First order kinetic approximation for a reactive gas mixture

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Abstract

A multicomponent reacting gas with an arbitrary number of chemical species and one reversible reaction is studied at a kinetic level in the frame of Discrete Velocity Models of the Boltzmann Equation, with the main objective of deriving the "reactive" Navier Stokes equations of the model, and characterizing the dissipative terms related to shear viscosity, thermal conductivity and thermal diffusion. The closure of the system formed by conservation and chemical rate equations is based on a first-order Chapman-Enskog method, to be applied in the strong reaction regime, and on a convenient representation of the density vector space in terms of the macroscopic variables. A mathematical procedure is proposed which leads to identify the transport coefficients and may be applied to a quite large variety of reactive gas flows. Moreover, it allows to characterize the functional form of the transport coefficients in dependence on the local gas concentrations, once the model is specified.

Keywords: Kinetic theory, mixtures, chemical reactions, discrete models, transport coefficients.

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1 Introduction

Kinetic approaches to the study of gas mixtures whose particles interact by elastic scattering and chemical reactions, essentially based on Boltzmann-like models, have motivated several research works since the last decades. More precisely, starting from the sixties, the first papers [1], [2], and the more recent ones [3], [4], [5], [6], [7] should be mentioned, among others, with reference to the full Boltzmann equation (BE) extended to a chemically reactive gas mixture. On the other hand, a large piece of research has been devoted also to the discrete velocity models of the Boltzmann equation (DVM) and the related main bibliography can be found, essentially, in the book by Monaco and Preziosi [8]; the renewed interest for DVM with care to gas mixtures, as tools to produce approximate solutions to the BE, is widely discussed in paper [9], but only for inert gases. Moreover, historical remarks, developments, relevant mathematical features, advantages and drawbacks of DVM for inert gases have been thoroughly outlined by Bobylev in his review paper [10]. For what concerns discrete and semi-continuous models, allowing also dissipative collisional processes, such as gas-photon interaction and chemical reactions, one may recall the recent papers [11], [12] by Schürrer et al. and [13] by the present authors.

In this last paper, the mathematical theory concerning collision laws, chemical kinetics and thermodynamical equilibrium has been formulated for a discrete kinetic model of a multicomponent mixture with general reversible reactions and velocity discretization. The treatment is exhaustive at microscopic scale; on the other hand, the macroscopic picture of the reactive flow is limited to the conservative processes described by the reactive Euler equations of the model. For this reason, it seems interesting to go further, extending the study of Ref. [13] to fluid dynamical processes with dissipative effects of viscosity, thermal conductivity and thermal diffusion due to chemical reactions. In the framework of DVM some previous efforts oriented in this sense are those of paper [14] for an inert gas and those of paper [15], where a bimolecular reaction and a Broadwell-type velocity discretization have been considered. On the other hand, in the context of the generalized BE extended to gas mixtures with reversible reactions, some other investigations on transport coefficients can be seen in papers [7], [16] and related bibliography.

Starting from the modeling of the reactive flow of Ref. [13], the theory here developed aims to demonstrate that DVM, extended to chemically reactive gas mixtures, have the capability to identify explicitly the transport coefficients.

The gas molecules during interactions are supposed to behave as Maxwell molecules and their internal degrees of freedom are not taken into account. A first-order perturbation scheme of Chapman-Enskog type is applied to the kinetic equations, in the chemical regime termed strong reaction regime, based on the assumption [2] that the mechanical relaxation time is shorter than the chemical one. The reactive Navier-Stokes equations for momentum, energy, progress variable and partial number densities are derived; their form is ready to handle for the deduction of transport coefficients, in view of fluid dynamical applications.

More in detail, the kinetic equations for a gas mixture formed by r reactants and s products, experiencing multiple elastic collisions and reversible reactions, are reported in Section 2, and the main aspects of the related chemical kinetics are recalled in Section 3. The reactive collision frequencies and the inelastic terms due to chemical interactions are introduced at the scope of recovering the laws of chemical kinetics and deriving the rate equation which specifies the evolution of the gas chemical composition.

The governing equations, resorting to some previous results stated by the authors in the quoted paper [13] and to the idea of representing the density vector space in a convenient orthonormal basis, are deduced in Section 4 and are shown to constitute a non closed set of partial differential equations.

The successive Sections 5 and 6 are dedicated to build the theory necessary to make solvable the system of the governing equations; its closure is achieved at the end of Section 6, thanks to lemmas and propositions proven in Section 5.

The reactive Navier-Stokes equations of the model are derived in Section 7 and then re-written for a pertinent choice of independent macroscopic variables in order to reproduce the classical hydrodynamic formulation.

Finally, in Section 8, the transport coefficients are formally identified by means of a mathematical procedure to be applied to a specific kinetic model.

2 Kinetic equations of the reactive flow

Consider a multicomponent gas mixture formed by r species $A_1, \ldots, A_r$ and s species $B_1, \ldots, B_s$, $r,\, s \in \mathbb{N}$; each M-species, $M = A_1, \ldots, A_r, B_1, \ldots, B_s$, is identified by its molecular mass m_M and chemical link energy ϵ_M. Besides multiple elastic collisions the gas particles experience inelastic collisions with reversible chemical reaction of type

$$A_1 + \ldots + A_r \rightleftarrows B_1 + \ldots + B_s \, . \tag{1}$$

Particles of $M-$species are supposed to move in the space with p selected velocities $\vec{v}_i^{\,M}$, $i = 1, \ldots, p$. The number density of particles with velocity $\vec{v}_i^{\,M}$ is denoted by $N_i^M(\vec{x}, t)$ with $\vec{x} \in \mathbb{R}^3$, $t \in \mathbb{R}_+$, and $\mathbf{N} \in \mathbb{R}^{p(r+s)}$ is the vector function defined by

$$\mathbf{N} = \left(N_1^{A_1}, \ldots, N_p^{A_1}, \ldots, N_1^{A_r}, \ldots, N_p^{A_r}, N_1^{B_1}, \ldots, N_p^{B_1}, \ldots, N_1^{B_s}, \ldots, N_p^{B_s}\right)^{\mathsf{T}}. \tag{2}$$

It is important to recall that multiple elastic collisions as well as inelastic collisions with chemical reaction contribute to adjust the number of collision invariants. Therefore, one can expect that the model under consideration possesses the correct independent collision invariants and consequently governing equations with only physically meaningful macroscopic variables.

The time-space evolution of the $p(r+s)$ number densities is given by the kinetic equations

$$\left(\frac{\partial}{\partial t} + \vec{v}_i^{\,M} \cdot \vec{\nabla}\right) N_i^M \;=\; Q_i^M(\mathbf{N}) \,+\, \mathcal{R}_i^M(\mathbf{N})\,, \tag{3a}$$

where $i = 1, \ldots, p$, $M = A_1, \ldots, A_r, B_1, \ldots, B_s$. The corresponding matrix form reads

$$\frac{\partial \mathbf{N}}{\partial t} + \mathcal{A}\,\mathbf{N} \;=\; \mathbf{Q}(\mathbf{N}) \,+\, \mathbf{R}(\mathbf{N})\,, \tag{3b}$$

where vectors $\mathbf{Q} = \left\{Q_i^M(\mathbf{N})\right\}$ and $\mathbf{R} = \left\{\mathcal{R}_i^M(\mathbf{N})\right\}$ are due to elastic collisions and chemical interactions, respectively. The matrix $\mathcal{A}$ is diagonal of order $p(r+s)$ with elements $\mathcal{A}_{ii}^M = \vec{v}_i^{\,M} \cdot \vec{\nabla}$.

In particular, $Q_i^M(\mathbf{N})$ are nonlinear mechanical terms known in literature for inert gases, see Ref. [8], whose extended expressions are here omitted for brevity. However, independently from their explicit expression, the property which states the vanishing of the summation over all admissible velocities, is recalled as

$$\sum_{i=1}^{p} Q_i^M = 0\,, \qquad i = 1, \ldots, p\,, \qquad M = A_1, \ldots, B_s. \tag{4}$$

Conversely some more details are needed for the reactive terms $\mathcal{R}_i^M(\mathbf{N})$ which will be characterized in the next section.

3 Chemical kinetics of the reactive flow

Some relevant features of chemical kinetics can be reproduced within the present modeling of the gas mixture. At this end, the chemical properties of the reacting gas mixture will be investigated in this section, on the basis of the inelastic interactions among the particles. More specifically, the inelastic interactions can be considered as collisions with chemical reaction of type (1) which result in a rearrangement of mass m such that the equality holds

$$m_{A_1} \,+\, \cdots \,+\, m_{A_r} \;=\; m_{B_1} \,+\, \cdots \,+\, m_{B_s}\,, \tag{5a}$$

and redistribution of total energy E, that is kinetic plus chemical link energy, such that

$$E_{A_1} \,+\, \cdots \,+\, E_{A_r} \;=\; E_{B_1} \,+\, \cdots \,+\, E_{B_s}. \tag{5b}$$

In the present kinetic model, the interaction with chemical reaction correspond to the inelastic collision represented by

$$\left(\vec{v}_{i_1}^{A_1}, \ldots, \vec{v}_{i_r}^{A_r}\right) \;\leftrightarrow\; \left(\vec{v}_{j_1}^{B_1}, \ldots, \vec{v}_{j_s}^{B_s}\right)\,, \tag{6}$$

where subscripts $i_1, \dots, i_r$ and $j_1, \dots, j_s$ assume any value $1, \dots, p$. Due to the reversibility of the chemical reaction, only collisions of type (6) which verify the microscopic reversibility principle (see Ref. [17]), and preserve mass, momentum and total energy, are considered as *admissible*.
Some preliminaries are briefly reported to go insight the chemical kinetics of the collisions. For further technical details, the reader is re-addressed to paper [13].

3.1 Reactive collision frequencies

The collision frequencies of the forward/backward reaction are in general functions, say g_f/g_b, depending on both incoming/outgoing velocities, and masses of reactants/products, respectively. They are defined by

$$\nu_{A_1\cdots A_r, i_1\cdots i_r}^{B_1\cdots B_s, j_1\cdots j_s} = g_f\left(m_{A_1}\vec{v}_{i_1}^{A_1}, \dots, m_{A_r}\vec{v}_{i_r}^{A_r}\right)\left[\sigma_f(g_f)\right]^{\frac{3r-4}{2}} , \tag{7a}$$

$$\nu_{B_1\cdots B_s, j_1\cdots j_s}^{A_1\cdots A_r, i_1\cdots i_r} = g_b\left(m_{B_1}\vec{v}_{i_1}^{B_1}, \dots, m_{B_s}\vec{v}_{j_s}^{B_s}\right)\left[\sigma_b(g_b)\right]^{\frac{3s-4}{2}} , \tag{7b}$$

where σ_f/σ_b denote the forward/backward cross sections, and the exponents assure the right dimension of the ν's. The effective expressions of the reactive collision frequencies depend on the intermolecular potential modeling molecular interactions, and geometry of the selected velocities.

3.2 Laws of chemical kinetics

The laws of chemical kinetics can be recovered once the concentration evolution of each $M-$species is determined. As known, see Ref. [18], such concentrations are measured by the individual number densities $n_{_M}$ defined by

$$n_{_M} = \sum_{i=1}^{p} N_i^M, \tag{8}$$

where N_i^M evolves according to kinetic equations (3a). The inelastic terms $\mathcal{R}_i^M(N)$ which figure in such equations will be now detailed and their relevant property recalled.

- **Inelastic terms**

  The terms $\mathcal{R}_i^M(N)$ for particles with velocity $\vec{v}_i^M$ involved in any inelastic collision of type (6) represent the balance between gain and loss contributions to N_i^M. The explicit expressions for species A_k, B_ℓ in the forward reaction are

$$\begin{aligned}
\mathcal{R}_{i_k}^{A_k}(\mathbf{N}) &= \sum_{j_1\cdots j_s} \sum_{\substack{i_1\cdots i_{k-1}\\ i_{k+1}\cdots i_r}} \left(\frac{1}{s!} A_{B_1\cdots B_s, j_1\cdots j_s}^{A_1\cdots A_r, i_1\cdots i_r} N_{j_1}^{B_1}\cdots N_{j_s}^{B_s} - \right.\\
&\qquad \left. \frac{1}{r!} A_{A_1\cdots A_r, i_1\cdots i_r}^{B_1\cdots B_s, j_1\cdots j_s} N_{i_1}^{A_1}\cdots N_{i_r}^{A_r}\right) ,\\
\mathcal{R}_{j_\ell}^{B_\ell}(\mathbf{N}) &= \sum_{i_1\cdots i_r} \sum_{\substack{j_1\cdots j_{\ell-1}\\ j_{\ell+1}\cdots j_s}} \left(\frac{1}{r!} A_{A_1\cdots A_r, i_1\cdots i_r}^{B_1\cdots B_s, j_1\cdots j_s} N_{i_1}^{A_1}\cdots N_{i_r}^{A_r} - \right.\\
&\qquad \left. \frac{1}{s!} A_{B_1\cdots B_s, j_1\cdots j_s}^{A_1\cdots A_r, i_1\cdots i_r} N_{j_1}^{B_1}\cdots N_{j_s}^{B_s}\right) ,
\end{aligned} \tag{9}$$

$i_k, j_\ell = 1, \ldots, p$. The coefficients A denote the transition rates of the admissible collisions, and result to be proportional to the reactive collision frequencies. Moreover, due to the microreversibility principle, they verify the equality

$$A_{A_1 \cdots A_r, i_1 \cdots i_r}^{B_1 \cdots B_s, j_1 \cdots j_s} = A_{B_1 \cdots B_s, j_1 \cdots j_s}^{A_1 \cdots A_r, i_1 \cdots i_r} . \tag{10}$$

- **Property of inelastic terms**

  Equations of chemical kinetics. Summing over the velocities the kinetic equations ($3a$) of each $M-$species, and taking into account property (4) of the elastic collision terms, one obtains the equations of chemical kinetics

$$\frac{dn_M}{dt} = \sum_{i=1}^{p} \mathcal{R}_i^M(N) , \quad M = A_1, \ldots, B_s , \tag{11}$$

  $\frac{d}{dt}$ being the Lagrangian derivative.

  Laws of chemical kinetics. Inserting the microreversibility equality (10) into expressions (9) of reactive terms, the property of inelastic terms reads

$$\sum_{i_k=1}^{p} \mathcal{R}_{i_k}^{A_k}(\mathbf{N}) = - \sum_{j_\ell=1}^{p} \mathcal{R}_{j_\ell}^{B_\ell}(\mathbf{N}) . \tag{12}$$

  As a direct consequence of the previous items, the concentrations of each reactant A_k and product B_ℓ satisfy the equations

$$\frac{dn_{A_1}}{dt} = \ldots = \frac{dn_{A_r}}{dt} = -\frac{dn_{B_1}}{dt} = \ldots = -\frac{dn_{B_\ell}}{dt} \tag{13}$$

  which recover the laws of chemical kinetics.

3.3 Rate equation

The number density of a given product of the forward reaction, say n_{B_1} without loss of generality, is assumed as the progress variable describing the chemical composition of the gas mixture. The rate equation is deduced as the time-space evolution of n_{B_1} which is proportional to the concentration of B_1-product. At this end, it is convenient to write Eqs. (11) for $M = B_1$, with the extended expression for the sum of the reactive terms, that is

$$\frac{dn_{B_1}}{dt} = \sum_{i_1 \cdots i_r} \sum_{j_1 \cdots j_s} A_{A_1 \cdots A_r, i_1 \cdots i_r}^{B_1 \cdots B_s, j_1 \cdots j_s} \left(\frac{1}{r!} N_{i_1}^{A_1} \cdots N_{i_r}^{A_r} - \frac{1}{s!} N_{j_1}^{B_1} \cdots N_{j_s}^{B_s} \right) . \tag{14a}$$

It is easy now to recognize at the *r.h.s.*, the difference between two terms, say r_f and r_b, which represent the rates of chemical formation and disappearance through the forward and backward reactions, respectively. Thus the rate equation reads

$$\frac{dn_{B_1}}{dt} = r_f - r_b . \tag{14b}$$

When the forward and backward reactions proceed with equal rates one has $r_f = r_b$ and the *chemical equilibrium* is reached.

It becomes evident that the rate equation of the model is a natural consequence of the microscopic description of the chemical transformations which ocurr during inelastic interactions.

- **Equation of chemical kinetics**

  Assuming that the gas particles behave as Maxwell molecules [19], the collision cross sections are inversely proportional to the relative speed, so that the reactive collision frequencies defined by expressions (7) do not depend anymore on the particle velocities. Consequently, it results

  $$\nu_{A_1\cdots A_r,i_1\cdots i_r}^{B_1\cdots B_s,j_1\cdots j_s} = \nu_A\,, \quad \nu_{B_1\cdots B_s,j_1\cdots j_s}^{A_1\cdots A_r,i_1\cdots i_r} = \nu_B\,, \tag{14c}$$

  with $\nu_A,\ \nu_B \in \mathbb{R}_+$. The rate equation (14$a$) takes the usual form of chemical kinetics

  $$\frac{dn_{B_1}}{dt} = \nu_A\, n_{A_1}\dots n_{A_r} - \nu_B\, n_{B_1}\dots n_{B_s}\,. \tag{14d}$$

Under the above said assumption of Maxwell molecules, the trend of the gas mixture to both mechanical and chemical equilibrium is assured, since an $\mathcal{H}$-theorem for a spatially non homogeneous gas evolution can be proven, as shown in Ref. [13].

4 Mathematical modeling

The reacting gas is governed by the conservation and rate equations, which will be here deduced in a pertinent form in view of the kinetic approximation of the next Section. Some preliminaries on the collision invariant spaces and their orthonormal basis, in accordance with the related results of paper [13], are first recalled in Subsection 4.1, whereas definitions and roles of macroscopic and microscopic variables are pointed out in Subsection 4.2. Finally in Subsection 4.3, the governing equations are formulated in dependence on microscopic and macroscopic variables.

4.1 Collision invariants

Introduce in $\mathbb{R}^{p(r+s)}$ the linear sub-spaces $\mathcal{F}$ of mechanical collision invariants and $\mathcal{M}$ of mechanical-reactive collision invariants, defined by

$$\mathcal{F} = \Big\{ \Upsilon \in \mathbb{R}^{p(r+s)} :\ \langle \Upsilon, \mathbf{Q}(\mathbf{N})\rangle = 0 \Big\}\,, \tag{15a}$$

$$\mathcal{M} = \Big\{ \Upsilon \in \mathbb{R}^{p(r+s)} :\ \langle \Upsilon, \mathbf{Q}(\mathbf{N})\rangle = 0\,,\ \langle \Upsilon, \mathbf{R}(\mathbf{N})\rangle = 0 \Big\}\,, \quad \mathcal{M} \subset \mathcal{F}. \tag{15b}$$

where $\langle\,\cdot\,,\,\cdot\,\rangle$ is the standard inner product.

The following results hold as immediate consequence of those proven in paper [13].

Lemma 1. *Let the vector* Υ *be a mechanical collision invariant,* $\Upsilon \in \mathcal{F}$*. Then* Υ *determines the conservation of the macroscopic quantity*

$$\langle \Upsilon, \mathbf{N}\rangle = \sum_M \sum_{i=1}^{p} [\Upsilon]_i^M\, \mathbf{N}_i^M \tag{16}$$

during elastic collisions. If in addition $\Upsilon \in \mathcal{M}$*, then* $\langle \Upsilon, \mathbf{N}\rangle$ *is preserved during inelastic interaction, as well.* ■

Lemma 2. *Let q denote the dimension of the linear sub-space $\mathcal{F}$. Then the dimension of $\mathcal{M}$ is $q-1$. Orthonormal basis $\mathcal{B}_{\mathcal{M}}$ of $\mathcal{M}$ and $\mathcal{B}_{\mathcal{F}}$ of $\mathcal{F}$ can be represented by*

$$\mathcal{B}_{\mathcal{M}} = \left\{ \Upsilon^{(1)}, \dots, \Upsilon^{(q-1)} \right\}, \tag{17a}$$

$$\mathcal{B}_{\mathcal{F}} = \left\{ \Upsilon^{(1)}, \dots, \Upsilon^{(q-1)}, \Upsilon^{(q)} \right\}, \;\; \mathcal{B}_{\mathcal{M}} \subset \mathcal{B}_{\mathcal{F}} \; . \tag{17b}$$

■

The choice of invariants $\Upsilon^{(1)}, \dots, \Upsilon^{(q-1)}$ in Eq. (17*a*) is fixed by the independent quantities preserved during both elastic and inelastic collisions, whereas the choice of $\Upsilon^{(q)}$ in Eq. (17*b*) is fixed by an independent quantity preserved during elastic collisions, only. The role played by the invariants will be more evident in the next subsections.

4.2 Macroscopic and microscopic variables of the model

In order to determine the functional dependence of the number densities on the macroscopic variables, the following definitions are needed.

Macroscopic variables. The inner products $\langle \Upsilon, \mathbf{N} \rangle$, when Υ varies in the basis $\mathcal{B}_{\mathcal{F}}$, define the q independent macroscopic variables of the model

$$a_k = \langle \Upsilon^{(k)}, \mathbf{N} \rangle , \qquad k = 1, \dots, q , \qquad q = dim\, \mathcal{F} \; . \tag{18}$$

Without loss of generality, as it will be seen in Section 7, such macroscopic variables can also assume a fluid dynamical meaning determined as follows.

For $k = 1, \dots, q-5$, a_k represent the independent partial number density $n^{[k]} = n_{A_{k_1}} + n_{B_{k_2}}$, where $k_1 \in \{1, \dots, r\}$ and $k_2 \in \{1, \dots, s\}$; $a_{q-4}, a_{q-3}, a_{q-2}$ denote the components of momentum $\rho \vec{U}$; a_{q-1} is the total energy $\rho e + \frac{1}{2} \rho |\vec{U}|^2$, detailed in Eqs. (56), and a_q the progress variable n_{B_1}.

Microscopic variables. Further inner products involving $\mathbf{N}$ and other vectors than Υ, say W, are considered microscopic variables of the model, that is $\langle W \, , \, \mathbf{N} \rangle$.

The following proposition can now be stated.

Proposition 1. *The number densities N_i^M, $i = 1, \dots, p$, $M = A_1, \dots, B_s$, admit representation in $\mathbb{R}^{p(r+s)}$ in terms of the q macroscopic variables $a_1, \dots, a_q$ and $p(r+s) - q$ microscopic variables $b_{q+1}, \dots, b_{p(r+s)}$.*

Proof. Consider a suitable orthonormal basis $\mathcal{B}$ of the whole space $\mathbb{R}^{p(r+s)}$, namely

$$\mathcal{B} = \left\{ \Upsilon^{(1)}, \dots, \Upsilon^{(q)}, W^{(q+1)}, \dots, W^{(p(r+s))} \right\} , \tag{19}$$

and let $\mathcal{B}_{\mathcal{F}^\perp}$ be an orthonormal basis of the space $\mathcal{F}^\perp$, orthogonal to $\mathcal{F}$,

$$\mathcal{B}_{\mathcal{F}^\perp} = \left\{ W^{(q+1)}, \dots, W^{(p(r+s))} \right\} . \tag{20}$$

Since $\mathcal{B} = \mathcal{B}_{\mathcal{F}} \cup \mathcal{B}_{\mathcal{F}^\perp}$, the vector $\mathbf{N} \in \mathbb{R}^{p(r+s)}$ defined in (2), splits in the basis $\mathcal{B}$ as

$$\mathbf{N} = \sum_{k=1}^{q} a_k \Upsilon^{(k)} + \sum_{\ell=q+1}^{p(r+s)} b_\ell W^{(\ell)} \; . \tag{21}$$

Thus the coefficients a_k in representation (21) turn out to be the macroscopic variables defined in (18) and b_ℓ the microscopic variables defined by

$$b_\ell = \langle W^{(\ell)} \, , \, \mathbf{N} \rangle , \quad \ell = q+1, \dots, p(r+s) \; . \tag{22}$$

■

4.3 Governing equations

After all contents of Subsections 4.1-4.2, the governing equations of the model can be deduced in the following proposition.

Proposition 2. *The governing equations of the model constitute a non closed set of* q *equations in* $p(r+s)$ *unknowns, and can be written as*

$$\frac{\partial a_k}{\partial t} + \langle \mathcal{A}\mathbf{N}\,,\,\Upsilon^{(k)}\rangle \;=\; 0\,, \qquad k=1,\ldots,q-1\,, \tag{23a}$$

$$\frac{\partial a_q}{\partial t} + \langle \mathcal{A}\mathbf{N}\,,\,\Upsilon^{(q)}\rangle \;=\; \langle \mathcal{R}\,(\mathbf{N})\,,\,\Upsilon^{(q)}\rangle\,. \tag{23b}$$

Proof. It is enough to project the matrix kinetic equation (3*b*) onto the space $\mathcal{F}$ defined in (15*a*), and remind definition (18) of the macroscopic variables. In particular, the mechanical-reactive invariants $\Upsilon^{(1)},\ldots,\Upsilon^{(q-1)}\in\mathcal{B}_{\mathcal{M}}$ generate the $q-1$ independent conservation equations (23*a*) for the macroscopic variables $a_1,\ldots,a_{q-1}$, whereas the mechanical invariant $\Upsilon^{(q)}\in\mathcal{F}\backslash\mathcal{M}$ generates the rate equation (23*b*) for the progress variable a_q. Since $\mathbf{N}$ is expressed by decomposition (21) in the basis $\mathcal{B}$, equations (23) constitute a non closed set of q equations in the unknowns $a_1,\ldots,a_q,b_{q+1},\ldots,b_{p(r+s)}$, that completes the proof. ■

The closure of the governing equations is achieved when each microscopic variable b_ℓ, given by (22), becomes a known function of the macroscopic ones $a_1,\ldots,a_q$. At this end, a detailed discussion will be articulated in the two next sections, the former dealing with the first-order approximation of $\mathbf{N}$, the latter containing the proof necessary to determine the functional dependence of the microscopic variables on the macroscopic ones.

5 Approximation procedure

A first-order approximation procedure of Chapman-Enskog type will be applied to the kinetic equations in the so called strong reaction regime [16] according to the assumption that the ratio of reactive to inert characteristic times is greater than unity. Therefore the dimensionless kinetic equations (3*b*) are expected to be written in the form

$$\varepsilon\left[\frac{\partial\mathbf{N}}{\partial t} + \mathcal{A}\mathbf{N} - \mathbf{R}(\mathbf{N})\right] \;=\; \mathbf{Q}(\mathbf{N})\,, \tag{24}$$

where $\varepsilon=\lambda/d$ is the Knudsen number, λ being the mean free path and d the scale length of the hydrodynamic gradients. Hereinafter $\mathbf{N}$ denotes the vector function of the dimensionless number densities, and $\mathbf{Q}(\mathbf{N})$ obeys to the decomposition law

$$\mathbf{Q}(\mathbf{N}) \;=\; \mathbf{Q}_2(\mathbf{N},\mathbf{N}) \;+\; \mathbf{Q}_3(\mathbf{N},\mathbf{N},\mathbf{N}) \;+\ldots\;+\mathbf{Q}_h(\mathbf{N},\ldots,\mathbf{N})\,, \tag{25}$$

each term $\mathbf{Q}_j$, $j=2,3,\ldots,h$, being the contribution due to all multiple elastic j–encounters, and index h being such that $h=\max\{r,s\}$.

The first-order expansions of the number densities and time derivatives of the macroscopic variables are provided by

$$\mathbf{N} \;=\; \mathbf{N}^{(0)} + \varepsilon\,\mathbf{N}^{(1)}, \tag{26}$$

$$\frac{\partial a_k}{\partial t} \;=\; \left(\frac{\partial a_k}{\partial t}\right)^{(0)} + \varepsilon\left(\frac{\partial a_k}{\partial t}\right)^{(1)}\,. \tag{27}$$

Under the Chapman-Enskog hypothesis, see Ref. [19], that the q independent macroscopic variables, defined by Eqs. (18), are exact at the zero-order approximation, the following equalities are verified

$$a_k \;=\; \langle \mathbf{N}^{(0)} \,,\, \Upsilon^{(k)} \rangle \,, \qquad 0 \;=\; \langle \mathbf{N}^{(1)} \,,\, \Upsilon^{(k)} \rangle \,, \qquad k = 1, \ldots, q \,. \tag{28}$$

Consequently, $\mathbf{N}^{(0)}$ and $\mathbf{N}^{(1)}$ can be written in the basis $\mathcal{B}$, defined in (19), as

$$\mathbf{N}^{(0)} \;=\; a_1 \Upsilon^{(1)} + \ldots a_q \Upsilon^{(q)} + b^{(0)}_{q+1} W^{(q+1)} + \ldots + b^{(0)}_{p(r+s)} W^{(p(r+s))} \,, \tag{29}$$

$$\mathbf{N}^{(1)} \;=\; b^{(1)}_{q+1} W^{(q+1)} + \ldots + b^{(1)}_{p(r+s)} W^{(p(r+s))} \,, \tag{30}$$

where

$$b^{(0)}_{\ell} \;=\; \langle\, W^{(\ell)} \,,\, \mathbf{N}^{(0)} \,\rangle \,, \;\; b^{(1)}_{\ell} \;=\; \langle\, W^{(\ell)} \,,\, \mathbf{N}^{(1)} \,\rangle \,, \quad \ell = q+1, \ldots, p(r+s) \,, \tag{31}$$

and approximation (26) of $\mathbf{N}$ becomes

$$\mathbf{N} \;=\; \sum_{k=1}^{q} a_k \Upsilon^{(k)} \;+\; \sum_{\ell=q+1}^{p(r+s)} (b^{(0)}_{\ell} + \varepsilon b^{(1)}_{\ell})\, W^{(\ell)} \,. \tag{32}$$

On the other hand, the density vector $\mathbf{N}$ has the representation (21) in the basis $\mathcal{B}$; therefore, the coefficients b_ℓ are given by

$$b_\ell = b^{(0)}_{\ell} + \varepsilon b^{(1)}_{\ell} \,, \qquad \ell = q+1, \ldots, p(r+s). \tag{33}$$

Both the zero-order and first-order approximations $b^{(0)}_{\ell}$ and $b^{(1)}_{\ell}$ of the microscopic variables b_ℓ result to be functions of the macroscopic variables $a_1, \ldots, a_q$, as it will be indicated by Eqs.(38), (49). The approximation technique proceeds according to the contents of the next three subsections.

5.1 Compatibility equations

The compatibility equations for $\mathbf{N}^{(0)}$ and $\mathbf{N}^{(1)}$ will be first deduced as pointed out in the next lemma.

Lemma 3. *The zero-order and first-order approximations* $\mathbf{N}^{(0)}$ *and* $\mathbf{N}^{(1)}$ *of the density vector* $\mathbf{N}$ *satisfy the compatibility equations*

$$\mathbf{Q}(\mathbf{N}^{(0)}) \;=\; 0 \,, \tag{34}$$

$$\begin{aligned} &2\mathbf{Q}_2(\mathbf{N}^{(0)}, \mathbf{N}^{(1)}) + \cdots + h\mathbf{Q}_h(\mathbf{N}^{(0)}, \ldots, \mathbf{N}^{(0)}, \mathbf{N}^{(1)}) \;= \\ &\qquad = \sum_{k=1}^{q} \frac{\partial \mathbf{N}^{(0)}}{\partial a_k} \left(\frac{\partial a_k}{\partial t} \right)^{(0)} + \mathcal{A}\mathbf{N}^{(0)} - \mathbf{R}(\mathbf{N}^{(0)}) \,, \end{aligned} \tag{35}$$

where

$$\mathbf{N}^{(0)} \;=\; \mathbf{N}^{(0)}\,(a_1, \ldots, a_q) \,. \tag{36}$$

Proof. Inserting expansion (26) into the dimensionless matrix kinetic equation (24), and neglecting terms with ε^2, yields

$$\begin{aligned} &\varepsilon \left[\frac{\partial \mathbf{N}^{(0)}}{\partial t} + \mathcal{A}\,\mathbf{N}^{(0)} \;-\; \mathbf{R}(\mathbf{N}^{(0)}) \right] = \\ &\qquad = \mathbf{Q}(\mathbf{N}^{(0)}) + 2\varepsilon \mathbf{Q}_2(\mathbf{N}^{(0)}, \mathbf{N}^{(1)}) + \cdots + h\varepsilon \mathbf{Q}_h(\mathbf{N}^{(0)}, \ldots, \mathbf{N}^{(0)}, \mathbf{N}^{(1)}) \,. \end{aligned} \tag{37}$$

The analysis of similar terms in ε will be performed in two items.

- Equating coefficients of zero-order in ε, the first compatibility equation (34) is immediately deduced. Furthermore, as known, the unique solution $\mathbf{N}^{(0)}$ to Eq. (34) is the Maxwellian density vector, see Ref. [20]. Thanks to the one-to-one map between the Maxwellian parameters and the macroscopic variables a_k, the coefficients $b_\ell^{(0)}$ in the expressions (29) of $\mathbf{N}^{(0)}$ become known functions of type

$$b_\ell^{(0)} \;=\; b_\ell^{(0)}\left(a_1, \dots, a_q\right), \qquad \ell = q+1, \dots, p(r+s), \tag{38}$$

and, consequentely, the zero-order approximation $\mathbf{N}^{(0)}$ verifies Eq. (36).

- Equating coefficients of first-order in ε, one gets

$$2\mathbf{Q}_2(\mathbf{N}^{(0)}, \mathbf{N}^{(1)}) + \cdots + h\mathbf{Q}_h(\mathbf{N}^{(0)}, \dots, \mathbf{N}^{(0)}, \mathbf{N}^{(1)}) \;=\; \frac{\partial \mathbf{N}^{(0)}}{\partial t} + \mathcal{A}\mathbf{N}^{(0)} - \mathbf{R}(\mathbf{N}^{(0)}) \,. \tag{39}$$

Since equality (36) holds, the time derivative of $\mathbf{N}^{(0)}$ at the zero-order approximation, reminding expansion (27), is

$$\frac{\partial \mathbf{N}^{(0)}}{\partial t} \;=\; \sum_{k=1}^{q} \frac{\partial \mathbf{N}^{(0)}}{\partial a_k} \left(\frac{\partial a_k}{\partial t}\right)^{(0)} , \tag{40}$$

and the second compatibility equation (35) of the lemma is implied. ■

5.2 The linearized mechanical operator

The particular form of the *l.h.s.* of the compatibility equation (35) for $\mathbf{N}^{(1)}$ can be seen as the peculiar one of the linearized mechanical operator $\mathbb{L}$ about the Maxwellian equilibrium $\mathbf{N}^{(0)}$. When multiple elastic collisions occur, $\mathbb{L}$ is such that

$$\mathbb{L}(\mathbf{N}^{(0)} + \varepsilon \mathbf{N}^{(1)}) \;=\; 2\mathbf{Q}_2(\mathbf{N}^{(0)}, \mathbf{N}^{(1)}) + \cdots + h\mathbf{Q}_h(\mathbf{N}^{(0)}, \dots, \mathbf{N}^{(0)}, \mathbf{N}^{(1)}) \,. \tag{41}$$

A relevant property of the operator $\mathbb{L}$ which will be fundamental in the sequel is stated in the next lemma.

Lemma 4. *The linearized operator* $\mathbb{L}$ *verifies the orthogonality property*

$$\langle \mathbb{L}(\mathbf{N}^{(0)} + \varepsilon \mathbf{N}^{(1)}) \,,\, \Phi \rangle = 0 \,, \quad \forall \Phi \in \mathcal{F}, \tag{42}$$

or, equivalently, $\mathbb{L}(\mathbf{N}^{(0)} + \varepsilon \mathbf{N}^{(1)}) \in \mathcal{F}^\perp$. *Thus, the equality holds*

$$\mathbb{L}(\mathbf{N}^{(0)} + \varepsilon \mathbf{N}^{(1)}) \;=\; \sum_{\ell=q+1}^{p(r+s)} \alpha_\ell \, W^{(\ell)} \,, \tag{43}$$

where the coefficients α_ℓ *are, in general, functions of type*

$$\alpha_\ell \;=\; \alpha_\ell(a_1, \dots, a_q, b_{q+1}^{(1)}, \dots, b_{p(r+s)}^{(1)}) \,. \tag{44}$$

Proof. The orthogonality property (42), from definitions (41) of operator $\mathbb{L}$ and (15*a*) of space $\mathcal{F}$, is an immediate extension to reactive mixtures of that demonstrated in Ref. [20] for inert gases. So the first part of Lemma 4 is valid. On the other hand, a suitable basis of $\mathcal{F}^\perp$ is provided by the set

(20). Thus, expanding the linear operator $\mathbb{L}(\mathbf{N}^{(0)}+\varepsilon\mathbf{N}^{(1)})$ in the basis $\mathcal{B}_{\mathcal{F}^\perp}$, decomposition (43) follows. Inserting expansions (29), (30) with relation (38) into (43), and then projecting onto space $\mathcal{F}^\perp$, coefficients α_ℓ result to be functions of type (44). ■

The features of linearized mechanical operator and the content of previous Lemmas 3, 4 allow to obtain a more convenient form for the compatibility equation for $\mathbf{N}^{(1)}$, as stated in the next proposition.

Proposition 3. *The first-order approximation of the microscopic variables $b_\ell^{(1)}$ satisfies the following condition*

$$\sum_{\ell=q+1}^{p(r+s)} \alpha_\ell(a_1,\ldots,a_q,b_{q+1}^{(1)},\ldots,b_{p(r+s)})\,W^{(\ell)} = \sum_{k=1}^{q} \frac{\partial \mathbf{N}^{(0)}}{\partial a_k}\left(\frac{\partial a_k}{\partial t}\right)^{(0)} + \mathcal{A}\mathbf{N}^{(0)} - \mathbf{R}(\mathbf{N}^{(0)})\,. \tag{45}$$

Proof. Having in mind definition (41) of the linearized operator $\mathbb{L}$ and its orthogonality property of Lemma 4, the compatibility equation (35) of Lemma 3 can straight away be written in the form (45). ■

Since $\mathbf{N}^{(1)}$ is expanded through decomposition (30), the compatibility equations (35) can be sustituted by Eq. (45).

5.3 Solubility conditions

The time derivatives of the macroscopic variables a_k, which figure in the compatibility equations (45), are still unknown at the zero level of the approximation. Such derivatives will be actually evaluated by means of the so called solubility conditions for $\mathbf{N}^{(1)}$. The next lemma supplies this requirement.

Lemma 5. *The time derivatives of the macroscopic variables a_k are given by the so called solubility conditions*

$$\left(\frac{\partial a_k}{\partial t}\right)^{(0)} = \langle -\mathcal{A}\mathbf{N}^{(0)} + \mathbf{R}(\mathbf{N}^{(0)})\,,\, \Upsilon^{(k)}\rangle\,, \qquad k=1,\ldots,q\,. \tag{46}$$

Proof. Projecting the compatibility equation (45) onto the space $\mathcal{F}$, one obtains

$$\begin{aligned}\sum_{k=1}^{q}\left(\frac{\partial a_k}{\partial t}\right)^{(0)} \langle \frac{\partial \mathbf{N}^{(0)}}{\partial a_k}\,,\,\Upsilon^{(j)}\rangle\, + \\ + \langle\,\mathcal{A}\mathbf{N}^{(0)} - \mathbf{R}(\mathbf{N}^{(0)})\,,\,\Upsilon^{(j)}\,\rangle \;=\; 0\,, \qquad j=1,\ldots,q\,.\end{aligned} \tag{47}$$

The derivatives of $\mathbf{N}^{(0)}$ can be easily evaluated reminding that, as stated by (36), $\mathbf{N}^{(0)}=\mathbf{N}^{(0)}(a_1,\ldots,a_q)$, and that $\mathbf{N}^{(0)}$, in the basis $\mathcal{B}$, admits representation (29) with coefficients $b_\ell^{(0)}=b_\ell^{(0)}(a_1,\ldots,a_q)$, as stated by (38), namely

$$\frac{\partial \mathbf{N}^{(0)}}{\partial a_k} \;=\; \Upsilon^{(k)} + \sum_{\ell=q+1}^{p(r+s)} \frac{\partial b_\ell^{(0)}}{\partial a_k}\,W^{(\ell)}\,, \qquad k=1,\ldots,q\,. \tag{48}$$

Casting the above expressions of the derivatives of $\mathbf{N}^{(0)}$ into Eq. (47), and reminding that vectors $\Upsilon^{(k)}$ are orthonormal, one immediately obtains Eq. (46) as required. ■

It can be pointed out that Eq. (46) play the role of solubility conditions for $\mathbf{N}^{(1)}$ in the compatibility equation (45).

6 Closure of the governing equations

As anticipated at the end of Section 4, the system (23) of the governing equations becomes closed when the unknowns reduce to the only q independent macroscopic variables, that is to say the density vector becomes a function of type $\mathbf{N} = \mathbf{N}(a_1, \dots, a_q)$. Since in the approximation procedure $\mathbf{N}$ results to be represented by Eq. (32), where the coefficients $b_\ell^{(0)}$ depend on $a_1, \dots, a_q$, as stated by Eq. (38), it is now necessary to express the first-order approximation $b_\ell^{(1)}$ in terms of the macroscopic variables, only. This is the objective of the next proposition.

Proposition 4 . *The first-order approximation* $b_\ell^{(1)}$ *of the microscopic variables* b_ℓ *can be univocally expressed in terms of the macroscopic variables, that is*

$$b_\ell^{(1)} = b_\ell^{(1)}(a_1, \dots, a_q), \qquad \ell = q+1, \dots, p(r+s) . \tag{49}$$

Proof. Insert expressions (48) into compatibility equations (45), that is

$$\begin{aligned} \sum_{\ell=q+1}^{p(r+s)} \alpha_\ell W^{(\ell)} &= \sum_{k=1}^{q} \left(\frac{\partial a_k}{\partial t}\right)^{(0)} \Upsilon^{(k)} + \\ & \sum_{\ell=q+1}^{p(r+s)} \frac{\partial b_\ell^{(0)}}{\partial t} W^{(\ell)} + \mathcal{A}\mathbf{N}^{(0)} - \mathbf{R}(\mathbf{N}^{(0)}) . \end{aligned} \tag{50}$$

If now one represents the term $\mathcal{A}\mathbf{N}^{(0)} - \mathbf{R}(\mathbf{N}^{(0)})$ in the basis $\mathcal{B}$, namely

$$\begin{aligned} \mathcal{A}\mathbf{N}^{(0)} - \mathbf{R}(\mathbf{N}^{(0)}) &= \sum_{k=1}^{q} \langle \mathcal{A}\mathbf{N}^{(0)} - \mathbf{R}(\mathbf{N}^{(0)}) \, , \, \Upsilon^{(k)} \rangle \, \Upsilon^{(k)} + \\ & \sum_{\ell=q+1}^{p(r+s)} \langle \mathcal{A}\mathbf{N}^{(0)} - \mathbf{R}(\mathbf{N}^{(0)}) \, , \, W^{(\ell)} \rangle \, W^{(\ell)} , \end{aligned} \tag{51}$$

and reminds the solubility conditions (46) of Lemma 5, the previous equality (50) reduces to

$$\sum_{\ell=q+1}^{p(r+s)} \alpha_\ell W^{(\ell)} = \sum_{\ell=q+1}^{p(r+s)} \left(\langle \mathcal{A}\mathbf{N}^{(0)} - \mathbf{R}(\mathbf{N}^{(0)}), W^{(\ell)} \rangle + \frac{\partial b_\ell^{(0)}}{\partial t} \right) W^{(\ell)}. \tag{52}$$

Reminding that $\mathbf{N}^{(0)}$, $b_\ell^{(0)}$ depend on the macroscopic variables, as specified by Eqs. (29), (38), and α_ℓ satisfies condition (44), Eq. (52) results to be equivalent to an algebraic system of type

$$\begin{aligned} \alpha_\ell(a_1, \dots, a_q, b_{q+1}^{(1)}, \dots, b_{p(r+s)}^{(1)}) &= \langle \mathcal{A}\mathbf{N}^{(0)} - \mathbf{R}(\mathbf{N}^{(0)}) \, , \, W^{(\ell)} \rangle + \frac{\partial b_\ell^{(0)}}{\partial t} \, , \\ & \qquad \ell = q+1, \dots, p(r+s) \end{aligned} \tag{53}$$

Since Lemma 3 assures that $b_\ell^{(0)} = b_\ell^{(0)}(a_1, \dots, a_q)$, system (53) can be regarded in the unknowns $b_{q+1}^{(1)}, \dots, b_{p(r+s)}^{(1)}$ and be actually solved in terms of the macroscopic variables, as required. ■

Remark. The existence and uniqueness of solutions $b_\ell^{(1)}(a_1, \dots, a_q)$ of system (53) may be stated resorting to the proof carried on in Ref. [20] for inert gases, and is here omitted for brevity.

7 Reactive Navier-Stokes equations

The results of the first-order approximation procedure of Section 6 will be applied to the governing equations. Re-write the conservation and rate equations (23) after inserting expansion (32) of $\mathbf{N}$ and expressions (38), (49) of $b_\ell^{(0)}$, $b_\ell^{(1)}$. One obtains the *reactive Navier-Stokes* equations of the model

$$
\begin{aligned}
&\frac{\partial a_k}{\partial t} \;+\; \langle \mathcal{A}\,(\sum_{\ell=1}^{q} a_\ell \Upsilon^{(\ell)} \;+\; \sum_{h=q+1}^{p(r+s)} b_h^{(0)} W^{(h)}\,)\,,\,\Upsilon^{(k)}\rangle \;+ \qquad (54a)\\
&\qquad +\,\varepsilon\,\langle \mathcal{A}\,(\sum_{h=q+1}^{p(r+s)} b_h^{(1)} W^{(h)}\,)\,,\,\Upsilon^{(k)}\rangle \;=\; 0\,, \quad k=1,\dots,q-1\,,\\
&\frac{\partial a_q}{\partial t} \;+\; \langle \mathcal{A}\,(\sum_{\ell=1}^{q} a_\ell \Upsilon^{(\ell)} \;+\; \sum_{h=q+1}^{p(r+s)} b_h^{(0)} W^{(h)}\,)\,,\,\Upsilon^{(q)}\rangle \;+ \qquad (54b)\\
&\qquad +\,\varepsilon\,\langle \mathcal{A}\,(\sum_{h=q+1}^{p(r+s)} b_h^{(1)} W^{(h)}\,)\,,\,\Upsilon^{(q)}\rangle \;=\\
&\qquad =\;\langle \mathbf{R}\,(\sum_{\ell=1}^{q} a_\ell \Upsilon^{(\ell)} \;+\; \sum_{h=q+1}^{p(r+s)} (b_h^{(0)} + \varepsilon b_h^{(1)}) W^{(h)}\,)\,,\,\Upsilon^{(q)}\rangle\;.
\end{aligned}
$$

Such equations result to form a closed system of q equations, since the unknowns are the q macroscopic variables $a_1,\dots,a_q$, only, as previously discussed.

On the other hand, when the macroscopic variables are specified as announced in Subsection 4.2, the reactive Navier-Stokes equations (54) reproduce the hydrodynamic formulation. In particular, let

$$
\begin{aligned}
&a_k = n^{[k]} = n_{A_{k_1}} + n_{B_{k_2}}\,, \quad k=1,\dots,q-5,\; k_1\in\{1,\dots,r\},\; k_2\in\{1,\dots,s\}\,,\\
&(a_{q-4}, a_{q-3}, a_{q-2}) = \rho\vec{U}\,, \qquad (55)\\
&a_{q-1} = \rho e + \frac{1}{2}\rho|\vec{U}|^2\,,\\
&a_q = n_{B_1}\,,
\end{aligned}
$$

where ρ is the total mass density, $\vec{U}$ the gas mean velocity, and ρe the internal energy, defined by

$$
\begin{aligned}
\rho \;&=\; \sum_{M} m_{_M}\, n_{_M}\,, \qquad \vec{U} \;=\; \frac{1}{\rho}\sum_{M} m_{_M} \sum_{i=1}^{p} N_i^M \vec{v}_i^M\,, \qquad (56)\\
\rho e \;&=\; \frac{1}{2}\sum_{M} m_{_M} \sum_{i=1}^{p} N_i^M |\vec{v}_i^M - \vec{U}|^2 \;+\; \left(\sum_{k=1}^{r}\epsilon_{A_k} - \sum_{\ell=1}^{s}\epsilon_{B_\ell}\right) n_{B_1}\,.
\end{aligned}
$$

Accordingly, the reactive equations (54) can be written in the hydrodynamic form

$$
\frac{\partial n^{[k]}}{\partial t} + \vec{\nabla}\cdot\left(\vec{I}^{[k]}\right) \;=\; 0\,, \qquad k=1,\dots,q-5\,, \qquad (57)
$$

$$\begin{aligned}&\frac{\partial}{\partial t}\left(\rho\vec{U}\right) + \vec{\nabla}\cdot\left(\rho\vec{U}\otimes\vec{U}+\mathbb{P}\right) + \\ &\qquad \varepsilon\,\vec{\nabla}\cdot\left(\sum_{M}\sum_{i}\sum_{h=q+1}^{p(r+s)} m_{_M}\, b_h^{(1)}\,[W^{(h)}]_i^M\,\vec{v}_i^{\,M}\otimes\vec{v}_i^{\,M}\right) = 0\,,\end{aligned}\tag{58}$$

$$\begin{aligned}&\frac{\partial}{\partial t}\left(\rho e+\frac{1}{2}\rho\mid\vec{U}\mid^2\right) + \vec{\nabla}\cdot\left[\rho\left(e+\frac{1}{2}\mid\vec{U}\mid^2\right)\vec{U}+\vec{U}\cdot\mathbb{P}+\vec{q}\right] + \\ &\qquad \varepsilon\,\vec{\nabla}\cdot\left(\sum_{M}\sum_{i}\sum_{h=q+1}^{p(r+s)} b_h^{(1)}\,[W^{(h)}]_i^M\,(\frac{1}{2}m_{_M}\mid\vec{v}_i^{\,M}\mid^2+\epsilon_{_M})\vec{v}_i^{\,M}\right) = 0\,,\end{aligned}\tag{59}$$

$$\frac{\partial n_{B_1}}{\partial t} + \vec{\nabla}\cdot\left(\vec{I}^{B_1}\right) + \varepsilon\,\vec{\nabla}\cdot\left(\sum_{i}\sum_{h=q+1}^{p(r+s)} b_h^{(1)}\,[W^{(h)}]_i^{B_1}\,\vec{v}_i^{B_1}\right) = \sum_i \mathcal{R}_i^{B_1}\,,\tag{60}$$

where $\vec{I}^{[k]}=\vec{I}^{A_{k_1}}+\vec{I}^{B_{k_2}}$, $\vec{I}^{M}$ being the current density of $M-$species, $\mathbb{P}$ is the stress tensor and $\vec{q}$ the heat flux which will be defined in equations (61). Note that equations (57)-(59) are conservation laws, whereas equation (60) is the balance equation for the B_1-species.

Remark 1. Equations (57) of partial number densities $n^{[k]}$ do not contain terms in ε; formally they coincide with the partial mass conservation laws in the Euler formulation. On the other hand, equations (58), (59) and (60) of momentum, energy and progress variable include terms in ε; formally they reproduce the corresponding equations in the Euler formulation when $\varepsilon = 0$.

Remark 2. In spite of the presence of microscopic quantities in terms with ε, Eqs. (57)-(60) are actually interpreted as the Navier-Stokes equations of the model. In fact, once the model and chemical reaction are specified, the procedure of Sections 5, 6 allows to express the microscopic variables $b_h^{(1)}$ in dependence on the macroscopic variables, as evidentiated by expressions (49) of Proposition 4.

8 Transport coefficients

The results of previous sections permit to identify the transport coefficients, according to the line that will be here proposed

– Remind first the kinetic definitions within discrete kinetic theory of the viscous stress tensor $\mathbb{P}$ ($-\mathbb{P}$ is the momentum flux tensor), current density $\vec{I}^M$ and heat flux vector $\vec{q}$

$$\begin{aligned}\mathbb{P} &= \sum_{M} m_{_M}\sum_{i=1}^{p} N_i^M\left(\vec{v}_i^{\,M}-\vec{U}\right)\otimes\left(\vec{v}_i^{\,M}-\vec{U}\right)\,,\\ \vec{I}^M &= \sum_{i=1}^{p} N_i^M\,\vec{v}_i^M\,,\\ \vec{q} &= \frac{1}{2}\sum_{M} m_{_M}\sum_{i=1}^{p} N_i^M\,|\vec{v}_i^{\,M}-\vec{U}|^2\left(\vec{v}_i^{\,M}-\vec{U}\right)\end{aligned}\tag{61}$$

$$+ \left(\epsilon_{A_1} + \cdots + \epsilon_{A_r} - \epsilon_{B_1} - \cdots - \epsilon_{B_s}\right) \vec{I}^{B_1} ,$$

where ϵ_M is the chemical link energy of M-species introduced in Section 2.

– Expand the densities N_i^M at the first-order level as in (32). Accordingly, the macroscopic quantities given by (61) split in the form

$$\begin{aligned} \mathbb{P} &= \mathbb{P}^{(0)} + \varepsilon\, \mathbb{P}^{(1)} , \\ \vec{I}^M &= \vec{I}^{M^{(0)}} + \varepsilon\, \vec{I}^{M^{(1)}} , \\ \vec{q} &= \vec{q}^{\,(0)} + \varepsilon\, \vec{q}^{\,(1)} . \end{aligned} \tag{62}$$

In Maxwellian equilibrium, the stress tensor $\mathbb{P}^{(0)}$ results to be spherical and the heat flux reduces to its reacting contribution, since the elastic one vanishes, so that

$$\begin{aligned} \mathbb{P}^{(0)} &= p^{(0)}\, \mathbb{I} , \quad \vec{I}^{M^{(0)}} = \sum_{i=1}^{p} N_i^{M^{(0)}} \vec{v}_i^M , \\ \vec{q}^{\,(0)} &= \left(\epsilon_{A_1} + \cdots + \epsilon_{A_r} - \epsilon_{B_1} - \cdots - \epsilon_{B_s}\right) \vec{I}^{B_1^{(0)}} , \end{aligned}$$

$p^{(0)}$, $\vec{I}^{M^{(0)}}$, $\vec{q}^{\,(0)}$ being the gas pressure, current density of species M and the heat flux in Maxwellian equilibrium, and $\mathbb{I}$ the unit tensor. Therefore the splitted form (62) reads

$$\begin{aligned} \mathbb{P} &= p^{(0)}\, \mathbb{I} + \varepsilon \left[\sum_M m_M \sum_{i=1}^{p} \left(\sum_{\ell=q+1}^{p(r+s)} b_\ell^{(1)} [W^{(\ell)}]_i^M \right) \vec{v}_i^{\,M} \otimes \vec{v}_i^{\,M} \right] , \\ \vec{I}^M &= \sum_{i=1}^{p} N_i^{M^{(0)}} \vec{v}_i^M + \varepsilon \left[\sum_{i=1}^{p} \sum_{\ell=q+1}^{p(r+s)} b_\ell^{(1)} [W^{(\ell)}]_i^M \, \vec{v}_i^{\,M} \right] , \\ \vec{q} &= \varepsilon \left[\frac{1}{2} \sum_M m_M \sum_{i=1}^{p} \left(\sum_{\ell=q+1}^{p(r+s)} b_\ell^{(1)} [W^{(\ell)}]_i^M \right) |\vec{v}_i^{\,M}|^2 \vec{v}_i^{\,M} \right] \\ &\qquad + \left(\epsilon_{A_1} + \cdots + \epsilon_{A_r} - \epsilon_{B_1} - \cdots - \epsilon_{B_s}\right) \vec{I}^{B_1^{(1)}} . \end{aligned} \tag{63}$$

In expansions (63), the terms within the large square brackets, defining $\mathbb{P}^{(1)}$, $\vec{I}^{M^{(1)}}$ and $\vec{q}^{\,(1)}$ involve $b_\ell^{(1)}$ and represent the dissipative contributions to the stress tensor, current density of M-species and heat flux vector due to transport effects. For this reason, expressions (63) can be interpreted as Navier-Stokes representation of the model for $\mathbb{P}$, $\vec{I}^M$, $\vec{q}$.

The actual computation of the transport coefficients of shear viscosity, thermal conductivity and thermal diffusivity may be achieved as outlined through the following steps.

1. Explicit the coefficients $b_\ell^{(1)}$ in terms of the macroscopic variables, according to Proposition 4 of Section 6, once the velocity discretization and chemical reaction have been specified for an assigned gas mixture.

2. Combine the explicit expressions obtained in step 1 with Eqs. (63) in order to express the first-order terms $\mathbb{P}^{(1)}$, $\vec{I}^{M^{(1)}}$ and $\vec{q}^{\,(1)}$ in the linear dependence on the gradients of mean velocity, energy and concentrations of each species, respectively, obtaining a more tractable Navier-Stokes representation for $\mathbb{P}$, $\vec{I}^M$ and $\vec{q}$, ready to be compared with the corresponding hydrodynamic representations.

3. Recall the hydrodynamic expressions of the dissipative terms known within the extended (BE), as deduced in paper [16], say $\mathbb{P}_*^{(1)}$, $\vec{I}_*^{M(1)}$ and $\vec{q}_*^{\,(1)}$, defined by

$$\begin{aligned}
\mathbb{P}_*^{(1)} &= \mu \sum_h \sum_k \vec{e}_h \otimes \vec{e}_k \left(\frac{\partial U_h}{\partial x_k} + \frac{\partial U_k}{\partial x_h} \right) - \frac{2}{3}\,\mu \left(\vec{\nabla} \cdot \vec{U} \right) \mathbb{I}\,, \\
\vec{I}_*^{M(1)} &= - \sum_{M' \neq M} D_{MM'} \left[\frac{\vec{\nabla}(k_B n_{M'} T)}{p} + \chi_{M'} \vec{\nabla} \log T \right] \\
\vec{q}_*^{\,(1)} &= -\kappa \vec{\nabla} T - p \sum_M \chi_M \vec{I}^M + \sum_M n_M \left(\frac{5}{2} k_B T + \epsilon_M \right)\,,
\end{aligned} \tag{64}$$

where μ, κ, χ_M, $D_{MM'}$ are the shear viscosity, thermal conductivity, thermal diffusion ratio of species M and diffusion coefficients defining the symmetric diffusion matrix; finally, $\vec{e}_h, \vec{e}_k$ are the unit vectors of the canonical basis in $\mathbb{R}^3$ and k_B the Boltzmann constant.

4. Match the dissipative contributions of the model representation, as obtained in step 2, with $\mathbb{P}_*^{(1)}$, $\vec{q}_*^{\,(1)}$ and $\vec{I}_*^{\,M(1)}$.

5. In the model expressions of $\mathbb{P}^{(1)}$, $\vec{q}^{\,(1)}$, $\vec{I}^{\,M(1)}$ of step 2, recognize then the multiplicative coefficients of the gradients of mean velocity, energy and concentrations of each species; interpret them as μ, κ and $D_{MM'}$, respectively.

To complete this section it should be underlined that the dependence of the transport coefficients on the temperature of the total mixture does not appear evident. In fact in DVM the quantity T defining the temperature, namely

$$T = \frac{1}{3nk_B} \sum_M m_M \sum_{i=1}^{p} N_i^M \, |\vec{v}_i^{\,M} - \vec{U}|^2,$$

is usually introduced as the kinetic temperature of the model, in order to reproduce the state equation in the usual form

$$p = \frac{2}{3}\rho e.$$

Thus, it seems to be clear that the dependence of transport coefficients on T is strictly joined to the set of selected velocities, both in direction and modulus, in other words the temperature is strictly related to the model. Such peculiarity of DVM has been widely discussed by Ernst in [21].

9 Concluding remarks

The content of the present paper furnishes a consistent methodology which can be applied to derive the Navier-Stokes equations and transport coefficients, starting from an arbitrary DVM for a reactive gas mixture with general reversible reaction. At the same time, the paper supplies the mathematical theory and the relevant modeling aspects necessary to set up the above said methodology.

As emphasized in Ref. [22], at the scope of studying the flow properties, it is important to know the functional form of the transport coefficients in dependence on the local concentrations of each species and whole mixture. This can be done in the present modeling, at formal level, trough steps 1-5 of Section 8.

Anyway, a first attempt has been done in this direction in the quoted paper [15] where a DVM for a gas with bimolecular reaction was considered. After rather cumbersome calculations, the transport coefficients of shear viscosity μ and thermal diffusivity $D_{MM'}$ only, could be analytically evaluated, showing an explicit dependence on local concentrations as well as on scattering collisional frequencies and speed of each gas species. Conversely, the thermal conductivity κ could not be recovered, since in the mentioned paper the macroscopic governing equations did not involve the energy equation, and the assumed independent macroscopic variables did not include the heat flux vector. This lack is due to the fact that a complete characterization of the transport coefficients can be realized only once the procedure of the present work is applied. In this sense, the proposed approach provides an improvement covering such lack.

On the other hand, as argued by Brun in paper [23], the computation of the transport terms suggests how crucial is the choice of good modelings for the collision terms, when chemical processes are included. The theory developed in the present paper yields feasible the study of fluid dynamical applications and real gases effects related to moderately dense gases, at small Knudsen number subjected to transport effects, when the chemical process is entirely considered at the molecular level. In fact, in the framework of DVM one can include multiple non reactive collisions in the scattering source term, as well as multiple collisions with chemical reaction in the chemical source term.

As future perspective, one can deal with the evaluation of transport coefficients for the Hydrogen-Oxygen system with reference to both bimolecular reaction

$$\mathrm{H} + \mathrm{O}_2 \rightleftharpoons \mathrm{OH} + \mathrm{O}$$

through which the radicals OH and O are formed from a stable species O_2 and a radical H, and autocathalytic reaction

$$\mathrm{OH} + \mathrm{M} \rightleftharpoons \mathrm{H} + \mathrm{O} + \mathrm{M}$$

of dissociation-recombination of the radicals OH, H, O.

Within DVM such reactions have been already considered in paper [15] and paper [24] where, in particular, a DVM with also triple elastic and inelastic collisions is used to study the steady detonation wave problem; but for the above mentioned perspective they still need to be modeled in a fashion more coherent with the line of the theory developed in the present paper. This task is not immediate and therefore will be matter of a next work.

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