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Reaction–Diffusion Equations for Chemically Reacting Gas Mixtures (*)

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Abstract. – *In this paper we aim at describing the hydrodynamic limit of a mixture of chemically reacting gases. Starting from kinetic Boltzmann–type equations, we derive Grad's 13–moments equations for single species. Then, after scaling such equations in terms of a suitable Knudsen number, we apply an asymptotic Chapman–Enskog procedure in order to build up hydrodynamic equations of Navier–Stokes type.*

1. – Introduction and description of the kinetic model.

Kinetic approaches to chemical reactions in a gas mixture have gained interest in past decades in the scientific literature [15, 17, 10]. An extensive bibliography may be found in the book [6] and in the survey papers [14, 13]. In particular, for a bimolecular chemical reaction, governing equations of Boltzmann type have been proposed in [16], where equilibria have been determined and an H–theorem has been proved. Then, this model has been extended to the case when reacting species exhibit an internal structure, in the sense that to each of them discrete energy levels [11] (or, equivalently, a continuous internal energy distribution [9]) are allowed.

For practical applications, a key point is the availability of closed sets of balance equations for the main macroscopic observables (number densities of gases, mass velocity, temperature and so on). A first step in this direction has been moved in [12], where Euler–type equations have been derived in the physical situation when elastic scattering plays the dominant role in the evolution. The range of validity of the macroscopic closed set has been then enlarged in [2], by using as approximating functions (instead of local Maxwellians) the ones proposed by Grad (suitably truncated Hermite polynomial expansions around Maxwellians), which lead to the so–called 13–moments closure. A Chapman–Enskog expansion in terms of suitable Knudsen numbers may be then applied in order to reduce the number of considered unknowns and to write

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down closed equations involving only the hydrodynamic variables determined by the operators driving the evolution [3]. The main available results on this subject have been collected in the survey [4].

Another way of modelling is based on phenomenological considerations: when the main process is the diffusion of concentrations (for instance when the considered species are traces in a background medium), one is led to write down reaction–diffusion equations for number densities [8]. First attempts to relate kinetic equations to macroscopic reaction–diffusion systems have been performed in [18, 19] for Fokker–Planck, BGK or discrete velocity models. These results have been then recently extended to more realistic chemical kernels like the ones introduced in [16, 11, 9]. More precisely, in [1, 5] the authors deal with a reacting mixture embedded in a much denser medium, considered as a fixed background whose evolution is not influenced by interactions with the other gases, thus it is assumed in local thermodynamical equilibrium. A scaling of the kinetic equations for the participating species is proposed, in which the collisions involving the background are dominant while reactive collisions are very rare, and it is shown that solution of the Boltzmann equations converges towards the solution of a suitable reaction–diffusion system involving only number densities.

In many physical experiments however it is evident that in a reacting mixture diffusion of concentrations is strongly depending also on the global temperature of the mixture, which is not a collision invariant in the evolution since chemical reactions involve transfer of internal energy of chemical link into kinetic energy and vice versa. One expects then the presence of a separate additional diffusive equation for the temperature, as typical indeed on physical grounds in all thermal processes. We aim here at building up a reaction–diffusion system of this kind starting from a suitably rescaled kinetic model. Precisely, we consider a mixture of five gases A^s, $s=1,\dots,5$ and we denote by $f^s \equiv f^s(t,\boldsymbol{x},\boldsymbol{v})$ the s–th one–particle distribution function (number density of molecules of the s–th species which at time t and point $\boldsymbol{x}$ have velocity $\boldsymbol{v}$). We assume that molecules of any species s can interact elastically with the molecules of whatever other species r (including the case $r=s$); in addition, we take into account also the effects of the following bimolecular reversible chemical reaction involving only the four species $A^1,\dots,A^4$:

$$A^1 + A^2 \rightleftharpoons A^3 + A^4\,. \tag{1}$$

For this physical situation, the extended set of Boltzmann equations reads as

$$\frac{\partial f^s}{\partial t} + \boldsymbol{v}\cdot\frac{\partial f^s}{\partial \boldsymbol{x}} = \sum_{r=1}^{5} Q^{sr}_{EL}(f^s,f^r) + Q^s_{CH}, \qquad s=1,\dots,5\,. \tag{2}$$

In this formula, the operator $Q^{sr}_{EL}(f^s,f^r)$ represents the net production of particles s (with velocity $\boldsymbol{v}$) due to elastic collisions with the species r, while the operator Q^s_{CH} stands for the net gain of molecules s due to chemical reactions. The bi–species elastic collision operator for the species s and r takes the form

$$Q^{sr}_{EL}(f^s,f^r)(\boldsymbol{v}) = \int\limits_{\mathbb{R}^3}\int\limits_{S^2} g\,\sigma^{sr}(g,\hat{\boldsymbol{\Omega}}\cdot\hat{\boldsymbol{\Omega}}')\left[f^s(\boldsymbol{v}')f^r(\boldsymbol{w}') - f^s(\boldsymbol{v})f^r(\boldsymbol{w})\right] d\boldsymbol{w}\, d\hat{\boldsymbol{\Omega}}. \tag{3}$$

Here $(\boldsymbol{v},\boldsymbol{w})$ stand for the pre–collision velocities, and $\boldsymbol{g} = g\hat{\boldsymbol{\Omega}}$ is the relative velocity $\boldsymbol{v}-\boldsymbol{w}$. The superscript prime affects the corresponding post–collision parameters: specifically, $(\boldsymbol{v}',\boldsymbol{w}')$ represent the post–collision velocities which, taking into account the conservations of momentum and of kinetic energy, can be suitably expressed in terms of $(\boldsymbol{v},\boldsymbol{w})$, of the unit vector $\hat{\boldsymbol{\Omega}}' = (\boldsymbol{v}'-\boldsymbol{w}')/g'$ and of particle masses m^s. Finally, σ^{sr} denotes the differential cross section and depends only on g and on $\hat{\boldsymbol{\Omega}}\cdot\hat{\boldsymbol{\Omega}}'$.

As concerns the chemical operators Q^s_{CH}, since the reaction (1) involves only the species $1,\ldots,4$, we have of course $Q^5_{CH} = 0$. Then, if we assume the direct reaction $A^1 + A^2 \longrightarrow A^3 + A^4$ to be endothermic, namely that internal energies of chemical link are such that $\Delta E = E^3 + E^4 - E^1 - E^2 > 0$, the operator Q^1_{CH} reads as

$$Q^1_{CH}(\boldsymbol{v}) = \int\limits_{\mathbb{R}^3}\int\limits_{S^2} U\!\left(g^2 - \frac{2\,\Delta E}{\mu^{12}}\right) g\,\sigma^{34}_{12}(g,\hat{\boldsymbol{\Omega}}\cdot\hat{\boldsymbol{\Omega}}')\left[\left(\frac{\mu^{12}}{\mu^{34}}\right)^{3} f^3(\tilde{\boldsymbol{v}})f^4(\tilde{\boldsymbol{w}}) - f^1(\boldsymbol{v})f^2(\boldsymbol{w})\right] d\boldsymbol{w}\, d\hat{\boldsymbol{\Omega}}. \tag{4}$$

Here the post–collision velocities are denoted by $(\tilde{\boldsymbol{v}},\tilde{\boldsymbol{w}})$, the symbol μ^{sr} represents the reduced mass $m^s m^r/(m^s + m^r)$, and U is the unit step function needed since the endothermic reaction can occur only if the kinetic energy overcomes the threshold ΔE. The expressions relevant to $s = 2,3,4$ may be obtained from (4) by suitable permutations of indices, bearing in mind the obvious symmetry $\sigma^{hk}_{rs} = \sigma^{kh}_{sr}$, and that the differential cross section of the exothermic reverse reaction is related to the direct one by the microreversibility condition [11].

In the following, we shall assume that all cross sections are of Maxwell molecules type, corresponding to “inverse power” kind intermolecular forces, for which the kernels $g\,\sigma^{sr}$ and $g\,\sigma^{34}_{12}$ depend only on the angle formed by pre– and post–collision relative velocities. Moreover, Einstein convention on repeated indices shall be adopted.

In Section 2 we extend the cumbersome derivation of Grad’s 13–moments equations, already developed for a four–species mixture [2], to the present five–species frame: we report all mechanical and chemical contributions in explicit form, and we point out the main features of such macroscopic equations. Then, in Section 3 we scale Boltzmann equations assuming that scattering involving gas A^5 is much more frequent than other elastic collisions, and chemical reaction is even rarer. Species 5 plays thus a crucial role in the evolution; unlike in [1, 5] however, it is not a fixed background medium but an actually participating species, and this shall imply that in the asymptotic procedure global temperature has to be included in the set of hydrodynamic variables. More precisely, here a Chapman–Enskog algorithm is consistently applied to Grad's equations, and the final result shall be an hydrodynamic system at the Navier–Stokes accuracy for species number densities, global mass velocity and temperature. Equations for concentrations turn out to be of reaction–diffusion type, but actually depending also on the diffusion of mixture temperature.

2. – Grad's equations.

In this Section we aim at deriving a closed set of balance equations for the major macroscopic fields (moments of the distribution function). As already pointed out in the Introduction, a first step in this direction has been performed in [12], in the physical situation when elastic scattering plays a crucial role in the evolution, and Euler–type equations for reacting mixtures have been achieved. A further step has been developed in [2], including physical situations farther from equilibrium. For a mixture of 4 gases, a closed set of 52 equations has been built up for the 4 number densities n^s, the 12 components of mass velocities u_i^s, the 4 temperatures T^s, the 20 independent entries of the viscosity tensors p_{ij}^s (symmetric and traceless matrices), and the 12 components of the heat flux vectors q_i^s. The closure procedure is based on replacing higher order moments and collision contributions by the ones corresponding to the following Grad's distribution functions, suitably truncated Hermite polynomial expansions around a local Maxwellian:

$$(5)\quad f_G^s(\boldsymbol{v}) = f_M^s(\boldsymbol{v})\left[1 + \frac{1}{n^s KT^s}\,\frac{m^s}{2KT^s}\,p_{ij}^s\,c_i^s c_j^s + \frac{4}{5}\,\frac{1}{n^s KT^s}\,\frac{m^s}{2KT^s}\,q_i^s\,c_i^s\left(\frac{m^s}{2KT^s}\,(c^s)^2 - \frac{5}{2}\right)\right]$$

where

$$f_M^s = n^s\left(\frac{m^s}{2\pi KT^s}\right)^{\frac{3}{2}}\exp\left(-\,\frac{m^s}{2KT^s}\,(c^s)^2\right),$$

K is the Boltzmann constant and $\boldsymbol{c}^s = \boldsymbol{v} - \boldsymbol{u}^s$ is the peculiar velocity of the species s.

The balance equations for n^s, u_i^s, T^s, p_{ij}^s, q_i^s follow from the weak forms of the Boltzmann equations, taking as weight functions 1, $m^s v_i$, $\frac{1}{2}\,m^s\,(c^s)^2$, $m^s\left(c_i^s\,c_j^s - \frac{1}{3}\,\delta_{ij}\,(c^s)^2\right)$, $\frac{1}{2}\,m^s\,c_i^s (c^s)^2$, respectively. The procedure described in [2] may be easily extended to the present frame of 5 scattering gases, thus technical details will be omitted here. The final Grad's 13–moments equations read, for $s = 1, \ldots, 5$, as

$$\frac{\partial n^s}{\partial t} + \frac{\partial (n^s u_i^s)}{\partial x_i} = Q^s \,, \tag{6a}$$

$$m^s n^s \left(\frac{\partial u_i^s}{\partial t} + u_j^s \, \frac{\partial u_i^s}{\partial x_j} \right) + \frac{\partial (n^s K T^s)}{\partial x_i} + \frac{\partial p_{ij}^s}{\partial x_j} = \mathcal{R}_i^s + R_i^s \,, \tag{6b}$$

$$\frac{3}{2} \, n^s \left(\frac{\partial (KT^s)}{\partial t} + u_i^s \, \frac{\partial (KT^s)}{\partial x_i} \right) + n^s K T^s \frac{\partial u_i^s}{\partial x_i} + p_{ij}^s \frac{\partial u_j^s}{\partial x_i} + \frac{\partial q_i^s}{\partial x_i} = \mathcal{S}^s + \mathsf{S}^s \,, \tag{6c}$$

$$\begin{aligned} & \frac{\partial p_{ij}^s}{\partial t} + \frac{\partial}{\partial x_k} (u_k^s \, p_{ij}^s) + p_{ik}^s \, \frac{\partial u_j^s}{\partial x_k} + p_{jk}^s \, \frac{\partial u_i^s}{\partial x_k} - \frac{2}{3} \delta_{ij} p_{kl}^s \, \frac{\partial u_l^s}{\partial x_k} \\ & + n^s K T^s \left(\frac{\partial u_i^s}{\partial x_j} + \frac{\partial u_j^s}{\partial x_i} - \frac{2}{3} \delta_{ij} \, \frac{\partial u_k^s}{\partial x_k} \right) + \frac{2}{5} \left(\frac{\partial q_i^s}{\partial x_j} + \frac{\partial q_j^s}{\partial x_i} - \frac{2}{3} \delta_{ij} \, \frac{\partial q_k^s}{\partial x_k} \right) = \mathcal{V}_{ij}^s + V_{ij}^s \,, \end{aligned} \tag{6d}$$

$$\begin{aligned} & \frac{\partial q_i^s}{\partial t} + \frac{\partial}{\partial x_j} (u_j^s \, q_i^s) + \frac{7}{5} \, q_j^s \, \frac{\partial u_i^s}{\partial x_j} + \frac{2}{5} \, q_j^s \, \frac{\partial u_j^s}{\partial x_i} + \frac{2}{5} \, q_i^s \, \frac{\partial u_j^s}{\partial x_j} + \frac{5}{2} \, n^s K T^s \frac{\partial}{\partial x_i} \left(\frac{K T^s}{m^s} \right) \\ & + \frac{5}{2} \, p_{ij}^s \, \frac{\partial}{\partial x_j} \left(\frac{K T^s}{m^s} \right) + n^s K T^s \frac{\partial}{\partial x_j} \left(\frac{p_{ij}^s}{m^s n^s} \right) - \frac{p_{ij}^s}{m^s n^s} \, \frac{\partial p_{kj}^s}{\partial x_k} = \mathcal{W}_i^s + W_i^s \,. \end{aligned} \tag{6e}$$

On the right hand side, we have mechanical and chemical collision contributions. Under the Maxwell molecules assumption, all elastic terms can be obtained exactly in closed form in terms of the selected moments (13 for each species), without any need of actually resorting to Grad's approximated functions (5). The final output is

$$\mathcal{R}_i^s \;=\; n^s \sum_{r=1}^{5} \nu_1^{sr} \mu^{sr} n^r (u_i^r - u_i^s) \,, \tag{7a}$$

$$\mathcal{S}^s \;=\; 2 \, n^s \sum_{r=1}^{5} \nu_1^{sr} \, \frac{\mu^{sr}}{m^s + m^r} \, n^r \left[\frac{3}{2} \, K (T^r - T^s) + \frac{1}{2} \, m^r (\boldsymbol{u}^r - \boldsymbol{u}^s)^2 \right] , \tag{7b}$$

$$\begin{aligned} \mathcal{V}_{ij}^s \;=\; & 2 \sum_{r=1}^{5} \nu_1^{sr} \, \frac{\mu^{sr}}{m^s + m^r} \left\{ n^s p_{ij}^r - n^r p_{ij}^s + n^s n^r m^r \left[(u_i^r - u_i^s)(u_j^r - u_j^s) \right. \right. \\ & \left. \left. - \frac{1}{3} \, \delta_{ij} (\boldsymbol{u}^r - \boldsymbol{u}^s)^2 \right] \right\} - \frac{3}{2} \sum_{r=1}^{5} \nu_2^{sr} \, \frac{m^r}{(m^s + m^r)^2} \left\{ m^s n^s p_{ij}^r + m^r n^r p_{ij}^s \right. \\ & \left. + m^s n^s m^r n^r \left[(u_i^r - u_i^s)(u_j^r - u_j^s) - \frac{1}{3} \, \delta_{ij} (\boldsymbol{u}^r - \boldsymbol{u}^s)^2 \right] \right\} , \end{aligned} \tag{7c}$$

$$\begin{aligned}\mathcal{W}_i^s \;=\; & -\frac{5}{2}\frac{n^s}{m^s}KT^s\sum_{r=1}^{5}\nu_1^{sr}\mu^{sr}n^r(u_i^r-u_i^s)-\frac{1}{m^s}\,p_{ij}^s\sum_{r=1}^{5}\nu_1^{sr}\mu^{sr}n^r(u_j^r-u_j^s)\\ & +\sum_{r=1}^{5}\frac{m^r n^r}{(m^s+m^r)^3}\left\{\beta_1^{sr}q_i^s+\frac{m^s n^s}{m^r n^r}\beta_4^{sr}q_i^r+(u_j^r-u_j^s)\left(\frac{1}{2}\,\beta_2^{sr}p_{ij}^s+\frac{m^s n^s}{m^r n^r}\beta_4^{sr}p_{ij}^r\right)\right.\\ & \left.+\frac{1}{2}(u_i^r-u_i^s)\left[(\beta_2^{sr}+3\,\beta_3^{sr})\,n^sKT^s+5\,\frac{m^s n^s}{m^r n^r}\beta_4^{sr}\,n^rKT^r+m^s n^s\beta_4^{sr}(\boldsymbol{u}^r-\boldsymbol{u}^s)^2\right]\right\},\end{aligned} \tag{7d}$$

where ν_1^{sr}, ν_2^{sr} are angular moments of the microscopic collision frequencies, and β_i^{sr} are the following coefficients involving masses m^s and constants ν_1^{sr}, ν_2^{sr}:

$$\begin{aligned}\beta_1^{sr} &= -\left\{\left[3(m^s)^2+(m^r)^2\right]\nu_1^{sr}+2\,m^s m^r\nu_2^{sr}\right\}\\ \beta_2^{sr} &= 2(m^s-m^r)^2\,\nu_1^{sr}+m^r(m^s-3\,m^r)\,\nu_2^{sr}\\ \beta_3^{sr} &= (m^s-m^r)^2\,\nu_1^{sr}+m^r(3\,m^s+m^r)\,\nu_2^{sr}\\ \beta_4^{sr} &= 2(m^r)^2\left[2\,\nu_1^{sr}-\nu_2^{sr}\right].\end{aligned} \tag{8}$$

As concerns chemical contributions, since species 5 is not involved in chemical reaction (1), we immediately get $Q^5=R_i^5=\mathsf{S}^5=V_{ij}^5=W_i^5=0$. The evaluation of contributions relevant to species $s=1,\dots,4$ is much more cumbersome. After some technical manipulations, in order to push the analytical treatment to the very end an additional assumption is introduced, besides Grad's approximation (5). Since chemical processes involve more complicated dynamics than elastic scattering (such as transfer of mass and of chemical energies), it seems reasonable to assume that relaxation to the elastic equilibrium occurs faster than to the chemical one. This implies that chemical terms may be made explicit by resorting to approximating functions given by local Maxwellians M^s accommodated at the mixture mean velocity $\boldsymbol{u}$ and at the global temperature T. In this way, chemical terms for $s=1,\dots,4$ take the form

$$Q^s \;=\; \lambda^s\,Q^1=\lambda^s\left[n^3n^4\left(\frac{m^1m^2}{m^3m^4}\right)^{\frac{3}{2}}\mathrm{e}^{\frac{\Delta E}{KT}}-n^1n^2\right]\nu_{12}^{34}\,\frac{2}{\sqrt{\pi}}\,\Gamma\left(\frac{3}{2},\frac{\Delta E}{KT}\right), \tag{9a}$$

$$R_i^s \;=\; -\,\lambda^s\,m^s(u_i^s-u_i)\,Q^1\,, \tag{9b}$$

$$\begin{aligned}\mathsf{S}^s=\lambda^s\,Q^1 & \left\{\frac{3}{2}\,(KT)\,\frac{m^s}{M}-\frac{1}{2}\,(1-\lambda^s)\,\Delta E\,\frac{M-m^s}{M}-\frac{3}{2}\,(KT^s)\right.\\ & \left.+\frac{1}{2}\,m^s(\boldsymbol{u}^s-\boldsymbol{u})^2+(KT)\,\frac{M-m^s}{M}\,\Gamma\left(\frac{5}{2},\frac{\Delta E}{KT}\right)\left[\Gamma\left(\frac{3}{2},\frac{\Delta E}{KT}\right)\right]^{-1}\right\},\end{aligned} \tag{9c}$$

$$V^s_{ij} = \lambda^s\, m^s\, Q^1 \left[(u^s_i - u_i)(u^s_j - u_j) - \frac{1}{3}\,\delta_{ij}\,(\boldsymbol{u}^s - \boldsymbol{u})^2\right], \tag{9d}$$

$$\begin{aligned} W^s_i = \lambda^s\, Q^1 \Bigg\{ & -\frac{5}{2}\,(u^s_i - u_i)\,(KT)\,\frac{m^s}{M} + \frac{5}{6}\,(1-\lambda^s)(u^s_i - u_i)\,\Delta E\,\frac{M - m^s}{M} \\ & + \frac{5}{2}\,(KT^s)\,(u^s_i - u_i) + \frac{p^s_{ij}}{n^s}\,(u^s_j - u_j) - \frac{1}{2}\,m^s(u^s_i - u_i)(\boldsymbol{u}^s - \boldsymbol{u})^2 \\ & - \frac{5}{3}\,(u^s_i - u_i)(KT)\,\frac{M - m^s}{M}\,\Gamma\!\left(\frac{5}{2},\frac{\Delta E}{KT}\right)\left[\Gamma\!\left(\frac{3}{2},\frac{\Delta E}{KT}\right)\right]^{-1}\Bigg\}. \end{aligned} \tag{9e}$$

Chemical contributions turn out to be all proportional to Q^1, which involves the total microscopic collision frequency ν^{34}_{12} and the incomplete Gamma function $\Gamma(a, y)$. Moreover, M is the total reacting mass $m^1 + m^2 = m^3 + m^4$ (mass is preserved by chemical reaction), and λ^s are the stoichiometric coefficients $\lambda^1 = \lambda^2 = -\lambda^3 = -\lambda^4 = 1$. Notice that Q^1 (and consequently all chemical terms) vanishes when number densities $n^1, \dots, n^4$ and temperature T are related by the so–called “mass action law” for chemical equilibrium:

$$\frac{n^1 n^2}{n^3 n^4} = \left(\frac{\mu^{12}}{\mu^{34}}\right)^{3/2} \exp\left(\frac{\Delta E}{KT}\right). \tag{10}$$

In spite of its cumbersome appearance, Grad’s system (6) preserves important features of the kinetic equations it comes from. First of all, it can be checked that suitable combinations of Grad’s equations correctly reproduce preservation of $n^1 + n^3$, $n^1 + n^4$, $n^2 + n^4$ (besides of course non–reacting species n^5), of global momentum, and of total (internal plus chemical) energy. Moreover, moments of kinetic collision equilibria, namely $\boldsymbol{u}^s = \boldsymbol{u}$, $T^s = T$, $\boldsymbol{p}^s = \boldsymbol{0}$, $\boldsymbol{q}^s = \boldsymbol{0}$ and number densities $n^1, \dots, n^4$ related by the mass action law (10), turn out to be collision equilibria for Grad’s equations.

3. – Asymptotic limit and hydrodynamic reaction–diffusion equations.

In hydrodynamic applications, it is usually not necessary a detailed knowledge of the macroscopic fields of all single species, but a closed balance system for the quantities preserved by the processes governing the evolution suffices. In order to build up consistent hydrodynamic equations, it is worth considering Boltzmann equations (2) in dimensionless form, measuring all quantities in terms of suitable characteristic values, and scaling space and time in terms of macroscopic units. We assume here that the non–reacting species A^5 is dominant with respect to other gases $A^1, \dots, A^4$, in the sense that elastic collisions involving A^5 are much more frequent than other scattering processes. Moreover, chemical reaction is taken much slower than elastic scattering, and this assumption seems reasonable from a physical point of view, as explained in [2, 1]. More precisely, if we measure the relative importance of each process in terms of a small parameter ε (playing the role of a Knudsen number), we have the elastic operator Q_{EL}^{55} playing the dominant role and then is taken in the scaling of order $1/\varepsilon^2$, while scattering terms Q_{EL}^{s5} involving A^5 and a different partner species are assumed $O(1/\varepsilon)$; finally, all remaining elastic contributions are taken $O(1)$, while chemical reaction is considerably slower ($O(\varepsilon)$). Rescaled kinetic equations read then as

$$\text{(11a)}\quad \frac{\partial f^s}{\partial t} + \boldsymbol{v}\cdot\frac{\partial f^s}{\partial \boldsymbol{x}} = \frac{1}{\varepsilon}\, Q_{EL}^{s5}(f^s,f^5) + \sum_{r=1}^{4} Q_{EL}^{sr}(f^s,f^r) + \varepsilon\, Q_{CH}^{s}, \qquad s = 1,\dots,4\,,$$

$$\text{(11b)}\quad \frac{\partial f^5}{\partial t} + \boldsymbol{v}\cdot\frac{\partial f^5}{\partial \boldsymbol{x}} = \frac{1}{\varepsilon^2}\, Q_{EL}^{55}(f^5,f^5) + \frac{1}{\varepsilon}\sum_{r=1}^{4} Q_{EL}^{5r}(f^5,f^r)\,.$$

The evolution of the mixture is driven by elastic scattering, and in particular by collisions with species 5. Dominant term ($O(1/\varepsilon^2)$) of equation (11b) yields that f^5 is, to the leading order, a local Maxwellian, equilibrium for the elastic operator. Therefore A^5 turns out to play somehow (to zero order accuracy) the role of a "background" (similarly to [1, 5]), in the sense that its distribution at this level is not affected by the interactions with the other particles $A^1,\dots,A^4$; corrections taking into account collisions with the remaining participating species will appear only to next order accuracy. The quantities which are conserved under dominant mechanical encounters are number densities of single species, global mass velocity, and total (kinetic plus chemical) energy. Thus, independent hydrodynamic variables are in number of nine, and they can be chosen as the five number densities n^s, $s = 1,\dots,5$, the three components of the mean velocity u_i, and the mixture temperature T ($K = 1$ in dimensionless equations). The relevant "conservation" equations to be considered in the present asymptotic algorithm follow from suitable weak forms of the Boltzmann equations: streaming part is well known in scientific literature [6], while chemical collision contributions are directly amenable to Q^1 given in (9a). The nine hydrodynamic equations read as

$$\text{(12)}\quad \begin{gathered} \frac{\partial n^s}{\partial t} + \frac{\partial (n^s\, u_i^s)}{\partial x_i} = \varepsilon\, \lambda^s Q^1, \qquad s = 1,\dots,4,\\ \frac{\partial n^5}{\partial t} + \frac{\partial (n^5\, u_i^5)}{\partial x_i} = 0\,,\\ \frac{\partial (\rho\, u_i)}{\partial t} + \frac{\partial}{\partial x_j}\Big(\rho\, u_i\, u_j + nT\,\delta_{ij} + p_{ij}\Big) = 0\,,\\ \frac{\partial}{\partial t}\left(\frac{1}{2}\,\rho\, u^2 + \frac{3}{2}\, nT\right) + \frac{\partial}{\partial x_i}\left[\left(\frac{1}{2}\,\rho\, u^2 + \frac{5}{2}\, nT\right)u_i + p_{ij}\, u_j + q_i\right] = \varepsilon\, Q^1\, \Delta E\,, \end{gathered}$$

where ρ is the total mass density, $\boldsymbol{p}$ stands for the global viscous stress tensor, and $\boldsymbol{q}$ for the global heat flux vector.

In order to close macroscopic equations (12), we have to express drift velocities $\boldsymbol{u}^s$, viscous stress $\boldsymbol{p}$ and heat flux $\boldsymbol{q}$ in terms of the hydrodynamic fields $n^s, \boldsymbol{u}, T$. To this aim, we will apply an asymptotic procedure of Chapman–Enskog type [7] with respect to the small parameter ε. We start from Grad's equations (6), rescaled according to the kinetic system (11). First of all, a factor $1/\varepsilon^2$ will affect elastic terms relevant to encounters between particles of species 5 themselves: notice that correspondingly to the option $r = 5$ we have vanishing contributions in $\mathcal{R}_i^5$ and in $\mathcal{S}^5$, while in $\mathcal{V}_{ij}^5$ we have $-\dfrac{3}{4}\,\nu_2^{55}\,n^5\,p_{ij}^5$ and in $\mathcal{W}_i^5$ there is $-\dfrac{1}{2}\,\nu_2^{55}\,n^5\,q_i^5$. Moreover, a factor $1/\varepsilon$ will appear in front of elastic contributions due to scattering between A^5 and whatever other species A^s $(s \neq 5)$, and a factor ε will multiply all non–vanishing chemical terms.

According to Chapman–Enskog method, all non–hydrodynamic quantities have to be expanded in powers of ε:

$$
\begin{aligned}
&u_i^s = u_i^{s(0)} + \varepsilon\, u_i^{s(1)} \qquad && T^s = T^{s(0)} + \varepsilon\, T^{s(1)} \\
&p_{ij}^s = p_{ij}^{s(0)} + \varepsilon\, p_{ij}^{s(1)} \qquad && q_i^s = q_i^{s(0)} + \varepsilon\, q_i^{s(1)}
\end{aligned}
\tag{13}
$$

leaving unexpanded the hydrodynamic fields. This requirement implies some constraints on first order corrections. In fact, u_i^s and T^s are actually expanded, but they must produce unexpanded u_i and T. Since $\rho\, u_i = \sum_{s=1}^{5} \rho^s u_i^s$, imposing that u_i remains unexpanded provides the constraint

$$
\sum_{s=1}^{5} \rho^s\, u_i^{s(1)} = 0\,;
\tag{14}
$$

analogously for temperature: $nT = \displaystyle\sum_{s=1}^{5}\left[n^s T^s + \frac{1}{3}\,\rho^s\left(u_k^s u_k^s - u_k u_k\right)\right]$, hence we get the condition

$$
\sum_{s=1}^{5} n^s\, T^{s(1)} + \frac{2}{3}\sum_{s=1}^{5} \rho^s\, u_k^{s(0)}\, u_k^{s(1)} = 0\,.
\tag{15}
$$

Finally, Chapman–Enskog method requires also the expansion versus ε of the temporal derivative [7]:

$$
\frac{\partial}{\partial t} = \frac{\partial_0}{\partial t} + \varepsilon\,\frac{\partial_1}{\partial t}\,.
\tag{16}
$$

In order to determine constitutive equations of Newton type and correspondingly Navier–Stokes–like fluid–dynamic equations, we substitute the expansions (13) and (16) into Grad's equations, and then in each equation we equate the coefficients of equal powers of ε. First of all, leading order ($O(1/\varepsilon^2)$) terms in Grad's equations imply that $p_{ij}^{5(0)} = 0$ and $q_i^{5(0)} = 0$, and these results are consistent with the fact that, to the zero order, distribution f^5 is a local Maxwellian. By considering then $O(1/\varepsilon)$ terms, from equations for mass velocities and temperatures we get

$$u_i^{s(0)} = u_i^{5(0)}, \qquad T^{s(0)} = T^{5(0)}, \qquad \forall s \neq 5\,,$$

hence, bearing in mind definitions of global $\boldsymbol{u}$ and T, we have

$$u_i^{s(0)} = u_i\,, \qquad T^{s(0)} = T\,, \qquad \forall s = 1, \ldots, 5\,. \tag{17}$$

Then, from equations for p_{ij}^s and q_i^s we get

$$\begin{gathered} p_{ij}^{s(0)} = 0\,, \qquad q_i^{s(0)} = 0\,, \qquad \forall s = 1, \ldots, 4, \\ p_{ij}^{5(1)} = 0\,, \qquad q_i^{5(1)} = 0\,. \end{gathered} \tag{18}$$

Owing to the constraints (14) and (15), global viscous stress and heat flux turn out to be, neglecting $O(\varepsilon^2)$ terms [4],

$$p_{ij} = \varepsilon \sum_{s=1}^{5} p_{ij}^{s(1)}, \qquad q_i = \varepsilon \left(\sum_{s=1}^{5} q_i^{s(1)} + \frac{5}{2}\, T \sum_{s=1}^{5} n^s\, u_i^{s(1)} \right), \tag{19}$$

hence in order to close the macroscopic system (12) we have to determine first order corrections $u_i^{s(1)}$, $p_{ij}^{s(1)}$ and $q_i^{s(1)}$. To this aim, we have to analyze $O(1)$ terms of Grad's system. From equations for u_i^s, we get the equalities

$$\begin{aligned} m^s n^s \left(\frac{\partial_0 u_i}{\partial t} + u_j\, \frac{\partial u_i}{\partial x_j} \right) + \frac{\partial (n^s T)}{\partial x_i} &= \nu_1^{s5} \mu^{s5} n^s n^5 \left(u_i^{5(1)} - u_i^{s(1)} \right), \qquad s = 1, \ldots, 4, \\ m^5 n^5 \left(\frac{\partial_0 u_i}{\partial t} + u_j\, \frac{\partial u_i}{\partial x_j} \right) + \frac{\partial (n^5 T)}{\partial x_i} &= \sum_{s=1}^{4} \nu_1^{s5}\, \mu^{s5}\, n^s\, n^5 \left(u_i^{s(1)} - u_i^{5(1)} \right). \end{aligned} \tag{20}$$

Since the sum of right hand sides vanishes, this system admits solution only if the same holds for left hand sides, and this "compatibility condition" is just what is required in order to determine the unknown operator $\dfrac{\partial_0 u_i}{\partial t}$:

$$\frac{\partial_0 u_i}{\partial t} + u_j\, \frac{\partial u_i}{\partial x_j} = -\, \frac{1}{\rho}\, \frac{\partial (nT)}{\partial x_i}\,.$$

By substituting into (20) we obtain, for $s = 1, \ldots, 4$,

$$u_i^{s(1)} = \frac{1}{\nu_1^{s5}\, \mu^{s5}\, n^s\, n^5} \left\{ \frac{m^s n^s}{\rho}\, \frac{\partial (nT)}{\partial x_i} - \frac{\partial (n^s T)}{\partial x_i} \right\} + u_i^{5(1)}, \tag{21}$$

where $u_i^{5(1)}$ may be now made explicit taking into account the constraint (14):

$$u_i^{5(1)} = -\frac{1}{\rho}\sum_{r=1}^{4}\frac{m^r + m^5}{\nu_1^{r5}\, m^5\, n^5}\left\{\frac{m^r n^r}{\rho}\,\frac{\partial(nT)}{\partial x_i} - \frac{\partial(n^r T)}{\partial x_i}\right\}. \tag{22}$$

Considering then $O(1)$ terms of equations (6d) we easily get, for $s = 1, \ldots, 4$,

$$p_{ij}^{s(1)} = -\frac{(m^s + m^5)^2}{m^5\, n^5}\,\frac{1}{2\,\nu_1^{s5}\, m^s + \frac{3}{2}\,\nu_2^{s5}\, m^5}\, n^s T\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3}\,\delta_{ij}\,\frac{\partial u_k}{\partial x_k}\right). \tag{23}$$

On the other hand, equations (6e) provide, to the same order,

$$\begin{aligned}\frac{5}{2}\, n^s T\,\frac{\partial}{\partial x_i}\left(\frac{T}{m^s}\right) = &-\frac{5}{2}\,\frac{\nu_1^{s5}\mu^{s5}}{m^s}\, n^5 n^s T\left(u_i^{5(1)} - u_i^{s(1)}\right) + \frac{m^5 n^5}{(m^s + m^5)^3}\,\beta_1^{s5}\, q_i^{s(1)}\\ &+ \frac{m^5 n^5}{(m^s + m^5)^3}\,\frac{1}{2}\left(\beta_2^{s5} + 3\,\beta_3^{s5} + 5\,\frac{m^s}{m^5}\,\beta_4^{s5}\right) n^s T\left(u_i^{5(1)} - u_i^{s(1)}\right),\end{aligned}$$

but resorting to the expressions (8) for β_i^{sr} it can be verified that the coefficient in front of $(u_i^{5(1)} - u_i^{s(1)})$ vanishes, hence

$$q_i^{s(1)} = -\frac{(m^s + m^5)^3}{m^5\, n^5}\,\frac{1}{\left[3(m^s)^2 + (m^5)^2\right]\nu_1^{s5} + 2\, m^s m^5\, \nu_2^{s5}}\,\frac{5}{2}\, n^s T\,\frac{\partial}{\partial x_i}\left(\frac{T}{m^s}\right) \tag{24}$$

for $s = 1, \ldots, 4$.

Now the sought closure of the balance equations (12) is obtained simply by replacing the non–hydrodynamic variables with the corresponding approximations (13), making use of the zero order solutions in (17)–(18) and of the first order constitutive equations (21)–(24). Thus reactive "Navier–Stokes" equations involve the nine variables n^s, $\boldsymbol{u}$, T, and read as

$$\begin{gathered}\frac{\partial n^s}{\partial t} + \frac{\partial(n^s\, u_i)}{\partial x_i} + \varepsilon\,\frac{\partial\left(n^s\, u_i^{s(1)}\right)}{\partial x_i} = \varepsilon\,\lambda^s Q^1, \qquad s = 1, \ldots, 4,\\ \frac{\partial n^5}{\partial t} + \frac{\partial(n^5\, u_i)}{\partial x_i} + \varepsilon\,\frac{\partial\left(n^5\, u_i^{5(1)}\right)}{\partial x_i} = 0\,,\\ \frac{\partial(\rho\, u_i)}{\partial t} + \frac{\partial(\rho\, u_i\, u_j)}{\partial x_j} + \frac{\partial(nT)}{\partial x_i} + \varepsilon\,\frac{\partial p_{ij}^{(1)}}{\partial x_j} = 0\,,\\ \frac{\partial}{\partial t}\left(\frac{1}{2}\,\rho\, u^2 + \frac{3}{2}\, nT\right) + \frac{\partial}{\partial x_i}\left[\left(\frac{1}{2}\,\rho\, u^2 + \frac{5}{2}\, nT\right) u_i\right] + \varepsilon\,\frac{\partial(p_{ij}^{(1)}\, u_j)}{\partial x_i} + \varepsilon\,\frac{\partial q_i^{(1)}}{\partial x_i} = \varepsilon\, Q^1 \varDelta E,\end{gathered} \tag{25}$$

with $u_i^{s(1)}$ given by (21) and (22), and $p_{ij}^{(1)}$ and $q_i^{(1)}$ derived from (21)–(24) bearing in mind the relations (19):

$$p_{ij}^{(1)} = -\left(\sum_{s=1}^{4} \frac{(m^s+m^5)^2}{\left[2\nu_1^{s5} m^s + \frac{3}{2}\,\nu_2^{s5} m^5\right] m^5}\,\frac{n^s}{n^5}\right) T\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3}\,\delta_{ij}\,\frac{\partial u_k}{\partial x_k}\right), \tag{26a}$$

$$\begin{aligned} q_i^{(1)} = &-\left(\sum_{s=1}^{4} \frac{(m^s+m^5)^3}{\left[\left(3(m^s)^2+(m^5)^2\right)\nu_1^{s5} + 2\,m^s m^5\,\nu_2^{s5}\right] m^s m^5}\,\frac{n^s}{n^5}\right) \frac{5}{2}\,T\,\frac{\partial T}{\partial x_i} \\ &+ \frac{5}{2}\,T\left\{\sum_{s=1}^{4} \frac{m^s+m^5}{\nu_1^{s5} m^5 n^5}\left(\frac{1}{m^s} - \frac{n}{\rho}\right)\left[\frac{m^s n^s}{\rho}\,\frac{\partial(nT)}{\partial x_i} - \frac{\partial(n^s T)}{\partial x_i}\right]\right\}. \end{aligned} \tag{26b}$$

In (25), 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. In equations for number densities and temperature there appear clearly diffusive terms with respect to both n^s and T, contributed by the constitutive equations (21)-(22) and (26b), respectively. Equations for n^s are then of reaction–diffusion type, but they take into account also the effects due to the temperature of the mixture to which they are coupled and to the non–vanishing global velocity. This is an evident difference with respect to reaction–diffusion systems recently derived from kinetic models for a reactive mixture embedded in a background [1, 5], in which mass velocity is assumed zero, and equations for n^s turn out to be self–consistent (independent from the temperature). Even in the present frame, in the particular case of vanishing mass velocity we can get rid of the third equation in (25), provided the compatibility condition $\dfrac{\partial(nT)}{\partial x_i} = 0$ is fulfilled; equations for n^s however maintain the presence of a Laplacian of the temperature, and this is physically consistent since, as well known in the literature, kinetic energy has a non–negligible influence on the evolution of concentrations of the gases.

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