

DERIVATION OF A BGK MODEL FOR REACTING GAS MIXTURES

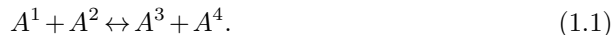
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Abstract. In this paper we derive a new relaxation model for reacting gas mixtures. We prove that this model satisfies the fundamental properties (equilibrium states, conservation laws, H-theorem, ...). We also consider the slow reaction regime. In this case a rigorous Chapman-Enskog procedure is performed and Navier-Stokes equations are derived.

Key words. Kinetic theory, gas mixtures, BGK models, entropy minimization, hydrodynamic limit

subject classifications 35Q20, 35Q35

1. Introduction The modeling of reacting gas mixtures is essentially based on the microscopic phenomena that occur when particles are colliding. Part of those collisions are non reactive while the others lead to different species and feature the chemical reactions. The same distinction is done at the kinetic level by adding to the classical collision operators for gas mixtures collision operators that only feature chemical reactions. A quite general setting of those equations can be found in [23]. It is however interesting to focus on the case where only one chemical reaction is considered. A simplified model has been proposed by Rossani and Spiga [32] where each species has only one degree of internal energy and where elastic collisions occur for the non reactive part of the collision operators. A generalization of this model to different degrees of internal energies was proposed in [25]. In particular they have considered a four species gas mixture with a reversible chemical reaction



(Here A^i stands for the species i).

The main motivation of this paper is the derivation of a relaxation model based on the simplified model of Rossani and Spiga. Our concerns are to include as much physical properties as possible (positivity, equilibrium states, conservation laws, H theorem) as well as minimizing computational cost. Such a model is the well known BGK model [4] for monoatomic gas. But its drawback is that it cannot lead to the proper Prandtl number at the Navier-Stokes level. This problem has been overcome by Holway [28] who introduced the so-called ES-BGK model. When inert gas mixtures are considered cross effects such as "mass" diffusion (Fick law) or thermo diffusion (Soret law) occur. The derivation of BGK models giving the right transport coefficients at the hydrodynamic limit is much more complicated. For example Kosuge [29] has derived a BGK operator that is able to approximate those coefficients but which guarantees neither the non negativity of the distribution functions nor the entropy decay. Andries & co-authors have successfully addressed the later problems [1] but their model is valid only for Maxwellian molecules and thus does not respond to the above requirements. The authors of the present paper have introduced a new concept of relaxation coefficients on non-conserved moments which allows to construct BGK type models. A first achievement was to recover the ES-BGK model in the

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monoatomic and polyatomic cases [12, 13]. But this idea extends to more general cases and we have derived in [14] a relaxation model allowing both to recover the correct Fick law at the hydrodynamic and enjoying the required mathematical (and physical) properties.

Coming back to reactive gas mixtures many BGK models were constructed by Groppi, Spiga and co-authors (see for example [9] for a complete bibliography) basing upon the "simplified" Boltzmann equation of Rossani and Spiga [32]. Those models always feature only one relaxation operator per species that includes both mechanical and chemical reactions. For the whole set of models the mechanical part is based on [1] where Maxwellian molecules are considered. Hence the hydrodynamic limits in the case of slow reactions lead to the Navier-Stokes equations with uncorrect transport coefficients. The chemical contributions depend on the approximation of the chemical collision operators. There are essentially two types of models. The first ones are constructed using estimations of the exchanges of mass, momentum and (kinetic plus internal energy) per species [26] and [9]. So in some sense those models mimic the one by Andries & al [1]. However those values cannot be computed in general even under the assumption of Maxwellian molecules and strong restrictions must be made -distribution functions at mechanical equilibrium (Maxwellian distributions)- to overcome this problem. This means that those models are essentially adapted to the case of slow reactions where the chemical reactions occur when the distribution of molecules are closed to mechanical equilibrium. The second model may be called "the" BGK model for mechanical plus chemical reactions [24]. The macroscopic parameters of the Maxwellian attractors are given under the requirements of number atoms conservation and conservation laws and bound together with some type of mass action law. This model enjoys the classical H-theorem for chemically reacting gas mixtures contrarily to the first class of models for which it is very unlikely that this property holds.

We intend in this paper to take advantage on one side on the modeling for inert gas mixtures and on the other side on the modeling for chemical reactions. Our methodology is based on a splitting between a mechanical operator and a chemical one as for the full Boltzmann equation. This procedure is particularly adapted to the case of slow reaction regime. More precisely we simply add to the model derived in [14] a chemical relaxation operator directly derived from [24]. However remark that while the chemical BGK operator seems to be more adapted to the case of fast chemical reactions, our choice relies upon the possibility to prove a H-theorem. In doing so the present paper must be considered more as an example of the splitting methodology than an attempt to match the best approximation of the chemical contribution in the case of slow reaction regime.

The paper is organized as follows. In section 3 we make a short review of different Boltzmann equations for reacting mixtures. In the next section we show that the construction of the mechanical model can be achieved either by using experimental values (Fick law) or by algorithms developed by Ern and Giovangigli [19]. Special attention is given as to the definition of the relaxation coefficients for the chemical model. Then we show that the whole relaxation model satisfies the H-theorem and that equilibrium states are Maxwellian functions which densities and temperature are bound together with the mass action law. Finally section 5 is devoted to the derivation of the Euler and the Navier-Stokes system in the slow reacting regime. The Chapman-Enskog procedure yields a first formulation of the Navier-Stokes. We focus on the calculation of the chemical terms at the first order. The second formulation of those

equations (section 5.3.2) is obtained by using the work of Kurochkin, Makarenko and Tirskaa [30] on the transport coefficients and the Onsager relations. Thus the Navier-Stokes equations are recast in the classical framework of polyatomic gases (see for example [23]). This makes possible the comparison between the different coefficients (species multicomponent diffusion, thermal diffusion, etc) that are obtained on one side with our model and on the other side with the usual theory. This also allows to determine entirely the definition of our model as already mentioned above.

2. Notations Consider a gas mixtures with p components. $f_i(t, x, v)$ (or for short $f_i, i \in [1, p]$ with $\mathbf{f} := (f_1, \dots, f_p)$) represents the distribution function of a given species i .

We denote with $n^i, \rho^i, u^i, \mathcal{E}^i$ and T^i the macroscopic quantities representing respectively the density and mass per unit volume, average velocity, internal energy per unit volume and finally temperature of a given species i . They are defined by the following relations:

$$\begin{aligned} n^i &= \int_{\mathbb{R}^3} f_i d\mathbf{v}, \quad \rho^i = m_i n^i, \quad n^i \mathbf{u}^i = \int_{\mathbb{R}^3} \mathbf{v} f_i d\mathbf{v}, \\ \mathcal{E}^i &= n^i \left(\frac{3}{2} k_B T^i + E_i \right) = \int_{\mathbb{R}^3} \left(\frac{m_i}{2} \|\mathbf{v} - \mathbf{u}^i\|^2 + E_i \right) f_i d\mathbf{v}, \end{aligned}$$

where k_B is the Boltzmann constant and $\|\cdot\|$ is the Euclidean norm in \mathbb{R}^3 . E_i represents the internal energy of species i due to chemical links. In the same way macroscopic quantities for the mixture are defined by

$$\begin{aligned} n &= \sum_{k=1}^p n^k, \quad \rho = \sum_{k=1}^p \rho^k, \quad \rho \mathbf{u} = \sum_{k=1}^p \rho^k \mathbf{u}^k, \\ \frac{\rho}{2} \|\mathbf{u}\|^2 + \mathcal{E} &= \sum_{i=1}^4 \left(\frac{1}{2} \rho^i \|\mathbf{u}^i\|^2 + n^i E_i \right), \quad \mathcal{E} = \sum_{i=1}^4 n^i \left(\frac{3}{2} k_B T + E_i \right). \end{aligned} \quad (2.1)$$

3. The Boltzmann equation for reactive gas mixtures In this section we recall some backgrounds about the Boltzmann equations for reacting mixtures. In the first subsection we recall the Boltzmann equation for inert gas mixtures which will be considered here. Next in subsection 3.2 we review some collision operators for reacting mixtures.

3.1. Inert monoatomic gas mixtures. For the sake of simplicity we are going to consider the mechanical Boltzmann equations for inert gas mixtures of p components, that is when collision between molecules are elastic. It reads [3]:

$$\forall i \in [1, p], \quad \partial_t f_i + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_i = \sum_{k=1}^{k=p} Q_{ki}(f_k, f_i) := Q_i(\mathbf{f}, \mathbf{f}),$$

where

$$Q_{ki}(f_k, f_i) = \int_{\mathbb{R}^3 \times \mathbb{S}^2} (f_k(\mathbf{w}_{ki}^*) f_i(\mathbf{v}_{ki}^*) - f_k(\mathbf{w}) f_i(\mathbf{v})) \sigma_{ik}(\boldsymbol{\omega} \cdot \mathbf{V}, \|\mathbf{V}\|) \|\mathbf{V}\| d\mathbf{w} d\boldsymbol{\omega}.$$

Here Q_{ki} is the Boltzmann collision operator between molecules of species i and k and $\sigma_{ik} = \sigma_{ki}$ is the differential cross section which depend on the interaction potential

between species i and k . Finally $\mathbf{V} = \mathbf{w} - \mathbf{v}$ is the relative velocity. The post collisional velocities are given by

$$\mathbf{v}_{ki}^* = \mathbf{v} - 2 \frac{m_k}{m_i + m_k} ((\mathbf{v} - \mathbf{w}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega}, \quad \mathbf{w}_{ki}^* = \mathbf{w} + 2 \frac{m_i}{m_i + m_k} ((\mathbf{v} - \mathbf{w}) \cdot \boldsymbol{\omega}) \boldsymbol{\omega},$$

where m_i represents the particle mass of species i . These equations satisfy the conservation of mass (per species) momentum and energy at microscopic level. The set of collisional invariants \mathbb{K} is spanned by the set of functions $(\phi^l)_{l \in \{1;8\}}$ defined by

$$\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}, \begin{pmatrix} m_1 v_\alpha \\ m_2 v_\alpha \\ m_3 v_\alpha \\ m_4 v_\alpha \end{pmatrix}, \begin{pmatrix} \frac{1}{2} m_1 \mathbf{v}^2 + E_1 \\ \frac{1}{2} m_2 \mathbf{v}^2 + E_2 \\ \frac{1}{2} m_3 \mathbf{v}^2 + E_3 \\ \frac{1}{2} m_4 \mathbf{v}^2 + E_4 \end{pmatrix}, \quad (3.1)$$

for $\alpha = x, y, z$.

Collision equilibria are given by Maxwellian distributions

$$f_i = \mathcal{M}_i = n_i \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(-\frac{m_i}{2k_B T} (\mathbf{v} - \mathbf{u})^2 \right), \quad (3.2)$$

for any densities $n_i \geq 0$, mean velocity $\mathbf{u} \in \mathbb{R}^3$ and positive temperature T . k_B is the Boltzmann constant.

Next we need to introduce the space $\mathbb{L}^2(\mathbf{M})$ equipped with its natural dot product:

$$\langle \Psi, \Phi \rangle = \sum_{i=1}^{i=p} \int_{\mathbb{R}^3} \psi_i \phi_i \mathcal{M}_i dv. \quad (3.3)$$

The i^{th} component of the linearized Boltzmann operator reads [3]

$$\mathcal{L}_{B_i}(\mathbf{g}) = \frac{1}{\mathcal{M}_i} \left(\sum_{j=1}^p Q_{ji}(\mathcal{M}_j, \mathcal{M}_i g_i) + Q_{ji}(\mathcal{M}_j g_j, \mathcal{M}_i) \right). \quad (3.4)$$

Then $\text{Ker}(\mathcal{L}_B) = \mathbb{K}$, \mathcal{L}_B is continuous, invertible and self adjoint negative on \mathbb{K}^\perp .

3.2. Reacting gas mixtures. In this subsection we recall the three main different approaches leading to collision operators for gas mixtures.

In [32] the authors consider a mixture of four gases undergoing a reversible bi-molecular chemical reaction together with mechanical binary collisions. Then the kinetic equation writes for the i^{th} species

$$\frac{\partial f_i}{\partial t} + \mathbf{v} \cdot \nabla f_i = Q_i + J_i, \quad i \in \{1;4\}, \quad (3.5)$$

where Q_i is the elastic collision operator and J_i represents the chemical collision term. Let us describe briefly J_i . Let m_i (resp. E_i) be the particle mass (resp. the energy of chemical link) for a given species i . Then J_1 is defined by

$$J_1(\mathbf{f}) = \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} U(V - \varepsilon_{12}) V I_{12}^{34}(V, \Omega, \Omega') \left(\left(\frac{m_{12}}{m_{34}} \right)^3 f_3(\mathbf{v}') f_4(\mathbf{w}') - f_1(\mathbf{v}) f_2(\mathbf{w}) \right) d\mathbf{w} d\Omega', \quad (3.6)$$

where $(\mathbf{v}', \mathbf{w}')$ are the post-collisional velocities and $m_{ij} = \frac{m_i m_j}{m_i + m_j}$ is the reduced mass. The quantity ε_{ij} is defined by

$$\varepsilon_{ij} = 2 \frac{\Delta E}{m_{ij}} \quad \text{with} \quad \Delta E = E_3 + E_4 - E_1 - E_2.$$

U denotes the unit step function and is a threshold for endothermic reactions. This term is linked to the energy of activation which must be given to the system in order that the endothermic reaction can happen.

$I_{12}^{34}(V, \Omega, \Omega')$ is the cross section where

$$V = \|\mathbf{w} - \mathbf{v}\|, \quad \Omega = (\mathbf{w} - \mathbf{v})/V, \quad \Omega' = (\mathbf{w}' - \mathbf{v}')/\|\mathbf{w}' - \mathbf{v}'\|.$$

The other chemical terms J_i for $i \in \{2; 3; 4\}$ can be obtained after suitable permutations.

Densities are not conserved but only the total mass. However one must also consider the conservation of atoms number during a reaction. In the case of bimolecular interactions this may be expressed by the following equalities (see [32])

$$\int J_i(\mathbf{f}) d\mathbf{v} = - \int J_j(\mathbf{f}) d\mathbf{v}, \quad (i, j) = (1, 3), (1, 4), (2, 4), \quad (3.7)$$

from which one also has

$$\int J_1(\mathbf{f}) d\mathbf{v} = \int J_2(\mathbf{f}) d\mathbf{v}, \quad \int J_3(\mathbf{f}) d\mathbf{v} = \int J_4(\mathbf{f}) d\mathbf{v}. \quad (3.8)$$

Finally the conservation of momentum and total energy $(\phi^l)_{l \in \{5; 8\}}$ must be added to this set of invariants.

A generalization of this operator for many levels of energy per particles ([25]) can be considered in the framework of Giovangigli and Ern ([20, 23]) and references therein. Each distribution function reads $f_i(t, x, v, I)$ where I is the index of the quantum internal energy states of the i^{th} . Then the chemical operator for f_1 reads

$$\mathcal{J}_i(\mathbf{f}) = \sum_{J, K, L} \int \left(f_3 f_4 \frac{\beta_{3K} \beta_{4L}}{\beta_{1I} \beta_{2J}} - f_i f_j \right) \mathcal{W}_{1234}^{IJKL} d\mathbf{w} d\mathbf{v}' d\mathbf{w}'. \quad (3.9)$$

J, K, L are all possible internal quantum energy states of species 2, 3, 4. In the case of [25] the ratio $\beta_{3K} \beta_{4L} / (\beta_{1I} \beta_{2J})$ does not depend upon I, J, K, L and simply takes the value $(m_{12}/m_{34})^3$ while in [23]

$$\beta_{iI} = \frac{\hbar}{a_{iI} m_i^3}.$$

\hbar is the Plank constant and a_{iI} is the degeneracy of the internal energy state I for species i . Within our framework we have on one side $a_{iI} = 1$ and $\beta_{iI} = \hbar/m_i^3$. However \hbar does not appear in (3.6) since we are considering bimolecular reaction. For the sake of simplicity we will set $\beta_{iI} = 1/m_i^3$.

REMARK 3.1. *The main difference between (3.6) and (3.9) is the interpretation of $\mathcal{W}_{1234}^{IJKL}$ which are probabilities of transition [20, 23]. However those values as well as differential cross sections $I_{12}^{34}(V, \Omega, \Omega')$ are unknown in general. But while angular deviation of the velocities are not accessible from experiments quite accurate evaluations of cross sections (as functions of the translational energy) have been carried out*

(see e.g [5]). They allow to compute the concentrations of the different species at any quantum energy states (vibrational, rotational) as soon as those quantum states can be evaluated for the molecules to be considered. This means that even under strong deviation from equilibrium (except for the translational energies) the chemical processes are quite well evaluated.

REMARK 3.2. One may consider the problem of finding relevant differential cross sections such as to obtain a correct hydrodynamical limit. In this vein one may cite the work of Desvillettes & co-authors [18, 11] who proposed a model for both mechanical and chemical reactions that allows to recover the energy law of polytropic gases at the Euler limit.

4. The relaxation model

4.1. Definition of the model. The distribution function $f_i(t, x, v)$ (or for short $f_i, i \in [1, 4]$ with $\mathbf{f} := (f_1, f_2, f_3, f_4)$) of a given species i evolves according to the kinetic equation:

$$\forall i \in [1, 4], \partial_t f_i + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_i = \mathcal{R}_i^{ME}(\mathbf{f}) + \mathcal{R}_i^{CE}(\mathbf{f}) := \mathcal{R}_i(\mathbf{f}), \quad (4.1)$$

where $\mathcal{R}_i^{ME}(\mathbf{f})$ (resp. $\mathcal{R}_i^{CE}(\mathbf{f})$) represents the mechanical (resp. chemical) part of the relaxation operator.

4.1.1. The mechanical BGK operators The mechanical part of the model is the one constructed in [14]. For the sake of clarity we recall how it is derived. Let us now consider the formalism of the thermodynamic of irreversible processes. Mass flux for the i^{th} species reads

$$\mathbf{J}_i = \sum_{j=1}^{j=4} L_{ij} \nabla (\mathcal{G}_i^{tr}) + L_{i5} \nabla \left(-\frac{1}{T} \right) \quad (4.2)$$

where the specific Gibbs functions \mathcal{G}_i^{tr} are defined by

$$\mathcal{G}_i^{tr} = \frac{k_B T}{m_i} \ln \left(\frac{n^i}{Q_i^{tr}} \right), \quad \text{with} \quad Q_i^{tr} = (2\pi m_i k_B T)^{\frac{3}{2}}. \quad (4.3)$$

We may as well consider the full specific Gibbs functions by including partition functions for internal energies. But the present definition is more suited to the derivation of the hydrodynamic limit of our model. We will later on use the full specific Gibbs functions to recast the Navier-Stokes equations in a classical way (section 5.3.2).

Remark here that L_{ij} and L_{i5} are of opposite sign of the traditional thermodynamic coefficients. The reason is that they are directly derived from the Boltzmann equation through a Chapman-Enskog expansion. Notice that the density fluxes are generally rather expressed in terms of the phenomenological coefficients in which case the dependence of the above fluxes on gradients of the densities is called the Fick law. Whatever is the expression the corresponding coefficients depend on temperature T and also on the number densities and molecular masses of each component.

Then in order to recover the matrix $(L_{ij})_{i,j=1,\dots,4}$ one performs the following steps:

1. Define the symmetric non positive matrix L^* whose elements are

$$L_{ij}^* := \frac{L_{ij}}{\sqrt{\rho_i \rho_j} T}. \quad (4.4)$$

In the case where the exact Fick coefficients F_{ij} can be measured from experiments one sets

$$L_{ij}^* = \frac{n_j}{k_B T} F_{ij} \frac{(m_i m_j)^{\frac{3}{2}}}{\sqrt{n_i n_j}}. \quad (4.5)$$

It is of course necessary that those coefficients are such that the matrix L^* remains symmetric non positive. L^* is also related to the diffusion matrix $(D_{ij})_{i,j=1,\dots,4}$ which definition is recalled in section . Then one also has

$$L_{ij}^* = -\frac{\sqrt{\rho_i \rho_j}}{n k_B T} D_{ij}, \quad i, j = 1, \dots, 4. \quad (4.6)$$

This second formula makes possible the computation of L^* by using the algorithms developed by Ern and Giovangigli [19].

2. Remark that L^* always diagonalizes in an orthonormal basis:

$$L^* = W^T K^* W$$

and that up to some permutation in W and K^* the corresponding eigenvalues $(k_r^*)_r$ are non null for $r=1,\dots,3$ while $k_4^*=0$ and corresponds to the conservation of the total mass ρ . Then set

$$\lambda_r = -k_r^{*-1} \text{ for } r=1,2,3 \text{ and } \lambda_4=0.$$

3. Define the vector of velocities $\underline{\mathbf{U}} = (\mathbf{u}_1, \dots, \mathbf{u}_4)^T$ with the relation

$$\underline{\mathbf{U}} - \mathbf{U} = \mathbf{N}^{-1} W^T \left(\mathbf{I} - \frac{1}{\nu^M} \Delta \right) W \mathbf{N} (\bar{\mathbf{U}} - \mathbf{U}), \quad (4.7)$$

where $\mathbf{U} = (\mathbf{u}, \mathbf{u}, \mathbf{u}, \mathbf{u})^T$, $\bar{\mathbf{U}} = (\mathbf{u}^1, \dots, \mathbf{u}^p)^T$ and \mathbf{N} and Δ are the diagonal matrix which diagonal terms are respectively $(\sqrt{\rho_1}, \dots, \sqrt{\rho_4})$ and $(\lambda_1, \dots, \lambda_4)$.

4. Set

$$T^* = T - \frac{1}{3n k_B} \|W^T \left(\mathbf{I} - \frac{1}{\nu^M} \Delta \right) W \mathbf{N} (\bar{\mathbf{U}} - \mathbf{U})\|^2. \quad (4.8)$$

DEFINITION 4.1. *The i^{th} component of the mechanical operator reads*

$$\mathcal{R}_i^{ME}(\mathbf{f}) = \nu^M (G_i - f_i), \quad i \in [1, 4], \quad (4.9)$$

with

$$\forall i \in [1, p], G_i = \frac{n^i}{(2\pi k_B T^* / m_i)^{3/2}} \exp\left(-\frac{m_i (\mathbf{v} - \mathbf{u}_i)^2}{2k_B T^*}\right), \quad (4.10)$$

where $\nu^M > 0$ represents the relaxation coefficient. This coefficient must be chosen with the constraint $\nu^M \geq \max_r \lambda_r / 2$ in order to ensure the positivity of T^* .

5. **Definition of ν^M :** In our case ν^M must be considered as a mean frequency of return to thermodynamic equilibria of the whole set of molecules. Assume

that the shear viscosity η is given by some formula or approximated by the algorithms of Ern and Giovangigli. Then if η satisfies the condition

$$\eta \leq \frac{nk_B T}{\max_r \lambda_r} \quad (4.11)$$

we set

$$\nu^M = nk_B T / \eta. \quad (4.12)$$

This definition allows to recover the viscosity η at the hydrodynamic limit. It is also classical for the BGK model with one component. However we also have

$$\lambda_r = \frac{nk_B T}{d_r^*}, \quad r = 1, 2, 3, \quad \text{and} \quad \lambda_4 = 0$$

where $(d_r^*)_r$ are the eigenvalues (up to some permutation) of the matrix $(\sqrt{\rho_i \rho_j} D_{ij})_{ij}$ (4.6). Then the condition (4.11) also reads $\eta \leq \min_{r=1,2,3} d_r^*$ and the definition (4.12) is subjected to the relative speed between the shear stress and diffusion phenomena. For want of anything better we set

$$\nu^M = \max \left(\frac{nk_B T}{\eta}, \max_r \lambda_r \right), \quad (4.13)$$

in such a way that the model is always well-posed.

4.1.2. The chemical BGK operators \mathcal{R}_i^{CE} represents the chemical part of the relaxation operator constructed in [24].

DEFINITION 4.2. *The i^{th} component of the chemical operator reads*

$$\mathcal{R}_i^{CE}(\mathbf{f}) = \nu_i^C (\tilde{\mathcal{M}}_i - f_i), \quad (4.14)$$

where $(\nu_i^C)_i$ are the chemical collision frequencies and

$$\tilde{\mathcal{M}}_i = \tilde{n}^i \left(\frac{m_i}{2\pi k_B \tilde{T}} \right)^{\frac{3}{2}} \exp \left(-\frac{m_i}{2k_B \tilde{T}} (\mathbf{v} - \tilde{\mathbf{u}})^2 \right). \quad (4.15)$$

It is clear that within the above framework the collision frequency of e.g the first species should read (see [26] or [24])

$$\frac{1}{n^1} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} U(V - \varepsilon_{12}) V I_{12}^{34}(V, \Omega, \Omega') f_1(\mathbf{v}) f_2(\mathbf{w}) d\mathbf{w} d\Omega', \quad (4.16)$$

(if the chemical collision integral is (3.6)). However neither the differential cross section nor the functions \mathbf{f} are known. Recall that the characteristic time of mechanical collisions is supposed to be much smaller than that of the chemical ones. In this case a possible approximation of the chemical terms $(J_i(\mathbf{f}))_i$ (3.6) consists in replacing \mathbf{f} with the set of functions at thermodynamical equilibrium \mathbf{M} . Further simplification - Maxwellian molecules [26] - allows to evaluate the collision frequencies which then read

$$\nu_1^C = \nu_{12}^{34} \frac{2}{\sqrt{2\pi}} \Gamma \left(\frac{3}{2}, \frac{\Delta E}{k_B T} \right) n^2, \quad (4.17)$$

$$\nu_3^C = \nu_{12}^{34} \frac{2}{\sqrt{2\pi}} \Gamma \left(\frac{3}{2}, \frac{\Delta E}{k_B T} \right) \left(\frac{m_{12}}{m_{34}} \right)^{\frac{3}{2}} \exp \left(\frac{\Delta E}{k_B T} \right) n^4. \quad (4.18)$$

Here ν_{12}^{34} is a physical constant depending on the species involved in the chemical reaction but not on the specified internal energy states $(E_i)_{i=1,\dots,4}$ which are considered here. $\Gamma(\alpha, x)$ is the uncomplete Gamma function defined by

$$\Gamma\left(\frac{3}{2}, \frac{\Delta E}{k_B T}\right) = \int_{\frac{\Delta E}{k_B T}}^{+\infty} \exp^{-t} t^{\frac{1}{2}} dt = \left(\frac{\Delta E}{k_B T}\right)^{\frac{1}{2}} \exp^{-\frac{\Delta E}{k_B T}} + \operatorname{erfc}\left(\sqrt{\frac{\Delta E}{k_B T}}\right).$$

Thus $\mathcal{N}\Delta E$ is somehow the activation energy of the reaction (1.1) when only one internal energy state per molecule is considered (\mathcal{N} is the Avogadro number).

NOTATION 4.1. *The set of functions $\tilde{\mathbf{M}} = (\tilde{\mathcal{M}}_1, \tilde{\mathcal{M}}_2, \tilde{\mathcal{M}}_3, \tilde{\mathcal{M}}_4)$ is denoted $\tilde{\mathbf{M}}(\mathbf{f})$ and respectively $\tilde{\mathcal{M}}_i(\mathbf{f})$ for each i . We will omit the dependance on \mathbf{f} when it is self evident.*

We recall how the parameters \tilde{n}^i , $\tilde{\mathbf{u}}$ and \tilde{T} are computed. The BGK models must satisfy the same laws than the chemical operators (3.6). That is the conservation of atoms number (3.7) together with the momentum and energy conservation.

$$\begin{aligned} \int (\mathcal{R}_i^{CE}(\mathbf{f}) + \mathcal{R}_j^{CE}(\mathbf{f})) d\mathbf{v} &= 0, & (i, j) &= (1, 3), (1, 4), (2, 4), \\ \sum_{i=1}^4 \int m_i \mathbf{v} \mathcal{R}_i^{CE}(\mathbf{f}) d\mathbf{v} &= 0, & \sum_{i=1}^4 \int \left(\frac{1}{2} m_i v^2 + E_i\right) \mathcal{R}_i^{CE}(\mathbf{f}) d\mathbf{v} &= 0. \end{aligned} \quad (4.19)$$

There are not enough equations to define all unknown densities $(\tilde{n}_i)_i$ but it is convenient to write them in the following form:

$$\tilde{n}_i = n^i + \Lambda^i \frac{\nu_1^C}{\nu_i^C} (\tilde{n}_1 - n^1), \quad i = 2, 3, 4, \quad (4.20)$$

where $(\Lambda^i)_i$ is the string of stoichiometric coefficients $(1, 1, -1, -1)$. Thus if \tilde{n}_1 is known all other densities are defined as well. Then the conservation of the mean velocity together with (4.20) allow to express $\tilde{\mathbf{u}}$ in term of the macroscopic fields:

$$\tilde{\mathbf{u}} = \sum_{i=1}^4 \nu_i^C m_i n^i \mathbf{u}^i / \sum_{i=1}^4 \nu_i^C m_i n^i. \quad (4.21)$$

Finally the conservation of the total energy together with (4.20), (4.21) gives the following equation for the temperature \tilde{T}

$$\tilde{T} = \left\{ \sum_{i=1}^4 \nu_i^C n^i \left[\frac{1}{2} m_i ((\mathbf{u}^i)^2 - \tilde{\mathbf{u}}^2) + \frac{3}{2} k_B T^i \right] + \nu_1^C \Delta E (\tilde{n}_1 - n^1) \right\} / \left(\frac{3}{2} k_B \sum_{i=1}^4 \nu_i^C n^i \right). \quad (4.22)$$

Thus \tilde{T} is also defined as soon as \tilde{n}_1 is. This last quantity is obtained by solving the implicit equation

$$\frac{\nu_3^C \nu_4^C \tilde{n}_1 (\nu_2^C n^2 + \nu_1^C (\tilde{n}_1 - n^1))}{\nu_2^C (\nu_3^C n^3 - \nu_1^C (\tilde{n}_1 - n^1)) (\nu_4^C n^4 - \nu_1^C (\tilde{n}_1 - n^1))} \exp\left(-\frac{\Delta E}{k_B \tilde{T}(\tilde{n}_1)}\right) = \left(\frac{m_{12}}{m_{34}}\right)^{\frac{3}{2}} \quad (4.23)$$

As mentioned by the authors "the left hand side is a monotonically increasing function of \tilde{n}_1 ranging from 0 to $+\infty$ when \tilde{n}_1 varies on its domain defined by the constraint of positivity of density and temperature fields. This guarantees existence and uniqueness of the solution to this equation" [24].

4.2. Properties of the model It is clear that those BGK models share the same collision invariants as the reacting Boltzmann equation itself. Now we show that the model satisfies an entropy dissipation property together with the H theorem. Let $\mathcal{H}(\mathbf{f})$ be defined by

$$\mathcal{H}(\mathbf{f}) = \sum_{i=1}^4 \int_{\mathbb{R}^3} f_i \ln \frac{f_i}{m_i^3} d\mathbf{v}. \quad (4.24)$$

PROPOSITION 4.3. *The relaxation operators $\mathcal{R}_i^{ME}(\mathbf{f})$ and $\mathcal{R}_i^{CE}(\mathbf{f})$ satisfy the following dissipative properties*

$$\sum_{i=1}^p \int_{\mathbb{R}^3} \mathcal{R}_i^{ME}(\mathbf{f}) \ln(f_i/m_i^3) d\mathbf{v} \leq 0, \quad \sum_{i=1}^p \int_{\mathbb{R}^3} \mathcal{R}_i^{CE}(\mathbf{f}) \ln(f_i/m_i^3) d\mathbf{v} \leq 0. \quad (4.25)$$

As a consequence \mathcal{H} defined in (4.24) is a Lyapounov function for the whole model.

Proof. On one side we have $\int \mathcal{R}_i^{ME}(\mathbf{f}) d\mathbf{v} = 0$ for all i so that

$$\sum_{i=1}^4 \int_{\mathbb{R}^3} \mathcal{R}_i^{ME}(\mathbf{f}) \ln(f_i/m_i^3) d\mathbf{v} = \sum_{i=1}^4 \int_{\mathbb{R}^3} \mathcal{R}_i^{ME}(\mathbf{f}) \ln f_i d\mathbf{v} \leq 0$$

as proved in [14]. On the other side [24] it holds that

$$\sum_{i=1}^4 \int_{\mathbb{R}^3} \mathcal{R}_i^{CE}(\mathbf{f}) \ln(f_i/m_i^3) d\mathbf{v} \leq 0.$$

So Proposition 4.3 follows \square

THEOREM 4.4. *The following assertions are equivalent:*

i) *the entropy production rate is equal to 0*

$$\sum_{i=1}^4 \int_{\mathbb{R}^3} (\mathcal{R}_i^{ME}(\mathbf{f}) + \mathcal{R}_i^{CE}(\mathbf{f})) \ln(f_i/m_i^3) d\mathbf{v} = 0. \quad (4.26)$$

ii) *For all i ,*

$$\mathcal{R}_i^{ME}(\mathbf{f}) + \mathcal{R}_i^{CE}(\mathbf{f}) = 0, \quad (4.27)$$

iii) *the distribution functions f_i are at mechanical and chemical equilibrium:*

$$\forall i \in [1, 4], f_i = \mathcal{M}_i = \frac{n_i}{(2\pi k_B T / m_i)^{3/2}} \exp\left(-\frac{m_i(\mathbf{v} - \mathbf{u})^2}{2k_B T}\right) \quad (4.28)$$

with the mass action law

$$\frac{n^1 n^2}{n^3 n^4} = \left(\frac{m_{12}}{m_{34}}\right)^{3/2} \exp\left(\frac{\Delta E}{KT}\right). \quad (4.29)$$

Proof. i) \Rightarrow iii) According to the above proposition 4.3 i) implies that

$$\sum_{i=1}^4 \int_{\mathbb{R}^3} \mathcal{R}_i^{ME}(\mathbf{f}) \ln(f_i/m_i^3) d\mathbf{v} = 0.$$

This holds [14] if and only if there exists macroscopic values $n_1, \dots, n_4, \mathbf{u}, T$ such that

$$\forall i \in \{1, 2, 3, 4\}, f_i = \mathcal{M}_i = \frac{n_i}{(2\pi k_B T / m_i)^{\frac{3}{2}}} \exp\left(-\frac{m_i(\mathbf{v} - \mathbf{u})^2}{2k_B T}\right).$$

However this condition is necessary but not sufficient for the entropy production rate to vanish. Plugging the above value of the distribution functions into the definition 4.2 of \mathcal{R}_i^{CE} , we obtain

$$\sum_{i=1}^4 \int_{\mathbb{R}^3} \nu_i^C (\tilde{\mathcal{M}}_i - \mathcal{M}_i) \ln(\mathcal{M}_i / m_i^3) d\mathbf{v} = 0.$$

A direct computation (see [24]) together with (4.23) gives

$$\begin{aligned} & \sum_{i=1}^4 \int_{\mathbb{R}^3} \nu_i^C (\tilde{\mathcal{M}}_i - f_i) \ln(\tilde{\mathcal{M}}_i / m_i^3) d\mathbf{v} \\ &= \nu_1 (\tilde{n}_1 - n_1) \left[\ln\left(\frac{\tilde{n}_1 \tilde{n}_2}{\tilde{n}_3 \tilde{n}_4} \left(\frac{m_3 m_4}{m_1 m_2}\right)^{\frac{3}{2}}\right) - \frac{\Delta E}{k_B \tilde{T}} \right] = 0, \quad \forall \mathbf{f} \geq 0. \end{aligned} \quad (4.30)$$

Subtracting the two previous equations with $f_i = \mathcal{M}_i$ gives

$$\sum_{i=1}^4 \int_{\mathbb{R}^3} \nu_i^C (\tilde{\mathcal{M}}_i - \mathcal{M}_i) \ln \frac{\tilde{\mathcal{M}}_i}{\mathcal{M}_i} d\mathbf{v} = 0.$$

The convexity of the function $x \rightarrow x \ln x$ yields $f_i = \mathcal{M}_i = \tilde{\mathcal{M}}_i$ for all $i \in \{1; 4\}$ which satisfy the mass action law (4.23).

ii) \Rightarrow i) is trivial.

iii) \Rightarrow ii). Assume that $(f_i)_i = (\mathcal{M}_i)_i$ such that density and temperature fields satisfy the mass action law

$$\frac{n^1 n^2}{n^3 n^4} \exp\left(-\frac{\Delta E}{k_B T}\right) = \left(\frac{m_{12}}{m_{34}}\right)^{3/2}. \quad (4.31)$$

One has firstly $G_i = \mathcal{M}_i$ from (4.7) and (4.8) so that $\mathcal{R}_i^{ME}(\mathbf{M}) = 0, \forall i$ (see Definition 4.1). Secondly equations (4.21) and (4.22) give $\tilde{\mathbf{u}} = \mathbf{u}$ and

$$\tilde{T} = T + \nu_1^C \Delta E (\tilde{n}_1 - n^1) / \left(\frac{3}{2} k_B \sum_{i=1}^4 \nu_i^C n^i\right). \quad (4.32)$$

One obtains the same equation as (4.31) by setting $\tilde{n}_1 = n_1$ into (4.23). Thus n_1 is the unique solution of (4.23) and $\tilde{n}_i = n_i, \forall i$ according to (4.20). One also has $\tilde{T} = T$ from (4.32) so that $\tilde{\mathcal{M}}_i = \mathcal{M}_i, \forall i$ and $\mathcal{R}_i^{CE}(\mathbf{f}) = 0$. \square

5. Hydrodynamic limit for slow reactions The slow reactions regime corresponds to the situation where the chemistry characteristic time is much smaller than the mechanical ones. This regime has been studied in ([19]) by estimating the ratio between the characteristic time of mechanical collisions and the chemistry characteristic time. This ratio is shown to be less than 0.16 for temperature varying between 300 and 1000 K. The hydrodynamic limit of our model is then obtained by studying the equations form

$$\forall i \in [1, 4], \partial_t f_i^\varepsilon + \mathbf{v} \cdot \nabla_x f_i^\varepsilon = \frac{1}{\varepsilon} \mathcal{R}_i^{ME}(\mathbf{f}) + \mathcal{R}_i^{CE}(\mathbf{f}), \quad (5.1)$$

as $\varepsilon \rightarrow 0$.

5.1. Asymptotic expansion The classical Chapman-Enskog expansion consists in setting

$$\forall i \in [1, 4], f_i^\varepsilon = f_i^0 + \varepsilon f_i^1 + \varepsilon f_i^2 \dots \quad (5.2)$$

and plugging those expressions in (5.1). Then we get at order -1 in ε $\mathcal{R}_i^M(\mathbf{f}) = 0$ for all i . So $f_i^0 = \mathcal{M}_i$ (see [14]).

Setting $f_i^1 = \mathcal{M}_i g_i$ the equations (5.1) at order 0 read:

$$\partial_t \mathcal{M}_i + \mathbf{v} \cdot \nabla_x \mathcal{M}_i = \mathcal{M}_i \mathcal{L}_i^{ME}(\mathbf{g}) + \mathcal{R}_i^{CE}(\mathbf{M}), \quad \forall i, \quad (5.3)$$

where \mathcal{L}_i^{ME} is the i^{th} component of the linearized operator of \mathcal{R}^{ME} around the Maxwellian distributions \mathbf{M} . Its i^{th} component is defined as usual by the formula:

$$D\mathcal{R}_i^{ME}(\mathbf{M}) \cdot \mathbf{Mg} = \mathcal{M}_i \mathcal{L}_i^{ME}(\mathbf{g}) = \lim_{\tau \rightarrow 0} \frac{\mathcal{R}_i^{ME}(\mathbf{M}(1 + \tau \mathbf{g})) - \mathcal{R}_i^{ME}(\mathbf{M})}{\tau}, \quad (5.4)$$

where $D\mathcal{R}^{ME}(\mathbf{M}) \cdot \mathbf{Mg}$ represents the differential of \mathcal{R}^{ME} at \mathbf{M} in the direction \mathbf{Mg} . After computing $\partial_t \mathcal{M}_i$ from the Euler system (5.9, 5.10, 5.11) in function of the space derivatives, the equations (5.3) will in turn be particularly easy to solve thanks to the exact formulation of the (pseudo-)inverse of \mathcal{L}^{ME} .

In order to obtain an asymptotic expansion of (5.1) up to order 1 in ε , the term $\mathcal{R}_i^{ME}(\mathbf{f})$ has to be expanded up to order 2. Set $f_i^2 = \mathcal{M}_i h_i$ then the equation (5.1) up to the order 1 is derived from

$$\begin{aligned} \partial_t(\mathcal{M}_i(1 + \varepsilon g_i)) + \mathbf{v} \cdot \nabla_x(\mathcal{M}_i(1 + \varepsilon g_i)) &= \frac{1}{\varepsilon} \mathcal{R}_i^{ME}(\mathbf{M}(1 + \varepsilon \mathbf{g} + \varepsilon^2 \mathbf{h})) \\ &+ \mathcal{R}_i^{CE}(\mathbf{M}(1 + \varepsilon \mathbf{g})). \end{aligned} \quad (5.5)$$

The Taylor expansion of $\mathcal{R}_i^{ME}(\mathbf{M}(1 + \varepsilon \mathbf{g} + \varepsilon^2 \mathbf{h}))$ gives

$$\begin{aligned} \mathcal{R}_i^{ME}(\mathbf{M}(1 + \varepsilon \mathbf{g} + \varepsilon^2 \mathbf{h})) &= \mathcal{R}_i^{ME}(\mathbf{M}) + \varepsilon \mathcal{L}_i^{ME}(\mathbf{g}) \\ &+ \varepsilon^2 \left(\mathcal{L}_i^{ME}(\mathbf{h}) + \frac{1}{2} D^2 \mathcal{R}_i^{ME}(\mathbf{M}) \cdot (\mathbf{Mg}, \mathbf{Mg}) \right) + \mathcal{O}(\varepsilon^3). \end{aligned} \quad (5.6)$$

Next one must expand $\mathcal{R}_i^{CE}(\mathbf{M}(1 + \varepsilon \mathbf{g}))$ as well. The linearized operator $\mathcal{L}^{CE}(\mathbf{g})$ around \mathbf{M} is defined with

$$\begin{aligned} D\mathcal{R}_i^{CE}(\mathbf{M}) \cdot \mathbf{Mg} = \mathcal{L}_i^{CE}(\mathbf{g}) &= \lim_{\tau \rightarrow 0} \frac{1}{\tau} (\mathcal{R}_i^{CE}(\mathbf{M}(1 + \tau \mathbf{g})) - \mathcal{R}_i^{CE}(\mathbf{M})) \\ &= \lim_{\tau \rightarrow 0} \frac{1}{\tau} (\tilde{\mathcal{M}}_i(\mathbf{M}(1 + \tau \mathbf{g})) - \tilde{\mathcal{M}}_i(\mathcal{M}) - \tau g_i \mathcal{M}_i). \end{aligned} \quad (5.7)$$

Remark that we have not factorized \mathcal{M}_i in front of \mathcal{L}_i^{CE} in this definition. The reason is that such a factor should not appear as suggests the last line of the above expression. Hence the expansion up to order 1 in ε of (5.5) gives

$$\begin{aligned} \partial_t(\mathcal{M}_i(1 + \varepsilon g_i)) + \mathbf{v} \cdot \nabla_x(\mathcal{M}_i(1 + \varepsilon g_i)) &= \mathcal{L}_i^{ME}(\mathbf{g}) + \mathcal{R}_i^{CE}(\mathbf{M}) + \varepsilon (\mathcal{L}_i^{CE}(\mathbf{g})) \\ &+ \mathcal{L}_i^{ME}(\mathbf{h}) + \frac{1}{2} D^2 \mathcal{R}_i^{ME}(\mathbf{M}) \cdot (\mathbf{Mg}, \mathbf{Mg}) + \mathcal{O}(\varepsilon^2). \end{aligned} \quad (5.8)$$

REMARK 5.1. According to their definition, the second order terms in ε of (5.6) conserve mass, total momentum and energy. Therefore they will neither contribute to the Euler system nor to the Navier-Stokes system.

5.2. The Euler system The Euler equations are classically obtained by integration of the 8 first moments of (5.3). They read:

$$\partial_t \rho^i + \nabla_x \cdot (\rho^i \mathbf{u}) = m_i \Lambda_i \nu_1^C (\tilde{n}_1 - n^1), \quad (5.9)$$

$$\partial_t (\rho \mathbf{u}) + \nabla_x \cdot (\rho \mathbf{u} \otimes \mathbf{u} + p \mathbb{I}) = 0, \quad (5.10)$$

$$\partial_t E_{tot} + \nabla \cdot (E_{tot} \mathbf{u} + \mathbb{P} \mathbf{u}) = 0, \quad (5.11)$$

where the total energy and the pressure are

$$E_{tot} = \frac{1}{2} \rho \mathbf{u}^2 + \mathcal{E}, \quad \mathbb{P} = nk_B T \mathbb{I}$$

and \mathbb{I} is the identity matrix.

5.3. The Navier-Stokes system.

5.3.1. Setting of the problem In order to obtain the Navier-Stokes system we have to perform the following steps:

1. compute \mathbf{g} solution to the equations (5.3) by using the Euler system,
2. compute the linearized operator \mathcal{L}^{CE} by using formula (5.7),
3. integrate (5.8) with respect to the elements of \mathbb{K} (3.1) and keep all terms up to the order 1 in ε .

Those steps are performed in the following sections and the final result is given in Proposition 5.1

PROPOSITION 5.1. *The Navier-Stokes system for slow chemical reactions of (5.1) reads:*

$$\partial_t \rho^i + \nabla \cdot (\rho^i \mathbf{u}) + \varepsilon \nabla \cdot \mathbf{J}_i = m_i \Lambda_i \nu_1^C (\tilde{n}_1 - n_1) + \varepsilon \omega_i^1, \quad (5.12)$$

$$\partial_t (\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u} + \mathbb{P}) + \varepsilon \nabla \cdot \mathbb{J}_{\mathbf{u}} = 0, \quad (5.13)$$

$$\partial_t E_{tot} + \nabla \cdot (E_{tot} \mathbf{u} + \mathbb{P} \mathbf{u}) + \varepsilon \nabla \cdot (\mathbb{J}_{\mathbf{u}}[\mathbf{u}]) + \varepsilon \nabla \cdot \mathbf{J}_q = 0, \quad (5.14)$$

where the fluxes are defined by

$$\mathbf{J}_i = \sum_{j=1}^{j=4} L_{ij} \nabla \left(\frac{\mathcal{G}_i^{tr}}{T} \right), \quad \mathbb{J}_{\mathbf{u}} = -\frac{nk_B T}{\nu^M} \mathbb{D}(\mathbf{u}), \quad \mathbf{J}_q = -\kappa \nabla T + \sum_i E_i \mathbf{J}_i, \quad (5.15)$$

and the partial thermal conductivity for monoatomic gases

$$\kappa = \frac{5k_B^2 T}{2\nu^M} \sum_{i=1}^4 \frac{n^i}{m_i}. \quad (5.16)$$

The matrix L_{ij} is defined in (4.2) and the Specific Gibbs functions $(\mathcal{G}_i^{tr})_i$ in (4.3). $\mathbb{D}(\mathbf{u})$ is the traceless part of the deformation tensor

$$\mathbb{D}(\mathbf{u}) = \frac{1}{2} \left[\nabla \mathbf{u} + (\nabla \mathbf{u})^T \right] - \frac{1}{3} (\nabla \cdot \mathbf{u}) \mathbb{I}.$$

$(m_i \Lambda_i \nu_1^C (\tilde{n}_1 - n_1))_i$ are the zero order chemical terms where \tilde{n}_1 is the unique solution to the equation (4.23). Finally the first order perturbation of the chemical term reads

$$\omega_i^1 = m_i \Lambda_i \nu_1^C \tau(\tilde{n}_1) \bar{h}(\mathbf{g}),$$

$$\tau(\tilde{n}_1) = \left(\frac{m_{12}}{m_{34}} \right)^{\frac{3}{2}} \frac{\Delta E}{k_B \tilde{T}^2} / \left(\xi'(\tilde{n}_1) + \xi(\tilde{n}_1) \frac{\nu_1 (\Delta E)^2}{\frac{3}{2} k_B^2 \tilde{T}^2 \sum_{i=1}^4 \nu_i^C n^i} \right), \quad (5.17)$$

$$\bar{h}(\mathbf{g}) = \frac{1}{\nu^M} \Delta E (\tilde{n}_1 - n^1) \frac{\sum_{i=1}^4 (\nu_i^C)^2 \rho_i}{\sum_{i=1}^4 \nu_i^C n^i} \left(\frac{\nu_1^C}{\sum_{i=1}^4 \nu_i^C n^i} - \frac{1}{n} \right). \quad (5.18)$$

REMARK 5.2. When all chemical relaxation frequencies are equal the first order chemical perturbation ω_i^1 vanishes. Moreover for fixed (t, \mathbf{x}) the densities $(\tilde{n}_i)_i$ are solutions to the local mass action law

$$\frac{\tilde{n}_1 \tilde{n}_2}{\tilde{n}_3 \tilde{n}_4} \exp\left(-\frac{\Delta E}{k_B \tilde{T}(\tilde{n}_1)}\right) = \left(\frac{m_{12}}{m_{34}} \right)^{\frac{3}{2}}$$

together with the relations

$$\begin{aligned} \tilde{n}_i - n^i &= \Lambda^i(\tilde{n}_1 - n^1), \quad i = 2, 3, 4, \\ \tilde{T} &= T + \Delta E (\tilde{n}_1 - n^1) / \left(\frac{3}{2} k_B n \right). \end{aligned}$$

In a thermodynamic framework -that is considering the space homogeneous problem related to (5.12) and (5.14) with initial conditions $n^i(0) = n^i, \forall i$ and $T(0) = T$ - those solutions correspond to the "true" chemical equilibrium states (when $t \rightarrow +\infty$) of the chemical reaction (1.1).

REMARK 5.3. According to the expression of the fluxes given in Proposition 5.1, the shear viscosity η and partial thermal conductivity for monoatomic species κ are equal to

$$\eta = \frac{nk_B T}{\nu^M}, \quad \kappa = \frac{5k_B^2 T}{2\nu^M} \sum_{i=1}^4 \frac{n^i}{m_i}.$$

Define the mean molar mass of the mixture \bar{m} as

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

Then the Prandtl number Pr in the monoatomic setting can be computed as

$$Pr = \frac{5 R \eta}{2 \bar{m} \kappa} = \frac{n^2}{\rho \sum_{i=1}^4 \frac{n^i}{m_i}},$$

where $R = \mathcal{N} k_B$ is the constant of perfect gases. Hence in the situation of indifferen- tiability - that is when all molecules are the same - the Prandtl number is equal to 1 which is a drawback of the classical BGK model for a single monoatomic species.

5.3.2. Other formulation of the Navier-Stokes equations It is clear that the present model does not pretend to reproduce all phenomena that occur for polyatomic gas mixtures. However it is possible to recast the above equations in a more familiar and useful framework such as that of the book of Giovangigli [23]. We first introduce the specific enthalpy and specific Gibbs free energy for each species. They are defined by

$$h_i = \frac{5}{2} \frac{k_B T}{m_i} + \frac{E_i}{m_i}, \quad \mathcal{G}_i = \frac{k_B T}{m_i} \ln \left(\frac{n^i}{Q_i} \right), \quad Q_i = (2\pi m_i k_B T)^{\frac{3}{2}} \exp \left(-\frac{E_i}{k_B T} \right),$$

where we have introduced the partition function for internal energy

$$Q_i^{int} = \exp(-E_i/k_B T)$$

of the species i . Those definitions are similar to those introduced in [23] when the molecules have multiple internal energy states. From this the mass fluxes can be conveniently rewritten in the following form

$$\mathbf{J}_i = \sum_{j=1}^4 \tilde{L}_{ij} \nabla \left(\frac{\mathcal{G}_j}{T} \right) + \tilde{L}_{i5} \nabla \left(-\frac{1}{T} \right) \quad (5.19)$$

where \mathbf{J}_i is defined in (4.2) and

$$\tilde{L}_{ij} = L_{ij}, \quad i, j = 1, \dots, 4, \quad \tilde{L}_{i5} = \sum_{j=1}^4 L_{ij} \frac{E_j}{m_j}, \quad i = 1, \dots, 4. \quad (5.20)$$

Then the heat flux \mathbf{J}_q (5.15) may be written in a "symmetric" form

$$\mathbf{J}_q = \sum_{i=1}^4 \tilde{L}_{5i} \nabla \left(\frac{\mathcal{G}_i}{T} \right) + \tilde{L}_{55} \nabla \left(-\frac{1}{T} \right), \quad (5.21)$$

where $\tilde{L}_{5i} = \tilde{L}_{i5}$ and

$$\tilde{L}_{55} = \sum_{i,j=1}^4 \frac{E_i}{m_i} L_{ij} \frac{E_j}{m_j} - \kappa T^2 < 0, \quad (5.22)$$

(κ is given in (5.16)). The null space of \tilde{L} is $\mathbb{R}(1, 1, 1, 1, 0)^T$ and \tilde{L} is symmetric non positive as shows the following decomposition $\tilde{L} = P^t \bar{L} P + M$ with

$$M = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \tilde{L}_{55} \end{bmatrix}, \quad P = \begin{bmatrix} 1 & 0 & 0 & 0 & \frac{E_1}{m_1} \\ 0 & 1 & 0 & 0 & \frac{E_2}{m_2} \\ 0 & 0 & 1 & 0 & \frac{E_3}{m_3} \\ 0 & 0 & 0 & 1 & \frac{E_4}{m_4} \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}, \quad \bar{L} = \begin{bmatrix} \tilde{L}_{11} & \tilde{L}_{12} & \tilde{L}_{13} & \tilde{L}_{14} & 0 \\ \tilde{L}_{21} & \tilde{L}_{22} & \tilde{L}_{23} & \tilde{L}_{24} & 0 \\ \tilde{L}_{31} & \tilde{L}_{32} & \tilde{L}_{33} & \tilde{L}_{34} & 0 \\ \tilde{L}_{41} & \tilde{L}_{42} & \tilde{L}_{43} & \tilde{L}_{44} & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}.$$

We are now going to use the work of Kurochkin & co-authors [30] that bridges the TIP formulations of the fluxes with more classical and practical ones. This comparison is still possible in our case since the thermodynamic functions are clearly defined. Denote with $A \in \mathbb{R}^{5 \times 5}$ the matrix

$$A = \begin{bmatrix} 1 & 0 & 0 & 0 & -h_1 \\ 0 & 1 & 0 & 0 & -h_2 \\ 0 & 0 & 1 & 0 & -h_3 \\ 0 & 0 & 0 & 1 & -h_4 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}.$$

Next we define with $\hat{L} = A^T \tilde{L} A$. Then it is easily checked that the mass and heat fluxes read also

$$J_i = - \sum_{j=1}^p \rho^i D_{ij} \frac{\nabla p_j}{p} - \rho^i \theta_i \frac{\nabla T}{T}, \quad \forall i \in \{1; 4\} \quad (5.23)$$

$$\mathbf{J}_q = -\hat{\lambda} \nabla T - p \sum_{i=1}^4 \theta_i \frac{\nabla p_i}{p} + \sum_{i=1}^4 h_i J_i. \quad (5.24)$$

Here $(p_i = n^i k_B T)_i$ are the partial pressures and the diffusion matrix $(D_{ij})_{i,j=1,\dots,4}$, thermal diffusion coefficients $(\theta_i)_{i=1,\dots,4}$ and partial thermal conductivity $\hat{\lambda}$ are respectively found to be

$$D_{ij} = -\frac{nk_B L_{ij}}{\rho_i \rho_j}, \quad \theta_i = \frac{\hat{L}_{i5}}{\rho_i T}, \quad \hat{\lambda} = \frac{\hat{L}_{55}}{T^2}. \quad (5.25)$$

Hence we recover the structural form of the fluxes in terms of phenomenological coefficients. Remark that the relation between the diffusion matrix and $(L_{ij})_{i,j=1,\dots,4}$ allows to approximate the later by using the algorithm developed by Ern and Giovangigli ([19]). As a consequence the mechanical model R^{ME} (section 4.1.1) is made explicit once the shear viscosity η is known. This is also given by the above approximation.

Nevertheless the thermal diffusion coefficients and partial thermal conductivity are uncorrect as it can be seen from the formulae (5.20) and (5.22). Indeed the values of $(\tilde{L}_{i5})_i$ and $(\tilde{L}_{55})_i$ are not the "real" value coming from the thermodynamics of irreversible processes since our mechanical model just allows to recover the matrix $(L_{ij})_{i,j=1,\dots,4}$ at the hydrodynamic limit.

Let us now compare $\mathbb{J}_{\mathbf{u}}$ in (5.15) with the general form that holds for a mixture of polyatomic gases with chemical reactions which writes

$$\mathbb{J}_{\mathbf{u}} = p^{reac} \mathbb{I} - \alpha \nabla \cdot \mathbf{u} \mathbb{I} - \eta \mathbb{D}(\mathbf{u}),$$

where p^{reac} is the chemical pressure, α is the volume viscosity and η the shear viscosity. In our case, since $\alpha = 0$ we are only considering elastic collisions. But it is possible to recover the exact shear viscosity under suitable conditions (see section 4.1.1). Finally there is no chemical pressure in our case. This is due to the (extremely) limited number of possible quantum energy states per molecules.

Finally the zero-order molecular production rate of the i^{th} species (5.12) is quite different from the Maxwellian production rate of the chemical operators (3.6). That is

$$\nu_i^C (\tilde{n}_i - n_i) \neq \Lambda_i \int_{\mathbb{R}^3} \mathcal{J}_1(\mathbf{M}) d\mathbf{v}.$$

Only the negative parts can be compared if the frequencies are chosen such as in (5.2).

5.3.3. Computation of \mathbf{g} Before we set the first result we need to introduce some notations.

DEFINITION 5.2. \mathbf{C}_i is the vector which i^{th} component is $\mathbf{v} - \mathbf{u}$ and others are 0. $\mathcal{P}_{\mathbb{K}}$ is the orthogonal projection on \mathbb{K} with respect to the scalar product (3.3) and \mathcal{I} is the identity operator.

LEMMA 5.3. The perturbation \mathbf{g} reads

$$\mathbf{g} = (\mathcal{L}^{ME})^{-1} (\Psi^{ME}) - \frac{1}{\nu^M} \Psi^{CE} = \mathbf{g}^{ME} + \mathbf{g}^{CE}, \quad (5.26)$$

where

$$\Psi_i^{ME} = \left(\sum_{j=1}^{j=p} k_B^{-1} (\mathcal{I} - \mathcal{P}_{\mathbb{K}}) \mathbf{C}_j \cdot \nabla \left(\frac{\mu_j}{k_B T} \right) + \mathbb{A} : \mathbb{D}(\mathbf{u}) + \mathbf{B} \cdot \nabla \left(\frac{1}{k_B T} \right) \right)_i, \quad (5.27)$$

$$\begin{aligned} \Psi_i^{CE} &= -\nu_i^C \frac{\tilde{\mathcal{M}}_i - \mathcal{M}_i}{\mathcal{M}_i} + \nu_i^C \frac{\tilde{n}_i - n_i}{n_i} \\ &+ \frac{2}{3nk_B^2 T^2} \left(\frac{1}{2} m_i (\mathbf{v} - \mathbf{u})^2 - \frac{3}{2} k_B T \right) \nu_1^C (\tilde{n}_1 - n_1) \Delta E. \end{aligned} \quad (5.28)$$

\mathbb{A} and \mathbf{B} are the list of tensors defined by

$$(\mathbb{A})_i = \frac{m_i}{k_B T} \left[(\mathbf{v} - \mathbf{u}) \otimes (\mathbf{v} - \mathbf{u}) - \frac{1}{3} (\mathbf{v} - \mathbf{u})^2 \mathbb{I} \right], \quad (\mathbf{B})_i = (\mathbf{v} - \mathbf{u}) \left[\frac{5}{2} k_B T - \frac{1}{2} m_i (\mathbf{v} - \mathbf{u})^2 \right].$$

\mathcal{I} is the identity and $\mathcal{P}_{\mathbb{K}}$ is the operator of projection on \mathbb{K} with respect to the scalar product (3.3). Finally \mathbf{C}_i is the vector in $\mathbb{R}^{3 \times 4}$ which i^{th} line is $\mathbf{v} - \mathbf{u}$ and the others are 0.

Proof. Using the Euler equations (5.9, 5.10, 5.11) the time derivatives of the macroscopic fields in (5.3) can be expressed in term of spatial derivatives. Then we use the formalism of [14] which can be easily extended to the case of slow chemical reactions. This reads:

$$\begin{aligned} \mathcal{L}^{ME}(\mathbf{g}) &= \sum_{j=1}^{j=p} k_B^{-1} (\mathcal{I} - \mathcal{P}_{\mathbb{K}}) m_i(\mathbf{C}_j) \cdot \nabla (\mathcal{G}_j^{tr}) + \mathbb{A} : \mathbb{D}(\mathbf{u}) + \mathbf{B} \cdot \nabla \left(\frac{1}{k_B T} \right) \\ &- (\mathcal{I} - \mathcal{P}_{\mathbb{K}}) \mathcal{R}^{CE}(\mathbf{M}). \end{aligned} \quad (5.29)$$

Let us first give more details on

$$\mathcal{R}_i^{CE}(\mathbf{M}) = \nu_i^C (\tilde{\mathcal{M}}_i - \mathcal{M}_i),$$

which corresponds to the chemical contribution. $\tilde{n}_i, \tilde{\mathbf{u}}$ and \tilde{T} are defined by the relations (4.20, 4.21, 4.22) corresponding to the fields of $\tilde{\mathbf{M}}$. Hence we have

$$\tilde{n}_i = n_i + \Lambda^i \frac{\nu_i^C}{\nu_i^C} (\tilde{n}_1 - n_1), \quad i = 2, 3, 4, \quad (5.30)$$

$$\tilde{\mathbf{u}} = \mathbf{u}, \quad \tilde{T} = T + \nu_1^C \Delta E (\tilde{n}_1 - n_1) / \left(\frac{3}{2} k_B \sum_{i=1}^4 \nu_i^C n_i \right), \quad (5.31)$$

where \tilde{n}_1 is the unique solution of the implicit equation (4.23). It is then an easy task to compute de i^{th} line of $(\mathcal{I} - \mathcal{P}_{\mathbb{K}}) \mathcal{R}^{CE}(\mathbf{M})$ by using the definition of \mathbb{K}^\perp and the result reads:

$$\begin{aligned} \Psi_i^{CE} &= -\nu_i^C \frac{\tilde{\mathcal{M}}_i - \mathcal{M}_i}{\mathcal{M}_i} + \nu_i^C \frac{\tilde{n}_i - n_i}{n_i} + \frac{2}{3nk_B^2 T^2} \left(\frac{1}{2} m_i (\mathbf{v} - \mathbf{u})^2 - \frac{3}{2} k_B T \right) \\ &\quad \times \nu_1^C (\tilde{n}_1 - n_1) \Delta E. \end{aligned}$$

We now need to compute $\mathcal{L}^{ME-1}(\Psi_i^{ME} + \Psi_i^{CE})$. Recall that

$$\forall \phi \in \mathbb{K}^\perp, \quad (\mathcal{L}^{ME})^{-1}(\phi) = \frac{1}{\nu^M} ((R - \mathcal{I}_C)^{-1} \circ \mathcal{P}_C + (\mathcal{P}_C - \mathcal{I}_C))(\phi), \quad (5.32)$$

(Lemma 8 in [14]) where \mathbb{C} is the space spanned by the vectors

$$(\mathcal{I} - \mathcal{P}_{\mathbb{K}})(\mathbf{C}_i), \quad i = 1, \dots, 4$$

and R is a linear operator acting on \mathbb{C} . Then one has $\mathbf{g}^{ME} = (\mathcal{L}^{ME})^{-1}(\Psi_i^{ME})$ from which one can compute the "elastic" part of the fluxes (see [14]). Next recall that

$$(\mathcal{I} - \mathcal{P}_{\mathbb{K}})\mathbf{C}_i = \sum_j a_{ij}\mathbf{C}_j, \quad (a_{ij})_{i,j} \in \mathbb{R}^4 \times \mathbb{R}^4,$$

and one can easily check that $\Psi^{CE} \in \mathbb{C}^\perp$. So Lemma 5.3 follows. \square

REMARK 5.4. *The decomposition of the perturbation \mathbf{g} into a mechanical and a chemical part corresponds to the usual decomposition that is valid for the reactive Boltzmann equation given in [23].*

5.4. Computation of \mathcal{L}^{CE} . In order to compute $\mathcal{L}^{CE}(\mathbf{g})$ from formula (5.7) we need a preliminary result.

LEMMA 5.4. *Let $\tilde{\mathcal{M}}_i^g$ be the "attractors" of the chemical term $\mathcal{R}_i^{CE}(\mathbf{M}(1 + \varepsilon\mathbf{g}))$ then*

$$\tilde{\mathcal{M}}_i^g(\mathbf{v}) = \tilde{n}_i^g \left(\frac{m_i}{2\pi k_B \tilde{T}_g} \right)^{\frac{3}{2}} \exp \left(-m_i \frac{(\mathbf{v} - \tilde{\mathbf{u}}_g)^2}{2k_B \tilde{T}_g} \right), \quad (5.33)$$

with

$$\tilde{n}_i^g = \tilde{n}_i + \varepsilon \Lambda_i \frac{\nu_1^C}{\nu_i^C} \tau(\tilde{n}_1) \bar{h}(\mathbf{g}) + \mathcal{O}(\varepsilon^2), \quad (5.34)$$

$$\tilde{\mathbf{u}}_g = \mathbf{u} + \varepsilon \frac{\sum_{i=1}^4 \nu_i^C m_i n_i u_i^g}{\sum_{i=1}^4 \nu_i^C m_i n_i}, \quad n_i u_i^g = \int_{\mathbb{R}^3} \mathcal{M}_i g_i \mathbf{v} d\mathbf{v}, \quad \mathbf{u}^g = (u_1^g, u_2^g, u_3^g, u_4^g), \quad (5.35)$$

$$\tilde{T}_g = \tilde{T} + \varepsilon \bar{h}(\mathbf{g}) \left(\frac{\nu_1^C \Delta E \tau(\tilde{n}_1)}{\frac{3}{2} k_B \sum_{i=1}^4 \nu_i^C n_i} + 1 \right) + \mathcal{O}(\varepsilon^2), \quad (5.36)$$

where

$$\tilde{T} = T + \nu_1^C \Delta E (\tilde{n}_1 - n^1) / \left(\frac{3}{2} k_B \sum_{i=1}^4 \nu_i^C n^i \right), \quad (5.37)$$

and

$$\bar{h}(\mathbf{g}) = \frac{1}{\nu^M} \Delta E (\tilde{n}_1 - n_1) \frac{\sum_{i=1}^4 (\nu_i^C)^2 \rho_i}{\sum_{i=1}^4 \nu_i^C n_i} \left(\frac{\nu_1^C}{\sum \nu_i^C n_i} - \frac{1}{n} \right).$$

This tedious and lengthy proof is left to appendix. Then expanding $\tilde{\mathcal{M}}_i^g$ around ε and using formula (5.7) we obtain

$$\begin{aligned} \mathcal{L}_i^{CE}(\mathbf{g}) &= \nu_i^C \tilde{\mathcal{M}}_i \left(\Lambda_i \frac{\nu_1^C}{\nu_i^C} \frac{\tau(\tilde{n}_1)}{\tilde{n}_i} \bar{h}(\mathbf{g}) - \frac{\bar{h}(\mathbf{g})}{2\pi k_B \tilde{T}} + \frac{m_i}{2\pi k_B \tilde{T}} (2\langle \mathbf{v} - \mathbf{u}, \mathbf{u}^g \rangle \right. \\ &\quad \left. + \frac{(\mathbf{v} - \mathbf{u})^2}{2k_B \tilde{T}} \bar{h}(\mathbf{g})) \right) - \nu_i^C \mathcal{M}_i g_i. \end{aligned} \quad (5.38)$$

REMARK 5.5. $\bar{h}(\mathbf{g}) = 0$ (5.18) when the collision frequencies (ν_i^C) are equal. Hence in this case there are no contribution of order ε to the chemical term in the Navier-Stokes equations for densities evolutions.

REMARK 5.6. The expression (5.38) of $\mathcal{L}_i^{CE}(\mathbf{g})$ does not depend on the mechanical perturbation \mathbf{g}^{ME} (5.26). Then contrarily to [23] there are no derivatives of the macroscopic fields in the first order production chemical terms.

5.5. Computation of the right-hand side of Navier Stokes system.

This subsection is devoted to the end of the proof of Proposition 5.1.

Proof. (Proposition 5.1). In order to obtain a Navier-Stokes system we have to consider for any $i \in \{1, 2, 3\}$ the moments of $\mathcal{M}_i(1 + \varepsilon g_i)$. Writing $g_i = g_i^{ME} + g_i^{CE}$ we remark that fluxes of order ε depend as expected only on g_i^{ME} . Hence we can directly infer that the left hand sides of the Navier-Stokes equations are those obtained in ([14]). Denote that one important point is the computation of matrix (L_{ij}) appearing in the definition of the mass flux J_i . More precisely, using (5.32) we obtain L_{ij} through the expression of the Ohnsager matrix from the Chapmann-Enskog expansion.

Next one has to compute the chemical terms up to order ε . As concerns the equations for densities those terms read

$$\int_{\mathbb{R}^3} (\mathcal{R}_i^{CE}(\mathbf{M}) + \varepsilon \mathcal{L}_i^{CE}(\mathbf{g})) d\mathbf{v} = \Lambda_i \nu_1^C (\tilde{n}_1 - n_1) + \varepsilon \Lambda_i \nu_1^C \tau(\tilde{n}_1) \bar{h}(\mathbf{g}).$$

Recall that

$$\mathcal{R}_i^{CE}(\mathbf{M}(1 + \varepsilon \mathbf{g})) = \mathcal{R}_i^{CE}(\mathbf{M}) + \varepsilon \mathcal{L}_i^{CE}(\mathbf{g}) + \mathcal{O}(\varepsilon^2)$$

and that $\mathcal{R}^{CE}(\mathbf{f})$ satisfies equations (4.19) for any function $\mathbf{f} = (f_1, f_2, f_3, f_4)$. Then we have on one side

$$\sum_i m_i \int_{\mathbb{R}^3} (\mathcal{R}_i^{CE}(\mathbf{M}) + \varepsilon \mathcal{L}_i^{CE}(\mathbf{g})) \mathbf{v} d\mathbf{v} = \mathcal{O}(\varepsilon^2),$$

and on the other side

$$\sum_i \int_{\mathbb{R}^3} \left(\frac{1}{2} m_i \mathbf{v}^2 + E_i \right) (\mathcal{R}_i^{CE}(\mathbf{M}) + \varepsilon \mathcal{L}_i^{CE}(\mathbf{g})) d\mathbf{v} = \mathcal{O}(\varepsilon^2),$$

which end the proof. \square

6. Discussion and conclusion The BGK model which is proposed here features the same structure as the simplified Boltzmann equation for reacting gas mixture proposed by Rossani and Spiga [32] or of the more general Boltzmann equation with different level of internal energies [23]. That is a sum of two different terms for the nonreactive and the reactive "collisions". Let us recall that our model is designed here to satisfy good mathematical properties (H-theorem, ...) and to present a splitting method that seems naturally adapted to the case of slow chemical reactions. The Chapman-Enskog expansion clearly outlines the respective contributions of the first order mechanical and chemical perturbations (5.26). As expected all transport coefficients (thermal diffusion, viscosity, Fourier law, ...) depend only on the modeling of the mechanical part of the BGK model. Its construction is based on the knowledge of the Fick law (4.5) or of the diffusion matrix (4.6) together with the shearn viscosity. In some cases the Fick law may be obtained from experiments but the corresponding

matrix of coefficients must be symmetrical non positive. This property is satisfied if the diffusion matrix is approximated by algorithms developed by Ern and Giovangigli [19]. The hydrodynamic limit of the model features good structural agreement (section 5.3.2) with the usual Navier-Stokes for polyatomic gases [23] (section 5.3.2) features a good structural agreement. The correct diffusion matrix is recovered by construction. This holds also true for the shear viscosity under suitable condition (4.11). But the thermal diffusion coefficients and partial thermal conductivity are uncorrect. There is no volume viscosity as expected since we are only dealing with elastic collisions and molecules with only one fixed internal energy state. As a consequence there is also no chemical pressure.

The zero order chemistry source terms (5.12) are not equal to the Maxwellian production rates of the real chemical operators contrarily to what is obtained from the theoretical BKG model of Bisi and Spiga [9] and for the Grad approximation in [8]. But positiveness of temperature of the attractors and H-theorem are guaranteed at the kinetic level contrarily to the model in [9]. Remark that perturbations of order ε are free from any derivatives of the spatial gradients as in [8]. One should also point out that those perturbations vanish when the chemical frequencies are equal.

Finally a generalization of the mechanical operator as well as a construction of a chemical operator allowing to recover the Maxwellian production rates in the general case of polyatomic gases are in progress.

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7. Appendix *Proof of Lemma 5.4.*

Proof. As $g \in \mathbb{K}^\perp$,

$$\int_{\mathbb{R}^3} \mathcal{M}_i(1 + \varepsilon g_i) d\mathbf{v} = n^i.$$

We first want to establish a transcendental equation as ([24]) whose \tilde{n}_1^g is a solution. By using the mass conservation for $i \in \{2; 3; 4\}$

$$\tilde{n}_i^g = n^i + \Lambda_i \frac{\nu_1^C}{\nu_i^C} (\tilde{n}_1^g - n^1). \quad (7.1)$$

Next the conservation of the impulsions for the chemical operator gives

$$\sum_{i=1}^4 m_i \nu_i^C \int_{\mathbb{R}^3} (\tilde{\mathcal{M}}_i^g - \mathcal{M}_i(1 + \varepsilon g_i)) \mathbf{v} d\mathbf{v} = 0.$$

So defining u_i^g by

$$n^i u_i^g = \int_{\mathbb{R}^3} \mathcal{M}_i g_i \mathbf{v} d\mathbf{v},$$

it holds that

$$\tilde{\mathbf{u}}_g = \mathbf{u} + \varepsilon \frac{\sum_{i=1}^4 \nu_i^C m_i n^i u_i^g}{\sum_{i=1}^4 \nu_i^C m_i n^i} = \mathbf{u} + \varepsilon f(u_g), \quad (7.2)$$

where

$$f(u_g) = \frac{\sum_{i=1}^4 \nu_i^C m_i n^i u_i^g}{\sum_{i=1}^4 \nu_i^C m_i n^i}.$$

Hence by setting

$$T_i^g = \frac{m_i}{3k_B n^i} \int_{\mathbb{R}^3} (\mathbf{v} - \mathbf{u} - \varepsilon \mathbf{u}_i^g)^2 \mathcal{M}_i(1 + \varepsilon g_i) d\mathbf{v}, \quad (7.3)$$

we finally obtain the following expression for \tilde{T}_g ,

$$\tilde{T}_g = \frac{\left(\sum_{i=1}^4 \frac{1}{2} \nu_i^C m_i n^i ((u + \varepsilon u_i^g)^2 - (u + \varepsilon f(u_g))^2) + \sum_{i=1}^4 \nu_i^C \frac{3}{2} k_B T_i^g + \nu_1^C \Delta E (\tilde{n}_1^g - n^1) \right)}{\frac{3}{2} k_B \sum_{i=1}^4 \nu_i^C n^i}. \quad (7.4)$$

In order to simplify (7.4) remark that

$$\begin{aligned} & \sum_{i=1}^4 \frac{1}{2} \nu_i^C m_i n^i ((u + \varepsilon u_i^g)^2 - (u + \varepsilon f(u_g))^2) \\ &= \sum_{i=1}^4 \nu_i^C m_i n^i (2\varepsilon u \cdot u_i^g - 2\varepsilon u \cdot f(u_g) + \varepsilon^2 u_i^{g2} - \varepsilon^2 f(u_g)^2) \\ &= 2\varepsilon u \cdot \left(\sum_{i=1}^4 \nu_i^C m_i n^i u_i^g - f(u_g) \sum_{i=1}^4 \nu_i^C m_i n^i \right) + \varepsilon^2 \sum_{i=1}^4 \nu_i^C m_i n^i (u_i^{g2} - f(u_g)^2) \\ &= \varepsilon^2 \sum_{i=1}^4 \nu_i^C m_i n^i (u_i^{g2} - f(u_g)^2) \end{aligned}$$

according to the definition of $f(u_g)$ (7.2). The relation (7.3) leads to

$$\begin{aligned} T_i^g &= \frac{m_i}{3k_B n^i} \left(\int_{\mathbb{R}^3} (\mathbf{v} - \mathbf{u})^2 \mathcal{M}_i(1 + \varepsilon g_i) d\mathbf{v} - 2\varepsilon u_i^g \cdot \int_{\mathbb{R}^3} (\mathbf{v} - \mathbf{u}) \mathcal{M}_i(1 + \varepsilon g_i) d\mathbf{v} \right. \\ &\quad \left. + \varepsilon^2 (u_i^g)^2 \int_{\mathbb{R}^3} \mathcal{M}_i(1 + \varepsilon g_i) d\mathbf{v} \right). \end{aligned}$$

Hence by setting

$$h_i^g = \frac{m_i}{3k_B n^i} \int_{\mathbb{R}^3} (\mathbf{v} - \mathbf{u})^2 \mathcal{M}_i g_i d\mathbf{v}, \quad (7.5)$$

it comes that

$$T_i^g = T + \varepsilon h_i^g - \frac{\varepsilon^2}{2k_B} (u_i^g)^2.$$

So

$$\frac{3}{2} k_B \sum_{i=1}^4 \nu_i^C n^i T_i^g = \frac{3}{2} k_B T \left(\sum_{i=1}^4 \nu_i^C n^i + \varepsilon \sum_{i=1}^4 \nu_i^C n^i h_i^g - \frac{\varepsilon^2}{3k_B} \sum_{i=1}^4 \nu_i^C n^i (u_i^g)^2 \right).$$

Finally, (7.4) leads to

$$\tilde{T}_g = T + \nu_1^C \frac{\Delta E(\tilde{n}_1^g - n^1)}{\frac{3}{2} k_B \sum_{i=1}^4 \nu_i^C n^i} + \varepsilon \bar{h}(\mathbf{g}) + \varepsilon^2 \bar{l}(\mathbf{g}), \quad (7.6)$$

with

$$\bar{h}(\mathbf{g}) = \frac{\sum_{i=1}^4 \nu_i^C n^i h_i^g}{\sum_{i=1}^4 \nu_i^C n^i},$$

$$\bar{l}(\mathbf{g}) = \frac{\sum_{i=1}^4 \nu_i^C n^i m_i ((u_i^g)^2 - (f(u_g))^2) - \frac{1}{2} \sum_{i=1}^4 \nu_i^C n^i m_i u_i^g}{\sum_{i=1}^4 \nu_i^C n^i}.$$

Next we aim to compute \tilde{n}_1^g . Let us write the implicit equation (4.23) in the following way

$$F(\varepsilon, \tilde{n}_1^g) = \xi(\tilde{n}_1^g) \exp\left(-\frac{\Delta E}{k_B(\tilde{T}_M(\tilde{n}_1^g) + \varepsilon \bar{h}(\mathbf{g}) + \varepsilon^2 \bar{l}(\mathbf{g}))}\right) - \left(\frac{m_{12}}{m_{34}}\right)^{\frac{3}{2}} = 0, \quad (7.7)$$

where

$$\xi(\tilde{n}_1^g) = \frac{\nu_3^C \nu_4^C \tilde{n}_1^g (\nu_2^C n^2 + \nu_1^C (\tilde{n}_1^g - n^1))}{\nu_2^C (\nu_3^C n^3 + \nu_1^C (\tilde{n}_1^g - n^1)) (\nu_4^C n^4 + \nu_1^C (\tilde{n}_1^g - n^1))}$$

and

$$\tilde{T}_M(\tilde{n}_1^g) = T + \nu_1^C \frac{\Delta E(\tilde{n}_1^g - n^1)}{\frac{3}{2} k_B \sum_{i=1}^4 \nu_i^C n^i}.$$

The computation of \tilde{n}_1^g is performed through the implicit function theorem at $\varepsilon = 0$. If $\varepsilon = 0$, $\tilde{n}_1^g = \tilde{n}_1$ and

$$F(0, \tilde{n}_1) = \xi(\tilde{n}_1) \exp\left(-\frac{\Delta E}{\tilde{T} k_B}\right) - \left(\frac{m_{12}}{m_{34}}\right)^{\frac{3}{2}} = 0. \quad (7.8)$$

So from (7.8) $\xi(\tilde{n}_1)$ reads

$$\xi(\tilde{n}_1) = \left(\frac{m_{34}}{m_{12}}\right)^{\frac{3}{2}} \exp\left(\frac{\Delta E}{\tilde{T} k_B}\right).$$

Then by using the implicit function theorem \tilde{n}_1^g can be expanded in ε .

$$\tilde{n}_1^g = \tilde{n}_1 + \varepsilon \frac{\frac{\partial}{\partial x} F(0, \tilde{n}_1)}{\frac{\partial}{\partial y} F(0, \tilde{n}_1)} + \mathcal{O}(\varepsilon^2).$$

From (7.7) it comes that

$$\begin{aligned}\frac{\partial}{\partial x} F(0, \tilde{n}_1) &= \xi(\tilde{n}_1) \frac{\Delta E \bar{h}(\mathbf{g})}{k_B \tilde{T}} \exp\left(-\frac{\Delta E}{k_B \tilde{T}}\right) \\ &= \left(\frac{m_{12}}{m_{34}}\right)^{\frac{3}{2}} \frac{\Delta E \bar{h}(\mathbf{g})}{k_B \tilde{T}^2} \exp\left(-\frac{\Delta E}{k_B \tilde{T}}\right)\end{aligned}$$

and

$$\frac{\partial}{\partial y} F(0, \tilde{n}_1) = \left(\xi'(\tilde{n}_1) + \xi(\tilde{n}_1) \frac{\nu_1 (\Delta E)^2}{\frac{3}{2} k_B^2 \tilde{T}^2 \sum_{i=1}^4 \nu_i^C n^i} \right) \exp\left(-\frac{\Delta E}{k_B \tilde{T}}\right).$$

Next by introducing $\tau(\tilde{n}_1)$ defined in (5.17), \tilde{n}_1^g writes $\tilde{n}_1^g = \tilde{n}_1 + \varepsilon \tau(\tilde{n}_1) \bar{h}(\mathbf{g}) + \mathcal{O}(\varepsilon^2)$. Hence according to (7.1) \tilde{n}_i^g satisfies for all $i \in \{2; 3; 4\}$ the relation (5.30). Moreover by plugging the expression of \tilde{n}_1^g into (7.6) it holds that \tilde{T}_g can be defined from relation (5.36)

Computation of $\bar{h}(\mathbf{g})$.

Firstly as

$$\begin{aligned}\int_{\mathbb{R}^3} (\mathbf{v} - \mathbf{u})(\mathbf{v} - \mathbf{u})^2 \mathcal{M}_i d\mathbf{v} &= 0, \quad \int_{\mathbb{R}^3} \mathbb{A}_i (\mathbf{v} - \mathbf{u})(\mathbf{v} - \mathbf{u})^2 \mathcal{M}_i d\mathbf{v} = 0, \\ \int_{\mathbb{R}^3} B_i (\mathbf{v} - \mathbf{u})(\mathbf{v} - \mathbf{u})^2 \mathcal{M}_i d\mathbf{v} &= 0,\end{aligned}$$

the mechanical part g_i^{ME} of g_i can be removed in (7.5) and h_i^g reduces to

$$h_i^g = \frac{m_i}{2k_B n^i} \int_{\mathbb{R}^3} \mathcal{M}_i (\mathbf{v} - \mathbf{u})^2 g_i^{CE} d\mathbf{v}.$$

That is

$$\begin{aligned}h_i^g &= \frac{m_i}{2\nu^M k_B n^i} \int_{\mathbb{R}^3} (\mathbf{v} - \mathbf{u})^2 \left(\nu_i^C (\tilde{\mathcal{M}}_i - \mathcal{M}_i) - \nu_i^C \mathcal{M}_i (\tilde{n}_i - n^i) \right. \\ &\quad \left. - \frac{\nu_1^{CE} \Delta E}{3n k_B^2 T^2} (\tilde{n}_1 - n^1) \left(\frac{1}{2} m_i (\mathbf{v} - \mathbf{u})^2 - \frac{3}{2} k_B T \right) \right) \mathcal{M}_i d\mathbf{v} \\ &= \frac{3\nu_i^C m_i}{2\nu^M n^i} \tilde{n}_i (\tilde{T}_M(\tilde{n}_1) - T) - \frac{\nu_i^C}{\nu^M n k_B} \Delta E (\tilde{n}_1 - n^1) \\ &= \frac{\nu_i^C}{\nu^M k_B} \Delta E (\tilde{n}_1 - n^1) \left(\frac{\nu_1^C}{\sum \nu_i^C n^i} - \frac{1}{n} \right)\end{aligned}$$

where we have used (5.37) in the last equation. Finally we obtain

$$\bar{h}(\mathbf{g}) = \Delta E (\tilde{n}_1 - n^1) \frac{\sum_{i=1}^4 (\nu_i^C)^2 \rho_i}{\nu^M \sum_{i=1}^4 \nu_i^C n^i} \left(\frac{\nu_1^C}{\sum \nu_i^C n^i} - \frac{1}{n} \right).$$

□