An ES–BGK Model for the Kinetic Analysis of a Chemically Reacting Gas Mixture

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Abstract

The paper deals with a partial relaxation–time–approximation of a simple Boltzmann kinetic model for a slow bimolecular chemical reaction when the process is driven by mechanical collisions. The dominant operator is in fact approximated by an ellipsoidal BGK–operator, recently introduced in the literature, which ensures correct constitutive equations for the diffusion velocities in the inert gas. The hydrodynamic limit up to the fluid–dynamic reactive Navier–Stokes equations is worked out by a Chapman–Enskog asymptotic procedure. Results indicate that transport coefficients are not affected by the (slow) chemical reaction, but reactive effects are described by additional source terms (integrals of the chemical cross sections), vanishing at chemical equilibrium, which appear in the non–conservative balance equations for species densities and for temperature.

1   Introduction

As widely recognized, several important regimes of gas dynamics and allied fields are best described at a kinetic level, and the appropriate mathematical tool is the nonlinear Boltzmann equation [1, 2, 3]. The complexity of the relevant collision operator stimulated quite rapidly the introduction of simplified kinetic models, which are being commonly and quite successfully used, mainly for practical purposes. Among them, relaxation–time–approximation of BGK type [4, 5, 6] constitute probably the most popular, flexible, and reliable, though ancient, working tool. Despite ignoring the details of the actual microscopic collisions, they retain the most significant mathematical and physical features of the actual Boltzmann equation (conservation laws, collision equilibria, H-theorem), and for this reason they have been attracting increasing interest for applications. However, one

of the main shortcomings of the BGK approach, pointed out since the very beginning, is its incapability in reproducing the correct Boltzmann hydrodynamic regime in the asymptotic continuum limit. The asymptotic procedure provides consistently, in the hydrodynamic limit, Newton's law for viscous stress and Fourier law for heat flux, but it is impossible to fit simultaneously the correct values of viscosity coefficient and thermal conductivity, and so, as well known, the Prandtl number is incorrectly predicted.

On the other hand, one of the most needed and natural extension of the BGK approach concerns the modelling of more realistic scenarios, like mixture of different gases, polyatomic molecules, and possible occurrence of chemical reactions. Unfortunately, it is well known that quite severe difficulties arise when trying to apply the BGK strategy to a gas made up by different species. Breakdown of positivity for density or temperature fields, and/or of the indifferentiability principle, may easily take place [7, 8]. In this respect we may quote the simple and ingenious idea proposed in [9] in order to avoid previous shortcomings, which consists in resorting to a single BGK collision operator for each given species, accounting for collisions of that species with any other species. As regards reactive mixtures, a quite deep and rigorous mathematical investigation of Boltzmann kinetic approaches to chemical reactions in a gas has been performed in a recent past, and we may quote for instance the excellent book [10]. In this paper we shall stick for simplicity to the reactive kinetic Boltzmann model proposed in [11] for a reversible bimolecular reaction

$$A_1 + A_2 \rightleftharpoons A_3 + A_4, \tag{1}$$
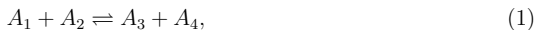
which was later generalized in [12] in order to account for the non–translational degrees of freedom of the participating molecules. Some reactive BGK models have been proposed indeed for the description of reaction (1) (see for instance [13, 14]), and, among them, we may quote [15, 16] (which follow the algorithm of [9] and are appropriate when the reaction is slow if compared to mechanical scattering), and [17] which, still in the line of [9], introduces a different algorithm well suited also for the case in which reactive and mechanical encounters are equally fast. All of the above BGK models for inert or reacting mixtures are affected by the previously mentioned shortcoming on the quantitative evaluation of transport coefficients.

Such crucial drawback has been overcome, in the basic case of mono–species and mono–atomic gas, by resorting to the so called ellipsoidal BGK (ES-BGK) model, introduced

first by Holway [18], which, in more recent times, has been cast in a consistent and elegant mathematical frame [19, 20]. Roughly speaking, the main idea consists in allowing some fundamental power moments of the distribution function to relax to its equilibrium value at a different (faster) rate than the distribution function itself, and to add this constraint to the other physical requirements imposed to the model (such as conservation of mass, momentum, energy and dissipation of entropy). Introducing then a second relaxation parameter quantifying the vanishing of viscous stress allows to fit quantitatively, via Chapman–Enskog expansion, both viscosity and thermal conductivity, and to reproduce correctly any given Prandtl number. The strategy can be extended to polyatomic gases [21], in which case the further constraint of equalization of translational and internal temperatures yields finally also a correct value for the bulk viscosity.

A substantial breakthrough towards the extension of the ES–BGK philosophy to gas mixtures has been performed very recently in [22]. The task is quite formidable, since now several transport coefficients are involved, pertinent to the Fick law for diffusion velocities, and to the Soret and Dufour effects, which show up in addition to the usual Newton and Fourier laws for viscous stress and heat flux, respectively [23]. The very clever procedure devised in [22] amounts to imposing equalization of the N species velocities, which introduces $N - 1$ independent relaxation parameters in addition to the standard collision frequency of the model. These parameters are cast in a one–to–one relationship with the $N - 1$ nonzero eigenvalues of the exact Fick matrix of the considered gas, in such a way that constitutive equations for diffusion velocities are correctly recovered by the proposed model. All necessary positivity and consistency requirements, under suitable restrictions on parameters, can be guaranteed, and the additional relaxation coefficient may be used to fit, for instance, Newton's law for viscosity.

Of course, the ES–BGK model in [22] can reproduce only qualitatively Soret, Fourier, and Dufour laws which make up the whole set of fluid–dynamic Navier–Stokes equations governing the gas mixture. More relaxation constraints, and then more free parameters, would be needed for that, but it is easily realized that one is very likely to run into breakdown of obvious physical requirements, like positivity. The point deserves certainly attention and investigation, as well as other issues of physical relevance, like consideration of polyatomic molecules and/or of possible chemical reactions among species. It is just this last problem that will be addressed here, with reference to a quaternary mixture

($N = 4$) in which reaction (1) takes place. For the Boltzmann scenario characterizing this reactive case the interested reader is referred to [11], and, as regards standard BGK approximations, to [17, 16]. However, main results will be summarized in the next Section for the readers' convenience, before proceeding with the task of putting together the inert ES–BGK modelling available so far and the reactive Boltzmann kinetic operator, aiming mainly at investigating preliminarily the chemical effects on the resulting reaction–diffusion Navier–Stokes equations. For simplicity reasons, the analysis will be confined to the case of slow chemistry, in which the process is dominated by mechanical elastic scattering, and the longer chemical characteristic time is comparable to the macroscopic scale. Other scalings will be hopefully matter of future research, as well as other points, including a rigorous treatment of the present (only formal) approach. The complete ES–BGK approximation will be presented in the next Section, together with the scaling and the relevant constraints. In the following Section the full asymptotic Chapman–Enskog expansion will be performed up to the Navier–Stokes fluid–dynamic level, emphasizing the chemical corrections with respect to the non–reacting frame. The final Section summarizes results and comments.

2 The ES–BGK model with chemical reaction

The kinetic Boltzmann equations governing the evolution of the distribution functions in the considered mixture read as (∇ standing for spatial gradient)

$$\frac{\partial f_i}{\partial t} + \mathbf{v} \cdot \nabla f_i = Q_i^{ME} + Q_i^{CH} \equiv Q_i \qquad i = 1, \ldots, 4 \tag{2}$$

where the mechanical and chemical collision integrals can be found elsewhere [12], and the crucial properties of the whole collision operator may be summarized as follows. Seven conservation laws hold for pair combinations of densities, for momentum, and for total (thermal plus chemical) energy

$$\int (Q_i + Q_j) \, d\mathbf{v} = 0, \qquad (i,j) = (1,3), (1,4), (2,4),$$

$$\sum_{i=1}^{4} \int m_i \mathbf{v} Q_i \, d\mathbf{v} = 0, \qquad \sum_{i=1}^{4} \int \left(\frac{1}{2} m_i v^2 + E_i \right) Q_i \, d\mathbf{v} = 0, \tag{3}$$

where $v = |\mathbf{v}|$ and E_i is the i–th energy of chemical bond. Collision equilibria are determined as a seven parameter family of local Maxwellians

$$M_i(\mathbf{v}) = n_i \left(\frac{m_i}{2\pi KT} \right)^{3/2} \exp \left(-\frac{m_i}{2KT} (\mathbf{v} - \mathbf{u})^2 \right) \qquad i = 1, \ldots, 4 \tag{4}$$

at a common mass velocity $\mathbf{u}$ and temperature T, with number densities related by the mass action law

$$\frac{n_1 n_2}{n_3 n_4} = \left(\frac{m_1 m_2}{m_3 m_4}\right)^{3/2} \exp\left(\frac{\Delta E}{KT}\right) \tag{5}$$

where K is the Boltzmann constant and the energy jump ΔE is defined as $-\sum_{i=1}^{4} \Lambda_i E_i$, where $\underline{\Lambda}$ is the string of stoichiometric coefficients $(1, 1, -1, -1)$. The kinetic model fulfils an H–theorem with respect to equilibrium (4) in terms of the entropy functional

$$H = \sum_{i=1}^{4} \int f_i \log \left(f_i/m_i^3\right) d\mathbf{v} \tag{6}$$

which is minimized by (4), and decreases monotonically along phase trajectories. The macroscopic fields for each species (including mass density ρ_i, pressure tensor $\mathbf{P}_i$ and heat flux $\mathbf{q}_i$) are defined in the standard way, and the corresponding quantities for the mixture follow as

$$n = \sum_{i=1}^{4} n_i, \qquad \rho = \sum_{i=1}^{4} \rho_i, \qquad \mathbf{u} = \frac{1}{\rho}\sum_{i=1}^{4} \rho_i \mathbf{u}_i,$$

$$nKT = \sum_{i=1}^{4} n_i KT_i + \frac{1}{3}\sum_{i=1}^{4} \rho_i(\mathbf{u}_i - \mathbf{u})^2,$$

$$\mathbf{P} = \sum_{i=1}^{4} \mathbf{P}_i + \sum_{i=1}^{4} \rho_i(\mathbf{u}_i - \mathbf{u}) \otimes (\mathbf{u}_i - \mathbf{u}), \tag{7}$$

$$\mathbf{q} = \sum_{i=1}^{4} \mathbf{q}_i + \sum_{i=1}^{4} \mathbf{P}_i \cdot (\mathbf{u}_i - \mathbf{u}) + \sum_{i=1}^{4} \frac{3}{2} n_i KT_i(\mathbf{u}_i - \mathbf{u})$$

$$+ \sum_{i=1}^{4} \frac{1}{2}\rho_i(\mathbf{u}_i - \mathbf{u})(\mathbf{u}_i - \mathbf{u})^2.$$

We consider here an ES–BGK model in which the actual Boltzmann collision operator Q_i^{ME} is replaced by a relaxation term $\hat{Q}_i^{ME}$, in physical regimes in which chemical reaction is a slow process, so that we shall write

$$\frac{\partial f_i}{\partial t} + \mathbf{v} \cdot \nabla f_i = \frac{1}{\epsilon}\hat{Q}_i^{ME} + Q_i^{CH} \qquad i = 1, \ldots, 4 \tag{8}$$

where ϵ is the small scaling parameter, representing the ratio between the mechanical and the chemical (or macroscopic) scales, making (8) a singular perturbation problem. The mechanical relaxation operator, as discussed in the Introduction, will be taken of the type

$$\hat{Q}_i^{ME} = \nu(G_i - f_i) \qquad i = 1, \ldots, 4 \tag{9}$$

with ν as a $\mathbf{v}$–independent collision frequency (inverse relaxation time), and where G_i is the attractor, that would coincide with equilibrium (4) in the standard BGK model, but is constructed here according to the algorithm of [22]. Precisely, the G_i are provided by the family of Gaussian functions

$$G_i(\mathbf{v}) = n_i \left(\frac{m_i}{2\pi K T^*}\right)^{\frac{3}{2}} \exp\left[-\frac{m_i}{2KT^*}(\mathbf{v} - \mathbf{u}_i^G)^2\right], \qquad i = 1,\ldots,4 \qquad (10)$$

which minimize the standard mechanical entropy

$$H_0 = \sum_{i=1}^{4} \int f_i \log f_i d\mathbf{v} \qquad (11)$$

in a suitable class of admissible distribution functions for which the relaxation operator (9) fulfils the standard mechanical conservation laws (densities of each species, momentum, thermal energy), plus the additional constraints that species velocities relax to mass velocity at paces given by three suitable inverse relaxation times $\lambda_1, \lambda_2, \lambda_3$, and that species temperatures are equal to each other. Referring to [22] for technical details, we simply mention here that macroscopic parameters relevant to the distribution function $\underline{G} = (G_1, G_2, G_3, G_4)$, labelled by a G superscript, may be cast in terms of the actual macroscopic parameters relevant to the distribution function $\underline{f}$ by means of the relaxation coefficients λ_k, with in particular $n^G = n$, $\rho^G = \rho$, $\mathbf{u}^G = \mathbf{u}$, $T^G = T$, and

$$\mathbf{u}_i^G - \mathbf{u} = \sum_{j=1}^{4} A_{ij}(\mathbf{u}_j - \mathbf{u}) \qquad i = 1,\ldots,4 \qquad (12)$$

where the matrix A_{ij} is given in [22] (see equation (35)), and is not repeated here for brevity. In addition we have

$$T^* = T - \frac{1}{3nK}\sum_{i=1}^{4}\rho_i(\mathbf{u}_i^G - \mathbf{u})^2, \qquad (13)$$

which completes the definition of the attractor $\underline{G}$. The parameters λ_k appearing in A_{ij} are determined by the three nonzero eigenvalues of the Fick matrix and, under a meaningful assumption on them, it is possible to prove [22] a contractive property for the matrix, yielding

$$\sum_{i=1}^{4}\rho_i(\mathbf{u}_i^G - \mathbf{u})^2 < \sum_{i=1}^{4}\rho_i(\mathbf{u}_i - \mathbf{u})^2. \qquad (14)$$

Since $T_i^G = T^*$ and $T^G = T$, on using the temperature equation in (7) and resorting to (14), one ends up with

$$T^* > \frac{1}{n}\sum_{i=1}^{4} n_i T_i \qquad (15)$$

which ensures the positivity requested to this temperature field.

As regards the reactive operator Q_i^{CH}, we shall stick to the kinetic Boltzmann model proposed in [11, 12], which fulfils the correct reactive conservation equations (3), and drives distribution functions towards an equilibrium (4) characterized by the mass action law (5). It reads, for $i = 1, \ldots, 4$, as a five-fold integral ($\mathbf{w} \in \mathbb{R}^3$, $\hat{\mathbf{\Omega}}' \in \mathbb{S}^2$)

$$Q_i^{CH} = \iint U(g^2 - \delta_{ij}^{hk}) B_{ij}^{hk}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') \left[\left(\frac{\mu_{ij}}{\mu_{hk}} \right)^3 f_h(\mathbf{v}_{ij}^{hk}) f_k(\mathbf{w}_{ij}^{hk}) - f_i(\mathbf{v}) f_j(\mathbf{w}) \right] d\mathbf{w} d\hat{\mathbf{\Omega}}' \quad (16)$$

where the i-th component is relevant to the event $(i, j) \to (h, k)$, and the allowed quadruplets are $(1, 2, 3, 4)$, $(2, 1, 4, 3)$, $(3, 4, 1, 2)$, $(4, 3, 2, 1)$. With $\Delta E_{ij}^{hk} = E_h + E_k - E_i - E_j$, $\mu_{ij} = m_i m_j / (m_i + m_j)$ standing for reduced mass, $\alpha_{ij} = \mu_{ij}/m_j$ for mass ratio, we have set $\delta_{ij}^{hk} = 2\Delta E_{ij}^{hk}/\mu_{ij}$, $g = |\mathbf{v} - \mathbf{w}|$, $\hat{\mathbf{\Omega}} = (\mathbf{v} - \mathbf{w})/g$, and $B_{ij}^{hk} = g\sigma_{ij}^{hk}$, where σ_{ij}^{hk} is the reactive differential cross section. The sign of δ_{ij}^{hk} determines a possibile threshold for the reaction, accounted for by the unit step function U; $\mathbf{v}_{ij}^{hk}$ and $\mathbf{w}_{ij}^{hk}$ are the post-collision velocities

$$\mathbf{v}_{ij}^{hk} = \alpha_{ij}\mathbf{v} + \alpha_{ji}\mathbf{w} + \alpha_{kh} g_{ij}^{hk} \hat{\mathbf{\Omega}}', \qquad \mathbf{w}_{ij}^{hk} = \alpha_{ij}\mathbf{v} + \alpha_{ji}\mathbf{w} - \alpha_{hk} g_{ij}^{hk} \hat{\mathbf{\Omega}}' \qquad (17)$$

and g_{ij}^{hk} is the post-collision relative speed

$$g_{ij}^{hk} = \left[\frac{\mu_{ij}}{\mu_{hk}} (g^2 - \delta_{ij}^{hk}) \right]^{1/2}. \qquad (18)$$

Moreover, we have used in (5) the notation ΔE for ΔE_{12}^{34}. In the ranges allowed for reaction, collision kernels B_{ij}^{hk} are related by the microreversibility condition

$$\mu_{ij}^2 \, g \, B_{ij}^{hk}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') = \mu_{hk}^2 \, g_{ij}^{hk} B_{hk}^{ij}(g_{ij}^{hk}, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') \qquad (19)$$

and the following Jacobian holds

$$d\mathbf{v}_{ij}^{hk} \, d\mathbf{w}_{ij}^{hk} \, d\hat{\mathbf{\Omega}} = \frac{\mu_{ij}}{\mu_{hk}} \frac{g_{ij}^{hk}}{g} d\mathbf{v} \, d\mathbf{w} \, d\hat{\mathbf{\Omega}}'. \qquad (20)$$

Taking a string of smooth test function φ_i, the weak form of the overall reactive operator reads as

$$\sum_{i=1}^{4} \int \varphi_i Q_i^{CH}(\mathbf{v}) d\mathbf{v} = -\iiint U(g^2 - \delta_{12}^{34}) B_{12}^{34}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') \left[\left(\frac{\mu_{12}}{\mu_{34}} \right)^3 f_3(\mathbf{v}_{12}^{34}) f_4(\mathbf{w}_{12}^{34}) \right. \qquad (21)$$

$$\left. - f_1(\mathbf{v}) f_2(\mathbf{w}) \right] \cdot \left[\varphi_3(\mathbf{v}_{12}^{34}) + \varphi_4(\mathbf{w}_{12}^{34}) - \varphi_1(\mathbf{v}) - \varphi_2(\mathbf{w}) \right] d\mathbf{v} d\mathbf{w} d\hat{\mathbf{\Omega}}'$$

where reference has been made to the event $(1,2) \to (3,4)$, and thus to the quadruplet $(1,2,3,4)$, but any other option, or combination of them, can be used, by simple permutation of indices. The interested reader is referred to [11, 12] or to the review [24] for more information and for technical details.

A complete analysis of mathematical and physical properties of the whole ES–BGK operator $\hat{\underline{Q}} = \frac{1}{\epsilon}\hat{\underline{Q}}^{ME} + \underline{Q}^{CH}$ is out of the purposes of the present work. However it is evident that it satisfies the correct conservation laws (3) of the Boltzmann equation. Also it is easy to verify that $\hat{\underline{Q}}$ vanishes if the f_i are the correct collision equilibria (4)–(5), since any distribution function of the form (4) is equilibrium for $\hat{\underline{Q}}^{ME}$, and also $\underline{Q}^{CH}$ vanishes if mass action law (5) additionally holds [12]. Finally, it is not difficult to check that an H–theorem holds in terms of the actual Boltzmann H–functional (6). In fact, the required minimum property of H, irrespective of the specific collision operator, was established in [12], and the negativity of $\dot{H}$ (Boltzmann lemma) follows easily from analogous pertinent results obtained in [22] and [12] for its mechanical and chemical parts, respectively.

In the sequel, we shall focus on the hydrodynamic limit of equations (8) for $\epsilon \to 0$ by performing a Chapman–Enskog asymptotic expansion up to the Navier–Stokes level. For such a purpose we need invariants and zeroes of the dominant operator $\hat{\underline{Q}}^{ME}$ alone, which are well known and coincide with those of $\underline{Q}^{ME}$. Weak forms to be closed are then represented by balance equations corresponding to the eight mechanically conserved macroscopic quantities (number density of each species, momentum vector, thermal energy), and are relevant to the "test functions" [22]

$$
\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}, \begin{pmatrix} m_1\mathbf{v} \\ m_2\mathbf{v} \\ m_3\mathbf{v} \\ m_4\mathbf{v} \end{pmatrix}, \begin{pmatrix} \frac{1}{2}m_1v^2 \\ \frac{1}{2}m_2v^2 \\ \frac{1}{2}m_3v^2 \\ \frac{1}{2}m_4v^2 \end{pmatrix}, \tag{22}
$$

while collision equilibria are provided by the 8–parameter family of Maxwellians (4) without any relationship among densities and temperature. Specifically, the set of exact macroscopic balance equations to be dealt with reads as

$$
\begin{cases}
\dfrac{\partial}{\partial t}(n_i) + \nabla \cdot (n_i\mathbf{u}_i) = \Lambda_i S & i = 1, \ldots, 4 \\[2mm]
\dfrac{\partial}{\partial t}(\rho\,\mathbf{u}) + \nabla \cdot (\rho\,\mathbf{u} \otimes \mathbf{u} + \mathbf{P}) = \mathbf{0} \\[2mm]
\dfrac{\partial}{\partial t}\left(\dfrac{1}{2}\rho\,u^2 + \dfrac{3}{2}nKT\right) + \nabla \cdot \left[\left(\dfrac{1}{2}\rho\,u^2 + \dfrac{3}{2}nKT\right)\mathbf{u} + \mathbf{P} \cdot \mathbf{u} + \mathbf{q}\right] = S\Delta E
\end{cases} \tag{23}
$$

where $S = S_1$ is defined by [12]

$$S_i = \int Q_i^{CH} \, d\mathbf{v}, \qquad S_i = \Lambda_i S \qquad (24)$$

and represents the net gain of molecules of type 1 by reaction. Inhomogeneous terms on the r.h.s. are in fact contributed by the slow collisions, and account for exchange of mass among species by chemical reaction, and for transfer between the thermal and the chemical forms of energy. Proper linear combinations would allow to recover the seven conservation equations (without reactive sources) holding for the whole problem, which are not written down here for brevity (see [12]).

Balance laws of the present type are indeed quite common in classical and extended thermodynamics for gas mixtures [25]. They are typically postulated from basic principles, even in a multi–temperature frame [26], rather than deduced from a kinetic level. In any case, the set (23) is not closed in the eight macroscopic fields n_1, n_2, n_3, n_4, $\mathbf{u}$, T because of the presence of the three independent diffusion velocities $\mathbf{u}_i - \mathbf{u}$, of the five independent components of the deviatoric part of the pressure tensor $\mathbf{P}$, of the heat flux vector $\mathbf{q}$, and of the reactive scalar unknown S. We shall search for constitutive equations for these extra fields, up to $O(\epsilon)$ terms, by expanding the kinetic unknowns as

$$f_i \equiv f_i^\epsilon = f_i^{(0)} + \epsilon f_i^{(1)} \qquad i = 1, \dots, 4 \qquad (25)$$

and plugging them into (8). It is clear that, to leading order, we get $\underline{\hat{Q}}_i^{ME(0)} = 0$, $i = 1, \dots, 4$, so that, as discussed above, the leading term in (25) is

$$f_i^{(0)} = M_i(\mathbf{v}) = n_i \left(\frac{m_i}{2\pi KT} \right)^{3/2} \exp\left(-\frac{m_i}{2KT}(\mathbf{v} - \mathbf{u})^2 \right) \qquad i = 1, \dots, 4, \qquad (26)$$

where hydrodynamic variables n_i, $\mathbf{u}$, T are unexpanded [2], and the same occurs then to ρ_i, n, ρ. Otherwise, (25) implies corresponding expansions

$$\mathbf{u}_i = \mathbf{u} + \epsilon \mathbf{u}_i^{(1)} \qquad T_i = T + \epsilon T_i^{(1)} \qquad S = S^{(0)} + \epsilon S^{(1)} \qquad (27)$$

with the constraints

$$\sum_{i=1}^{4} \rho_i \mathbf{u}_i^{(1)} = \mathbf{0}, \qquad \sum_{i=1}^{4} n_i T_i^{(1)} = 0. \qquad (28)$$

3   Hydrodynamic limit

Euler equations would correspond to retaining only $O(1)$ contributions, and so they differ from the standard inert Euler equations for a mixture only by the presence of reactive

source terms on the r.h.s., namely $S^{(0)}\Lambda_i$ in the i-th continuity equation, and $S^{(0)}\Delta E$ in the energy equation. Retaining only $O(1)$ terms in (24) leads to the integral representation

$$S^{(0)} = \left[\left(\frac{\mu_{12}}{\mu_{34}}\right)^{3/2} e^{\Delta E/KT}\frac{n_3 n_4}{n_1 n_2} - 1\right] \iint U\left(g^2 - \frac{2\Delta E}{\mu_{12}}\right) \bar{B}_{12}^{34}(g)\tilde{M}_1(\mathbf{v})\tilde{M}_2(\mathbf{w})\,d\mathbf{v}\,d\mathbf{w} \tag{29}$$

where

$$\bar{B}_{ij}^{hk}(g) = \int B_{ij}^{hk}(g, \hat{\boldsymbol{\Omega}}\cdot\hat{\boldsymbol{\Omega}}')\,d\hat{\boldsymbol{\Omega}}' \tag{30}$$

and $\tilde{M}_i(\mathbf{v}) = M_i(\mathbf{v} + \mathbf{u})$. The chemical source in the reactive Euler equations is then a kind of Gaussian average of the reactive collision kernel, that can be put in analytical closed form for some specialization of the collision model, with a multiplicative factor vanishing under mass action law.

Inserting (25) into (8) and ordering in powers of ϵ we get then

$$f_i^\epsilon = G_i[\underline{f}^\epsilon] - \frac{\epsilon}{\nu}\left(\frac{\partial M_i}{\partial t} + \mathbf{v}\cdot\nabla M_i\right) + \frac{\epsilon}{\nu}Q_i^{CH(0)} + O(\epsilon^2), \tag{31}$$

where $Q_i^{CH(0)}$ is the i-th reactive operator corresponding to the option $f_i = M_i$ for the distribution functions. A little algebra yields

$$Q_i^{CH(0)} = M_i(\mathbf{v})\left[\left(\frac{\mu_{ij}}{\mu_{hk}}\right)^{3/2}\exp\left(\frac{\Delta E_{ij}^{hk}}{KT}\right)\frac{n_h n_k}{n_i n_j} - 1\right]\chi_i(\mathbf{v}), \tag{32}$$

where

$$\chi_i(\mathbf{v}) = \int U\left(g^2 - \delta_{ij}^{hk}\right)\bar{B}_{ij}^{hk}(g)M_j(\mathbf{w})\,d\mathbf{w} \tag{33}$$

is a function accounting for the relevant collision kernel, which depends on $\mathbf{v}$ only via $|\mathbf{v} - \mathbf{u}|$, and is thus, like the Maxwellians M_i, isotropic in the peculiar velocity $\mathbf{c}$. Once more, all $Q_i^{CH(0)}$ vanish at chemical equilibrium, where mass action law (5) holds.

The derivatives of Maxwellians appearing in (31) may be performed by usual techniques and, according to the Chapman-Enskog procedure [1, 19], we use (23) themselves in order to eliminate time derivatives to leading order (Euler equations). We have

$$\frac{\partial n_i}{\partial t} = -\nabla\cdot(n_i\mathbf{u}) + \Lambda_i S^{(0)} + O(\epsilon)$$

$$\frac{\partial\mathbf{u}}{\partial t} = -\mathbf{u}\cdot\nabla\mathbf{u} - \frac{1}{\rho}\nabla(nKT) + O(\epsilon) \tag{34}$$

$$\frac{\partial T}{\partial t} = -\mathbf{u}\cdot\nabla T - \frac{2}{3}T\nabla\cdot\mathbf{u} + \frac{2\Delta E}{3Kn}S^{(0)} + O(\epsilon)$$

and the final result reads

$$
\frac{\partial M_i}{\partial t} + \mathbf{v} \cdot \nabla M_i = M_i \left[\frac{1}{n_i} \mathbf{c} \cdot \nabla n_i - \frac{m_i}{\rho} \mathbf{c} \cdot \nabla n + \frac{m_i}{KT} \left(c_s c_r - \frac{1}{3} c^2 \delta_{sr} \right) \frac{\partial u_s}{\partial x_r} \right.
$$
$$
+ \frac{1}{T} \mathbf{c} \cdot \nabla T \left(\frac{m_i c^2}{2KT} - \frac{3}{2} - \frac{m_i n}{\rho} \right) \Big] + M_i \left[\frac{\Lambda_i}{n_i} + \frac{2}{3} \frac{\Delta E}{KT} \left(\frac{m_i c^2}{2KT} - \frac{3}{2} \right) \frac{1}{n} \right] S^{(0)} + O(\epsilon) \tag{35}
$$

where Einstein convention on repeated indices s, r has been used. This contribution to $f_i^{(1)}$ in (31) may be then split into a mechanical part, typical of inert mixtures, and a reactive one, isotropic in $\mathbf{c}$, proportional to $S^{(0)}$ and thus vanishing at chemical equilibrium.

Expanding finally also G_i yields

$$
G_i[\underline{f}^\epsilon] = G_i^{(0)} + \epsilon G_i^{(1)} + O(\epsilon^2), \qquad G_i^{(0)} = G_i \mid_{\epsilon=0}, \qquad G_i^{(1)} = \frac{\partial G_i}{\partial \epsilon} \mid_{\epsilon=0} \tag{36}
$$

and an easy calculation, bearing (12) in mind, leads to

$$
G_i^{(0)} = M_i, \qquad G_i^{(1)} = M_i \frac{m_i}{KT} \mathbf{u}_i^{G(1)} \cdot (\mathbf{v} - \mathbf{u}) = M_i \frac{m_i}{KT} \mathbf{c} \cdot \sum_{j=1}^{4} A_{ij} \mathbf{u}_j^{(1)} \tag{37}
$$

with appearance of the velocity corrections $\mathbf{u}_i^{(1)}$, which are moments of the unknown $f_i^{(1)}$ themselves. Putting all expansions together and disregarding higher order terms we end up with

$$
f_i^{(1)} = f_{iME}^{(1)} + f_{iCH}^{(1)} = M_i(\psi_i^{ME} + \psi_i^{CH}) = M_i \psi_i
$$
$$
\psi_i^{ME} = \frac{m_i}{KT} \mathbf{c} \cdot \sum_{j=1}^{4} A_{ij} \mathbf{u}_j^{(1)} - \frac{1}{\nu} \left[\frac{1}{n_i} \mathbf{c} \cdot \nabla n_i - \frac{m_i}{\rho} \mathbf{c} \cdot \nabla n + \frac{m_i}{KT} \left(c_s c_r - \frac{1}{3} c^2 \delta_{sr} \right) \frac{\partial u_s}{\partial x_r} \right.
$$
$$
\left. + \frac{1}{T} \mathbf{c} \cdot \nabla T \left(\frac{m_i c^2}{2KT} - \frac{3}{2} - \frac{m_i n}{\rho} \right) \right] \tag{38}
$$
$$
\psi_i^{CH} = -\frac{S^{(0)}}{\nu} \left[\frac{\Lambda_i}{n_i} + \frac{2}{3} \frac{\Delta E}{KT} \left(\frac{m_i c^2}{2KT} - \frac{3}{2} \right) \frac{1}{n} \right] + \frac{\chi_i(\mathbf{v})}{\nu} \left[\left(\frac{\mu_{ij}}{\mu_{hk}} \right)^{3/2} \exp \left(\frac{\Delta E_{ij}^{hk}}{KT} \right) \frac{n_h n_k}{n_i n_j} - 1 \right]
$$

which is not explicit because of the presence of the $\mathbf{u}_i^{(1)}$, with

$$
\mathbf{u}_i^{(1)} = \frac{1}{n_i} \int \mathbf{v} f_i^{(1)} \, d\mathbf{v} = \frac{1}{n_i} \int \mathbf{c} f_i^{(1)} \, d\mathbf{c} \tag{39}
$$

(densities are unexpanded). Therefore, one has to take the weak form of (38) corresponding to the weight $\frac{1}{n_i} \mathbf{c}$ in order to compute all $\mathbf{u}_i^{(1)}$ from the resulting linear algebraic equations. In doing that, the contributions from $f_{iCH}^{(1)}$ all disappear, since they are isotropic functions of $\mathbf{c}$, so that one is left exactly with the same problem that would occur for the

inert mixture modelled according to the ES-BGK approximation [22]. We take then from that paper the final result, which, in our notation, reads as

$$\mathbf{u}_i^{(1)} = \sum_{j=1}^{4} F_{ij} \nabla n_j + D_i \nabla T \tag{40}$$

where F_{ij} is the Fick matrix (exact by this approach) and D_i accounts for thermal diffusion. By resorting to (40), the mechanical part of the first order corrections to distribution functions becomes explicitly

$$
\begin{aligned}
\psi_i^{ME} &= \frac{m_i}{KT} \mathbf{c} \cdot \sum_{j=1}^{4} \tilde{F}_{ij} \nabla n_j + \frac{m_i}{KT} \tilde{D}_i \mathbf{c} \cdot \nabla T - \frac{1}{\nu} \left[\frac{1}{n_i} \mathbf{c} \cdot \nabla n_i - \frac{m_i}{\rho} \mathbf{c} \cdot \nabla n \right. \\
&\quad + \frac{m_i}{KT} \left(c_s c_r - \frac{1}{3} c^2 \delta_{sr} \right) \frac{\partial u_s}{\partial x_r} + \frac{1}{T} \mathbf{c} \cdot \nabla T \left. \left(\frac{m_i c^2}{2KT} - \frac{3}{2} - \frac{m_i n}{\rho} \right) \right]
\end{aligned} \tag{41}
$$

where

$$\tilde{F}_{ij} = \sum_{k=1}^{4} A_{ik} F_{kj}, \qquad \tilde{D}_i = \sum_{j=1}^{4} A_{ij} D_j, \tag{42}$$

so that the $f_i^{(1)}$ are expressed, to leading order, in terms of hydrodynamic fields and of their space derivatives.

We are then ready to calculate all $O(\epsilon)$ corrections appearing in the exact balance equations (23), building up the sought reactive Navier-Stokes fluid-dynamic equations. An important remark is that, in the usual L_2 norm, $f_{iME}^{(1)}$ (given by (38) and (41)) is orthogonal to all test functions which are isotropic in $\mathbf{c}$, and conversely $f_{iCH}^{(1)}$ in (38) is actually isotropic in $\mathbf{c}$. In particular, as already observed, there is no chemical correction to species velocities, which remain the same as for the inert mixture. When looking instead for temperature corrections, no contribution arises from $f_{iME}^{(1)}$, since the test functions $\frac{1}{2} m_i c^2$ are isotropic (in fact, $T_i = T + O(\epsilon^2)$ in the non reactive case), whereas the reaction does contribute an $O(\epsilon)$ correction. Precisely, since

$$\epsilon \int \frac{1}{2} m_i c^2 f_i^{(1)} \, d\mathbf{v} = \frac{3}{2} n_i K (T_i - T) + O(\epsilon^2) = \epsilon \frac{3}{2} n_i K T_i^{(1)} + O(\epsilon^2), \tag{43}$$

we get from (38), again to leading order,

$$
\begin{aligned}
\frac{3}{2} n_i K T_i^{(1)} &= -\frac{S^{(0)}}{\nu} \left(\frac{3}{2} \Lambda_i KT + \frac{n_i}{n} \Delta E \right) + \frac{1}{\nu} \left[\left(\frac{\mu_{ij}}{\mu_{hk}} \right)^{3/2} \exp \left(\frac{\Delta E_{ij}^{hk}}{KT} \right) \frac{n_h n_k}{n_i n_j} - 1 \right] \\
&\quad \cdot \iint \frac{1}{2} m_i c^2 U \left(g^2 - \delta_{ij}^{hk} \right) \bar{B}_{ij}^{hk}(g) M_i(\mathbf{v}) M_j(\mathbf{w}) \, d\mathbf{v} d\mathbf{w}
\end{aligned} \tag{44}
$$

involving once more a weighted integration of the collision kernel, that could be made explicit for simple collision models (like Maxwell molecules). After suitable manipulations,

resorting repeatedly to (19), (20) and applying energy conservation in each encounter, it is possible to prove that

$$\sum_{i=1}^{4} \left[\left(\frac{\mu_{ij}}{\mu_{hk}} \right)^{3/2} \exp \left(\frac{\Delta E_{ij}^{hk}}{KT} \right) \frac{n_h n_k}{n_i n_j} - 1 \right]$$
$$\cdot \iint \frac{1}{2} m_i c^2 U \left(g^2 - \delta_{ij}^{hk} \right) \bar{B}_{ij}^{hk}(g) M_i(\mathbf{v}) M_j(\mathbf{w}) \, d\mathbf{v} d\mathbf{w} = S^{(0)} \Delta E \tag{45}$$

ensuring that

$$\sum_{i=1}^{4} n_i T_i^{(1)} = -\frac{S^{(0)} T}{\nu} \sum_{i=1}^{4} \Lambda_i - \frac{2\Delta E}{3K\nu} S^{(0)} \frac{1}{n} \sum_{i=1}^{4} n_i + \frac{2\Delta E}{3K\nu} S^{(0)} = 0 \tag{46}$$

in agreement with constraint (28).

A crucial term in the fluid-dynamic equations is the chemical source correction $S^{(1)}$ in (27). On using definition (24), expansion (25), expression (38), and neglecting higher order terms we have first

$$Q_i^{CH(1)} = M_i(\mathbf{v}) \iint U \left(g^2 - \delta_{ij}^{hk} \right) B_{ij}^{hk}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') M_j(\mathbf{w}) \tag{47}$$
$$\cdot \left\{ \left(\frac{\mu_{ij}}{\mu_{hk}} \right)^{3/2} \exp \left(\frac{\Delta E_{ij}^{hk}}{KT} \right) \frac{n_h n_k}{n_i n_j} \left[\psi_h(\mathbf{v}_{ij}^{hk}) + \psi_k(\mathbf{w}_{ij}^{hk}) \right] - \left[\psi_i(\mathbf{v}) + \psi_j(\mathbf{w}) \right] \right\} d\mathbf{w} d\hat{\mathbf{\Omega}}'$$

and then, resorting again to (19), (20)

$$S^{(1)} = \iint U \left(g^2 + \frac{2\Delta E}{\mu_{34}} \right) \bar{B}_{34}^{12}(g) \left[\psi_3(\mathbf{v}) + \psi_4(\mathbf{w}) \right] M_3(\mathbf{v}) M_4(\mathbf{w}) \, d\mathbf{v} d\mathbf{w}$$
$$- \iint U \left(g^2 - \frac{2\Delta E}{\mu_{12}} \right) \bar{B}_{12}^{34}(g) \left[\psi_1(\mathbf{v}) + \psi_2(\mathbf{w}) \right] M_1(\mathbf{v}) M_2(\mathbf{w}) \, d\mathbf{v} d\mathbf{w} \tag{48}$$

or, recalling (33) and setting $\tilde{\psi}_i(\mathbf{v}) = \psi_i(\mathbf{v} + \mathbf{u})$ and $\tilde{\chi}_i(\mathbf{v}) = \chi_i(\mathbf{v} + \mathbf{u})$

$$S^{(1)} = -\sum_{i=1}^{4} \Lambda_i R_i, \qquad R_i = \int \tilde{\psi}_i(\mathbf{v}) \tilde{\chi}_i(\mathbf{v}) \tilde{M}_i(\mathbf{v}) \, d\mathbf{v}. \tag{49}$$

It is important to notice that both $\tilde{\chi}_i$ and $\tilde{M}_i$ are isotropic functions of $\mathbf{v}$, and to recall that the addend $\tilde{\psi}_i^{ME}$ of $\tilde{\psi}_i$ vanishes when integrated against an isotropic function. This implies that there is no mechanical contribution to R_i (and to $S^{(1)}$), which is entirely made up by the reactive addend $\tilde{\psi}_i^{CH}$, namely

$$R_i = \int \tilde{\psi}_i^{CH}(\mathbf{v}) \tilde{\chi}_i(\mathbf{v}) \tilde{M}_i(\mathbf{v}) \, d\mathbf{v} \tag{50}$$

with

$$\tilde{\psi}_i^{CH}(\mathbf{v}) = -\frac{S^{(0)}}{\nu} \left[\frac{\Lambda_i}{n_i} + \frac{2}{3} \frac{\Delta E}{nKT} \left(\frac{m_i v^2}{2KT} - \frac{3}{2} \right) \right] + \frac{\tilde{\chi}_i(\mathbf{v})}{\nu} \left[\left(\frac{\mu_{ij}}{\mu_{hk}} \right)^{3/2} \exp \left(\frac{\Delta E_{ij}^{hk}}{KT} \right) \frac{n_h n_k}{n_i n_j} - 1 \right]$$
$$\tag{51}$$

and

$$\tilde{\chi}_i(\mathbf{v}) = \tilde{M}_j(\mathbf{v}) \frac{4\pi}{v} \frac{KT}{m_j} \int_0^{+\infty} U(g^2 - \delta_{ij}^{hk}) \bar{B}_{ij}^{hk}(g) \exp\left(-\frac{m_j g^2}{2KT}\right) \sinh\left(\frac{m_j}{KT} vg\right) g\, dg. \quad (52)$$

Notice that $\tilde{\psi}_i^{CH}$ vanishes at chemical equilibrium, since both $S^{(0)}$ and the square bracket in the second addend are equal to zero. The $O(\epsilon)$ contribution to the reaction rate S in (23) is then completely defined by (49)-(52), where again integrations involve the reactive collision kernels, and could be made explicit for suitable specialization of them.

The other constitutive equations needed for the closure of the set (23) of balance laws concern the diffusion velocities $\mathbf{u}_i - \mathbf{u}$, the viscous stress tensor $\mathbf{P} - nKT\mathbf{I}$, and the heat flux $\mathbf{q}$, which are all $O(\epsilon)$. We found already that diffusion velocities are the same as for the inert mixture, and are provided by (40). Indeed, the same happens to the other sought fields. In fact, they are merely moments of the distributions $f_i^{(1)}$ in (38) with test functions like $c_s c_r - \frac{1}{3} c^2 \delta_{sr}$ or $c_s c^2$, whose integral against an isotropic function of $\mathbf{c}$ is bound to vanish, as already observed. Since $f_i^{CH(1)}$ is indeed isotropic in the peculiar velocity, there is no contribution at all from the chemical reaction, neither to viscous stress nor to heat flux. All relevant transport coefficients are then the same as for the non reactive mixture, and so, in our scheme, Fick diffusion law, Newton law for viscosity, Fourier law for heat conduction, as well as Soret and Dufour effects, coincide with those of [22]. Reactive effects are confined to the chemical source $S = S^{(0)} + \epsilon S^{(1)}$, with $S^{(0)}$ given by (29) and $S^{(1)}$ by (49)-(52), which vanishes at chemical equilibrium, namely when (5) holds. The chemical reaction rate S depends of course on the reactive collision kernel B_{12}^{34} (related to its reciprocal B_{34}^{12} by (19)), and is expressed in terms of integrals of known functions. Some of these integrals can be put in closed analytical form for some simple collision model. Just as an example, if we take Maxwell-like interaction potential for the endothermic direction ($\bar{B}_{12}^{34} = $ constant, $\Delta E > 0$) we can write, in terms of error functions and incomplete Gamma functions,

$$S^{(0)} = \bar{B}_{12}^{34} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \frac{\Delta E}{KT}\right) \left[n_3 n_4 \left(\frac{\mu_{12}}{\mu_{34}}\right)^{3/2} e^{\Delta E/KT} - n_1 n_2 \right] \quad (53)$$

and, after some algebra, we have for instance for species 1

$$
T_1^{(1)} = -\frac{S^{(0)}}{\nu}\frac{1}{n_1}T - \frac{2}{3}\frac{S^{(0)}}{\nu}\frac{1}{n}\frac{\Delta E}{K} + \frac{\bar{B}_{12}^{34}}{\nu}\left[n_3 n_4\left(\frac{\mu_{12}}{\mu_{34}}\right)^{3/2}e^{\Delta E/KT} - n_1 n_2\right]
$$
$$
\cdot\frac{2}{\sqrt{\pi}}\left[\frac{2}{3}\alpha_{21}\Gamma\left(\frac{5}{2},\frac{\Delta E}{KT}\right) + \alpha_{12}\Gamma\left(\frac{3}{2},\frac{\Delta E}{KT}\right)\right]\frac{1}{n_1}T \tag{54}
$$

$$
\tilde{\chi}_1(\mathbf{v}) = \frac{1}{2\sqrt{\pi}}\bar{B}_{12}^{34}n_2\left\{\frac{\exp\left(-\frac{m_2}{2KT}(\sqrt{2\Delta E/\mu_{12}}-v)^2\right) - \exp\left(-\frac{m_2}{2KT}(\sqrt{2\Delta E/\mu_{12}}+v)^2\right)}{\sqrt{m_2/(2KT)}\,v}\right.
$$
$$
\left. +\sqrt{\pi}\,\mathrm{erfc}\left[\sqrt{\frac{m_2}{2KT}}\left(\sqrt{\frac{2\Delta E}{\mu_{12}}}-v\right)\right] + \sqrt{\pi}\,\mathrm{erfc}\left[\sqrt{\frac{m_2}{2KT}}\left(\sqrt{\frac{2\Delta E}{\mu_{12}}}+v\right)\right]\right\}.
$$

Simpler expressions are in order for Maxwellian molecules relevant to the exothermic direction ($\bar{B}_{12}^{34} = $ constant, $\Delta E < 0$)

$$
S^{(0)} = \bar{B}_{12}^{34}\left[n_3 n_4\left(\frac{\mu_{12}}{\mu_{34}}\right)^{3/2}e^{\Delta E/KT} - n_1 n_2\right]
$$
$$
T_1^{(1)} = -\frac{2}{3}\frac{S^{(0)}}{\nu}\frac{1}{n}\frac{\Delta E}{K}, \qquad \tilde{\chi}_1(\mathbf{v}) = \bar{B}_{12}^{34}n_2. \tag{55}
$$

Unfortunately, once B_{12}^{34} is assigned, B_{34}^{12} follows from (19), and takes typically a form leading to integrations of rational functionals and quadratic exponentials which are not amenable to standard transcendental or special functions. In other words, under any assumption on cross sections, one should expect that at least some of the integrals must be computed numerically.

4 Conclusions

We have examined the Navier–Stokes hydrodynamic limit of the reactive kinetic ES–BGK model equations (8), where the dominant mechanical operator is the ellipsoidal one recently proposed by Brull, Pavan, and Schneider in [22], and the slow chemical operator, according to the Boltzmann model introduced in [11], accounts additionally for exchange of mass and of energy of chemical link among species. Exact macroscopic equations for the eight hydrodynamic fields n_i ($i = 1, \ldots, 4$), $\mathbf{u}$, T are provided by the set (23) of eight reactive partial differential equations, where constitutive relations have been obtained for the extra fields $\mathbf{u}_i - \mathbf{u}$, $\mathbf{P} - nKT\mathbf{I}$, $\mathbf{q}$, and S, up to first order accuracy in the small parameter ϵ, yielding then a closed set of reaction diffusion equations. Chemical corrections to the inert scenario are confined to the reactive source terms on the r.h.s. of equations (23), all determined by the single scalar parameter $S = S^{(0)} + \epsilon S^{(1)}$. Fick matrix, viscosity, thermal

conductivity, as well as Soret and Dufour effects, are not affected by chemical reactions, and are the same as in [22]. This conclusion is in agreement with previous results from slow (standard) reactive BGK models [16], and at variance with conclusions drawn from fast reactive BGK models [17], where chemical microscopic parameters do affect transport coefficients, and reactions are further taken into account by an additional scalar pressure (not present here), rather than by inhomogeneous source terms. In particular, the present analysis shows that first order corrections to species temperatures (missing in the inert frame) actually arise in the presence of reactions, as given by (44). There are instead no chemical contributions to the mechanical first order corrections of species velocities. The dominant reactive contribution $S^{(0)}$ is given here in explicit form by equation (29). The first order correction $S^{(1)}$ to chemical sources is given by (49)-(52). Both of them are expressed in terms of integrals of the reactive collision kernels, with Maxwellian weights and other suitable weighting functions. Chemical collision kernels appear linearly in $S^{(0)}$ and quadratically in $S^{(1)}$, whereas mechanical macroscopic parameters do not affect these fluid-dynamic reaction rates. All chemical contributions vanish if mass action law (5) holds, namely at chemical equilibrium. A deeper analysis of the present results, and their extension to more realistic situations is scheduled as future work.

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