

Kinetic approach to transport properties of a reacting gas

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Abstract

A multicomponent reacting gas with reversible reactions is studied at a kinetic level with the main objective of deriving the reactive Navier-Stokes equations in dependence on the macroscopic variables, and characterizing the dissipative terms related to shear viscosity, heat conduction and thermal diffusion. A step-by-step procedure, which can be applied to a quite large variety of reactive flows, is proposed in order to identify the transport coefficients, basically resorting to a first-order density approximation of Chapman-Enskog type.

1 Introduction

Kinetic approaches to the study of gas mixtures with chemical reactions, have motivated several research works since the last decades, essentially based on Boltzmann-like models, as documented in paper [1] with reference to the full Boltzmann equation, and in paper [2] with reference to the discrete one. In the latter the mathematical theory concerning collision laws, chemical kinetics and thermodynamical equilibrium has been formulated for a kinetic model of a multicomponent mixture with general reversible reaction and velocity discretization. The study is exhaustive at microscopic scale, whereas the macroscopic picture of the reactive flow is limited to the conservative processes described by the reactive Euler equations. For this reason it seems interesting to extend the above treatment to fluid dynamical processes with dissipative effects due to chemical reactions.

Based on the modeling of Ref. [2], the set of conservation and rate equations

$$\frac{\partial}{\partial t} \langle \mathbf{N}, \Upsilon^{(k)} \rangle + \langle \mathcal{A} \mathbf{N}, \Upsilon^{(k)} \rangle = 0 \quad k = 1, \dots, q-1, \quad (1)$$

$$\frac{\partial}{\partial t} \langle \mathbf{N}, \Upsilon^{(q)} \rangle + \langle \mathcal{A} \mathbf{N}, \Upsilon^{(q)} \rangle = \langle \mathcal{R}(\mathbf{N}), \Upsilon^{(q)} \rangle, \quad (2)$$

can be deduced starting from the matrix kinetic equation

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

for a gas formed by $r + s$ M -species, $M = A_1, \dots, A_r, B_1, \dots, B_s$, whose particles move in the space with p selected velocities and undergo multiple elastic collisions and inelastic

interactions with reversible chemical reaction



The meaning of symbols involved in Eqs. (1-3) is briefly recalled.

- $\mathbf{N}, \mathbf{Q}(\mathbf{N}), \mathbf{R}(\mathbf{N}) \in \mathbb{R}^{p(r+s)}$ denote the vector of the number densities $N_i^M(\vec{x}, t)$, $\vec{x} \in \mathbb{R}^3$, $t \in \mathbb{R}_+$, of particles with velocity \vec{v}_i^M , $i = 1, \dots, p$, and the nonlinear vector functions related to elastic collisions and chemical reactions.

- \mathcal{A} is a diagonal matrix of order $p(r+s)$ with elements $\mathcal{A}_{ii}^M = \vec{v}_i^M \cdot \vec{\nabla}$.

- $\Upsilon^{(k)} \in \mathbb{R}^{p(r+s)}$, $k = 1, \dots, q$, with $q = \dim \mathcal{F}$, are o.n. vectors of the basis

$$\mathcal{B}_{\mathcal{M}} = \{\Upsilon^{(1)}, \dots, \Upsilon^{(q-1)}\} \subset \mathcal{M}, \quad \mathcal{B}_{\mathcal{F}} = \mathcal{B}_{\mathcal{M}} \cup \{\Upsilon^{(q)}\} \subset \mathcal{F}, \quad (5)$$

where \mathcal{M} is the space of *mechanical-reactive* collision invariants and \mathcal{F} the space of *mechanical* collision invariants [2].

In the extended version [3] of the present paper, it is proven that the closure of the governing equations (1-2) requires the choice of an appropriate orthonormal basis \mathcal{B} of $\mathbb{R}^{p(r+s)}$, represented by

$$\mathcal{B} = \mathcal{B}_{\mathcal{F}} \cup \mathcal{B}_{\mathcal{F}^\perp}, \quad \mathcal{F} \oplus \mathcal{F}^\perp = \mathbb{R}^{p(r+s)}. \quad (6)$$

Consequently, the vector $\mathbf{N} \in \mathbb{R}^{p(r+s)}$ can be splitted in the basis \mathcal{B} as

$$\mathbf{N} = \sum_{k=1}^q a_k(\vec{x}, t) \Upsilon^{(k)} + \sum_{\ell=q+1}^{p(r+s)} b_\ell(\vec{x}, t) W^{(\ell)}, \quad (7)$$

where the coefficients a_k, b_ℓ are macroscopic and microscopic variables, respectively, defined for $k = 1, \dots, q$ and $\ell = q+1, \dots, p(r+s)$ by

$$a_k = \langle \mathbf{N}, \Upsilon^{(k)} \rangle, \quad b_\ell = \langle \mathbf{N}, W^{(\ell)} \rangle. \quad (8)$$

It is evident that Eqs. (1-2), when \mathbf{N} is given by expansion (7), form a non closed set of q equations in the unknowns $a_1, \dots, a_q, b_{q+1}, \dots, b_{p(r+s)}$. The closure is achieved when $b_{q+1}, \dots, b_{p(r+s)}$ become known functions of the macroscopic variables a_1, \dots, a_q . The next section deals with the mathematical strategy which leads to the closure of the above said set.

2 Approximation procedure

A first order Chapman-Enskog method can be applied to Eqs. (1-2), introducing the approximation for the number density vector given by

$$\mathbf{N} = \mathbf{N}^{(0)} + \varepsilon \mathbf{N}^{(1)}, \quad (9)$$

ε being the Knudsen number, and taking into account the classical hypothesis that the macroscopic variables are exact at the zero-order approximation (i.e. unexpanded [4]), namely

$$a_k = \langle \mathbf{N}^{(0)}, \Upsilon^{(k)} \rangle, \quad 0 = \langle \mathbf{N}^{(1)}, \Upsilon^{(k)} \rangle, \quad k = 1, \dots, q. \quad (10)$$

These last equalities permit to represent the density vector \mathbf{N} as

$$\mathbf{N} = \sum_{k=1}^q a_k \Upsilon^{(k)} + \sum_{\ell=q+1}^{p(r+s)} (b_\ell^{(0)} + \varepsilon b_\ell^{(1)}) W^{(\ell)}. \quad (11)$$

The approximations $\mathbf{N}^{(0)}$ and $\mathbf{N}^{(1)}$ satisfy the compatibility equations

$$\mathbf{Q}(\mathbf{N}^{(0)}) = 0, \quad (12)$$

$$\begin{aligned} & 2\mathbf{Q}_2(\mathbf{N}^{(0)}, \mathbf{N}^{(1)}) + \dots + h\mathbf{Q}_h(\mathbf{N}^{(0)}, \dots, \mathbf{N}^{(0)}, \mathbf{N}^{(1)}) = \\ & = \mathbb{L}(\mathbf{N}^{(0)} + \varepsilon \mathbf{N}^{(1)}) = \sum_{k=1}^q \frac{\partial a_k}{\partial t} \Upsilon^{(k)} + \mathcal{A}\mathbf{N}^{(0)} - \mathbf{R}(\mathbf{N}^{(0)}), \end{aligned} \quad (13)$$

where $h = \max\{r, s\}$, \mathbf{Q}_j , $j = 1, \dots, h$, is the nonlinear term due to elastic j -encounters and \mathbb{L} the linearized mechanical operator [3].

The approximation procedure is based on the contents of next items.

- Equation (12) characterizes the zero-order approximation $\mathbf{N}^{(0)}$ as the Maxwellian number density in dependence on the q macroscopic variables, $\mathbf{N}^{(0)} = \mathbf{N}^{(0)}(a_1, \dots, a_q)$. Thanks to the one-to-one map between the a_k variables and the Maxwellian parameters, the coefficients $b_\ell^{(0)}$ of Eq. (11) become known functions of type

$$b_\ell^{(0)} = b_\ell^{(0)}(a_1, \dots, a_q), \quad \ell = q+1, \dots, p(r+s), \quad (14)$$

which are strictly related to the kinetic model assumed to describe the gas.

- Equation (13) determines the first approximation $\mathbf{N}^{(1)}$ in terms of q parameters, as well, provided that the time derivatives of the macroscopic variables are evaluated through the reactive Euler equations in the form

$$\frac{\partial a_k}{\partial t} = \langle -\mathcal{A}\mathbf{N}^{(0)} + \mathcal{R}(\mathbf{N}^{(0)}), \Upsilon^{(k)} \rangle, \quad k = 1, \dots, q, \quad (15)$$

which play the role of solubility conditions for $\mathbf{N}^{(1)}$ in Eq. (13). Projecting Eq. (13) on the space \mathcal{F} and reminding the orthogonality property [3, 5] of \mathbb{L} , the microscopic variables become functions of type

$$b_\ell^{(1)} = b_\ell^{(1)}(a_1, \dots, a_q) \quad \ell = q+1, \dots, p(r+s), \quad (16)$$

whose explicit form depends on the specific kinetic model. Thus one has $\mathbf{N}^{(1)} = \mathbf{N}^{(1)}(a_1, \dots, a_q)$ and the system (1-2) can actually be closed.

3 Reactive Navier Stokes equations

After inserting expressions (11) of \mathbf{N} and (14,16) of $b_\ell^{(0)}$, $b_\ell^{(1)}$ into the governing equations (1-2), one obtains the closed system of the reactive Navier--Stokes equations of the model.

When the macroscopic variables a_1, \dots, a_q are specified in a convenient manner, such equations reproduce the hydrodynamic formulation of the Navier-Stokes equations. In particular, let

$$\begin{aligned} a_k &= n^{[k]} = n_{A_{k_1}} + n_{B_{k_2}}, \quad k = 1, \dots, q-5, \\ &\quad k_1 \in \{1, \dots, r\}, \quad k_2 \in \{1, \dots, s\}, \\ (a_{q-4}, a_{q-3}, a_{q-2}) &= \rho \vec{U}, \\ a_{q-1} &= \rho e + \frac{1}{2} \rho |\vec{U}|^2 + \gamma, \quad a_q = n_{B_1}, \end{aligned} \quad (17)$$

where ρ , \vec{U} , ρe and γ are the total mass density, mean velocity, internal energy and chemical energy per unit volume. Accordingly, Eqs. (1-2) become

$$\frac{\partial n^{[k]}}{\partial t} + \vec{\nabla} \cdot (\vec{I}^{[k]}) = 0, \quad k = 1, \dots, q-5, \quad (18)$$

$$\begin{aligned} \frac{\partial}{\partial t} (\rho \vec{U}) + \vec{\nabla} \cdot (\rho \vec{U} \otimes \vec{U} + \mathbb{P}) + \\ \varepsilon \vec{\nabla} \cdot \left(\sum_M \sum_i \sum_{h=q+1}^{p(r+s)} m_M b_h^{(1)} [W^{(h)}]_i^M \vec{v}_i^M \otimes \vec{v}_i^M \right) = 0, \end{aligned} \quad (19)$$

$$\begin{aligned} \frac{\partial}{\partial t} \left(\rho e + \frac{1}{2} \rho |\vec{U}|^2 + \gamma \right) + \vec{\nabla} \cdot \left[\rho \left(e + \frac{1}{2} |\vec{U}|^2 \right) \vec{U} + \vec{U} \cdot \mathbb{P} + \vec{q} + \vec{\Gamma} \right] + \\ \varepsilon \vec{\nabla} \cdot \left(\sum_M \sum_i \sum_{h=q+1}^{p(r+s)} b_h^{(1)} [W^{(h)}]_i^M \left(\frac{1}{2} m_M |\vec{v}_i^M|^2 + \epsilon_M \right) \vec{v}_i^M \right) = 0, \end{aligned} \quad (20)$$

$$\frac{\partial n_{B_1}}{\partial t} + \vec{\nabla} \cdot (\vec{I}^{B_1}) + \varepsilon \vec{\nabla} \cdot \left(\sum_i \sum_{h=q+1}^{p(r+s)} b_h^{(1)} [W^{(h)}]_i^{B_1} \vec{v}_i^{B_1} \right) = \sum_i \mathcal{R}_i^{B_1}, \quad (21)$$

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, \vec{q} the heat flux and $\vec{\Gamma}$ the flux of chemical energy. Note that Eqs. (18-20) are conservation laws, whereas Eq. (21) is a balance equation. Moreover, Eqs. (18) 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. Equations (19-21) of momentum, energy and progress variable include terms in ε ; formally, they reproduce the corresponding equations in the Euler formulation, when $\varepsilon = 0$.

4 Transport coefficients

The transport coefficients of viscosity, heat conductivity and thermal diffusivity will be identified through a step-by-step procedure, on the basis of the Navier-Stokes representation

of the model for \mathbb{P} , \vec{q} and \vec{I}^M . Their first-order kinetic definitions, since in Maxwellian equilibrium the stress tensor $\mathbb{P}^{(0)}$ is spherical and the heat flux $\vec{q}^{(0)}$ vanishes, read

$$\begin{aligned}\mathbb{P} &= p^{(0)} \mathbb{I} + \varepsilon \left[\sum_M m_M \sum_{i=1}^p \left(\sum_{\ell=q+1}^{p(r+s)} b_\ell^{(1)} [W^{(\ell)}]_i^M \right) \vec{v}_i^M \otimes \vec{v}_i^M \right], \\ \vec{q} &= \varepsilon \left[\frac{1}{2} \sum_M m_M \sum_{i=1}^p \left(\sum_{\ell=q+1}^{p(r+s)} b_\ell^{(1)} [W^{(\ell)}]_i^M \right) |\vec{v}_i^M|^2 \vec{v}_i^M \right], \\ \vec{I}^M &= \sum_{i=1}^p N_i^{M(0)} \vec{v}_i^M + \varepsilon \left[\sum_{i=1}^p \sum_{\ell=q+1}^{p(r+s)} b_\ell^{(1)} [W^{(\ell)}]_i^M \vec{v}_i^M \right].\end{aligned}\tag{22}$$

The terms within the large square brackets involve $b_\ell^{(1)}$ and represent the dissipative contributions to \mathbb{P} , \vec{q} and \vec{I}^M , due to transport effects.

The actual computation of the transport coefficients may be achieved as outlined through the following steps.

1. Explicit coefficients $b_\ell^{(1)}$ in terms of the macroscopic variables, according to Eq. (16), once the model has been specified for an assigned gas.
2. Combine the expressions obtained in step 1. with Eqs. (22) in order to express the dissipative contributions to \mathbb{P} , \vec{q} , \vec{I}^M in dependence on the gradients of mean velocity, energy and concentrations of each species, obtaining a more tractable Navier-Stokes representation for \mathbb{P} , \vec{q} , \vec{I}^M , ready to be compared with the corresponding hydrodynamic representations.
3. Recall the hydrodynamic expressions [6] of the dissipative terms known for real gases, say $\mathbb{P}_*^{(1)}$, $\vec{q}_*^{(1)}$ and $\vec{I}_*^{M(1)}$,

$$\begin{aligned}\mathbb{P}_*^{(1)} &= \mu \sum_h \sum_k \vec{e}_h \otimes \vec{e}_k \left(\frac{\partial U_h}{\partial x_k} + \frac{\partial U_k}{\partial x_h} \right) - \frac{2}{3} \mu (\vec{\nabla} \cdot \vec{U}) \mathbb{I}, \\ \vec{q}_*^{(1)} &= -\kappa \vec{\nabla} e, \quad \vec{I}_*^{M(1)} = \sum_{M' \neq M} D_{MM'} \vec{\nabla} n_{M'},\end{aligned}\tag{23}$$

where μ , κ and $D_{MM'}$ are the shear viscosity, conductivity and diffusivity, and \vec{e}_h, \vec{e}_k the unit vectors of the canonical basis in \mathbb{R}^3 .

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 for the dissipative contributions of step 2. recognize the multiplicative coefficients of the gradients of mean velocity, energy and species concentrations, and interpret them as μ , κ and $D_{MM'}$, respectively.

Acknowledgments

The present paper has been partially supported by PRIN 2003 (Coordinator: T. Ruggeri) and Minho University Mathematics Centre (Fundação para a Ciência e Tecnologia/Programa Operacional “Ciência, Tecnologia, Inovação”).

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