A WELL-POSED SIMULATION MODEL FOR MULTICOMPONENT REACTING GASES[*]

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Abstract. We aim to present a relaxation model that can be used in real simulations of dilute multicomponent reacting gases. The kinetic framework is the semi-classical approach with only one variable for the internal energy modes. The relaxation times for the internal energy modes are assumed to be smaller than the chemistry characteristic times. The strategy is the same as in [S. Brull and J. Schneider, Commun. Math. Sci., 12, 1199–1223, 2014]. That is, a sum of operators for respectively the mechanical and chemical processes. The mechanical operator(s) is the "natural" extension to polyatomic gases of the method of moment relaxations presented in [S. Brull and J. Schneider, Cont. Mech. Thermodyn. 20(2), 63–74, 2008] [S. Brull, V. Pavan, and J. Schneider, Eur. J. Mech. (B-Fluids), 33, 74–86, 2012]. The derivation of the chemical model lies on the chemical processes at thermal equilibria. It is shown that this BGK approach features the same properties as the Boltzmann equation: conservations and entropy production. Moreover, null entropy production states are characterized by vanishing chemical production rates. We also study the hydrodynamic limit in the slow chemistry regime. Finally, we show that the whole set of parameters that are used in the derivation of the model can be calculated by softwares such as EGlib [A. Ern, V. Giovangigli, http://www.cmap.polytechnique.fr/www.eglib/] or STANJAN [B. Reynolds, http://www.stanford.edu/].

Key words. Kinetic theory, BGK models, polyatomic gases, chemical reactions, entropy production, hydrodynamic limit.

AMS subject classifications. 35Q20, 35Q35.

1. Introduction

The Boltzmann equation for multicomponent reacting gases features many phenomena that may occur at the microscopic level: elastic and nonelastic collisions, transfer of energy between the different internal energy modes, chemical collisions, etc. An extensive literature on the different Boltzmann equations, as well as mathematical modeling, can be found in the book of Nagnibeda and Kustova [33]. Simplified models under strong non-equilibrium assumptions rely essentially on the Chapman–Enskog expansion in a state-to-state approach or, equivalently, under the different time scales of each phenomena. Once the relative scales are set, this requires one to evaluate the corresponding transport coefficients on one side and to write evolution equations for the densities on the other side. For example, one can consider the evolution of the concentrations of rotational quantum levels for each species. The collisions resulting in vibrational exchanges and/or chemical reactions are then averaged on the velocity space under suitable assumptions on the translational and rotational distributions (Maxwell–Boltzmann). This results in source terms that can be evaluated by analytical methods and/or experiments (see for example [14]).

In the present article, we will not address the strong non-equilibrium regime. The physical framework will be that of a moderately non-equilibrium regime with slow chemical reactions. The corresponding Boltzmann equation is stated in the semi-classical approach for which the internal energy states for a given species are described by a single variable. This theory was derived by Waldmann and Trüdenbacher [37] for a nonreactive gas mixture. Ludwig and Heil [31] would eventually include reactive collisions

(dissociation). The generalization to dissociation and recombination, including triple collisions, was given by Kŭscer [29] and Grunfeld [25] and can also be found in classical textbooks [16, 19]. In the present paper, we intend to derive a simplified model for dilute polyatomic gases undergoing chemical reactions. For the Navier–Stokes system of equations for reactive collisions, BGK [4] type relaxtion operators may bring more information than the corresponding moment method. Notice also that those moment equations are the "simplest" model in the hierarchy of Nagnibeda and Kustova [33]. Our aim is to construct a kinetic model based on one side on mechanical relaxation processes and on the other side on chemical reactions near thermal equilibria. The seminal model of Bhatnagar, Gross, and Krook must be generalized and improved in order to keep as much information as possible coming from the non-equilibrium distribution functions. We only retain some of the advances that were obtained in the case of gas of monatomic gas mixtures, namely the works of Garsó, Santos, and Brey [24], Andriès, Aoki, and Perthame [1], and finally Brull, Pavan, and the author [11]. The first of these models is actually used in practical applications. The second has brought a nice mathematical setting — positivity of its solutions, H-theorem, etc. — together with the right collision frequencies in the case of Maxwellian molecules. The last one proposes a systematic way to construct well-posed relaxation models based, more or less, on the study of the linearized Boltzmann operator and on the transport coefficients of the hydrodynamic limit (Navier–Stokes equations). To our knowledge, BGK type models addressing chemical reactions have been mainly investigated by Groppi, Spiga, and other researchers in Parma [5, 6, 21, 22]. In the same vein, one should also cite the works of Kremer, Pandolfi, and Soares [28]. Their framework is that of a four component gas mixture undergoing a bimolecular reversible reaction

$$\mathfrak{M}_1 + \mathfrak{M}_2 \rightleftharpoons \mathfrak{M}_3 + \mathfrak{M}_4$$
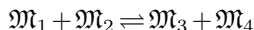
with only one quantum internal energy per molecule. Thus mechanical collisions are elastic and treated as in [1]. Those pioneering works constitute a solid basis for further investigations despite the fact that they are unlikely to be generalized to real polyatomic gases. A good analysis of them, as well as a perception of their drawbacks, can provide insight about what could be done.

The aim of this article is to introduce a BGK model that goes beyond such an analysis. We do not only intend to design a well-posed simulation model (H-theorem, etc.) but also to address physical simulations of multicomponent reacting gases. We adopt the strategy that was introduced in [10] and employ a sum of BGK models that features the natural distinction between nonreactive and reactive collisions. This strategy applies especially in the case where the difference between the respective characteristic times of each phenomena is of a sufficiently large order of magnitude. The founding idea is to bring information from the macroscopic level to the kinetic one. In this vein, we extend to polyatomic gases the method of moments relaxation introduced in [8, 11]. The real novelty lies in the derivation of the chemical operators by making use of chemical processes at thermal equilibrium. We construct for a given species i a single BGK type model that takes into account all chemical reactions where i is either a reactant or a product (or both).

The paper is organized as follows. We first introduce the notations and all necessary materials for the rest of the paper. In particular, the semi-classical approach is briefly described for the sake of consistency. In Section 3, we recall two formulations of the Navier–Stokes equations for polyatomic mixtures after a short introduction on the method of moments relaxation (MMR). In the first one, the fluxes are expressed using

the thermodynamics of irreversible processes [32, 13, 18, 11]. It is the natural framework of the MMR. Yet, our method is for the moment incomplete and is constructed assuming that only the diffusion matrix is known (second formulation [37, 31, 20, 16]). We then present the derivation of the mechanical operator in two steps. Some necessary assumptions are proved a posteriori in the third step together with the H-theorem. Section 4 is devoted to the chemical relaxation model. We firstly address the case of a single reaction and secondly construct the operator for a full chain of reactions. Finally, we prove that all physical properties are satisfied: conservation of atom mass concentrations, mean velocity, and total energy together with entropy production. In Section 5, we study the whole model: 1 - states corresponding to null entropy production, 2 - hydrodynamic limit. We also summarize the steps of the whole construction. In particular, we show that the whole set of parameters that are used in the construction of the model can be calculated by softwares such as EGlib [17] or STANJAN [36].

2. Boltzmann equation and notations

2.1. Notations. We consider a set S of polyatomic gases composed of p species. For the purpose of notation, we often use the same letter/index i to denote either a species in S or its number in $\{1, \cdots, p\}$. Then for each species $i \in S$, we denote with $f_i(t, \mathbf{x}, \mathbf{v}, I)$ the distribution function where $t, \mathbf{x}, \mathbf{v}, I$ are respectively the time, position, velocity, and index for the internal energy states of the ith species. Each internal energy is denoted with E_{iI} which includes both the Ith quantum energy state together with the energy of formation. Macroscopic quantities are obtained, as usual, from the distribution functions f_i in the following way. The number density of the ith species is given by

$$n^i = \sum_{I \in \Omega_i} \int f_i d\mathbf{v}$$

so that its mass density per unit volume is

$$\rho^i = m_i n^i = \sum_{I \in \Omega_i} \int m_i f_i d\mathbf{v}$$

where m_i denotes the mass of the molecules of the ith species. The hydrodynamic velocity $\mathbf{u}$ is given by

$$\rho \mathbf{u} = \sum_{\substack{i \in S \\ I \in \Omega_i}} \int m_i \mathbf{v} f_i d\mathbf{v}$$

where $\rho = \sum_{i \in S} \rho_i$ is the total mass density. We may also define the total density $n = \sum_{i \in S} n^i$ which is often used when there are no chemical reactions. The internal energy $\mathcal{E}$ per unit volume is given by

$$\frac{1}{2}\rho \mathbf{u}^2 + \mathcal{E} = \sum_{\substack{i \in S \\ I \in \Omega_i}} \int (\frac{1}{2} m_i \mathbf{v}^2 + E_{iI}) f_i(t, x, v, E_{iI}) d\mathbf{v}. \tag{2.1}$$

The kinetic entropy $\mathcal{S}^{\text{kin}}$ per unit volume is defined by

$$\mathcal{S}^{\text{kin}}(\mathbf{f}) = -k_{\text{B}} \sum_{\substack{i \in S \\ I \in \Omega_i}} \int f_i \big(\log(\beta_{iI} f_i) - 1\big) d\mathbf{v}$$

where the statistical weight β_{iI} is given by

$$\beta_{iI} = \frac{h_{\mathrm{P}}^3}{a_{iI} m_i^3}.$$

Here h_{P} is the Planck constant and a_{iI} is the degeneracy of the Ith quantum energy shell of the ith species. Let us point out that $\mathcal{S}^{\mathrm{kin}}$ corresponds to the physical kinetic entropy, contrary to the mathematical entropy H which is often used for mathematical convenience and is of the **opposite sign**.

2.2. Boltzmann equation.   In this section, we briefly recall the reactive kinetic Boltzmann equations in the semi-classical approach. The non reactive Boltzmann equation for polyatomic gas mixtures that we consider is obtained in a semiclassical approach. It was derived by Waldmann and Trüdenbacher [37] and can be found in different textbooks [16, 19], etc. The chemical source terms were derived by Ludwig and Heil [31] and generalized by different authors [29, 25] and can be found again in the above textbooks. This operator will not be detailed because it is required in the present work. The Boltzmann equation without external forces reads as

$$\partial_t f_i + \mathbf{v}.\nabla_x f_i = S_i(f) + C_i(f), \qquad i \in S, \tag{2.2}$$

where $S_i(f)$ is the nonreactive, or scattering, source term and $C_i(f)$ is the reactive, or chemistry, source term.

The nonreactive collision term. This term reads as

$$S_i(f) = \sum_{j \in S} \sum_{\substack{I' \in \Omega_i \\ J \in \Omega_j \\ J' \in \Omega_j}} \int \left(f_i' f_j' \frac{a_{iI} a_{jJ}}{a_{iI'} a_{jJ'}} - f_i f_j\right) W_{ij}^{IJI'J'} d\mathbf{v}_j d\mathbf{v}_i' d\mathbf{v}_j' \tag{2.3}$$

where I and J are the indices for the internal energy states of the ith and j^{th} species before collision and I' and J' are the corresponding numbers after collision. The symbols f_i' and f_j' are the classical notations for the distribution functions after collisions, that is $f_i' = f_i(t, \mathbf{x}, \mathbf{v}_i', I')$ and $f_j' = f_j(t, \mathbf{x}, \mathbf{v}_j', J')$. Finally $W_{ij}^{IJI'J'}$ is the transition probability for for the above collisions. In the case where collisions are possible, the following condition on reversible collisions holds:

$$W_{ij}^{IJI'J'} a_{iI} a_{jJ} = W_{ij}^{I'J'IJ} a_{iI'} a_{jJ'}. \tag{2.4}$$

Finally, we recall that other formulations involving cross sections, and thus angular deviation in the integral, are possible (see e.g [34, 23]).

The chemistry collision term. For a given species $i \in S$, the chemical process is composed by an arbitrary number of elementary reactions. Those reactions occur at the microscopic level collisions between two molecules. Collisions involving more molecules are, in principle, very unlikely to occur. However, triple reactive collisions may be considered in an abstract kinetic framework and will be considered here. All chemical reactions are of the form

$$\sum_{k \in \mathfrak{F}^r} \mathfrak{M}_k \rightleftharpoons \sum_{l \in \mathfrak{B}^r} \mathfrak{M}_l, \qquad r \in R \tag{2.5}$$

where $\mathfrak{F}^r$ and $\mathfrak{B}^r$ are respectively the indices for the reactant and product species. Correspondingly, the stoichiometric coefficients of the ith species in this reaction are

respectively denoted by ν_{ir}^{f} and ν_{ir}^{b}, and we set $\nu_{ir} = \nu_{ir}^{\mathrm{b}} - \nu_{ir}^{\mathrm{f}}$. We also denote with S_r the set of reactants, products, or both in the reaction r. Finally, the reactive source term in (2.2) reads as

$$C_i(f) = \sum_{r \in R} C_i^r(f) \tag{2.6}$$

where $C_i^r(f)$ is the term corresponding to the chemical reaction r for the species i.

2.3. Collisional invariants of the non-reactive collision operator. This space is of particular interest in the case of slow chemical reaction. It is spanned by the following list of vectors:

$$\begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \cdots, \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 1 \end{pmatrix}, \begin{pmatrix} m_1 v_x \\ m_2 v_x \\ \vdots \\ m_n v_x \end{pmatrix}, \begin{pmatrix} m_1 v_y \\ m_2 v_y \\ \vdots \\ m_n v_y \end{pmatrix}, \begin{pmatrix} m_1 v_z \\ m_2 v_z \\ \vdots \\ m_n v_z \end{pmatrix}, \begin{pmatrix} \frac{1}{2} m_1 \mathbf{v}^2 + E_{1I} \\ \frac{1}{2} m_2 \mathbf{v}^2 + E_{2I} \\ \vdots \\ \frac{1}{2} m_n \mathbf{v}^2 + E_{nI} \end{pmatrix}.$$

This space is of dimension $p+4$, and the above list of functions is denoted $\boldsymbol{\psi}^l$, $l \in [1, p+4]$.

DEFINITION 2.1. *The space of collisional invariants of the non reactive collision terms is*

$$\mathbb{K} = \mathrm{Span}\{ \boldsymbol{\psi}^l, l = 1, \ldots, n+4 \}. \tag{2.7}$$

The momentum invariants $\boldsymbol{\psi}^{p+\nu}$, $\nu = 1, 2, 3$, and the energy invariant $\boldsymbol{\psi}^{p+4}$ are also collisional invariants for the reactive collision operator C. But this is not the case for the species type invariants ψ^l, $l = 1, \cdots, p$, and one must rather consider conservation of atom mass concentrations. However, the description of those invariants is not required in our work as will be shown later on.

2.4. Entropy production and Maxwellian distributions. The entropy source term can be split into

$$\mathfrak{v}^{\mathrm{kin}} = \mathfrak{v}^S + \mathfrak{v}^C$$

where $\mathfrak{v}^S$ is the nonreactive contribution

$$\mathfrak{v}^S = -k_{\mathrm{B}} \sum_{\substack{i \in S \\ I \in \Omega_i}} \int S_i(f) \log(\beta_{iI} f_i) d\mathbf{v}_i$$

and $\mathfrak{v}^C$ is the reactive contribution

$$\mathfrak{v}^C = -k_{\mathrm{B}} \sum_{\substack{i \in S \\ I \in \Omega_i}} \int C_i(f) \log(\beta_{iI} f_i) d\mathbf{v}_i.$$

Each quantity is nonnegative and thus yields a generalization of the celebrated H-theorem. In particular, one can specify the form of the distribution functions for which $\mathfrak{v}^S = 0$ or equivalently $S_i(f) = 0$ for all i by using (2.4) and the specification of the space of collisional invariants $\mathbb{K}$. We denote with $\mathbf{M} = (\mathcal{M}^1, ..., \mathcal{M}^p)$ the set of those functions with

$$\mathcal{M}^i = \frac{1}{\beta_{iI}} \frac{n_i}{Q_i} \exp\left\{ -\frac{m_i}{2k_{\mathrm{B}}T} (\mathbf{v}_i - \mathbf{v})^2 - \frac{E_{iI}}{k_{\mathrm{B}}T} \right\} \tag{2.8}$$

where Q_i is the full partition function of the species i per unit volume. This function is the product of the partition function for internal energy

$$Q_i^{\text{int}} = \sum_{I \in \Omega_i} a_{iI} \exp\left(-\frac{E_{iI}}{k_{\text{B}}T}\right) \tag{2.9}$$

with

$$Q_i^{\text{tr}} = \left(\frac{2\pi m_i k_{\text{B}} T}{h_{\text{P}}^2}\right)^{3/2}.$$

2.5. The linearized non reactive source term.   For any list of functions $\boldsymbol{\Psi} = (\psi_1, \cdots, \psi_p)$ and $\boldsymbol{\Phi} = (\phi_1, \cdots, \phi_p)$, we introduce the dot product

$$\langle \boldsymbol{\Psi}, \boldsymbol{\Phi} \rangle = \sum_{i=1}^{i=p} \int_{\mathbb{R}^3} \psi_i \phi_i \mathcal{M}^i \, dv.$$

This definition extends to lists of tensors by applying tensor contraction. Next we denote with $\mathcal{L}_S := (\mathcal{L}_{S,1}, \cdots, \mathcal{L}_{S,p})$ the linearized operator of the non-reactive source term. Without entering too much into detail, $\mathcal{L}_S$ satisfies the properties

$$\text{Ker}(\mathcal{L}_S) = \mathbb{K}, \tag{2.10}$$

$$\mathcal{L}_S \text{ is continuous, invertible and self adjoint negative on } \mathbb{K}^\perp. \tag{2.11}$$

A mathematical proof for monoatomic mixtures can be found in [3].

3. A relaxation operator for mechanical processes

In this section, we extend the BGK model derived in [11] to polyatomic gas mixtures. This approach was developed in different steps which are presented here.

1. In the simple case of a monoatomic gas, the collision term reads $Q(f,f) = Q^+(f,f) - \nu(f)f$ where $\nu(f)$ is the collision frequency. In particular, when ν does not depend on f (Maxwellian molecules), the above form is very close to a BGK model $R(f) = \nu(G - f)$. The comparison between $Q^+(f,f)$ and $R(f)$ not only suggests that one consider G as a relaxation function (the classical BGK model [4]) but as an approximation of $Q^+(f,f)$. This founding idea was presented in [35] as a Galerkin method where G is defined via a maximization problem under constraints. More precisely, G is the nonnegative function that is the maximum of the entropy of all functions whose moments are equal to those of $Q^+(f,f)$. The number of moments is chosen arbitrarily.

2. Unfortunately, this idea cannot be generalized to any type of interaction potentials. Then, the second idea consists of considering the formal linearized form of $R(f)$ in such a way that its eigenvalues are more or less those of the linearized operator of $Q(f,f)$. This leads one to set constraints such as

$$\int R(f) m_i(v) \, d\mathbf{v} = -\lambda_i \int f m_i(v) \, d\mathbf{v}, \qquad i = 1, ..., N$$

where $(1/\lambda_i)_i, (m_i(v))_i$ are more ore less equivalent to the eigenvalues and eigenvectors of the linearized operator of $Q(f,f)$. With those constraints at hand, one can perform a Chapman–Enskog under suitable assumptions. The corresponding Navier–Stokes equations are then compared with those obtained from

the Boltzmann equation. Then a proper choice of $(\lambda_i, m_i(v))_i$ allows one to match the first system of equations with the second. In a previous publication [8, 9], we were able to reinterpret classical relaxation models such as the ESBGK model [26] and its generalization to polyatomic molecules [2].

3. Yet, this new interpretation becomes a systematic method for constructing relaxation models. This was applied with success in the case of monoatomic gas mixtures [11].

In our method, the formulation of the fluxes is very important. The mass and heat fluxes are written as

$$
\mathbf{J}_i = -\sum_{j=1}^{j=p} L_{ij} \nabla \left(\frac{g_j}{T} \right) - L_{i,p+1} \nabla \left(-\frac{1}{T} \right),
$$
$$
\mathbf{J_q} = -\sum_{j=1}^{j=p} L_{p+1,j} \nabla \left(\frac{g_j}{T} \right) - L_{p+1,p+1} \nabla \left(-\frac{1}{T} \right)
$$
(3.1)

where $(g_i)_i$ are the specific Gibbs free energies per species. Finally the momentum flux is

$$
\mathbb{J}_{\mathbf{u}} = -\alpha \nabla \cdot \mathbf{u} \mathbb{I} - \eta \mathbb{D}(\mathbf{u})
$$
(3.2)

where α is the volume viscosity and η is the shear viscosity. We denote with $\mathbb{D}(\mathbf{u})$ the classical Reynolds tensor

$$
\mathbb{D}(\mathbf{u}) = \left[\nabla_{\mathbf{x}} \mathbf{u} + (\nabla_{\mathbf{x}} \mathbf{u})^T \right] - \frac{1}{3} (\nabla_{\mathbf{x}} \cdot \mathbf{u}) \mathbb{I}.
$$
(3.3)

This formualtion was derived from the thermodynamics of irreversible processes (TIP) by Meixner [32] and from the Boltzmann equation for monatomic gas mixtures by Chapman and Cowling [13] and De Groot and Mazur [18]. We quickly describe in an appendix the derivation of the coefficients from the kinetic theory of polyatomic gas mixtures (see Remark A.2 in Appendix A.4). Yet, another formulation of the above fluxes is more suited to real applications since it is written in terms of phenomenological forces:

$$
\mathbf{J}_i = -\sum_{j=1}^{p} \rho^i D_{ij} \frac{\nabla p_j}{p} - \rho^i \theta_i \frac{\nabla T}{T}, \qquad \forall i \in \{1;4\},
$$
$$
\mathbf{J_q} = -\hat{\lambda} \nabla T - p \sum_{i=1}^{4} \theta_i \frac{\nabla p_i}{p} + \sum_{i=1}^{4} h_i J_i.
$$
(3.4)

Here, $D = (D_{ij})_{ij}$ is the diffusion matrix, $(\theta_i)_i$ are the thermal diffusion coefficients and $\hat{\lambda}$ is the partial thermal conductivity. This formulation was derived from a kinetic theory of polyatomic gas mixtures by Waldmann and Trudenbacher [37]. Rigorous derivation of these equations was then given by Ludwig and Heil [31] and later on by different authors (see e.g [13, 20, 16, 19]). The set of coefficients in the two formulations are related by algebraic relations that were found by Kurochkin, Makarenko, and Tirskii [27]. In our approach, if the above coefficients are approximated by some formulae or algorithms (see e.g [16]), the Onsager matrix $L = (L_{i,j})_{i,j=1,\cdots,p+1}$ obtained from those relations must be symmetric nonnegative, α nonnegative, and η positive.

3.1. The mechanical operator. It will have the form

$$
\mathcal{R}^M(\mathbf{f}) = \varrho^M \left(\mathbf{M}^M - \mathbf{f} \right)
$$
(3.5)

where ϱ^M is a mechanical relaxation frequency and $\mathbf{M}^M = (\mathcal{M}_1^M, ..., \mathcal{M}_p^M)$ is the set of relaxation functions. We impose constraints on this operator such that the Chapman–Enskog expansion of the kinetic equations

$$\partial_t f_i^\varepsilon + \mathbf{v}.\nabla_x f_i^\varepsilon = \frac{1}{\varepsilon} \mathcal{R}_i^M (f_i^\varepsilon), \qquad i \in S, \tag{3.6}$$

coincides with that of the Boltzmann equation (2.2) (without chemical terms). To this end, we set

$$\varrho^M \sum_{\substack{j \in S \\ J \in \Omega_j}} \int_{\mathbb{R}^3} \left(\mathcal{M}_j^M - f_j \right) \mathbf{w}_{r,j} = -\lambda_r \sum_{\substack{j \in S \\ J \in \Omega_j}} \int_{\mathbb{R}^3} f_j \mathbf{w}_{r,j}. \tag{3.7}$$

Up to now, we were only able to construct an operator based on the matrix $L = (L_{ij})_{i,j=1,...,p}$. It is not our purpose to go beyond this result but just to extend it to the case of polyatomic molecules. Note that the symmetric nonnegative matrix L is related to the symmetric nonnegative diffusion matrix $D = (D_{ij})_{i,j=1,...,p}$ by the formula [27]

$$D_{ij} = \frac{R\rho L_{ij}}{\rho^i \rho^j \bar{m}}, \qquad i, j \in S, \tag{3.8}$$

where R is the perfect gas constant and $\bar{m}$ is the mean molar mass of the mixture:

$$\bar{m} = \frac{\mathcal{N}\rho}{\sum_{i=1}^4 \frac{\rho^i}{m_i}}$$

($\mathcal{N}$ is the Avogadro number). We are now going to briefly recall and eventually modify the results obtained in [11] in the next sections.

3.2. Step 1: Definition of the relaxation coefficients and related moments.

DEFINITION 3.1. *Let $\boldsymbol{C}_i$ be the vector whose i^{th} component is $\boldsymbol{v} - \boldsymbol{u}$ and whose other components are 0. Denote by $\mathcal{P}_{\mathbb{K}}$ the orthogonal projection on $\mathbb{K}$ and by $\mathcal{I}$ the identity operator. Then we define $\mathbb{C}$ as the space generated by the vectors $(\mathcal{I} - \mathcal{P}_{\mathbb{K}})(\boldsymbol{C}_i), i \in [1, p]$.*

The following lemma and proposition were proven in [11].

LEMMA 3.2. *The symmetric nonnegative matrix D^* defined by*

$$D_{ij}^* := \frac{\sqrt{\rho_i \rho_j}}{n k_B T} D_{ij}, \qquad i, j \in [1, p], \tag{3.9}$$

always diagonalizes in an orthonormal basis,

$$D^* = W^T A W.$$

Up to some permutation in W and A, the corresponding eigenvalues $(d_r^*)_r$ are non null for $r = 1, ..., p-1$ and $d_n^* = 0$. Moreover, the vectors defined by

$$\boldsymbol{w}_r = \sum_{s=1}^n W_{rs} \frac{\boldsymbol{C}_s}{||\boldsymbol{C}_s||}, \qquad r = 1, ..., p-1 \tag{3.10}$$

form an orthonormal basis of $\mathbb{C}$ *while*

$$\boldsymbol{w}_n = \sum_s \sqrt{\frac{\rho_s}{\rho}} \frac{\boldsymbol{C}_s}{\|\boldsymbol{C}_s\|} = \pm \sum_{s=1}^{s=n} W_{ps} \frac{\boldsymbol{C}_s}{\|\boldsymbol{C}_s\|} = \frac{1}{\sqrt{\rho k_{\mathrm{B}} T}} (\boldsymbol{\Psi}^{p+1}, \boldsymbol{\Psi}^{p+2}, \boldsymbol{\Psi}^{p+3})^T. \qquad (3.11)$$

PROPOSITION 3.3. *Set*

$$\lambda_r = d_r^{*\,-1}, \quad \lambda_p = 0, \qquad (3.12)$$

in (3.7) where $(\boldsymbol{w}_r)_r$ *is defined as above. Then under suitable properties on the linearized operator of* $\mathcal{R}(\boldsymbol{f})$, *the mass fluxes obtained from the Chapman–Enskog expansion of (the rescaled) Equation (3.6) are*

$$J_i = -\sum_{j=1}^p \rho^i D_{ij} \frac{\nabla p_j}{p}, \qquad i \in S. \qquad (3.13)$$

We refer the reader to the proof given in [11]. The required conditions on $\mathcal{R}^M(\mathbf{f})$ will be further detailed and proven.

3.3. Step 2: Defining $\mathcal{R}^M(\mathbf{f})$. The form of $\mathcal{R}^M(\mathbf{f})$ in (3.5), together with the constraints (3.7) and the conservation laws, imply that $\mathbf{M}^M$ must be in the set of functions

$$\mathbf{g} \in \mathbf{K}(\mathbf{f}) \Leftrightarrow \begin{cases} g \geq 0 \, a.e, \forall l \in [1, n+4], \sum_{\substack{i \in S \\ I \in \Omega_i}} \int_{\mathbb{R}^3} \Psi_i^l (g_i - f_i) \, d\mathbf{v} = 0, \\ \forall r \in [1, n-1], \sum_{\substack{i \in S \\ I \in \Omega_i}} \int_{\mathbb{R}^3} \mathbf{w}_{r,i} \left(g_i - \left(1 - \frac{\lambda_r}{\varrho^M}\right) f_i \right) d\mathbf{v} = \mathbf{0}. \end{cases} \qquad (3.14)$$

Denote respectively with $\overline{\mathbf{U}} = (\mathbf{u}^1, ..., \mathbf{u}^p)^T$ and $\underline{\mathbf{U}} = (\mathbf{u}_1, ..., \mathbf{u}_p)^T$ the mean velocities of $\mathbf{f}$ and $\mathbf{g}$ and with $\mathbf{N}$ and Λ the diagonal matrices whose diagonal terms are respectively $(\sqrt{\rho_1}, ..., \sqrt{\rho_p})$ and $(\lambda_1, ..., \lambda_p)$. Then one can deduce from Lemma 3.2 and (3.7) that

$$\underline{\mathbf{U}} - \mathbf{U} = \mathbf{N}^{-1} W^T \left(\mathbf{I} - \frac{1}{\varrho^M} \Lambda \right) W \mathbf{N} (\overline{\mathbf{U}} - \mathbf{U}) \qquad (3.15)$$

where $\mathbf{U} = (\mathbf{u}, \cdots, \mathbf{u})^T$. Now we need to prove that $\mathbf{K}(\mathbf{f})$ is non-empty. The conservation of internal energy reads as

$$\mathcal{E} = \sum_{\substack{i \in S \\ I \in \Omega_i}} \int \left(\frac{1}{2} m_i (\mathbf{v} - \mathbf{u})^2 + E_{iI} \right) f_i d\mathbf{v} = \sum_{i=1}^p \frac{1}{2} \rho^i (\mathbf{u}^i - \mathbf{u})^2 + \mathcal{E}^* \qquad (3.16)$$

$$= \sum_{\substack{i \in S \\ I \in \Omega_i}} \int \left(\frac{1}{2} m_i (\mathbf{v} - \mathbf{u})^2 + E_{iI} \right) g_i d\mathbf{v} = \sum_{i=1}^p \frac{1}{2} \rho^i (\mathbf{u}_i - \mathbf{u})^2 + \mathcal{E}_*$$

where

$$\mathcal{E}^* = \sum_{\substack{i \in S \\ I \in \Omega_i}} \frac{1}{2} m_i \int (\mathbf{v} - \mathbf{u}^i)^2 f_i d\mathbf{v}, \quad \mathcal{E}_* = \sum_{\substack{i \in S \\ I \in \Omega_i}} \frac{1}{2} m_i \int (\mathbf{v} - \mathbf{u}_i)^2 g_i d\mathbf{v}. \qquad (3.17)$$

It is clear that a necessary condition for $\mathbf{K}(\mathbf{f})$ to be non-empty is

$$\mathcal{E}_* - \mathcal{E}^* = \frac{1}{2} \sum_{i=1}^p \rho^i (\mathbf{u}^i - \mathbf{u})^2 - \frac{1}{2} \sum_{i=1}^p \rho^i (\mathbf{u}_i - \mathbf{u})^2 \geq 0 \qquad (3.18)$$

(we will see in Definition 3.4 that this condition is actually sufficient by exhibiting a set $(g_i)_i$ of nonnegative functions satisfying all constraints). The constraint it imposes is that ϱ^M must be larger than

$$\tilde{\varrho}^M = \frac{\sum_i \lambda_i^2 \|\overline{\mathbf{V}}_i\|^2}{\sum_i \lambda_i \|\overline{\mathbf{V}}_i\|^2} \quad \text{where} \quad \overline{\mathbf{V}} = W\mathbf{N}\left(\overline{\mathbf{U}} - \mathbf{U}\right) \tag{3.19}$$

which is obtained by minimizing

$$\sum_{i=1}^{p} \rho^i (\mathbf{u}_i - \mathbf{u})^2 = \|W^T \left(\mathbf{I} - \frac{1}{\varrho^M}\Lambda\right)\overline{\mathbf{V}}\|^2.$$

Equation (3.18) is then satisfied since

$$\sum_{i=1}^{p} \rho^i (\mathbf{u}_i - \mathbf{u})^2 \le \max_r (1 - \frac{\lambda_r}{\varrho^M})^2 \sum_{i=1}^{p} \rho^i (\mathbf{u}^i - \mathbf{u})^2, \qquad \forall \varrho^M > 0, \tag{3.20}$$

(W is orthonormal). We will see later on that the entropy production is more or less maximal when $\varrho^M = \tilde{\varrho}^M$ (Proposition 3.6). Yet, $1/\varrho^M$ should be considered as the mean relaxation time of the mixture for the translational and internal degrees of freedom to come to equilibrium. For a single polyatomic gas, this time is proportional to the volume viscosity [20]

$$\alpha = \frac{2}{3}p\frac{\mathbf{c}^{\text{int}}}{\mathbf{c}_v}\frac{1}{\varrho^M}$$

where p is the pressure, $\mathbf{c}^{\text{int}}$ is the internal specific heat per molecule and $\mathbf{c}_v$ is the constant-volume specific heat per molecule. We may as well consider the same quantities for the mixture with

$$p = \rho\frac{R}{\overline{m}}T \tag{3.21}$$

and define ϱ^M with the above formula. This is, of course, subject to the condition $\varrho^M \ge \tilde{\varrho}^M$ and leads us to the definition of our model.

DEFINITION 3.4.   *Set*

$$\varrho^M = \max\left(\frac{2}{3}\frac{p}{\alpha}\frac{\mathbf{c}^{\text{int}}}{\mathbf{c}_v}, \tilde{\varrho}^M\right). \tag{3.22}$$

Denote with $\boldsymbol{M}^M = (\mathcal{M}_1^M, \cdots, \mathcal{M}_p^M)$ *the set of functions such that*

$$\mathcal{S}^{\text{kin}}(\boldsymbol{M}^M) = \max_{\boldsymbol{g} \in \boldsymbol{K}(\boldsymbol{f})} \mathcal{S}^{\text{kin}}(\boldsymbol{g}). \tag{3.23}$$

Those functions read as

$$\mathcal{M}_i^M = \frac{1}{\beta_{iI}}\frac{n_i}{Q_i(T_*)}\exp\left\{-\frac{m_i}{2k_{\text{B}}T_*}(\boldsymbol{v} - \boldsymbol{u}_i)^2 - \frac{E_{iI}}{k_{\text{B}}T_*}\right\} \tag{3.24}$$

where T_* *is implicitly defined by*

$$\mathcal{E}_* = \sum_{i \in S} n_i(\frac{3}{2}k_{\text{B}}T_* + \overline{E}_i(T_*)), \quad \overline{E}_i(T_*) = \frac{1}{Q_i^{\text{int}}(T_*)}\sum_{I \in \Omega_i} a_{iI} E_{iI}\exp\left(-\frac{E_{iI}}{k_{\text{B}}T_*}\right) \tag{3.25}$$

(see (2.9) for the definition of Q_i^{int}) together with

$$\mathcal{E}_* = \mathcal{E} - \frac{1}{2} \| \left(\boldsymbol{I} - \frac{1}{\varrho^M} \Lambda \right) W \boldsymbol{N} \left(\overline{\boldsymbol{U}} - \boldsymbol{U} \right) \|^2. \tag{3.26}$$

Then the mechanical relaxation operator $\mathcal{R}^M(\boldsymbol{f})$ reads as

$$\mathcal{R}^M(\boldsymbol{f}) = \varrho^M \left(\boldsymbol{M}^M - \boldsymbol{f} \right). \tag{3.27}$$

REMARK 3.5.   In [1] different collision frequencies are considered for each molecules. However their model is only valid for Maxwellian molecules and its derivation is very different from the essence of the method of moments relaxation. We may impose in (3.22) that $\varrho^M \geq \max_r \varrho_r^M$ where ϱ_r^M is a typical mechanical collision frequency of the rth species. This is important as regards the assumption of slow chemistry but it seems somehow artificial. Thus considering multiple collision frequencies in our framework should be investigated.

3.4. Step 3: General properties and linearized operator.   The whole construction of the model $\mathcal{R}(\mathbf{f})$ relies on its ad-hoc linearized form and on the derivation of the hydrodynamic limit. The required conditions of Proposition 3.3 are given in the sequel. It is firstly necessary that the order -1 in the Chapman–Enskog expansion of (the re-scaled) Equation (3.6) vanishes if and only if

$$\mathcal{R}(\mathbf{f}) = 0 \Longleftrightarrow \mathbf{f}^0 = \mathbf{M}.$$

PROPOSITION 3.6. *The non-reactive entropy source term $\mathbf{v}^M$ is nonnegative and vanishes if and only if $\boldsymbol{f} = \boldsymbol{M}$ or, equivalently, $\mathcal{R}(\boldsymbol{f}) = 0$.*

The proof, which differs from that given in the monoatomic case, is left to the appendix. Then, the second conditions are given in the following lemma (see [11]).

LEMMA 3.7. *The linearized operator $\mathcal{L}_M$ of $\mathcal{R}^M$ reads as*

$$\mathcal{L}_M = \varrho^M \left(\mathcal{P}_{\mathbb{K}} + R \circ \mathcal{P}_{\mathbb{C}} - \mathcal{I} \right)$$

where $\mathcal{P}_{\mathbb{C}}$ denotes the orthogonal projection $\mathbb{C}$ and R is the linear operator defined on $\mathbb{C}$ by the formula

$$\forall r \in [1, p-1], R(\boldsymbol{w}_r) = \left(1 - \frac{\lambda_r}{\varrho^M} \right) \boldsymbol{w}_r.$$

As a conclusion, $\mathcal{L}_M$ satisfies the same properties as $\mathcal{L}_S$. Moreover, $\mathrm{Ker}\,\mathcal{L}_M = \mathbb{K}$, and $\mathcal{L}_M$ is continuous and self-adjoint negative.

4. A BGK model for chemical reactions

In this section, we firstly construct a BGK model for a single reaction $r \in R$ (2.5) and secondly consider the whole set of reactions. Then we prove the conservation laws and the H-theorem. Finally, we reflect upon the meaning of this model.

4.1. A single reaction.   The aim is to construct a relaxation model that allows us to approximate the molecular production rates of $\int C_i^r(\mathbf{f}) d\mathbf{v}$ and still satisfies conservation laws and entropy production. In the slow chemistry regime, it is reasonable to assume that $\int C_i^r(\mathbf{f}) d\mathbf{v} \approx \int C_i^r(\mathbf{M}) d\mathbf{v}$. However, the slight departure of the averaged macroscopic fields in a subset S_r from those of the Maxwellian functions in the same set

does not allow us to make this approximation. More precisely, macroscopic quantities in the subset S_r are defined by

$$\rho^r = \sum_{i \in S_r} \sum_{I \in \Omega_i} \int m_i f_i d\mathbf{v},$$
$$\rho^r \mathbf{u}^r = \sum_{i \in S_r} \sum_{I \in \Omega_i} \int m_i \mathbf{v} f_i d\mathbf{v}, \tag{4.1}$$
$$\tfrac{1}{2}\rho^r |\mathbf{u}^r|^2 + \mathcal{E}^r = \sum_{i \in S_r} \sum_{I \in \Omega_i} \int (\tfrac{1}{2} m_i \mathbf{v}^2 + E_{iI}) f_i(t, x, v, E_{iI}) d\mathbf{v}$$

where ρ^r, $\mathbf{u}^r$, and $\mathcal{E}^r$ are respectively the total mass per unit volume, the mean hydrodynamic velocity, and the internal energy of the species. It is easily seen that, in general, $\mathbf{u}^r \neq \mathbf{u}$ and

$$\mathcal{E}^r \neq \sum_{i \in S_r} n^i (\frac{3}{2} k_{\mathrm{B}} T + \overline{E}_i(T))$$

(see (3.25) for the definition of $\overline{E}_i$). We may associate to the above quantities Maxwellian distributions $\mathbf{M}^r = (\mathcal{M}^{i,r})_{i \in S_r}$, which we do not define here, and the corresponding molecular production rates $\int C_i^r(\mathbf{M}^r) d\mathbf{v}$. The latter can be considered, to a certain extent, as approximations of $\int C_i^r(\mathbf{f}) d\mathbf{v}$ in the slow chemistry regime. They read as

$$\int C_i^r(\mathbf{M}^r) d\mathbf{v} = \nu_{ir} \overline{\tau}_r(t, \mathbf{x}), \quad i \in S_r,$$

where $\overline{\tau}_r$ is the zero-order rate of progress of the reaction at $(t, \mathbf{x})$ defined by

$$\overline{\tau}_r = \mathcal{K}_r \left\{ \prod_{k \in S} \left(\frac{n^k}{Q^k} \right)^{\nu_{kr}^{\mathrm{f}}} - \prod_{k \in S} \left(\frac{n^k}{Q^k} \right)^{\nu_{kr}^{\mathrm{b}}} \right\} \tag{4.2}$$

(here the dependance of all quantities on $(t, \mathbf{x})$ is omitted for the sake of brevity). Essentially, $\mathcal{K}_r$ is an average of all reactive collisions (either forward or backward but not both) with respect to the distribution functions

$$\exp \left\{ -\frac{m_i}{2k_{\mathrm{B}} T^r} (\mathbf{v} - \mathbf{u}^r)^2 - \frac{E_{iI}}{k_{\mathrm{B}} T^r} \right\}, \quad i \in S_r,$$

where T^r is implicitly defined through the equation

$$\mathcal{E}^r = \sum_{i \in S_r} n^i (\frac{3}{2} k_{\mathrm{B}} T^r + \overline{E}_i(T^r)). \tag{4.3}$$

Then we consider S_r as an isolated system. The construction of our model relies on the evolution equations of those species at thermodynamical equilibria and constant internal energy when only chemical reactions occur. Those equations read as

$$d_s \rho_i(s) = m_i \nu_{ir} \overline{\tau}_r(s), \quad \forall i \in S_r,$$
$$\rho_i(0) = m_i n^i(t, \mathbf{x}), \tag{4.4}$$
$$\mathcal{E}^r(s) = \mathcal{E}^r(t, \mathbf{x}), \quad \forall s \geq 0,$$

where $\overline{\tau}_r(s)$ now depends on $n_i(s)$ and $T_r(s)$ is implicitly defined through (4.3) replacing (n^i) with $(n_i(s))$. The usual progress of this reaction at time s is, in absolute value,

$$\xi^r(s) = \int_0^s \overline{\tau}_r(u) \, du.$$

Here, the time s is independent from t and d_s is the classical derivative with respect to s. Note that the temperature $T_r(s)$ is implicitly defined at any time through Equation (4.3) (replacing n^i with $n_i(s)$) and the conservation of internal energy $\mathcal{E}^r$. We may as well write the evolution equation for $T_r(s)$ coupled with the ones for $(\rho_i(s))_{i \in S_r}$ taking into account the conservation of internal energy. However, we will see that the construction of the model relies essentially upon the conservation of mass atoms concentrations and internal energy all along the chemical process. So as a first step, we are suggesting the following definition.

DEFINITION 4.1. *Set*

$$n_i = n^i + \nu_{ir} \xi^r(s), \qquad \forall i \in S_r, \tag{4.5}$$

and

$$\mathcal{M}_i^r = \frac{1}{\beta_{iI}} \frac{n_i}{Q_i(T_r)} \exp\left\{ -\frac{1}{2} \frac{m_i(\boldsymbol{v} - \boldsymbol{u}^r)^2}{k_B T_r} - \frac{E_{iI}}{k_B T_r} \right\}, \quad i \in S_r, \tag{4.6}$$

where $T_r = T_r(s)$. Then the chemistry BGK model for the reaction r is defined by

$$\mathcal{R}_i^r(f_i) = \frac{\overline{\tau}_r(0)}{\xi^r(s)} (\mathcal{M}_i^r - f_i). \tag{4.7}$$

The whole construction allows one to recover the averaged Maxwellian production rate of the rth reaction at $(t, \mathbf{x})$ whatever the choice of s:

$$\sum_{I \in \Omega_i} \int \mathcal{R}_i^r(f_i) \, d\mathbf{v} = \nu_{ir} \overline{\tau}_r(t, \mathbf{x}), \qquad \forall i \in S_r.$$

The instantaneous variation of higher "physical" moments of the distribution functions should be recovered for the smallest values of s. But this is true only if those functions were at thermal equilibrium. As an example, we have

$$\sum_{I \in \Omega_i} \int m_i \mathbf{v} \mathcal{R}_i^r(\mathbf{f}) d\mathbf{v} = m_i \mathbf{u}^r \nu_{ir} \overline{\tau}_r(0) + \frac{\overline{\tau}_r(0)}{\xi^r(s)} \rho^i(\mathbf{u}^r - \mathbf{u}^i),$$

$$= \mathbf{u}^r \frac{d\rho^i}{ds}(0) + \frac{\overline{\tau}_r(0)}{\xi^r(s)} \rho^i(\mathbf{u}^r - \mathbf{u}^i).$$

The first term is an approximation of $\sum_{I \in \Omega_i} \int m_i \mathbf{v} C_i^r(\mathbf{f}) d\mathbf{v}$ (2.6) in the thermal limit $\mathbf{f} \rightarrow \mathbf{M}^r$, but the second one features a spurious relaxation of $\mathbf{u}^i$ toward $\mathbf{u}^r$. As a consequence, s must be chosen in such a way that this non-physical relaxation is as small as possible. The best we can do is to set $s = +\infty$. We denote with $\xi^{r,eq}$ and (n_i^{eq}) the following quantities:

$$\xi^{r,eq} = \int_0^{+\infty} \overline{\tau}_r(u) \, du \Longleftrightarrow n_i^{eq} = n^i + \nu_{ir} \xi^{r,eq}, \quad \forall i \in S_r. \tag{4.8}$$

We do not know exactly the order of magnitude of $\overline{\tau}_r(0)/\xi^{r,eq}$, but we have the following stability property whose proof is left to the appendix.

PROPOSITION 4.2. *The model (4.7) is well-posed in the sense that*

$$\lim_{\xi^{r,eq} \to 0} \frac{\overline{\tau}_r(0)}{\xi^{r,eq}} = \alpha^{r,eq} < +\infty$$

where $\alpha^{r,eq}$ depends on macroscopic values at equilibrium. In particular, for bimolecular reactions — $\mathbf{M}_i + \mathbf{M}_j \rightleftharpoons \mathbf{M}_k + \mathbf{M}_l$ — we have

$$\alpha^{r,eq} = \mathcal{K}_r \left\{ \frac{n_i^{eq} + n_j^{eq}}{Q_i Q_j} + \frac{n_k^{eq} + n_l^{eq}}{Q_k Q_l} \right\}$$

$$+ \mathcal{K}_r \frac{n_i^{eq} n_j^{eq}}{Q_i Q_j} \frac{\left(\overline{E}_i + \overline{E}_j - \overline{E}_j - \overline{E}_j \right)^2}{\left(\sum_{j \in S_r} \rho_j \mathbf{c}_{vj}(T^{r,eq}) \right) k_B (T^{r,eq})^2}$$

where $\mathbf{c}_{vj}(T^{r,eq})$ is the constant-volume specific heat of the jth species defined by

$$\mathbf{c}_{vj} = \frac{\frac{3}{2} k_B + \frac{d\overline{E}_j}{dT}(T^{r,eq})}{m_j} \tag{4.9}$$

(here we have omitted all dependance on $T^{r,eq}$ when it is self-evident).

If the distribution functions were at thermal equilibrium when the mass action holds, then the reactive term (4.7) would vanish. Unfortunately, the above proposition shows that $\mathcal{R}_i^r(\mathbf{f})$ may not vanish even when $\overline{\tau}_r = 0$. So, finally, we propose the following definition.

DEFINITION 4.3.   *Let $(n_i^{eq})_{i \in S_r}$ (see (4.8)) and $T^{r,eq}$ be respectively the equilibrium densities and temperature of the system (4.4). Set*

$$\mathcal{M}_i^{r,eq} = \frac{1}{\beta_{iI}} \frac{n_i^{eq}}{Q_i(T^{r,eq})} \exp \left\{ -\frac{1}{2} \frac{m_i(\boldsymbol{v} - \boldsymbol{u}^r)^2}{k_B T^{r,eq}} - \frac{E_{iI}}{k_B T^{r,eq}} \right\}, \quad i \in S_r. \tag{4.10}$$

Then the chemistry BGK model for the reaction r is defined by

$$\mathcal{R}_i^r(f_i) = \frac{\overline{\tau}_r(0)}{\xi^{r,eq}} H(\overline{\tau}_r) \, (\mathcal{M}_i^{r,eq} - f_i) \tag{4.11}$$

$$= \varrho^r \, (\mathcal{M}_i^{r,eq} - f_i) \tag{4.12}$$

where $H(\cdot)$ is the Heaviside function.

REMARK 4.4.   Note that $\varrho^r > 0$ varies all along the reaction process and vanishes artificially at equilibrium. Moreover, ϱ^r is not a collision frequency. It is the exact rate of relaxation of a mass specie's to its equilibrium value, i.e when the mass action holds. To our knowledge, this variable is never considered in classical chemistry.

REMARK 4.5.   This model may be compared, to some extent, to the relaxation model derived by Bisi, Groppi, and Spiga [7]. In their article, the Maxwellian functions $\mathcal{M}_i^{r,eq}$ are defined under the constraints of atom mass concentrations, mean velocity and energy conservation. The corresponding macroscopic fields are bound together with the mass action law. Finally, the H-theorem is satisfied, but the use of different collision frequencies does not allow one to approximate the chemistry production rates. Another approach was proposed by Groppi and Spiga [22] which takes into account those production rates. The also model features different chemical collision frequencies. On the one hand, this eliminates the spurious relaxation terms; on the other hand, the model is not well-posed. In particular, the H-theorem is only satisfied when the distribution functions are at thermal equilibria. We believe the main reason is that atom mass concentrations of the relaxation functions are different from those of the distribution functions.

4.2. A model for all chemical reactions. The quantities that must be calculated to design the whole chemistry model are summarized here.

1. For each reaction r, consider the set of distributions functions $(f_i)_{i \in S_r}$ as an isolated system with corresponding macroscopic quantities ρ^r, $\mathbf{u}^r$, $\mathcal{E}^r$, and T^r.
2. Calculate the zero-order macroscopic rate of progress at $(t, \mathbf{x})$,

$$\overline{\tau}_r = \mathcal{K}_r \left\{ \prod_{k \in S} \left(\frac{n^k}{Q_k} \right)^{\nu_{kr}^{\mathrm{f}}} - \prod_{k \in S} \left(\frac{n^k}{Q_k} \right)^{\nu_{kr}^{\mathrm{b}}} \right\}, \tag{4.13}$$

and the densities $(n_i^{r,eq})_{i \in S_r}$ and temperature $T^{r,eq}$ of the system (4.4) at chemical equilibrium. Finally, set

$$n_i^{r,eq} = n^i + \nu_{ir} \xi^{r,eq}, \qquad \forall i \in S_r.$$

Let us now define some macroscopic quantities of the following weighted sum of Maxwellian functions, $(\mathcal{M}_i^{r,eq})_r$, for the ith species: the density n_i^C

$$n_i^C = \frac{1}{\sum_{r/\ i \in S_r} \varrho^r} \sum_{r/\ i \in S_r} \varrho^r \sum_{I \in \Omega_i} \int \mathcal{M}_i^{r,eq}\ d\mathbf{v}$$

$$= \frac{1}{\sum_{r/\ i \in S_r} \varrho^r} \sum_{r/\ i \in S_r} \varrho^r\ n_i^{r,eq}, \tag{4.14}$$

the velocity $\mathbf{u}_i^C$

$$\rho_i^C \mathbf{u}_i^C = \frac{m_i}{\sum_{r/\ i \in S_r} \varrho^r} \sum_{r/\ i \in S_r} \varrho^r \sum_{I \in \Omega_i} \int \mathbf{v}\ \mathcal{M}_i^{r,eq}\ d\mathbf{v}$$

$$= \frac{m_i}{\sum_{r/\ i \in S_r} \varrho^r} \sum_{r/\ i \in S_r} \varrho^r\ n_i^{r,eq}\ \mathbf{u}^r, \tag{4.15}$$

and the internal energy per unit volume $\mathcal{E}_i^C$

$$\mathcal{E}_i^C = \frac{1}{\sum_{r/\ i \in S_r} \varrho^r} \sum_{r/\ i \in S_r} \varrho^r \sum_{I \in \Omega_i} \int (\frac{1}{2} m_i (\mathbf{v} - \mathbf{u}_i^C)^2 + E_{iI})\ \mathcal{M}_i^{r,eq}\ d\mathbf{v}$$

$$= \frac{1}{\sum_{r/\ i \in S_r} \varrho^r} \sum_{r/\ i \in S_r} \varrho^r \left[n_i^{r,eq} \left(\frac{3}{2} k_{\mathrm{B}} T^{r,eq} + \overline{E}_i(T^{r,eq}) \right) + (\mathbf{u}^r - \mathbf{u}_i^C)^2 \right] \tag{4.16}$$

(in these equations $\sum_{r/\ i \in S_r} \varrho^r$ only applies to the relaxation rates ϱ^r which are different from 0). Finally, the temperature T_i^C is defined implicitly by the relation

$$\mathcal{E}_i^C = n_i^C \left(\frac{3}{2} k_{\mathrm{B}} T_i^C + \overline{E}_i(T_i^C) \right). \tag{4.17}$$

DEFINITION 4.6. *Set*

$$\mathcal{M}_i^C = \frac{1}{\beta_{iI}} \frac{n_i^C}{Q_i(T_i^C)} \exp \left\{ -\frac{m_i}{2 k_{\mathrm{B}} T_i^C} (\boldsymbol{v} - \boldsymbol{u}_i^C)^2 - \frac{E_{iI}}{k_{\mathrm{B}} T_i^C} \right\}. \tag{4.18}$$

Then the chemical model for the species i is defined by

$$\mathcal{R}_i^C(f_i) = (\sum_{r/\ i\in S_r} \varrho^r)\,(\mathcal{M}_i^C - f_i) \tag{4.19}$$

$$= \varrho_i^C\,(\mathcal{M}_i^C - f_i). \tag{4.20}$$

The whole construction allows one to recover the zero-order molecular production rate of the ith species at $(t,\mathbf{x})$,

$$\varrho_i^C \sum_{I\in\Omega_i} \int (\mathcal{M}_i^C - f_i)\,d\mathbf{v} = (\sum_{r/\ i\in S_r} \varrho^r)(n_i^C - n^i) = \sum_{r/\ i\in S_r} \varrho^r\,(n_i^{r,eq} - n^i)$$

$$= \sum_{r/\ i\in S_r} \nu_{ir}\,\bar{\tau}_r((n^i)_i,\mathcal{E}^r) \tag{4.21}$$

where we have used (4.14) and (4.11).

4.3. General properties.   The solution $(\rho_i(s))_{i\in S_r}$ to the Euler system (4.4) conserves atom mass concentrations by construction. As a consequence, this is also the case for the sum of the reactions. The whole construction of the chemical model (4.12) also preserves the other collisional invariants $\boldsymbol{\psi}^l$ $(l=p+1,\ldots,p+4)$. We have

$$\sum_{i\in S} \varrho_i^C \sum_{I\in\Omega_i} \int (\mathcal{M}_i^C - f_i)\,\psi_i^l\,d\mathbf{v} = \sum_{i\in S}(\sum_{r/\ i\in S_r} \varrho^r)\int (\mathcal{M}_i^C - f_i)\,\psi_i^l\,d\mathbf{v}$$

$$= \sum_r \varrho^r \sum_{i\in S_r} \int (\mathcal{M}_i^{r,eq} - f_i)\,\psi_i^l\,d\mathbf{v} = 0 \tag{4.22}$$

where we have used (4.15) and (4.16) and the construction of the models (4.11) for all reactions r.

PROPOSITION 4.7.   *The reactive entropy source term $\mathbf{v}^C$ is nonnegative.*

The proof is left to the appendix.

4.4. Discussion.   We have considered each reaction separately in the construction of this model which seems incorrect at first sight. Let us now consider the full chain of reactions assuming that $\mathbf{f}=\mathbf{M}$. In the homogeneous case, the equations of the chemical reactions are

$$d_s\rho_i = \sum_r \nu_{ir}\bar{\tau}_r, \qquad \forall i\in S_r,$$

$$\rho_i(0) = \rho^i, \tag{4.23}$$

$$\mathcal{E}(s) = \sum_{i\in S} n^i(\tfrac{3}{2}k_{\mathrm{B}}T + \overline{E}_i(T)), \quad \forall s\geq 0,$$

where T is the temperature at thermal equilibrium at $s=0$. Denote with $(\mathcal{M}_i^{eq})_i$ the equilibrium distribution functions obtained as $s\to+\infty$ in these equations. It would thus be tempting to set

$$\tilde{\mathcal{R}}_i^C(f_i) = \tilde{\varrho}_i^C\,(\mathcal{M}_i^{eq} - f_i)$$

where $\tilde{\varrho}_i^C\,(n_i^{eq} - n^i) = \sum_r \nu_{ir}\bar{\tau}_r(0)$. But there is no reason why $\sum_r \nu_{ir}\bar{\tau}_r(0)\,/(n_i^{eq} - n^i) > 0$, so that the model is ill-posed. In some sense, the best relaxation model is obtained

when replacing ϱ^r in (4.11) with $\overline{\tau}_r(0)/\xi^r(s)$, defined in (4.7) for s small. Indeed, $(\mathcal{M}_i^C)_i$ would thus tend to the thermal distributions all along the chemical process as $s \rightarrow 0$. We have already seen that such a choice is not possible and want to go further in the analysis of $\mathcal{R}_i^C(f_i)$. One can deduce from (4.8), (4.12), and (4.14) that

$$n_i^C = n^i + \frac{\sum_r \nu_{ir} \overline{\tau}_r(0)}{\sum_{r/ \ i \in S_r} \varrho^r} = n^i + \frac{1}{\sum_{r/ \ i \in S_r} \varrho^r} \frac{dn_i}{ds}(0), \qquad i \in S.$$

Thus, the faster the relaxation rates ϱ^r are, the smaller the "time step" $\Delta s_i = 1/(\sum_{r/ \ i \in S_r} \varrho^r)$ is. Hence, n_i^C can be seen as an approximation of $n_i(\Delta s_i)$, the solution to the system (4.23).

5. The whole BGK model: properties and hydrodynamic limit
The modified Boltzmann equation reads as

$$\partial t f_i + \mathbf{v}.\nabla_x f_i = \varrho^M \left(\mathcal{M}_i^M - f_i \right) + \varrho_i^C \left(\mathcal{M}_i^C - f_i \right), \qquad \forall i \in S, \tag{5.1}$$

where the mechanical and chemical operators are respectively defined in (3.27) and (4.19).

5.1. Properties.   We have seen that the mechanical operator"s construction is based on a maximization of the entropy $\mathcal{S}^{\mathrm{kin}}$ under constraints (3.14). Recall then that those constraints include the conservation of all moments in the set of mechanical collisional invariants $\mathbb{K}$. Moreover, mass atom concentrations, mean velocity, and energy are conserved by definition of the chemical operators. We now want to characterize the states of null entropy production.

THEOREM 5.1. *The entropy source term,*

$$\mathbf{v}^{\mathrm{kin}} = \mathbf{v}^M + \mathbf{v}^C,$$

is nonnegative. Moreover, the three following assertions are equivalent:

i) $f_i = \mathcal{M}^i, \quad \forall i \in S$ *and all molecular production rates* $\overline{\tau}_r = 0$,

ii) $\varrho^M \left(\mathcal{M}_i^M - f_i \right) + \varrho_i^C \left(\mathcal{M}_i^C - f_i \right) = 0, \qquad \forall i \in S,$

iii) $\mathbf{v}^{\mathrm{kin}} = 0$.

   Proof.
   i) $\Rightarrow$ ii) We have that

$$f_i = \mathcal{M}^i, \forall i \in S \Rightarrow \mathcal{M}_i^M = \mathcal{M}^i$$

by construction of the mechanical operators. Finally,

$$\varrho_i^C = \sum_{r/ \ i \in S_r} \frac{\overline{\tau}_r}{\xi^{r,eq}} H(|\overline{\tau}_r|) = 0, \qquad \forall i \in S.$$

   ii) $\Rightarrow$ iii) This is straightforward.

   iii) $\Rightarrow$ i) We have already proven that $\mathbf{v}^M \geq 0$ and vanishes if and only if $\mathbf{f} = \mathbf{M}$ (Proposition 3.6). Besides, $\mathbf{v}^C \geq 0$ (Proposition 4.7). Hence, $\mathbf{v}^{\mathrm{kin}} = 0$ if and only if $\mathbf{v}^C = 0$ with $\mathbf{f} = \mathbf{M}$. Following the proof of Proposition 4.7, it must hold that

$$0 = \mathbf{v}^C \geq \sum_r \varrho^r \sum_{i \in S_r} \left(\mathcal{S}^{\mathrm{kin}}(\mathcal{M}^i) - \mathcal{S}^{\mathrm{kin}}(\mathcal{M}_i^{r,eq}) \right) \geq 0$$

Thus either $\varrho^r = 0$ or $f_i = \mathcal{M}^i = \mathcal{M}_i^{r,eq}$ for each reaction r. In each case, this means that $\overline{\tau}_r = 0$ by construction of the models $\mathcal{R}_i^r(f_i)$ (4.11). Hence, $\overline{\tau}_r = 0$ for all r which ends the proof. □

5.2. Hydrodynamic limit for slow reactions.   The slow reactions regime corresponds to the situation where the chemistry characteristic time is much less than the mechanical time. The hydrodynamic limit of our model is then obtained by studying the equations

$$\partial t f_i^\varepsilon + \mathbf{v}.\nabla_x f_i^\varepsilon = \frac{1}{\varepsilon}\varrho^M\left(\mathcal{M}_i^M - f_i^\varepsilon\right) + \varrho_i^C\left(\mathcal{M}_i^C - f_i^\varepsilon\right), \qquad i \in S, \tag{5.2}$$

as $\varepsilon \to 0$.

5.2.1. Euler equations.   Equation (5.2) at order -1 implies that $f_i = \mathcal{M}^i$ for all species i thanks to Proposition 3.6. Then, the zero-order macroscopic equations read as

$$\partial_t \rho^i + \nabla_x \cdot (\rho^i \mathbf{u}) = m_i\,\overline{\omega}_i^0,$$
$$\partial_t(\rho\mathbf{u}) + \nabla_x \cdot (\rho\mathbf{u}\otimes\mathbf{u} + p\mathbb{I}) = 0, \tag{5.3}$$
$$\partial_t(\tfrac{1}{2}\rho u^2 + \mathcal{E}) + \nabla\cdot\left((\tfrac{1}{2}\rho u^2 + \mathcal{E} + p)\,\mathbf{u}\right) = 0$$

where the pressure p is defined in (3.21). Additionally, $\overline{\omega}_i^0$ is the zero-order molecular production rate of the species i with

$$\overline{\omega}_i^0 = \sum_r \nu_{ir}\overline{\tau}_r \tag{5.4}$$

where $(\overline{\tau}_r)_r$ are the set of Maxwellian rates of progress (4.13) with $T^r = T$.

5.2.2. The Navier–Stokes equations.   We may write the Navier–Stokes equations in the general form

$$\partial_t \rho^i + \nabla\cdot(\rho^i\mathbf{u}) + \varepsilon\nabla\cdot\mathbf{J}_i = m_i\overline{\omega}_i^0 + \varepsilon m_i\overline{\omega}_i^1,$$
$$\partial_t(\rho\mathbf{u}) + \nabla\cdot(\rho\mathbf{u}\otimes\mathbf{u} + p\mathbb{I}) + \varepsilon\nabla\cdot\mathbb{J}_\mathbf{u}) = 0, \tag{5.5}$$
$$\partial_t(\tfrac{1}{2}\rho u^2 + \mathcal{E}) + \nabla\cdot\left((\tfrac{1}{2}\rho u^2 + \mathcal{E} + p)\,\mathbf{u}\right) + \varepsilon\nabla\cdot\mathbf{J}_\mathbf{q} = 0.$$

The fluxes are given by

$$J_i = -\sum_{j=1}^p \rho^i D_{ij}\frac{\nabla p_j}{p}, \qquad i \in S, \tag{5.6}$$
$$\mathbb{J}_\mathbf{u} = p^{\text{reac}}\mathbb{I} - \tilde{\alpha}(\nabla_x.u)\mathbb{I} - \tilde{\eta}\mathbb{D}(\mathbf{u}), \tag{5.7}$$
$$\mathbf{J}_\mathbf{q} = -\hat{\lambda}\nabla T + \sum_{i=1}^p h_i J_i. \tag{5.8}$$

Here, $(D_{ij})_{ij}$ is the diffusion matrix computed with the linearized Boltzmann operator. The volume and shear viscosities are equal to

$$\tilde{\alpha} = \frac{2}{3}\frac{p}{\varrho^M}\frac{\mathbf{c}^{\text{int}}}{\mathbf{c}_v}, \qquad \tilde{\eta} = \frac{p}{\varrho^M}$$

where $\mathbf{c}^{\text{int}} = \sum_{i \in S} \frac{n^i}{n} \mathbf{c}_i^{\text{int}}$ is the mixture internal specific heat per molecule with $\mathbf{c}_i^{\text{int}} = d\overline{E}_i/dT$ and $\mathbf{c}_{\text{v}} = \frac{3}{2}k_{\text{B}} + \mathbf{c}^{\text{int}}$ is the mixture constant-volume specific heat per molecule. We have the following formula for the reactive pressure:

$$p^{\text{reac}} = \frac{1}{2\varrho^M} \sum_{i \in S} \varrho_i^C (n_i^C k_{\text{B}} T_i^C - n^i k_{\text{B}} T) - \frac{k_{\text{B}} T}{2\varrho^M} \sum_{i \in S} \overline{\omega}_i^0 + \frac{k_{\text{B}}}{2\varrho^M \mathbf{c}_{\text{v}}} \sum_{i \in S} m_i \overline{\omega}_i^0 \ e_i$$

where ϱ_i^C, n_i^C and T_i^C are defined in (4.19), (4.14), (4.17) and $e_i = (\frac{3}{2}k_{\text{B}} T + \overline{E}_i)/m_i$ is the specific energy of the ith species. The partial thermal conductivity is equal to

$$\hat{\lambda} = k_{\text{B}} T \sum_{i \in S} \frac{n^i}{m_i} \left(\frac{5}{2} k_{\text{B}} + \frac{d\overline{E}_i}{dT} \right) = k_{\text{B}} T \sum_{i \in S} \frac{n^i}{m_i} (\frac{5}{2} k_{\text{B}} + \mathbf{c}_i^{\text{int}}),$$

and $h_i = (\frac{5}{2}k_{\text{B}} T + \overline{E}_i)/m_i$ is the specific enthalpy of the ith species. Finally, perturbations of the chemical source terms are explicitly given in the following lemma.

LEMMA 5.2. *We have that*

$$\overline{\omega}_i^1 = \sum_{r/ \ i \in S_r} \frac{\alpha_r}{\sum_{k \in S_r} \rho_k \mathbf{c}_{\text{vk}}(T)} \ \nu_{ir} \frac{d\overline{\tau}_r}{dT} \tag{5.9}$$

where $\mathbf{c}_{\text{vk}}$ is the constant-volume specific heat of the kth species defined in (4.9). Furthermore,

$$\alpha_r = -\frac{1}{\varrho^M} k_{\text{B}} T \left((\sum_{j \in S_r} n^j) \frac{\mathbf{c}^{\text{int}}}{\mathbf{c}_{\text{v}}} - n \sum_{j \in S_r} \frac{\mathbf{c}_j^{\text{int}}}{\mathbf{c}_{\text{v}}} \right) \nabla . \boldsymbol{u}$$
$$+ \frac{1}{\varrho^M} \sum_{j \in S_r} \varrho_j^C (\mathcal{E}_j^C - \mathcal{E}_j) - \frac{1}{\varrho^M} \sum_{j \in S_r} m_j \overline{\omega}_j^0 \ e_j$$
$$+ \frac{1}{\varrho^M} \left(\sum_{j \in S} m_j \overline{\omega}_j^0 \ e_j \right) \times (\sum_{j \in S_r} \rho_j \mathbf{c}_{\text{vj}}(T))/(\sum_{j \in S} \rho_j \mathbf{c}_{vj}(T))$$

where $\mathcal{E}_j^C$ is defined in (4.16) with $\boldsymbol{u}^r = \boldsymbol{u}^i = \boldsymbol{u}$ and $\mathcal{E}_j = \rho^j e_j$ is the internal energy of the species j.

The computation of the transport coefficients together with the proof of this lemma are left to the appendix.

Comment. The diffusion matrix is the one derived from the Chapman–Enskog expansion of the true Boltzmann equation (2.2) in the slow chemistry regime, but the thermal diffusion coefficients are equal to 0. All other transport coefficients depend on ϱ^M. However, if ϱ^M is the first argument in (3.22), then $\tilde{\alpha}$ is equal to the true volume viscosity α. Note finally, that there is a bulk viscosity in the first order correction of the the molecular production rates and a chemical pressure p^{reac} as in the "true" Navier–Stokes equations. As a conclusion, one may obtain all transport coefficients in (3.4) by diagonalizing the whole Onsager Matrix $(L_{ij})_{i,j=1,\cdots,p+1}$ (see (3.1) and the introduction of Section 3).

5.3. Calculation of the coefficients. As already mentioned in the introduction, the present model is not just a well-posed mathematical model. Many softwares and formulae provide us with tools for calculating its coefficients.

The mechanical operator: Let us recall that its derivation essentially requires one to diagonalize the symmetric nonnegative matrix D^* defined by (3.9),

$$D_{ij}^* := \frac{\sqrt{\rho_i \rho_j}}{n k_B T} D_{ij}, \qquad i,j \in [1,p].$$

Ern and Giovangigli [16] have derived algorithms to compute the modified diffusion matrix $\tilde{D} = (\frac{\rho_i}{\rho} D_{ij})_{ij}$ that preserve the required property of D. Those algorithms have been implemented in the free access software EGlib [17]. Moreover, their iterative procedure is numerically stable for vanishing mass fractions. In this case, D^* is not defined, but we need, essentially, to compute the inverse of its eigenvalues (Proposition 1). This problem must be investigated within the framework of [16].

The chemical operator: It depends on different coefficients which are either directly given by the macroscopic fields or must be calculated.

1. The first step consists of calculating $\mathbf{u}^r$ and $\mathcal{E}^r$ (4.1) for each reaction.

2. At this stage, the molecular production rate may be rewritten in a more familiar form (molar production rate):

$$\frac{\overline{\tau}_r}{\mathcal{N}} = K_r^f \prod_{k \in S} \left(\gamma^k\right)^{\nu_{kr}^{\mathrm{f}}} - K_r^b \prod_{k \in S} \left(\gamma^k\right)^{\nu_{kr}^{\mathrm{b}}} \tag{5.10}$$

where $\gamma^k = n^k/\mathcal{N} = \rho^k/(\mathcal{N} m_k)$. The forward rate constant $K_r^f(T)$ can be approximated by Arrhenius empirical relation. The backward rate constant must then be defined by $K_r^b(T) = K_r^f(T)/K_r^e(T)$ where $K_r^e(T)$ is the equilibrium constant of the rth reaction. This constant is related to the standard Gibbs free energy change

$$-RT \ln K_r^e(T) = \sum_{i \in S_r} \nu_{ir} \mathcal{N} m_i \left(g_k^{\mathrm{atm}}(T) - \frac{k_{\mathrm{B}} T}{m_i} ln(\frac{p^{\mathrm{atm}}}{RT}) \right)$$

where the quantities in parenthesis are the Gibbs free energy of each species at unit concentration.

3. The next step consists of calculating the concentrations and temperatures at equilibrium for the whole set of chemical reactions. Softwares such as STANJAN [36] are dedicated to such computations. In our case, it is done by maximizing the thermodynamic entropy $\mathcal{S}$ in the set

$$X = \{(n^i + \nu_{ir} x)_{i \in S_r}, \quad \forall x \in \mathbb{R}\} \cap (\mathbb{R}^+)^{\dim S_r}, \tag{5.11}$$

where $\dim S_r$ is the total number of species in the reaction — reactants and products (see the proof of Lemma 5.2 in the appendix). Note that $\mathcal{S}$ is different from the entropy $\mathcal{S}^{\mathrm{kin}}$ which depends on the partition functions $(Q_i)_{i \in S_r}$ and thus on quantum mechanics. In practice, this means that the H-theorem will be satisfied only up to some small error.

4. The final step just consists of calculating the weighted macroscopic quantities (4.14), (4.15), (4.16), and (4.17).

6. Discussion and conclusion

We have presented a kinetic simulation model for dilute polyatomic gases undergoing chemical reactions. It is the sum of mechanical and chemical operators for each species. The mechanical part is the extension to polyatomic gases of the method of moment relaxations for monatomic gas mixtures [11]. This method allows us to construct a well-posed BGK model based on the knowledge of the "true" transport coefficients at the hydrodynamic limit (diffusion matrix, etc). In some sense, this operator mimics the behavior of the linearized Boltzmann operator as concerns its restriction to a limited number of functions, not only in its restriction to the collisional invariants $\mathbb{K}$

(see Definition 2.1) but also in its restriction to other physically relevant moments. The chemical relaxation models feature many interesting properties and a certain simplicity in regards to the unlimited number of reactions. The production rate of a given reaction r is approximated by a Maxwellian production rate, an assumption which makes sense in the case of slow chemistry. The H-theorem is proved and the entropy production vanishes if and only if the distribution functions are at thermal equilibrium and all production rates are null (Theorem 5.1). The hydrodynamic limit is very close to that of the Boltzmann equation for reacting gas mixtures [16, 19]. Finally, we have summarized the derivation of the whole model in Section 5.3. Softwares such as EGlib [17] or STANJAN [36] allow us to calculate the whole set of parameters of the two operators. Thus, the model can be utilized in a real physical context, especially in the so-called moderately non-equilibrium regime. The mechanical operator may be subject to some restrictions, however. On one side, it would be necessary to include different relaxation frequencies (see Remark 3.5, Section 3.3) in the framework of the method of moments relaxation (Section 3). This is a required condition to make sure that the characteristic times of relaxation of internal energy are larger than the chemistry characteristic times. On the other side, the derivation of the mechanical BGK model should take into account the whole set of transport coefficients; that is, not only the diffusion matrix and the shear viscosity but also the thermal diffusion coefficients, the partial thermal conductivity, and the volume viscosity should be accounted for. A work is in progress as concerns this last point.

Appendix A.

A.1. Proof of Proposition 3.6.
Proof. We have

$$\mathbf{v}^M = -k_{\mathrm{B}} \; \varrho^M \sum_{\substack{i \in S \\ I \in \Omega_i}} \int (\mathcal{M}_i^M - f_i) \log(\beta_{iI} f_i) d\mathbf{v} \geq \varrho^M \left(\mathcal{S}^{\mathrm{kin}}(\mathbf{M}^M) - \mathcal{S}^{\mathrm{kin}}(\mathbf{f}) \right) \quad \text{(A.1)}$$

by concavity of the function $x \rightarrow -x \ln x$. Let $\tilde{\mathbf{M}}^*$ be the set of functions

$$\tilde{\mathcal{M}}_i^* = \frac{1}{\beta_{iI}} \frac{n_i}{Q_i(T^*)} \exp\left\{ -\frac{m_i}{2k_{\mathrm{B}} T^*} (\mathbf{v} - \mathbf{u}^i)^2 - \frac{E_{iI}}{k_{\mathrm{B}} T^*} \right\}$$

where T^* is implicitly defined by

$$\mathcal{E}^* = \sum_{i \in S} n_i \left(\frac{3}{2} k_{\mathrm{B}} T^* + \overline{E}_i(T^*) \right)$$

and $\mathcal{E}^*$ is defined in (3.17). It holds that

$$\mathcal{S}^{\mathrm{kin}}(\mathbf{f}) \leq \mathcal{S}^{\mathrm{kin}}(\tilde{\mathbf{M}}^*). \quad \text{(A.2)}$$

Denote with $\mathbf{M}_*$ and $\mathbf{M}^*$ the set of functions obtained by setting $\mathbf{u}_i = 0$ in $\mathcal{M}_i^M$ and $\mathbf{u}^i = 0$ in $\tilde{\mathcal{M}}_i^*$ for all species $i \in S$. Those functions are two states of the gas at rest and at thermal equilibrium. One may define the corresponding thermodynamics functions

— entropy $\mathcal{S}$, volumetric energy $\mathcal{E}$, etc — from the kinetic framework and state the celebrated fundamental thermodynamic relation

$$\mathbb{D}\mathcal{S} = \frac{1}{T}\mathbb{D}\mathcal{E} - \sum_{i \in S} \frac{g_i}{T}\mathbb{D}\rho^i \tag{A.3}$$

where $g_i = (k_{\mathrm{B}}T/m_i)\ln(n^i/Q_i)$ are the specific Gibbs functions and $\mathbb{D}$ denotes the total derivative. Next, we set $A = (\mathcal{E}^*, \rho^1, ..., \rho^p)$, $B = (\mathcal{E}_*, \rho^1, ..., \rho^p)$, and $\gamma(t) = (1-t)A + tB$ with $t \in [0,1]$. Then, integrating the exact differential 1-form (A.3) on the path γ, one obtains

$$\mathcal{S}(B) - \mathcal{S}(A) = \int_{\gamma} dS = \int_0^1 \frac{\partial S}{\partial \mathcal{E}}(\gamma(t))\,(\mathcal{E}_* - \mathcal{E}^*)\,dt = (\mathcal{E}_* - \mathcal{E}^*) \int_0^1 \frac{1}{T(\gamma(t))}dt.$$

Recall that $\mathcal{E}_* \geq \mathcal{E}^*$ by construction of $\mathcal{R}^M(\mathbf{f})$, so that using (A.1), (A.2), and the definitions of $\mathbf{M}_*$ and $\mathbf{M}^*$ one obtains

$$\mathbf{v}^M \geq \varrho^M \left(\mathcal{S}^{\mathrm{kin}}(\mathbf{M}^M) - \mathcal{S}^{\mathrm{kin}}(\tilde{\mathbf{M}}^*)\right) = \varrho^M\,(\mathcal{S}(B) - \mathcal{S}(A)) \geq 0.$$

Note that $\mathcal{S}^{\mathrm{kin}}(\mathbf{f}) < \mathcal{S}^{\mathrm{kin}}(\tilde{\mathbf{M}}^*)$ (A.2) unless $\mathbf{f} = \tilde{\mathbf{M}}^*$. Next, it is easily checked by using (3.20) and (3.22) that $\mathcal{E}_* = \mathcal{E}^*$ if and only if $\mathbf{u}^i = \mathbf{u}_i = \mathbf{u}, \forall i \in S$. Therefore, $\mathbf{v}^M = 0$ if and only if $\mathbf{f} = \mathbf{M} = \mathbf{M}^M$.

Finally, it is easily seen that

$$\mathbf{f} = \mathbf{M} = \mathbf{M}^M \Longrightarrow \mathbf{R}^M(\mathbf{f}) \Longrightarrow \mathbf{v}^M = 0,$$

which ends the proof. $\square$

A.2. Proof of Proposition 4.2.

Proof.   Let $(n_j^{eq})_j$ and $T^{r,eq}$ be respectively the densities and temperature obtained as $t \to +\infty$ in (4.4). Consider the function

$$f(x,y) = \sum_{j \in S_r} (n_j^{eq} - \nu_{jr}x)\left(\frac{3}{2}k_{\mathrm{B}}(T^{r,eq}+y) + \overline{E}_j(T^{r,eq}+y)\right) - \mathcal{E}^r.$$

We naturally have $f(0,0) = 0$ due to the conservation of internal energy in (4.4). Recall that (see (2.9))

$$Q_j^{\mathrm{int}}(T^{r,eq}) = \sum_{J \in \Omega_j} a_{jJ}\exp\left(-\frac{E_{jJ}}{k_{\mathrm{B}}T^{r,eq}}\right).$$

Then we have

$$\frac{\partial f}{\partial y}(0,0) = \sum_{j \in S_r} \rho_j \mathbf{c}_{\mathrm{vj}}(T^{r,eq}) > 0$$

where $\mathbf{c}_{\mathrm{vj}}$ is the constant-volume specific heat of the jth species defined by

$$\mathbf{c}_{\mathrm{vj}} = \frac{\frac{3}{2}k_{\mathrm{B}} + \frac{d\overline{E}_j}{dT}(T^{r,eq})}{m_j}.$$

Without entering too much into detail, the implicit function theorem states that there exists an open set W containing 0, an open set U containing 0, and a unique C^∞ function φ from W to U such that $f(x, \varphi(x)) = 0$. Note that one can apply the same theorem any time $s \geq 0$ in (4.4) so that φ can be extended to the bounded set $I =]0, \xi^{r,eq}[$ (if $\overline{\tau}_r(0) > 0$) and $I =]\xi^{r,eq}, 0[$ (if $\overline{\tau}_r(0) < 0$). Set $x = \xi^{r,eq}$ and

$$\overline{\tau}_r^{eq}(x) = \overline{\tau}_r(0) = \mathcal{K}_r(\varphi(x) + T^{r,eq})$$

$$\times \left\{ \prod_{k \in S} \left(\frac{n_k^{eq} - \nu_{kr} x}{Q_k(\varphi(x) + T^{r,eq})} \right)^{\nu_{kr}^{\mathrm{f}}} - \prod_{k \in S} \left(\frac{n_k^{eq} - \nu_{kr} x}{Q_k(\varphi(x) + T^{r,eq})} \right)^{\nu_{kr}^{\mathrm{b}}} \right\}. \tag{A.4}$$

It is easily seen that $\overline{\tau}_r^{eq}$ is a C^∞ function of x in I. Using a Taylor expansion, one has

$$\overline{\tau}_r^{eq}(x) = \overline{\tau}_r^{eq}(0) + x \frac{d\overline{\tau}_r^{eq}}{dx}(0) + O(x^2) = x \frac{d\overline{\tau}_r^{eq}}{dx}(0) + O(x^2).$$

As a consequence,

$$\lim_{\xi^{r,eq} \to 0} \frac{\overline{\tau}_r(0)}{\xi^{r,eq}} = \lim_{x \to 0} \frac{\overline{\tau}_r^{eq}(x)}{x} = \frac{d\overline{\tau}_r^{eq}}{dx}(0).$$

This limit can be easily calculated by differentiating (A.4) at $x = 0$. We just consider, for the sake of clarity, the case of a bimolecular reaction $\mathbf{M}_i + \mathbf{M}_j \rightleftharpoons \mathbf{M}_k + \mathbf{M}_l$. Then one finds after some calculation that

$$\alpha^{r,eq} = \frac{d\overline{\tau}_r^{eq}}{dx}(0) = \mathcal{K}_r \left\{ \frac{n_i^{eq} + n_j^{eq}}{Q_i Q_j} + \frac{n_k^{eq} + n_l^{eq}}{Q_k Q_l} \right\}$$

$$+ \mathcal{K}_r \frac{n_i^{eq} n_j^{eq}}{Q_i Q_j} \frac{\left(\overline{E}_i + \overline{E}_j - \overline{E}_j - \overline{E}_j \right)^2}{\left(\sum_{j \in S_r} \rho_j \mathbf{c}_{\mathrm{vj}}(T^{r,eq}) \right) k_B (T^{r,eq})^2}$$

where we have omitted the dependance upon $T^{r,eq}$ when it is self evident. □

A.3. Proof of Proposition 4.7.

Proof. We firstly recall a result due to Giovangigli which we adapt to our case (Proposition 6.5.1 [19]).

PROPOSITION A.1 ([19]). *The entropy of the system* (4.4) *is defined by*

$$\mathcal{S}^{\mathrm{kin},r} = \sum_{i \in S_r} n_i \left(\frac{5}{2} k_{\mathrm{B}} + \frac{\overline{E}_i}{T_r} - k_{\mathrm{B}} \log \frac{n_i}{Q_i(T_r)} \right) \tag{A.5}$$

where $T_r = T_r(s)$ *is defined implicitly thanks to the conservation of internal energy,*

$$\mathcal{E}^r = \sum_{i \in r} n_i(s) \left(\frac{3}{2} k_{\mathrm{B}} T_r + \overline{E}_i(T_r) \right).$$

Then the entropy production $\mathbf{v}^{C,r}$ *is equal to*

$$\mathbf{v}^{C,r} = -\frac{k_{\mathrm{B}}}{T_r} \sum_{i \in S_r} g_i m_i \nu_{ir} \overline{\tau}_r$$

where g_i *is the specific Gibbs function of the* i^{th} *species. It is nonnegative and vanishes if and only if* $\overline{\tau}_r = 0$.

Let us first remark that

$$\mathcal{S}^{\text{kin}}(\mathcal{M}_i^C) \geq \mathcal{S}^{\text{kin}}\left(\frac{1}{\sum_{r/\ i\in S_r}\varrho^r}\sum_{r/\ i\in S_r}\varrho^r(\mathcal{M}_i^{r,eq})\right)$$

$$\geq \frac{1}{\sum_{r/\ i\in S_r}\varrho^r}\sum_{r/\ i\in S_r}\varrho^r\mathcal{S}^{\text{kin}}(\mathcal{M}_i^{r,eq})$$

where we have used on one side the definition of $\mathcal{M}_i^C$ (4.18) and on the other side the concavity of the function $\mathcal{S}^{\text{kin}}$. Thus,

$$\mathbf{v}^C = -k_{\text{B}}\sum_i\varrho_i^C\sum_{I\in\Omega_i}\int(\mathcal{M}_i^C - f_i)\ \log(\beta_{iI}f_i)\,d\mathbf{v} \tag{A.6}$$

$$\geq \sum_i\varrho_i^C\left(\mathcal{S}^{\text{kin}}(\mathcal{M}_i^C) - \mathcal{S}^{\text{kin}}(f_i)\right)$$

$$\geq \sum_r\varrho^r\sum_{i\in S_r}\left(\mathcal{S}^{\text{kin}}(\mathcal{M}_i^{r,eq}) - \mathcal{S}^{\text{kin}}(f_i)\right) \tag{A.7}$$

where we have used the concavity of the function $x\leftarrow -x\ln x$. Set

$$\mathcal{M}^{ir} = \frac{1}{\beta_{iI}}\frac{n^i}{Q_i(T^r)}\exp\left\{-\frac{m_i}{2k_{\text{B}}T^r}(\mathbf{v}-\mathbf{u}^r)^2 - \frac{E_{iI}}{k_{\text{B}}T^r}\right\}, \quad i\in S_r, \tag{A.8}$$

where $T^r = T^r(0)$ in (4.4). Then,

$$\sum_{i\in S_r}\mathcal{S}^{\text{kin}}(f_i) \leq \sum_{i\in S_r}\mathcal{S}^{\text{kin}}(\mathcal{M}^{ir})$$

by definition. Finally, using Proposition A.1 it holds that

$$\sum_{i\in S_r}\left(\mathcal{S}^{\text{kin}}(\mathcal{M}_i^{r,eq}) - \mathcal{S}^{\text{kin}}(\mathcal{M}^{ir})\right) \geq 0, \qquad \forall r\in R,$$

which ends the proof. □

A.4. Derivation of the Navier–Stokes Equation (4.2).   One can compute the first order perturbation $\mathbf{g}$ in the same way that it is done when coming from the Boltzmann equation (see e.g [20] or [19]). This is essentially due to the properties of the linearized mechanical operator $\mathcal{L}_M$ (see Lemma **??**) and to the ad-hoc form of the Euler equation (5.3). So we will not recall the calculations that lead to the equation

$$\mathcal{L}_M(\mathbf{g}) = \sum_{j=1}^{j=p}\mathbf{\Phi}^{D_j}\cdot\nabla_x p_j + \frac{1}{2}\mathbb{A}:\mathbb{D}(\mathbf{u}) + \frac{1}{3}\mathbb{A}^V:\nabla_x\mathbf{u} + \mathbf{B}\cdot\nabla\left(\frac{1}{k_{\text{B}}T}\right) + \mathbf{\Psi}^C. \tag{A.9}$$

The list of tensors $\mathbf{\Psi}^{D_j}$, $\mathbb{A}$, A^V, and $\mathbf{B}$ belong to $\mathbb{K}^\perp$ (2.7) and read on their i^{th} line as

$$\mathbf{\Phi}_i^{D_j} = \frac{1}{p_i}\left(\delta_{ji} - \frac{\rho_i}{\rho}\right)(\mathbf{v}-\mathbf{u}), \qquad j\in S$$

$$(\mathbb{A})_i = \frac{m_i}{k_{\text{B}}T}\left[(\mathbf{v}-\mathbf{u})\otimes(\mathbf{v}-\mathbf{u}) - \frac{1}{3}\|\mathbf{v}-\mathbf{u}\|^2\mathbb{I}\right],$$

$$\mathbb{A}_i^V = \left(\frac{2\mathbf{c}^{\text{int}}}{\mathbf{c}_v k_{\text{B}} T} \left(\frac{1}{2} m_i (\mathbf{v} - \mathbf{u})^2 - \frac{3}{2} k_{\text{B}} T \right) + \frac{2\mathbf{c}_v^{\text{tr}}}{\mathbf{c}_v k_{\text{B}} T} (\overline{E}_i - E_{iI}) \right) \mathbb{I},$$

$$(\mathbf{B})_i = \left(\frac{5 k_{\text{B}} T}{2} - \frac{1}{2} m_i (\mathbf{v} - \mathbf{u})^2 + \overline{E}_i - E_{iI} \right) (\mathbf{v} - \mathbf{u}).$$

Finally,

$$\boldsymbol{\Psi}_i^C = -\frac{\varrho_i^C (\mathcal{M}_i^C - \mathcal{M}^i)}{\mathcal{M}^i} + \frac{\overline{\omega}_i^0}{n^i} + \frac{\sum_{j \in S} (\frac{3}{2} k_{\text{B}} T + \bar{E}_j) \overline{\omega}_i^0}{p \mathbf{c}_v T}$$

$$\times (\frac{3}{2} k_{\text{B}} T - \frac{1}{2} m_i |\mathbf{v} - \mathbf{u}|^2 + \bar{E}_i - E_{iI}).$$

Here $\boldsymbol{\Psi}_i^C$ is simply obtained by calculating the ith line of $(\mathcal{I} - \mathcal{P}_{\mathbb{K}}) \mathbf{V}^C$ with $\mathbf{V}^C = \left(-\varrho_1^C (\mathcal{M}_1^C - \mathcal{M}_1) / \mathcal{M}_1, \cdots, -\varrho_p^C (\mathcal{M}_p^C - \mathcal{M}_p) / \mathcal{M}_p \right)^T$ (recall that $\mathcal{I}$ is the identity operator on $\mathbb{L}^2(\boldsymbol{M})$ and $\mathcal{P}_{\mathbb{K}}$ is the orthogonal projection on $\mathbb{K}$).

Then the computation of the transport coefficients is easily obtained thanks to Proposition 3.3 and the explicit formulation of the pseudo inverse of $\mathcal{L}_M$

$$\forall \mathbf{g} \in \mathbb{K}^\perp, \mathcal{L}_M^{-1}(\mathbf{g}) = \frac{1}{\varrho^M} \left((R - \mathcal{I}_{\mathbb{C}})^{-1} \circ \mathcal{P}_{\mathbb{C}} + (\mathcal{P}_{\mathbb{C}} - \mathcal{I}) \right) (\mathbf{g}) \tag{A.10}$$

where $\mathcal{I}_{\mathbb{C}}$ denotes the restriction on $\mathbb{C}$ of the identity operator.

REMARK A.2.   Yet another formulation of (A.9) is more suited to the computation of the Onsager matrix (thermodynamics of irreversible processes). This formulation was introduced in [11] in the case of monoatomic gas mixtures following an interpretation of the Euler equations by Levermore in [30]. This formulation reads

$$\mathcal{L}_i^S(\mathbf{g}) = \sum_{j=1}^{j=p} (\mathcal{I} - \mathcal{P}_{\mathbb{K}})(\mathbf{C}_j) \cdot \nabla_x \left(\ln \frac{n_j}{Q_j} \right) + \frac{1}{2} \mathbb{A} : \mathbb{D}(\mathbf{u}) + \frac{1}{3} \mathbb{A}^V : \nabla_x \mathbf{u} + \tilde{\mathbf{B}} \cdot \nabla \left(\frac{1}{k_{\text{B}} T} \right) + \boldsymbol{\Psi}^C$$

where $\mathbf{C}_j$ is the vector whose j^{th} component is $\mathbf{v} - \mathbf{u}$ and whose other components are 0 and $\tilde{\mathbf{B}}$ is given by

$$\tilde{\mathbf{B}}_i = m_i (\mathbf{v} - \mathbf{u}) \left(\frac{5 n k_{\text{B}} T}{2\rho} - \frac{1}{2} (\mathbf{v} - \mathbf{u})^2 + \overline{E}_i - E_{iI} \right).$$

Note that $\tilde{\mathbf{B}}$ is no longer orthogonal to $\mathbb{C}$ (Definition 3.1), contrary to $\mathbf{B}$. Then,

$$L_{ij} = -k_B^{-1} m_i m_j \left\langle \mathcal{L}_S^{-1} [(\mathcal{I} - \mathcal{P}_{\mathbb{K}})(\mathbf{C}_j)], (\mathcal{I} - \mathcal{P}_{\mathbb{K}})(\mathbf{C}_i) \right\rangle,$$

$$L_{i,p+1} = L_{p+1,i} \mathbb{I} = -k_{\text{B}}^{-1} m_i \left\langle \mathcal{L}_S^{-1} \left(\tilde{\mathbf{B}} \right), (\mathcal{I} - \mathcal{P}_{\mathbb{K}})(\mathbf{C}_i) \right\rangle, \tag{A.11}$$

$$L_{p+1,p+1} = -k_{\text{B}}^{-1} \left\langle \mathcal{L}_S^{-1} \left(\tilde{\mathbf{B}} \right), \tilde{\mathbf{B}} \right\rangle.$$

Finally, the matrix $(L_{ij})_{i,j=1,\ldots,p+1}$ is symmetric nonpositive thanks to the property (2.11), and one can easily check that its kernel is $(1, \cdots, 1, 0)^T \in \mathbb{R}^{p+1}$.

A.5. Proof of Lemma 5.2.
Proof.   Our aim is to calculate

$$\overline{\omega}_i^1 = \sum_{I \in \Omega_i} \int \mathcal{L}_i^C(\mathbf{g}) d\mathbf{v} \tag{A.12}$$

where

$$\mathcal{L}_i^C(\mathbf{g}) = \lim_{s \to 0} \frac{1}{s} \left(\mathcal{R}_i^C(\mathbf{M}(1+s\mathbf{g})) - \mathcal{R}_i^C(\mathbf{M}) \right) \tag{A.13}$$

$$= \lim_{s \to 0} \frac{1}{s} \left[\varrho_{i,s}^C \left(\mathcal{M}_{i,s}^C - \mathcal{M}_i(1+sg_i) \right) - \varrho_i^C \left(\mathcal{M}_i^C - \mathcal{M}_i \right) \right] \tag{A.14}$$

and $\varrho_{i,s}^C$ and $\mathcal{M}_{i,s}^C$ are respectively the rate of relaxation and equilibrium function of the ith species defined in (4.19) and (4.18). They depend on the relaxation models $\mathcal{R}_i^r$ (4.7) and, therefore, on the initial distribution functions $\mathbf{M}(1+s\mathbf{g})$. So let us consider a single reaction r and calculate the perturbed rate of relaxation ϱ_s^r together with the Maxwellian function $\mathcal{M}_{i,s}^{r,eq}$ at chemical equilibrium where

$$\mathcal{M}_{i,s}^{r,eq} = \frac{1}{\beta_{iI}} \frac{n_{i,s}^{eq}}{Q_i(T_s^{eq})} \exp \left\{ -\frac{m_i}{2k_{\mathrm{B}}T_s^{r,eq}}(\mathbf{v} - \mathbf{v})^2 - \frac{E_{iI}}{k_{\mathrm{B}}T_s^{r,eq}} \right\}. \tag{A.15}$$

Let us now consider the system (4.4) and calculate its initial conditions. Note that the mass species $(\rho^i)_{i \in S_r}$ remain unchanged since $\mathcal{L}_M^{-1} \colon \mathbb{K}^\perp \to \mathbb{K}^\perp$. Hence, $\rho^r = \sum_{i \in S_r} \rho^i$. Other macroscopic quantities for this reaction (see (4.1)) are found to be equal to

$$\rho^r \mathbf{u}_s^r = \rho^r \mathbf{u}_s^r + \sum_{i \in S_r} \sum_{j=1}^p \rho^i D_{ij} \frac{\nabla p_j}{p}, \tag{A.16}$$

$$\mathcal{E}_s^r = \mathcal{E}^r + s\alpha_r + s^2 \beta_r \tag{A.17}$$

where

$$\alpha_r = -\frac{1}{\varrho^M} \sum_{\substack{j \in S_r \\ I \in \Omega_j}} \int \left(\frac{1}{2}m_j(\mathbf{v}-\mathbf{u})^2 + E_{iI} \right) \left(\frac{1}{3}\mathbb{A}_j^V : \nabla_x \mathbf{u} + \boldsymbol{\Psi}_j^C \right) \mathcal{M}_j d\mathbf{v},$$

$$= -\frac{1}{\varrho^M} k_{\mathrm{B}} T \left((\sum_{j \in S_r} n^j) \frac{\mathbf{c}^{\mathrm{int}}}{\mathbf{c}_{\mathrm{v}}} - n \sum_{j \in S_r} \frac{\mathbf{c}_j^{\mathrm{int}}}{\mathbf{c}_{\mathrm{v}}} \right) \nabla.\mathbf{u}$$

$$+ \frac{1}{\varrho^M} \sum_{j \in S_r} \varrho_j^C(\mathcal{E}_j^C - \mathcal{E}_j) - \frac{1}{\varrho^M} \sum_{j \in S_r} m_j \overline{\omega}_j^0 \, e_j$$

$$+ \frac{1}{\varrho^M} \left(\sum_{j \in S} m_j \overline{\omega}_j^0 \, e_j \right) \times (\sum_{j \in S_r} \rho_j \mathbf{c}_{\mathrm{vj}}(T))/(\sum_{j \in S} \rho_j \mathbf{c}_{vj}(T)),$$

β_r is some constant depending on $\boldsymbol{\Psi}^C$, and $(\nabla p_j)_j$. $e_j = (\frac{3}{2}k_{\mathrm{B}}T + \bar{E}_j)/m_j$ is the specific energy of the jth species. Additionally, $\mathcal{E}_j^C$ is defined in (4.16) with $\mathbf{u}^r = \mathbf{u}^i = \mathbf{u}$, and $\mathcal{E}_j$ is the internal energy of the species j. It is well known (see for example [12]) that the entropy is a concave function of the number densities per unit volume once the internal energy is fixed. This still applies to thermodynamics functions defined from the kinetic entropy such as $\mathcal{S}^{\mathrm{kin},r}$ (A.5). In the case where a chemical reaction occurs at fixed internal energy, the usual thermodynamics function used for characterizing the equilibrium is the entropy [12]. We are now going to prove it in a mathematical framework. Let us consider the concave function $\phi(x) = \mathcal{S}^{\mathrm{kin},r}((n^i + \nu_{ir} x)_{i \in S_r}, \mathcal{E}^r)$ which is defined for all values of x such that $n^i + \nu_{ir} x \geq 0$, $\forall i \in S_r$, or equivalently for all number densities in the set

$$X = \{(n^i + \nu_{ir} x)_{i \in S_r}, \quad \forall x \in \mathbb{R}\} \cap (\mathbb{R}^+)^{\dim S_r}.$$

Here $\dim S_r$ is the total number of species in the reaction — reactants and products. Atom mass concentrations are conserved in this set, and X contains the solutions of (4.4) as s varies (see (4.5)). Using the second law of thermodynamics (A.3) and the implicit theorem that was used in the proof of Proposition 4.2, one has

$$d\phi = k_{\text{B}} \sum_{i \in S_r} \nu_{ir} \ln\left(\frac{n^i + \nu_{ir} x}{Q_i(T_r(x, \mathcal{E}^r))}\right) dx$$

in such a way that $\phi'(x) = 0$ if and only if $\bar{\tau}_r(x) = 0$ (see (4.2) for the definition of the macroscopic rate of progress $\bar{\tau}_r$). Thus, the maximum value of ϕ in X is obtained for $x = \xi^{r,eq}$ (here we avoid some technical arguments to prove that the densities at equilibrium are in the interior of X).

Let us now study the variation of densities and temperature at chemical equilibrium with respect to the variation of internal energy. This can be done by calculating the variation of x and y with respect to the variation of $\mathcal{E}^r$ in the manifold

$$g(x,y) = \sum_{i \in S_r} \nu_{ir} \ln\left(\frac{n_i^{eq} + \nu_{ir} x}{T^{r,eq} + y}\right) = 0.$$

Clearly, x is a strictly monotonic function of the variation of $\mathcal{E}^r$ in its vicinity since $\frac{\partial g}{\partial x}(0,0) > 0$. It is even shown in [19] that this function is smooth, and we may write $n_{i,s}^{eq} = n_i^{eq} + \phi_r(\mathcal{E}_s^r - \mathcal{E}^r)$. The behavior of y with respect to this variation is less clear since $\frac{\partial g}{\partial y}(0,0) = \sum_i \nu_{ir} \bar{E}_i(T^{r,eq})$ which might be null. So let us consider the problem from another point of view. The mass atoms concentrations $\tilde{\rho}_r = (\tilde{\rho}_{1,r}, ..., \tilde{\rho}_{n^{a,r}})$ and temperature T are the "natural" variables in the study of chemical equilibrium flows [16, 19] (here $n^{a,r}$ is the number of atoms in the set of reactants (or products) in the reaction r). As concerns the homogeneous problem, $\tilde{\rho}_r$ is determined by the initial mass species $(\rho^j)_{j \in S_r}$ and is kept constant during the reaction, that is $(n_i)_{i \in S_r} \in X$ (5.11). Then one may consider the internal energy and the densities as functions of $(T, \tilde{\rho}_r)$, and one has, in particular,

$$n_i^{eq} = n_i(T^{r,eq}, \tilde{\rho}_r), \forall i \in S_r, \qquad \mathcal{E}^r = \mathcal{E}(T^{r,eq}, \tilde{\rho}_r).$$

It is shown in this framework ([19], Lemma 10.2.3) that $\partial_T \mathcal{E}$ is positive (not infinite) at chemical equilibrium points, and $\mathcal{E}$ is also a smooth function of T. Hence, we also have $T_s^{r,eq} = T^{r,eq} + \psi_r(\mathcal{E}_s^r - \mathcal{E}^r)$ for $\tilde{\rho}_r$ fixed. The calculation of the macroscopic fields defining $\mathcal{M}_{i,s}^C$ is then performed using (4.14), (4.15), (4.16), and (4.17). They depend smoothly on the perturbation $s\mathbf{Mg}$ thanks to the above results. Denote with $F_{i,s}$ the function in the limit (A.14). Skipping all technical details, $F_{i,s}$ is bounded by a function $G \in L^1(\mathbb{R}^3)$ for $0 \le s \le \delta$ with δ fixed and sufficiently small. Moreover, $F_{i,s}$ converges point-wise to a function $F_i = \mathcal{L}_i^C(\mathbf{g}) \in L^1(\mathbb{R}^3)$, so that we can use the dominated convergence theorem to compute $\overline{\omega}_i^1$. More precisely,

$$\overline{\omega}_i^1 = \sum_{r/\ i \in S_r} \lim_{s \to 0} \frac{\nu_{ir} \left(\overline{\tau}_{r,s} - \overline{\tau}_r\right)}{s} \tag{A.18}$$

where we have used (4.21). Here, $\overline{\tau}_{r,s} = \overline{\tau}_r((\rho^i)_i, \mathcal{E}_s^r)$. Next, consider the perturbed initial condition in (4.4). For $(\rho^i)_i$ fixed, one has

$$\mathcal{E}_s^r(T_s^r) = \mathcal{E}^r(T) + (T_s^r - T) \sum_{j \in S_r} \rho_j \, \mathbf{c}_{vj}(T) + O((T_s^r - T)^2).$$

For a given reaction r, one sets $s = (T_s^r - T) \left(\sum_{j \in S_r} \rho_j \, \mathbf{c}_{vj}(T) \right) / \alpha_r$ in (A.18) if $\alpha_r \neq 0$. Otherwise the limit is 0. Then the final result is

$$\overline{\omega}_i^1 = \sum_{r/\ i \in S_r} \frac{\alpha_r}{\sum_{k \in S_r} \rho_k \mathbf{c}_{vk}(T)} \ \nu_{ir} \frac{d\overline{\tau}_r}{dT}.$$

$\Box$

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