

Applications of Mathematics

Marzia Bisi; Maria Groppi; Giampiero Spiga
Fluid-dynamic equations for reacting gas mixtures

Applications of Mathematics, Vol. 50 (2005), No. 1, 43–62

Persistent URL: <http://dml.cz/dmlcz/134589>

Terms of use:

© Institute of Mathematics AS CR, 2005

Institute of Mathematics of the Czech Academy of Sciences provides access to digitized documents strictly for personal use. Each copy of any part of this document must contain these *Terms of use*.



This document has been digitized, optimized for electronic delivery and stamped with digital signature within the project *DML-CZ: The Czech Digital Mathematics Library* <http://dml.cz>

FLUID-DYNAMIC EQUATIONS FOR REACTING GAS MIXTURES*

MARZIA BISI, MARIA GROPPI, GIAMPIERO SPIGA, Parma

(Received March 26, 2003, in revised version September 9, 2003)

Abstract. Starting from the Grad 13-moment equations for a bimolecular chemical reaction, Navier-Stokes-type equations are derived by asymptotic procedure in the limit of small mean paths. Two physical situations of slow and fast reactions, with their different hydrodynamic variables and conservation equations, are considered separately, yielding different limiting results.

Keywords: kinetic theory, chemical reaction, Chapman-Enskog expansion

MSC 2000: 82C40, 76P05

1. INTRODUCTION

Mathematical modeling of multicomponent gaseous flows with chemical reactions in view of practical applications is a fundamental problem in scientific literature [1], [2]. Consideration of the kinetic equations [3], [4] is essential in order to properly account for the molecular aspects of the flows and to go deeper into the physical understanding of the process; moreover, kinetic equations represent also the starting point for a consistent derivation, via suitable expansion algorithms and closure strategies, of hydrodynamic equations at a macroscopic level [2], [4]. The task is quite formidable even in the absence of chemical reactions [5], [6], and is typically accomplished by an asymptotic procedure of Hilbert or Chapman-Enskog type with respect to the small parameter constituted by the Knudsen number, labeling the

*This work was performed in the frame of the activities sponsored by MIUR (Project “Mathematical Problems of Kinetic Theories”), by INdAM, by GNFM, by the University of Parma (Italy), and by the European TMR Network “Hyperbolic and Kinetic Equations: Asymptotics, Numerics, Analysis”.

importance of collision terms in collision dominated regimes [3], [7], [8]. The approach is rather cumbersome and requires the solution of linearized Boltzmann-like integral equations; results are available in general only in implicit or approximate forms [2], [5].

The present paper follows the kinetic scheme proposed in [9], [10] for the description of a simple bimolecular chemical reaction, assuming further that the typical relaxation time for mechanical encounters (elastic scattering) and/or the characteristic time relevant to chemical interactions are much shorter than the typical macroscopic times. In particular, we aim at pushing explicit analytical manipulations as far as possible in the Chapman-Enskog expansion, and therefore we confine ourselves to the so-called Maxwellian molecule approximation for all intermolecular potentials [4], [7], though in this way, as is well known, effects like thermal diffusion are neglected [3], [5]. In such a frame, some steps have been already done towards the derivation of a closed set of balance equations for the main macroscopic observables (moments of the distribution functions). It is desirable in fact to obtain a set of partial differential equations properly describing the bulk evolution of the reacting system after the fast initial transient dominated by collisions, which improves the simplest zero-order level represented by the reactive Euler equations, corresponding to the assumption of Maxwellian distribution for the unknown distribution functions. More precisely, a Grad 13-moment approximation [11] has been used in [12] for each of the four distribution functions involved in the bimolecular reaction, and it has been possible to express all mechanical and chemical collision integrals in terms of those moments, achieving thus a closed set of partial differential equations for the 52 unknown macroscopic fields. They include density, mean velocity, temperature, viscous stress, and heat flux for each species. The main features of such Grad's equations have been already discussed in [12]. They do retain collision terms, and it is remarkable that they reproduce the exact conservation equations as well as the correct collision equilibria (including the mass action law) of the kinetic level.

They can also be handled asymptotically by a Chapman-Enskog expansion in terms of suitable Knudsen number(s), and indeed such a task, leading hopefully to Navier-Stokes-type approximations, was mentioned but left for future work in [12]. This is what this paper is about, and it has to be considered as a preliminary step towards a general asymptotic analysis for an arbitrary interaction law, leading from the kinetic to the hydrodynamic level. Hydrodynamic variables are determined by the dominant operator driving the process, and quite different scenarios occur in different physical situations. In particular we shall examine here those which appear as most significant, namely the case of dominant elastic scattering only (slow chemical reaction), and the situation in which the dominant role is played by the whole collision term, namely by both the mechanical and chemical interactions. Our approach

is essentially formal, but it provides a foundation for further developments of the analysis (convergence and so on) that seem premature at this point and will be considered in future investigation.

Statement of the problem and governing equations are presented in Section 2. Then the quite heavy machinery of the Chapman-Enskog expansion (to first order) is applied separately to two cases of slow and fast chemical reaction in the next sections. The mathematical algorithm is different in the two cases, and even the number of independent variables changes from 8 to 7. In both cases, the correction terms obtained represent the sought constitutive equations and allow the desired hydrodynamic closure, even though some coefficients remain necessarily expressed only in implicit form.

2. GOVERNING EQUATIONS

We consider a mixture of four gases A^s , $s = 1, \dots, 4$ which, beside all elastic collisions, can interact according to the bimolecular chemical reaction



as described in [12], to which the reader is referred for details on the physical framework and on notation. Moments of the distribution functions which constitute the dependent variables in the Grad equations are number densities n^s , mean velocities u_i^s , temperatures T^s , viscous stresses p_{ij}^s , and heat fluxes q_i^s , for each species. Indexial notation for vectors and tensors and Einstein convention will be used throughout. Global quantities of major importance for the mixture are

$$\begin{aligned} n &= \sum_{s=1}^4 n^s && \text{total number density} \\ \varrho &= \sum_{s=1}^4 m^s n^s && \text{mass density} \\ u_i &= \frac{1}{\varrho} \sum_{s=1}^4 m^s n^s u_i^s && \text{mass velocity} \\ KT &= \frac{1}{n} \sum_{s=1}^4 n^s KT^s + \frac{1}{3n} \sum_{s=1}^4 \varrho^s (u_k^s u_k^s - u_k u_k) && \text{gas temperature} \\ p_{ij} &= \sum_{s=1}^4 p_{ij}^s + \sum_{s=1}^4 \varrho^s \left[(u_i^s u_j^s - u_i u_j) - \frac{1}{3} \delta_{ij} (u_k^s u_k^s - u_k u_k) \right] && \text{viscosity tensor} \end{aligned}$$

$$q_i = \sum_{s=1}^4 q_i^s + \sum_{s=1}^4 p_{ij}^s (u_j^s - u_j) + \frac{5}{2} \sum_{s=1}^4 n^s KT^s (u_i^s - u_i) \quad \text{thermal heat flux}$$

$$+ \frac{1}{2} \sum_{s=1}^4 \rho^s (u_k^s - u_k)(u_k^s - u_k)(u_i^s - u_i)$$

while the symbol P_{ij} will be adopted to label the pressure tensor $nKT\delta_{ij} + p_{ij}$, and U is used to denote the total internal energy density $\frac{3}{2}nKT + \sum_{s=1}^4 E^s n^s$ (thermal plus chemical).

We start from Grad's equations, which will be written here for Maxwellian molecules in dimensionless form by measuring all quantities in terms of characteristic values and by scaling time and space variables in terms of macroscopic units, with the Strouhal number assumed to be unity [4]. Their derivation from the kinetic level is explicitly given in [12]. The integro-differential nonlinear kinetic equations may be found in [10], where their properties are investigated in detail, and therefore are not repeated here for the sake of brevity. Two Knudsen numbers automatically appear, namely the ratios of the mechanical and of the chemical characteristic times, respectively, to the macroscopic one. It is not restrictive to write them as ε^p and ε^q , where ε is the chosen small parameter, and p and q are suitable non-negative integers. The equations to be dealt with read then as

$$(2a) \quad \frac{\partial n^s}{\partial t} + \frac{\partial(n^s u_i^s)}{\partial x_i} = \frac{1}{\varepsilon^q} Q^s,$$

$$(2b) \quad m^s n^s \left(\frac{\partial u_i^s}{\partial t} + u_j^s \frac{\partial u_i^s}{\partial x_j} \right) + \frac{\partial(n^s KT^s)}{\partial x_i} + \frac{\partial p_{ij}^s}{\partial x_j} = \frac{1}{\varepsilon^p} \mathcal{R}_i^s + \frac{1}{\varepsilon^q} R_i^s,$$

$$(2c) \quad \frac{3}{2} n^s \left(\frac{\partial(KT^s)}{\partial t} + u_i^s \frac{\partial(KT^s)}{\partial x_i} \right) + n^s KT^s \frac{\partial u_i^s}{\partial x_i} + p_{ij}^s \frac{\partial u_j^s}{\partial x_i} + \frac{\partial q_i^s}{\partial x_i}$$

$$= \frac{1}{\varepsilon^p} \mathcal{S}^s + \frac{1}{\varepsilon^q} \mathcal{S}^s,$$

$$(2d) \quad \frac{\partial p_{ij}^s}{\partial t} + \frac{\partial}{\partial x_k} (u_k^s p_{ij}^s) + p_{ik}^s \frac{\partial u_j^s}{\partial x_k} + p_{jk}^s \frac{\partial u_i^s}{\partial x_k} - \frac{2}{3} \delta_{ij} p_{kl}^s \frac{\partial u_l^s}{\partial x_k}$$

$$+ n^s KT^s \left(\frac{\partial u_i^s}{\partial x_j} + \frac{\partial u_j^s}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial u_k^s}{\partial x_k} \right) + \frac{2}{5} \left(\frac{\partial q_i^s}{\partial x_j} + \frac{\partial q_j^s}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial q_k^s}{\partial x_k} \right)$$

$$= \frac{1}{\varepsilon^p} \mathcal{V}_{ij}^s + \frac{1}{\varepsilon^q} V_{ij}^s,$$

$$\begin{aligned}
(2e) \quad & \frac{\partial q_i^s}{\partial t} + \frac{\partial}{\partial x_j} (u_j^s q_i^s) + \frac{7}{5} q_j^s \frac{\partial u_i^s}{\partial x_j} + \frac{2}{5} q_j^s \frac{\partial u_j^s}{\partial x_i} + \frac{2}{5} q_i^s \frac{\partial u_j^s}{\partial x_j} \\
& + \frac{5}{2} n^s K T^s \frac{\partial}{\partial x_i} \left(\frac{K T^s}{m^s} \right) + \frac{5}{2} p_{ij}^s \frac{\partial}{\partial x_j} \left(\frac{K T^s}{m^s} \right) \\
& + n^s K T^s \frac{\partial}{\partial x_j} \left(\frac{p_{ij}^s}{m^s n^s} \right) - \frac{p_{ij}^s}{m^s n^s} \frac{\partial p_{kj}^s}{\partial x_k} \\
& = \frac{1}{\varepsilon^p} \mathcal{W}_i^s + \frac{1}{\varepsilon^q} W_i^s
\end{aligned}$$

where the mechanical ‘‘collision terms’’ are given by

$$(3a) \quad \mathcal{R}_i^s = n^s \sum_{r=1}^4 \nu_1^{sr} \mu^{sr} n^r (u_i^r - u_i^s),$$

$$(3b) \quad \mathcal{S}^s = 2n^s \sum_{r=1}^4 \nu_1^{sr} \frac{\mu^{sr}}{m^s + m^r} n^r \left[\frac{3}{2} K (T^r - T^s) + \frac{1}{2} m^r (\mathbf{u}^r - \mathbf{u}^s)^2 \right],$$

$$\begin{aligned}
(3c) \quad \mathcal{V}_{ij}^s &= 2 \sum_{r=1}^4 \nu_1^{sr} \frac{\mu^{sr}}{m^s + m^r} \left\{ n^s p_{ij}^r - n^r p_{ij}^s + n^s n^r m^r \left[(u_i^r - u_i^s)(u_j^r - u_j^s) \right. \right. \\
& \left. \left. - \frac{1}{3} \delta_{ij} (\mathbf{u}^r - \mathbf{u}^s)^2 \right] \right\} - \frac{3}{2} \sum_{r=1}^4 \nu_2^{sr} \frac{m^r}{(m^s + m^r)^2} \left\{ m^s n^s p_{ij}^r + m^r n^r p_{ij}^s \right. \\
& \left. + m^s n^s m^r n^r \left[(u_i^r - u_i^s)(u_j^r - u_j^s) - \frac{1}{3} \delta_{ij} (\mathbf{u}^r - \mathbf{u}^s)^2 \right] \right\},
\end{aligned}$$

$$\begin{aligned}
(3d) \quad \mathcal{W}_i^s &= -\frac{5}{2} \frac{n^s}{m^s} K T^s \sum_{r=1}^4 \nu_1^{sr} \mu^{sr} n^r (u_i^r - u_i^s) \\
& - \frac{1}{m^s} p_{ij}^s \sum_{r=1}^4 \nu_1^{sr} \mu^{sr} n^r (u_j^r - u_j^s) \\
& + \sum_{r=1}^4 \frac{m^r n^r}{(m^s + m^r)^3} \left\{ \beta_1^{sr} q_i^s + \frac{m^s n^s}{m^r n^r} \beta_4^{sr} q_i^r \right. \\
& + (u_j^r - u_j^s) \left(\frac{1}{2} \beta_2^{sr} p_{ij}^s + \frac{m^s n^s}{m^r n^r} \beta_4^{sr} p_{ij}^r \right) \\
& + \frac{1}{2} (u_i^r - u_i^s) \left[(\beta_2^{sr} + 3\beta_3^{sr}) n^s K T^s \right. \\
& \left. \left. + 5 \frac{m^s n^s}{m^r n^r} \beta_4^{sr} n^r K T^r + m^s n^s \beta_4^{sr} (\mathbf{u}^r - \mathbf{u}^s)^2 \right] \right\}
\end{aligned}$$

and the chemical “collision terms” take the form

$$(4a) \quad Q^s = \lambda^s Q^1 = \lambda^s \left[n^3 n^4 \left(\frac{m^1 m^2}{m^3 m^4} \right)^{\frac{3}{2}} e^{\Delta E / KT} - n^1 n^2 \right] \nu_{12}^{34} \frac{2}{\sqrt{\pi}} \Gamma \left(\frac{3}{2}, \frac{\Delta E}{KT} \right),$$

$$(4b) \quad R_i^s = -\lambda^s m^s (u_i^s - u_i) Q^1,$$

$$(4c) \quad \mathcal{S}^s = \lambda^s Q^1 \left\{ \frac{3}{2} (KT) \frac{m^s}{M} - \frac{1}{2} (1 - \lambda^s) \Delta E \frac{M - m^s}{M} - \frac{3}{2} (KT^s) \right. \\ \left. + \frac{1}{2} m^s (\mathbf{u}^s - \mathbf{u})^2 + (KT) \frac{M - m^s}{M}, \Gamma \left(\frac{5}{2}, \frac{\Delta E}{KT} \right) \left[\Gamma \left(\frac{3}{2}, \frac{\Delta E}{KT} \right) \right]^{-1} \right\},$$

$$(4d) \quad V_{ij}^s = \lambda^s m^s Q^1 \left[(u_i^s - u_i)(u_j^s - u_j) - \frac{1}{3} \delta_{ij} (\mathbf{u}^s - \mathbf{u})^2 \right],$$

$$(4e) \quad W_i^s = \lambda^s Q^1 \left\{ -\frac{5}{2} (u_i^s - u_i) (KT) \frac{m^s}{M} \right. \\ \left. + \frac{5}{6} (1 - \lambda^s) (u_i^s - u_i) \Delta E \frac{M - m^s}{M} \right. \\ \left. + \frac{5}{2} (KT^s) (u_i^s - u_i) + \frac{p_{ij}^s}{n^s} (u_j^s - u_j) - \frac{1}{2} m^s (u_i^s - u_i) (\mathbf{u}^s - \mathbf{u})^2 \right. \\ \left. - \frac{5}{3} (u_i^s - u_i) (KT) \frac{M - m^s}{M} \Gamma \left(\frac{5}{2}, \frac{\Delta E}{KT} \right) \left[\Gamma \left(\frac{3}{2}, \frac{\Delta E}{KT} \right) \right]^{-1} \right\}.$$

Here $\lambda^1 = \lambda^2 = -\lambda^3 = -\lambda^4 = 1$, and $\Delta E = E^3 + E^4 - E^1 - E^2 > 0$ represents the energy absorbed (released) in the direct (reverse) reaction (1) due to the chemical bonds. For the other symbols, μ^{sr} is the reduced mass for an (s, r) encounter, ν_{12}^{34} the microscopic, angle integrated, collision frequency for the direct chemical reaction (constant in our hypothesis [12]), while ν_1^{sr} and ν_2^{sr} denote the angular moments of the microscopic collision frequency for elastic scattering between species s and r . In general, they would depend on the relative molecular speed g via the general expressions involving the cross section σ^{sr} :

$$(5) \quad \nu_k^{sr}(g) = 2\pi \int_0^\pi g \sigma^{sr}(g, \chi) (1 - \cos^k \chi) \sin \chi d\chi, \quad k = 1, 2$$

where χ is the deflection angle. In our Maxwell molecule approximation, they turn out to be constant due to the $1/g$ dependence of σ^{sr} [4]. Finally, the coefficients β_k^{sr}

are linear combinations of ν_1^{sr} and ν_2^{sr} [12]:

$$(6) \quad \begin{aligned} \beta_1^{sr} &= -\{[3(m^s)^2 + (m^r)^2]\nu_1^{sr} + 2m^s m^r \nu_2^{sr}\}, \\ \beta_2^{sr} &= 2(m^s - m^r)^2 \nu_1^{sr} + m^r(m^s - 3m^r)\nu_2^{sr}, \\ \beta_3^{sr} &= (m^s - m^r)^2 \nu_1^{sr} + m^r(3m^s + m^r)\nu_2^{sr}, \\ \beta_4^{sr} &= 2(m^r)^2[2\nu_1^{sr} - \nu_2^{sr}], \end{aligned}$$

Γ stands for the incomplete gamma function [13] and $M = m^1 + m^2 = m^3 + m^4$ (mass conservation). Of course, only five independent pairs of indices need to be considered in the equations for p_{ij}^s , since the deviatoric part of the pressure tensor is symmetric and trackless.

The above set of partial differential equations is the starting point of the analysis to be developed in the present article. The appearance is quite cumbersome, and the interested reader should consult again [12] for more detail. However, proper combinations of Eqs. (2) allow us to get rid of the complicated collision terms (3) and (4) and to obtain seven scalar conservation equations

$$(7) \quad \begin{aligned} \frac{\partial}{\partial t}(n^1 + n^3) + \frac{\partial}{\partial \mathbf{x}} \cdot (n^1 \mathbf{u}^1 + n^3 \mathbf{u}^3) &= 0, \\ \frac{\partial}{\partial t}(n^1 + n^4) + \frac{\partial}{\partial \mathbf{x}} \cdot (n^1 \mathbf{u}^1 + n^4 \mathbf{u}^4) &= 0, \\ \frac{\partial}{\partial t}(n^2 + n^4) + \frac{\partial}{\partial \mathbf{x}} \cdot (n^2 \mathbf{u}^2 + n^4 \mathbf{u}^4) &= 0, \\ \frac{\partial}{\partial t}(\rho \mathbf{u}) + \frac{\partial}{\partial \mathbf{x}} \cdot (\rho \mathbf{u} \otimes \mathbf{u} + \mathbf{P}) &= \mathbf{0}, \\ \frac{\partial}{\partial t} \left(\frac{1}{2} \rho u^2 + \frac{3}{2} n K T + \sum_{s=1}^4 E^s n^s \right) \\ + \frac{\partial}{\partial \mathbf{x}} \cdot \left[\left(\frac{1}{2} \rho u^2 + \frac{3}{2} n K T + \sum_{s=1}^4 E^s n^s \right) \mathbf{u} + \mathbf{P} \cdot \mathbf{u} + \mathbf{q} + \sum_{s=1}^4 E^s n^s (\mathbf{u}^s - \mathbf{u}) \right] &= 0 \end{aligned}$$

accounting for conservation of particles in species 1+3, 1+4, 2+4, of momentum, and of total energy. These equations are indeed exact in the sense that the conserved quantities correspond to the seven collision invariants which are in order for the Boltzmann-like equations governing the problem [10]. As a byproduct they also provide the continuity equation

$$(8) \quad \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i}(\rho u_i) = 0.$$

Below, we shall perform an asymptotic Chapman-Enskog analysis of Eqs. (2) versus the small parameter ε . The cases of upmost physical relevance correspond, as discussed in Introduction, to slow or fast chemical reactions in a collision dominated regime. They may be represented by options of parameters $p = 1$ and $q = 0$, and $p = 1$ and $q = 1$, respectively, so that ε bears the meaning of an actual Knudsen number. In both cases all unknowns will be expanded to the first order:

$$(9) \quad n^s = n^{s(0)} + \varepsilon n^{s(1)}, \quad u_i^s = u_i^{s(0)} + \varepsilon u_i^{s(1)}, \quad T^s = T^{s(0)} + \varepsilon T^{s(1)}, \\ p_{ij}^s = p_{ij}^{s(0)} + \varepsilon p_{ij}^{s(1)}, \quad q_i^s = q_i^{s(0)} + \varepsilon q_i^{s(1)}$$

with the constraints which are implied by the Chapman-Enskog procedure [4]. We aim thus at determining constitutive equations of Newton type and correspondingly the Navier-Stokes-like fluid-dynamic equations.

3. SLOW CHEMICAL REACTION

In the case $p = 1, q = 0$, the process is driven by elastic scattering, and the kernel of the relevant collision operator is made up by 8 collision invariants [10], which correspond to the quantities which are conserved under such mechanical encounters, namely the number of each species, the momentum, and the thermal energy. Of course other conservations follow from the previous ones, like for instance the total number of particles, the total mass, the total internal energy. However, hydrodynamic variables are in number of eight, and they can be chosen as the four number densities n^s , the three components of the mass velocity vector u_i , and the gas temperature T . Correspondingly, the “conservation” equations to be considered in the asymptotic algorithm follow from the weak forms of the Boltzmann equations, relevant to the same collision invariants, taken as test functions. Therefore [10], the first four of such equations coincide exactly with the Grad equations (2a), the next three are nothing but the momentum equation, and the last one is easily seen [12] to be an equivalent form of the last equation in (7):

$$(10) \quad \frac{\partial n^s}{\partial t} + \frac{\partial(n^s u_i^s)}{\partial x_i} = \lambda^s Q^1, \\ \frac{\partial}{\partial t}(\rho \mathbf{u}) + \frac{\partial}{\partial \mathbf{x}} \cdot (\rho \mathbf{u} \otimes \mathbf{u} + \mathbf{P}) = \mathbf{0}, \\ \frac{\partial}{\partial t} \left(\frac{1}{2} \rho u^2 + \frac{3}{2} nKT \right) + \frac{\partial}{\partial \mathbf{x}} \cdot \left[\left(\frac{1}{2} \rho u^2 + \frac{3}{2} nKT \right) \mathbf{u} + \mathbf{P} \cdot \mathbf{u} + \mathbf{q} \right] = Q^1 \Delta E.$$

It is not surprising that these equations contain chemical terms, since elastic collision invariants are not necessarily conserved in the chemical reaction, so that chemical

collision integrals contribute terms in these balance equations, like streaming, the other slow process.

At this point, all hydrodynamic quantities are left unexpanded [4] so that $n^{s(1)} = 0$ and $n^{s(0)} = n^s$ in (9), whereas u_i^s and T^s are actually expanded, but must produce unexpanded u_i and T , which yields the constraints

$$(11) \quad \sum_{s=1}^4 \varrho^s u_i^{s(1)} = 0, \quad \sum_{s=1}^4 n^s K T^{s(1)} + \frac{2}{3} \sum_{s=1}^4 \varrho^s u_k^{s(0)} u_k^{s(1)} = 0.$$

With $p = 1$ and $q = 0$, Eqs. (2) to leading order read

$$(12) \quad \mathcal{R}_i^{s(0)} = 0, \quad \mathcal{S}^{s(0)} = 0, \quad \mathcal{V}_{ij}^{s(0)} = 0, \quad \mathcal{W}_i^{s(0)} = 0.$$

The first is a linear algebraic equation of the form $\underline{\Phi} \cdot \underline{\mathbf{u}}_i^{(0)} = \mathbf{0}$, where $\underline{\mathbf{u}}_i^{(0)}$ is the four dimensional vector of $u_i^{s(0)}$, and the matrix elements of $\underline{\Phi}$ read

$$(13) \quad \Phi^{sr} = \nu_1^{sr} \mu^{sr} n^s n^r - \delta^{sr} \sum_{l=1}^4 \nu_1^{sl} \mu^{sl} n^s n^l.$$

The matrix is singular, since each diagonal term is exactly the opposite of the sum of the non-diagonal entries of the same column, and hence allows a non-zero solution. There are indeed ∞^1 solutions, provided by $u_i^{r(0)} = u_i^{s(0)} \forall s, r$ (all equal component vectors), as discussed in [12], since the rank of $\underline{\Phi}$ is equal to 3, due to the fact that the matrix made up by the first three rows and columns is strictly diagonally dominant, and hence its determinant is different from zero. At this point, the definition of mass velocity and the first of constraints (11) imply that the common value of all $u_i^{s(0)}$ must coincide with the (as yet unknown) value of u_i . The second of (12) turns out to be an algebraic equation of the same kind, with a matrix $\underline{\Psi}$ given by

$$(14) \quad \Psi^{sr} = 3K \nu_1^{sr} \frac{\mu^{sr}}{m^s + m^r} n^s n^r - \delta^{sr} 3K \sum_{l=1}^4 \nu_1^{sl} \frac{\mu^{sl}}{m^s + m^l} n^s n^l,$$

showing the same crucial property of $\underline{\Phi}$. Therefore this algebraic equation provides the analogous result $T^{s(0)} = T^{r(0)} \forall s, r$, which, combined with (11) and the definition of gas temperature, yields $T^{s(0)} = T \forall s$. At the next step, the third of (12) is a linear algebraic equation of the form $\underline{\Upsilon} \cdot \underline{\mathbf{p}}_{ij}^{(0)} = \mathbf{0}$, where $\underline{\mathbf{p}}_{ij}^{(0)}$ is the vector of the $p_{ij}^{s(0)}$ and $\underline{\Upsilon}$ is defined by

$$(15) \quad \Upsilon^{sr} = 2\nu_1^{sr} \frac{\mu^{sr}}{m^s + m^r} n^s - \delta^{sr} 2 \sum_{l=1}^4 \nu_1^{sl} \frac{\mu^{sl}}{m^s + m^l} n^l \\ - \frac{3}{2} \nu_2^{sr} \frac{\mu^{sr}}{m^s + m^r} n^s - \delta^{sr} \frac{3}{2} \sum_{l=1}^4 \nu_2^{sl} \left(\frac{m^l}{m^s + m^l} \right)^2 n^l.$$

Now it is a matter of very lengthy and heavy manipulations to show that the matrix $\underline{\Upsilon}$ is regular, with a positive determinant. It is in fact possible to single out the negative contributions, which all come from products involving off-diagonal entries, and to verify that they are canceled out by some positive addends, mostly originating from the products of the diagonal elements (each of them is indeed the sum of eight negative terms). In any case, we may conclude that the unique solution is provided by $p_{ij}^{s(0)} = 0 \ \forall s$. Finally, the fourth of (12) is again a linear algebraic equation $\underline{\Xi} \cdot \underline{\mathbf{q}}_i^{(0)} = \mathbf{0}$, where $\underline{\mathbf{q}}_i^{(0)}$ is the vector of the $q_i^{s(0)}$ and $\underline{\Xi}$ reads

$$(16) \quad \Xi^{sr} = \frac{m^s n^s}{(m^s + m^r)^3} \beta_4^{sr} + \delta^{sr} \sum_{l=1}^4 \frac{m^l n^l}{(m^s + m^l)^3} \beta_1^{sl}.$$

The matrix $\underline{\Xi}$ can be analyzed in the same way as the matrix $\underline{\Upsilon}$, and shows similar properties, in the sense that negative addends in the determinant can be all singled out, and a patient and careful investigation allows one to realize that they are compensated by positive contributions, and only positive addends are left. Regularity of $\underline{\Xi}$ implies then, as before, uniqueness of the trivial solution $q_i^{s(0)} = 0$ for all s .

Notice that all the matrices depend on physical parameters like collision frequencies and masses, as well as on some of the unknowns, namely the number densities n^s . In particular, matrix coefficients are homogeneous functions of the above quantities. So, Φ^{sr} is homogeneous of order 1 with respect to masses, and of order 2 with respect to densities. As regards densities, the order of homogeneity is 2 in Ψ^{sr} , and 1 in Υ^{sr} and Ξ^{sr} , whereas for masses it is 0 in all of them. Collision frequencies appear everywhere in (13), (14), (15), (16) in a linearly homogeneous fashion.

In conclusion, coming back to the asymptotic procedure, the zero order solution is provided by

$$(17) \quad u_i^{s(0)} = u_i, \quad T^{s(0)} = T, \quad p_{ij}^{s(0)} = 0, \quad q_i^{s(0)} = 0.$$

Now it is readily seen that the sought first order accuracy in (10) requires only the determination of $u_i^{s(1)}$, $p_{ij}^{s(1)}$ and $q_i^{s(1)}$. To this end, we resort to the next step of the asymptotic procedure, where it suffices to consider the (still algebraic) equations

$$(18) \quad \begin{aligned} \mathcal{R}_i^{s(1)} &= -R_i^{s(0)} + \varrho^s \left(\frac{\partial_0 u_i}{\partial t} + u_j \frac{\partial u_i}{\partial x_j} \right) + \frac{\partial(n^s K T)}{\partial x_i}, \\ \mathcal{V}_{ij}^{s(1)} &= -V_{ij}^{s(0)} + n^s K T \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial u_k}{\partial x_k} \right), \\ \mathcal{W}_i^{s(1)} &= -W_i^{s(0)} + \frac{5}{2} n^s K T \frac{\partial}{\partial x_i} \left(\frac{K T}{m^s} \right) \end{aligned}$$

with the first of the constraints (11). Indices at the time derivative refer to expansion versus ε of such operator [4]. We get easily $R_i^{s(0)} = 0$, $V_{ij}^{s(0)} = 0$, $W_i^{s(0)} = 0$ and

$$(19) \quad \mathcal{R}_i^{s(1)} = \sum_{r=1}^4 \Phi^{sr} u_i^{r(1)}, \quad \mathcal{V}_{ij}^{s(1)} = \sum_{r=1}^4 \Upsilon^{sr} p_{ij}^{r(1)}, \quad \mathcal{W}_i^{s(1)} = \sum_{r=1}^4 \Xi^{sr} q_i^{r(1)},$$

so that we have to deal with the same matrices as previously introduced. It is remarkable that the matrix Φ is singular, so that the first algebraic system in (18) needs a compatibility condition on the inhomogeneous terms for existence of a solution, and this is just what is required in order to determine the unknown operator $\partial_0/\partial t$. More precisely, from $\sum_{s=1}^4 \Phi^{sr} = 0$ we get the sought expression of $\partial_0/\partial t$ in the form

$$(20) \quad \varrho \left(\frac{\partial_0 u_i}{\partial t} + u_j \frac{\partial u_i}{\partial x_j} \right) = - \frac{\partial(nKT)}{\partial x_i},$$

from which the consistent algebraic system for the unknowns $u_i^{s(1)}$ follows:

$$(21) \quad \sum_{r=1}^4 \Phi^{sr} u_i^{r(1)} = - \frac{\varrho^s}{\varrho} \frac{\partial(nKT)}{\partial x_i} + \frac{\partial(n^s KT)}{\partial x_i}, \quad s = 1, 2, 3, 4,$$

involving only spatial gradients of hydrodynamic variables. Now (21) is not uniquely solvable, but its ∞^1 solutions are made unique by imposing the additional constraint (11) on the velocities $u_i^{s(1)}$. In fact, it may be reduced to the 3×3 system

$$(22) \quad \sum_{r=1}^3 \Gamma^{sr} u_i^{r(1)} = \sum_{l=1}^4 \mathcal{C}^{sl} \frac{\partial(n^l KT)}{\partial x_i}, \quad s = 1, 2, 3$$

where

$$(23) \quad \Gamma^{sr} = \Phi^{sr} - \frac{\Phi^{s4} \varrho^r}{\varrho^4}, \quad \mathcal{C}^{sl} = \delta^{sl} - \frac{\varrho^s}{\varrho}$$

and the matrix Γ can be verified, with a little algebra, to be invertible. The solution can be formally cast as

$$(24) \quad u_i^{s(1)} = \sum_{r=1}^4 \mathcal{K}^{sr} \frac{\partial(n^r KT)}{\partial x_i}$$

with

$$(25) \quad \mathcal{K}^{sr} = \sum_{l=1}^3 (\Gamma^{-1})^{sl} \mathcal{C}^{lr}, \quad s = 1, 2, 3,$$

$$\mathcal{K}^{4r} = - \frac{1}{\varrho^4} \sum_{l=1}^3 \varrho^l \mathcal{K}^{lr}.$$

It is not difficult to check that the matrix coefficients \mathcal{K}^{sr} are homogeneous functions of order -1 with respect to collision frequencies and masses, and of order -2 with respect to number densities.

The solution of the other algebraic systems in (19) is much easier, since the relevant matrices are regular. So, upon setting

$$(26) \quad \mathcal{H}^s = \sum_{r=1}^4 (\Upsilon^{-1})^{sr} n^r$$

one readily obtains

$$(27) \quad p_{ij}^{s(1)} = \mathcal{H}^s KT \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial u_k}{\partial x_k} \right)$$

where coefficients \mathcal{H}^s are homogeneous functions of order -1 with respect to collision frequencies, and of order 0 with respect to masses and number densities. Analogously, for heat fluxes one can write

$$(28) \quad q_i^{s(1)} = \mathcal{J}^s KT \frac{\partial(KT)}{\partial x_i}$$

where

$$(29) \quad \mathcal{J}^s = \sum_{r=1}^4 (\Xi^{-1})^{sr} \frac{5}{2} \frac{n^r}{m^r}$$

is homogeneous of order -1 with respect to collision frequencies and masses, and of order 0 versus number densities.

Now the sought reactive ‘‘Navier-Stokes’’ equations are obtained from (10) by simply expressing the non-hydrodynamic variables u_i^s , p_{ij}^s and q_i^s by means of their first order approximations (9) and making use of the constitutive equations (17), (24), (27), (28), which yield in particular

$$(30) \quad p_{ij}^{(1)} = \left(\sum_{s=1}^4 \mathcal{H}^s \right) KT \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial u_k}{\partial x_k} \right),$$

$$q_i^{(1)} = \left(\sum_{s=1}^4 \mathcal{J}^s \right) KT \frac{\partial(KT)}{\partial x_i} + \frac{5}{2} KT \sum_{s,r=1}^4 \mathcal{K}^{sr} n^s \frac{\partial(n^r KT)}{\partial x_i}.$$

They involve the eight variables n^s , u_i , T , and read

$$(31) \quad \begin{aligned} \frac{\partial n^s}{\partial t} + \frac{\partial}{\partial x_i} (n^s u_i) + \varepsilon \frac{\partial}{\partial x_i} (n^s u_i^{s(1)}) &= \lambda^s Q^1, \\ \frac{\partial}{\partial t} (\varrho \mathbf{u}) + \frac{\partial}{\partial \mathbf{x}} \cdot (\varrho \mathbf{u} \otimes \mathbf{u}) + \frac{\partial}{\partial \mathbf{x}} (nKT) + \varepsilon \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{p}^{(1)} &= \mathbf{0}, \\ \frac{\partial}{\partial t} \left(\frac{1}{2} \varrho u^2 + \frac{3}{2} nKT \right) + \frac{\partial}{\partial \mathbf{x}} \cdot \left[\left(\frac{1}{2} \varrho u^2 + \frac{5}{2} nKT \right) \mathbf{u} \right] \\ + \varepsilon \frac{\partial}{\partial \mathbf{x}} \cdot (\mathbf{p}^{(1)} \cdot \mathbf{u}) + \varepsilon \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{q}^{(1)} &= Q^1 \Delta E \end{aligned}$$

with $u_i^{s(1)}$, $\mathbf{p}^{(1)}$ and $\mathbf{q}^{(1)}$ expressed respectively by (24) and (30) in terms of the above fields.

On the other hand, the Euler equations would be obtained from the conservation equations (10) by simply replacing all other moments by their equilibrium (in the sense of mechanical equilibrium) values. This amounts to setting there $\mathbf{u}^s = \mathbf{u} \forall s$, $\mathbf{p} = \mathbf{0}$, $\mathbf{q} = \mathbf{0}$. The result is nothing but the set (31) for $\varepsilon = 0$, so that, as is well known in this kind of approach, Navier-Stokes equations provide first order corrections to the Euler equations.

In (31) there appear clearly, in addition to the derivatives of the strain-rate tensor, diffusive terms with respect to both the temperature and the densities, contributed by the constitutive equations (24) and (30). Chemical effects are all included in the collision term Q^1 , which does not need any correction since it depends only on n^s and T . Additional dependence on the densities is accounted for in the coefficients \mathcal{K}^{sr} , \mathcal{H}^s , \mathcal{J}^s , but it is quite impossible to make it more explicit, as is typical indeed also in the existing literature [5], [3], [2]. Dependence on masses and collision frequencies shares the same level of complexity, but at least it is nice to see that going back to dimensional variables leads merely (and correctly) to absorbing the parameter ε , as implied by the order -1 of homogeneity with respect to collision frequencies. It is also comforting to realize that results available in literature are reproduced by the present ones when comparison is possible. This occurs for instance for a binary mixture (without chemical reaction) in which case all coefficients \mathcal{K}^{sr} , \mathcal{H}^s , \mathcal{J}^s can be made explicit, though only in a cumbersome form which is omitted here for brevity. The interested reader can find more details in [14]. We only mention that, for a single species, viscosity η and thermal conductivity λ , for a Maxwellian intermolecular potential of the kind $(\gamma/r)^4$, turn out to be given by

$$(32) \quad \eta = \varepsilon \frac{4}{3} \frac{KT}{\nu_2}, \quad \lambda = \varepsilon \frac{5K}{m} \frac{KT}{\nu_2}.$$

They coincide with those quoted in [5], on the basis of the fact that the numerical factors \mathcal{A}_k (to be computed numerically), used there, are simply related to our

weighted collision frequencies by

$$(33) \quad \nu_k = 4\sqrt{2}\pi \frac{\gamma^2}{\sqrt{\mu}} \mathcal{A}_k.$$

4. FAST CHEMICAL REACTION

The process is driven now by all collision terms, namely mechanical and chemical ones. Knudsen numbers are both small, so that $p = q = 1$ is the proper option in the governing equations (2). Now chemical terms are expected to deeply affect the asymptotic procedure itself, while they appeared only as additional inhomogeneous terms in the previous section. The kernel of the dominant operator is 7-dimensional [10], and hydrodynamic variables may be chosen as $n^1 + n^3$, $n^1 + n^4$, $n^2 + n^4$, the mass velocity \mathbf{u} , and the total internal energy $U = \frac{3}{2}nKT + \sum_{s=1}^4 E^s n^s$ (any linear combination of them could be used equivalently). Suitable combinations of the first three reproduce also the total number density n and the mass density ϱ . The same is not in order for T , since kinetic energy alone is not a conserved quantity. With such a choice of collision invariants, the macroscopic equations to be used in the asymptotic algorithm are just the conservation equations (7), which consistently do not keep any trace of collision integrals. Our strategy will consist in working with the same 52 unknowns as before, expanding them again according to (9), and pretending simply that the present hydrodynamic variables remain unexpanded. We shall apply such a strategy step by step while proceeding with the asymptotic machinery towards the closure of the system. At first, from the densities we get the constraints $n^{1(1)} + n^{3(1)} = n^{1(1)} + n^{4(1)} = n^{2(1)} + n^{4(1)} = 0$, which are solved by

$$(34) \quad n^{s(1)} = \lambda^s n^{1(1)}, \quad s = 1, 2, 3, 4.$$

This yields easily $n^1 + n^3 = n^{1(0)} + n^{3(0)}$, $n^1 + n^4 = n^{1(0)} + n^{4(0)}$, $n^2 + n^4 = n^{2(0)} + n^{4(0)}$ and

$$(35) \quad n = \sum_{s=1}^4 n^{s(0)}, \quad \varrho = \sum_{s=1}^4 m^s n^{s(0)}.$$

With $p = q = 1$, the leading order terms in (2) provide the equations

$$(36) \quad \begin{aligned} Q^{1(0)} &= 0, & \mathcal{R}_i^{s(0)} + R_i^{s(0)} &= 0, & \mathcal{S}^{s(0)} + \mathcal{S}^{s(0)} &= 0, \\ \mathcal{V}_{ij}^{s(0)} + V_{ij}^{s(0)} &= 0, & \mathcal{W}_i^{s(0)} + W_i^{s(0)} &= 0. \end{aligned}$$

The first of them reads

$$(37) \quad \frac{2}{\sqrt{\pi}} \nu_{12}^{34} \Gamma\left(\frac{3}{2}, \frac{\Delta E}{KT^{(0)}}\right) \left[n^{3(0)} n^{4(0)} \left(\frac{\mu^{12}}{\mu^{34}}\right)^{\frac{3}{2}} e^{\Delta E/KT^{(0)}} - n^{1(0)} n^{2(0)} \right] = 0$$

and has significant bearing on the whole procedure. To begin with, it implies

$$(38) \quad \frac{n^{1(0)} n^{2(0)}}{n^{3(0)} n^{4(0)}} = \left(\frac{\mu^{12}}{\mu^{34}}\right)^{\frac{3}{2}} e^{\Delta E/KT^{(0)}},$$

which represents a zero order truncation of the well known mass action law for chemical equilibrium [9], [10], and also allows to evaluate explicitly the zero order gas temperature $T^{(0)}$ in terms of the zero order number densities. Moreover, once (37) is fulfilled, it is easy to check that all chemical contributions of the remaining equations in (36) vanish, and only the mechanical ones are left, which are nothing but those of the previous section, only with $n^{s(0)}$ replacing n^s . Therefore such equations may be rewritten as homogeneous algebraic systems

$$(39) \quad \sum_{r=1}^4 \Phi_0^{sr} u_i^{r(0)} = 0, \quad \sum_{r=1}^4 \Psi_0^{sr} T^{r(0)} = 0, \quad \sum_{r=1}^4 \Upsilon_0^{sr} p_{ij}^{r(0)} = 0, \quad \sum_{r=1}^4 \Xi_0^{sr} q_i^{r(0)} = 0,$$

where the subscript zero in the matrices simply means that they are related to $n^s = n^{s(0)}$. Bearing all algebra of the previous section in mind, this means that $u_i^{s(0)}$ and $T^{s(0)}$ are independent of s , and $p_{ij}^{s(0)}$ and $q_i^{s(0)}$ vanish, i. e.

$$(40) \quad u_i^{s(0)} = u_i^0, \quad T^{s(0)} = T^0, \quad p_{ij}^{s(0)} = 0, \quad q_i^{s(0)} = 0.$$

Now, by using the definition of u_i , the second equality of (35), the constraint (34) and the requirement of keeping u_i unexpanded, it is not difficult to show that $u_i^0 = u_i$ and

$$(41) \quad \sum_{s=1}^4 m^s n^{s(0)} u_i^{s(1)} = 0.$$

Moreover, from (40) we get

$$(42) \quad nKT = nKT^0 + \varepsilon \left(\sum_{s=1}^4 n^{s(0)} KT^{s(1)} \right),$$

implying $T^{(0)} = T^0$, and the fact that U must remain unexpanded yields

$$(43) \quad U = \frac{3}{2} nKT^{(0)} + \sum_{s=1}^4 E^s n^{s(0)}$$

and the additional constraint

$$(44) \quad \frac{3}{2} \sum_{s=1}^4 n^{s(0)} K T^{s(1)} + \sum_{s=1}^4 E^s \lambda^s n^{1(1)} = 0.$$

Our purpose is the closure of the set (7) of seven conservation equations, and we choose as seven dependent variables the quantities $n^{s(0)}$ and u_i . The temperature $T^{(0)}$ follows then from (38), and all hydrodynamic variables are expressed in terms of these quantities. For the other variables, we have to the leading order

$$(45) \quad u_i^{s(0)} = u_i, \quad T^{s(0)} = T^{(0)}.$$

First order corrections needed in the closure are only $n^{1(1)}$, $u_i^{s(1)}$, $p_{ij}^{s(1)}$ and $q_i^{s(1)}$, since, in addition to (34), we get from (44)

$$(46) \quad T^{(1)} = \frac{2\Delta E}{3K} \frac{n^{1(1)}}{n}$$

for the correction to the global temperature.

We proceed further and equate the next equal powers of ε . A crucial point is the chemical term $Q^{1(1)}$, coming from the expansion of all n^s and of T , appearing also in $\exp(\Delta E/KT)$. Due to (46), one ends up with

$$(47) \quad \begin{aligned} Q^{1(1)} = n^{1(1)} \tilde{Q} = & -n^{1(1)} \nu_{12}^{34} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \frac{\Delta E}{KT^{(0)}}\right) \\ & \times \left[\left(n^{3(0)} + n^{4(0)} + \frac{2}{3} \frac{n^{3(0)} n^{4(0)}}{n} \left(\frac{\Delta E}{KT^{(0)}} \right)^2 \right) \right. \\ & \left. \times \left(\frac{\mu^{12}}{\mu^{34}} \right)^{\frac{3}{2}} e^{\Delta E/KT^{(0)}} + n^{1(0)} + n^{2(0)} \right] \end{aligned}$$

so that Grad's equations (2a) become

$$(48) \quad \lambda^s \tilde{Q} n^{1(1)} = \frac{\partial_0 n^{s(0)}}{\partial t} + \frac{\partial(n^{s(0)} u_i)}{\partial x_i}.$$

Concerning chemical contributions, it is easy to show that $R_i^{s(1)} = V_{ij}^{s(1)} = W_i^{s(1)} = 0$, while the chemical term does not disappear from the equations for temperatures, which now have to be considered, contrary to the previous case, in order to make $\partial_0/\partial t$ explicit. Therefore the Grad equations for mass velocities, viscous stresses and heat fluxes are the same as for the previous scenario, apart from the substitution

of $n^{s(0)}$ for n^s and of $T^{(0)}$ for T . For completeness, the final result takes the form

$$(49) \quad \begin{aligned} u_i^{s(1)} &= \sum_{r=1}^4 \mathcal{K}_0^{sr} \frac{\partial(n^{r(0)}KT^{(0)})}{\partial x_i}, \\ p_{ij}^{(1)} &= \left(\sum_{s=1}^4 \mathcal{H}_0^s \right) KT^{(0)} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial u_k}{\partial x_k} \right), \\ q_i^{(1)} &= \left(\sum_{s=1}^4 \mathcal{J}_0^s \right) KT^{(0)} \frac{\partial(KT^{(0)})}{\partial x_i} + \frac{5}{2} KT^{(0)} \sum_{s,r=1}^4 \mathcal{K}_0^{sr} n^{s(0)} \frac{\partial(n^{r(0)}KT^{(0)})}{\partial x_i} \end{aligned}$$

with the obvious meaning for subscript 0. Moreover, a little algebra shows that

$$(50) \quad \begin{aligned} \mathcal{S}^{s(1)} = \lambda^s n^{1(1)} \tilde{\mathcal{S}}^s = \lambda^s n^{1(1)} \tilde{Q} \frac{M - m^s}{M} \left\{ -\frac{3}{2} KT^{(0)} - \frac{1}{2} (1 - \lambda^s) \Delta E \right. \\ \left. + KT^{(0)} \Gamma\left(\frac{5}{2}, \frac{\Delta E}{KT^{(0)}}\right) \left[\Gamma\left(\frac{3}{2}, \frac{\Delta E}{KT^{(0)}}\right) \right]^{-1} \right\} \end{aligned}$$

and thus the equations completing this level of approximation are

$$(51) \quad \begin{aligned} \sum_{r=1}^4 \Psi_0^{sr} T^{r(1)} + \lambda^s \tilde{\mathcal{S}}^s n^{1(1)} = \frac{3}{2} n^{s(0)} \left(\frac{\partial_0(KT^{(0)})}{\partial t} + u_i \frac{\partial(KT^{(0)})}{\partial x_i} \right) \\ + n^{s(0)} KT^{(0)} \frac{\partial u_i}{\partial x_i}. \end{aligned}$$

Equations (49) determine all needed corrections except $n^{1(1)}$ in terms of the actual dependent variables. The $T^{s(1)}$ appearing in (51) are not needed, and we may get rid of them by simply summing up with respect to s , taking advantage of the singularity of Ψ_0 . Bearing in mind that $\sum_{s=1}^4 \lambda^s (M - m^s) = 0$ and $\sum_{s=1}^4 \lambda^s (1 - \lambda^s) (M - m^s) = -2M$, we find

$$(52) \quad \tilde{Q} \Delta E n^{1(1)} = \frac{3}{2} n \frac{\partial_0(KT^{(0)})}{\partial t} + \frac{3}{2} n u_i \frac{\partial(KT^{(0)})}{\partial x_i} + n KT^{(0)} \frac{\partial u_i}{\partial x_i}.$$

This must be compatible with equations (48), and such a condition allows again elimination of the unknown operator $\partial_0/\partial t$, even though a trickier argument must be invoked as compared to the previous section. Rearrangement of (38) and differentiation with respect to t truncated to zero order yields in fact

$$(53) \quad \frac{\partial_0(KT^{(0)})}{\partial t} = -\frac{(KT^{(0)})^2}{\Delta E} \sum_{s=1}^4 \lambda^s \frac{1}{n^{s(0)}} \frac{\partial_0 n^{s(0)}}{\partial t}$$

so that $\partial_0(KT^{(0)})/\partial t$ may be reconstructed from the set (48) by suitable linear combinations. Equating the different expressions of such a derivative yields finally a linear algebraic equation for $n^{1(1)}$, with solution

$$(54) \quad n^{1(1)} = \left\{ \tilde{Q} \left[1 + \frac{3}{2} n \left(\frac{KT^{(0)}}{\Delta E} \right)^2 \sum_{s=1}^4 \frac{1}{n^{s(0)}} \right] \right\}^{-1} \\ \times \left\{ \frac{3}{2} n u_i \left(\frac{KT^{(0)}}{\Delta E} \right)^2 \sum_{s=1}^4 \frac{\lambda^s}{n^{s(0)}} \frac{\partial n^{s(0)}}{\partial x_i} + \frac{3}{2} n u_i \frac{\partial}{\partial x_i} \left(\frac{KT^{(0)}}{\Delta E} \right) \right. \\ \left. + n \frac{KT^{(0)}}{\Delta E} \frac{\partial u_i}{\partial x_i} \right\}$$

showing the dependence of the density correction on the gradients of densities and temperature and on the divergence of mass velocity.

The presence of \tilde{Q} , namely of ν_{12}^{34} , in the denominator of (54) shows that the small parameter disappears when going back to dimensional variables. The main difference, along with the presence of $n^{s(0)}$ instead of n^s , is the lack of one equation (on particle balance) and of one unknown (temperature). The leading order temperature is deduced from the (approximated) mass action law (38), describing closeness to chemical equilibrium, obviously absent for slow reactions. Further difference is the need for an additional correction term for densities and temperature, as represented by (34), (46), (54). However, since

$$(55) \quad n^1 u_i^1 + n^3 u_i^3 = (n^{1(0)} + n^{3(0)}) u_i + \varepsilon (n^{1(0)} u_i^{1(1)} + n^{3(0)} u_i^{3(1)})$$

(and analogously for the combinations 1 + 4 and 2 + 4) and

$$(56) \quad \sum_{s=1}^4 E^s n^s (u_i^s - u_i) = \varepsilon \sum_{s=1}^4 E^s n^{s(0)} u_i^{s(1)},$$

such new correction affects only the scalar pressure nKT as a part of the pressure tensor \mathbf{P} , namely $nKT = nKT^{(0)} + \frac{2}{3}\varepsilon\Delta E n^{1(1)}$. Such effect has been already pointed out in phenomenological approaches to chemical reactions [15].

The structure of the resulting reacting ‘‘Navier-Stokes’’ equations is again implicit and quite cumbersome, like in the previous case. Explicitly, they are written as a set

of seven partial differential equations for the seven variables $n^{s(0)}$, u_i

$$\begin{aligned}
(57) \quad & \frac{\partial}{\partial t} (n^{1(0)} + n^{3(0)}) + \frac{\partial}{\partial \mathbf{x}} \cdot [(n^{1(0)} + n^{3(0)}) \mathbf{u}] \\
& + \varepsilon \frac{\partial}{\partial \mathbf{x}} \cdot (n^{1(0)} \mathbf{u}^{1(1)} + n^{3(0)} \mathbf{u}^{3(1)}) = 0, \\
& \frac{\partial}{\partial t} (n^{1(0)} + n^{4(0)}) + \frac{\partial}{\partial \mathbf{x}} \cdot [(n^{1(0)} + n^{4(0)}) \mathbf{u}] \\
& + \varepsilon \frac{\partial}{\partial \mathbf{x}} \cdot (n^{1(0)} \mathbf{u}^{1(1)} + n^{4(0)} \mathbf{u}^{4(1)}) = 0, \\
& \frac{\partial}{\partial t} (n^{2(0)} + n^{4(0)}) + \frac{\partial}{\partial \mathbf{x}} \cdot [(n^{2(0)} + n^{4(0)}) \mathbf{u}] \\
& + \varepsilon \frac{\partial}{\partial \mathbf{x}} \cdot (n^{2(0)} \mathbf{u}^{2(1)} + n^{4(0)} \mathbf{u}^{4(1)}) = 0, \\
& \frac{\partial}{\partial t} (\varrho \mathbf{u}) + \frac{\partial}{\partial \mathbf{x}} \cdot (\varrho \mathbf{u} \otimes \mathbf{u}) + \frac{\partial}{\partial \mathbf{x}} (nKT^{(0)}) + \varepsilon \frac{\partial}{\partial \mathbf{x}} (nKT^{(1)}) + \varepsilon \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{p}^{(1)} = \mathbf{0}, \\
& \frac{\partial}{\partial t} \left(\frac{1}{2} \varrho u^2 + \frac{3}{2} nKT^{(0)} + \sum_{s=1}^4 E^s n^{s(0)} \right) \\
& + \frac{\partial}{\partial \mathbf{x}} \cdot \left[\left(\frac{1}{2} \varrho u^2 + \frac{5}{2} nKT^{(0)} + \sum_{s=1}^4 E^s n^{s(0)} \right) \mathbf{u} \right] \\
& + \varepsilon \frac{\partial}{\partial \mathbf{x}} \cdot (nKT^{(1)} \mathbf{u}) + \varepsilon \frac{\partial}{\partial \mathbf{x}} \cdot (\mathbf{p}^{(1)} \cdot \mathbf{u}) + \varepsilon \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{q}^{(1)} \\
& + \varepsilon \frac{\partial}{\partial \mathbf{x}} \cdot \left(\sum_{s=1}^4 E^s n^{s(0)} \mathbf{u}^{s(1)} \right) = 0
\end{aligned}$$

where $T^{(0)}$ follows from (38), $T^{(1)}$ is provided by (46) and (54), and $\mathbf{u}^{s(1)}$, $\mathbf{p}^{(1)}$, $\mathbf{q}^{(1)}$ are given by (49).

Finally, it is easy to check that the reactive Euler equations in this case of fast chemical reaction are obtained from (7) by introducing mechanical and chemical equilibrium, namely by setting $\mathbf{u}^s = \mathbf{u} \forall s$, $\mathbf{p} = \mathbf{0}$, $\mathbf{q} = \mathbf{0}$, and using the mass action law in order to express T in terms of the n^s . They are a set of seven partial differential equations for the unknowns n^s and \mathbf{u} , with temperature provided by an additional algebraic equation. Like in the case of slow reaction, this set may be regarded as the limit for $\varepsilon \rightarrow 0$ of the reactive Navier-Stokes equations (57).

References

- [1] *C. Cercignani*: Rarefied Gas Dynamics. From Basic Concepts to Actual Calculations. Cambridge University Press, Cambridge, 2000.
- [2] *V. Giovangigli*: Multicomponent Flow Modeling. Birkhäuser-Verlag, Boston, 1999.
- [3] *M. N. Kogan*: Rarefied Gas Dynamics. Plenum Press, New York, 1969.

- [4] *C. Cercignani*: The Boltzmann Equation and its Applications. Springer-Verlag, New York, 1988.
- [5] *J.H. Ferziger, H.G. Kaper*: Mathematical Theory of Transport Processes in Gases. North Holland, Amsterdam, 1972.
- [6] *S. Takata, K. Aoki*: The ghost effect in the continuum limit for a vapor-gas mixture around condensed phases: Asymptotic analysis of the Boltzmann equation. *Transport Theory Statist. Phys.* *30* (2001), 205–237.
- [7] *S. Chapman, T.G. Cowling*: The Mathematical Theory of Non-Uniform Gases. Cambridge University Press, Cambridge, 1970.
- [8] *Y. Sone*: Kinetic Theory and Fluid Dynamics. Birkhäuser-Verlag, Boston, 2002.
- [9] *A. Rossani, G. Spiga*: A note on the kinetic theory of chemically reacting gases. *Physica A* *272* (1999), 563–573.
- [10] *M. Groppi, G. Spiga*: Kinetic approach to chemical reactions and inelastic transitions in a rarefied gas. *J. Math. Chem.* *26* (1999), 197–219.
- [11] *I. Müller, T. Ruggeri*: Extended Thermodynamics. Springer-Verlag, New York, 1993.
- [12] *M. Bisi, M. Groppi, G. Spiga*: Grad's distribution functions in the kinetic equations for a chemical reaction. *Contin. Mech. Thermodyn.* *14* (2002), 207–222.
- [13] Handbook of Mathematical Functions (M. Abramowitz, I. A. Stegun, eds.). Dover, New York, 1965.
- [14] *M. Bisi*: Kinetic equations for non-conservative interactions. PhD. Thesis. Università di Milano, 2004, in press.
- [15] *I. Samohýl*: Comparison of classical and rational thermodynamics of reacting fluid mixtures with linear transport properties. *Collection Czechoslov. Chem. Commun.* *40* (1975), 3421–3435.

Authors' address: M. Bisi, M. Groppi, and G. Spiga, Dipart. di Matematica, Università di Parma, Via D'Azeglio 85, 43100 Parma, Italy, e-mail: giampiero.spiga@unipr.it.