(r)}}}{\prod_{\mathcal{P}^{(r)}} \beta_{kK}}. \tag{2.18}$$

2.2 Entropy production

We now show that the nonreactive source term (2.3) and the reactive source term (2.17) are both compatible with the H-theorem or, in other words, that they yield a positive entropy production. To this purpose, we introduce the kinetic entropy per unit volume given by

$$S = -k_{\text{B}} \sum_{i,I} \int f_i \big(\log(\beta_{iI} f_i) - 1\big) d\boldsymbol{c}_i. \tag{2.19}$$

Multiplying the Boltzmann equation (2.1) by $\log(\beta_{iI} f_i) - 1$, integrating over $d\boldsymbol{c}_i$ and summing over i and $_I$ yields the entropy conservation equation in the form

$$\partial_t S + \partial_{\boldsymbol{x}} \cdot (S\boldsymbol{v}) + \partial_{\boldsymbol{x}} \cdot \boldsymbol{J}_s = \sigma, \tag{2.20}$$

where $\boldsymbol{v}$ is the mean average velocity defined later, $\boldsymbol{J}_s$ the entropy diffusive flux given by

$$\boldsymbol{J}_s = -k_{\text{B}} \sum_{i,I} \int (\boldsymbol{c}_i - \boldsymbol{v}) f_i \big(\log(\beta_{iI} f_i) - 1\big) d\boldsymbol{c}_i, \tag{2.21}$$

and σ the entropy source term. The entropy source term may be written

$$\sigma = \sigma^{\mathcal{B}} + \sigma^{\mathcal{C}}, \tag{2.22}$$

with the nonreactive source term given by

$$\begin{aligned}\sigma^{\mathcal{B}} =& -k_{\text{B}} \sum_{i,I} \int \mathcal{B}_i(f)\big(\log(\beta_{iI} f_i) - 1\big) d\boldsymbol{c}_i \\ =& \frac{1}{4} k_{\text{B}} \sum_{i,j \in \mathcal{S}} \sum_{I,J,I',J'} \int f_i f_j \; \Omega\big(\frac{f_i' f_j'}{a_{iI'} a_{jJ'}}; \frac{f_i f_j}{a_{iI} a_{jJ}}\big) \; W_{ij}^{IJI'J'} d\boldsymbol{c}_i d\boldsymbol{c}_j d\boldsymbol{c}_i' d\boldsymbol{c}_j',\end{aligned} \tag{2.23}$$

and the reactive source term by

$$\begin{aligned}\sigma^{\mathcal{C}} =& -k_{\text{B}} \sum_{i,I} \int \mathcal{C}_i(f)\big(\log(\beta_{iI} f_i) - 1\big) d\boldsymbol{c}_i \\ =& k_{\text{B}} \sum_{(r)} \sum_{R,P} \int \Big(\prod_{\mathcal{R}^{(r)}} f_j\Big) \; \Omega\big(\prod_{\mathcal{P}^{(r)}} \beta_{kK} f_k; \prod_{\mathcal{R}^{(r)}} \beta_{jJ} f_j\big) \; \mathcal{W}_{\mathcal{R}^{(r)}\mathcal{P}^{(r)}}^{RP} \prod_{\mathcal{R}^{(r)},\mathcal{P}^{(r)}} d\boldsymbol{c}_j d\boldsymbol{c}_k,\end{aligned} \tag{2.24}$$

with $\Omega(x;y) = \log(x/y)(x-y)$. It is readily seen that both $\sigma^{\mathcal{B}}$ and $\sigma^{\mathcal{C}}$ are a sum of positive terms. In other words, all the collisions arising at the microscopic level, either nonreactive or reactive, yield a positive contribution to the kinetic entropy production. The generalized Boltzmann equation (2.1) is thus compatible with the H-theorem and yields a dissipative structure. This property is particularly important in the modeling of reactive gas mixtures where special care should be taken so that all the terms arising in the entropy production yield a positive contribution.

2.3 Collisional invariants and macroscopic properties

As opposed to the nonreactive case where species, momentum and energy are conserved by any microscopic collision, in the reactive case only elements, momentum and energy are conserved. We denote by n_e the number of elements in the mixture and by $\mathcal{E} = [1, n_e]$ the set of element indices. The n_e+4 collisional invariants are then given by

$$\psi^l = \begin{cases} (\mathcal{E}_{il})_{i \in \mathcal{S}}, & l \in \mathcal{E}, \\ (m_i c_{\nu i})_{i \in \mathcal{S}}, & l = n_e + \nu, \; \nu = 1,2,3, \\ (\frac{1}{2} m_i \boldsymbol{c}_i \cdot \boldsymbol{c}_i + E_{iI})_{i \in \mathcal{S}}, & l = n_e + 4, \end{cases} \tag{2.25}$$

where $\mathcal{E}_{il}$ is the number of element l in the i^{th} species, $c_{\nu i}$ the component of $\boldsymbol{c}_i$ in the ν^{th} spatial coordinate, and E_{iI} the total internal energy of the i^{th} species in the I^{th} quantum energy shell, given by the sum of the energy of formation plus the internal energy. For later convenience, we denote by $\mathcal{I}$ the space spanned by the collisional invariants.

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

$$\langle\!\langle \xi, \zeta \rangle\!\rangle = \sum_{i,I} \int \xi_i \zeta_i d\boldsymbol{c}_i. \tag{2.26}$$

The macroscopic properties are then given by

$$\langle\!\langle f, \psi^l \rangle\!\rangle = \begin{cases} \widetilde{n}_l, & l \in \mathcal{E}, \\ \rho \boldsymbol{v}, & l = n_e + \nu,\ \nu = 1, 2, 3, \\ \frac{1}{2}\rho \boldsymbol{v}\cdot\boldsymbol{v} + E, & l = n_e + 4, \end{cases} \tag{2.27}$$

where $\widetilde{n}_l$ denotes the number density for the l^{th} element, $\rho = \sum_{l\in\mathcal{E}} \widetilde{m}_l \widetilde{n}_l$ the density of the mixture, $\widetilde{m}_l$ the molecular mass of the l^{th} element, $\boldsymbol{v}$ the mean average velocity and E the total internal energy per unit volume of the mixture. We introduce the partition function for internal energy Q_i^{int} for the i^{th} species

$$Q_i^{\text{int}} = \sum_I a_{iI} \exp(-\beta E_{iI}), \tag{2.28}$$

with $\beta = 1/(k_{\text{B}} T)$, k_{B} being the Boltzmann constant and T the temperature, as well as the translational and full partition functions

$$Q_i^{\text{tr}} = \left(\frac{2\pi m_i}{\beta h_{\text{P}}^2}\right)^{3/2}, \qquad Q_i = Q_i^{\text{tr}}\, Q_i^{\text{int}}. \tag{2.29}$$

The averaged internal energy of the i^{th} species reads

$$\overline{E}_i = \frac{1}{Q_i^{\text{int}}} \sum_I a_{iI} E_{iI} \exp(-\beta E_{iI}) = -\frac{d}{d\beta} \log Q_i^{\text{int}}. \tag{2.30}$$

We also introduce the internal energy of the i^{th} species and its enthalpy given by

$$E_i = \tfrac{3}{2} k_{\text{B}} T + \overline{E}_i, \qquad H_i = \tfrac{5}{2} k_{\text{B}} T + \overline{E}_i, \qquad i \in \mathcal{S}. \tag{2.31}$$

The species number densities are defined as

$$n_i = \sum_I \int f_i d\boldsymbol{c}_i, \qquad i \in \mathcal{S}, \tag{2.32}$$

in such a way that

$$\widetilde{n}_l = \sum_{i\in\mathcal{S}} n_i \mathcal{E}_{il}, l \in \mathcal{E}. \tag{2.33}$$

The total internal energy per unit volume of the mixture then reads

$$E = \sum_{i\in\mathcal{S}} n_i E_i. \tag{2.34}$$

2.4 The kinetic chemical equilibrium regime

In this work we are concerned with the kinetic chemical equilibrium regime in which both the chemistry times and the relaxation times for translational and internal energy are much smaller than the characteristic times of the flow. An approximate solution to the Boltzmann equation (2.1) is then obtained using an Enskog expansion. Rewriting (2.1) in the form

$$\mathcal{D}_i(f_i) = \frac{1}{\varepsilon}\left(\mathcal{B}_i(f) + \mathcal{C}_i(f)\right), \qquad i \in \mathcal{S}, \tag{2.35}$$

where ε is a formal expansion parameter, the species distribution functions are expanded as

$$f_i = f_i^0\big(1 + \varepsilon\phi_i + \mathcal{O}(\varepsilon^2)\big), \qquad i \in \mathcal{S}. \tag{2.36}$$

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

$$\mathcal{B}_i(f^0) + \mathcal{C}_i(f^0) = 0, \qquad i \in \mathcal{S}. \tag{2.37}$$

In order to determine f^0 uniquely, it is classical to impose that f^0 yield the local macroscopic properties

$$\langle\!\langle f^0, \psi^l \rangle\!\rangle = \langle\!\langle f, \psi^l \rangle\!\rangle, \qquad \psi^l \in \mathcal{I}. \tag{2.38}$$

We will see in section 3 that (2.37) and (2.38) uniquely determine the zeroth order distribution functions f^0 and give rise to the Euler equilibrium regime.

The first order perturbations $\phi = (\phi_i)_{i\in\mathcal{S}}$ are the solution of non-homogeneous integral equations written in the form

$$\Im_i(\phi) = \Psi_i, \qquad i \in \mathcal{S}, \tag{2.39}$$

where the right member Ψ_i uniquely depends on f^0 and reads

$$\Psi_i = -\mathcal{D}_i(\log f_i^0), \qquad i \in \mathcal{S}. \tag{2.40}$$

In addition, $\Im_i$ denotes the linearized collision operator for the i^{th} species, which reads

$$\Im_i(\phi) = \Im_i^{\mathcal{B}}(\phi) + \Im_i^{\mathcal{C}}(\phi), \tag{2.41}$$

where the nonreactive and reactive collision operators are given by

$$\begin{aligned} \Im_i^{\mathcal{B}}(\phi) =& -\frac{1}{f_i^0}\langle\, \partial_f \mathcal{B}_i(f^0), f^0\phi \,\rangle \\ =& \sum_{j\in\mathcal{S}} \sum_{J,I',J'} \int f_j^0(\phi_i + \phi_j - \phi_i' - \phi_j') W_{ij}^{IJI'J'} d\boldsymbol{c}_j d\boldsymbol{c}_i' d\boldsymbol{c}_j', \end{aligned} \tag{2.42}$$

and

$$\begin{aligned}\Im_i^{\mathcal{C}}(\phi) = & -\frac{1}{f_i^0}\langle\, \partial_f \mathcal{C}_i(f^0), f^0\phi\,\rangle \\ & = \nu_i^{\mathcal{R}^{(r)}} \sum_{R_I,P} \int \prod_{\mathcal{R}_i^{(r)}} f_j^0 \big(\sum_{\mathcal{R}^{(r)}} \phi_j - \sum_{\mathcal{P}^{(r)}} \phi_k\big) \mathcal{W}^{RP}_{\mathcal{R}^{(r)}\mathcal{P}^{(r)}} \prod_{\mathcal{R}_i^{(r)},\mathcal{P}^{(r)}} d\boldsymbol{c}_j d\boldsymbol{c}_k \\ & + \nu_i^{\mathcal{P}^{(r)}} \sum_{R,P_I} \int \prod_{\mathcal{P}_i^{(r)}} f_k^0 \big(\sum_{\mathcal{P}^{(r)}} \phi_k - \sum_{\mathcal{R}^{(r)}} \phi_j\big) \mathcal{W}^{RP}_{\mathcal{R}^{(r)}\mathcal{P}^{(r)}} \prod_{\mathcal{R}^{(r)},\mathcal{P}_i^{(r)}} d\boldsymbol{c}_j d\boldsymbol{c}_k.\end{aligned} \tag{2.43}$$

Note that the linearized collision operator has important structure properties which generalize those discussed in [12] for nonreactive mixtures. Indeed, upon introducing the bracket operator

$$[\![\xi,\zeta]\!] = \langle\!\langle f^0\xi, \Im(\zeta)\rangle\!\rangle, \tag{2.44}$$

it is readily seen from (2.42) and (2.43) that the bracket operator has the following fundamental properties.

(i) it is symmetic: $[\![\xi,\zeta]\!] = [\![\zeta,\xi]\!]$,

(ii) it is positive semi-definite: $[\![\xi,\xi]\!] \geq 0$,

(iii) its kernel is spanned by the collisional invariants: $[\![\xi,\xi]\!] = 0 \Longleftrightarrow \xi \in \mathcal{I}$.

In order to determine uniquely the perturbation ϕ, the integral equations (2.39) are completed with the $n_e + 4$ constraints

$$\langle\!\langle f^0\phi, \psi^l\rangle\!\rangle = 0, \qquad \psi^l \in \mathcal{I}. \tag{2.45}$$

The first order species distribution functions $f^1 = (f_i^1)_{i\in\mathcal{S}}$ given by

$$f_i^1 = f_i^0(1+\phi_i), \qquad i \in \mathcal{S}, \tag{2.46}$$

are then such that

$$\langle\!\langle f^1, \psi^l\rangle\!\rangle = \langle\!\langle f^0, \psi^l\rangle\!\rangle = \langle\!\langle f, \psi^l\rangle\!\rangle, \qquad \psi^l \in \mathcal{I}, \tag{2.47}$$

and give rise to the Navier-Stokes equilibrium regime discussed in Section 4.

3 The Euler equilibrium regime

In this section we discuss the Euler equilibrium regime for reactive mixtures in kinetic chemical equilibrium. This regime results from the zeroth order Enskog expansion discussed in Section 2.4.

3.1 Generalized Maxwellian distribution functions

The zeroth order distribution functions f^0 are generalized Maxwellian distribution functions. Indeed, we have seen in Section 2.4 that they satisfy Eqs. (2.37) and (2.38). Using (2.37), we first deduce that

$$\sigma^0 = -k_{\mathrm{B}} \sum_{i,I} \int \big(\mathcal{B}_i(f^0) + \mathcal{C}_i(f^0)\big) \big(\log(\beta_{iI} f_i^0) - 1\big) d\boldsymbol{c}_i = 0, \tag{3.1}$$

and hence the entropy production corresponding to f^0 is zero. Since σ^0 is a sum of nonnegative terms, it is readily seen from (2.23) and (2.24) that σ^0 can vanish if and only if the vector $\big(\log(\beta_{iI} f_i^0)\big)_{i\in\mathcal{S}}$ is conserved in both nonreactive and reactive collisions. We may therefore write

$$\big(\log(\beta_{iI} f_i^0)\big)_{i\in\mathcal{S}} \in \mathcal{I}. \tag{3.2}$$

Using (2.25) we obtain that

$$\log(\beta_{iI} f_i^0) = \sum_{l\in\mathcal{E}} \alpha_l \mathcal{E}_{il} - \boldsymbol{w}\cdot m_i \boldsymbol{c}_i - \gamma(\tfrac{1}{2} m_i \boldsymbol{c}_i\cdot\boldsymbol{c}_i + E_{iI}), \tag{3.3}$$

for $i \in \mathcal{S}$. The constants α_l for $l \in E$, $\boldsymbol{w} \in \mathbb{R}^3$ and γ in (3.3) are determined from the macroscopic constraints (2.38). After some algebra we get $\boldsymbol{w} = \beta\boldsymbol{v}$, $\gamma = \beta$ and the following expression for the zeroth order species distribution functions

$$\begin{aligned} f_i^0 &= \frac{a_{iI} m_i^3}{h_{\mathrm{P}}^3} \frac{n_i}{Q_i} \exp\left\{-\frac{m_i\beta}{2}(\boldsymbol{c}_i - \boldsymbol{v})^2 - \beta E_{iI}\right\} \\ &= \left(\frac{m_i\beta}{2\pi}\right)^{3/2} \frac{a_{iI} n_i}{Q_i^{\mathrm{int}}} \exp\left\{-\frac{m_i\beta}{2}(\boldsymbol{c}_i - \boldsymbol{v})^2 - \beta E_{iI}\right\}. \end{aligned} \tag{3.4}$$

These expressions are similar to those obtained for flows in both tempered and slow reaction regimes, except that the species number densities are now constrained by the relations

$$\left(\log\frac{n_i}{Q_i}\right)_{i\in\mathcal{S}} \in \mathbb{E}, \tag{3.5}$$

where we have introduced the element space

$$\mathbb{E} = \mathrm{Vect}(\mathcal{E}_1, \ldots, \mathcal{E}_{n_e}), \tag{3.6}$$

where $\mathcal{E}_l = (\mathcal{E}_{il})_{i\in\mathcal{S}}$ for $l \in \mathcal{E}$.

It is important to point out that the constraints (3.5) actually yield the usual chemical equilibrium conditions for the species number densities. Indeed, upon introducing the zeroth order entropy

$$S^0 = -k_{\rm B} \sum_{i,I} \int f_i^0 \big(\log(\beta_{iI} f_i^0) - 1\big) d\boldsymbol{c}_i, \tag{3.7}$$

we obtain after some algebra that

$$S^0 = \sum_{i \in \mathcal{S}} n_i S_i^0, \tag{3.8}$$

with the zeroth order molecular entropies S_i^0 given by

$$S_i^0 = \frac{H_i}{T} - k_{\rm B} \log \frac{n_i}{Q_i}, \qquad i \in \mathcal{S}. \tag{3.9}$$

At the zeroth order, the species chemical potentials read

$$\mu_i^0 = \frac{1}{m_i}(H_i - T S_i^0) = \frac{k_{\rm B} T}{m_i} \log \frac{n_i}{Q_i}, \tag{3.10}$$

and it is readily seen from (3.5) that the vector $M\mu^0$ with components $m_i \mu_i^0$ is in the element space

$$M\mu^0 = (m_i \mu_i^0)_{i \in \mathcal{S}} \in \mathbb{E}. \tag{3.11}$$

This relation simply states the usual equilibrium conditions for the chemical reactions, as detailed for instance in [13,14]. In addition, the resulting equilibrium constant is exactly the same as would be obtained using the rules of statistical mechanics [1,15].

3.2 Macroscopic conservation equations

The macroscopic conservation equations in the Euler regime are obtained from the relations

$$\langle\!\langle \psi^l, \mathcal{D}(f^0) \rangle\!\rangle = 0, \qquad \psi^l \in \mathcal{I}, \tag{3.12}$$

where we have introduced the family $\mathcal{D}(f^0) = \big(\mathcal{D}_i(f_i^0)\big)_{i \in \mathcal{S}}$. After some algebra, we obtain

$$\partial_t \widetilde{n}_l + \partial_{\boldsymbol{x}} \cdot (\widetilde{n}_l \boldsymbol{v}) = 0, \qquad l \in \mathcal{E}, \tag{3.13}$$

$$\partial_t (\rho \boldsymbol{v}) + \partial_{\boldsymbol{x}} \cdot (\rho \boldsymbol{v} \otimes \boldsymbol{v}) = \partial_{\boldsymbol{x}} p + \sum_{i \in \mathcal{S}} \rho_i \boldsymbol{b}_i, \tag{3.14}$$

$$\partial_t (\tfrac{1}{2} \rho \boldsymbol{v}^2 + E) + \partial_{\boldsymbol{x}} \cdot \big((\tfrac{1}{2} \rho \boldsymbol{v}^2 + E) \boldsymbol{v} \big) = -\partial_{\boldsymbol{x}} \cdot (p \boldsymbol{v}) + \sum_{i \in \mathcal{S}} \rho_i \boldsymbol{b}_i \cdot \boldsymbol{v}, \tag{3.15}$$

where $\rho_i = n_i m_i$ is the density of the i^{th} species. These equations express conservation of element densities, momentum and energy.

An equation for the temperature is easily recovered from the energy equation (3.15). Upon introduing the particular derivative $D_t = \partial_t + \boldsymbol{v}\cdot\partial_{\boldsymbol{x}}$, a straightforward calculation yields

$$c^{\text{mol}}\, D_t T = \left\{ -(p+E) + \sum_{l\in\mathcal{E}} \Big(\widetilde{n}_l \sum_{i\in\mathcal{S}} \frac{\partial n_i}{\partial \widetilde{n}_l} E_i \Big) \right\} \partial_{\boldsymbol{x}}\cdot\boldsymbol{v}. \tag{3.16}$$

The molecular heat capacity c^{mol} which appears in (3.16) consists of three contributions

$$c^{\text{mol}} = \tfrac{3}{2}k + \sum_{i\in\mathcal{S}} n_i c_i^{\text{int,mol}} + \sum_{i\in\mathcal{S}} n_i c_i^{\text{chem,mol}}. \tag{3.17}$$

The first term accounts for the translational heat capacity, while $c_i^{\text{int,mol}}$ and $c_i^{\text{chem,mol}}$ are, respectively the internal and chemical molecular heat capacity of the i^{th} species given by

$$c_i^{\text{int,mol}} = \frac{d\overline{E}_i}{dT}, \qquad c_i^{\text{chem,mol}} = \frac{1}{n_i}\frac{\partial n_i}{\partial T} E_i. \tag{3.18}$$

4 The Navier-Stokes equilibrium regime

In this section we discuss the Navier-Stokes equilibrium regime for reactive mixtures in kinetic chemical equilibrium. This regime results from the first order Enskog expansion discussed in Section 2.4.

4.1 Linearized Boltzmann equations

We restate that the species perturbed distribution functions $\phi = (\phi_i)_{i\in\mathcal{S}}$ are the solution of the integral equations (2.39) completed by the constraints (2.45). The right member Ψ_i in (2.39) may now be evaluated using the zeroth order macroscopic conservation equations derived in Section 3.2. For convenience, we introduce the partial pressure of the l^{th} element and the partial pressure of the i^{th} species given by

$$\widetilde{p}_l = \widetilde{n}_l k_{\text{B}} T,\ l\in\mathcal{E}, \qquad\qquad p_i = n_i k_{\text{B}} T,\ i\in\mathcal{S}. \tag{4.1}$$

With the $n_e + 4$ macroscopic variables β^l given by

$$\beta^l = \begin{cases} \widetilde{p}_l, & l\in\mathcal{E}, \\ v_\nu, & l = n_e + \nu,\ \nu = 1,2,3, \\ \beta, & l = n_e + 4 \end{cases} \tag{4.2}$$

we obtain

$$\Psi_i = \sum_{l=1}^{n_e+4} \Upsilon_i^l \big(D_t\beta^l + (\boldsymbol{c}_i - \boldsymbol{v})\cdot\partial_{\boldsymbol{x}}\beta^l\big) - m_i\beta(\boldsymbol{c}_i - \boldsymbol{v})\cdot\boldsymbol{b}_i, \tag{4.3}$$

with

$$\Upsilon_i^l = \frac{1}{f_i^0}\frac{\partial f_i^0}{\partial \beta^l} = \begin{cases} \frac{1}{p_i}\frac{\partial p_i}{\partial \widetilde{p}_l}, & l \in \mathcal{E}, \\ m_i\beta(c_{i\nu} - v_\nu), & l = n_e + \nu,\ \nu = 1,2,3, \\ H_i - \frac{k_{\mathrm{B}}T^2}{p_i}\frac{\partial p_i}{\partial T} - \frac{1}{2}m_i(\boldsymbol{c}_i - \boldsymbol{v})^2 - E_{iI}, & l = n_e + 4, \end{cases} \tag{4.4}$$

for $i \in \mathcal{S}$. Using the relations presented in the appendix, it is easily verified that for all $l = 1, \ldots, n_e+4$, the vector $\big(\Upsilon_i^l\big)_{i\in\mathcal{S}}$ is a linear combination of the collisional invariants (2.25). After some lengthy calculations, we obtain the following expansion for Ψ_i in terms of the macroscopic variable gradients

$$\Psi_i = -\boldsymbol{\Psi}_i^\eta : \partial_{\boldsymbol{x}}\boldsymbol{v} - \tfrac{1}{3}\Psi_i^\kappa\ \partial_{\boldsymbol{x}}\cdot\boldsymbol{v} - \sum_{l\in\mathcal{E}} \boldsymbol{\Psi}_i^{\widetilde{D}_l}\cdot\partial_{\boldsymbol{x}}\widetilde{p}_l - \boldsymbol{\Psi}_i^{\lambda'}\cdot\partial_{\boldsymbol{x}}\beta + \sum_{j\in\mathcal{S}} \boldsymbol{\Psi}_i^{D_j}\cdot(\rho_j\boldsymbol{b}_j), \tag{4.5}$$

with

$$\begin{aligned}
\boldsymbol{\Psi}_i^\eta &= m_i\beta\left\{(\boldsymbol{c}_i - \boldsymbol{v})\otimes(\boldsymbol{c}_i - \boldsymbol{v}) - \tfrac{1}{3}(\boldsymbol{c}_i - \boldsymbol{v})^2\boldsymbol{I}\right\}, \\
\Psi_i^\kappa &= \tfrac{1}{3}m_i\beta(\boldsymbol{c}_i - \boldsymbol{v})^2 - \sum_{l\in\mathcal{E}}\frac{\widetilde{p}_l}{p_i}\frac{\partial p_i}{\partial \widetilde{p}_l} + \frac{1}{k_{\mathrm{B}}T^2 c^{\mathrm{mol}}}\left\{p + \sum_{j\in\mathcal{S}}\Big(n_j - \sum_{l\in\mathcal{E}}\widetilde{n}_l\frac{\partial n_j}{\partial \widetilde{n}_l}\Big)E_j\right\} \\
&\qquad \times\left\{H_i - \frac{k_{\mathrm{B}}T^2}{p_i}\frac{\partial p_i}{\partial T} - \sum_{l\in\mathcal{E}} k_{\mathrm{B}}T\frac{\widetilde{p}_l}{p_i}\frac{\partial p_i}{\partial \widetilde{p}_l} - \tfrac{1}{2}m_i(\boldsymbol{c}_i - \boldsymbol{v})^2 - E_{iI}\right\}, \\
\boldsymbol{\Psi}_i^{\widetilde{D}_l} &= \frac{1}{p_i}\left\{\frac{\partial p_i}{\partial \widetilde{p}_l} - Y_i\sum_{j\in\mathcal{S}}\frac{\partial p_j}{\partial \widetilde{p}_l}\right\}(\boldsymbol{c}_i - \boldsymbol{v}), \\
\boldsymbol{\Psi}_i^{\lambda'} &= \left\{H_i - \frac{k_{\mathrm{B}}T^2}{p_i}\Big(\frac{\partial p_i}{\partial T} - Y_i\sum_{j\in\mathcal{S}}\frac{\partial p_j}{\partial T}\Big) - \tfrac{1}{2}m_i(\boldsymbol{c}_i - \boldsymbol{v})^2 - E_{iI}\right\}(\boldsymbol{c}_i - \boldsymbol{v}), \\
\boldsymbol{\Psi}_i^{D_j} &= \frac{1}{p_i}\Big(\delta_{ij} - Y_i\Big)(\boldsymbol{c}_i - \boldsymbol{v}),
\end{aligned} \tag{4.6}$$

where $\boldsymbol{I}$ is the identity matrix. Letting $\mu = \eta$, κ, $\widetilde{D}_l$ for $l \in \mathcal{E}$, λ', or D_j for $j \in \mathcal{S}$, we deduce from the expansion (4.5) for Ψ_i a similar expansion for ϕ_i, namely

$$\phi_i = -\boldsymbol{\phi}_i^\eta : \partial_{\boldsymbol{x}}\boldsymbol{v} - \tfrac{1}{3}\phi_i^\kappa\ \partial_{\boldsymbol{x}}\cdot\boldsymbol{v} - \sum_{l\in\mathcal{E}} \boldsymbol{\phi}_i^{\widetilde{D}_l}\cdot\partial_{\boldsymbol{x}}\widetilde{p}_l - \boldsymbol{\phi}_i^{\lambda'}\cdot\partial_{\boldsymbol{x}}\beta + \sum_{j\in\mathcal{S}} \boldsymbol{\phi}_i^{D_j}\cdot(\rho_j\boldsymbol{b}_j), \tag{4.7}$$

and each of the expansion coefficients $\phi^\mu = (\phi_i^\mu)_{i\in\mathcal{S}}$ in (4.7) is the solution of the constrained integral equations

$$\begin{cases} \Im_i(\phi^\mu) = \Psi_i^\mu, & i \in \mathcal{S}, \\ \langle\!\langle f^0\phi^\mu, \psi^l\rangle\!\rangle = 0, & \psi^l \in \mathcal{I}. \end{cases} \tag{4.8}$$

It is easily verified that the above systems are well posed for all μ, i.e., the right member Ψ_i^μ is in the range of the operator $\Im_i$ and the solution ϕ^μ is unique.

4.2 Macroscopic conservation equations

The macroscopic equations in the Navier-Stokes regime are obtained from the relations

$$\langle\!\langle \psi^l, \mathcal{D}\big(f^1\big)\rangle\!\rangle = 0, \qquad \psi^l \in \mathcal{I}, \tag{4.9}$$

where we have introduced the family $\mathcal{D}(f^1) = \big(\mathcal{D}_i(f_i^1)\big)_{i\in\mathcal{S}}$. We introduce two types of diffusion fluxes, the classical species diffusion fluxes given by

$$n_i \boldsymbol{V}_i = \sum_I \int (\boldsymbol{c}_i - \boldsymbol{v}) f_i^0 \phi_i d\boldsymbol{c}_i, \qquad i \in \mathcal{S}, \tag{4.10}$$

and the element diffusion fluxes defined as

$$\widetilde{n}_l \widetilde{\boldsymbol{V}}_l = \sum_{i,I} \int \mathcal{E}_{il}(\boldsymbol{c}_i - \boldsymbol{v}) f_i^0 \phi_i d\boldsymbol{c}_i, \qquad l \in \mathcal{E}, \tag{4.11}$$

in such a way that

$$\widetilde{n}_l \widetilde{\boldsymbol{V}}_l = \sum_{i\in\mathcal{S}} \mathcal{E}_{il} n_i \boldsymbol{V}_i, \qquad l \in \mathcal{E}. \tag{4.12}$$

After some algebra, we obtain the macroscopic conservation equations in the following form

$$\partial_t \widetilde{n}_l + \partial_{\boldsymbol{x}} \cdot (\widetilde{n}_l \boldsymbol{v}) + \partial_{\boldsymbol{x}} \cdot (\widetilde{n}_l \widetilde{\boldsymbol{V}}_l) = 0, \qquad l \in \mathcal{E}, \tag{4.13}$$

$$\partial_t(\rho \boldsymbol{v}) + \partial_{\boldsymbol{x}} \cdot (\rho \boldsymbol{v} \otimes \boldsymbol{v}) + \partial_{\boldsymbol{x}} \cdot \boldsymbol{P} = \sum_{i\in\mathcal{S}} \rho_i \boldsymbol{b}_i, \tag{4.14}$$

$$\partial_t(\tfrac{1}{2}\rho \boldsymbol{v}^2 + E) + \partial_{\boldsymbol{x}} \cdot \big((\tfrac{1}{2}\rho \boldsymbol{v}^2 + E)\boldsymbol{v}\big) + \partial_{\boldsymbol{x}} \cdot (\boldsymbol{q} + \boldsymbol{P} \cdot \boldsymbol{v}) = \sum_{i\in\mathcal{S}} \rho_i \boldsymbol{b}_i \cdot (\boldsymbol{v} + \boldsymbol{V}_i). \tag{4.15}$$

These equations express conservation of element densities, momentum and energy.

With the element diffusion velocities given by (4.12), we still need to specify the species diffusion velocities $\boldsymbol{V}_i$ for $i \in \mathcal{S}$, the heat flux vector $\boldsymbol{q}$ and the pressure tensor

$\boldsymbol{P}$. These transport fluxes are expressed in terms of the species perturbed distribution functions as follows

$$\boldsymbol{V}_i = \frac{1}{\beta}\langle\langle \boldsymbol{\Psi}^{D_i}, f^0\phi\rangle\rangle, \qquad i \in \mathcal{S}, \tag{4.16}$$

$$\boldsymbol{P} = p\boldsymbol{I} + \boldsymbol{\Pi}, \qquad \boldsymbol{\Pi} = \frac{1}{\beta}\langle\langle \boldsymbol{\Psi}^{\eta}, f^0\phi\rangle\rangle + \frac{1}{3\beta}\langle\langle \Psi^{\kappa}, f^0\phi\rangle\rangle \boldsymbol{I}, \tag{4.17}$$

$$\boldsymbol{q} = -\langle\langle \boldsymbol{\Psi}^{\lambda'}, f^0\phi\rangle\rangle + \sum_{i\in\mathcal{S}}\Big(H_i - \frac{k_{\mathrm{B}}T^2}{p_i}\frac{\partial p_i}{\partial T}\Big) n_i \boldsymbol{V}_i, \tag{4.18}$$

where $\boldsymbol{\Pi}$ is the viscous stress tensor. In the next section we express the transport fluxes (4.16)–(4.18) in terms of various transport coefficients.

4.3 Transport coefficients

We first consider the viscous stress tensor $\boldsymbol{\Pi}$. We introduce the shear viscosity η and the volume viscosity κ given by

$$\begin{cases} \eta = \dfrac{k_{\mathrm{B}}T}{10}[\![\boldsymbol{\phi}^{\eta}, \boldsymbol{\phi}^{\eta}]\!], \\ \kappa = \dfrac{k_{\mathrm{B}}T}{9}[\![\phi^{\kappa}, \phi^{\kappa}]\!], \end{cases} \tag{4.19}$$

and the viscous stress tensor then reads

$$\boldsymbol{\Pi} = -\eta\left(\partial_{\boldsymbol{x}}\boldsymbol{v} + (\partial_{\boldsymbol{x}}\boldsymbol{v})^t - \tfrac{2}{3}(\partial_{\boldsymbol{x}}\cdot\boldsymbol{v})\boldsymbol{I}\right) - \kappa\,(\partial_{\boldsymbol{x}}\cdot\boldsymbol{v})\boldsymbol{I}. \tag{4.20}$$

We next turn to the species diffusion velocities $\boldsymbol{V}_i$, $i \in \mathcal{S}$, and the heat flux vector $\boldsymbol{q}$. We define the species multicomponent and the thermal diffusion coefficients as

$$\begin{cases} D_{ij} = \dfrac{p}{3\beta}[\![\boldsymbol{\phi}^{D_i}, \boldsymbol{\phi}^{D_j}]\!], \qquad i,j \in \mathcal{S}, \\ \theta_i = -\dfrac{1}{3}[\![\boldsymbol{\phi}^{\lambda'}, \boldsymbol{\phi}^{D_i}]\!], \qquad i \in \mathcal{S}, \end{cases} \tag{4.21}$$

the partial thermal conductivity as

$$\lambda' = \frac{1}{3k_{\mathrm{B}}T^2}[\![\boldsymbol{\phi}^{\lambda'}, \boldsymbol{\phi}^{\lambda'}]\!], \tag{4.22}$$

and the diffusion driving forces as

$$\boldsymbol{d}_j = \frac{1}{p}\left(\sum_{l\in\mathcal{E}}\frac{\partial p_j}{\partial \widetilde{p}_l}\partial_{\boldsymbol{x}}\widetilde{p}_l - \rho_j \boldsymbol{b}_j\right), \qquad j \in \mathcal{S}. \tag{4.23}$$

The species diffusion velocities may then be written as

$$\boldsymbol{V}_i = -\sum_{j\in\mathcal{S}} D_{ij}\,\boldsymbol{d}_j - \theta_i \partial_{\boldsymbol{x}} \log T, \qquad i \in \mathcal{S}, \tag{4.24}$$

and the heat flux vector as

$$\boldsymbol{q} = -\lambda' \partial_{\boldsymbol{x}} T - p \sum_{i\in\mathcal{S}} \theta_i \boldsymbol{d}_i + \sum_{i\in\mathcal{S}} \Big(H_i - \frac{k_{\text{B}} T^2}{p_i} \frac{\partial p_i}{\partial T} \Big) n_i \boldsymbol{V}_i. \tag{4.25}$$

It is also possible to use a formalism identical to the one arising for mixtures with nonequilibrium chemistry. We first notice that

$$\boldsymbol{\Psi}^{\widetilde{D}_l} = \sum_{j\in\mathcal{S}} \boldsymbol{\Psi}^{D_j} \frac{\partial p_j}{\partial \widetilde{p}_l}. \tag{4.26}$$

Thus, by linearity, the corresponding solutions of the integral Boltzmann equations (4.8) are such that

$$\boldsymbol{\phi}^{\widetilde{D}_l} = \sum_{j\in\mathcal{S}} \boldsymbol{\phi}^{D_j} \frac{\partial p_j}{\partial \widetilde{p}_l}. \tag{4.27}$$

We also introduce the quantities

$$\widehat{\boldsymbol{\Psi}}_i^{\lambda'} = \big(H_i - \tfrac{1}{2} m_i (\boldsymbol{c}_i - \boldsymbol{v})^2 - E_{iI} \big) (\boldsymbol{c}_i - \boldsymbol{v}), \qquad i \in \mathcal{S}, \tag{4.28}$$

in such a way that

$$\boldsymbol{\Psi}^{\lambda'} = \widehat{\boldsymbol{\Psi}}^{\lambda'} - k_{\text{B}} T^2 \sum_{j\in\mathcal{S}} \boldsymbol{\Psi}^{D_j} \frac{\partial p_j}{\partial T}. \tag{4.29}$$

Upon introducing the integral equations

$$\begin{cases} \Im_i(\widehat{\boldsymbol{\phi}}^{\lambda'}) = \widehat{\boldsymbol{\Psi}}_i^{\lambda'}, & i \in \mathcal{S}, \\ \langle\!\langle f^0 \widehat{\boldsymbol{\phi}}^{\lambda'}, \psi^l \rangle\!\rangle = 0, & \psi^l \in \mathcal{I}, \end{cases} \tag{4.30}$$

we obtain by linearity that

$$\boldsymbol{\phi}^{\lambda'} = \widehat{\boldsymbol{\phi}}^{\lambda'} - k_{\text{B}} T^2 \sum_{j\in\mathcal{S}} \boldsymbol{\phi}^{D_j} \frac{\partial p_j}{\partial T}. \tag{4.31}$$

We then define the thermal diffusion coefficients as

$$\widehat{\theta}_i = -\frac{1}{3} [\![\widehat{\boldsymbol{\phi}}^{\lambda'}, \boldsymbol{\phi}^{D_i}]\!] = \theta_i - \frac{T}{p} \sum_{j\in\mathcal{S}} D_{ij} \frac{\partial p_j}{\partial T}, \qquad i \in \mathcal{S}, \tag{4.32}$$

the partial thermal conductivity as

$$\widehat{\lambda}' = \frac{1}{3 k_{\text{B}} T^2} [\![\widehat{\boldsymbol{\phi}}^{\lambda'}, \widehat{\boldsymbol{\phi}}^{\lambda'}]\!], \tag{4.33}$$

and the species diffusion driving forces as

$$\widehat{\boldsymbol{d}}_j = \frac{1}{p}\left(\sum_{l\in\mathcal{E}} \frac{\partial p_j}{\partial \widetilde{p}_l}\partial_{\boldsymbol{x}}\widetilde{p}_l + \frac{\partial p_j}{\partial T}\partial_{\boldsymbol{x}}T - \rho_j \boldsymbol{b}_j\right), \qquad j \in \mathcal{S}. \tag{4.34}$$

The species diffusion velocities $\boldsymbol{V}_i$ are then given by

$$\boldsymbol{V}_i = -\sum_{j\in\mathcal{S}} D_{ij}\widehat{\boldsymbol{d}}_j - \widehat{\theta}_i \partial_{\boldsymbol{x}} \log T, \qquad i \in \mathcal{S}, \tag{4.35}$$

and the heat flux vector by

$$\boldsymbol{q} = -\widehat{\lambda}'\partial_{\boldsymbol{x}}T - p\sum_{i\in\mathcal{S}}\widehat{\theta}_i\widehat{\boldsymbol{d}}_i + \sum_{i\in\mathcal{S}} H_i n_i \boldsymbol{V}_i. \tag{4.36}$$

It is possible to rewrite the species diffusion velocities and the heat flux vector in terms of the thermal diffusion ratios and the thermal conductivity [16]. The thermal diffusion ratios $\widehat{\chi}_i$, for $i \in \mathcal{S}$, are the unique solution of the constrained singular system

$$\begin{cases} \displaystyle\sum_{j\in\mathcal{S}} D_{ij}\widehat{\chi}_j = \widehat{\theta}_i, \quad i \in \mathcal{S}, \\ \displaystyle\sum_{j\in\mathcal{S}} \widehat{\chi}_j = 0, \end{cases} \tag{4.37}$$

while the thermal conductivity reads

$$\widehat{\lambda} = \widehat{\lambda}' - \frac{p}{T}\sum_{j\in\mathcal{S}}\widehat{\theta}_j\widehat{\chi}_j. \tag{4.38}$$

Upon introducing

$$\widehat{\boldsymbol{\phi}}^{\lambda} = \widehat{\boldsymbol{\phi}}^{\lambda'} + p k_{\mathrm{B}} T \sum_{j\in\mathcal{S}} \widehat{\chi}_j \boldsymbol{\phi}^{D_j}, \tag{4.39}$$

we may write

$$\begin{cases} \widehat{\lambda} = \dfrac{1}{3k_{\mathrm{B}}T^2}[\![\widehat{\boldsymbol{\phi}}^{\lambda}, \widehat{\boldsymbol{\phi}}^{\lambda}]\!], \\ \widehat{\chi}_i = \dfrac{m_i}{3pk_{\mathrm{B}}T}[\![\boldsymbol{\Xi}_i, \widehat{\boldsymbol{\phi}}^{\lambda}]\!], \qquad i \in \mathcal{S}, \end{cases} \tag{4.40}$$

with $\boldsymbol{\Xi}_i = \big((\boldsymbol{c}_i - \boldsymbol{v})\delta_{ij}\big)_{i\in\mathcal{S}}$, and we recover the formalism derived in [16] for nonreactive mixtures. Using the thermal conductivity and the thermal diffusion ratios, the species diffusion velocities and the heat flux vector read

$$\begin{cases} \boldsymbol{V}_i = -\displaystyle\sum_{j\in\mathcal{S}} D_{ij}(\widehat{\boldsymbol{d}}_j + \widehat{\chi}_j \partial_{\boldsymbol{x}} \log T), \qquad i \in \mathcal{S}, \\ \boldsymbol{q} = -\widehat{\lambda}\partial_{\boldsymbol{x}}T - p\displaystyle\sum_{i\in\mathcal{S}}\widehat{\chi}_i\boldsymbol{V}_i + \sum_{i\in\mathcal{S}} H_i n_i \boldsymbol{V}_i. \end{cases} \tag{4.41}$$

The transport coefficients introduced above satisfy several important properties which result from those of the bracket operator $[\![\,,]\!]$. First, the matrix of order $n+1$

$$\begin{pmatrix} \frac{1}{T^2}\widehat{\lambda}' & \frac{p}{T}(\widehat{\theta}_i)_{i\in\mathcal{S}} \\ \frac{p}{T}(\widehat{\theta}_i)_{i\in\mathcal{S}} & \frac{p}{T}(D_{ij})_{i,j\in\mathcal{S}} \end{pmatrix}, \tag{4.42}$$

is symmetric positive semi-definite with kernel spanned by the vector $(0, Y_1, \ldots, Y_n)$. Equivalently, we may state that the thermal conductivity $\widehat{\lambda}$ is positive and that the diffusion matrix $D = (D_{ij})_{i,j\in\mathcal{S}}$ is symmetric positive semi-definite with kernel spanned by the mass fraction vector $(Y_1, \ldots, Y_n)$. On the other hand, the shear vicosity η is positive and the volume viscosity κ is nonnegative, the latter being zero only if there are no polyatomic species in the mixture.

Finally, we point out that it is possible to define multicomponent and thermal diffusion coefficients for the elements. Indeed, we may write the element diffusion velocities $\widetilde{\boldsymbol{V}}_k$, $k \in \mathcal{E}$, as follows

$$\widetilde{\boldsymbol{V}}_k = -\sum_{l\in\mathcal{E}} \widetilde{D}_{kl}\frac{1}{p}\partial_{\boldsymbol{x}}\widetilde{p}_l - \widetilde{\theta}_k\partial_{\boldsymbol{x}}\log T + \sum_{i,j\in\mathcal{S}} \frac{n_i}{\widetilde{n}_k}\mathcal{E}_{ik}\frac{D_{ij}}{p}\rho_j\boldsymbol{b}_j, \tag{4.43}$$

where we have introduced the element multicomponent diffusion coefficients

$$\widetilde{D}_{kl} = \sum_{i,j\in\mathcal{S}} \frac{n_i}{\widetilde{n}_k} D_{ij}\frac{\partial p_j}{\partial \widetilde{p}_l}\mathcal{E}_{ik}, \qquad k,l \in \mathcal{E}, \tag{4.44}$$

and the thermal diffusion coefficients for the elements

$$\widetilde{\theta}_k = \sum_{i\in\mathcal{S}} \frac{n_i}{\widetilde{n}_k}\theta_i\mathcal{E}_{ik}, \qquad k \in \mathcal{E}. \tag{4.45}$$

Note also that when all the species external forces are equal, i.e., $\boldsymbol{b}_i = \boldsymbol{b}$ for $i \in \mathcal{S}$, the last term in (4.43) vanishes. Introducing the matrix $(\gamma_{lm})_{l,m\in\mathcal{E}}$ defined in the appendix, the element multicomponent diffusion coefficients may be expressed as

$$\widetilde{D}_{kl} = \sum_{m\in\mathcal{E}} k_{\mathrm{B}}T\gamma_{lm} \sum_{i,j\in\mathcal{S}} \frac{1}{\widetilde{n}_k} D_{ij}\, n_i\mathcal{E}_{ik}\, n_j\mathcal{E}_{jm}. \tag{4.46}$$

As opposed to the diffusion matrix D, the element diffusion matrix $\widetilde{D} = (\widetilde{D}_{kl})_{k,l\in\mathcal{E}}$ does not appear to have any simple structure properties, such as symmetry or positive definiteness. We will see in the next section that this matrix does not appear directly in the framework of Onsager's reciprocal relations. As a result, it is more convenient to use the species diffusion matrix D rather than the element diffusion matrix $\widetilde{D}$.

4.4 Entropy production and Onsager's reciprocal relations

It is well-known that at the first order in the Enskog expansion, the entropy may be evaluated using the zeroth order Maxwellian distribution functions. The first order entropy per unit volume S^1 then reads

$$\begin{aligned} S^1 = & -k_{\text{B}} \sum_{i,I} \int f_i^1 \big(\log(\beta_{iI} f_i^1) - 1\big) d\boldsymbol{c}_i \\ = & \sum_{i \in \mathcal{S}} n_i S_i^0 + \mathcal{O}(\varepsilon^2), \end{aligned} \tag{4.47}$$

where the zeroth order molecular entropies are given by (3.9). The Gibbs free energy per unit volume of the species

$$G_i = H_i - T S_i^0 = k_{\text{B}} T \log \frac{n_i}{Q_i}, \tag{4.48}$$

has several important properties. First, as a result of the chemical equilibrium conditions (3.5) we have

$$(G_i)_{i \in \mathcal{S}} \in \mathbb{E}. \tag{4.49}$$

In addition, as a direct consequence of the first relation in (A.2), we obtain the orthogonality property

$$\sum_{i \in \mathcal{S}} G_i \frac{\partial n_i}{\partial T} = 0. \tag{4.50}$$

We then define the Gibbs free energy per unit volume for the elements as

$$\widetilde{G}_l = \sum_{i \in \mathcal{S}} G_i \frac{\partial p_i}{\partial \widetilde{p}_l}, \qquad l \in \mathcal{E}, \tag{4.51}$$

as well as the enthalpy per unit volume for the elements

$$\widetilde{H}_l = \sum_{i \in \mathcal{S}} H_i \frac{\partial p_i}{\partial \widetilde{p}_l}, \qquad l \in \mathcal{E}. \tag{4.52}$$

Using the relations given in the appendix, one can easily show that

$$G = \sum_{i \in \mathcal{S}} n_i G_i = \sum_{l \in \mathcal{E}} \widetilde{n}_l \widetilde{G}_l, \tag{4.53}$$

and that

$$H = \sum_{i \in \mathcal{S}} n_i H_i = \sum_{l \in \mathcal{E}} \widetilde{n}_l \widetilde{H}_l + T \left(\frac{\partial p}{\partial T} \right)_{\widetilde{p}_l}. \tag{4.54}$$

Using the above relations, we deduce that the differential of the volumetric entropy in the kinetic chemical equilibrium regime is given by the relation

$$TdS = dE - \sum_{l\in\mathcal{E}} \widetilde{G}_l d\widetilde{n}_l. \tag{4.55}$$

This relation generalizes the Gibbs differential relation to the kinetic chemical equilibrium regime. A conservation equation for S is then easily obtained from (4.55) and the macroscopic conservation equations stated in Section 4.2. This equation can be also directly obtained from the Boltzmann equation satisfied by f^1 and proceeding as in Section 2.2. A straightforward calculation yields that

$$\partial_t S + \partial_{\boldsymbol{x}}\cdot(\boldsymbol{v}S) + \partial_{\boldsymbol{x}}\cdot\boldsymbol{J}_s^1 = \sigma^1, \tag{4.56}$$

where $\boldsymbol{J}_s^1$ is the entropy flux vector given by

$$\boldsymbol{J}_s^1 = \frac{1}{T}(\boldsymbol{q} - \sum_{l\in\mathcal{E}} \widetilde{G}_l \widetilde{n}_l \widetilde{\boldsymbol{V}}_l), \tag{4.57}$$

and the entropy source term σ^1 reads

$$\sigma^1 = -\frac{\boldsymbol{q}\cdot\partial_{\boldsymbol{x}}T}{T^2} - \frac{\boldsymbol{\Pi}:\partial_{\boldsymbol{x}}\boldsymbol{v}}{T} + \frac{1}{T}\sum_{i\in\mathcal{S}} \rho_i \boldsymbol{V}_i\cdot\boldsymbol{b}_i - \sum_{l\in\mathcal{E}} \widetilde{n}_l \widetilde{\boldsymbol{V}}_l\cdot\partial_{\boldsymbol{x}}\Big(\frac{\widetilde{G}_l}{T}\Big). \tag{4.58}$$

For the sake of simplicity, we assume that all the external forces are equal, $\boldsymbol{b}_i = \boldsymbol{b}$ for $i \in \mathcal{S}$, so that the third term in the right member of (4.58) vanishes.

In order to expand the last term in (4.58), we use the following relations

$$\frac{\partial}{\partial T}\left(\frac{\widetilde{G}_l}{T}\right)_{\widetilde{p}_l} = -\frac{\widetilde{H}_l}{T^2}, \qquad l \in \mathcal{E}, \tag{4.59}$$

and

$$\frac{\partial}{\partial \widetilde{p}_k}\left(\frac{\widetilde{G}_l}{T}\right)_{T,\,\widetilde{p}_m,\,m\neq k} = k_{\mathrm{B}}\gamma_{kl}, \qquad k,l \in \mathcal{E}, \tag{4.60}$$

where the matrix $(\gamma_{kl})_{k,l\in\mathcal{E}}$ is symmetric and given explicitly in the appendix. The entropy source term may now be written as

$$\sigma^1 = -\frac{\boldsymbol{q} - \sum_{l\in\mathcal{E}} \widetilde{H}_l \widetilde{n}_l \widetilde{\boldsymbol{V}}_l}{T^2}\cdot\partial_{\boldsymbol{x}}T - \frac{\boldsymbol{\Pi}:\partial_{\boldsymbol{x}}\boldsymbol{v}}{T} - \sum_{k,l\in\mathcal{E}} k_{\mathrm{B}}\gamma_{kl}\widetilde{n}_l\widetilde{\boldsymbol{V}}_l\cdot\partial_{\boldsymbol{x}}\widetilde{p}_l. \tag{4.61}$$

Using the expressions for the transport fluxes obtained in the previous section, we may write

$$\boldsymbol{q} - \sum_{l\in\mathcal{E}} \widetilde{H}_l\widetilde{n}_l\widetilde{\boldsymbol{V}}_l = -\alpha^{0,0}\frac{\partial_{\boldsymbol{x}}T}{T^2} - \sum_{k\in\mathcal{E}} \alpha^{0,k}\partial_{\boldsymbol{x}}\widetilde{p}_k, \tag{4.62}$$

and

$$\sum_{l\in\mathcal{E}} k_{\mathrm{B}}\gamma_{kl}\widetilde{n}_l\widetilde{\boldsymbol{V}}_l = -\alpha^{k,0}\frac{\partial_{\boldsymbol{x}}T}{T^2} - \sum_{m\in\mathcal{E}}\alpha^{k,m}\partial_{\boldsymbol{x}}\widetilde{p}_m, \qquad k\in\mathcal{E}, \tag{4.63}$$

and the coefficients $\alpha^{k,m}$, $0\leq k,m\leq n_e$, read

$$\begin{cases} \alpha^{0,0} = T^2\lambda', \\ \alpha^{0,k} = \alpha^{k,0} = \displaystyle\sum_{i\in\mathcal{S}}\theta_i\frac{\partial p_i}{\partial\widetilde{p}_k}, \qquad k\in\mathcal{E}, \\ \alpha^{k,m} = \dfrac{1}{pT}\displaystyle\sum_{i,j\in\mathcal{S}} D_{ij}\frac{\partial p_i}{\partial\widetilde{p}_k}\frac{\partial p_j}{\partial\widetilde{p}_m}, \qquad k,m\in\mathcal{E}. \end{cases} \tag{4.64}$$

The above relations show that the entropy source term in the Navier-Stokes equilibrium regime is compatible with Onsager's reciprocal relations.

Finally, we point out that the entropy source term may also be written using the same formalism as for gas mixtures in chemical nonequilibrium. After some algebra, we get

$$\begin{aligned}\sigma^1 = \widehat{\lambda}\frac{\partial_{\boldsymbol{x}}T\cdot\partial_{\boldsymbol{x}}T}{T^2} + \frac{p}{T}\sum_{i,j\in\mathcal{S}} D_{ij}(\widehat{\boldsymbol{d}}_i + \widehat{\chi}_i\partial_{\boldsymbol{x}}\log T)\cdot(\widehat{\boldsymbol{d}}_j + \widehat{\chi}_j\partial_{\boldsymbol{x}}\log T) + \frac{\kappa}{T}(\partial_{\boldsymbol{x}}\cdot\boldsymbol{v})^2 + \\ \frac{\eta}{2T}\big(\partial_{\boldsymbol{x}}\boldsymbol{v} + (\partial_{\boldsymbol{x}}\boldsymbol{v})^t - \tfrac{2}{3}(\partial_{\boldsymbol{x}}\cdot\boldsymbol{v})\boldsymbol{I}\big):\big(\partial_{\boldsymbol{x}}\boldsymbol{v} + (\partial_{\boldsymbol{x}}\boldsymbol{v})^t - \tfrac{2}{3}(\partial_{\boldsymbol{x}}\cdot\boldsymbol{v})\boldsymbol{I}\big).\end{aligned} \tag{4.65}$$

From the properties of the transport coefficients stated in Section 4.3, we readily obtain that the entropy production term σ^1 is a sum of positive terms.

4.5 Concluding remarks

In this paper we have derived a theoretical framework for the kinetic chemical equilibrium regime introduced formally by Ludwig and Heil and we have presented a detailed investigation of the associated Euler and Navier-Stokes regimes. As a conclusion, it is interesting to consider the following points.

(1) The preceeding sections show that the underlying structure of the governing equations for gas mixtures in the kinetic chemical equilibrium regime is formally identical to the one obtained for gas mixtures in chemical nonequilibrium and then letting the chemical reactions approach equilibrium. This remark is valid for both the transport fluxes and the entropy production. It is important to notice, however, that the actual value of the transport coefficients is different in each case. Indeed, in the kinetic chemical equilibrium regime, the linearized Boltzmann operator $\Im$

contains terms accounting for reactive collisions, as opposed to the linearized Boltzmann operator that would be obtained if the chemical reactions were considered as a slow process.

(2) It is also interesting to point out that although the macroscopic governing equations in the kinetic equilibrium regime express conservation of element densities instead of species densities, the simplest structure in these equations is recovered by introducing species diffusion velocities. It is actually impossible to eliminate completely the species from the governing equations since the volumetric energy of the mixture cannot be expressed as a combination of quantities only depending on the elements.

Appendix. Differential relations

In this appendix, we present some useful differential relations needed in this work. We restate that in the kinetic chemical equilibrium regime the macroscopic independent variables are the element number densities, the mean average flow velocity, and the temperature. As a result, the species number densities n_i, $i \in \mathcal{S}$, are functions of the element number densities $\widetilde{n}_l$, $l \in \mathcal{E}$, and the temperature T. They are given by

$$\begin{cases} \displaystyle\sum_{i\in\mathcal{S}} n_i \mathcal{E}_{il} = \widetilde{n}_l, \\ \displaystyle\left(\log \frac{n_i}{Q_i}\right)_{i\in\mathcal{S}} \in \mathbb{E}, \end{cases} \tag{A.1}$$

recalling that $\mathbb{E}$ is the element space defined by (3.6). Differentiating (A.1) with respect to T first yields

$$\begin{cases} \displaystyle\left(\frac{\partial n_i}{\partial T}\right)_{i\in\mathcal{S}} \in \mathbb{E}^\perp, \\ \displaystyle\left(E_i - \frac{k_\mathrm{B} T^2}{n_i}\frac{\partial n_i}{\partial T}\right)_{i\in\mathcal{S}} \in \mathbb{E}, \end{cases} \tag{A.2}$$

while differentiating (A.1) with respect to n_m, for $m \in \mathcal{E}$, yields

$$\begin{cases} \displaystyle\sum_{i\in\mathcal{S}} \frac{\partial n_i}{\partial \widetilde{n}_m}\mathcal{E}_{il} = \delta_{lm}, \qquad m \in \mathcal{E}, \\ \displaystyle\left(\frac{1}{n_i}\frac{\partial n_i}{\partial \widetilde{n}_m}\right)_{i\in\mathcal{S}} \in \mathbb{E}, \qquad m \in \mathcal{E}. \end{cases} \tag{A.3}$$

Rather than number densities, it is also possible to consider partial pressures for the elements and the species, as given by (4.1). With the macroscopic variables (4.2), the species partial pressures are functions of the element partial pressures $\widetilde{p}_l$, $l \in \mathcal{E}$, and the temperature T. Eqs. (A.1) now read

$$\begin{cases} \displaystyle\sum_{i\in\mathcal{S}} p_i \mathcal{E}_{il} = \widetilde{p}_l, \\ \displaystyle\left(\log \frac{p_i}{k_\mathrm{B} T Q_i}\right)_{i\in\mathcal{S}} \in \mathbb{E}, \end{cases} \tag{A.4}$$

and differentiating (A.4) with respect to T and $\widetilde{p}_m$, for $m \in \mathcal{E}$, yields

$$\begin{cases} \displaystyle\left(\frac{\partial p_i}{\partial T}\right)_{i\in\mathcal{S}} \in \mathbb{E}^\perp, \\ \displaystyle\left(H_i - \frac{k_\mathrm{B} T^2}{p_i}\frac{\partial p_i}{\partial T}\right)_{i\in\mathcal{S}} \in \mathbb{E}, \end{cases} \tag{A.5}$$

and

$$\begin{cases} \displaystyle\sum_{i\in\mathcal{S}} \frac{\partial p_i}{\partial \widetilde{p}_m}\mathcal{E}_{il} = \delta_{lm}, \qquad m \in \mathcal{E}, \\ \\ \displaystyle\left(\frac{1}{p_i}\frac{\partial p_i}{\partial \widetilde{p}_m}\right)_{i\in\mathcal{S}} \in \mathbb{E}, \qquad m \in \mathcal{E}. \end{cases} \tag{A.6}$$

From the second relation in (A.6) we deduce that there exist a matrix $\gamma = (\gamma_{kl})_{k,l\in\mathcal{E}}$ such that

$$\frac{1}{p_i}\frac{\partial p_i}{\partial \widetilde{p}_l} = \sum_{l\in\mathcal{E}} \gamma_{kl}\mathcal{E}_{il}, \qquad i \in \mathcal{S},\ l \in \mathcal{E}, \tag{A.7}$$

and a straightforward calculation shows that

$$\gamma_{kl} = \gamma_{lk} = \sum_{i\in\mathcal{S}} \frac{1}{p_i}\frac{\partial p_i}{\partial \widetilde{p}_k}\frac{\partial p_i}{\partial \widetilde{p}_l}. \tag{A.8}$$

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