

From Reactive Boltzmann Equations to Reaction–Diffusion Systems

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Abstract

We consider the reactive Boltzmann equations for a mixture of different species of molecules, including a fixed background. We propose a scaling in which the collisions involving this background are predominant, while the inelastic (reactive) binary collisions are very rare. We show that, at the formal level, the solutions of the Boltzmann equations converge toward the solutions of a reaction-diffusion system. The coefficients of this system can be expressed in terms of the cross sections of the Boltzmann kernels. We discuss various possible physical settings (gases having internal energy, presence of a boundary, etc.), and present one rigorous mathematical proof in a simplified situation (for which the existence of strong solutions to the Boltzmann equation is known).

1 Introduction

Gases in which chemical reactions are present can be described by various types of equations. When one is interested only in global quantities (that is, quantities which do not depend on the space variable $\mathbf{x}$), systems of ODEs can be used (the unknowns are then the global concentrations at time t).

We are interested here in situations when the spatial variable $\mathbf{x}$ has to be taken into account, so that PDEs are used. In many papers, the gas is assumed to follow a (reactive) Euler or Navier-Stokes system (Cf. [5]). These systems can in turn be obtained (at the formal level) from (reactive) kinetic equations of Boltzmann type (Cf. [4], [5]).

Another possibility of modelling consists in considering that the main process (apart from chemical reactions) is the diffusion of the concentration of the species (this is particularly meaningful when the considered species are traces in a background medium). One is then led to write down reaction-diffusion equations (Cf. [16]). Equations of this kind can in some cases be obtained in a rigorous mathematical way starting from particle systems (Cf. [9], [10] and [20]).

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In this paper, we show how one can relate (reactive) kinetic equations of Boltzmann type to such reaction-diffusion systems, by a suitable scaling. Such a connection was explored in the 90s in a series of papers by R. Spigler and D. H. Zanette (Cf. [17], [18], [19], [21]), in the case when the (reactive) collision operators are phenomenological models such as Fokker-Planck or BGK (or for discrete velocities models). We introduce here more realistic reactive collision kernels (of Boltzmann type), such as those devised by A. Rossani and G. Spiga (Cf. [15]), M. Groppi and G. Spiga (Cf. [14]) or L. Desvillettes, R. Monaco and F. Salvarani (Cf. [12]).

The scaling which is used consists in considering that the dominant process to which the various species are submitted is (elastic) scattering with a fixed background, while advection and elastic collisions between the considered species are of lower order, and reactive collisions of even lower order. Finally, the time is rescaled in order to recover the time-scale of diffusion. This scaling is very close in spirit to the diffusive approximation of neutron transport (Cf. [6]) or the Rosseland approximation of radiative transfer (Cf. [13]).

More precisely, we consider a mixture of $N + 1$ gases A^s , $s = 1, \dots, N + 1$, and we assume that one of them (for instance A^{N+1}) is much denser than all the others, so that it plays the role of a “background”. This background is assumed to be distributed according to a fixed Maxwellian M . Then, we denote by $f^s \equiv f^s(t, \mathbf{x}, \mathbf{v})$ the s -th one-particle distribution function (number density of particles which at time t and point $\mathbf{x}$ have velocity $\mathbf{v}$) of the remaining species A^s , $s = 1, \dots, N$.

We assume that f^s satisfies the following rescaled (reactive) Boltzmann equation :

$$\epsilon \frac{\partial f^s}{\partial t} + \mathbf{v} \cdot \frac{\partial f^s}{\partial \mathbf{x}} = \frac{1}{\epsilon} Q_{EL}^s(f^s, M) + \epsilon^p \sum_{r=1}^N Q_{EL}^{sr}(f^s, f^r) + \epsilon Q_{CH}^s(\mathbf{f}), \quad (1)$$

where Q_{EL}^s and Q_{EL}^{sr} denote the elastic Boltzmann kernels (defined precisely in next section) and Q_{CH}^s denotes the reactive Boltzmann kernel (also defined in next section) which depends on the whole set $\mathbf{f}$ of densities. Finally, p can be any real number bigger or equal to 0.

We study in this paper the limit $\epsilon \rightarrow 0$ and relate eq. (1) to systems of reaction-diffusion equations for the number densities ρ^s , of the type :

$$\frac{\partial \rho^s}{\partial t} - \Lambda^s \Delta_{\mathbf{x}} \rho^s = \pm \Xi (\Pi \rho^3 \rho^4 - \rho^1 \rho^2), \quad (2)$$

where Λ^s , Ξ and Π are constants which are computed in terms of the masses, link chemical energy, and cross sections of the Boltzmann kernels appearing in (1). Eq. (2) corresponds to the case when $N = 4$ and one binary reversible reaction only is considered.

The paper is structured as follows. In section 2, we describe in a precise way the various kernels and we recall their main properties (conservations, H-theorem, etc.). Then, we detail in section 3 the formal computation allowing to recover the reaction-diffusion system (2) from the (rescaled) kinetic equation (1). For pedagogical reasons, we first perform the computation in the so-called Maxwell molecules case (subsection 3.1), before treating general cross sections (subsection 3.2). Section 4 is devoted to various extensions,

including more complex chemistry than just binary reversible reactions, reactions involving the background, gases having degrees of internal energy, treatment of the boundaries. Finally, we prove in a mathematically rigorous way in section 5 that the convergence holds in a special case in which the existence of solutions to the kinetic equation is known (that is, when the equation is linear).

2 Description of the (rescaled) kinetic model

We recall here that we consider a mixture of $N + 1$ gases A^s , $s = 1, \dots, N + 1$, and we assume that one of them (for instance A^{N+1}) is much denser than all the other ones, so that it plays the role of a “background”. In the sequel, this background is assumed to be distributed according to the reduced centered Maxwellian :

$$M(\mathbf{v}) = \left(\frac{1}{2\pi} \right)^{\frac{3}{2}} \exp \left(- \frac{|\mathbf{v}|^2}{2} \right). \quad (3)$$

Without loss of generality we have set particle mass, number density and temperature of the background equal to 1, and mean velocity equal to $\mathbf{0}$.

We denote by $f^s \equiv f^s(t, \mathbf{x}, \mathbf{v})$ the s -th one-particle distribution function (number density of molecules of the s -th species which at time t and point $\mathbf{x}$ have velocity $\mathbf{v}$) of the remaining species A^s , $s = 1, \dots, N$, while the symbol $\mathbf{f}$ will stand for the vector $(f^1, \dots, f^N)$. We assume that molecules of any species s can interact elastically both with the molecules of whatever other species r (including the case $r = s$), and with the particles of the fixed background. Moreover, we shall also take into account a suitable bimolecular reversible chemical reaction of type



We shall assume the direct reaction to be endothermic, in the sense that it provides an increase of chemical energy. For this physical situation, the extended set of Boltzmann equations reads as

$$\frac{\partial f^s}{\partial t} + \mathbf{v} \cdot \frac{\partial f^s}{\partial \mathbf{x}} = Q_{EL}^s(f^s, M) + \sum_{r=1}^N Q_{EL}^{sr}(f^s, f^r) + Q_{CH}^s(\mathbf{f}), \quad s = 1, \dots, N. \quad (5)$$

In this formula, the operators $Q_{EL}^s(f^s, M)$ and $Q_{EL}^{sr}(f^s, f^r)$ represent the net production of particles s (with velocity $\mathbf{v}$) due to elastic collisions with the background and with the species r , respectively, while the operator $Q_{CH}^s(\mathbf{f})$ 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

$$Q_{EL}^{sr}(f^s, f^r)(\mathbf{v}) = \int_{\mathbb{R}^3} \int_{S^2} \mathcal{B}^{sr}(\mathbf{v} - \mathbf{v}_*, \hat{\omega}) \left[f^s(\mathbf{v}') f^r(\mathbf{v}_*) - f^s(\mathbf{v}) f^r(\mathbf{v}_*) \right] d\mathbf{v}_* d\hat{\omega}. \quad (6)$$

Here, $(\mathbf{v}, \mathbf{v}_*)$ stand for the pre-collision velocities, while $(\mathbf{v}', \mathbf{v}'_*)$ stand for the post-collision ones. Taking into account the conservations of momentum and of kinetic energy, $(\mathbf{v}', \mathbf{v}'_*)$ can be expressed in terms of $(\mathbf{v}, \mathbf{v}_*)$ and of the unit vector $\hat{\omega} \in S^2$ as :

$$\begin{aligned}\mathbf{v}' &= \frac{m^s}{m^s + m^r} \mathbf{v} + \frac{m^r}{m^s + m^r} \mathbf{v}_* + \frac{m^r}{m^s + m^r} |\mathbf{v} - \mathbf{v}_*| T_{\hat{\omega}} \left(\frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \right), \\ \mathbf{v}'_* &= \frac{m^s}{m^s + m^r} \mathbf{v} + \frac{m^r}{m^s + m^r} \mathbf{v}_* - \frac{m^s}{m^s + m^r} |\mathbf{v} - \mathbf{v}_*| T_{\hat{\omega}} \left(\frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \right),\end{aligned}\tag{7}$$

where m^s denotes the particle mass of the species s , and $T_{\hat{\omega}}$ denotes the symmetry with respect to $\hat{\omega}^\perp$:

$$T_{\hat{\omega}} \mathbf{y} = \mathbf{y} - 2(\hat{\omega} \cdot \mathbf{y}) \hat{\omega}.\tag{8}$$

The function $\mathcal{B}^{sr}$ in (6) stands for the so-called differential cross section multiplied by the relative speed, and it depends on the impact parameter of the collision and the modulus of the relative velocity of the incoming particles (that is, $\left| \frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \cdot \hat{\omega} \right|$ and $|\mathbf{v} - \mathbf{v}_*|$).

The linear Boltzmann collision operator $Q_{EL}^s(f^s, M)$, which involves only one species A^s together with the background, can be obtained as particular case of the general bi-species elastic operator (6), by replacing the distribution function f^r by the Maxwellian M :

$$Q_{EL}^s(f^s, M)(\mathbf{v}) = \int_{\mathbb{R}^3} \int_{S^2} \mathcal{B}^s(\mathbf{v} - \mathbf{v}_*, \hat{\omega}) \left[f^s(\mathbf{v}') M(\mathbf{v}'_*) - f^s(\mathbf{v}) M(\mathbf{v}_*) \right] d\mathbf{v}_* d\hat{\omega}.\tag{9}$$

The expressions of $(\mathbf{v}', \mathbf{v}'_*)$ are again (7) with 1 instead of m^r , and $\mathcal{B}^s$ depends only on $\left| \frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \cdot \hat{\omega} \right|$ and $|\mathbf{v} - \mathbf{v}_*|$.

Considering now a chemical reaction of the type



the total mass is conserved, so we have $m := m^l + m^r = m^h + m^k$. We assume the direct reaction to be endothermic, thus, if E^s denotes the energy of chemical link of the species s , we have $\Delta E_{lr}^{hk} = E^h + E^k - E^l - E^r \geq 0$. Bearing in mind conservation of total (kinetic plus chemical) energy, to a variation of chemical energy there corresponds an opposite variation of kinetic energy. As a consequence, contrary to elastic collisions, the relative speed varies during a chemical reaction. More precisely, with reference to the process $A^l + A^r \rightarrow A^h + A^k$ with $(\mathbf{v}, \mathbf{v}_*)$ standing for the velocities of the ingoing particles (l, r) , the post-collision velocities are such that :

$$|\mathbf{v}' - \mathbf{v}'_*| = |\mathbf{v}_{lr}^{hk} - \mathbf{v}_{*lr}^{hk}| = \left[\frac{\mu^{lr}}{\mu^{hk}} \left(|\mathbf{v} - \mathbf{v}_*|^2 - \frac{2\Delta E_{lr}^{hk}}{\mu^{lr}} \right) \right]^{\frac{1}{2}},\tag{11}$$

where μ^{lr} , μ^{hk} are the reduced masses $\mu^{lr} = (m^l m^r)/m$, $\mu^{hk} = (m^h m^k)/m$. So, a threshold effect arises in the endothermic reaction : this reaction cannot happen in case of insufficient impinging kinetic energy, namely if $|\mathbf{v} - \mathbf{v}_*|^2 < \frac{2\Delta E_{lr}^{hk}}{\mu^{lr}}$. Taking into account the

conservation of momentum, the velocities after collision are provided by

$$\begin{aligned}\mathbf{v}' &= \mathbf{v}_{lr}^{hk} = \alpha^l \mathbf{v} + \alpha^r \mathbf{v}_* + \alpha^k \left[\frac{\mu^{lr}}{\mu^{hk}} \left(|\mathbf{v} - \mathbf{v}_*|^2 - \frac{2 \Delta E_{lr}^{hk}}{\mu^{lr}} \right) \right]^{\frac{1}{2}} T_{\hat{\omega}} \left(\frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \right), \\ \mathbf{v}'_* &= \mathbf{v}_{*lr}^{hk} = \alpha^l \mathbf{v} + \alpha^r \mathbf{v}_* - \alpha^h \left[\frac{\mu^{lr}}{\mu^{hk}} \left(|\mathbf{v} - \mathbf{v}_*|^2 - \frac{2 \Delta E_{lr}^{hk}}{\mu^{lr}} \right) \right]^{\frac{1}{2}} T_{\hat{\omega}} \left(\frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \right),\end{aligned}\tag{12}$$

where $\alpha^l = m^l/m$, $\alpha^r = m^r/m$, etc.

The net production of molecules l due to the reaction (10) is given by

$$\begin{aligned}Q_{CH}^l(\mathbf{f})(\mathbf{v}) &= \int_{\mathbb{R}^3} \int_{S^2} H \left(|\mathbf{v} - \mathbf{v}_*|^2 - \frac{2 \Delta E_{lr}^{hk}}{\mu^{lr}} \right) \mathcal{B}_{lr}^{hk}(\mathbf{v} - \mathbf{v}_*, \hat{\omega}) \\ &\quad \times \left[\left(\frac{\mu^{lr}}{\mu^{hk}} \right)^3 f^h(\mathbf{v}_{lr}^{hk}) f^k(\mathbf{v}_{*lr}^{hk}) - f^l(\mathbf{v}) f^r(\mathbf{v}_*) \right] d\mathbf{v}_* d\hat{\omega},\end{aligned}\tag{13}$$

where H denotes the unit step function :

$$H(x) = \begin{cases} 1 & \text{if } x \geq 0, \\ 0 & \text{if } x < 0, \end{cases}$$

and $\mathcal{B}_{lr}^{hk}$ depends only on $\left| \frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \cdot \hat{\omega} \right|$ and $|\mathbf{v} - \mathbf{v}_*|$. Since the differential cross sections have to satisfy the indistinguishableness condition

$$\mathcal{B}_{lr}^{hk}(\mathbf{v} - \mathbf{v}_*, \hat{\omega}) = \mathcal{B}_{rl}^{kh}(\mathbf{v} - \mathbf{v}_*, \hat{\omega}),$$

the chemical operator for the species r may be obtained from (13) simply by permutations of indices :

$$\begin{aligned}Q_{CH}^r(\mathbf{f})(\mathbf{v}) &= \int_{\mathbb{R}^3} \int_{S^2} H \left(|\mathbf{v} - \mathbf{v}_*|^2 - \frac{2 \Delta E_{lr}^{hk}}{\mu^{lr}} \right) \mathcal{B}_{lr}^{hk}(\mathbf{v} - \mathbf{v}_*, \hat{\omega}) \\ &\quad \times \left[\left(\frac{\mu^{lr}}{\mu^{hk}} \right)^3 f^k(\mathbf{v}_{rl}^{kh}) f^h(\mathbf{v}_{*rl}^{kh}) - f^r(\mathbf{v}) f^l(\mathbf{v}_*) \right] d\mathbf{v}_* d\hat{\omega}\end{aligned}\tag{14}$$

where $(\mathbf{v}_{rl}^{kh}, \mathbf{v}_{*rl}^{kh})$ are provided by (12) by exchanging the indices $l \leftrightarrow r$, $h \leftrightarrow k$. On the other hand, $Q_{CH}^h(\mathbf{f})$ is a bit different because the reverse exothermic reaction can occur whatever pre-collision relative speed is, so that we do not need a unit step function in the integrand :

$$Q_{CH}^h(\mathbf{f})(\mathbf{v}) = \int_{\mathbb{R}^3} \int_{S^2} \mathcal{B}_{hk}^{lr}(\mathbf{v} - \mathbf{v}_*, \hat{\omega}) \left[\left(\frac{\mu^{hk}}{\mu^{lr}} \right)^3 f^l(\mathbf{v}_{hk}^{lr}) f^r(\mathbf{v}_{*hk}^{lr}) - f^h(\mathbf{v}) f^k(\mathbf{v}_*) \right] d\mathbf{v}_* d\hat{\omega},\tag{15}$$

where the function $\mathcal{B}_{hk}^{lr}$ is related to $\mathcal{B}_{lr}^{hk}$ by the so-called “microreversibility condition” :

$$|\mathbf{v} - \mathbf{v}_*| \mathcal{B}_{lr}^{hk}(\mathbf{v} - \mathbf{v}_*, \hat{\omega}) = \left(\frac{\mu^{hk}}{\mu^{lr}} \right)^2 |\mathbf{v}_{lr}^{hk} - \mathbf{v}_{*lr}^{hk}| \mathcal{B}_{hk}^{lr}(\mathbf{v}_{lr}^{hk} - \mathbf{v}_{*lr}^{hk}, \hat{\omega}).$$

Finally, $Q_{CH}^k(\mathbf{f})$ can be cast as (15) with obvious permutations of indices :

$$Q_{CH}^k(\mathbf{f})(\mathbf{v}) = \int_{\mathbb{R}^3} \int_{S^2} \mathcal{B}_{hk}^{lr}(\mathbf{v} - \mathbf{v}_*, \hat{\omega}) \left[\left(\frac{\mu^{hk}}{\mu^{lr}} \right)^3 f^r(\mathbf{v}_{kh}^{rl}) f^l(\mathbf{v}_{*kh}^{rl}) - f^k(\mathbf{v}) f^h(\mathbf{v}_*) \right] d\mathbf{v}_* d\hat{\omega}. \quad (16)$$

In the sequel, we shall also use the weak forms of the elastic and chemical collision operators. For the bi-species elastic operator $Q_{EL}^{sr}(f^s, f^r)$, it can be shown (by means of simple changes of variables) that for each function $\varphi^s(\mathbf{v})$ with suitable properties of integrability :

$$\begin{aligned} & \int_{\mathbb{R}^3} \varphi^s(\mathbf{v}) Q_{EL}^{sr}(f^s, f^r)(\mathbf{v}) d\mathbf{v} = \\ &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} \mathcal{B}^{sr}(\mathbf{v} - \mathbf{v}_*, \hat{\omega}) \left[\varphi^s(\mathbf{v}') - \varphi^s(\mathbf{v}) \right] f^s(\mathbf{v}) f^r(\mathbf{v}_*) d\mathbf{v} d\mathbf{v}_* d\hat{\omega}, \end{aligned} \quad (17)$$

or, in equivalent form,

$$\begin{aligned} & \int_{\mathbb{R}^3} \varphi^s(\mathbf{v}) Q_{EL}^{sr}(f^s, f^r)(\mathbf{v}) d\mathbf{v} = \\ &= -\frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} \mathcal{B}^{sr}(\mathbf{v} - \mathbf{v}_*, \hat{\omega}) \left[\varphi^s(\mathbf{v}') - \varphi^s(\mathbf{v}) \right] \left[f^s(\mathbf{v}') f^r(\mathbf{v}_*) - f^s(\mathbf{v}) f^r(\mathbf{v}_*) \right] d\mathbf{v} d\mathbf{v}_* d\hat{\omega}. \end{aligned} \quad (18)$$

We have the same formulas for the linear operator $Q_{EL}^s(f^s, M)$:

$$\begin{aligned} & \int_{\mathbb{R}^3} \varphi^s(\mathbf{v}) Q_{EL}^s(f^s, M)(\mathbf{v}) d\mathbf{v} = \\ &= -\frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} \mathcal{B}^s(\mathbf{v} - \mathbf{v}_*, \hat{\omega}) \left[\varphi^s(\mathbf{v}') - \varphi^s(\mathbf{v}) \right] \left[f^s(\mathbf{v}') M(\mathbf{v}_*) - f^s(\mathbf{v}) M(\mathbf{v}_*) \right] d\mathbf{v} d\mathbf{v}_* d\hat{\omega}. \end{aligned} \quad (19)$$

In particular, taking $\varphi^s(\mathbf{v}) = 1$ in (17) and (19) yields the conservation of number density for each species :

$$\int_{\mathbb{R}^3} Q_{EL}^{sr}(f^s, f^r)(\mathbf{v}) d\mathbf{v} = 0, \quad \int_{\mathbb{R}^3} Q_{EL}^s(f^s, M)(\mathbf{v}) d\mathbf{v} = 0. \quad (20)$$

On the other hand, for the chemical operators corresponding to the reaction (10), it can be proven [15] that if we denote by $K_{CH}^l(\mathbf{v}, \mathbf{v}_*, \hat{\omega})$ the whole integrand of (13), the following

relations hold :

$$\begin{aligned}
\int_{\mathbb{R}^3} \varphi^l(\mathbf{v}) Q_{CH}^l(\mathbf{f})(\mathbf{v}) d\mathbf{v} &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} \varphi^l(\mathbf{v}) K_{CH}^l(\mathbf{v}, \mathbf{v}_*, \hat{\omega}) d\mathbf{v} d\mathbf{v}_* d\hat{\omega}, \\
\int_{\mathbb{R}^3} \varphi^r(\mathbf{v}) Q_{CH}^r(\mathbf{f})(\mathbf{v}) d\mathbf{v} &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} \varphi^r(\mathbf{v}_*) K_{CH}^l(\mathbf{v}, \mathbf{v}_*, \hat{\omega}) d\mathbf{v} d\mathbf{v}_* d\hat{\omega}, \\
\int_{\mathbb{R}^3} \varphi^h(\mathbf{v}) Q_{CH}^h(\mathbf{f})(\mathbf{v}) d\mathbf{v} &= - \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} \varphi^h(\mathbf{v}_{lr}^{hk}) K_{CH}^l(\mathbf{v}, \mathbf{v}_*, \hat{\omega}) d\mathbf{v} d\mathbf{v}_* d\hat{\omega}, \\
\int_{\mathbb{R}^3} \varphi^k(\mathbf{v}) Q_{CH}^k(\mathbf{f})(\mathbf{v}) d\mathbf{v} &= - \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} \varphi^k(\mathbf{v}_{lr}^{hk}) K_{CH}^l(\mathbf{v}, \mathbf{v}_*, \hat{\omega}) d\mathbf{v} d\mathbf{v}_* d\hat{\omega}.
\end{aligned} \tag{21}$$

From now on, we shall study the set of Boltzmann equations (5) in a physical situation in which the fixed background is assumed denser than other species, the dominant role in the evolution of each species s being played by the elastic collisions with background particles. We therefore study in detail the following rescaled Boltzmann equations :

$$\epsilon \frac{\partial f^s}{\partial t} + \mathbf{v} \cdot \frac{\partial f^s}{\partial \mathbf{x}} = \frac{1}{\epsilon} Q_{EL}^s(f^s, M) + \epsilon^p \sum_{r=1}^N Q_{EL}^{sr}(f^s, f^r) + \epsilon Q_{CH}^s(\mathbf{f}), \tag{22}$$

with the power $p \geq 0$. Here, the main assumption is that the chemical kernel is of order ϵ . By keeping any possible power $p \geq 0$, we only assume that the interspecies collisions are much less frequent than the collisions with the background. Since the chemical reactions are very slow processes, and since we are interested in their time scale, we put the same scaling in front of the temporal derivative.

We shall see that, in this regime dominated by the collisions with the background, the final macroscopic equations we shall build up are not influenced by the particular scaling (that is, the power p) that we choose for the other bimolecular elastic encounters.

For the dominant operator, that is the elastic linear one, the following dissipation estimate (H-theorem) holds [3] :

$$\int_{\mathbb{R}^3} \frac{f^s(\mathbf{v})}{M^s(\mathbf{v})} Q_{EL}^s(f^s, M)(\mathbf{v}) d\mathbf{v} \leq 0, \tag{23}$$

where $M^s(\mathbf{v})$ is the Maxwellian having the same macroscopic parameters (density, mean velocity and temperature) as the background distribution (3), but involving the particle mass m^s :

$$M^s(\mathbf{v}) = \left(\frac{m^s}{2\pi} \right)^{\frac{3}{2}} \exp \left(- \frac{m^s |\mathbf{v}|^2}{2} \right). \tag{24}$$

More precisely, by applying (19) with $\varphi^s(\mathbf{v}) = f^s(\mathbf{v})/M^s(\mathbf{v})$, we get

$$\begin{aligned}
& \int_{\mathbb{R}^3} \frac{f^s(\mathbf{v})}{M^s(\mathbf{v})} Q_{EL}^s(f^s, M)(\mathbf{v}) d\mathbf{v} = \\
& = -\frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} \mathcal{B}^s \left[\frac{f^s(\mathbf{v}')}{M^s(\mathbf{v}')} - \frac{f^s(\mathbf{v})}{M^s(\mathbf{v})} \right] \left[f^s(\mathbf{v}') M(\mathbf{v}_*) - f^s(\mathbf{v}) M(\mathbf{v}_*) \right] d\mathbf{v} d\mathbf{v}_* d\hat{\omega} \\
& = -\frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} \mathcal{B}^s \left[\frac{f^s(\mathbf{v}')}{M^s(\mathbf{v}')} - \frac{f^s(\mathbf{v})}{M^s(\mathbf{v})} \right]^2 M^s(\mathbf{v}) M(\mathbf{v}_*) d\mathbf{v} d\mathbf{v}_* d\hat{\omega} \leq 0.
\end{aligned} \tag{25}$$

Thanks to (25), as soon as $\mathcal{B}^s > 0$ a.e., the equality in (23) holds if and only if $f^s(\mathbf{v}) = \rho^s M^s(\mathbf{v})$, where ρ^s corresponds to the number density of the gas A^s , and also if and only if $Q_{EL}^s(f^s, M) = 0$. So, in our scaling, after an initial time layer (of duration ϵ^2), collisions force the distributions f^s towards a Maxwellian configuration.

3 Formal derivation of reaction–diffusion equations

In this section we focus our attention on a mixture of five gases, A^1, A^2, A^3, A^4 , plus the background, that, besides all elastic collisions, can interact according to the bimolecular reversible chemical reaction



with the direct one endothermic.

We show that in this case, at the formal level, the solution of eq. (22) converges to the solution of a reaction-diffusion system like (2). In subsection 3.1, we concentrate on the Maxwell molecules case, in which all the constants can be computed. Then, we extend the result to all kinds of cross sections in subsection 3.2.

3.1 The Maxwell molecules case

In this subsection, we assume that all cross sections are of Maxwell molecules type, which means that the intermolecular forces are of “inverse power” kind, precisely proportional to $1/d^5$, where d is the intermolecular distance. This assumption implies (Cf. [3]) that the differential cross sections (both the elastic and the chemical ones) depend only on the angle formed by $\hat{\omega}$ and the relative velocity :

$$\begin{aligned}
\mathcal{B}^s(\mathbf{v} - \mathbf{v}_*, \hat{\omega}) &= \tilde{\mathcal{B}}^s \left(\left| \hat{\omega} \cdot \frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \right| \right), \quad \mathcal{B}^{sr}(\mathbf{v} - \mathbf{v}_*, \hat{\omega}) = \tilde{\mathcal{B}}^{sr} \left(\left| \hat{\omega} \cdot \frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \right| \right), \\
\mathcal{B}_{12}^{34}(\mathbf{v} - \mathbf{v}_*, \hat{\omega}) &= \tilde{\mathcal{B}}_{12}^{34} \left(\left| \hat{\omega} \cdot \frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \right| \right).
\end{aligned} \tag{27}$$

For each species $s = 1, \dots, 4$, let us consider the rescaled Boltzmann equation introduced in the previous section :

$$\epsilon \frac{\partial f_\epsilon^s}{\partial t} + \mathbf{v} \cdot \frac{\partial f_\epsilon^s}{\partial \mathbf{x}} = \frac{1}{\epsilon} Q_{EL}^s(f_\epsilon^s, M) + \epsilon^p \sum_{r=1}^4 Q_{EL}^{sr}(f_\epsilon^s, f_\epsilon^r) + \epsilon Q_{CH}^s(\mathbf{f}_\epsilon). \tag{28}$$

We first see that the linear elastic operator is the dominant one, in the sense that

$$Q_{EL}^s(f_\epsilon^s, M) = O(\epsilon). \quad (29)$$

But the linear operator $L^s = Q_{EL}^s(\cdot, M)$ is bounded, self-adjoint and Fredholm in $L^2(M^{-1}(\mathbf{v}) d\mathbf{v})$ (this is a consequence of the computations in [3] for example). Moreover, according to the H-theorem (23), the spectrum of L^s is included in $\mathbb{R}^-$, and 0 is an eigenvalue of order 1 whose eigenvector is the function M^s . As a consequence, f_ϵ^s is a perturbation of order 1 of a collision equilibrium :

$$f_\epsilon^s(t, \mathbf{x}, \mathbf{v}) = n_\epsilon^s(t, \mathbf{x}) M^s(\mathbf{v}) + \epsilon \tilde{g}_\epsilon^s(t, \mathbf{x}, \mathbf{v}), \quad (30)$$

with $\tilde{g}_\epsilon^s = O(1)$. Now, since ρ_ϵ^s denotes the number density of the distribution function f_ϵ^s , i.e. $\rho_\epsilon^s = \int_{\mathbb{R}^3} f_\epsilon^s(\mathbf{v}) d\mathbf{v}$, by integrating the equality (30) we get :

$$\rho_\epsilon^s = n_\epsilon^s + \epsilon \int_{\mathbb{R}^3} \tilde{g}_\epsilon^s(\mathbf{v}) d\mathbf{v}. \quad (31)$$

This allows to express n_ϵ^s as ρ_ϵ^s plus some $O(\epsilon)$ perturbation. By inserting this result into (30) we obtain :

$$f_\epsilon^s = \left(\rho_\epsilon^s - \epsilon \int_{\mathbb{R}^3} \tilde{g}_\epsilon^s(\mathbf{v}) d\mathbf{v} \right) M^s + \epsilon \tilde{g}_\epsilon^s = \rho_\epsilon^s M^s + \epsilon g_\epsilon^s, \quad (32)$$

where g_ϵ^s stands for

$$g_\epsilon^s = \tilde{g}_\epsilon^s - M^s \int_{\mathbb{R}^3} \tilde{g}_\epsilon^s(\mathbf{v}) d\mathbf{v}$$

and obviously fulfills the constraint

$$\int_{\mathbb{R}^3} g_\epsilon^s(\mathbf{v}) d\mathbf{v} = 0.$$

Let us now write down the macroscopic evolution equations for the number density and for the mean velocity starting from the kinetic equation (28).

Integrating (28) over the velocity variable, that is multiplying (28) by the weight function $\varphi^s(\mathbf{v}) = 1$, we get :

$$\epsilon \frac{\partial}{\partial t} \int_{\mathbb{R}^3} f_\epsilon^s(\mathbf{v}) d\mathbf{v} + \frac{\partial}{\partial \mathbf{x}} \cdot \int_{\mathbb{R}^3} \mathbf{v} f_\epsilon^s(\mathbf{v}) d\mathbf{v} = \epsilon \int_{\mathbb{R}^3} Q_{CH}^s(\mathbf{f}_\epsilon)(\mathbf{v}) d\mathbf{v}, \quad (33)$$

where the conservation of mass (20) for elastic collisions has been used.

Then, multiplying (28) by $\varphi^s(\mathbf{v}) = \mathbf{v}$, we get :

$$\begin{aligned} & \epsilon \frac{\partial}{\partial t} \int_{\mathbb{R}^3} \mathbf{v} f_\epsilon^s(\mathbf{v}) d\mathbf{v} + \frac{\partial}{\partial \mathbf{x}} \cdot \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v}) f_\epsilon^s(\mathbf{v}) d\mathbf{v} = \\ & = \frac{1}{\epsilon} \int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^s(f_\epsilon^s, M)(\mathbf{v}) d\mathbf{v} + \epsilon^p \sum_{r=1}^4 \int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^{sr}(f_\epsilon^s, f_\epsilon^r)(\mathbf{v}) d\mathbf{v} + \epsilon \int_{\mathbb{R}^3} \mathbf{v} Q_{CH}^s(\mathbf{f}_\epsilon)(\mathbf{v}) d\mathbf{v}. \end{aligned} \quad (34)$$

Let us compute the collision contribution due to the dominant operator (the linear elastic one). From formulas (7), we get :

$$\mathbf{v}' - \mathbf{v} = -\frac{2}{m^s + 1} |\mathbf{v} - \mathbf{v}_*| \left(\hat{\boldsymbol{\omega}} \cdot \frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \right) \hat{\boldsymbol{\omega}}.$$

So, bearing in mind the Maxwell molecule assumption (27), the angular integration in the weak form (17) relevant to $\varphi^s(\mathbf{v}) = \mathbf{v}$ provides

$$\begin{aligned} & \int_{S^2} \mathcal{B}^s(\mathbf{v} - \mathbf{v}_*, \hat{\boldsymbol{\omega}})(\mathbf{v}' - \mathbf{v}) d\hat{\boldsymbol{\omega}} = \\ &= -\frac{2}{m^s + 1} |\mathbf{v} - \mathbf{v}_*| \int_{S^2} \tilde{\mathcal{B}}^s \left(\left| \hat{\boldsymbol{\omega}} \cdot \frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \right| \right) \left(\hat{\boldsymbol{\omega}} \cdot \frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \right) \hat{\boldsymbol{\omega}} d\hat{\boldsymbol{\omega}} = \\ &= -\nu^s (\mathbf{v} - \mathbf{v}_*). \end{aligned} \quad (35)$$

Performing the integral above in polar coordinates, we get for the constant ν^s the value :

$$\nu^s = \frac{4\pi}{m^s + 1} \int_0^\pi \tilde{\mathcal{B}}^s(\cos \theta) \cos^2 \theta \sin \theta d\theta.$$

Finally, we obtain

$$\int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^s(f_\epsilon^s, M)(\mathbf{v}) d\mathbf{v} = -\nu^s \int_{\mathbb{R}^3} \mathbf{v} f_\epsilon^s(\mathbf{v}) d\mathbf{v}. \quad (36)$$

This last integral also appears in eq. (33) for number density, hence we can “insert” the momentum equation (34) into (33), ending up with :

$$\begin{aligned} & \frac{\partial}{\partial t} \int_{\mathbb{R}^3} f_\epsilon^s(\mathbf{v}) d\mathbf{v} + \frac{\partial}{\partial \mathbf{x}} \cdot \left\{ -\frac{\epsilon}{\nu^s} \frac{\partial}{\partial t} \int_{\mathbb{R}^3} \mathbf{v} f_\epsilon^s(\mathbf{v}) d\mathbf{v} - \frac{1}{\nu^s} \frac{\partial}{\partial \mathbf{x}} \cdot \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v}) f_\epsilon^s(\mathbf{v}) d\mathbf{v} \right. \\ & \left. + \frac{\epsilon^p}{\nu^s} \sum_{r=1}^4 \int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^{sr}(f_\epsilon^s, f_\epsilon^r)(\mathbf{v}) d\mathbf{v} + \frac{\epsilon}{\nu^s} \int_{\mathbb{R}^3} \mathbf{v} Q_{CH}^s(\mathbf{f}_\epsilon)(\mathbf{v}) d\mathbf{v} \right\} = \int_{\mathbb{R}^3} Q_{CH}^s(\mathbf{f}_\epsilon)(\mathbf{v}) d\mathbf{v} \end{aligned} \quad (37)$$

(all terms have been divided by ϵ).

At this point, let us recall that each distribution function f_ϵ^s takes the form (32), thus at the leading order it coincides with a Maxwellian with number density ρ_ϵ^s , zero mean velocity and normalized temperature. Therefore

$$\int_{\mathbb{R}^3} \mathbf{v} f_\epsilon^s(\mathbf{v}) d\mathbf{v} = O(\epsilon), \quad \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v}) f_\epsilon^s(\mathbf{v}) d\mathbf{v} = \frac{1}{m^s} \rho_\epsilon^s \mathbf{I} + O(\epsilon), \quad (38)$$

where $\mathbf{I}$ is the identity tensor. Moreover, since $Q_{EL}^{sr}(M^s, M^r) = 0$, we see that the elastic collision contributions on the left-hand side of (37) vanish (to the leading order) :

$$\int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^{sr}(f_\epsilon^s, f_\epsilon^r)(\mathbf{v}) d\mathbf{v} = O(\epsilon). \quad (39)$$

Therefore, even in the case $p = 0$, eq. (37) does not contain this term among the $O(1)$ contributions. Finally, following the strategy of [2], we compute the remaining chemical term (right-hand side of (37)). Note first that thanks to relations (21),

$$\int_{\mathbb{R}^3} Q_{CH}^s(\mathbf{f}_\epsilon)(\mathbf{v}) d\mathbf{v} = \pm \int_{\mathbb{R}^3} Q_{CH}^1(\mathbf{f}_\epsilon)(\mathbf{v}) d\mathbf{v}$$

with positive sign for $s = 1, 2$ and negative for $s = 3, 4$. Then, notice that when $f_\epsilon^s = \rho_\epsilon^s M^s + O(\epsilon)$ for each s , the content of the square brackets in the chemical collision operator $Q_{CH}^1(\mathbf{f}_\epsilon)$ becomes

$$\begin{aligned} & \left(\frac{\mu^{12}}{\mu^{34}} \right)^3 f_\epsilon^3(\mathbf{v}_{12}^{34}) f_\epsilon^4(\mathbf{v}_{*12}^{34}) - f_\epsilon^1(\mathbf{v}) f_\epsilon^2(\mathbf{v}_*) = \\ &= \frac{1}{(2\pi)^3} \left\{ \frac{(m^1 m^2)^3}{(m^3 m^4)^{\frac{3}{2}}} \rho_\epsilon^3 \rho_\epsilon^4 \exp \left[\frac{1}{2} \left(m^1 |\mathbf{v}|^2 + m^2 |\mathbf{v}_*|^2 - m^3 |\mathbf{v}_{12}^{34}|^2 - m^4 |\mathbf{v}_{*12}^{34}|^2 \right) \right] \right. \\ & \quad \left. - (m^1 m^2)^{\frac{3}{2}} \rho_\epsilon^1 \rho_\epsilon^2 \right\} \exp \left[-\frac{1}{2} \left(m^1 |\mathbf{v}|^2 + m^2 |\mathbf{v}_*|^2 \right) \right] + O(\epsilon). \end{aligned}$$

Taking into account the conservation of kinetic plus chemical energy, the argument of the exponential function inside the brackets reduces to ΔE_{12}^{34} . So, if we denote by

$$\nu_{12}^{34} = \int_{S^2} \hat{\mathcal{B}}_{12}^{34} \left(\left| \hat{\omega} \cdot \frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \right| \right) d\hat{\omega},$$

the sought chemical contribution results in :

$$\begin{aligned} \int_{\mathbb{R}^3} Q_{CH}^1(\mathbf{f}_\epsilon)(\mathbf{v}) d\mathbf{v} &= \nu_{12}^{34} \frac{(m^1 m^2)^{\frac{3}{2}}}{(2\pi)^3} \left[\left(\frac{\mu^{12}}{\mu^{34}} \right)^{\frac{3}{2}} \exp(\Delta E_{12}^{34}) \rho_\epsilon^3 \rho_\epsilon^4 - \rho_\epsilon^1 \rho_\epsilon^2 \right] \\ &\quad \times \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} H \left(|\mathbf{v} - \mathbf{v}_*|^2 - \frac{2\Delta E_{12}^{34}}{\mu^{12}} \right) \exp \left[-\frac{1}{2} \left(m^1 |\mathbf{v}|^2 + m^2 |\mathbf{v}_*|^2 \right) \right] d\mathbf{v} d\mathbf{v}_* + O(\epsilon) = \\ &= \nu_{12}^{34} \frac{2}{\sqrt{\pi}} \Gamma \left(\frac{3}{2}, \Delta E_{12}^{34} \right) \left[\left(\frac{\mu^{12}}{\mu^{34}} \right)^{\frac{3}{2}} \exp(\Delta E_{12}^{34}) \rho_\epsilon^3 \rho_\epsilon^4 - \rho_\epsilon^1 \rho_\epsilon^2 \right] + O(\epsilon), \end{aligned} \tag{40}$$

where $\Gamma(\alpha, x)$ is the incomplete Euler gamma function (cf. [1]) :

$$\Gamma(\alpha, x) = \int_x^\infty t^{\alpha-1} e^{-t} dt.$$

Finally, by inserting results (38), (39), (40) into the macroscopic equations (37), we obtain the set of approximated reaction–diffusion equations :

$$\frac{\partial \rho_\epsilon^s}{\partial t} - \frac{1}{m^s \nu^s} \Delta_{\mathbf{x}} \rho_\epsilon^s = \lambda^s \nu_{12}^{34} \frac{2}{\sqrt{\pi}} \Gamma \left(\frac{3}{2}, \Delta E_{12}^{34} \right) \left[\left(\frac{\mu^{12}}{\mu^{34}} \right)^{\frac{3}{2}} \exp(\Delta E_{12}^{34}) \rho_\epsilon^3 \rho_\epsilon^4 - \rho_\epsilon^1 \rho_\epsilon^2 \right] + O(\epsilon), \tag{41}$$

where $\lambda^1 = \lambda^2 = -\lambda^3 = -\lambda^4 = 1$.

Of course, any limit point ρ^s of the sequence ρ_ϵ^s satisfies

$$\frac{\partial \rho^s}{\partial t} - \frac{1}{m^s \nu^s} \Delta_{\mathbf{x}} \rho^s = \lambda^s \nu_{12}^{34} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Delta E_{12}^{34}\right) \left[\left(\frac{\mu^{12}}{\mu^{34}}\right)^{\frac{3}{2}} \exp(\Delta E_{12}^{34}) \rho^3 \rho^4 - \rho^1 \rho^2 \right]. \quad (42)$$

Notice that the chemical contributions vanish only if the content of the square brackets involving $\rho^3 \rho^4$ and $\rho^1 \rho^2$ vanishes. This reproduces exactly the “mass action law” corresponding to chemical collision equilibria [15, 2].

3.2 Case of general cross sections

A system of reaction–diffusion equations like (42) can be derived from the rescaled kinetic model (28) without the particular assumption (27) on the differential cross sections. The procedure in this case is a bit different from before, since the elastic contribution $\int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^s(f_\epsilon^s, M)(\mathbf{v}) d\mathbf{v}$ is not directly computable in terms of the momentum of f_ϵ^s as in (36).

We first note that if Maxwell molecules are replaced by hard potentials or hard spheres with cutoff (that is the usual assumption for rarefied gases, Cf. [3]), it is still possible to resort to the spectral properties of the operator L^s . This operator is not bounded anymore, but it is still possible (Cf. [3]) to show that the solution to the rescaled equation (28) takes the form (32) :

$$f_\epsilon^s = \rho_\epsilon^s M^s + \epsilon g_\epsilon^s, \quad (43)$$

with g_ϵ^s an $O(1)$ function with vanishing number density. Inserting this formula into the macroscopic equation (33), we get :

$$\frac{\partial \rho_\epsilon^s}{\partial t} + \frac{\partial}{\partial \mathbf{x}} \cdot \int_{\mathbb{R}^3} \mathbf{v} g_\epsilon^s(\mathbf{v}) d\mathbf{v} = \int_{\mathbb{R}^3} Q_{CH}^s(\mathbf{f}_\epsilon)(\mathbf{v}) d\mathbf{v}. \quad (44)$$

In order to express the streaming contribution in terms of the number density, we need more information about the correction g_ϵ^s . By inserting the expression (43) into the kinetic equation (28), we obtain that g_ϵ^s is solution to

$$Q_{EL}^s(g_\epsilon^s, M)(\mathbf{v}) = \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{x}} \left(\rho_\epsilon^s M^s \right) + O(\epsilon). \quad (45)$$

Let us define the function $\mathbf{g}_1^s$ as the solution to the problem

$$Q_{EL}^s(\mathbf{g}_1^s, M)(\mathbf{v}) = \mathbf{v} M^s(\mathbf{v}), \quad (46)$$

fulfilling the constraint

$$\int_{\mathbb{R}^3} \mathbf{g}_1^s(\mathbf{v}) d\mathbf{v} = \mathbf{0}. \quad (47)$$

According to the spectral properties of L^s (and still for hard potentials or hard spheres), the property

$$\int_{\mathbb{R}^3} \mathbf{v} M^s(\mathbf{v}) d\mathbf{v} = \mathbf{0}$$

implies that the linear problem (46) has a unique solution (Cf. [3, 6]), apart from a constant that is univocally determined by the constraint (47). By comparing the two equations (45) and (46), and bearing in mind that g_ϵ^s has zero number density, we have

$$g_\epsilon^s = \frac{\partial \rho_\epsilon^s}{\partial \mathbf{x}} \cdot \mathbf{g}_1^s + O(\epsilon). \quad (48)$$

We now give standard information for the problem (46). Notice that for each isometry $R \in O(\mathbb{R}^3)$,

$$Q_{EL}^s(R \circ \mathbf{g}_1^s, M) = R \circ Q_{EL}^s(\mathbf{g}_1^s, M). \quad (49)$$

Moreover, as extensively discussed in [11], it can be shown (by means of suitable changes of variables) that for all $R \in O(\mathbb{R}^3)$,

$$Q_{EL}^s(\mathbf{g}_1^s \circ R, M)(\mathbf{v}) = Q_{EL}^s(\mathbf{g}_1^s, M)(R\mathbf{v}). \quad (50)$$

Recalling eq. (46), the right-hand side of (50) can be rewritten as

$$Q_{EL}^s(\mathbf{g}_1^s, M)(R\mathbf{v}) = (R\mathbf{v}) M^s(\mathbf{v}) = R \circ Q_{EL}^s(\mathbf{g}_1^s, M)(\mathbf{v}). \quad (51)$$

Thus finally, collecting equalities (49), (50), (51) we have

$$Q_{EL}^s(R \circ \mathbf{g}_1^s, M) = Q_{EL}^s(\mathbf{g}_1^s \circ R, M).$$

Then, thanks to the uniqueness of the solution to the problem

$$Q_{EL}^s(\mathbf{z}, M)(\mathbf{v}) = (R\mathbf{v}) M^s(\mathbf{v}) \quad \text{with} \quad \int_{\mathbb{R}^3} \mathbf{z}(\mathbf{v}) d\mathbf{v} = \mathbf{0},$$

we see that

$$R(\mathbf{g}_1^s(\mathbf{v})) = \mathbf{g}_1^s(R\mathbf{v}), \quad \forall R \in O(\mathbb{R}^3). \quad (52)$$

This allows to conclude (see Lemma 3 of [11]) that the unknown function $\mathbf{g}_1^s$ takes the form

$$\mathbf{g}_1^s(\mathbf{v}) = -h^s(|\mathbf{v}|) \mathbf{v}, \quad (53)$$

where the function h^s depends only on the modulus of $\mathbf{v}$. By substituting this result into (48), the streaming contribution in the macroscopic equation (44) turns out to be

$$\begin{aligned} \frac{\partial}{\partial \mathbf{x}} \cdot \int_{\mathbb{R}^3} \mathbf{v} g_\epsilon^s(\mathbf{v}) d\mathbf{v} &= - \sum_{i,j=1}^3 \frac{\partial}{\partial x_i} \frac{\partial \rho_\epsilon^s}{\partial x_j} \int_{\mathbb{R}^3} h^s(|\mathbf{v}|) v_i v_j d\mathbf{v} + O(\epsilon) = \\ &= - \Delta_{\mathbf{x}} \left[\rho_\epsilon^s \int_{\mathbb{R}^3} h^s(|\mathbf{v}|) \frac{|\mathbf{v}|^2}{3} d\mathbf{v} \right] + O(\epsilon). \end{aligned} \quad (54)$$

Note that the diffusion coefficient, which from now on will be denoted by Υ^s , is actually strictly positive :

$$\begin{aligned}\Upsilon^s &= \frac{1}{3} \int_{\mathbb{R}^3} h^s(|\mathbf{v}|) |\mathbf{v}|^2 d\mathbf{v} = -\frac{1}{3} \int_{\mathbb{R}^3} \mathbf{g}_1^s(\mathbf{v}) \cdot \mathbf{v} d\mathbf{v} \\ &= -\frac{1}{3} \int_{\mathbb{R}^3} \frac{\mathbf{g}_1^s(\mathbf{v})}{M^s(\mathbf{v})} \cdot Q_{EL}^s(\mathbf{g}_1^s, M)(\mathbf{v}) d\mathbf{v}\end{aligned}$$

(where the last equality follows from (46)), and a computation analogous to (25) shows that the right-hand side is strictly positive (since $\mathbf{g}_1^s$ is not a Maxwellian).

The evaluation of the chemical contributions appearing in (44) does not involve substantial complications with respect to the previous subsection. Of course, for non Maxwell molecules, the integration over the angular variable does not yield a constant, therefore the final result cannot be completely explicit. Precisely, the reaction–diffusion system can be cast as

$$\frac{\partial \rho^s}{\partial t} - \Upsilon^s \Delta_{\mathbf{x}} \rho^s = \lambda^s \mathcal{K}(m^1, m^2, \Delta E_{12}^{34}) \left[\left(\frac{\mu^{12}}{\mu^{34}} \right)^{\frac{3}{2}} \exp(\Delta E_{12}^{34}) \rho^3 \rho^4 - \rho^1 \rho^2 \right], \quad (55)$$

where the coefficient $\mathcal{K}(m^1, m^2, \Delta E_{12}^{34})$ stands for

$$\begin{aligned}\mathcal{K}(m^1, m^2, \Delta E_{12}^{34}) &= \frac{(m^1 m^2)^{\frac{3}{2}}}{(2\pi)^3} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} H \left(|\mathbf{v} - \mathbf{v}_*|^2 - \frac{2 \Delta E_{12}^{34}}{\mu^{12}} \right) \mathcal{B}_{12}^{34}(\mathbf{v} - \mathbf{v}_*, \hat{\omega}) \\ &\quad \times \exp \left[-\frac{1}{2} \left(m^1 |\mathbf{v}|^2 + m^2 |\mathbf{v}_*|^2 \right) \right] d\mathbf{v} d\mathbf{v}_* d\hat{\omega} .\end{aligned} \quad (56)$$

4 Extensions

In this section, we shall extend the formal derivation of reaction–diffusion equations described in section 3 to some more complicated physical situations. We shall systematically focus our attention on the differences with respect to section 3.

4.1 Chemical reactions involving the background

The derivation of equations of reaction–diffusion type starting from the kinetic model (22) can be extended to different kinds of chemical reactions. In particular, particles of the fixed background may be involved in chemical interactions, with considerable consequences on the chemical terms of the relevant reaction–diffusion equations. This subsection will be mainly devoted to two examples. In the first one, we shall consider a bimolecular reversible reaction analogous to (26) but in which one of the species is the background. Then, in the second one, we shall investigate a non–reversible reaction. These two situations are chosen only for illustrative purposes, and obviously do not span the whole range of possible interactions.

4.1.1 A reversible reaction involving the background

We consider a mixture of four gases, A^1 , A^2 , A^3 plus the background B whose particles are taken with unitary mass and with vanishing energy of chemical link. These species can interact, besides elastic encounters, according to



This chemical reaction is assumed reversible, and the conservation of total mass implies that particle masses are such that $m^1 + m^2 = m^3 + 1 = m$. If the direct reaction is endothermic, the structure of the chemical collision operators Q_{CH}^s for $s = 1, 2, 3$ is very similar to (13)–(15), only with the fixed Maxwellian M replacing the distribution function f^k :

$$\begin{aligned} Q_{CH}^1(\mathbf{f})(\mathbf{v}) &= \int_{\mathbb{R}^3} \int_{S^2} H \left(|\mathbf{v} - \mathbf{v}_*|^2 - \frac{2\Delta E_{12}^3}{\mu^{12}} \right) \mathcal{B}_{12}^{3B}(\mathbf{v} - \mathbf{v}_*, \hat{\omega}) \\ &\quad \times \left[\left(\frac{\mu^{12}}{\mu^{3B}} \right)^3 f^3(\mathbf{v}_{12}^{3B}) M(\mathbf{v}_*^{3B}) - f^1(\mathbf{v}) f^2(\mathbf{v}_*) \right] d\mathbf{v}_* d\hat{\omega}. \end{aligned} \quad (58)$$

Then, Q_{CH}^2 can be obtained by means of suitable permutations of indices, and analogously Q_{CH}^3 , recalling that in the reverse exothermic reaction the unit step function H disappears. The weak forms of such chemical operators can be cast analogously to (21) :

$$\begin{aligned} \int_{\mathbb{R}^3} \varphi^1(\mathbf{v}) Q_{CH}^1(\mathbf{f})(\mathbf{v}) d\mathbf{v} &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} \varphi^1(\mathbf{v}) K_{CH}^1(\mathbf{v}, \mathbf{v}_*, \hat{\omega}) d\mathbf{v} d\mathbf{v}_* d\hat{\omega}, \\ \int_{\mathbb{R}^3} \varphi^2(\mathbf{v}) Q_{CH}^2(\mathbf{f})(\mathbf{v}) d\mathbf{v} &= \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} \varphi^2(\mathbf{v}_*) K_{CH}^1(\mathbf{v}, \mathbf{v}_*, \hat{\omega}) d\mathbf{v} d\mathbf{v}_* d\hat{\omega}, \\ \int_{\mathbb{R}^3} \varphi^3(\mathbf{v}) Q_{CH}^3(\mathbf{f})(\mathbf{v}) d\mathbf{v} &= - \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \int_{S^2} \varphi^3(\mathbf{v}_{12}^{3B}) K_{CH}^1(\mathbf{v}, \mathbf{v}_*, \hat{\omega}) d\mathbf{v} d\mathbf{v}_* d\hat{\omega}, \end{aligned} \quad (59)$$

where $K_{CH}^1(\mathbf{v}, \mathbf{v}_*, \hat{\omega})$ denotes the integrand of (58). Notice that, contrary to the classical chemical reactions of type (10), in the present chemical frame involving also background particles, we lose conservation of total number density and of momentum, in the sense that :

$$\sum_{s=1}^3 \int_{\mathbb{R}^3} Q_{CH}^s(\mathbf{f})(\mathbf{v}) d\mathbf{v} \neq 0, \quad \sum_{s=1}^3 \int_{\mathbb{R}^3} m^s \mathbf{v} Q_{CH}^s(\mathbf{f})(\mathbf{v}) d\mathbf{v} \neq \mathbf{0}. \quad (60)$$

In fact, during each direct chemical reaction (57), a part of the ingoing mass and momentum is absorbed by the fixed background, thus it disappears from our considered system; on the other hand, in the reverse reaction, the background causes a gain of mass and momentum to the system. We would reobtain the classical conservation laws if the background were not assumed fixed, and its evolution were governed by a kinetic Boltzmann equation.

For the present physical situation, if we rescale the Boltzmann equation as in (22), then the procedure described in section 3 yields the following reaction–diffusion equations :

$$\frac{\partial \rho^s}{\partial t} - \Upsilon^s \Delta_{\mathbf{x}} \rho^s = \lambda^s \mathcal{K}(m^1, m^2, \Delta E_{12}^3) \left[\left(\frac{\mu^{12}}{\mu^{3B}} \right)^{\frac{3}{2}} \exp(\Delta E_{12}^3) \rho^3 - \rho^1 \rho^2 \right], \quad s = 1, 2, 3 \quad (61)$$

with $\lambda^1 = \lambda^2 = -\lambda^3 = 1$, and the coefficient $\mathcal{K}$ given in (56). Note that the first part of the term inside the square brackets presents only a linear dependence on the unknown field ρ^3 , since the partner of the gas A^3 in the chemical reaction is the fixed background. If the background had been involved in both sides of the chemical reaction, for instance $A^1 + B \rightleftharpoons A^2 + B$, we would have ended up with a completely linear reaction–diffusion system. This system will be extensively discussed from a mathematical point of view in section 5.

4.1.2 An irreversible reaction involving three species in the products of reaction

Let us now describe the evolution of a mixture of five gases, A^s , $s = 1, \dots, 4$, plus the background B , undergoing mechanical encounters and the following irreversible chemical reaction :



This means that a collision between two particles of the species A^1 , A^2 may give rise to three particles, of species A^3 , A^4 and B respectively, but the reverse phenomenon cannot happen. Consequently, the chemical operators relevant to species A^1 , A^2 will consist only of a loss term, since each chemical reaction causes a loss of a particle 1 and of a particle 2, while, on the other hand, the chemical operators relevant to species A^3 , A^4 shall take into account only gain of molecules. Since the reaction is not reversible, in this part of the paper it is convenient to change a bit the notations : we shall denote by $\mathcal{B}$ the scattering kernel, the vectors $(\mathbf{v}^1, \mathbf{v}^2)$ shall stand for the velocities of the ingoing particles (A^1, A^2), and $(\mathbf{v}^3, \mathbf{v}^4, \mathbf{v}^B)$ for the velocities of the outgoing particles (A^3, A^4, B). Conservation of total mass implies that $m^1 + m^2 = m^3 + m^4 + 1 = m$, while conservations of momentum and total energy write as

$$m^1 \mathbf{v}^1 + m^2 \mathbf{v}^2 = m^3 \mathbf{v}^3 + m^4 \mathbf{v}^4 + \mathbf{v}^B, \quad (63)$$

$$\frac{1}{2} m^1 |\mathbf{v}^1|^2 + E^1 + \frac{1}{2} m^2 |\mathbf{v}^2|^2 + E^2 = \frac{1}{2} m^3 |\mathbf{v}^3|^2 + E^3 + \frac{1}{2} m^4 |\mathbf{v}^4|^2 + E^4 + \frac{1}{2} |\mathbf{v}^B|^2. \quad (64)$$

If we assume the reaction (62) exothermic, the chemical operator for the species 1 reads as

$$Q_{CH}^1(\mathbf{f})(\mathbf{v}^1) = - \int_{D^1} \mathcal{B}(\mathbf{v}^1, \mathbf{v}^2, \mathbf{v}^3, \mathbf{v}^4, \mathbf{v}^B) f^1(\mathbf{v}^1) f^2(\mathbf{v}^2) d\mathbf{v}^2 d\mathbf{v}^3 d\mathbf{v}^4 d\mathbf{v}^B, \quad (65)$$

where D^1 denotes the set of all vectors $(\mathbf{v}^2, \mathbf{v}^3, \mathbf{v}^4, \mathbf{v}^B)$ such that the constraints (63) and (64) are fulfilled. Thus, unlike the classical quintuple integral operator (13), in the present frame the quantity $\mathcal{B}$ is a distribution with an 8-dimensional support (twelve components of the vector $(\mathbf{v}^2, \mathbf{v}^3, \mathbf{v}^4, \mathbf{v}^B)$ minus four constraints). This is due to the fact that with respect to the classical reaction $A^1 + A^2 \longrightarrow A^3 + A^4$, we have here three more additional free parameters : the components of the background velocity $\mathbf{v}^B$. The operator for the species 2 is analogous, but now we have to integrate over the velocity variable $\mathbf{v}^1$ instead of $\mathbf{v}^2$:

$$Q_{CH}^2(\mathbf{f})(\mathbf{v}^2) = - \int_{D^2} \mathcal{B}(\mathbf{v}^1, \mathbf{v}^2, \mathbf{v}^3, \mathbf{v}^4, \mathbf{v}^B) f^1(\mathbf{v}^1) f^2(\mathbf{v}^2) d\mathbf{v}^1 d\mathbf{v}^3 d\mathbf{v}^4 d\mathbf{v}^B, \quad (66)$$

where D^2 contains the vectors $(\mathbf{v}^1, \mathbf{v}^3, \mathbf{v}^4, \mathbf{v}^B)$ fulfilling the equalities (63) and (64). The corresponding operators for species 3 and 4 have the same structure but the opposite sign, since each chemical reaction causes a gain of two particles (A^3, A^4) :

$$Q_{CH}^3(\mathbf{f})(\mathbf{v}^3) = \int_{D^3} \mathcal{B}(\mathbf{v}^1, \mathbf{v}^2, \mathbf{v}^3, \mathbf{v}^4, \mathbf{v}^B) f^1(\mathbf{v}^1) f^2(\mathbf{v}^2) d\mathbf{v}^1 d\mathbf{v}^2 d\mathbf{v}^4 d\mathbf{v}^B, \quad (67)$$

$$Q_{CH}^4(\mathbf{f})(\mathbf{v}^4) = \int_{D^4} \mathcal{B}(\mathbf{v}^1, \mathbf{v}^2, \mathbf{v}^3, \mathbf{v}^4, \mathbf{v}^B) f^1(\mathbf{v}^1) f^2(\mathbf{v}^2) d\mathbf{v}^1 d\mathbf{v}^2 d\mathbf{v}^3 d\mathbf{v}^B, \quad (68)$$

with obvious meaning for the sets D^3, D^4 .

For this irreversible chemical reaction, the reaction–diffusion equations following from the rescaled Boltzmann equations (22) are :

$$\frac{\partial \rho^s}{\partial t} - \Upsilon^s \Delta_{\mathbf{x}} \rho^s = -\lambda^s \mathcal{K} \rho^1 \rho^2, \quad (69)$$

with $\lambda^1 = \lambda^2 = -\lambda^3 = -\lambda^4 = 1$, and the coefficient $\mathcal{K}$ standing for :

$$\mathcal{K} = \frac{(m^1 m^2)^{\frac{3}{2}}}{(2\pi)^3} \int_{\mathbb{R}^3} \int_{D^1} \mathcal{B}(\mathbf{v}^1, \mathbf{v}^2, \mathbf{v}^3, \mathbf{v}^4, \mathbf{v}^B) \exp \left[-\frac{1}{2} \left(m^1 |\mathbf{v}^1|^2 + m^2 |\mathbf{v}^2|^2 \right) \right] d\mathbf{v}^1 d\mathbf{v}^2 d\mathbf{v}^3 d\mathbf{v}^4 d\mathbf{v}^B. \quad (70)$$

4.2 Gases with internal energy

It is possible to build up a reactive kinetic model of Boltzmann type which also takes into account the internal energy of the species. This is achieved for example in [14] with a discrete set of internal energies. It is also achieved in [12] assuming that for each species A^s , the distribution function f^s depends (besides on time, position and velocity) on a continuous internal energy parameter I which varies in $\mathbb{R}^+$.

The incoming energy corresponding to an elastic encounter between two molecules A^s, A^r with velocity and internal energy $(\mathbf{v}, I)$ and $(\mathbf{v}_*, I_*)$ respectively is :

$$\mathcal{E} = \frac{1}{2} m^s |\mathbf{v}|^2 + \frac{1}{2} m^r |\mathbf{v}_*|^2 + I + I_*.$$

Then, a proportion $1 - R$ (with $R \in [0, 1]$) of this energy is attributed to the internal energy of the outgoing molecules, in the sense that

$$I' + I'_* = (1 - R) \mathcal{E}.$$

This internal energy is distributed to the two particles according to

$$I' = r(1 - R) \mathcal{E}, \quad I'_* = (1 - r)(1 - R) \mathcal{E},$$

with $r \in [0, 1]$. This procedure is sometimes called “Borgnakke–Larsen model”. Therefore the kinetic energy of the outgoing molecules is $R \mathcal{E}$, and as a consequence the post-collision velocities are provided by the relations :

$$\begin{aligned} \mathbf{v}' &= \frac{m^s}{m^s + m^r} \mathbf{v} + \frac{m^r}{m^s + m^r} \mathbf{v}_* + \frac{m^r}{m^s + m^r} \sqrt{\frac{2R\mathcal{E}}{\mu^{sr}}} T_{\hat{\omega}} \left(\frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \right), \\ \mathbf{v}'_* &= \frac{m^s}{m^s + m^r} \mathbf{v} + \frac{m^r}{m^s + m^r} \mathbf{v}_* - \frac{m^s}{m^s + m^r} \sqrt{\frac{2R\mathcal{E}}{\mu^{sr}}} T_{\hat{\omega}} \left(\frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \right). \end{aligned} \quad (71)$$

The non-reactive Boltzmann collision operator for this physical situation is given by [12] :

$$\begin{aligned} Q_{EL}^{sr}(f^s, f^r)(\mathbf{v}, I) &= \int_{\mathcal{D}} \left[f^s(\mathbf{v}', I') f^r(\mathbf{v}'_*, I'_*) - f^s(\mathbf{v}, I) f^r(\mathbf{v}_*, I_*) \right] \\ &\quad \times \mathcal{B}^{sr}(\mathbf{v}, \mathbf{v}_*, I, I_*, R, r, \hat{\omega}) \frac{(1 - R)}{|\mathbf{v} - \mathbf{v}_*| \psi^s(I)} d\mathbf{v}_* dI_* dR dr d\hat{\omega} \end{aligned} \quad (72)$$

where $\mathcal{D} = \{\mathbf{v}_* \in \mathbb{R}^3; I_* \geq 0; r, R \in [0, 1]; \hat{\omega} \in S^2\}$, and $\psi^s(I) dI$ is a nonnegative measure which is a parameter of the model.

Analogous considerations allow to also build up the chemical scattering operators corresponding to the chemical reaction $A^1 + A^2 \rightleftharpoons A^3 + A^4$. Skipping further details, the reactive collision kernel for the species 1 is defined (Cf. [12]) as :

$$\begin{aligned} Q_{CH}^1(\mathbf{f})(\mathbf{v}, I) &= \\ &= \int_{\mathcal{D}} H^1 \left[\left(\frac{\mu^{12}}{\mu^{34}} \right)^3 f^3 \left(\alpha^1 \mathbf{v} + \alpha^2 \mathbf{v}_* + \alpha^4 \sqrt{\frac{2}{\mu^{34}}} \left(R\mathcal{E} - \frac{\Delta E_{12}^{34}}{6} \right) T_{\hat{\omega}} \left(\frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \right), (1 - R)r\mathcal{E} - \frac{\Delta E_{12}^{34}}{6} \right) \right. \\ &\quad \times f^4 \left(\alpha^1 \mathbf{v} + \alpha^2 \mathbf{v}_* - \alpha^3 \sqrt{\frac{2}{\mu^{34}}} \left(R\mathcal{E} - \frac{\Delta E_{12}^{34}}{6} \right) T_{\hat{\omega}} \left(\frac{\mathbf{v} - \mathbf{v}_*}{|\mathbf{v} - \mathbf{v}_*|} \right), (1 - R)(1 - r)\mathcal{E} - \frac{\Delta E_{12}^{34}}{6} \right) \\ &\quad \left. - f^1(\mathbf{v}, I) f^2(\mathbf{v}_*, I_*) \right] \mathcal{B}_{12}^{34}(\mathbf{v}, \mathbf{v}_*, I, I_*, R, r, \hat{\omega}) \frac{(1 - R)}{(m^1 m^2)^2 |\mathbf{v} - \mathbf{v}_*| \psi^1(I)} d\mathbf{v}_* dI_* dR dr d\hat{\omega}, \end{aligned} \quad (73)$$

where the unit step function H^1 takes into account the threshold effects involved in the endothermic direct reaction. The operators Q_{CH}^2 , Q_{CH}^3 , Q_{CH}^4 , not reported here for the sake of brevity, present a similar structure.

It is worth remarking that the Maxwellian collision equilibrium of the elastic operator also depends on the internal energy I . More precisely, the solution to the equation $\sum_{r=1}^4 Q_{EL}^{sr}(f^s, f^r) = 0$ turns out to be (Cf. [12]) :

$$f^s(\mathbf{v}, I) = \frac{\rho^s}{q^s(T)} \left(\frac{m^s}{2\pi T} \right)^{\frac{3}{2}} \exp \left\{ -\frac{1}{T} \left(\frac{m^s |\mathbf{v} - \mathbf{u}|^2}{2} + I \right) \right\},$$

where $\mathbf{u}$, T are the mean velocity and the global temperature of the mixture, and q^s (as a function of $1/T$) is the Laplace transform of ψ^s :

$$q^s(T) = \int_0^{+\infty} \psi^s(I) e^{-I/T} dI.$$

The derivation of reaction–diffusion equations outlined in section 3 may be performed even starting from this model. The chemical contribution appearing in the resulting equations has already been discussed, in the context of hydrodynamic equations, in [12], to which the reader is addressed for further details. The final reaction–diffusion system is

$$\frac{\partial \rho^s}{\partial t} - \Upsilon^s \Delta_{\mathbf{x}} \rho^s = \lambda^s \mathcal{K} \left[\frac{\rho^3 \rho^4}{q^3(1)q^4(1)} - \left(\frac{\mu^{34}}{\mu^{12}} \right)^{\frac{3}{2}} \exp(-\Delta E_{12}^{34}) \frac{\rho^1 \rho^2}{q^1(1)q^2(1)} \right], \quad (74)$$

where the coefficient $\mathcal{K}$ stands for

$$\begin{aligned} \mathcal{K} = & \frac{(m^3 m^4)^{\frac{3}{2}}}{(2\pi)^3} \int_{\mathcal{D}'} \exp \left[- \left(\frac{1}{2} m^3 |\mathbf{v}_{12}^{34}|^2 + I' + \frac{1}{2} m^4 |\mathbf{v}_{*12}^{34}|^2 + I'_* \right) \right] \\ & \times \mathcal{B}_{34}^{12}(\mathbf{v}_{12}^{34}, \mathbf{v}_{*12}^{34}, I', I'_*, R', r', \hat{\omega}) \frac{(1 - R')}{(m^3 m^4)^2 |\mathbf{v}_{12}^{34} - \mathbf{v}_{*12}^{34}|} d\mathbf{v}_{12}^{34} d\mathbf{v}_{*12}^{34} dI' dI'_* dR' dr' d\hat{\omega}, \end{aligned} \quad (75)$$

and where $\mathcal{D}' = \{\mathbf{v}_{12}^{34}, \mathbf{v}_{*12}^{34} \in \mathbb{R}^3; I', I'_* \in \mathbb{R}^+; r', R' \in [0, 1]; \hat{\omega} \in S^2\}$.

4.3 Boundary and initial conditions

In this subsection, we explain what happens when the gases are confined in a domain Ω of $\mathbb{R}^3$. We also comment on the initial condition, noting that it is not necessarily compatible with the macroscopic equation. We start again from equation (28) :

$$\epsilon \frac{\partial f_\epsilon^s}{\partial t} + \mathbf{v} \cdot \frac{\partial f_\epsilon^s}{\partial \mathbf{x}} = \frac{1}{\epsilon} Q_{EL}^s(f_\epsilon^s, M) + \epsilon^p \sum_{r=1}^4 Q_{EL}^{sr}(f_\epsilon^s, f_\epsilon^r) + \epsilon Q_{CH}^s(\mathbf{f}_\epsilon),$$

but we now assume that $\mathbf{x}$ lives in a regular open set Ω of $\mathbb{R}^3$, and that the densities f_ϵ^s satisfy the specular reflection boundary condition :

$$\forall t > 0, \mathbf{x} \in \partial\Omega, \mathbf{v} \in \mathbb{R}^3, \quad f_\epsilon^s(t, \mathbf{x}, \mathbf{v}) = f_\epsilon^s(t, \mathbf{x}, R\mathbf{v}), \quad (76)$$

where

$$R\mathbf{v} = \mathbf{v} - 2(\mathbf{v} \cdot \hat{\mathbf{n}}(\mathbf{x})) \hat{\mathbf{n}}(\mathbf{x}),$$

and $\hat{\mathbf{n}}(\mathbf{x})$ is the outward normal vector to $\partial\Omega$ at point $\mathbf{x}$. Finally, we introduce the initial datum

$$\forall \mathbf{x} \in \Omega, \quad \mathbf{v} \in \mathbb{R}^3, \quad f_\epsilon^s(0, \mathbf{x}, \mathbf{v}) = f_0^s(\mathbf{x}, \mathbf{v}), \quad (77)$$

where $f_0^s(\mathbf{x}, \mathbf{v})$ does not depend on ϵ .

Then, we rewrite formula (37) in a weak form, using a smooth test function $\psi \equiv \psi(t, \mathbf{x})$ having a compact support in $[0, +\infty[\times \overline{\Omega}$:

$$\begin{aligned} & - \int_0^{+\infty} \int_\Omega \int_{\mathbb{R}^3} f_\epsilon^s(t, \mathbf{x}, \mathbf{v}) \frac{\partial \psi}{\partial t}(t, \mathbf{x}) dt d\mathbf{x} d\mathbf{v} - \int_\Omega \int_{\mathbb{R}^3} f_\epsilon^s(0, \mathbf{x}, \mathbf{v}) \psi(0, \mathbf{x}) d\mathbf{x} d\mathbf{v} \\ & + \frac{1}{\epsilon} \int_0^{+\infty} \int_{\partial\Omega} \int_{\mathbb{R}^3} (\mathbf{v} \cdot \hat{\mathbf{n}}(\mathbf{x})) f_\epsilon^s(t, \mathbf{x}, \mathbf{v}) \psi(t, \mathbf{x}) dt d\mathbf{x} d\mathbf{v} \\ & + \frac{1}{\nu_s} \left\{ - \epsilon \int_0^{+\infty} \int_\Omega \int_{\mathbb{R}^3} \mathbf{v} f_\epsilon^s(t, \mathbf{x}, \mathbf{v}) \cdot \frac{\partial}{\partial t} \frac{\partial}{\partial \mathbf{x}} \psi(t, \mathbf{x}) dt d\mathbf{x} d\mathbf{v} \right. \\ & - \epsilon \int_\Omega \int_{\mathbb{R}^3} \mathbf{v} f_\epsilon^s(0, \mathbf{x}, \mathbf{v}) \cdot \frac{\partial}{\partial \mathbf{x}} \psi(0, \mathbf{x}) d\mathbf{x} d\mathbf{v} \\ & + \int_0^{+\infty} \int_{\partial\Omega} \int_{\mathbb{R}^3} (\mathbf{v} \cdot \hat{\mathbf{n}}(\mathbf{x})) \mathbf{v} f_\epsilon^s(t, \mathbf{x}, \mathbf{v}) \cdot \frac{\partial}{\partial \mathbf{x}} \psi(t, \mathbf{x}) dt d\mathbf{x} d\mathbf{v} \\ & - \int_0^{+\infty} \int_\Omega \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v}) f_\epsilon^s(t, \mathbf{x}, \mathbf{v}) : \frac{\partial}{\partial \mathbf{x}} \frac{\partial}{\partial \mathbf{x}} \psi(t, \mathbf{x}) dt d\mathbf{x} d\mathbf{v} \\ & - \epsilon^p \sum_{r=1}^4 \int_0^{+\infty} \int_\Omega \int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^{sr}(f_\epsilon^s, f_\epsilon^r)(t, \mathbf{x}, \mathbf{v}) \cdot \frac{\partial}{\partial \mathbf{x}} \psi(t, \mathbf{x}) dt d\mathbf{x} d\mathbf{v} \\ & \left. - \epsilon \int_0^{+\infty} \int_\Omega \int_{\mathbb{R}^3} \mathbf{v} Q_{CH}^s(\mathbf{f}_\epsilon)(t, \mathbf{x}, \mathbf{v}) \cdot \frac{\partial}{\partial \mathbf{x}} \psi(t, \mathbf{x}) dt d\mathbf{x} d\mathbf{v} \right\} \\ & = \int_0^{+\infty} \int_\Omega \int_{\mathbb{R}^3} Q_{CH}^s(\mathbf{f}_\epsilon)(t, \mathbf{x}, \mathbf{v}) \psi(t, \mathbf{x}) dt d\mathbf{x} d\mathbf{v}. \end{aligned} \quad (78)$$

Using the boundary condition (76), we see that $\int_{\mathbb{R}^3} (\mathbf{v} \cdot \hat{\mathbf{n}}(\mathbf{x})) f_\epsilon^s(t, \mathbf{x}, \mathbf{v}) d\mathbf{v} = 0$, so that the third term in the above equation is cancelled.

Then, passing to the limit in (78), and remembering that at first order $f_\epsilon^s(t, \mathbf{x}, \mathbf{v}) \sim \rho^s(t, \mathbf{x}) M^s(\mathbf{v})$, we get

$$\begin{aligned} & - \int_0^{+\infty} \int_\Omega \rho^s(t, \mathbf{x}) \frac{\partial \psi}{\partial t}(t, \mathbf{x}) dt d\mathbf{x} - \int_\Omega \int_{\mathbb{R}^3} f_0^s(\mathbf{x}, \mathbf{v}) \psi(0, \mathbf{x}) d\mathbf{x} d\mathbf{v} \\ & + \frac{1}{\nu_s} \int_0^{+\infty} \int_{\partial\Omega} \int_{\mathbb{R}^3} (\mathbf{v} \cdot \hat{\mathbf{n}}(\mathbf{x})) \mathbf{v} \rho^s(t, \mathbf{x}) M^s(\mathbf{v}) \cdot \frac{\partial}{\partial \mathbf{x}} \psi(t, \mathbf{x}) dt d\mathbf{x} d\mathbf{v} \\ & - \frac{1}{m^s \nu^s} \int_0^{+\infty} \int_\Omega \rho^s(t, \mathbf{x}) \Delta_{\mathbf{x}} \psi(t, \mathbf{x}) dt d\mathbf{x} \\ & = \int_0^{+\infty} \int_\Omega \int_{\mathbb{R}^3} Q_{CH}^s(\boldsymbol{\rho}(t, \mathbf{x}) \mathbf{M}(\mathbf{v})) \psi(t, \mathbf{x}) dt d\mathbf{x} d\mathbf{v}. \end{aligned} \quad (79)$$

We now observe that

$$\int_{\mathbb{R}^3} (\mathbf{v} \cdot \hat{\mathbf{n}}(\mathbf{x})) \mathbf{v} M^s(\mathbf{v}) d\mathbf{v} = \frac{1}{m^s} \hat{\mathbf{n}}(\mathbf{x}),$$

and that the last term in (79) is given by (40). As a consequence, (79) is nothing but the weak formulation of the reaction-diffusion (42) together with the initial datum

$$\rho^s(0, \mathbf{x}) = \int_{\mathbb{R}^3} f_0^s(\mathbf{x}, \mathbf{v}) d\mathbf{v},$$

and the homogeneous Neumann boundary condition

$$\forall \mathbf{x} \in \partial\Omega, \quad \frac{\partial}{\partial \mathbf{x}} \rho^s(t, \mathbf{x}) \cdot \hat{\mathbf{n}}(\mathbf{x}) = 0.$$

Note that whenever $f_0^s(\mathbf{x}, \mathbf{v})$ is not a Maxwellian function of the variable $\mathbf{v}$, then there is the formation of an initial layer.

4.4 Different scaling for different chemical reactions

Finally, it is possible to extend the derivation of reaction–diffusion systems to physical situations involving chemical reactions which occur with rates having different orders of magnitude.

If we add a chain of n slower chemical reactions to the rescaled Boltzmann equations (22) :

$$\epsilon \frac{\partial f_\epsilon^s}{\partial t} + \mathbf{v} \cdot \frac{\partial f_\epsilon^s}{\partial \mathbf{x}} = \frac{1}{\epsilon} Q_{EL}^s(f_\epsilon^s, M) + \epsilon^p \sum_{r=1}^N Q_{EL}^{sr}(f_\epsilon^s, f_\epsilon^r) + \epsilon Q_{CH}^s(\mathbf{f}_\epsilon) + \epsilon^2 \sum_{i=1}^n \left(Q_{CH}^s(\mathbf{f}_\epsilon) \right)_i \quad (80)$$

(where $\left(Q_{CH}^s(\mathbf{f}_\epsilon) \right)_i$ denotes the net production due to the chemical reaction i), obviously the additional chemical operators do not influence the final reaction–diffusion equations, which retain only the $O(\epsilon)$ terms. On the other hand, interesting modifications arise if one (or more) chemical reaction becomes faster than in the scaling (22), for instance $O(1)$ instead of $O(\epsilon)$, and this will be the main subject of this subsection.

We consider for example a mixture of eight gases, A^s , $s = 1, \dots, 7$, plus the background, undergoing the following two reversible chemical reactions :



In our regime dominated by the elastic collisions with the background (of order $1/\epsilon$), we assume that the reaction (81a) is $O(1)$ as the streaming operator, while the reaction (81b)

remains slow ($O(\epsilon)$) as the temporal derivative. Thus, the rescaled kinetic equations read as

$$\epsilon \frac{\partial f_\epsilon^s}{\partial t} + \mathbf{v} \cdot \frac{\partial f_\epsilon^s}{\partial \mathbf{x}} = \frac{1}{\epsilon} Q_{EL}^s(f_\epsilon^s, M) + \epsilon^p \sum_{r=1}^7 Q_{EL}^{sr}(f_\epsilon^s, f_\epsilon^r) + \left(Q_{CH}^s(\mathbf{f}_\epsilon) \right)_a + \epsilon \left(Q_{CH}^s(\mathbf{f}_\epsilon) \right)_b, \quad (82)$$

where $\left(Q_{CH}^s(\mathbf{f}_\epsilon) \right)_a$ and $\left(Q_{CH}^s(\mathbf{f}_\epsilon) \right)_b$ denote the chemical terms corresponding to the reactions (81a) and (81b) respectively. Since we still have $Q_{EL}^s(f_\epsilon^s, M) = O(\epsilon)$, the distribution functions are again perturbations of Maxwellian distributions : $f_\epsilon^s = \rho_\epsilon^s M^s + \epsilon g_\epsilon^s$ with $g_\epsilon^s = O(1)$. If we assume that the intermolecular forces are of Maxwell molecules type, in the present scaling the equation (37), obtained inserting the momentum equation into the number density equation, becomes

$$\begin{aligned} & \frac{\partial}{\partial t} \int_{\mathbb{R}^3} f_\epsilon^s(\mathbf{v}) d\mathbf{v} + \frac{\partial}{\partial \mathbf{x}} \cdot \left\{ -\frac{\epsilon}{\nu^s} \frac{\partial}{\partial t} \int_{\mathbb{R}^3} \mathbf{v} f_\epsilon^s(\mathbf{v}) d\mathbf{v} - \frac{1}{\nu^s} \frac{\partial}{\partial \mathbf{x}} \cdot \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v}) f_\epsilon^s(\mathbf{v}) d\mathbf{v} \right. \\ & \left. + \frac{\epsilon^p}{\nu^s} \sum_{r=1}^7 \int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^{sr}(f_\epsilon^s, f_\epsilon^r)(\mathbf{v}) d\mathbf{v} + \frac{1}{\nu^s} \int_{\mathbb{R}^3} \mathbf{v} \left(Q_{CH}^s(\mathbf{f}_\epsilon) \right)_a(\mathbf{v}) d\mathbf{v} + \frac{\epsilon}{\nu^s} \int_{\mathbb{R}^3} \mathbf{v} \left(Q_{CH}^s(\mathbf{f}_\epsilon) \right)_b(\mathbf{v}) d\mathbf{v} \right\} = \\ & = \frac{1}{\epsilon} \int_{\mathbb{R}^3} \left(Q_{CH}^s(\mathbf{f}_\epsilon) \right)_a(\mathbf{v}) d\mathbf{v} + \int_{\mathbb{R}^3} \left(Q_{CH}^s(\mathbf{f}_\epsilon) \right)_b(\mathbf{v}) d\mathbf{v}. \end{aligned} \quad (83)$$

The first chemical contribution on the right-hand side is the dominant term :

$$\int_{\mathbb{R}^3} \left(Q_{CH}^s(\mathbf{f}_\epsilon) \right)_a(\mathbf{v}) d\mathbf{v} = O(\epsilon).$$

This implies that the leading order of such contribution, given explicitly in (40), has to vanish, hence the number densities of the four species A^1, A^2, A^3, A^4 fulfill

$$\frac{\rho_\epsilon^1 \rho_\epsilon^2}{\rho_\epsilon^3 \rho_\epsilon^4} = \left(\frac{\mu^{12}}{\mu^{34}} \right)^{\frac{3}{2}} \exp(\Delta E_{12}^{34}) + O(\epsilon), \quad (84)$$

that represents the mass action law for the chemical collision equilibrium corresponding to the reaction (81a). So, since the number densities $\rho_\epsilon^1, \rho_\epsilon^2, \rho_\epsilon^3, \rho_\epsilon^4$ are related by the constraint (84), their evolution is completely described by means of only three independent balance equations. We shall choose as independent variables $\rho_\epsilon^1 + \rho_\epsilon^3, \rho_\epsilon^2 + \rho_\epsilon^3, \rho_\epsilon^2 + \rho_\epsilon^4$, but any combination of them could be used equivalently. The corresponding evolution equations are provided by summing up the eqs. (83) relevant to the species (1,3), (2,3), (2,4), respectively. Notice that, thanks to some parity arguments, both elastic and chemical terms on the left-hand side of (83) do not yield $O(1)$ contributions.

Moreover, bearing in mind the weak forms (21), we have

$$\int_{\mathbb{R}^3} \left\{ \left(Q_{CH}^1(\mathbf{f}_\epsilon) \right)_a(\mathbf{v}) + \left(Q_{CH}^3(\mathbf{f}_\epsilon) \right)_a(\mathbf{v}) \right\} d\mathbf{v} = 0,$$

and analogously for the species (2,3) and (2,4). In conclusion, the reaction–diffusion system corresponding to the kinetic model (82) can be cast as

$$\begin{aligned}
\frac{\rho^1 \rho^2}{\rho^3 \rho^4} &= \left(\frac{\mu^{12}}{\mu^{34}} \right)^{\frac{3}{2}} \exp(\Delta E_{12}^{34}), \\
\frac{\partial}{\partial t}(\rho^1 + \rho^3) - \frac{1}{m^1 \nu^1} \Delta_{\mathbf{x}} \rho^1 - \frac{1}{m^3 \nu^3} \Delta_{\mathbf{x}} \rho^3 &= \\
= \nu_{15}^{67} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Delta E_{15}^{67}\right) \left[\left(\frac{\mu^{15}}{\mu^{67}} \right)^{\frac{3}{2}} \exp(\Delta E_{15}^{67}) \rho^6 \rho^7 - \rho^1 \rho^5 \right], \\
\frac{\partial}{\partial t}(\rho^2 + \rho^3) - \frac{1}{m^2 \nu^2} \Delta_{\mathbf{x}} \rho^2 - \frac{1}{m^3 \nu^3} \Delta_{\mathbf{x}} \rho^3 &= 0, \\
\frac{\partial}{\partial t}(\rho^2 + \rho^4) - \frac{1}{m^2 \nu^2} \Delta_{\mathbf{x}} \rho^2 - \frac{1}{m^4 \nu^4} \Delta_{\mathbf{x}} \rho^4 &= 0, \\
\frac{\partial \rho^s}{\partial t} - \frac{1}{m^s \nu^s} \Delta_{\mathbf{x}} \rho^s = \lambda^s \nu_{15}^{67} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Delta E_{15}^{67}\right) \left[\left(\frac{\mu^{15}}{\mu^{67}} \right)^{\frac{3}{2}} \exp(\Delta E_{15}^{67}) \rho^6 \rho^7 - \rho^1 \rho^5 \right],
\end{aligned} \tag{85}$$

for $s = 5, 6, 7$, with $\lambda^5 = -\lambda^6 = -\lambda^7 = 1$. This is a set of seven independent macroscopic equations. The main difference with respect to previous subsections is the constraint (84), consistent with the fact that the relaxation to the equilibrium corresponding to (81a) is assumed faster than other scattering effects. Then, contributions relevant to the slower reaction (81b) affect the evolution of the involved species $s = 1, 5, 6, 7$ as in the eqs. (42).

4.5 Remarks

In this subsection, we indicate some possibilities of different (but related) scalings.

1. We first notice that the Maxwellian (3) used as background distribution could have its macroscopic parameters different from $\rho = 1$, $T = 1$. Note however that it is not possible to take a mean velocity $\mathbf{u}$ different from $\mathbf{0}$, except if this velocity is of order ϵ . In this last case, we expect the appearance in the macroscopic equations of convection terms involving this velocity.
2. One other possibility is that one of the parameters occurring in the chemical kernels, for example the exchanged energy of chemical link ΔE_{12}^{34} or some masses (typically if one of the species is electrons while others are ions or molecules), be rescaled. This can change the macroscopic equations (Cf. [7], [8] for scalings involving very different masses).

5 Mathematical results in the linear case

In this section, we consider a mixture of three gases, A^1 , A^2 plus the background B , that can interact according to the following reversible chemical reaction :



The kinetic chemical operators corresponding to this reaction present a linear dependence on the distribution functions f^1 , f^2 , since in each reaction the partner molecule belongs to the fixed background, with Maxwellian distribution (3). More precisely, if we assume the direct reaction endothermic, we have

$$\begin{aligned} Q_{CH}^1(\mathbf{f})(\mathbf{v}) &= \int_{\mathbb{R}^3} \int_{S^2} H \left(|\mathbf{v} - \mathbf{v}_*|^2 - \frac{2\Delta E_1^2}{\mu^{1B}} \right) \mathcal{B}_{1B}^{2B}(\mathbf{v} - \mathbf{v}_*, \hat{\omega}) \\ &\quad \times \left[f^2(\mathbf{v}_{1B}^{2B}) M(\mathbf{v}_{*1B}^{2B}) - f^1(\mathbf{v}) M(\mathbf{v}_*) \right] d\mathbf{v}_* d\hat{\omega}, \end{aligned} \quad (87)$$

where $\Delta E_1^2 = E^2 - E^1$. Notice that, thanks to the conservation of total mass in the reaction (86), $m^1 = m^2$, and consequently the factor (appearing in (58)) which involves the ratio between reduced masses is unitary in the present frame. The operator $Q_{CH}^2(\mathbf{f})$ can be obtained by permutating the indices in (87), and recalling that the reverse exothermic reaction does not need a threshold. For any species $s = 1, 2$, in the sequel we shall neglect elastic collisions with particles of whatever species $r = 1, 2$, since in our scaling these elastic encounters do not influence the final macroscopic reaction-diffusion equations. Thus, the rescaled Boltzmann equation we shall deal with is

$$\epsilon \frac{\partial f_\epsilon^s}{\partial t} + \mathbf{v} \cdot \frac{\partial f_\epsilon^s}{\partial \mathbf{x}} = \frac{1}{\epsilon} Q_{EL}^s(f_\epsilon^s, M) + \epsilon Q_{CH}^s(\mathbf{f}_\epsilon), \quad s = 1, 2. \quad (88)$$

We shall treat from a mathematical point of view the diffusive limit $\epsilon \rightarrow 0$ of this linear kinetic problem, with initial conditions

$$f_\epsilon^s(0, \mathbf{x}, \mathbf{v}) = f_0^s(\mathbf{x}, \mathbf{v}) \in L^2 \left(\mathbb{R}^3 \times \left(\mathbb{R}^3, \frac{d\mathbf{v}}{M^s(\mathbf{v})} \right) \right), \quad (89)$$

and under the Maxwell molecules assumptions (27) on the cross sections.

We prove the

Theorem 1 :

Let f_ϵ^s be the unique solution of eq. (88), (89) in $L^\infty \left(\mathbb{R}^+; L^2 \left(\mathbb{R}^3 \times \left(\mathbb{R}^3, \frac{d\mathbf{v}}{M^s(\mathbf{v})} \right) \right) \right)$, where Q_{CH}^s is given by (87), Q_{EL}^s is defined by (9), and the cross sections in Q_{CH}^s , Q_{EL}^s satisfying the Maxwell molecules assumption (27). When ϵ goes to 0, f_ϵ^s converges in $L^\infty \left(\mathbb{R}^+; L^2 \left(\mathbb{R}^3 \times \left(\mathbb{R}^3, \frac{d\mathbf{v}}{M^s(\mathbf{v})} \right) \right) \right)$ weak * towards $\rho^s(t, \mathbf{x}) M^s(\mathbf{v})$, where ρ^s is the unique solution (in $L^\infty(\mathbb{R}^+; L^2(\mathbb{R}^3))$) of the reaction-diffusion system

$$\frac{\partial \rho^s}{\partial t} - \frac{1}{m^s \nu^s} \Delta_{\mathbf{x}} \rho^s = -\lambda^s \nu_{1B}^{2B} \frac{2}{\sqrt{\pi}} \Gamma \left(\frac{3}{2}, \Delta E_1^2 \right) \left[\exp(\Delta E_1^2) \rho^2(t, \mathbf{x}) - \rho^1(t, \mathbf{x}) \right], \quad (90)$$

$$\rho^s(0, \mathbf{x}) = \int_{\mathbb{R}^3} f_0^s(\mathbf{x}, \mathbf{v}) d\mathbf{v},$$

with $\lambda^1 = -\lambda^2 = 1$.

Proof of theorem 1 : Note first that the existence and uniqueness of a solution to eq. (88), (89) in $L^\infty\left(\mathbb{R}^+; L^2\left(\mathbb{R}^3 \times \left(\mathbb{R}^3, \frac{d\mathbf{v}}{M^s(\mathbf{v})}\right)\right)\right)$ is a direct consequence of Cauchy-Lipschitz theorem (once one has made the change of variable $(\mathbf{x}, \mathbf{v}) \rightarrow (\mathbf{x} + \mathbf{v}t, \mathbf{v})$ related to the characteristics of the free transport) since both elastic and chemical collision kernels are bounded in $L^2\left(\mathbb{R}^3, \frac{d\mathbf{v}}{M^s(\mathbf{v})}\right)$ (as operators on functions acting on the variable $\mathbf{v}$ only).

We now recall the main a priori estimate (directly related to the H-theorem) for eq. (88), (89). For a smooth enough test function $\varphi^s(t, \mathbf{x}, \mathbf{v})$, we multiply the s -th equation (88) by φ^s and then integrate on $[0, T] \times \mathbb{R}^3 \times \mathbb{R}^3$. We obtain

$$\begin{aligned} & \epsilon \int_0^T \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \varphi^s \frac{\partial f_\epsilon^s}{\partial t} dt d\mathbf{x} d\mathbf{v} + \int_0^T \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \varphi^s \mathbf{v} \cdot \frac{\partial f_\epsilon^s}{\partial \mathbf{x}} dt d\mathbf{x} d\mathbf{v} = \\ & = \frac{1}{\epsilon} \int_0^T \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \varphi^s Q_{EL}^s(f_\epsilon^s, M) dt d\mathbf{x} d\mathbf{v} + \epsilon \int_0^T \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \varphi^s Q_{CH}^s(\mathbf{f}_\epsilon) dt d\mathbf{x} d\mathbf{v}. \end{aligned} \quad (91)$$

Specializing this formula for

$$\varphi^s = \frac{f_\epsilon^s}{M^s} \exp(E^s), \quad (92)$$

and summing then equalities (91) over s , we first see that

$$\begin{aligned} & \epsilon \sum_{s=1}^2 \exp(E^s) \int_0^T \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{f_\epsilon^s}{M^s} \frac{\partial f_\epsilon^s}{\partial t} dt d\mathbf{x} d\mathbf{v} = \\ & = \epsilon \sum_{s=1}^2 \frac{\exp(E^s)}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\left(f_\epsilon^s(T, \mathbf{x}, \mathbf{v})\right)^2}{M^s(\mathbf{v})} d\mathbf{x} d\mathbf{v} - \epsilon \sum_{s=1}^2 \frac{\exp(E^s)}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\left(f_0^s(\mathbf{x}, \mathbf{v})\right)^2}{M^s(\mathbf{v})} d\mathbf{x} d\mathbf{v}. \end{aligned} \quad (93)$$

Analogously, the second term in (91) provides

$$\sum_{s=1}^2 \exp(E^s) \int_0^T \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{f_\epsilon^s}{M^s} \mathbf{v} \cdot \frac{\partial f_\epsilon^s}{\partial \mathbf{x}} dt d\mathbf{x} d\mathbf{v} = 0. \quad (94)$$

Then, with calculations very similar to (25), the elastic contribution in (91) can be rearranged (this is the H-theorem) as

$$\begin{aligned} & \frac{1}{\epsilon} \sum_{s=1}^2 \exp(E^s) \int_0^T \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{f_\epsilon^s}{M^s} Q_{EL}^s(f_\epsilon^s, M) dt d\mathbf{x} d\mathbf{v} = \\ & = -\frac{1}{\epsilon} \sum_{s=1}^2 \frac{e^{E^s}}{2} \int_{\mathcal{R}} \tilde{\mathcal{B}}^s \left[\frac{f_\epsilon^s(\mathbf{v}')}{M^s(\mathbf{v}')} - \frac{f_\epsilon^s(\mathbf{v})}{M^s(\mathbf{v})} \right]^2 M^s(\mathbf{v}) M(\mathbf{v}_*) dt d\mathbf{x} d\mathbf{v} d\mathbf{v}_* d\hat{\omega} \leq 0, \end{aligned} \quad (95)$$

where the domain $\mathcal{R} = \{t \in [0, T]; \mathbf{x} \in \mathbb{R}^3; \mathbf{v} \in \mathbb{R}^3; \mathbf{v}_* \in \mathbb{R}^3; \hat{\omega} \in S^2\}$. It can be shown that the chemical contribution is also less or equal to zero. In fact, bearing in mind the weak forms of the chemical operators (21), we have (this is the H-theorem for the reactive Boltzmann kernels)

$$\begin{aligned}
& \epsilon \sum_{s=1}^2 \int_0^T \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{f_\epsilon^s}{M^s} \exp(E^s) Q_{CH}^s(\mathbf{f}_\epsilon) dt d\mathbf{x} d\mathbf{v} = \\
& = \epsilon \int_{\mathcal{R}} H \left(|\mathbf{v} - \mathbf{v}_*|^2 - \frac{2\Delta E_1^2}{\mu^{1B}} \right) \tilde{\mathcal{B}}_{1B}^{2B} \left[\frac{f_\epsilon^1(\mathbf{v})}{M^1(\mathbf{v})} e^{E^1} - \frac{f_\epsilon^2(\mathbf{v}_{1B}^{2B})}{M^1(\mathbf{v}_{1B}^{2B})} e^{E^2} \right] \\
& \quad \times \left[\frac{f_\epsilon^2(\mathbf{v}_{1B}^{2B})}{M^1(\mathbf{v}_{1B}^{2B})} M^1(\mathbf{v}_{1B}^{2B}) M(\mathbf{v}_{*1B}^{2B}) - \frac{f_\epsilon^1(\mathbf{v})}{M^1(\mathbf{v})} M^1(\mathbf{v}) M(\mathbf{v}_*) \right] dt d\mathbf{x} d\mathbf{v} d\mathbf{v}_* d\hat{\omega} \quad (96) \\
& = -\epsilon e^{E^1} \int_{\mathcal{R}} H \left(|\mathbf{v} - \mathbf{v}_*|^2 - \frac{2\Delta E_1^2}{\mu^{1B}} \right) \tilde{\mathcal{B}}_{1B}^{2B} \left[\frac{f_\epsilon^1(\mathbf{v})}{M^1(\mathbf{v})} - \frac{f_\epsilon^2(\mathbf{v}_{1B}^{2B})}{M^1(\mathbf{v}_{1B}^{2B})} e^{\Delta E_1^2} \right]^2 \\
& \quad \times M^1(\mathbf{v}) M(\mathbf{v}_*) dt d\mathbf{x} d\mathbf{v} d\mathbf{v}_* d\hat{\omega} \leq 0
\end{aligned}$$

(the Maxwellians M^1 and M^2 coincide, since $m^1 = m^2$). In conclusion, taking into account (93)–(96), we get the basic a priori estimate

$$\begin{aligned}
& \sum_{s=1}^2 \exp(E^s) \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|f_\epsilon^s(T, \mathbf{x}, \mathbf{v})|^2}{M^s(\mathbf{v})} d\mathbf{x} d\mathbf{v} \\
& + \frac{1}{\epsilon^2} \sum_{s=1}^2 e^{E^s} \int_{\mathcal{R}} \tilde{\mathcal{B}}^s \left[\frac{f_\epsilon^s(\mathbf{v}')}{M^s(\mathbf{v}')} - \frac{f_\epsilon^s(\mathbf{v})}{M^s(\mathbf{v})} \right]^2 M^s(\mathbf{v}) M(\mathbf{v}_*) dt d\mathbf{x} d\mathbf{v} d\mathbf{v}_* d\hat{\omega} \\
& + 2 e^{E^1} \int_{\mathcal{R}} H \left(|\mathbf{v} - \mathbf{v}_*|^2 - \frac{2\Delta E_1^2}{\mu^{1B}} \right) \tilde{\mathcal{B}}_{1B}^{2B} \left[\frac{f_\epsilon^1(\mathbf{v})}{M^1(\mathbf{v})} - \frac{f_\epsilon^2(\mathbf{v}_{1B}^{2B})}{M^1(\mathbf{v}_{1B}^{2B})} e^{\Delta E_1^2} \right]^2 \\
& \quad \times M^1(\mathbf{v}) M(\mathbf{v}_*) dt d\mathbf{x} d\mathbf{v} d\mathbf{v}_* d\hat{\omega} \quad (97) \\
& \leq \sum_{s=1}^2 \exp(E^s) \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|f_0^s(\mathbf{x}, \mathbf{v})|^2}{M^s(\mathbf{v})} d\mathbf{x} d\mathbf{v}.
\end{aligned}$$

Thanks to the assumption (89) on the initial datum, all the terms on the left-hand side turn out to be uniformly bounded by the (weighted) L^2 -norm of the initial datum. Thus we have proven that f_ϵ^s is a bounded sequence in $L^\infty \left(\mathbb{R}^+; L^2 \left(\mathbb{R}^3 \times \left(\mathbb{R}^3, \frac{d\mathbf{v}}{M^s(\mathbf{v})} \right) \right) \right)$. Consequently there exists a subsequence f_ϵ^s that is weakly $*$ convergent in this space to some f^s . This exactly means that

$$\begin{aligned}
& \int_0^{+\infty} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{f_\epsilon^s \varphi^s}{M^s} dt d\mathbf{x} d\mathbf{v} \longrightarrow \int_0^{+\infty} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{f^s \varphi^s}{M^s} dt d\mathbf{x} d\mathbf{v}, \\
& \forall \varphi^s \in L^1 \left(\mathbb{R}^+; L^2 \left(\mathbb{R}^3 \times \left(\mathbb{R}^3, \frac{d\mathbf{v}}{M^s(\mathbf{v})} \right) \right) \right).
\end{aligned}$$

Hence, taking test functions of the form

$$\varphi^s(t, \mathbf{x}, \mathbf{v}) = \psi(t, \mathbf{x}) M^s(\mathbf{v}), \quad \psi(t, \mathbf{x}) \mathbf{v} M^s(\mathbf{v}), \quad \psi(t, \mathbf{x}) (\mathbf{v} \otimes \mathbf{v}) M^s(\mathbf{v}),$$

with $\psi(t, \mathbf{x}) \in L^1(\mathbb{R}^+; L^2(\mathbb{R}^3))$, we get

$$\int_0^{+\infty} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi(t, \mathbf{x}) \begin{pmatrix} 1 \\ \mathbf{v} \\ \mathbf{v} \otimes \mathbf{v} \end{pmatrix} f_\epsilon^s dt d\mathbf{x} d\mathbf{v} \longrightarrow \int_0^{+\infty} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi(t, \mathbf{x}) \begin{pmatrix} 1 \\ \mathbf{v} \\ \mathbf{v} \otimes \mathbf{v} \end{pmatrix} f^s dt d\mathbf{x} d\mathbf{v}. \quad (98)$$

For Maxwell molecules, the same also holds for the chemical linear operator :

$$\int_0^{+\infty} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi(t, \mathbf{x}) \begin{pmatrix} 1 \\ \mathbf{v} \end{pmatrix} Q_{CH}^s(\mathbf{f}_\epsilon) dt d\mathbf{x} d\mathbf{v} \longrightarrow \int_0^{+\infty} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi(t, \mathbf{x}) \begin{pmatrix} 1 \\ \mathbf{v} \end{pmatrix} Q_{CH}^s(\mathbf{f}) dt d\mathbf{x} d\mathbf{v} \quad (99)$$

since in the kernel, f_ϵ^s is multiplied by a Maxwellian and by the bounded function $\tilde{\mathcal{B}}_{1B}^{2B}$.

Therefore, passing to the limit $\epsilon \rightarrow 0$ in the weak form of the macroscopic equation (37), we get that the limit function f^s fulfills the equation, for any $\psi \in \mathcal{D}(\mathbb{R}^+ \times \mathbb{R}^3)$:

$$\begin{aligned} & - \int_0^{+\infty} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} f^s(t, \mathbf{x}, \mathbf{v}) \frac{\partial \psi}{\partial t}(t, \mathbf{x}) dt d\mathbf{x} d\mathbf{v} - \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} f_0^s(\mathbf{x}, \mathbf{v}) \psi(0, \mathbf{x}) d\mathbf{x} d\mathbf{v} \\ & - \frac{1}{\nu_s} \int_0^{+\infty} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v}) f^s(t, \mathbf{x}, \mathbf{v}) : \frac{\partial}{\partial \mathbf{x}} \frac{\partial}{\partial \mathbf{x}} \psi(t, \mathbf{x}) dt d\mathbf{x} d\mathbf{v} \\ & = \int_0^{+\infty} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} Q_{CH}^s(\mathbf{f})(t, \mathbf{x}, \mathbf{v}) \psi(t, \mathbf{x}) dt d\mathbf{x} d\mathbf{v}. \end{aligned} \quad (100)$$

Coming back to estimate (97), we obtain

$$\mathcal{J}(f_\epsilon^s) := \int_{\mathcal{R}} \tilde{\mathcal{B}}^s \left[\frac{f_\epsilon^s(\mathbf{v}')}{M^s(\mathbf{v}')} - \frac{f_\epsilon^s(\mathbf{v})}{M^s(\mathbf{v})} \right]^2 M^s(\mathbf{v}) M(\mathbf{v}_*) dt d\mathbf{x} d\mathbf{v} d\mathbf{v}_* d\hat{\omega} \leq C \epsilon^2, \quad (101)$$

hence $\lim_{\epsilon \rightarrow 0} \mathcal{J}(f_\epsilon^s) = 0$.

Let $\psi \equiv \psi(t, \mathbf{x}, \mathbf{v}, \mathbf{v}_*, \hat{\omega})$ be a test function in L_c^∞ . Then

$$\left| \int_{\mathcal{R}} \left(\frac{f_\epsilon^s(\mathbf{v}')}{M^s(\mathbf{v}')} - \frac{f_\epsilon^s(\mathbf{v})}{M^s(\mathbf{v})} \right) \psi(t, \mathbf{x}, \mathbf{v}, \mathbf{v}_*, \hat{\omega}) dt d\mathbf{x} d\mathbf{v} d\mathbf{v}_* d\hat{\omega} \right| \leq C \mathcal{J}(f_\epsilon^s)^{1/2}$$

if $\tilde{\mathcal{B}}^s$ is bounded below by some strictly positive number (if it is not the case, one uses $\int \tilde{\mathcal{B}}^s d\hat{\omega}$ instead of $\tilde{\mathcal{B}}^s$). This implies that

$$\frac{f^s(\mathbf{v}')}{M^s(\mathbf{v}')} = \frac{f^s(\mathbf{v})}{M^s(\mathbf{v})} \quad a.e.$$

Therefore, $f^s = \rho^s M^s$.

By substituting this formula into the evolution equation (100), the evolution of the number density ρ^s is governed by the following weak form of the reaction–diffusion equation :

$$\begin{aligned} & \int_0^{+\infty} \int_{\mathbb{R}^3} \rho^s(t, \mathbf{x}) \frac{\partial \psi}{\partial t}(t, \mathbf{x}) dt d\mathbf{x} + \int_{\mathbb{R}^3} \rho^s(0, \mathbf{x}) \psi(0, \mathbf{x}) d\mathbf{x} \\ & + \frac{1}{m^s \nu^s} \int_0^{+\infty} \int_{\mathbb{R}^3} \rho^s(t, \mathbf{x}) \Delta_{\mathbf{x}} \psi(t, \mathbf{x}) dt d\mathbf{x} \\ & = -\lambda^s \nu_{1B}^{2B} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Delta E_1^2\right) \int_0^{+\infty} \int_{\mathbb{R}^3} \left[\exp(\Delta E_1^2) \rho^2(t, \mathbf{x}) - \rho^1(t, \mathbf{x}) \right] \psi(t, \mathbf{x}) dt d\mathbf{x}, \end{aligned} \quad (102)$$

with $\lambda^1 = -\lambda^2 = 1$. By uniqueness of the weak solution of this equation, we see that the whole sequence f_ϵ^s converges, and this concludes the proof of theorem 1.

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