The kinetic chemical equilibrium regime

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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. © 1998 Elsevier Science B.V. All rights reserved.

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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 equilibrium 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 isotropic reactive gas mixture consisting of \( n \) chemical species having internal degrees of freedom. The starting point of our analysis is the Boltzmann equation derived in [8] for polyatomic gas mixtures without chemical reactions. This equation is obtained in a semiclassical framework, i.e., the translational motion of the particles 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]. For a relativistic kinetic gas theory, we refer to [11].

The state of the mixture is described by the species distribution functions denoted by \( f_i(t,x;c_i;l) \), where \( t \) is the time, \( x \) the three-dimensional spatial coordinate, \( c_i \) the velocity of the \( i \)th species and \( l \) the index for the internal energy state. For brevity, the dependence on \( (t,x) \) is made implicit. For a family of functions \( i \in \mathcal{S} \), where \( i \) depends on \( c_i \) and \( l \), we introduce the compact notation \( f_i \). 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

\[
\mathcal{D}_i(f_i) = \mathcal{B}_i(f) + \mathcal{C}_i(f); \quad i \in \mathcal{S};
\]

(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

\[
\mathcal{D}_i(f_i) = \mathcal{B}(f) + \mathcal{C}_i(f);
\]

(2.2)

where \( \mathcal{B}(f) \) and \( \mathcal{C}_i(f) \) are, respectively, the nonreactive and reactive source terms. The nonreactive source term is given by [1,8]

\[
\mathcal{B}_i(f) = \sum_{j \in \mathcal{S}} \sum_{l:j:J} \int \left( f_j f' \frac{\hat{a}_i \hat{a}_j}{\hat{a}_i \cdot \hat{a}_j} - f_i f_j \right) W_{lj}^{l'j'} \; dc_i \; dc_j \; dc_i' \; dc_j';
\]

(2.3)

where \( l \) and \( J \) are the indices for the quantum energy states of the \( i \)th and \( j \)th species before collision, \( l' \) and \( J' \) the corresponding numbers after collision, \( \hat{a}_i \) the degeneracy
of the \textit{i}th quantum energy shell of the \textit{i}th species and \( W_{ij}^{(I')} \) 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]

\[ W_{ij}^{(I')} a_i a_j = W_{ij}^{(I)} a_i a_j ; \]  

(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 [6,12]. 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

\[ i + j \rightleftharpoons k + l ; \]  

(2.5)

with species indices \( i; j; k; l \) assumed to be distinct and with \( i \) 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 [1,2,6,11,12]

\[ \mathcal{C}_i(f) = \sum_{j; K; L} \int \left( f_k f_i \frac{kK_{il}}{Ij} - f_i f_j \right) \gamma_{ijkl}^{K}_{gL} d\epsilon_l d\epsilon_k d\epsilon_l ; \]  

(2.6)

where the statistical weight \( iI \) is given by

\[ iI = \frac{\hbar^2}{a_i m_i} ; \]  

(2.7)

and where \( \hbar \) is the Planck constant, \( m \) the mass of the particles of the \( i \)th species and \( \gamma_{ijkl}^{K}_{gL} \) the transition probability for the forward reaction in Eq. (2.5). In Eq. (2.6), we have used the reciprocity relation between the forward and reverse transition probabilities which reads [1,2,6,12]

\[ \gamma_{ijkl}^{K}_{gL} = \gamma_{klij}^{I}_{iil} ; \]  

(2.8)

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

\[ i + i \rightleftharpoons k + i ; \]  

(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 [2,6,12]

\[ \mathcal{C}_i(f) = 2 \sum_{k; K; L} \int \left( f_k f_i \frac{kK_{il}}{iI} - f_i f_i \right) \gamma_{ijkl}^{K}_{gL} d\epsilon_l d\epsilon_k d\epsilon_l ; \]  

(2.10)
with \( f_i \) denoting \( f_i(x;\tilde{c};\tilde{f}) \). In the case of a chemical reaction involving three products, as in

\[
i + j \rightleftharpoons k + i + m;
\]

with all the indices assumed to be distinct, the reactive source term reads [2,6,12]

\[
q_i(f) = \sum_{j;K;L;M} \int \left( f_k f_i f_m \frac{\partial K L M}{\partial j j j} - f_i f_j \right) \frac{\partial K L M}{\partial i j j} \, \text{d}c_k \text{d}c_l \text{d}c_m; \tag{2.12}
\]

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

\[
i + j \rightleftharpoons i + i ; \tag{2.13}
\]

the forward and reverse reactions do not account for the same statistical event regarding species \( i \) so that the source term reads [2,6,12]

\[
q_i(f) = \sum_{j;L} \int \left( f_i f_j - f_i f_j \right) \frac{\partial L}{\partial i j j} \, \text{d}c_i \text{d}c_j \text{d}c_l + \sum_{L;f} \int \left( f_i f_j - f_i f_j \right) \frac{\partial L}{\partial i i j} \, \text{d}c_i \text{d}c_j \text{d}c_l ; \tag{2.14}
\]

We now generalize the above expressions into a single formalism valid for arbitrary reaction mechanisms. The reactive source term for the \( i \)th species reads

\[
q_i(f) = \sum_{(r)} q_i^{(r)}(f) ; \tag{2.15}
\]

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

\[
\sum_{j \in \mathcal{R}^{(r)}} j \rightleftharpoons \sum_{k \in \mathcal{P}^{(r)}} k ; \tag{2.16}
\]

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 \( \mathcal{R}^{(r)} = \{i;\} \) and \( \mathcal{P}^{(r)} = \{k;1\} \). We denote by \( i^{(r)} \) and \( j^{(r)} \) the stoichiometric coefficients of the \( i \)th species among reactants and products, respectively, and we also denote by \( \mathcal{R} \) and \( \mathcal{P} \) 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 $\mathcal{R}_i^{(r)}$, $\mathcal{R}_i$ and $\mathcal{P}_1$. With this notation, the source term for the $r$th elementary reaction reads

$$
\mathcal{E}_i^{(r)}(f) = \sum_{R_i \in \mathcal{R}_i} \int \left( \prod_{j \in \mathcal{R}_i} \mathcal{R}_i f_k - \prod_{j \in \mathcal{P}_1} \mathcal{P}_1 f_j \right) \frac{\mathcal{W}_{\mathcal{R}_i^{(r)}, \mathcal{P}_1^{(r)}}}{\prod_{j \in \mathcal{P}_1^{(r)}}} \
\times \prod_{j \in \mathcal{P}_1^{(r)}} \delta c_j \delta c_k + \sum_{R_i \in \mathcal{R}_i} \int \left( \prod_{j \in \mathcal{R}_i} f_j - \prod_{j \in \mathcal{R}_i} \mathcal{R}_i f_k \right) \frac{\mathcal{W}_{\mathcal{P}_1^{(r)}, \mathcal{R}_i^{(r)}}}{\prod_{j \in \mathcal{R}_i^{(r)}}} \
\times \prod_{j \in \mathcal{R}_i^{(r)}} \delta c_j \delta c_k ;
$$

(2.17)

with, for instance, $\prod_{j \in \mathcal{R}_i^{(r)}} \delta c_j \delta c_k$ standing for $\prod_{j \in \mathcal{R}_i^{(r)}} \delta c \prod_{j \in \mathcal{R}_i^{(r)}} \delta c$. In addition, $\mathcal{W}_{\mathcal{R}_i^{(r)}, \mathcal{P}_1^{(r)}}$ is the transition probability for a reactive collision in which the reactants $\mathcal{R}_i$ with internal energy states $\mathcal{R}_i$ are transformed into products $\mathcal{P}_1$ with internal energy states $\mathcal{P}_1$. Note that the following reciprocity relation holds for the transition probabilities [2]:

$$
\frac{\mathcal{W}_{\mathcal{R}_i^{(r)}, \mathcal{P}_1^{(r)}}}{\prod_{j \in \mathcal{P}_1^{(r)}}} = \frac{\mathcal{W}_{\mathcal{P}_1^{(r)}, \mathcal{R}_i^{(r)}}}{\prod_{j \in \mathcal{R}_i^{(r)}}} ;
$$

(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

$$
S^{\text{kin}} = -k_B \sum_{i,l} \int f_i (\log(\mathcal{R}_i f_i) - 1) \delta c_l ;
$$

(2.19)

Multiplying the Boltzmann equation (2.1) by $-k_B \log(\mathcal{R}_i f_i)$, integrating over $\delta c_l$ and summing over $i$ and $l$ yields the entropy conservation equation in the form

$$
@ S^{\text{kin}} + @ \cdot (S^{\text{kin}} v) + @ \cdot J^{\text{kin}} = ^{\text{kin}} ;
$$

(2.20)

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

$$
J^{\text{kin}} = -k_B \sum_{i,l} \int (\mathcal{R}_i - v) f_i (\log(\mathcal{R}_i f_i) - 1) \delta c_l ;
$$

(2.21)

and $^{\text{kin}}$ the kinetic entropy source term. The source term reads

$$
^{\text{kin}} = ^{\text{kin};\mathcal{R}_i} + ^{\text{kin};\mathcal{P}_1} ;
$$

(2.22)
with the nonreactive source term given by

\[
\text{kin}^\text{ND} = -k_B \sum_{i,l} \int \mathcal{B}(f_i) \log(f_i f_i) \, dc_i \\
= \frac{1}{4} k_B \sum_{i,j \in \mathcal{I}} \sum_{l,j' \in \mathcal{I}} \int \left( \frac{f_i' f_j'}{a_i a_j} : \frac{f_i f_j}{a_i a_j} \right) \frac{W_{ij}^j}{(a_i a_j)^{-1}} \, dc_i \, dc_j' \, dc_j';
\]

(2.23)

and the reactive source term by

\[
\text{kin}^\text{R} = -k_B \sum_{i,l} \int \mathcal{D}(f_i) \log(f_i f_i) \, dc_i \\
= k_B \sum_{i} \sum_{R,P} \int \left( \prod_{\rho} f_i \right) \frac{\mathcal{F}_{R}[R]}{\prod_{\rho} f_j} \, dc_i \, dc_j;
\]

(2.24)

with \((x,y) = \log(x/y)(x-y)\). It is readily seen that both \text{kin}^\text{ND} and \text{kin}^\text{R} 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

\[
I = \begin{cases} 
(\delta_{i1})_{i \in \mathcal{I}}; & l \in \mathcal{E}; \\
(\mathcal{M}c_i)_{i \in \mathcal{I}}; & l = n_e + 1; \\
(\mathcal{M}c_i + \mathcal{E}_i)_{i \in \mathcal{I}}; & l = n_e + 4;
\end{cases}
\]

(2.25)

where \(\delta_{i1}\) is the number of element \(l\) in the \(i\)th species, \(c_i\) the component of \(c_i\) in the \(th\) spatial coordinate, and \(\mathcal{E}_i\) the total internal energy of the \(i\)th species in the \(l\)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 \((i)_{i \in \mathcal{I}} = (j)_{j \in \mathcal{J}}\) and \((l)_{l \in \mathcal{L}} = (m)_{m \in \mathcal{M}}\), we introduce the scalar product

\[
\langle i, l \rangle = \sum_{i,l} \int \langle f_i f_l \rangle \, dc_i.
\]

(2.26)
More generally, when dealing with tensor quantities $\xi$ and $\zeta$, the scalar product becomes
\[(\langle \xi ; \zeta \rangle) = \sum_{i;\ell} \int \xi_i \otimes \zeta_i \, d\mathbf{c}_{\ell},\]
where $\xi_i \otimes \zeta_i$ denotes the maximum contracted product between tensors $\xi_i$ and $\zeta_i$.

The macroscopic properties are given by
\[
\langle \langle f ; \mathbf{l} \rangle \rangle = \left\{ \begin{array}{ll}
\bar{n}_i; & l \in \mathcal{E}; \\
v_i; & l = n_e + \ell = 1; 2; 3; \\
\frac{1}{2} \mathbf{v} \cdot \mathbf{v} + E_i; & l = n_e + 4;
\end{array} \right.
\]  \quad (2.27)
where $\bar{n}_i$ denotes the number density for the $l$th element, $\mathbf{v}_i$ the velocity of the mixture, $\bar{m}$ the molecular mass of the $l$th element, $v$ the component in the $\ell$th spatial coordinate of the mean average velocity $\mathbf{v}$, and $E$ the total internal energy per unit volume of the mixture. We introduce the partition function for internal energy $Q_i^{\text{int}}$ for the $i$th species
\[
Q_i^{\text{int}} = \sum_l a_l \exp(-E_i \& k_B T); \quad (2.28)
\] where $k_B$ is the Boltzmann constant and $T$ the temperature, as well as the translational and full partition functions
\[
Q_i^T = \left( \frac{2 \bar{m} k_B T}{\bar{n}_i} \right)^{3d}; \quad Q_i = Q_i^T Q_i^{\text{int}}; \quad (2.29)
\]
We also introduce the averaged internal energy of the $i$th species
\[
E_i = \frac{1}{Q_i^{\text{int}}} \sum_l a_l E_i \exp(-E_i \& k_B T) \quad (2.30)
\] as well as the internal energy of the $i$th species and its enthalpy
\[
E_i = \frac{3}{2} k_B T + E_i; \quad H_i = \frac{3}{2} k_B T + E_i; \quad i \in \mathcal{E}; \quad (2.31)
\]
The species number densities are defined as
\[
n_i = \sum_l \int f_i \, d\mathbf{c}_{\ell}; \quad i \in \mathcal{E}; \quad (2.32)
\] in such a way that
\[
\bar{n}_i = \sum_{l \in \mathcal{E}} n_i \delta_l; \quad l \in \mathcal{E}; \quad (2.33)
\] The total internal energy per unit volume of the mixture then reads
\[
E = \sum_{i \in \mathcal{E}} n_i E_i; \quad (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 Eq. (2.1) in the form

$$D_i(f_i) = \frac{1}{\pi}( \mathcal{B}_i(f) + \mathcal{G}_i(f) ); \quad i \in \mathcal{S};$$

(2.35)

where $\alpha$ is a formal expansion parameter, the species distribution functions are expanded as

$$f_i = f_{i0}(1 + \alpha_i + O(\alpha^2)); \quad i \in \mathcal{S};$$

(2.36)

The family of zeroth-order distribution functions $f_0 = (f_0_i)_{i \in \mathcal{S}}$ is the solution of

$$\mathcal{B}_i(f_0) + \mathcal{G}_i(f_0) = 0; \quad i \in \mathcal{S};$$

(2.37)

In order to determine $f_0$ uniquely, it is classical to impose that $f_0$ yield the local macroscopic properties

$$\langle \langle f_0; l \rangle \rangle = \langle \langle f; l \rangle \rangle; \quad 1 \in \mathcal{S};$$

(2.38)

We will see in Section 3 that Eqs. (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 $f_1 = (f_1_i)_{i \in \mathcal{S}}$ are the solution of non-homogeneous integral equations written in the form

$$\mathcal{B}_i(f_1) + \mathcal{G}_i(f_0) = \Xi_i(f_0); \quad i \in \mathcal{S};$$

(2.39)

where the right member uniquely depends on $f_0$ and reads

$$\Xi_i = -D_i(\log f_0^0); \quad i \in \mathcal{S};$$

(2.40)

In addition, $\Xi_i$ denotes the linearized collision operator for the $i$th species, which reads

$$\Xi_i(\cdot) = \Xi_i^\#(\cdot) + \Xi_i^\#(\cdot);$$

(2.41)

where the nonreactive and reactive collision operators are given by

$$\Xi_i^\#(\cdot) = -\frac{1}{f_0^0} \langle \mathcal{B}_i(f_0) f_0^0 \rangle; \quad \Xi_i^\#(\cdot) = -\frac{1}{f_0^0} \langle \mathcal{G}_i(f_0) f_0^0 \rangle;$$

(2.42)

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

$$\langle \langle f_0; l \rangle \rangle = 0; \quad 1 \in \mathcal{S};$$

(2.43)

The first-order species distribution functions $f_1 = (f_1_i)_{i \in \mathcal{S}}$ given by

$$f_1_i = f_0_i(1 + \alpha_i); \quad i \in \mathcal{S};$$

(2.44)
are then such that
\[ \langle \langle f^1 \rangle \rangle = \langle \langle f^0 \rangle \rangle = \langle \langle f \rangle \rangle; \quad 1 \in \mathcal{S}; \]

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 Eq. (2.37), we first deduce that

\[ 0 = -k_B \sum_{i,l} \int (\mathcal{B}_l(f^0) + \mathcal{C}_l(f^0)) \log(\|f^0_l \|) \, dc_l = 0; \]

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

\[ (\log(\|f^0_i \|))_{i \in \mathcal{S}} \in \mathcal{S}; \]

Using Eq. (2.25) we obtain that

\[ \log(\|f^0_i \|) = \sum_{l=1}^{n+4} \begin{pmatrix} 1 \\ i \end{pmatrix} \exp \left\{ -\frac{m}{2k_B T}(c_l - v)^2 - \frac{E_i}{k_B T} \right\}; \]

and the constants \( i \) are determined from the macroscopic constraints (2:38). After some algebra we get

\[ f^0_i = \frac{a_i m^3}{\hbar^3 Q_i} \exp \left\{ -\frac{m}{2k_B T}(c_l - v)^2 - \frac{E_i}{k_B T} \right\} \]

\[ = \left( \frac{m}{2k_B T} \right)^{3/2} \frac{a_i n_i}{Q_i^{\text{int}}} \exp \left\{ -\frac{m}{2k_B T}(c_l - v)^2 - \frac{E_i}{k_B T} \right\}; \]

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

\[ \left( \log \frac{n}{Q_i} \right)_{i \in \mathcal{S}} \in \mathcal{E}; \]
where we have introduced the element space

\[ E = \text{Vect}(\delta_1; \cdots; \delta_n); \]  

(3.6)

where \( \delta_l = (\delta_{il}) \in \mathcal{E} \) for \( l \in \mathcal{L} \).

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 per unit volume

\[ S^0 = -k_B \sum_{l=1}^n \int f_i^0 \left( \log(f_i^0) - 1 \right) d\mathcal{L}; \]  

(3.7)

we obtain after some algebra that

\[ S^0 = \sum_{i \in \mathcal{I}} n_i S^0_i; \]  

(3.8)

with the zeroth order molecular entropies \( S^0_i \) given by

\[ S^0_i = \frac{H_i}{T} - k_B \log \frac{n_i}{Q_i}; \]  

(3.9)

At the zeroth order, the species chemical potentials read

\[ \psi^0_i = \frac{1}{m_i} \left( H_i - TS^0_i \right) = \frac{k_B T}{m_i} \log \frac{n_i}{Q_i}; \]  

(3.10)

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

\[ M^0 = (m_i^0)_{i \in \mathcal{I}} \in E: \]  

(3.11)

This relation simply states the usual equilibrium conditions for the chemical reactions, as detailed for instance in [14,15]. In addition, the resulting equilibrium constant is exactly the same as would be obtained using the rules of statistical mechanics [1,16].

3.2. Macroscopic conservation equations

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

\[ \langle \langle \mathcal{L}; \mathcal{D}(f^0) \rangle \rangle = 0; \quad \mathcal{L} \in \mathcal{I}; \]  

(3.12)

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

\[ \mathcal{G}n + \mathcal{G} \cdot (n \mathbf{v}) = 0; \quad \mathcal{L} \in \mathcal{E}; \]  

(3.13)

\[ \mathcal{G}(\mathbf{v}) + \mathcal{G} \cdot (\mathbf{v} \otimes \mathbf{v}) = \mathcal{G}p + \sum_{i \in \mathcal{I}} \mathbf{b}_i; \]  

(3.14)
\[
\frac{1}{2} \frac{\partial v^2}{\partial t} + E + \frac{\partial \cdot ((\frac{1}{2} v^2 + E) v)}{\partial t} = - \nabla \cdot (\rho v) + \sum_{i \in S} \mathbf{b}_i \cdot v; \tag{3.15}
\]

where \( \mathbf{n}_i = n_i \mathbf{m} \) 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 introducing the particular derivative \( \frac{\partial}{\partial t} = \frac{\partial}{\partial t} + v \cdot \nabla \), a straightforward calculation yields

\[
\mathbf{c}_{\text{mol}} \frac{\partial v}{\partial T} = \left\{ -(p + E) + \sum_{i \in S} \left( n_i \sum_{i \in S} \frac{\partial}{\partial \mathbf{m}} E_i \right) \right\} \cdot v; \tag{3.16}
\]

The molecular heat capacity \( \mathbf{c}_{\text{mol}} \) which appears in Eq. (3.16) consists of three contributions

\[
\mathbf{c}_{\text{mol}} = \frac{1}{2} k_0 \mathbf{n} + \sum_{i \in S} n_i \mathbf{c}_{\text{int;mol}} + \sum_{i \in S} n_i \mathbf{c}_{\text{chem;mol}}; \tag{3.17}
\]

where \( \mathbf{n} = \sum_{i \in S} n_i \) is the total number density. The first term in Eq. (3.17) accounts for the translational heat capacity, while \( \mathbf{c}_{\text{int;mol}} \) and \( \mathbf{c}_{\text{chem;mol}} \) are, respectively, the internal and chemical molecular heat capacity of the \( i \)-th species given by

\[
\mathbf{c}_{\text{int;mol}} = \frac{d E_i}{d T}; \quad \mathbf{c}_{\text{chem;mol}} = \frac{1}{n_i} \frac{\partial}{\partial \mathbf{m}} E_i; \tag{3.18}
\]

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

The species perturbed distribution functions \( \mathbf{f}_{\text{pert}(i)} \) are the solution of the integral equations (2.39) completed by the constraints (2.43). Using Eq. (3.2), the non-reactive and reactive collision operators now read

\[
\mathcal{S}_{\text{pert}}(i) = \sum_{j \in S} \sum_{j' \in S} \int f_j^0(i + j) \delta_{ij} \delta_{ij'} \mathbf{c}_{ij} \mathbf{d}_{ij}; \tag{4.1}
\]

and

\[
\mathcal{S}_{\text{pert}}(i) = 2(\mathbf{p}) \sum_{j \in \mathcal{A}_{\text{pert}}} \int \prod_{j \in \mathcal{A}_{\text{pert}}} f_j^0 \left( \sum_{j} - \sum_{j' \in \mathcal{A}_{\text{pert}}} k \right) W_{\mathbf{p}} \prod_{j \in \mathcal{A}_{\text{pert}}} \mathbf{d}_{ij} \mathbf{d}_{k};
\]
The linearized collision operator \( \mathcal{Z} = \mathcal{Z}^R + \mathcal{Z}^\lambda \) has important structure properties which generalize those discussed in [13] for nonreactive mixtures. We introduce the bracket operator

\[
[ ; ] = \langle f^0 ; \mathcal{Z}( ) \rangle ;
\]

keeping in mind that \( f^0 \) and \( \mathcal{Z} \) may be either scalar or tensor quantities. It is readily seen from Eqs. (4.1) and (4.2) that the bracket operator has the following fundamental properties.

(i) it is symmetric: \([ ; ] = [ ; ]\),
(ii) it is positive semi-definite: \([ ; ] \geq 0\),
(iii) its kernel is spanned by the collisional invariants: \([ ; ] = 0 \Leftrightarrow \mathcal{Z} \).

On the other hand, the right member \( H_i \) in Eq. (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

\[
\bar{p}_l = n_l k_l T ; \quad l \in \mathcal{E} ; \quad p_i = n_i k_i T ; \quad i \in \mathcal{I} ;
\]

With the \( n_e + 4 \) macroscopic variables \( \mathbf{l} \) given by

\[
\mathbf{l} = \begin{cases} 
\bar{p}_l ; & l \in \mathcal{E} ; \\
\nu ; & l = n_e + ; \\
1 k_l T ; & l = n_e + 4 
\end{cases} \quad = 1;2;3 ;
\]

we obtain

\[
\mathbf{i} = \sum_{l=1}^{n_e+4} \mathbf{l} | (\mathbf{D}_l \mathbf{i} + (c_l - \nu) \cdot \mathbf{G}^0 ) - \frac{m}{k_l T} (c_l - \nu) \cdot \mathbf{b}_l ;
\]

with

\[
\mathbf{i} = \frac{1}{\mathbf{f}^0} \frac{\mathbf{G}^0}{\mathbf{G}^0} \mathbf{l} = \begin{cases} 
1 \mathbf{G}_l \bar{p}_l / \bar{p}_l ; & l \in \mathcal{E} ; \\
\frac{m}{k_l T} (c_l - \nu) ; & l = n_e + ; \\
H_i - \frac{k_l T^2 \mathbf{G}_l \mathbf{G}_l}{p_i} - \frac{1}{2} m (c_l - \nu)^2 - E_i ; & l = n_e + 4 ;
\end{cases} \quad = 1;2;3 ;
\]

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

$$i = -\mathbf{\Psi}_i : \mathbf{\bar{\nabla}} \mathbf{r} - \frac{1}{3} \mathbf{i} \cdot \mathbf{\bar{\nabla}} \cdot \mathbf{r} - \sum_{l \in \mathcal{E}} \mathbf{\Psi}_i^\mathcal{E} : \mathbf{\bar{\nabla}} \mathbf{p}_l - \mathbf{\Psi}_i' : \mathbf{\bar{\nabla}}(1 - k_0 T)$$

$$+ \sum_{j \in \mathcal{F}} \mathbf{\Psi}_i^\mathcal{F} : \mathbf{\bar{\nabla}} \mathbf{b}_j;$$

(4.8)

with

$$\mathbf{\Psi}_i = \frac{m_i}{k_0 T} \left\{ (c_i - v) \otimes (c_i - v) - \frac{1}{3}(c_i - v)^2 I \right\};$$

$$i = \frac{1}{3} \frac{m_i}{k_0 T} (c_i - v)^2 - \frac{1}{k_0 T^2} \sum_{l \in \mathcal{E}} \frac{\mathbf{\bar{p}}_l}{\mathbf{p}_l} \otimes \mathbf{\bar{\nabla}} \mathbf{p}_l$$

$$+ \frac{1}{k_0 T^3} \sum_{j \in \mathcal{F}} \left( n_j - \sum_{l \in \mathcal{E}} \frac{n_l}{\mathbf{\bar{\nabla}} \mathbf{p}_l} \right) E_j$$

$$\times \left\{ H_l - k_0 T^2 \frac{\mathbf{\bar{p}}_l}{\mathbf{p}_l} \otimes \mathbf{\bar{\nabla}} \mathbf{p}_l - \sum_{l \in \mathcal{E}} k_0 T \frac{\mathbf{\bar{p}}_l}{\mathbf{p}_l} \otimes \mathbf{\bar{\nabla}} \mathbf{p}_l - \frac{1}{2} m(c_i - v)^2 - E_l \right\};$$

$$\mathbf{\Psi}_i^\mathcal{E} = \frac{1}{p_i} \left\{ \frac{\Phi_i}{\mathbf{\bar{\nabla}} \mathbf{p}_i} - \gamma_i \sum_{j \in \mathcal{F}} \frac{\Phi_j}{\mathbf{\bar{\nabla}} \mathbf{p}_j} \right\} (c_i - v);$$

$$\mathbf{\Psi}_i' = \left\{ H_l - k_0 T^2 \frac{\mathbf{\bar{p}}_l}{\mathbf{p}_l} \otimes \mathbf{\bar{\nabla}} \mathbf{p}_l - \gamma_i \sum_{j \in \mathcal{F}} \frac{\Phi_j}{\mathbf{\bar{\nabla}} \mathbf{p}_j} \right\} - \frac{1}{2} m(c_i - v)^2 - E_l \right\} (c_i - v);$$

$$\mathbf{\Psi}_i^\mathcal{F} = \frac{1}{p_i}( i - \gamma_i)(c_i - v);$$

(4.9)

where $I$ is the identity matrix and $ij$ the Kronecker symbol. Letting $\mathcal{E}$, $\mathcal{F}$, or $\mathcal{D}_j$ for $j \in \mathcal{F}$, or $\mathcal{D}_j$ for $j \in \mathcal{F}$, we deduce from the expansion (4.8) for $i$ a similar expansion for $i$, namely

$$i = -\phi_i : \mathbf{\bar{\nabla}} \mathbf{r} - \frac{1}{3} \mathbf{i} \cdot \mathbf{\bar{\nabla}} \cdot \mathbf{r} - \sum_{l \in \mathcal{E}} \phi_i^\mathcal{E} : \mathbf{\bar{\nabla}} \mathbf{p}_l - \phi_i' : \mathbf{\bar{\nabla}}(1 - k_0 T)$$

$$+ \sum_{j \in \mathcal{F}} \phi_i^\mathcal{F} : \mathbf{\bar{\nabla}} \mathbf{b}_j;$$

(4.10)

and each of the expansion coefficients $\phi_i^\mathcal{F} = \phi_i( i )_{\in \mathcal{F}}$ in Eq. (4.10) is the solution of the constrained integral equations

$$\left\{ \begin{array}{c}
\langle f \rangle = i; \\
\langle f \rangle = i\\n\langle f \rangle = i
\end{array} \right\} = 0; \\
\langle f \rangle = i;$$

(4.11)
It is easily verified that the above systems are well posed for all , i.e., the right member is in the range of the operator and the solution is unique.

4.2. Macroscopic conservation equations

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

\[ \left\langle \langle 1; D(f_i) \rangle \right\rangle = 0; \quad i \in \mathcal{I}; \]  

(4.12)

where we have introduced the family \( D(f_i) = (D_i(f_i^0))_{i \in \mathcal{I}} \). We introduce two types of diffusion fluxes, the classical species diffusion fluxes given by

\[ n_i V_i = \sum_i \int (c_i - v) f_i^0 \, dc_i; \quad i \in \mathcal{I}; \]  

(4.13)

and the element diffusion fluxes defined as

\[ \tilde{n}_i \tilde{V}_i = \sum_{i,j} \delta_{ij} n_i V_i; \quad i \in \mathcal{I}; \]  

(4.14)

in such a way that

\[ \tilde{n}_i \tilde{V}_i = \sum_{i \in \mathcal{I}} \delta_{ij} n_i V_i; \quad i \in \mathcal{I}; \]  

(4.15)

After some algebra, we obtain the macroscopic equations expressing conservation of element densities, momentum and energy in the form

\[ \begin{align*}
\nabla \tilde{n} + \nabla \cdot (\tilde{n} v) + \nabla \cdot (\tilde{n} \tilde{V}_i) &= 0; \quad i \in \mathcal{I}; \\
\nabla \cdot (v) + \nabla \cdot (v \otimes v) + \nabla \cdot P &= \sum_{i \in \mathcal{I}} \delta_{ij} \left[ \left( \frac{1}{2} v^2 + E \right) \right] + \nabla \cdot (Q + P \cdot v) \\
\ &= \sum_{i \in \mathcal{I}} \delta_{ij} \left[ (v + V_i) \right]; 
\end{align*} \]  

(4.16)

(4.17)

(4.18)

With the element diffusion velocities given by Eq. (4.15), we still need to specify the species diffusion velocities \( V_i \) for \( i \in \mathcal{I} \), the heat flux vector \( Q \) and the pressure tensor \( P \). These transport fluxes are expressed in terms of the species perturbed distribution functions as follows:

\[ V_i = k_B T \left\langle \langle D_i^0; f^0 \rangle \right\rangle; \quad i \in \mathcal{I}; \]  

(4.19)

\[ P = p I + \Pi; \quad \Pi = k_B T \left\langle \langle \Psi; f^0 \rangle \right\rangle + \frac{k_B T}{3} \left\langle \langle f^0 \rangle \right\rangle I; \]  

(4.20)
\[
Q = - \left( \sum_{i \in \mathcal{S}} \left( H_i - \frac{k_B T^2 \phi_i}{p_i} \right) \right) \nabla V_i \tag{4.21}
\]

where \( \Pi \) is the viscous stress tensor. In the next section we express the transport fluxes Eqs. (4.19)–(4.21) in terms of various transport coefficients.

### 4.3. Transport coefficients

We first consider the viscous stress tensor \( \Pi \). We introduce the shear viscosity and the volume viscosity given by

\[
\begin{align*}
\nu &= \frac{k_B T}{10} \left[ \phi ; \phi \right]; \\
\nu_v &= \frac{k_B T}{9} \left[ \phi ; \phi \right];
\end{align*}
\]

and the viscous stress tensor then reads

\[
\Pi = - \left( \nabla \mathbf{v} + (\nabla \mathbf{v})^T - \frac{2}{3} (\nabla \cdot \mathbf{v}) I \right) - (\nabla \cdot \mathbf{v}) I. \tag{4.23}
\]

We next turn to the species diffusion velocities \( V_i, i \in \mathcal{S} \), and the heat flux vector \( Q \). We define the species multicomponent and the thermal diffusion coefficients as

\[
D_{ij} = \frac{\rho k_B T}{3} \left[ \phi^{D_i} ; \phi^{D_j} \right]; \quad i,j \in \mathcal{S};
\]

\[
i = - \frac{1}{3} \left[ \phi ; \phi^{D_i} \right]; \quad i \in \mathcal{S}; \tag{4.24}
\]

the partial thermal conductivity as

\[
\lambda' = \frac{1}{3 k_B T^2} \left[ \phi ; \phi' \right]; \tag{4.25}
\]

and the diffusion driving forces as

\[
d_j = \frac{1}{p} \left( \sum_{i \in \mathcal{S}} \frac{\phi_i}{\phi_i} \nabla p_i - j b_j \right); \quad j \in \mathcal{S}. \tag{4.26}
\]

The species diffusion velocities may then be written as

\[
V_i = - \sum_{j \in \mathcal{S}} D_{ij} d_j - i \nabla \log T; \quad i \in \mathcal{S}; \tag{4.27}
\]

and the heat flux vector as

\[
Q = - \lambda T - \rho \sum_{i \in \mathcal{S}} d_i + \sum_{i \in \mathcal{S}} \left( H_i - \frac{k_B T^2 \phi_i}{p_i} \right) \nabla V_i. \tag{4.28}
\]
It is also possible to use a formalism identical to the one arising for mixtures with nonequilibrium chemistry. We first notice that

\[ \mathbf{\psi}^D = \sum_{j \in \mathcal{S}} \mathbf{\psi}^D_j \left( \mathbf{\Phi}^D_j / \mathbf{\Phi}^D \right) ; \quad (4.29) \]

Thus, by linearity, the corresponding solutions of the integral Boltzmann equations (4.11) are such that

\[ \phi^D = \sum_{j \in \mathcal{S}} \phi^D_j \left( \mathbf{\Phi}^D_j / \mathbf{\Phi}^D \right) ; \quad (4.30) \]

We also introduce the quantities

\[ \bar{\psi}_i' = (H_i - \frac{1}{2}m(c_i - v)^2 - E_i/c_i - v) ; \quad i \in \mathcal{S} ; \quad (4.31) \]

in such a way that

\[ \mathbf{\psi}' = \bar{\psi}' - k_B T^2 \sum_{j \in \mathcal{S}} \mathbf{\psi}^D_j \left( \mathbf{\Phi}^D_j / \mathbf{\Phi}^D \right) ; \quad (4.32) \]

Upon introducing the integral equations

\[ \mathcal{R}_i(\phi') = \bar{\psi}_i' ; \quad i \in \mathcal{S} ; \quad \left\langle \left\langle f^0 \phi' ; j \right\rangle \right\rangle = 0 ; \quad j \in \mathcal{S} ; \quad (4.33) \]

we obtain by linearity that

\[ \phi' = \bar{\phi}' - k_B T^2 \sum_{j \in \mathcal{S}} \phi^D_j \left( \mathbf{\Phi}^D_j / \mathbf{\Phi}^D \right) ; \quad (4.34) \]

We then define the thermal diffusion coefficients as

\[ \hat{\phi}_i = -\frac{1}{3} \left[ \mathbf{\phi}' ; \phi^D \right] = \mathbf{\phi}' - \frac{T}{p} \sum_{j \in \mathcal{S}} \mathbf{D}_{ij} \left( \mathbf{\Phi}^D_j / \mathbf{\Phi}^D \right) ; \quad i \in \mathcal{S} ; \quad (4.35) \]

the partial thermal conductivity as

\[ \hat{c}' = \frac{1}{3k_B T^2} \left[ \mathbf{\phi}' ; \mathbf{\phi}' \right] ; \quad (4.36) \]

and the species diffusion driving forces as

\[ \hat{d}_j = \frac{1}{p} \left( \sum_{i \in \mathcal{S}} \frac{\mathbf{\Phi}^D_j}{\mathbf{\Phi}^D} \mathbf{\Phi}_{ij} + \frac{\mathbf{\Phi}^D_j}{\mathbf{\Phi}^D} \mathbf{\Phi}^T - \mathbf{\phi}_j \right) ; \quad j \in \mathcal{S} ; \quad (4.37) \]

The species diffusion velocities \( V_i \) are then given by

\[ V_i = -\sum_{j \in \mathcal{S}} \mathbf{D}_{ij} \hat{d}_j - \hat{c}_i \log T ; \quad i \in \mathcal{S} ; \quad (4.38) \]
and the heat flux vector by
\[ Q = -\hat{\gamma} \otimes T - p \sum_{i \in \Omega} \hat{\gamma} d_i + \sum_{i \in \Omega} H_i n V_i : \]  
\[ (4.39) \]

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 [17]. The thermal diffusion ratios \( \hat{\gamma}_i \), for \( i \in \Omega \), are the unique solution of the constrained singular system
\[ \sum_{j \in \Omega} D_{ij} \hat{\gamma}_j = \hat{\gamma}_i ; \quad i \in \Omega ; \] 
\[ \sum_{j \in \Omega} \hat{\gamma}_j = 0 ; \]  
\[ (4.40) \]

while the thermal conductivity reads
\[ \hat{\gamma} = \hat{\gamma} - \frac{p}{T} \sum_{j \in \Omega} \hat{\gamma} \hat{j} ; \]  
\[ (4.41) \]

Upon introducing
\[ \hat{\phi} = \hat{\phi}^T + pk_0 T \sum_{j \in \Omega} \hat{\gamma}_j \hat{\phi}_j ) ; \]  
\[ (4.42) \]
we may write
\[ \hat{\gamma} = \frac{1}{3k_0 T^2} [\hat{\phi} : \hat{\phi}] ; \]  
\[ \hat{\gamma}_i = \frac{m}{3p k_0 T} [\mathbf{E}_i : \hat{\phi}] ; \quad i \in \Omega ; \]  
\[ (4.43) \]

with \( \mathbf{E}_i = (c_i - v) \hat{j} \) \( i \in \Omega \), and we recover the formalism derived in [17] for nonreactive mixtures. Using the thermal conductivity and the thermal diffusion ratios, the species diffusion velocities and the heat flux vector read
\[ V_i = -\sum_{j \in \Omega} D_{ij} (d_i + \hat{\gamma} \hat{j} \otimes \log T) ; \quad i \in \Omega ; \]  
\[ Q = -\hat{\gamma} \otimes T - p \sum_{i \in \Omega} \hat{\gamma} V_i + \sum_{i \in \Omega} H_i n V_i : \]  
\[ (4.44) \]

The transport coefficients introduced above satisfy several important properties which result from those of the bracket operator \([\cdot, \cdot] \). First, the matrix of order \( n + 1 \)
\[ \left( \begin{array}{cc} \hat{\gamma} & \hat{p} \\ \hat{p} & \hat{D}_{ij} \end{array} \right)_{i \in \Omega, j \in \Omega} \]  
\[ (4.45) \]
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 \( \hat{\gamma} \) is positive and that the
diffusion matrix $D = (D_{ij})_{i,j \in S}$ is symmetric positive semi-definite with kernel spanned by the mass fraction vector $(Y_1; \ldots; Y_n)$. On the other hand, the shear viscosity is positive and the volume viscosity 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 $\bar{V}_k$, $k \in \mathcal{E}$, as follows:

$$
\bar{V}_k = - \sum_{l \in \mathcal{E}} \bar{D}_{kl} \frac{1}{p} \partial p_l - \bar{\kappa} \log T + \sum_{ij \in S} \frac{n}{f_k} \epsilon_{ik} D_{ij} \frac{j b_j}{p};
$$

(4.46)

where we have introduced the element multicomponent diffusion coefficients

$$
\bar{D}_{kl} = \sum_{ij \in S} \frac{n}{f_k} D_{ij} \left( \frac{\partial j}{\partial l} \right) \epsilon_{ik}; \quad k \in \mathcal{E};
$$

(4.47)

and the thermal diffusion coefficients for the elements

$$
\bar{\kappa} = \sum_{i \in S} \frac{n}{f_k} \epsilon_{ik}; \quad k \in \mathcal{E};
$$

(4.48)

Note also that when all the species external forces are equal, i.e., $b_i = b$ for $i \in S$, the last term in Eq. (4.46) vanishes. Introducing the matrix $(\bar{D}_{kl})_{k,l \in \mathcal{E}}$ defined in the appendix, the element multicomponent diffusion coefficients may be expressed as

$$
\bar{D}_{kl} = \sum_{m \in \mathcal{E}} k_T l m \sum_{ij \in S} \frac{1}{f_k} D_{ij} n \epsilon_{ik} n \epsilon_{jm};
$$

(4.49)

As opposed to the diffusion matrix $D$, the element diffusion matrix $\bar{D} = (\bar{D}_{kl})_{k,l \in \mathcal{E}}$ 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 $\bar{D}$.

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, denoted by $S$, reads

$$
S = -k_B \sum_{i=1} \int f_i^0 \left( \log(f_i^0) - 1 \right) d\Omega_i
$$

$$
= \sum_{i \in S} n S_i^0 + \mathcal{E}(n^2);
$$

(4.50)
where the zeroth-order molecular entropies are given by Eq. (3.9). The Gibbs free energy per unit volume of the species

$$G_i = H_i - TS_i^0 = k_BT log \frac{n_i}{Q_i};$$

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

$$(G_i)_{i \in \mathcal{E}} \in \mathcal{E}: \quad (4.52)$$

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

$$\sum_i G_i \frac{\partial n_i}{\partial \theta} = 0: \quad (4.53)$$

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

$$\tilde{G}_l = \sum_{i \in \mathcal{E}} G_i \frac{\partial \Phi_i}{\partial \theta}; \quad l \in \mathcal{E}; \quad (4.54)$$

as well as the enthalpy per unit volume for the elements

$$\tilde{H}_l = \sum_{i \in \mathcal{E}} H_i \frac{\partial \Phi_i}{\partial \theta}; \quad l \in \mathcal{E}; \quad (4.55)$$

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

$$G = \sum_{i \in \mathcal{E}} n_i G_i = \sum_{l \in \mathcal{E}} \tilde{n}_l \tilde{G}_l; \quad (4.56)$$

and that

$$H = \sum_{i \in \mathcal{E}} n_i H_i = \sum_{l \in \mathcal{E}} \tilde{n}_l \tilde{H}_l + T \left( \frac{\partial \Phi}{\partial \theta} \right)_{\theta}; \quad (4.57)$$

Using the above relations, we deduce that the differential of the volumetric entropy in the Navier-Stokes equilibrium regime is given by the relation

$$T dS = dE - \sum_{l \in \mathcal{E}} \tilde{G}_l d\tilde{n}_l: \quad (4.58)$$

This relation generalizes the Gibbs differential relation to the kinetic chemical equilibrium regime. A conservation equation for $S$ is then easily obtained from Eq. (4.58) and the macroscopic conservation equations stated in Section 4.2. A straightforward calculation yields that

$$\nabla \cdot S + \nabla \cdot (\nu S) + \nabla \cdot J_S = 0; \quad (4.59)$$
where $J_s$ is the entropy flux vector given by

$$J_s = \frac{1}{T} \left( Q - \sum_{l \in \mathcal{E}} \nabla_l \tilde{V}_l \right);$$

(4.60)

and the entropy source term reads

$$= -\frac{Q}{T^2} \frac{\partial T}{\partial \bar{p}_l} - \frac{\Pi \cdot \nabla \bar{V}_l}{T} + \frac{1}{T} \sum_{i \in \mathcal{F}} \bar{V}_l \cdot \bar{b}_i - \sum_{l \in \mathcal{E}} \bar{n} \tilde{V}_l \cdot \nabla \left( \frac{\bar{G}_l}{T} \right);$$

(4.61)

For the sake of simplicity, we assume that all the external forces are equal, $\bar{b}_i = \bar{b}$ for $i \in \mathcal{F}$, so that the third term in the right member of Eq. (4.61) vanishes.

In order to expand the last term in Eq. (4.61), we use the following relations:

$$\frac{\partial}{\partial T} \left( \frac{\bar{G}_l}{T} \right)_{\bar{p}_l} = -\frac{\bar{H}_l}{T^2}; \quad l \in \mathcal{E};$$

(4.62)

and

$$\frac{\partial}{\partial \bar{p}_l} \left( \frac{\bar{G}_l}{T} \right)_{T, \bar{p}_m, \mu_l k} = k_0 \mu_l; \quad k_l \in \mathcal{E};$$

(4.63)

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

$$= -\frac{Q}{T^2} \frac{\partial T}{\partial \bar{p}_l} - \frac{\Pi \cdot \nabla \bar{V}_l}{T} - \sum_{k_l \in \mathcal{E}} k_0 \mu_l \bar{n} \tilde{V}_l \cdot \bar{p}_l;$$

(4.64)

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

$$Q - \sum_{l \in \mathcal{E}} \bar{H}_l \tilde{n}_{\bar{V}_l} = -\frac{Q}{T^2} \frac{\partial T}{\partial \bar{p}_l} - \sum_{k \in \mathcal{E}} k_0 \bar{p}_k;$$

(4.65)

and

$$\sum_{l \in \mathcal{E}} k_0 \mu_l \bar{n} \tilde{V}_l = -\frac{k_0}{T^2} \frac{\partial T}{\partial \bar{p}_l} - \sum_{m \in \mathcal{E}} k_m \frac{\partial \bar{p}_m}{\partial \bar{p}_l}; \quad k \in \mathcal{E};$$

(4.66)

and the coefficients $k_m$, $0 \leq k_m \leq n_0$, read

$$^0_{0} = T^2;$$

$$^0_{k_0} = \frac{k_0}{T^2} \sum_{i \in \mathcal{F}} \bar{I}_i \bar{p}_k; \quad k \in \mathcal{E};$$

(4.67)

$$^0_{k_m} = \frac{1}{\partial T} \sum_{ij \in \mathcal{F}} D_{ij} \bar{I}_i \bar{I}_k \bar{I}_m; \quad k \in \mathcal{E};$$

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

\[
\frac{\partial T}{\partial t} + \nabla \cdot \mathbf{S} = \frac{\partial T}{\partial t} + \sum_{i,j} \left( D_{ij} \left( \frac{\partial \rho_i}{\partial t} + \mathbf{v} \cdot \nabla \rho_i \right) + \frac{\rho_i}{T} \left( \mathbf{v} \cdot \nabla T \right) \right) + \frac{\rho_i}{T} \mathbf{S}_{ij} \left( \mathbf{v} \cdot \nabla \rho_i \right) + \frac{\rho_i}{T} \mathbf{S}_{ij} \left( \mathbf{v} \cdot \nabla T \right)
\]

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

### 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 preceding 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 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 $n_l, l \in \mathcal{E}$, and the temperature $T$. They are given by

$$\sum_{i \in \mathcal{S}} n_i = n; \tag{A.1}$$

$$\left( \log \frac{n_i}{Q_i} \right)_{i \in \mathcal{S}} \in \mathcal{E};$$

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

$$\left( \frac{\partial n_i}{\partial T} \right)_{i \in \mathcal{S}} \in \mathcal{E}^{-}; \tag{A.2}$$

$$\left( E_i - k_B T^2 \frac{\partial n_i}{n} \right)_{i \in \mathcal{S}} \in \mathcal{E};$$

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

$$\sum_{i \in \mathcal{S}} \frac{\partial n_i}{\partial n_m} = n_m; \quad m \in \mathcal{E}; \tag{A.3}$$

$$\left( \frac{1}{n} \frac{\partial n_i}{\partial n_m} \right)_{i \in \mathcal{S}} \in \mathcal{E}; \quad m \in \mathcal{E};$$

Rather than number densities, it is also possible to consider partial pressures for the
elements and the species, as given by Eq. (4.4). With the macroscopic variables (4.5),
the species partial pressures are functions of the element partial pressures $p_l, l \in \mathcal{E}$,
and the temperature $T$. Eqs. (A.1) now read

$$\sum_{i \in \mathcal{S}} p_i = p_l; \tag{A.4}$$

$$\left( \log \frac{p_i}{k_B T Q_i} \right)_{i \in \mathcal{S}} \in \mathcal{E};$$

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

$$\left( \frac{\partial \tilde{p}_i}{\partial \tilde{p}_m} \right)_{i \in \mathcal{S}} \in \mathcal{E}^{-}; \tag{A.5}$$

$$\left( \frac{H_i - k_B T^2 \frac{\partial \tilde{p}_i}{p_i \mathcal{E}}} \right)_{i \in \mathcal{S}} \in \mathcal{E};$$

and

$$\sum_{i \in \mathcal{S}} \frac{\partial \tilde{p}_i}{\partial \tilde{p}_m} = n_m; \quad m \in \mathcal{E}; \tag{A.6}$$

$$\left( \frac{1}{p_l} \frac{\partial \tilde{p}_i}{\partial \tilde{p}_m} \right)_{i \in \mathcal{S}} \in \mathcal{E}; \quad m \in \mathcal{E};$$
From the second relation in Eq. (A.6) we deduce that there exist a matrix

\[ \left( \frac{1}{p_i} \frac{\partial \rho_i}{\partial \rho_i} \right) = \left( \frac{1}{p_i} \frac{\partial \rho_i}{\partial \rho_i} \right) \]

such that

\[ \frac{1}{p_i} \frac{\partial \rho_i}{\partial \rho_i} = \sum_{i \in \mathcal{I}} \frac{1}{p_i} \frac{\partial \rho_i}{\partial \rho_i} \]

(A.7)

and a straightforward calculation shows that

\[ \frac{1}{p_i} \frac{\partial \rho_i}{\partial \rho_i} = \sum_{i \in \mathcal{I}} \frac{1}{p_i} \frac{\partial \rho_i}{\partial \rho_i} \]

(A.8)

References