

# AN INTERNAL STATE KINETIC MODEL FOR CHEMICALLY REACTING MIXTURES OF MONATOMIC AND POLYATOMIC GASES

MARZIA BISI, THOMAS BORSONI, AND MARIA GROPPI\*

**ABSTRACT.** We propose a general kinetic framework for the description of a mixture of non-relativistic mono- or polyatomic gases undergoing any number of bi-molecular reactions. The description of the internal structure of the molecules is kept general, in order to model it according to the physical properties of the considered species. The possibility of keeping separate rotational and vibrational energies of polyatomic particles is thus included in the present framework. Moreover, activation energy for chemical reactions is taken into account, allowing to accurately describe the kinetics of the chemical process. We prove the validity of the H-Theorem, we recover the expected Maxwellian equilibrium distributions joint with the mass-action laws of chemical reactions, and we obtain an explicit formula for the rate constant of a given chemical reaction. The system of Euler equations in the case of moderately slow chemical reactions is also derived.

**Keywords:** kinetic theory; gas mixtures; polyatomic gases; chemical reactions; internal energy; H-theorem

## 1. INTRODUCTION

Kinetic models of Boltzmann type for gas mixtures are well known in the literature [40, 23], and suitable simpler BGK approximations have also been proposed and investigated [1, 42, 39, 13]. Many of the models for inert mixtures have been generalized to gas species undergoing chemical reactions; however, the major part of existing kinetic descriptions of reactive frames assumes the presence of only one bimolecular and reversible reaction, involving monatomic gases [48, 36, 33, 45, 22]. These models are thus too simplistic, since it is well known that each real bimolecular reaction involves at least a polyatomic species; even in simpler transitions of dissociation or recombination type, one needs to model polyatomic molecules. For this reason, the kinetic approach has been extended also to polyatomic gases, modelling the non-translational degrees of freedom by means of an internal energy variable, that could be assumed discrete or continuous. The Boltzmann model with discrete energy levels may be found for instance in [29, 35], while the model with a continuous internal energy has been proposed and investigated in [27, 28]. Consistent BGK kinetic equations have been built up for a single polyatomic gas [50, 2, 21, 44], but also for inert or reactive mixtures of polyatomic gases [8, 46, 10, 51]. In case of continuous internal energy, the Boltzmann collision operator involves an integral over the energy variable, with a suitable weight function related to the number of degrees of freedom of the considered species, that diverges in case of a monatomic gas; consequently, the kinetic description of mixtures of monatomic and polyatomic species needs to model collisions involving atoms separately, by means of classical Boltzmann operators [28]. A Chapman–Enskog closure and a BGK approximation of this model have been recently investigated [6, 20]. On the other hand, in the discrete energy frame a monatomic

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\*Corresponding author: Maria Groppi.

gas could be easily recovered as a species having only one energy level, but even in this simpler case a BGK model allowing to involve mixtures of monatomic and polyatomic species (namely, with each gas characterized by its own number of energy levels) has been only recently built up [11].

As concerns reacting mixtures, it is well known that a collision may change the nature of the molecules only if the total energy of the impinging particles exceeds the activation energy which characterizes the considered chemical reaction [5], but this threshold is taken into account only in some of the existing kinetic models [32, 41, 47]. Moreover, the generalization of the kinetic approach to mixtures involving chains of chemical reactions is not straightforward, even if the possible presence of several reacting species is already taken into account in some classical references [49, 29]. In this respect, some specific problems have been faced at Boltzmann level for monatomic gases in [24, 26] and macroscopic equations have been constructed owing to suitable entropy principles [19]; moreover, as concerns polyatomic species, dissociation and recombination processes affecting a diatomic gas have been investigated [43, 34], a BGK model involving two separate reactions has been recently built up [12], and a general kinetic model for an arbitrary number of reactions on crystal surfaces involving monatomic or polyatomic species has been dealt with in [3].

In order to improve the generality of the kinetic description of polyatomic gases, we have recently proposed [15] a kinetic Boltzmann model where the internal structure of a molecule is described by a single internal state parameter, belonging to a suitable space. Proper options for such a space of internal states and for the measure defined on it allow to reproduce some models commonly used in kinetic theory for polyatomic particles: the description based on a set of discrete internal energy levels [35, 29], and the one involving a continuous internal energy variable [28]. Moreover, it has been shown that within this general framework it is possible to build up new models desirable in physical applications, including the possibility to separate the internal energy into two different components, the rotational and the vibrational ones. We are able to recover the existing attempts of separating these two internal energies using different discrete indices [29] or two continuous energy variables [25, 4], and also to approximate rotational energy by means of a continuous variable keeping the vibrational one discrete; this way of modelling turns out to be physically reasonable, since the gap between two subsequent discrete levels is much lower for rotational than for vibrational energy [38]. The consistency of our kinetic Boltzmann model for polyatomic gases has been proved, together with the validity of the H-theorem for each choice of the space of internal states and of its measure. We have also shown that, under suitable assumptions on the Boltzmann cross sections, it is possible to reduce the models fitting our general internal state setting to a one-real-variable description with a suitable measure, similar to the classical continuous model with integration weight.

The aim of this work is to extend the Boltzmann model proposed in [15] to a mixture of monatomic and polyatomic gases, possibly undergoing bimolecular and reversible chemical reactions. Each gas is characterized by its own space of internal states, endowed with a suitable measure; in this way we could manage simultaneously monatomic species (with a fixed internal energy) and polyatomic constituents with discrete or continuous internal energy structure (or even both, if rotational and vibrational energies are kept separate). Unlike many existing kinetic models described above, in our general framework an arbitrary number of bimolecular reactions could be taken into account, and each species could be involved in more than one reaction; even the activation energy of each chemical reaction is included in the relevant Boltzmann cross section. Of course collision rules are more complicated than for a single polyatomic gas investigated in [15], due to the presence of mass ratios and of the amount of energy produced or consumed by chemical reactions. After the presentation of our setting and of the Boltzmann operators for elastic and chemical interactions, the collision invariants of mechanical scattering and of global (mechanical plus chemical) Boltzmann operators are determined and the Boltzmann H-theorem is proved, leading to the expected Maxwellian equilibria depending also on the internal energy, with suitable mass

action laws relating number densities of gases involved in the admissible chemical reactions with temperature of the mixture. Euler equations in case of moderately slow chemical reactions (namely, in an elastic dominated regime) are also derived.

In more detail, the article is organized as follows. In Section 2, the general setting considered in this paper is described, as well as the admissible collisions. Section 3 is devoted to the collision rules and to their properties, while Section 4 deals with the Boltzmann equations; specifically, after introducing main macroscopic fields and elastic and chemical Boltzmann operators together with the assumptions on the cross sections, mechanical and global collision invariants are determined and the H-theorem is proved. In Section 5, the equilibrium configurations are discussed, focusing the attention at first on the mechanical equilibria and on the corresponding thermodynamic properties (internal degrees of freedom, specific heat at constant volume, and macroscopic fields of each species), and then on the global collision equilibria, involving the mass action laws relevant to the admissible chemical reactions. The Euler limit in a mechanical dominated regime is then investigated in Section 6. The following short sections are devoted to possible applications of our framework: Section 7 shows an example of a computation of a rate of reaction, in Section 8 we discuss the possibility of reducing our general description to a model with only one continuous variable (at the price of complicating the measure space), and in Section 9 we provide an explicit realistic example involving three gas species undergoing a bimolecular reversible reaction. Section 10 contains some concluding remarks and perspectives. We have collected in two appendices a technical result (in Appendix A) and, for readers' convenience, some tables summarizing all physical and chemical quantities used in this paper (in Appendix B).

## 2. SETTING

We describe our non-relativistic kinetic framework for the study of mixture of gases (mono- or polyatomic), with or without chemical reactions. We consider a gas mixture composed of  $N$  species. Each molecule of the gas is described by its species label  $i$  and its state, namely its velocity  $v$  and internal state  $\zeta$ , representing for instance rotation and vibration. The species or state of a molecule is assumed to possibly change only because of a binary interaction, which can be a mechanical collision or a chemical reaction.

While it is common to consider from the beginning the energy of reaction in the study of chemical reactions, we decide not to adopt this point of view in this paper. Indeed, our approach consists in considering that the reacting molecules form an isolated system, with no exchange of matter or energy with the environment, in contrast with the option that the reacting molecules form a closed system, possibly exchanging energy with its environment. This choice is motivated by a wish of simplicity and generality of the formulation. As can be seen in [37, Chapter 1], the energy of reaction is the difference between the fundamental potential energy of the products and of the reactants, that is of the two local minima on Fig. 1, and this is how the energy of reaction appears in our framework. Figure 1 is borrowed from [37, Chapter 1] and illustrates the evolution of the potential energy during an exothermic chemical reaction. Here, some of the potential energy of the reactants is converted into kinetic, or rotational, vibrational, etc., energy for the products, so that the chemical reaction induces an overall growth of temperature. In our framework, the potential energy of configuration is taken into account in the internal description, so that there is no need to a priori introduce any energy of reaction. The equivalence of our formulation with others used in kinetic theory regarding this consideration will be investigated in Section 8.

Another feature appearing in Figure 1 is the existence of a transition state. It is a state of maximum potential energy, and the chemical reaction may occur only if the reactants have enough energy to get to this state [37, Chapter 1]. In the Boltzmann framework, collisions are considered instantaneous, so that species transition state does not have to be studied and does not appear in the conservation laws. This feature is taken into account here as a potential barrier, linked to

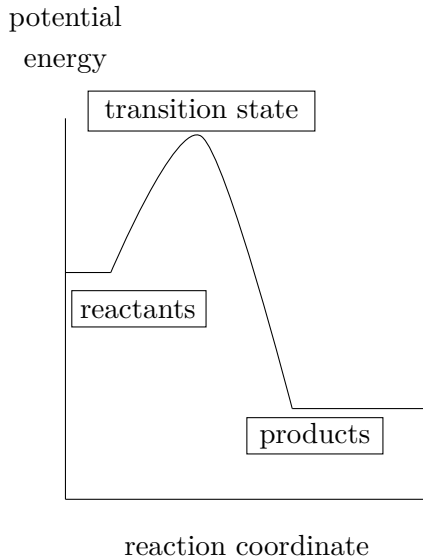


FIGURE 1. Reaction coordinate diagram

the activation energy, to overcome for a chemical reaction to be possible, as it will be explained in Section 3.

Following [15], we associate to each species of the gas, labelled by  $i \in \llbracket 1, N \rrbracket$  (the set of integer numbers such that  $1 \leq i \leq N$ ), a measured space of internal states  $(\mathcal{E}_i, \mathcal{A}_i, \mu_i)$ , with  $\mathcal{E}_i$  the set of internal states,  $\mathcal{A}_i$  a  $\sigma$ -algebra on  $\mathcal{E}_i$  and  $\mu_i$  a measure on  $\mathcal{E}_i$  adapted to  $\mathcal{A}_i$ , an  $\mathcal{A}_i$ -measurable internal energy function  $\varepsilon_i : \mathcal{E}_i \rightarrow \mathbb{R}$ , and we denote by  $m_i$  the mass of a molecule of this species. Hence each species can be described with its own adapted model. For instance, we may study a mixture of three gases, the first one described by the monatomic model, the second by the weighted continuous internal energy model [14, 27, 28] and the third by a discrete internal energy model [35, 9].

Following [15], we assume that  $\varepsilon_i$  admits a finite essential infimum under  $\mu_i$  denoted by  $\varepsilon_i^0$ , and define the grounded internal energy function

$$(2.1) \quad \bar{\varepsilon}_i = \varepsilon_i - \varepsilon_i^0.$$

We define  $Z_i$ , the partition function of the species  $i$ , by

$$(2.2) \quad Z_i(\beta) = \int_{\mathcal{E}_i} e^{-\beta \bar{\varepsilon}_i(\zeta)} d\mu_i(\zeta),$$

and assume that  $Z_i(\beta) < \infty$  for any  $\beta > 0$ . The choice of  $\bar{\varepsilon}_i$  in the definition of the partition function  $Z_i$  is motivated by physical considerations, as explained in [15, Remark 4.2].

The quantity  $\varepsilon_i^0$  corresponds to the fundamental energy of the molecule, hence to its potential energy of configuration. It plays a role in chemical reactions.

The way we handle an arbitrary number of chemical reactions is the following. We consider a space of allowed collisions, denoted by  $\Omega$ . When the collision of particles of species  $i$  and  $j$  transforming them into particles  $k$  and  $l$  is possible, we write  $\{(i, j) \rightarrow (k, l)\} \in \Omega$ . We assume that

- mechanical collisions are allowed collisions, that is, for any  $1 \leq i, j \leq N$ ,

$$(2.3) \quad \{(i, j) \rightarrow (i, j)\} \in \Omega.$$

- collisions are symmetric and can happen in both directions, that is

$$(2.4) \quad \{(i, j) \rightarrow (k, l)\} \in \Omega \iff \{(j, i) \rightarrow (l, k)\} \in \Omega \iff \{(k, l) \rightarrow (i, j)\} \in \Omega.$$

- a redundant symmetry property, implying that every collision is accounting for exactly once when  $k = l$  and twice when  $k \neq l$

$$(2.5) \quad \{(i, j) \rightarrow (k, l)\} \in \Omega \iff \{(i, j) \rightarrow (l, k)\} \in \Omega.$$

- collisions are mass conserving, that is for any  $\{(i, j) \rightarrow (k, l)\} \in \Omega$ ,

$$(2.6) \quad m_i + m_j = m_k + m_l.$$

For any allowed collision  $\{(i, j) \rightarrow (k, l)\} \in \Omega$ , we denote by  $\kappa_{ij}^{kl} \in \mathbb{R}$  the energy of the transition state of the collision. We make the following assumptions on  $\kappa_{ij}^{kl}$ .

- For any  $\{(i, j) \rightarrow (k, l)\} \in \Omega$ ,

$$(2.7) \quad \kappa_{ij}^{kl} \geq \max(\varepsilon_i^0 + \varepsilon_j^0, \varepsilon_k^0 + \varepsilon_l^0).$$

- For any  $\{(i, j) \rightarrow (k, l)\} \in \Omega$ ,

$$(2.8) \quad \kappa_{ij}^{kl} = \kappa_{ji}^{lk} = \kappa_{ik}^{lj} = \kappa_{kl}^{ij}.$$

- We assume no transition states for mechanical collisions, that is, for any  $(i, j) \in \llbracket 1, N \rrbracket^2$ ,

$$(2.9) \quad \kappa_{ij}^{ij} = \varepsilon_i^0 + \varepsilon_j^0.$$

We illustrate in Figure 2 the role of the quantities  $\varepsilon_i^0, \varepsilon_j^0, \varepsilon_k^0, \varepsilon_l^0$  and  $\kappa_{ij}^{kl}$  in the case of a chemical reaction; we highlight in particular that the potential energy of configuration of the system of the two molecules labelled respectively by  $i$  and  $j$  is  $\varepsilon_i^0 + \varepsilon_j^0$ .

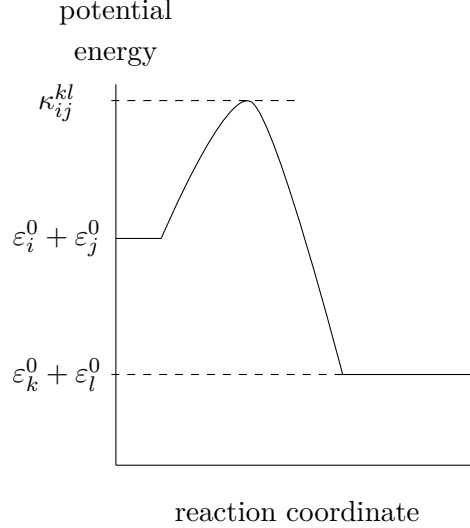


FIGURE 2. Reaction coordinate diagram with reference energy thresholds

### 3. COLLISION MODEL

We consider a collision  $\{(i, j) \rightarrow (k, l)\} \in \Omega$ . The states of the pre-collision molecules are denoted by  $(v, \zeta) \in \mathbb{R}^3 \times \mathcal{E}_i$  and  $(v_*, \zeta_*) \in \mathbb{R}^3 \times \mathcal{E}_j$ , and the states of the post-collision molecules are denoted by  $(v', \zeta') \in \mathbb{R}^3 \times \mathcal{E}_k$  and  $(v'_*, \zeta'_*) \in \mathbb{R}^3 \times \mathcal{E}_l$ . Writing the conservation of momentum and energy of the isolated system yields

$$(3.1) \quad \begin{cases} m_i v + m_j v_* = m_k v' + m_l v'_* \\ \frac{1}{2} m_i |v|^2 + \varepsilon_i(\zeta) + \frac{1}{2} m_j |v_*|^2 + \varepsilon_j(\zeta_*) = \frac{1}{2} m_k |v'|^2 + \varepsilon_k(\zeta') + \frac{1}{2} m_l |v'_*|^2 + \varepsilon_l(\zeta'_*). \end{cases}$$

Notice that in this state-based formulation no energy of chemical reaction appears in (3.1). An explanation and link with the usual formulation of the energy conservation law for chemical reactions [28, 35] is provided in Section 8.

**3.1. Collision rules and transformation.** We set  $m_{ij}^* = \frac{m_i m_j}{m_i + m_j}$  and  $M_{ij} = m_i + m_j$ . Notice that

$$\frac{1}{2} m_i |v|^2 + \frac{1}{2} m_j |v_*|^2 = \frac{m_{ij}^*}{2} |v - v_*|^2 + \frac{M_{ij}}{2} \left| \frac{m_i v + m_j v_*}{m_i + m_j} \right|^2.$$

Using the conservation laws (2.6) and (3.1), we have  $\frac{M_{ij}}{2} \left| \frac{m_i v + m_j v_*}{m_i + m_j} \right|^2 = \frac{M_{kl}}{2} \left| \frac{m_k v' + m_l v'_*}{m_k + m_l} \right|^2$  from which we deduce that

$$\frac{m_{ij}^*}{2} |v - v_*|^2 + \varepsilon_i(\zeta) + \varepsilon_j(\zeta_*) = \frac{m_{kl}^*}{2} |v' - v'_*|^2 + \varepsilon_k(\zeta') + \varepsilon_l(\zeta'_*).$$

Let us set

$$(3.2) \quad \Delta_{ij}^{kl}(v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*) = \frac{m_{ij}^*}{m_{kl}^*} |v - v_*|^2 + \frac{2}{m_{kl}^*} (\varepsilon_i(\zeta) + \varepsilon_j(\zeta_*) - \varepsilon_k(\zeta') - \varepsilon_l(\zeta'_*)),$$

which satisfies the symmetry property

$$(3.3) \quad \Delta_{ij}^{kl}(v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*) = \Delta_{ji}^{lk}(v_*, v, \zeta_*, \zeta, \zeta'_*, \zeta').$$

We then have

$$(3.4) \quad |v' - v'_*|^2 = \Delta_{ij}^{kl}(v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*),$$

and by a classical argument we conclude that there exists  $\omega \in \mathbb{S}^2$  such that

$$(3.5) \quad \begin{cases} v' = \frac{m_i v + m_j v_*}{M_{ij}} + \frac{m_l}{M_{kl}} \sqrt{\Delta_{ij}^{kl}} T_\omega \left[ \frac{v - v_*}{|v - v_*|} \right] \\ v'_* = \frac{m_i v + m_j v_*}{M_{ij}} - \frac{m_k}{M_{kl}} \sqrt{\Delta_{ij}^{kl}} T_\omega \left[ \frac{v - v_*}{|v - v_*|} \right], \end{cases}$$

where  $T_\omega$  is the symmetry with respect to  $(\mathbb{R}\omega)^\perp$ ,

$$(3.6) \quad \forall V \in \mathbb{S}^2, \quad T_\omega[V] := V - 2(\omega \cdot V)\omega \in \mathbb{S}^2.$$

Note that (3.5) makes sense if and only if  $\Delta_{ij}^{kl}(v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*) \geq 0$ .

For any allowed collision  $\{(i, j) \rightarrow (k, l)\} \in \Omega$  and  $(\zeta, \zeta_*, \zeta', \zeta'_*) \in \mathcal{E}_i \times \mathcal{E}_j \times \mathcal{E}_k \times \mathcal{E}_l$ , we define the set of pre-collision velocities  $(v, v_*)$  such that the collision

$$(v, \zeta) \in \mathbb{R}^3 \times \mathcal{E}_i, (v_*, \zeta_*) \in \mathbb{R}^3 \times \mathcal{E}_j \quad \longrightarrow \quad (\cdot, \zeta') \in \mathbb{R}^3 \times \mathcal{E}_k, (\cdot, \zeta'_*) \in \mathbb{R}^3 \times \mathcal{E}_l$$

is possible, namely

$$(3.7) \quad E_{ij}^{kl}[\zeta, \zeta_*, \zeta', \zeta'_*] = \left\{ (v, v_*) \in \mathbb{R}^3 \times \mathbb{R}^3 \left| \frac{m_{ij}^*}{2} |v - v_*|^2 + \varepsilon_i(\zeta) + \varepsilon_j(\zeta_*) \geq \max \left( \varepsilon_k(\zeta') + \varepsilon_l(\zeta'_*), \kappa_{ij}^{kl} \right) \right. \right\}.$$

Notice that  $\kappa_{ij}^{kl}$  appears in the definition of  $E_{ij}^{kl}[\zeta, \zeta_*, \zeta', \zeta'_*]$  as a potential barrier.

**Definition 1.** For any allowed collision  $\{(i, j) \rightarrow (k, l)\} \in \Omega$ ,  $(\zeta, \zeta_*, \zeta', \zeta'_*) \in \mathcal{E}_i \times \mathcal{E}_j \times \mathcal{E}_k \times \mathcal{E}_l$  and  $\omega \in \mathbb{S}^2$ , we define the transformation

$$(3.8) \quad S_\omega^{ijkl}[\zeta, \zeta_*, \zeta', \zeta'_*] : \begin{cases} E_{ij}^{kl}[\zeta, \zeta_*, \zeta', \zeta'_*] & \rightarrow & E_{kl}^{ij}[\zeta', \zeta'_*, \zeta, \zeta_*] \\ (v, v_*) \mapsto \left( \frac{m_i v + m_j v_*}{M_{ij}} + \frac{m_l}{M_{kl}} \sqrt{\Delta_{ij}^{kl}} T_\omega \left[ \frac{v - v_*}{|v - v_*|} \right], \frac{m_i v + m_j v_*}{M_{ij}} - \frac{m_k}{M_{kl}} \sqrt{\Delta_{ij}^{kl}} T_\omega \left[ \frac{v - v_*}{|v - v_*|} \right] \right), \end{cases}$$

where  $\Delta_{ij}^{kl}$  and  $T_\omega$  are respectively defined in (3.2) and (3.6).

The transformation  $S_\omega^{ijkl}[\zeta, \zeta_*, \zeta', \zeta'_*]$  links, at fixed angle  $\omega$  and internal states  $\zeta, \zeta_*, \zeta', \zeta'_*$ , the pre- and post-collision velocities.

**Lemma 1.** For any allowed collision  $\{(i, j) \rightarrow (k, l)\} \in \Omega$ ,  $(\zeta, \zeta_*, \zeta', \zeta'_*) \in \mathcal{E}_i \times \mathcal{E}_j \times \mathcal{E}_k \times \mathcal{E}_l$  and  $\omega \in \mathbb{S}^2$ ,  $S_\omega^{ijkl}[\zeta, \zeta_*, \zeta', \zeta'_*]$  is well-defined and is a bijection, with

$$\left( S_\omega^{ijkl}[\zeta, \zeta_*, \zeta', \zeta'_*] \right)^{-1} = S_\omega^{klij}[\zeta', \zeta'_*, \zeta, \zeta_*].$$

**Lemma 2.** The Jacobian of the transformation  $S_\omega^{ijkl}[\zeta, \zeta_*, \zeta', \zeta'_*]$  is given by the formula

$$(3.9) \quad J \left[ S_\omega^{ijkl}[\zeta, \zeta_*, \zeta', \zeta'_*] \right] = \frac{m_i m_j}{m_k m_l} \times \frac{|v' - v'_*|}{|v - v_*|}.$$

The proofs are similar to those of [15, Lemmas 2.1 and 2.2].

#### 4. THE BOLTZMANN MODEL

**Distribution function and kinetic equation.** We study the function  $F$  describing the density of molecules of every species. For  $i \in \llbracket 1, N \rrbracket$ , the density associated with the species  $i$  is denoted by  $F_i$ . It depends on four variables:

- 2 macroscopic variables: the time  $t \in \mathbb{R}$  or  $\mathbb{R}_+$  and the position in space  $x \in \mathbb{R}^3$  or  $\mathbb{T}^3$
- 2 kinetic variables: the velocity  $v \in \mathbb{R}^3$  and the internal state  $\zeta \in \mathcal{E}_i$

As a distribution function,  $F_i$  is non-negative, so that we study  $F_i(t, x, v, \zeta) \in \mathbb{R}_+$ . Moreover, we assume that for any  $(t, x)$ ,  $F_i(t, x, \cdot, \cdot) \in L^1(\mathbb{R}^3 \times \mathcal{E}_i, dv d\mu_i(\zeta))$ . The evolution of this distribution function is governed by the Boltzmann equation

$$(4.1) \quad \partial_t F_i(t, x, v, \zeta) + v \cdot \nabla_x F_i(t, x, v, \zeta) = \mathcal{B}(F, F)_i(t, x, v, \zeta),$$

where  $\mathcal{B}$  is the Boltzmann collision operator we define in a following subsection.

**Macroscopic quantities.** From the density function we can compute the macroscopic quantities. Let  $i \in \llbracket 1, N \rrbracket$ . If  $\phi$  defined on  $\mathbb{R}^3 \times \mathcal{E}_i$  is a molecular property, then the associated macroscopic quantity for the species  $i$  is

$$\int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \phi(v, \zeta) F_i(t, x, v, \zeta) dv d\mu_i(\zeta).$$

Typically,  $\phi = m_i$ ,  $\phi = m_i v$  and  $\phi = \frac{1}{2} m_i |v|^2 + \varepsilon_i(\zeta)$  give respectively the macroscopic mass density  $\rho_i$  (and macroscopic number density  $n_i$ ), velocity  $u_i$  and specific energy density  $e_i$  of the species  $i$

$$\rho_i(t, x) = \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} m_i F_i(t, x, v, \zeta) dv d\mu_i(\zeta) \quad \text{and} \quad n_i(t, x) = \frac{\rho_i(t, x)}{m_i}$$

$$u_i(t, x) = \frac{1}{\rho_i(t, x)} \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} m_i v F_i(t, x, v, \zeta) \, dv \, d\mu_i(\zeta)$$

$$e_i(t, x) = \frac{1}{n_i(t, x)} \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \left( \frac{1}{2} m_i |v|^2 + \varepsilon_i(\zeta) \right) F_i(t, x, v, \zeta) \, dv \, d\mu_i(\zeta).$$

The total (number and mass) density, average velocity and specific energy density are given by

$$\bar{n} = \sum_{i=1}^N n_i, \quad \bar{\rho} = \sum_{i=1}^N \rho_i, \quad \underline{u} = \sum_{i=1}^N \frac{n_i}{\bar{n}} u_i, \quad \bar{e} = \sum_{i=1}^N \frac{n_i}{\bar{n}} e_i.$$

Finally, one can define the temperature of the species  $i$  by

$$(4.2) \quad T_i = \Theta_i^{-1} \left( \frac{1}{n_i} \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \left( \frac{1}{2} m_i |v - u_i|^2 + \bar{\varepsilon}_i(\zeta) \right) F_i(v, \zeta) \, dv \, d\mu_i(\zeta) \right),$$

where  $\Theta_i(T) = \frac{3}{2} k_B T - \log(Z_i)' \left( \frac{1}{k_B T} \right)$ , as well as the temperature of the whole gas

$$(4.3) \quad T = \bar{\Theta} \left[ \left( \frac{n_i}{\bar{n}} \right) \right]^{-1} \left( \frac{1}{\bar{n}} \sum_{i=1}^N \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \left( \frac{1}{2} m_i |v - u_i|^2 + \bar{\varepsilon}_i(\zeta) \right) F_i(v, \zeta) \, dv \, d\mu_i(\zeta) \right),$$

where  $\bar{\Theta} \left[ \left( \frac{n_i}{\bar{n}} \right) \right] (T) = \sum_{i=1}^N \frac{n_i}{\bar{n}} \Theta_i(T)$ . Justifications for the definitions (4.2) and (4.3) and the proof that they coincide with the species and global temperatures defined in classical kinetic models will be provided in Section 5.

**4.1. Boltzmann operator.** The Boltzmann operator acts as a source term in Equation (4.1) and represents the fact that collisions between molecules change their velocities and internal states.

*Collision kernel.* When two molecules collide, not all possible post-collision states are equiprobable. This idea is translated in the concept of the collision kernel, linked with the cross-section. This kernel encapsulates the information on the interaction potential, for example a hard sphere or Lennard-Jones one [23]. The collision kernel  $B$  is a family of measurable functions

$$(4.4) \quad B_{ij}^{kl} : \begin{cases} \mathbb{R}^3 \times \mathbb{R}^3 \times \mathcal{E}_i \times \mathcal{E}_j \times \mathcal{E}_k \times \mathcal{E}_l \times \mathbb{S}^2 \rightarrow \mathbb{R}_+ \\ (v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*, \omega) \mapsto B_{ij}^{kl}(v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*, \omega), \end{cases}$$

for any  $i, j, k, l \in \llbracket 1, N \rrbracket$ .

**Assumption 2. Symmetry.** The kernel  $B$  is symmetric in the following sense: if  $\{(i, j) \rightarrow (k, l)\} \in \Omega$ , then for a.e.  $v, v_* \in \mathbb{R}^3$ , for  $\mu_i \otimes \mu_j \otimes \mu_k \otimes \mu_l$ -a.e.  $(\zeta, \zeta_*, \zeta', \zeta'_*) \in \mathcal{E}_i \times \mathcal{E}_j \times \mathcal{E}_k \times \mathcal{E}_l$  and a.e.  $\omega \in \mathbb{S}^2$ ,

$$(4.5) \quad B_{ij}^{kl}(v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*, \omega) = B_{ji}^{lk}(v_*, v, \zeta_*, \zeta, \zeta'_*, \zeta', \omega) = B_{ij}^{lk}(v, v_*, \zeta, \zeta_*, \zeta'_*, \zeta', \omega).$$

When  $k \neq l$ , due to the redundancy (2.5), one should think of  $B_{ij}^{kl}$  as half the physical collision kernel.

**Assumption 3. Micro-reversibility.** For  $\{(i, j) \rightarrow (k, l)\} \in \Omega$ , for a.e.  $v, v_* \in \mathbb{R}^3$ , for  $\mu_i \otimes \mu_j \otimes \mu_k \otimes \mu_l$ -a.e.  $(\zeta, \zeta_*, \zeta', \zeta'_*) \in \mathcal{E}_i \times \mathcal{E}_j \times \mathcal{E}_k \times \mathcal{E}_l$  and a.e.  $\omega \in \mathbb{S}^2$ ,

$$(4.6) \quad m_i^2 m_j^2 |v - v_*| B_{ij}^{kl}(v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*, \omega) = m_k^2 m_l^2 |v' - v'_*| B_{kl}^{ij}(v', v'_*, \zeta', \zeta'_*, \zeta, \zeta_*, \omega).$$

where  $(v', v'_*) = S_\omega^{ijkl}[\zeta, \zeta_*, \zeta', \zeta'_*](v, v_*)$ .



The kernel  $B$  is positive when a collision is possible, and equal to zero when it is not admissible. The following positivity assumption 4 also links our way of dealing with transition states with the approach used in [31, 32, 41], where the energy of the transition state is taken into account in the kernel through the introduction of a step function relative to the activation energy.

**Definition and assumption 4.** For  $\{(i, j) \rightarrow (k, l)\} \in \Omega$ , for a.e.  $v, v_* \in \mathbb{R}^3$ , for  $\mu_i \otimes \mu_j \otimes \mu_k \otimes \mu_l$ -a.e.  $(\zeta, \zeta_*, \zeta', \zeta'_*) \in \mathcal{E}_i \times \mathcal{E}_j \times \mathcal{E}_k \times \mathcal{E}_l$ , we define  $\mathbb{S}_{ijkl}^2[v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*]$  as the subset of  $\mathbb{S}^2$  such that for any  $\omega \in \mathbb{S}^2$ ,

$$\omega \in \mathbb{S}_{ijkl}^2[v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*] \iff B_{ij}^{kl}(v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*, \omega) > 0.$$

We assume that

$$(v, v_*) \in E_{ij}^{kl}[\zeta, \zeta_*, \zeta', \zeta'_*] \iff \mathbb{S}_{ijkl}^2[v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*] \text{ contains a neighbourhood of } \frac{v - v_*}{|v - v_*|}$$

and  $\mathbb{S}^2 \setminus \mathbb{S}_{iii}^2[v, v_*, \zeta, \zeta, \zeta, \zeta]$  has zero measure.

*Modified density and kernel.* The density  $F_i$  and kernel  $B$  are physically meaningful, however, in order to lighten the calculations later on, it is useful to define the following modified density  $f_i$  and modified kernel  $b$ .

**Definition 5.** For  $i \in \llbracket 1, N \rrbracket$ , let  $c_i = \frac{1}{m_i^3}$ . We define

$$(4.7) \quad f_i = c_i F_i, \quad b_{ij}^{kl} = \frac{B_{ij}^{kl}}{c_i c_j}.$$

We notice that  $b$  satisfies the same positivity and symmetry conditions as  $B$ , Assumptions 4 and 2. Moreover,  $b$  satisfies the following micro-reversibility condition: for  $\{(i, j) \rightarrow (k, l)\} \in \Omega$ , for a.e.  $v, v_* \in \mathbb{R}^3$ , for  $\mu_i \otimes \mu_j \otimes \mu_k \otimes \mu_l$ -a.e.  $(\zeta, \zeta_*, \zeta', \zeta'_*) \in \mathcal{E}_i \times \mathcal{E}_j \times \mathcal{E}_k \times \mathcal{E}_l$  and a.e.  $\omega \in \mathbb{S}^2$ ,

$$(4.8) \quad \frac{|v - v_*|}{m_i m_j} b_{ij}^{kl}(v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*, \omega) = \frac{|v' - v'_*|}{m_k m_l} b_{kl}^{ij}(v', v'_*, \zeta', \zeta'_*, \zeta, \zeta_*, \omega).$$

where  $(v', v'_*) = S_\omega^{ijkl}[\zeta, \zeta_*, \zeta', \zeta'_*](v, v_*)$ .

*Boltzmann collision operator.* Writing  $B_{ij}^{kl} \equiv B_{ij}^{kl}(v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*, \omega)$  to lighten the notations, we define the Boltzmann collision operator for the species  $i$  by, for any  $v \in \mathbb{R}^3$  and  $\zeta \in \mathcal{E}_i$ ,

$$(4.9) \quad \mathcal{B}(F, F)_i(v, \zeta) = \sum_{j, k, l=1}^N \int_{\mathcal{E}_i} \int_{\mathcal{E}_k} \int_{\mathcal{E}_j} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} \left( \left( \frac{m_i m_j}{m_k m_l} \right)^3 F_k(v', \zeta') F_l(v'_*, \zeta'_*) - F_i(v, \zeta) F_j(v_*, \zeta_*) \right) \\ \times B_{ij}^{kl} d\omega dv_* d\mu_j(\zeta_*) d\mu_k(\zeta') d\mu_l(\zeta'_*).$$

Recall that collisions with  $k \neq l$  are redundantly accounted for twice here, see (2.5), but in this case the kernel  $B_{ij}^{kl}$  equals half the physical collision kernel. In terms of  $f_i$  and  $b_{ij}^{kl}$ , (4.9) writes more symmetrically

$$\mathcal{B}(F, F)_i(v, \zeta) = \sum_{j, k, l=1}^N \int_{\mathcal{E}_i} \int_{\mathcal{E}_k} \int_{\mathcal{E}_j} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} (f_k(v', \zeta') f_l(v'_*, \zeta'_*) - f_i(v, \zeta) f_j(v_*, \zeta_*)) \\ \times b_{ij}^{kl} d\omega dv_* d\mu_j(\zeta_*) d\mu_k(\zeta') d\mu_l(\zeta'_*),$$

where we write  $b_{ij}^{kl} \equiv b_{ij}^{kl}(v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*, \omega)$  to lighten the notations. We finally denote respectively

$$\mathcal{B}_+(F, F)_i(v, \zeta) = \sum_{j,k,l=1}^N \int_{\mathcal{E}_l} \int_{\mathcal{E}_k} \int_{\mathcal{E}_j} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} f_k(v', \zeta') f_l(v'_*, \zeta'_*) b_{ij}^{kl} d\omega dv_* d\mu_j(\zeta_*) d\mu_k(\zeta') d\mu_l(\zeta'_*)$$

and

$$\mathcal{B}_-(F, F)_i(v, \zeta) = \sum_{j,k,l=1}^N \int_{\mathcal{E}_l} \int_{\mathcal{E}_k} \int_{\mathcal{E}_j} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} f_i(v, \zeta) f_j(v_*, \zeta_*) b_{ij}^{kl} d\omega dv_* d\mu_j(\zeta_*) d\mu_k(\zeta') d\mu_l(\zeta'_*)$$

the gain and loss parts of the operator, so that formally,

$$\mathcal{B} = \mathcal{B}_+ - \mathcal{B}_-.$$

**Mechanical and chemical collision operators.** In our framework, there is no need to clearly distinguish chemical reactions from mechanical collisions. However, it can be useful to make this distinction, notably for the derivation of the Euler equations and the study of *moderately slow chemical reactions*, for which mechanical equilibrium is reached way before chemical equilibrium.

We define the set of mechanical collisions  $\Omega_{mech}$  and the set of chemical collisions  $\Omega_{chem}$  by

$$(4.10) \quad \Omega_{mech} = \left\{ \{(i, j) \rightarrow (i, j)\}, (i, j) \in \llbracket 1, N \rrbracket^2 \right\}, \quad \Omega_{chem} = \Omega \setminus \Omega_{mech}.$$

**Definition 6.** We define the mechanical collision Boltzmann operator  $\mathcal{B}_{mech}(F, F)$ , for any  $i \in \llbracket 1, N \rrbracket$ ,  $v \in \mathbb{R}^3$  and  $\zeta \in \mathcal{E}_i$ , by

$$\begin{aligned} & \mathcal{B}_{mech}(F, F)_i(v, \zeta) \\ &= \sum_{j=1}^N \int_{\mathcal{E}_j^2} \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} (f_i(v', \zeta') f_j(v'_*, \zeta'_*) - f_i(v, \zeta) f_j(v_*, \zeta_*)) b_{ij}^{ij} d\omega dv d\mu_j(\zeta_*) d\mu_i(\zeta') d\mu_j(\zeta'_*) \\ &= \sum_{\substack{j,k,l \\ \{(i,j) \rightarrow (k,l)\} \in \Omega_{mech}}} \int_{\mathcal{E}_l} \int_{\mathcal{E}_k} \int_{\mathcal{E}_j} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} (f_k(v', \zeta') f_l(v'_*, \zeta'_*) - f_i(v, \zeta) f_j(v_*, \zeta_*)) b_{ij}^{kl} d\omega dv d\mu_j(\zeta_*) d\mu_k(\zeta') d\mu_l(\zeta'_*), \end{aligned}$$

and the chemical collision Boltzmann operator  $\mathcal{B}_{chem}(F, F)$ , for any  $i \in \llbracket 1, N \rrbracket$ ,  $v \in \mathbb{R}^3$  and  $\zeta \in \mathcal{E}_i$ , by

$$\begin{aligned} & \mathcal{B}_{chem}(F, F)_i(v, \zeta) \\ &= \sum_{\substack{j,k,l \\ \{(i,j) \rightarrow (k,l)\} \in \Omega_{chem}}} \int_{\mathcal{E}_l} \int_{\mathcal{E}_k} \int_{\mathcal{E}_j} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} (f_k(v', \zeta') f_l(v'_*, \zeta'_*) - f_i(v, \zeta) f_j(v_*, \zeta_*)) b_{ij}^{kl} d\omega dv d\mu_j(\zeta_*) d\mu_k(\zeta') d\mu_l(\zeta'_*). \end{aligned}$$

Since  $\{\Omega_{mech}, \Omega_{chem}\}$  is a partition of  $\Omega$ ,

$$\mathcal{B}(F, F)_i(v, \zeta) = \mathcal{B}_{mech}(F, F)_i(v, \zeta) + \mathcal{B}_{chem}(F, F)_i(v, \zeta).$$

A weak formulation of the collision operator holds with the following proposition.

**Proposition 3.** For all  $i \in \llbracket 1, N \rrbracket$ , let  $\psi_i : \mathbb{R}^3 \times \mathcal{E}_i \rightarrow \mathbb{R}$  be a measurable function such that

$$\int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \left[ \mathcal{B}_-(F, F)_i(v, \zeta) + \mathcal{B}_+(F, F)_i(v, \zeta) \right] |\psi_i(v, \zeta)| dv d\mu_i(\zeta) < \infty,$$

then

$$\begin{aligned}
(4.11) \quad & \sum_{i=1}^N \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \mathcal{B}(F, F)_i(v, \zeta) \psi_i(v, \zeta) \, dv \, d\mu_i(\zeta) \\
&= -\frac{1}{4} \sum_{i,j,k,l=1}^N \int_{\mathcal{E}_i} \int_{\mathcal{E}_j} \int_{\mathcal{E}_k} \int_{\mathcal{E}_l} \iint_{(\mathbb{R}^3)^2} \int_{\mathbb{S}^2} (f_k(v', \zeta') f_l(v'_*, \zeta'_*) - f_i(v, \zeta) f_j(v_*, \zeta_*)) \\
&\quad \times \left[ \psi_k(v', \zeta') + \psi_l(v'_*, \zeta'_*) - \psi_i(v, \zeta) - \psi_j(v_*, \zeta_*) \right] b_{ij}^{kl} \, d\omega \, dv \, dv_* \, d\mu_i(\zeta) \, d\mu_j(\zeta_*) \, d\mu_k(\zeta') \, d\mu_l(\zeta'_*).
\end{aligned}$$

The proof, relying on the symmetry and micro-reversibility of the kernel  $b$ , is analogous to the one in [15, Proposition 3.1].

**4.2. Mechanical and global collision invariants.** In this subsection, we study the *mechanical* and *collision* invariants. Mechanical invariants are related to the equilibrium of mechanical collisions only, whereas global collision invariants are related to the equilibrium of both mechanical collisions and chemical reactions.

**Definition 7.** We say that  $\psi = (\psi_i)$ , where  $\psi_i : \mathbb{R}^3 \times \mathcal{E}_i \rightarrow \mathbb{R}$ , is a *mechanical invariant* if for any  $i, j$ , for  $\mu_i \otimes \mu_j \otimes \mu_i \otimes \mu_j$ -a.e.  $(\zeta, \zeta_*, \zeta', \zeta'_*) \in \mathcal{E}_i \times \mathcal{E}_j \times \mathcal{E}_i \times \mathcal{E}_j$ , a.e.  $(v, v_*) \in E_{ij}^{ij}[\zeta, \zeta_*, \zeta', \zeta'_*]$  and a.e.  $\omega \in \mathbb{S}_{ijij}^2[v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*]$ ,

$$(4.12) \quad \psi_i(v', \zeta') + \psi_j(v'_*, \zeta'_*) = \psi_i(v, \zeta) + \psi_j(v_*, \zeta_*),$$

where  $(v', v'_*)$  are defined by  $(v', v'_*) = S_{\omega}^{ijij}[\zeta, \zeta_*, \zeta', \zeta'_*](v, v_*)$ .

**Definition 8.** We say that  $\psi = (\psi_i)$ , where  $\psi_i : \mathbb{R}^3 \times \mathcal{E}_i \rightarrow \mathbb{R}$ , is a *global collision invariant* if for any allowed collision  $\{(i, j) \rightarrow (k, l)\} \in \Omega$ , for  $\mu_i \otimes \mu_j \otimes \mu_k \otimes \mu_l$ -a.e.  $(\zeta, \zeta_*, \zeta', \zeta'_*) \in \mathcal{E}_i \times \mathcal{E}_j \times \mathcal{E}_k \times \mathcal{E}_l$ , a.e.  $(v, v_*) \in E_{ij}^{kl}[\zeta, \zeta_*, \zeta', \zeta'_*]$  and a.e.  $\omega \in \mathbb{S}_{ijkl}^2[v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*]$ ,

$$(4.13) \quad \psi_k(v', \zeta') + \psi_l(v'_*, \zeta'_*) = \psi_i(v, \zeta) + \psi_j(v_*, \zeta_*),$$

where  $(v', v'_*)$  are defined by  $(v', v'_*) = S_{\omega}^{ijkl}[\zeta, \zeta_*, \zeta', \zeta'_*](v, v_*)$ .

Since  $\Omega$  contains all collisions, a collision invariant is also a mechanical invariant.

Let  $(\alpha_i) \in \mathbb{R}^N$  and  $(\beta, \gamma) \in \mathbb{R}^3 \times \mathbb{R}$ . Let us define  $\psi$  such that for any  $\zeta \in \mathcal{E}_i$  and  $v \in \mathbb{R}^3$

$$\psi_i(v, \zeta) = \alpha_i + \beta \cdot m_i v + \gamma \left( \frac{1}{2} m_i |v|^2 + \varepsilon_i(\zeta) \right).$$

Then the conservation laws (3.1) straightforwardly imply that  $\psi$  is a mechanical invariant. If moreover, for any  $\{(i, j) \rightarrow (k, l)\} \in \Omega_{chem}$ ,  $\alpha_i + \alpha_j = \alpha_k + \alpha_l$ , then  $\psi$  is a collision invariant.

**Proposition 4.** Let  $\psi$  be a mechanical invariant, such that for any  $i \in \llbracket 1, N \rrbracket$  and  $\mu_i$ -a.e.  $\zeta \in \mathcal{E}_i$  there exists  $r_\zeta > 0$  such that  $\psi_i(\cdot, \zeta) \in L^1(\mathbb{R}^3, e^{-|v|^2/r_\zeta} dv)$ . Then there exists  $(\alpha_i) \in \mathbb{R}^N$  and  $(\beta, \gamma) \in \mathbb{R}^3 \times \mathbb{R}$  such that for any  $i \in \llbracket 1, N \rrbracket$ , for  $\mu_i$ -a.e.  $\zeta \in \mathcal{E}_i$  and a.e.  $v \in \mathbb{R}^3$ ,

$$(4.14) \quad \psi_i(v, \zeta) = \alpha_i + \beta \cdot m_i v + \gamma \left( \frac{1}{2} m_i |v|^2 + \varepsilon_i(\zeta) \right).$$

*Proof.* First, we consider Equation (4.12) for  $i = j = k = l$  (since by hypothesis  $\{(i, i) \rightarrow (i, i)\} \in \Omega$ ). The assumption on the potential barrier for mechanical collisions (2.9) yields  $\kappa_{ii}^{ii} = \varepsilon_i^0 + \varepsilon_i^0$ , hence we obtain from [15, Theorem 3.2] that there exists  $(\alpha_i, \beta_i, \gamma_i) \in \mathbb{R} \times \mathbb{R}^3 \times \mathbb{R}$  such that for any  $i \in \llbracket 1, N \rrbracket$  and  $\mu_i$ -a.e.  $\zeta \in \mathcal{E}_i$  and a.e.  $v \in \mathbb{R}^3$ ,

$$(4.15) \quad \psi_i(v, \zeta) = \alpha_i + \beta_i \cdot v + \gamma_i \left( \frac{1}{2} m_i |v|^2 + \varepsilon_i(\zeta) \right).$$

Let us now consider again Equation (4.12), using formula (4.15), with  $i = k$ ,  $j = l$  (since by hypothesis  $\{(i, j) \rightarrow (i, j)\} \in \Omega$ ),  $\zeta = \zeta' \in \mathcal{E}_i$ ,  $\zeta_* = \zeta'_* \in \mathcal{E}_j$ , with  $\zeta$  and  $\zeta_*$  such that equality (4.15) holds. By definition, the set of allowed pre-collision velocities writes in this case

$$E_{ij}^{ij}[\zeta, \zeta_*, \zeta, \zeta_*] = \left\{ (v, v_*) \in \mathbb{R}^3 \times \mathbb{R}^3 \text{ s.t. } \frac{m_{ij}^*}{2} |v - v_*|^2 \geq \kappa_{ij}^{ij} - \varepsilon_i(\zeta) - \varepsilon_j(\zeta_*) \right\}.$$

Using the assumption on the potential barrier for mechanical collisions (2.9) thus yields

$$(4.16) \quad E_{ij}^{ij}[\zeta, \zeta_*, \zeta, \zeta_*] = \mathbb{R}^3 \times \mathbb{R}^3.$$

Moreover, we have

$$\sqrt{\Delta_{ij}^{ij}(v, v_*, \zeta, \zeta_*, \zeta, \zeta_*)} = |v - v_*|,$$

so that

$$v' = \frac{m_i v + m_j v_*}{M_{ij}} + \frac{m_j}{M_{ij}} T_\omega [v - v_*],$$

hence  $v'$  is a continuous function of  $v, v_*, \omega$ . The same applies for  $v'_*$ .

Now combining (4.15) with (4.12), we get

$$\begin{aligned} & \alpha_i + \alpha_j + \beta_i \cdot v + \beta_j \cdot v_* + \gamma_i \left( \frac{1}{2} m_i |v|^2 + \varepsilon_i(\zeta) \right) + \gamma_j \left( \frac{1}{2} m_j |v_*|^2 + \varepsilon_j(\zeta_*) \right) \\ &= \alpha_i + \alpha_j + \beta_i \cdot v' + \beta_j \cdot v'_* + \gamma_i \left( \frac{1}{2} m_i |v'|^2 + \varepsilon_i(\zeta) \right) + \gamma_j \left( \frac{1}{2} m_j |v'_*|^2 + \varepsilon_j(\zeta_*) \right), \end{aligned}$$

simplifying into

$$(4.17)$$

$$\beta_i \cdot v - \beta_i \cdot v' + \beta_j \cdot v_* - \beta_j \cdot v'_* + \gamma_i \left( \frac{1}{2} m_i |v|^2 \right) - \gamma_i \left( \frac{1}{2} m_i |v'|^2 \right) + \gamma_j \left( \frac{1}{2} m_j |v_*|^2 \right) - \gamma_j \left( \frac{1}{2} m_j |v'_*|^2 \right) = 0.$$

By hypothesis and from Equation (4.16), the above expression holds for a.e.  $(v, v_*) \in \mathbb{R}^3 \times \mathbb{R}^3$  and a.e.  $\omega \in \mathbb{S}_{ijij}^2[v, v_*, \zeta, \zeta_*, \zeta, \zeta_*]$ . Since it is continuous in  $v, v_*, \omega$ , and from assumption 4,  $\mathbb{S}_{ijij}^2[v, v_*, \zeta, \zeta_*, \zeta, \zeta_*]$  contains a neighbourhood of  $\frac{v-v_*}{|v-v_*|}$ , Equation (4.17) actually holds for all  $(v, v_*) \in \mathbb{R}^3 \times \mathbb{R}^3$  and  $\omega$  in some neighbourhood of  $\frac{v-v_*}{|v-v_*|}$ . We can thus consider  $\omega = \frac{v-v_*}{|v-v_*|}$  in the equation, so that

$$T_\omega \left[ \frac{v - v_*}{|v - v_*|} \right] = - \frac{v - v_*}{|v - v_*|},$$

implying

$$v' = \frac{m_i v + m_j v_*}{M_{ij}} - \frac{m_j}{M_{ij}} (v - v_*) = \frac{m_i - m_j}{M_{ij}} v + \frac{2m_j}{M_{ij}} v_*$$

and

$$v'_* = \frac{m_i v + m_j v_*}{M_{ij}} + \frac{m_i}{M_{ij}} (v - v_*) = \frac{2m_i}{M_{ij}} v + \frac{m_j - m_i}{M_{ij}} v_*.$$

Equation (4.17) becomes

$$\begin{aligned} & \beta_i \cdot v + \beta_j \cdot v_* - \beta_i \cdot \left( \frac{m_i - m_j}{M_{ij}} v + \frac{2m_j}{M_{ij}} v_* \right) - \beta_j \cdot \left( \frac{2m_i}{M_{ij}} v + \frac{m_j - m_i}{M_{ij}} v_* \right) + \gamma_i \left( \frac{1}{2} m_i |v|^2 \right) \\ &+ \gamma_j \left( \frac{1}{2} m_j |v_*|^2 \right) - \gamma_i \left( \frac{1}{2} m_i \left| \frac{m_i - m_j}{M_{ij}} v + \frac{2m_j}{M_{ij}} v_* \right|^2 \right) - \gamma_j \left( \frac{1}{2} m_j \left| \frac{2m_i}{M_{ij}} v + \frac{m_j - m_i}{M_{ij}} v_* \right|^2 \right) = 0. \end{aligned}$$

The above equality holds for all  $(v, v_*) \in \mathbb{R}^3 \times \mathbb{R}^3$ . Since it is a polynomial in  $v$  and  $v_*$ , all coefficients must be equal to 0. Focusing on the coefficient in front of  $v$  yields

$$\beta_i - \left( \frac{m_i - m_j}{M_{ij}} \right) \beta_i - \frac{2m_i}{M_{ij}} \beta_j = 0 \iff (m_i + m_j - (m_i - m_j))\beta_i = 2m_i\beta_j \iff \frac{\beta_i}{m_i} = \frac{\beta_j}{m_j}.$$

We deduce that there exists  $\beta \in \mathbb{R}^3$  such that for any  $1 \leq i \leq N$ ,  $\beta_i = m_i\beta$ . Now focusing on the coefficient in front of  $|v|^2$  yields

$$\begin{aligned} \frac{m_i}{2}\gamma_i - \frac{m_i}{2}\gamma_i \left( \frac{m_i - m_j}{M_{ij}} \right)^2 - \frac{m_j}{2}\gamma_j \left( \frac{2m_i}{M_{ij}} \right)^2 = 0 &\iff \left( (m_i + m_j)^2 - (m_i - m_j)^2 \right) \gamma_i = 4m_i m_j \gamma_j \\ &\iff \gamma_i = \gamma_j. \end{aligned}$$

We conclude that there exists  $\gamma \in \mathbb{R}$  such that for any  $1 \leq i \leq N$ ,  $\gamma_i = \gamma$ , ending the proof.  $\square$

**Corollary 5.** *Let  $\psi$  be a collision invariant, such that for any  $i \in \llbracket 1, N \rrbracket$  and  $\mu_i$ -a.e.  $\zeta \in \mathcal{E}_i$  there exists  $r_\zeta > 0$  such that  $\psi_i(\cdot, \zeta) \in L^1(\mathbb{R}^3, e^{-|v|^2/r_\zeta} dv)$ . Then there exists  $(\alpha_i) \in \mathbb{R}^N$  such that  $\alpha_i + \alpha_j = \alpha_k + \alpha_l$  for any  $\{(i, j) \rightarrow (k, l)\} \in \Omega_{chem}$  and  $(\beta, \gamma) \in \mathbb{R}^3 \times \mathbb{R}$ , such that for any  $i \in \llbracket 1, N \rrbracket$ ,  $\mu_i$ -a.e.  $\zeta \in \mathcal{E}_i$  and a.e.  $v \in \mathbb{R}^3$ ,*

$$(4.18) \quad \psi_i(v, \zeta) = \alpha_i + \beta \cdot m_i v + \gamma \left( \frac{1}{2} m_i |v|^2 + \varepsilon_i(\zeta) \right).$$

*Proof.* Since  $\psi$  is a collision invariant, it is also a mechanical invariant. From Proposition 4, there exists  $(\alpha_i) \in \mathbb{R}^N$  and  $(\beta, \gamma) \in \mathbb{R}^3 \times \mathbb{R}$  such that for any  $i \in \llbracket 1, N \rrbracket$ , for  $\mu_i$ -a.e.  $\zeta \in \mathcal{E}_i$  and a.e.  $v \in \mathbb{R}^3$ ,

$$\psi_i(v, \zeta) = \alpha_i + \beta \cdot m_i v + \gamma \left( \frac{1}{2} m_i |v|^2 + \varepsilon_i(\zeta) \right).$$

We have to prove that functions of this form are collision invariants also of the non mechanical collisions if and only if, for any  $\{(i, j) \rightarrow (k, l)\} \in \Omega_{chem}$ , we have

$$\alpha_i + \alpha_j = \alpha_k + \alpha_l.$$

Let  $\{(i, j) \rightarrow (k, l)\} \in \Omega_{chem}$ . There exists  $(\zeta, \zeta_*, \zeta', \zeta'_*) \in \mathcal{E}_i \times \mathcal{E}_j \times \mathcal{E}_k \times \mathcal{E}_l$  and  $(v, v_*) \in E_{ij}^{kl}[\zeta, \zeta_*, \zeta', \zeta'_*]$  such that Equation (4.13) holds, because for any  $\xi, \xi_*, \xi', \xi'_*$ ,  $E_{ij}^{kl}[\xi, \xi_*, \xi', \xi'_*]$  has non-zero Lebesgue measure. Equation (4.13) now writes

$$\begin{aligned} &\alpha_i + \alpha_j + \beta \cdot (m_i v + m_j v_*) + \gamma \left( \frac{1}{2} m_i |v|^2 + \varepsilon_i(\zeta) + \frac{1}{2} m_j |v_*|^2 + \varepsilon_j(\zeta_*) \right) \\ &= \alpha_k + \alpha_l + \beta \cdot (m_k v' + m_l v'_*) + \gamma \left( \frac{1}{2} m_k |v'|^2 + \varepsilon_k(\zeta') + \frac{1}{2} m_l |v'_*|^2 + \varepsilon_l(\zeta'_*) \right), \end{aligned}$$

and from the conservation laws (3.1), we get  $\alpha_i + \alpha_j = \alpha_k + \alpha_l$ .  $\square$

**4.3. H-Theorem.** The collision equilibrium can be characterized with the following theorem.

**Theorem 1.** *Let  $F \in \prod_{i=1}^N L^1(\mathbb{R}^3 \times \mathcal{E}_i, dv d\mu_i(\zeta))$  such that for any  $i \in \llbracket 1, N \rrbracket$ , a.e.  $v \in \mathbb{R}^3$  and  $\mu_i$ -a.e.  $\zeta \in \mathcal{E}_i$ ,  $F_i(v, \zeta) > 0$ . We assume that for any  $i \in \llbracket 1, N \rrbracket$ ,*

$$\int_{\mathcal{E}_i} \int_{\mathbb{R}^3} [\mathcal{B}_-(F, F)_i(v, \zeta) + \mathcal{B}_+(F, F)_i(v, \zeta)] |\log(F_i)(v, \zeta)| dv d\mu_i(\zeta) < \infty.$$

We have, recalling that  $c_i = \frac{1}{m_i^3}$ ,

$$(4.19) \quad \sum_{i=1}^N \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \mathcal{B}(F, F)_i(v, \zeta) \log(c_i F_i)(v, \zeta) dv d\mu_i(\zeta) \leq 0.$$

Moreover,

$$\begin{aligned}
& \sum_{i=1}^N \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \mathcal{B}(F, F)_i(v, \zeta) \log(c_i F_i)(v, \zeta) \, dv \, d\mu_i(\zeta) = 0 \\
& \quad \Downarrow \\
(4.20) \quad & \mathcal{B}(F, F)_i(v, \zeta) = 0 \text{ for any } i \in \llbracket 1, N \rrbracket, \text{ for a.e. } v \in \mathbb{R}^3 \text{ and } \mu_i\text{-a.e. } \zeta \in \mathcal{E}_i \\
& \quad \Downarrow \\
& (\log(c_i F_i))_{1 \leq i \leq N} \text{ is a collision invariant.}
\end{aligned}$$

The proof is similar to the one of [15, Theorem 4.1].

Moreover, the mechanical equilibrium can be characterized with the following theorem.

**Corollary 6.** *Let  $F \in \prod_{i=1}^N L^1(\mathbb{R}^3 \times \mathcal{E}_i, dv \, d\mu_i(\zeta))$  such that for any  $i \in \llbracket 1, N \rrbracket$ , a.e.  $v \in \mathbb{R}^3$  and  $\mu_i$ -a.e.  $\zeta \in \mathcal{E}_i$ ,  $F_i(v, \zeta) > 0$ . We assume that for any  $i \in \llbracket 1, N \rrbracket$ ,*

$$\int_{\mathcal{E}_i} \int_{\mathbb{R}^3} [\mathcal{B}_{mech,-}(F, F)_i(v, \zeta) + \mathcal{B}_{mech,+}(F, F)_i(v, \zeta)] |\log(F_i)(v, \zeta)| \, dv \, d\mu_i(\zeta) < \infty.$$

We have, recalling that  $c_i = \frac{1}{m_i^3}$ ,

$$(4.21) \quad \sum_{i=1}^N \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \mathcal{B}_{mech}(F, F)_i(v, \zeta) \log(c_i F_i)(v, \zeta) \, dv \, d\mu_i(\zeta) \leq 0.$$

Moreover,

$$\begin{aligned}
& \sum_{i=1}^N \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \mathcal{B}_{mech}(F, F)_i(v, \zeta) \log(c_i F_i)(v, \zeta) \, dv \, d\mu_i(\zeta) = 0 \\
& \quad \Downarrow \\
& \mathcal{B}_{mech}(F, F)_i(v, \zeta) = 0 \text{ for any } i \in \llbracket 1, N \rrbracket, \text{ for a.e. } v \in \mathbb{R}^3 \text{ and } \mu_i\text{-a.e. } \zeta \in \mathcal{E}_i \\
& \quad \Downarrow \\
& (\log(c_i F_i))_{1 \leq i \leq N} \text{ is a mechanical invariant.}
\end{aligned}$$

Since  $\Omega_{mech}$  satisfies the assumptions of our framework, Theorem 1 is still valid when  $\Omega$  is replaced by  $\Omega_{mech}$ . In this case, the invariants involved are the mechanical invariants.

## 5. EQUILIBRIUM

The H-Theorem along with the characterization of invariants allow to obtain the form of the equilibrium distribution, and to compute usual thermodynamic quantities, such as the number of degrees of freedom or the specific heat at constant volume.

**Definition 9.** *We define the extended Maxwellian family of distributions  $(\mathcal{M}_i)_{1 \leq i \leq N}$  associated to the densities  $(n_i)_{1 \leq i \leq N} \in \mathbb{R}_+^{*N}$  (where  $\mathbb{R}_+^* = \mathbb{R}_+ - \{0\}$ ), velocity  $\underline{u} \in \mathbb{R}^3$  and temperature  $T > 0$  by, for any  $1 \leq i \leq N$ ,  $v \in \mathbb{R}^3$  and  $\zeta \in \mathcal{E}_i$ ,*

$$(5.1) \quad \mathcal{M}_i[n_i, \underline{u}, T](v, \zeta) = n_i \left( \frac{m_i}{2\pi k_B T} \right)^{3/2} Z_i^{-1} \left( \frac{1}{k_B T} \right) \exp \left( -\frac{m_i |v - \underline{u}|^2}{2k_B T} - \frac{\bar{\varepsilon}_i(\zeta)}{k_B T} \right),$$

where  $k_B$  stands for the Boltzmann constant and  $Z_i$  is the partition function of the species  $i$  defined in (2.2).

**5.1. Mechanical equilibrium.** We consider at first mechanical equilibrium configurations, namely suitable sets of distributions  $F$  such that  $\mathcal{B}_{mech}(F, F) = 0$ . We have the following proposition.

**Proposition 7.** *When mechanical equilibrium is reached, that is when  $\mathcal{B}_{mech}(F, F) = 0$ , there exists  $(n_i)_{1 \leq i \leq N} \in \mathbb{R}_+^{*N}$ ,  $\underline{u} \in \mathbb{R}^3$  and  $T > 0$  such that, for any  $1 \leq i \leq N$ , a.e.  $v \in \mathbb{R}^3$  and  $\mu_i$ -a.e.  $\zeta \in \mathcal{E}_i$ ,*

$$F_i(v, \zeta) = \mathcal{M}_i[n_i, \underline{u}, T](v, \zeta).$$

This result is quite classical and the proof is similar to the one shown in [15, Section 4].

**Definition 10.** *We define  $\delta_i$ , the thermodynamic number of internal degrees of freedom of the species  $i$ , and  $c_V^i$ , the specific heat at constant volume of the species  $i$ , for any  $T > 0$ , by*

$$(5.2) \quad \delta_i(T) = \frac{2}{k_B T} \left( \frac{\int_{\mathcal{E}_i} \bar{\varepsilon}_i(\zeta) \exp\left(-\frac{\bar{\varepsilon}_i(\zeta)}{k_B T}\right) d\mu_i(\zeta)}{\int_{\mathcal{E}_i} \exp\left(-\frac{\bar{\varepsilon}_i(\zeta)}{k_B T}\right) d\mu_i(\zeta)} \right),$$

and

$$(5.3) \quad c_V^i(T) = \frac{3 + D_i(T)}{2},$$

with

$$(5.4) \quad D_i(T) = \frac{d(T\delta_i(T))}{dT}.$$

Recall that the partition function  $Z_i$  defined by Equation (2.2) is  $\mathcal{C}^\infty$ . Remarking that, from (5.2),

$$T\delta_i(T) = -\frac{2}{k_B} (\log(Z_i))' \left( \frac{1}{k_B T} \right),$$

the function  $T \mapsto T\delta_i(T)$  is  $\mathcal{C}^\infty$  on  $\mathbb{R}_+^*$  and  $D_i$  is indeed well-defined.

We recall in the following propositions and corollaries various mathematical properties of  $\delta_i$  and  $D_i$  studied in [15].

**Proposition 8.** *If  $\mu_i(\varepsilon_i = \varepsilon_i^0) > 0$ , then*

$$\delta_i(T) \xrightarrow{T \rightarrow 0^+} 0 \quad \text{and} \quad D_i(T) \xrightarrow{T \rightarrow 0^+} 0.$$

**Proposition 9.** *For any  $T > 0$ ,*

$$\delta_i(T) = \frac{1}{T} \int_0^T D_i(T') dT'.$$

A probabilistic interpretation may also be provided for the functions  $\delta_i(T)$  and  $D_i(T)$ . For  $T > 0$ , define the Gibbs probability measure  $\nu_T^i$  on  $(\mathcal{E}_i, \mathcal{A}_i)$  by

$$(5.5) \quad \frac{d\nu_T^i}{d\mu_i}(\zeta) = Z_i \left( \frac{1}{k_B T} \right)^{-1} \exp\left(-\frac{\bar{\varepsilon}_i(\zeta)}{k_B T}\right),$$

where  $Z_i$  is the partition function defined by Equation (2.2). Then for any  $T > 0$ ,  $(\mathcal{E}_i, \mathcal{A}_i, \nu_T^i)$  is a probability space. Since  $\bar{\varepsilon}_i : \mathcal{E}_i \rightarrow \mathbb{R}_+$  is  $(\mathcal{A}_i, \text{Bor}(\mathbb{R}))$ -measurable, it is a real random variable on  $(\mathcal{E}_i, \mathcal{A}_i, \nu_T^i)$ .

**Proposition 10.** *For any  $T > 0$ ,*

$$(5.6) \quad \delta_i(T) = 2 \mathbb{E}_{\nu_T^i} \left[ \frac{\bar{\varepsilon}_i}{k_B T} \right],$$

and

$$(5.7) \quad D_i(T) = 2 \operatorname{Var}_{\nu_T^i} \left[ \frac{\bar{\varepsilon}_i}{k_B T} \right],$$

where  $\mathbb{E}_{\nu_T^i}$  and  $\operatorname{Var}_{\nu_T^i}$  are respectively the expectation and the variance under the probability  $\nu_T^i$ .

**Corollary 11.** *For any  $T > 0$ , we have  $\delta_i(T) \geq 0$  and  $D_i(T) \geq 0$ .*

**Corollary 12.** *If there exists  $R \in \mathbb{R}$  such that  $\varepsilon_i \leq R$   $\mu_i$ -a.e., then*

$$\delta_i(T) \xrightarrow{T \rightarrow \infty} 0, \quad \text{and} \quad D_i(T) \xrightarrow{T \rightarrow \infty} 0.$$

We set  $\rho_i = m_i n_i$ . We easily verify that

$$\int_{\mathcal{E}_i} \int_{\mathbb{R}^3} m_i \mathcal{M}_i[n_i, \underline{u}, T](v, \zeta) \, dv \, d\mu_i(\zeta) = \rho_i,$$

and

$$\int_{\mathcal{E}_i} \int_{\mathbb{R}^3} m_i v \mathcal{M}_i[n_i, \underline{u}, T](v, \zeta) \, dv \, d\mu_i(\zeta) = \rho_i \underline{u}.$$

**Definition 11.** *We define  $\Theta_i$ , the microscopic energy function of the species  $i$ , for any  $T > 0$ , by*

$$(5.8) \quad \Theta_i(T) = \frac{3}{2} k_B T - \log(Z_i)' \left( \frac{1}{k_B T} \right).$$

By definition (5.2), we also have  $\Theta_i(T) = \frac{3 + \delta_i(T)}{2} k_B T$ , and from (5.3)-(5.4),  $\Theta_i(T) = \int_0^T c_V^i(T') k_B \, dT'$ .

We now define the specific energy density associated to the species  $i$  at equilibrium as

$$(5.9) \quad e_i^{eq}[\underline{u}, T] = \frac{1}{n_i} \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \left( \frac{1}{2} m_i |v|^2 + \varepsilon_i(\zeta) \right) \mathcal{M}_i[n_i, \underline{u}, T](v, \zeta) \, dv \, d\mu_i(\zeta).$$

A straightforward computation leads to

$$(5.10) \quad e_i^{eq}[\underline{u}, T] = \varepsilon_i^0 + \frac{1}{2} m_i |\underline{u}|^2 + \Theta_i(T).$$

Notice that  $\Theta_i$  is continuous on  $\mathbb{R}_+^*$ , can be extended by continuity to  $\mathbb{R}_+$  setting  $\Theta_i(0) = 0$ , is increasing on  $\mathbb{R}_+$ , with  $\Theta_i(T) \xrightarrow{T \rightarrow \infty} \infty$ , and thus is a bijection from  $\mathbb{R}_+$  to  $\mathbb{R}_+$ .

We then have for any  $i$ ,

$$T_i = \Theta_i^{-1} \left( \frac{1}{n_i} \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \left( \frac{1}{2} m_i |v - \underline{u}|^2 + \bar{\varepsilon}_i(\zeta) \right) F_i(v, \zeta) \, dv \, d\mu_i(\zeta) \right),$$

justifying (4.2), the definition of temperature of the species  $i$ , noticing that here, at mechanical equilibrium,  $(u_i, T_i) = (\underline{u}, T)$ .

Letting  $a_i = \frac{n_i}{\bar{n}}$  be the density fraction of the species  $i$ , we define the average specific energy at equilibrium by

$$(5.11) \quad \bar{e}^{eq}[(a_i), \underline{u}, T] = \sum_{i=1}^N a_i e_i^{eq}[\underline{u}, T].$$

We have

$$\bar{e}^{eq}[(a_i), \underline{u}, T] = \underbrace{\sum_{i=1}^N a_i \varepsilon_i^0}_{\text{potential}} + \underbrace{\sum_{i=1}^N a_i \frac{1}{2} m_i |\underline{u}|^2}_{\text{bulk}} + \underbrace{\sum_{i=1}^N a_i \Theta_i(T)}_{\text{micro}}$$



where we notice the separation of the potential energy, bulk kinetic energy and "microscopic" energy (coming from the contribution of both kinetic and internal contributions at microscopic level). We define

$$(5.12) \quad \bar{\Theta}[(a_i)](T) = \sum_{i=1}^N a_i \Theta_i(T).$$

The function  $\bar{\Theta}[(a_i)]$  is continuous on  $\mathbb{R}_+^*$ , can be extended by continuity to  $\mathbb{R}_+$ , setting  $\bar{\Theta}[(a_i)](0) = 0$ , is increasing on  $\mathbb{R}_+$ , with  $\bar{\Theta}[(a_i)](T) \xrightarrow{T \rightarrow \infty} \infty$ , and thus it is a bijection from  $\mathbb{R}_+$  to  $\mathbb{R}_+$ .

We then have

$$T = \bar{\Theta} \left[ \left( \frac{n_i}{\bar{n}} \right) \right]^{-1} \left( \frac{1}{\bar{n}} \sum_{i=1}^N \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \left( \frac{1}{2} m_i |v - \underline{u}|^2 + \bar{\varepsilon}_i(\zeta) \right) F_i(v, \zeta) \, dv \, d\mu_i(\zeta) \right),$$

justifying the definition of the mean temperature in (4.3) when noticing that here, at mechanical equilibrium,  $u_i = \underline{u}$ .

**5.2. Mechanical and chemical equilibrium.** We now consider global steady states, namely mechanical and chemical equilibrium. Obviously, every proposition of the previous subsection still holds. We now obtain in addition the mass-action law for each admissible reaction.

**Definition 12.** We define  $C_i^0$ , the chemical constant of the species  $i$ , for any  $T > 0$ , by

$$(5.13) \quad C_i^0(T) = (2\pi m_i k_B T)^{3/2} Z_i \left( \frac{1}{k_B T} \right) e^{-\frac{\varepsilon_i^0}{k_B T}}.$$

We also define, for any chemical reaction  $\{(i, j) \rightarrow (k, l)\} \in \Omega_{chem}$ , the equilibrium constant

$$(5.14) \quad \mathcal{K}_{ij}^{kl}(T) = \frac{C_k^0(T) C_l^0(T)}{C_i^0(T) C_j^0(T)} = \prod_{p \in \{i, j, k, l\}} \left\{ (2\pi m_p k_B T)^{3\sigma_p/2} Z_p \left( \frac{1}{k_B T} \right)^{\sigma_p} \right\} \exp \left( -\frac{(\Delta\varepsilon^0)_{ij}^{kl}}{k_B T} \right),$$

with stoichiometric coefficients  $\sigma_k = \sigma_l = -\sigma_i = -\sigma_j = 1$  and we recall that  $(\Delta\varepsilon^0)_{ij}^{kl} = \varepsilon_k^0 + \varepsilon_l^0 - \varepsilon_i^0 - \varepsilon_j^0$  is interpreted as the energy consumed by the chemical reaction.

We now state the mass-action law of chemistry.

**Theorem 2. Mass-action law.** When collision equilibrium is reached, that is when  $\mathcal{B}(F, F) = 0$ , there exists  $(n_i^{eq})_{1 \leq i \leq N} \in \mathbb{R}_+^{*N}$ ,  $\underline{u} \in \mathbb{R}^3$  and  $T > 0$  such that, for any  $1 \leq i \leq N$ , a.e.  $v \in \mathbb{R}^3$  and  $\mu_i$ -a.e.  $\zeta \in \mathcal{E}_i$ ,

$$F_i(v, \zeta) = \mathcal{M}_i[n_i^{eq}, \underline{u}, T](v, \zeta),$$

with  $\mathcal{M}_i$  given in (5.1), and for any chemical reaction  $\{(i, j) \rightarrow (k, l)\} \in \Omega_{chem}$ , the following mass-action law holds

$$(5.15) \quad \frac{n_k^{eq} n_l^{eq}}{n_i^{eq} n_j^{eq}} = \mathcal{K}_{ij}^{kl}(T).$$

*Proof.* Theorem 1 ensures that  $(\log(c_i F_i))_{1 \leq i \leq N}$  is a collision invariant and Corollary 5 yields the existence of  $(\alpha_i) \in \mathbb{R}^N$ ,  $\beta \in \mathbb{R}^3$  and  $\gamma \in \mathbb{R}$  such that  $\alpha_k + \alpha_l = \alpha_i + \alpha_j$  for any  $\{(i, j) \rightarrow (k, l)\} \in \Omega_{chem}$ , and for any  $i \in \llbracket 1, N \rrbracket$ , for a.e.  $v \in \mathbb{R}^3$  and  $\mu_i$ -a.e.  $\zeta \in \mathcal{E}_i$ ,

$$\log(c_i F_i)(v, \zeta) = \alpha_i + \beta \cdot m_i v + \gamma \left( \frac{1}{2} m_i |v|^2 + \varepsilon_i(\zeta) \right).$$

Setting  $T = -\frac{1}{k_B \gamma}$ ,  $\underline{u} = -\frac{1}{\gamma} \beta$  and  $A_i = \exp\left(\alpha_i + m_i \frac{|\beta|^2}{2\gamma}\right)$  for any  $i$ , we get

$$F_i(v, \zeta) = \frac{1}{c_i} A_i \exp\left(-\frac{m_i |v - \underline{u}|^2}{2k_B T} - \frac{\varepsilon_i(\zeta)}{k_B T}\right).$$

We set  $n_i^{eq} = \frac{C_i^0(T)}{A_i}$ , and recover, recalling that  $c_i = \frac{1}{m_i^3}$ ,  $F_i = \mathcal{M}_i[n_i^{eq}, \underline{u}, T]$ , where  $\mathcal{M}_i$  is given in (5.1).

We consider a chemical reaction  $\{(i, j) \rightarrow (k, l)\} \in \Omega_{chem}$ . Since  $\alpha_k + \alpha_l = \alpha_i + \alpha_j$  and  $m_k + m_l = m_i + m_j$ , we obtain  $A_i A_j = A_k A_l$ , leading to

$$\frac{n_k^{eq} n_l^{eq}}{n_i^{eq} n_j^{eq}} = \frac{C_k^0(T) C_l^0(T)}{C_i^0(T) C_j^0(T)},$$

which ends the proof.  $\square$

### 5.3. Rate of reaction.

**Assumption 13.** *From now on, we assume that the dependence on  $(v, v_*)$  in the kernel is through  $v - v_*$ , i.e. there exists  $\tilde{B}_{ij}^{kl}$  such that*

$$(5.16) \quad \tilde{B}_{ij}^{kl}(v - v_*, \zeta, \zeta_*, \zeta', \zeta'_*, \omega) = B_{ij}^{kl}(v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*, \omega).$$

We assume the chemical reaction to be *moderately slow* compared to the effect of mechanical collisions, which leads us to investigate the case where mechanical equilibrium has already been reached, implying  $F_i = \mathcal{M}_i[n_i, u, T]$  for any  $i$ , but not chemical equilibrium. Since in this case  $\mathcal{B}_{mech}(F, F) = 0$ , the Boltzmann equation for the species  $i$  writes, for  $(t, x, v, \zeta) \in \mathbb{R}_+ \times \mathbb{R}^3 \times \mathbb{R}^3 \times \mathcal{E}_i$ ,

$$\partial_t F_i(t, x, v, \zeta) + v \cdot \nabla_x F_i(t, x, v, \zeta) = \mathcal{B}_{chem}(F(t, x, \cdot, \cdot), F(t, x, \cdot, \cdot))_i(v, \zeta).$$

In order to lighten the notations, we do not write the variables  $t, x$  in the following. Recall that, using the notation  $f_i = c_i F_i$  and  $b_{ij}^{kl} = \frac{B_{ij}^{kl}}{c_i c_j}$ ,

$$\begin{aligned} & \mathcal{B}_{chem}(F, F)_i(v, \zeta) \\ &= \sum_{j, k, l} \int_{\mathcal{E}_l} \int_{\mathcal{E}_k} \int_{\mathcal{E}_j} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} (f_k(v', \zeta') f_l(v'_*, \zeta'_*) - f_i(v, \zeta) f_j(v_*, \zeta_*)) b_{ij}^{kl} d\omega dv_* d\mu_j(\zeta_*) d\mu_k(\zeta') d\mu_l(\zeta'_*). \\ & \{(i, j) \rightarrow (k, l)\} \in \Omega_{chem} \end{aligned}$$

**Definition 14.** *We define  $r_{ij}^{kl}$ , the rate of the reaction  $\{(i, j) \rightarrow (k, l)\}$ , by*

$$(5.17) \quad r_{ij}^{kl} = \int_{\mathcal{E}_l} \int_{\mathcal{E}_k} \int_{\mathcal{E}_j} \int_{\mathcal{E}_i} \int_{(\mathbb{R}^3)^2} \int_{\mathbb{S}^2} (f_k(v', \zeta') f_l(v'_*, \zeta'_*) - f_i(v, \zeta) f_j(v_*, \zeta_*)) b_{ij}^{kl}(v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*, \omega) d\omega dv dv_* d\mu_i(\zeta) d\mu_j(\zeta_*) d\mu_k(\zeta') d\mu_l(\zeta'_*).$$

*We also define  $r_i$ , the reaction rate of the species  $i$  by*

$$(5.18) \quad r_i = \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \mathcal{B}_{chem}(F, F)_i(v, \zeta) dv d\mu_i(\zeta) = \sum_{j, k, l} r_{ij}^{kl} \cdot \{(i, j) \rightarrow (k, l)\} \in \Omega_{chem}$$

**Lemma 13.** *For any  $\{(i, j) \rightarrow (k, l)\} \in \Omega_{chem}$ ,*

$$(5.19) \quad r_{ij}^{kl} = r_{ij}^{lk} = r_{ji}^{lk} = -r_{kl}^{ij}.$$

*Proof.* The symmetry assumption (4.5) on  $B$ , and thus on  $b$ , straightforwardly implies  $r_{ij}^{kl} = r_{ij}^{lk} = r_{ji}^{lk}$ , while the Jacobian formula of  $S_\omega^{ijkl}[\zeta, \zeta_*, \zeta', \zeta'_*]$  along with the micro-reversibility condition (4.8) on  $b$  also straightforwardly implies  $r_{ij}^{kl} = -r_{kl}^{ij}$ .  $\square$

We define  $\bar{B}_{ij}^{kl}$ , the average kernel relevant to the reaction  $\{(i, j) \rightarrow (k, l)\}$ , for any  $g \in \mathbb{R}^3$  and  $(\zeta, \zeta_*) \in \mathcal{E}_i \times \mathcal{E}_j$ ,

$$(5.20) \quad \bar{B}_{ij}^{kl}(g, \zeta, \zeta_*) = \int_{\mathcal{E}_i} \int_{\mathcal{E}_k} \int_{\mathbb{S}^2} \tilde{B}_{ij}^{kl}(g, \zeta, \zeta_*, \zeta', \zeta'_*, \omega) d\omega d\mu_k(\zeta') d\mu_l(\zeta'_*),$$

with  $\tilde{B}_{ij}^{kl}$  defined in (5.16).

Define the relative kinetic Gibbs probability of the species  $i$  and  $j$  at temperature  $T > 0$  on  $\mathbb{R}^3$  by

$$(5.21) \quad d\lambda_T^{ij}(g) = \left( \frac{m_{ij}^*}{2\pi k_B T} \right)^{3/2} \exp\left( -\frac{m_{ij}^* |g|^2}{2k_B T} \right) dg,$$

where  $m_{ij}^*$  is the reduced mass. Then, for any  $T > 0$ ,  $\bar{B}_{ij}^{kl}$  is a real random variable on the space  $\mathbb{R}^3 \times \mathcal{E}_i \times \mathcal{E}_j$  endowed with the probability  $\lambda_T^{ij} \otimes \nu_T^i \otimes \nu_T^j$ .

**Definition 15.** We define  $\mathsf{K}_{ij}^{kl}$ , the rate constant of the chemical reaction  $\{(i, j) \rightarrow (k, l)\}$ , for any  $T > 0$ , by

$$(5.22) \quad \mathsf{K}_{ij}^{kl}(T) = \mathbb{E}_{\lambda_T^{ij} \otimes \nu_T^i \otimes \nu_T^j} [\bar{B}_{ij}^{kl}],$$

where  $\mathbb{E}_{\lambda_T^{ij} \otimes \nu_T^i \otimes \nu_T^j}$  stands for the expectation under the probability  $\lambda_T^{ij} \otimes \nu_T^i \otimes \nu_T^j$ .

The rate constant only depends on the considered species, the collision kernel and the temperature.

**Definition 16.** We say that  $\bar{B}_{ij}^{kl}$  is energy-non-decreasing (resp. energy-non-increasing) if for a.e.  $g, g' \in \mathbb{R}^3$ ,  $\mu_i$ -a.e.  $\zeta, \zeta' \in \mathcal{E}_i$  and  $\mu_j$ -a.e.  $\zeta_*, \zeta'_* \in \mathcal{E}_j$ ,

$$\begin{aligned} \frac{m_{ij}^*}{2} |g|^2 + \varepsilon_i(\zeta) + \varepsilon_j(\zeta_*) \leq \frac{m_{ij}^*}{2} |g'|^2 + \varepsilon_i(\zeta') + \varepsilon_j(\zeta'_*) &\implies \bar{B}_{ij}^{kl}(g, \zeta, \zeta_*) \leq \bar{B}_{ij}^{kl}(g', \zeta', \zeta'_*) \\ \text{(resp. } \implies \bar{B}_{ij}^{kl}(g, \zeta, \zeta_*) \geq \bar{B}_{ij}^{kl}(g', \zeta', \zeta'_*) \text{)}. \end{aligned}$$

**Proposition 14.** If  $\bar{B}_{ij}^{kl}$  is energy-non-decreasing and  $\text{Leb}_{\mathbb{R}^3} \otimes \mu_i \otimes \mu_j$ -non-constant, then  $\mathsf{K}_{ij}^{kl}$  is an increasing function of temperature. If  $\bar{B}_{ij}^{kl}$  is  $\text{Leb}_{\mathbb{R}^3} \otimes \mu_i \otimes \mu_j$ -constant, then  $\mathsf{K}_{ij}^{kl}$  is a constant function of temperature. If  $\bar{B}_{ij}^{kl}$  is energy-non-increasing and  $\text{Leb}_{\mathbb{R}^3} \otimes \mu_i \otimes \mu_j$ -non-constant, then  $\mathsf{K}_{ij}^{kl}$  is a decreasing function of temperature.

This is a straightforward consequence of Lemma 18 in Appendix A, with  $\mathcal{X} = \mathbb{R}^3 \times \mathcal{E}_i \times \mathcal{E}_j$ ,  $\eta = \text{Leb}_{\mathbb{R}^3} \otimes \mu_i \otimes \mu_j$ ,  $\varphi = \bar{B}_{ij}^{kl}$  and  $\psi(g, \zeta, \zeta_*) = \frac{1}{k_B} \left( \frac{m_{ij}^*}{2} |g|^2 + \bar{\varepsilon}_i(\zeta) + \bar{\varepsilon}_j(\zeta_*) \right)$ .

**Proposition 15.** The rate of reaction writes

$$(5.23) \quad r_{ij}^{kl} = \mathsf{K}_{kl}^{ij}(T) n_k n_l - \mathsf{K}_{ij}^{kl}(T) n_i n_j,$$

and the following relation holds

$$(5.24) \quad \mathsf{K}_{kl}^{ij}(T) = \frac{\mathsf{K}_{ij}^{kl}(T)}{\mathcal{K}_{ij}^{kl}(T)},$$

where  $\mathcal{K}_{ij}^{kl}$  has been defined in (5.14).

*Proof.* Let us fix  $j, k, l$  such that  $\{(i, j) \rightarrow (k, l)\} \in \Omega_{chem}$ . We denote

$$\mathcal{I}_{ij}^{kl}(v, \zeta) = \int_{\mathcal{E}_i} \int_{\mathcal{E}_k} \int_{\mathcal{E}_j} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} (f_k(v', \zeta') f_l(v'_*, \zeta'_*) - f_i(v, \zeta) f_j(v_*, \zeta_*)) b_{ij}^{kl} d\omega dv_* d\mu_j(\zeta_*) d\mu_k(\zeta') d\mu_l(\zeta'_*).$$

Since we assumed mechanical equilibrium,  $F$  has a Maxwellian form, and we deduce from the conservation laws (3.1) that

$$f_k(v', \zeta') f_l(v'_*, \zeta'_*) = \frac{n_k n_l}{n_i n_j} \frac{1}{\mathcal{K}_{ij}^{kl}(T)} f_i(v, \zeta) f_j(v_*, \zeta_*).$$

We set

$$R_{ij}^{kl}(T) = \frac{n_k n_l}{\mathcal{K}_{ij}^{kl}(T)} - n_i n_j.$$

Then, recalling that  $f_i f_j b_{ij}^{kl} = F_i F_j B_{ij}^{kl}$  and the assumption (5.16) on  $B$ , we have

$$\begin{aligned} \mathcal{I}_{ij}^{kl}(v, \zeta) &= \\ \frac{R_{ij}^{kl}(T)}{n_i n_j} &\int_{\mathcal{E}_i} \int_{\mathcal{E}_k} \int_{\mathcal{E}_j} \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} F_i(v, \zeta) F_j(v_*, \zeta_*) \tilde{B}_{ij}^{kl}(v - v_*, \zeta, \zeta_*, \zeta', \zeta'_*, \omega) d\omega dv_* d\mu_j(\zeta_*) d\mu_k(\zeta') d\mu_l(\zeta'_*), \end{aligned}$$

simplifying into

$$\mathcal{I}_{ij}^{kl}(v, \zeta) = \frac{R_{ij}^{kl}(T)}{n_i n_j} \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} F_i(v, \zeta) F_j(v_*, \zeta_*) \bar{B}_{ij}^{kl}(v - v_*, \zeta, \zeta_*) dv_* d\mu_j(\zeta_*).$$

The rate of the reaction  $\{(i, j) \rightarrow (k, l)\}$  then writes

$$\begin{aligned} r_{ij}^{kl} &= \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \mathcal{I}_{ij}^{kl}(v, \zeta) dv d\mu_i(\zeta) \\ &= \frac{R_{ij}^{kl}(T)}{n_i n_j} \int_{\mathcal{E}_i} \int_{\mathcal{E}_j} \iint_{(\mathbb{R}^3)^2} \mathcal{M}_i[n_i, \underline{u}, T] \mathcal{M}_j[n_j, \underline{u}, T] \bar{B}_{ij}^{kl}(v - v_*, \zeta, \zeta_*) dv dv_* d\mu_j(\zeta_*) d\mu_i(\zeta). \end{aligned}$$

Applying the change of variables  $v, v_* \rightarrow v + \underline{u}, v_* + \underline{u}$  yields

$$\begin{aligned} r_{ij}^{kl} &= \frac{R_{ij}^{kl}(T)}{n_i n_j} \int_{\mathcal{E}_i} \int_{\mathcal{E}_j} \iint_{(\mathbb{R}^3)^2} \mathcal{M}_i[n_i, 0, T] \mathcal{M}_j[n_j, 0, T] \bar{B}_{ij}^{kl}(v - v_*, \zeta, \zeta_*) dv dv_* d\mu_j(\zeta_*) d\mu_i(\zeta) \\ &= R_{ij}^{kl}(T) \left( \frac{m_i}{2\pi k_B T} \right)^{3/2} \left( \frac{m_j}{2\pi k_B T} \right)^{3/2} Z_i^{-1} \left( \frac{1}{k_B T} \right) Z_j^{-1} \left( \frac{1}{k_B T} \right) \\ &\quad \times \int_{\mathcal{E}_i} \int_{\mathcal{E}_j} e^{-\frac{\varepsilon_i(\zeta) + \varepsilon_j(\zeta_*)}{k_B T}} \iint_{(\mathbb{R}^3)^2} e^{-\frac{m_i |v|^2 + m_j |v_*|^2}{2k_B T}} \bar{B}_{ij}^{kl}(v - v_*, \zeta, \zeta_*) dv dv_* d\mu_i(\zeta) d\mu_j(\zeta_*). \end{aligned}$$

In the integral in  $(v, v_*)$ , we perform the change of variables

$$(v, v_*) \mapsto \left( v - v_*, \frac{m_i v + m_j v_*}{m_i + m_j} \right) = (g, G)$$

of Jacobian 1. Recalling that  $m_{ij}^* = \frac{m_i m_j}{m_i + m_j}$  and  $M_{ij} = m_i + m_j$ , we have

$$\frac{1}{2} m_{ij}^* |g|^2 + \frac{1}{2} M_{ij} |G|^2 = \frac{1}{2} m_i |v|^2 + \frac{1}{2} m_j |v_*|^2,$$

and we obtain that the integral over the relative velocity  $g$  writes as

$$\left( \frac{2\pi k_B T}{M_{ij}} \right)^{3/2} \int_{\mathbb{R}^3} e^{-\frac{m_{ij}^* |g|^2}{2k_B T}} \bar{B}_{ij}^{kl}(g, \zeta, \zeta_*) dg.$$

It follows that

$$\begin{aligned} r_{ij}^{kl} &= R_{ij}^{kl}(T) \left( \frac{m_{ij}^*}{2\pi k_B T} \right)^{3/2} Z_i \left( \frac{1}{k_B T} \right)^{-1} Z_j \left( \frac{1}{k_B T} \right)^{-1} \\ &\times \int_{\mathcal{E}_i} \int_{\mathcal{E}_j} \int_{\mathbb{R}^3} \exp \left( -\frac{m_{ij}^* |g|^2}{2k_B T} - \frac{\bar{\varepsilon}_i(\zeta) + \bar{\varepsilon}_j(\zeta_*)}{k_B T} \right) \bar{B}_{ij}^{kl}(g, \zeta, \zeta_*) \, dg \, d\mu_i(\zeta) d\mu_j(\zeta_*), \end{aligned}$$

which rewrites as

$$r_{ij}^{kl} = R_{ij}^{kl}(T) \mathbb{E}_{\lambda_T^{ij} \otimes \nu_T^i \otimes \nu_T^j} [\bar{B}_{ij}^{kl}] = \left( \frac{n_k n_l}{\mathcal{K}_{ij}^{kl}(T)} - n_i n_j \right) \mathcal{K}_{ij}^{kl}(T).$$

Finally, since  $r_{ij}^{kl} = -r_{kl}^{ij}$  and the above expression is a polynomial in  $n_i, n_j, n_k, n_l$ , we obtain (5.24) by identification and (5.23) follows.  $\square$

**Corollary 16.** *The reaction rate of the species  $i$  writes*

$$r_i = \sum_{\substack{j,k,l \\ \{(i,j) \rightarrow (k,l)\} \in \Omega_{chem}}} \mathcal{K}_{kl}^{ij}(T) n_k n_l - \mathcal{K}_{ij}^{kl}(T) n_i n_j.$$

This corollary is a straightforward consequence of Proposition 15.

**Redundancy-free quantities.** Let us recall that since the reaction  $\{(i, j) \rightarrow (k, l)\}$  is technically the same as  $\{(i, j) \rightarrow (l, k)\}$ , the physical rate of this reaction actually writes, when  $k \neq l$ ,

$$(5.25) \quad \bar{r}_{ij}^{kl} = r_{ij}^{kl} + r_{ij}^{lk}.$$

Similarly, the physical rate constant of this reaction actually writes, when  $k \neq l$ ,

$$(5.26) \quad \bar{\mathcal{K}}_{ij}^{kl} = \mathcal{K}_{ij}^{kl} + \mathcal{K}_{ij}^{lk}.$$

We highlight that this is coherent, as we already pointed out that in the case  $k \neq l$  the kernel  $B_{ij}^{kl}$  may be thought of as half the physical one, and both the rate of reaction and the rate constant linearly depend on it.

## 6. EULER LIMIT

In this section we derive the system of Euler equations in the case of moderately slow chemical reactions, that is, when mechanical equilibrium is assumed. Then Corollary 6 ensures that  $\mathcal{B}_{mech}(F, F) = 0$  a.e., and for any  $i \in \llbracket 1, N \rrbracket$ , all  $t \in \mathbb{R}_+$ ,  $x \in \mathbb{R}^3$ , a.e.  $v \in \mathbb{R}^3$  and  $\mu_i$ -a.e.  $\zeta \in \mathcal{E}_i$ ,

$$F_i(t, x, v, \zeta) = \mathcal{M}_i [n_i(t, x), \underline{u}(t, x), T(t, x)](v, \zeta).$$

We define  $(\Delta \varepsilon^0)_{ij}^{kl}$ , the energy consumed by the chemical reaction  $\{(i, j) \rightarrow (k, l)\}$ , by

$$(6.1) \quad (\Delta \varepsilon^0)_{ij}^{kl} = \varepsilon_k^0 + \varepsilon_l^0 - \varepsilon_i^0 - \varepsilon_j^0.$$

Now we define the set of families of chemical reactions

$$\bar{\Omega}_{chem} = \left\{ \{ \{i, j\} \rightleftharpoons \{k, l\} \} \text{ s.t. } \{(i, j) \rightarrow (k, l)\} \in \Omega_{chem} \right\},$$

accounting exactly once for each different chemical reaction, in the sense that

$$\begin{aligned} \{ \{i, j\} \rightleftharpoons \{k, l\} \} &= \{ \{j, i\} \rightleftharpoons \{l, k\} \} = \{ \{k, l\} \rightleftharpoons \{i, j\} \} = \{ \{l, k\} \rightleftharpoons \{j, i\} \} \\ &= \{ \{i, j\} \rightleftharpoons \{l, k\} \} = \{ \{j, i\} \rightleftharpoons \{k, l\} \} = \{ \{k, l\} \rightleftharpoons \{j, i\} \} = \{ \{l, k\} \rightleftharpoons \{i, j\} \}. \end{aligned}$$

The symmetry properties of  $(\Delta\varepsilon^0)_{ij}^{kl}$  and of  $r_{ij}^{kl}$ , (5.19), straightforwardly imply

$$(6.2) \quad \begin{aligned} (\Delta\varepsilon^0)_{ij}^{kl} r_{ij}^{kl} &= (\Delta\varepsilon^0)_{ji}^{lk} r_{ji}^{lk} = (\Delta\varepsilon^0)_{kl}^{ij} r_{kl}^{ij} = (\Delta\varepsilon^0)_{lk}^{ji} r_{lk}^{ji} \\ &= (\Delta\varepsilon^0)_{ij}^{lk} r_{ij}^{lk} = (\Delta\varepsilon^0)_{ji}^{kl} r_{ji}^{kl} = (\Delta\varepsilon^0)_{kl}^{ji} r_{kl}^{ji} = (\Delta\varepsilon^0)_{lk}^{ij} r_{lk}^{ij}, \end{aligned}$$

allowing the following (6.6) to make sense.

**Theorem 3.** *We set*

$$(6.3) \quad \bar{n} = \sum_{i=1}^N n_i, \quad \bar{\rho} = \sum_{i=1}^N m_i n_i, \quad \bar{\delta} = \frac{1}{\bar{n}} \sum_{i=1}^N n_i \delta_i(T), \quad p = \bar{n} k_B T.$$

The Euler system of equations at mechanical equilibrium is given by

$$(6.4) \quad \forall i \in \llbracket 1, N \rrbracket, \quad \partial_t n_i + \operatorname{div}_x(n_i \underline{u}) = r_i,$$

$$(6.5) \quad \partial_t(\bar{\rho} \underline{u}) + \operatorname{div}_x(\bar{\rho} \underline{u} \otimes \underline{u}) + \nabla_x p = 0,$$

(6.6)

$$\partial_t \left( \frac{1}{2} \bar{\rho} |\underline{u}|^2 + \bar{n} \frac{3 + \bar{\delta}}{2} k_B T \right) + \operatorname{div}_x \left( \frac{1}{2} \bar{\rho} |\underline{u}|^2 \underline{u} + \bar{n} \frac{3 + \bar{\delta}}{2} k_B T \underline{u} + p \underline{u} \right) = \sum_{\{(i,j) \rightleftharpoons (k,l)\} \in \bar{\Omega}_{chem}} (\Delta\varepsilon^0)_{ij}^{kl} \bar{r}_{ij}^{kl},$$

where, recalling that  $\bar{r}_{ij}^{kl}$  and  $\bar{K}_{ij}^{kl}$  are the redundancy-free quantities defined in (5.25)–(5.26),

$$\bar{r}_{ij}^{kl} = r_{ij}^{kl} + r_{ij}^{lk} = \bar{K}_{kl}^{ij}(T) n_k n_l - \bar{K}_{ij}^{kl}(T) n_i n_j, \quad \text{and} \quad r_i = \sum_{\substack{j,k,l \\ \{(i,j) \rightarrow (k,l)\} \in \Omega_{chem}}} r_{ij}^{kl}.$$

*Proof.* Since  $\mathcal{B}_{mech}(F, F) = 0$ , the Boltzmann equation now writes, for any  $1 \leq i \leq N$ ,

$$(6.7) \quad \partial_t F_i(t, x, v, \zeta) + v \cdot \nabla_x F_i(t, x, v, \zeta) = \mathcal{B}_{chem}(F(t, x, \cdot, \cdot), F(t, x, \cdot, \cdot))_i(v, \zeta).$$

By definition of  $r_i$ , given in (5.18), integrating (6.7) in  $v \in \mathbb{R}^3$  and  $\zeta \in \mathcal{E}_i$  straightforwardly yields (6.4).

Now let  $\psi$  such that for any  $i \in \llbracket 1, N \rrbracket$ ,  $v \in \mathbb{R}^3$  and  $\zeta \in \mathcal{E}_i$ ,  $\psi_i(v, \zeta) = m_i v$ . Since  $\psi$  is a collision invariant, we have for any  $t$  and  $x$

$$(6.8) \quad \sum_{i=1}^N \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \mathcal{B}_{chem}(F(t, x, \cdot, \cdot), F(t, x, \cdot, \cdot))_i(v, \zeta) \psi_i(v, \zeta) dv d\mu_i(\zeta) = 0.$$

Combining (6.7) and (6.8) yields

$$\partial_t \left( \sum_{i=1}^N \rho_i \underline{u} \right) + \operatorname{div}_x \left( \sum_{i=1}^N \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \mathcal{M}_i[n_i, \underline{u}, T](v, \zeta) m_i v \otimes v dv d\mu_i(\zeta) \right) = 0.$$

By a standard computation (see [17, Chapter 2]),

$$\begin{aligned} \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \mathcal{M}_i[n_i, \underline{u}, T](v, \zeta) m_i v \otimes v dv d\mu_i(\zeta) &= m_i n_i \left( \frac{m_i}{2\pi k_B T} \right)^{3/2} \int_{\mathbb{R}^3} \exp\left(-\frac{m_i |v - \underline{u}|^2}{2k_B T}\right) v \otimes v dv \\ &= \rho_i \underline{u} \otimes \underline{u} + n_i k_B T \mathbf{I}_d, \end{aligned}$$

where  $\mathbf{I}_d$  stands for the identity matrix of dimension 3, which allows to conclude for (6.5).

Finally, let  $\psi$  such that for any  $i \in \llbracket 1, N \rrbracket$ ,  $v \in \mathbb{R}^3$  and  $\zeta \in \mathcal{E}_i$ ,  $\psi_i(v, \zeta) = \frac{1}{2} m_i |v|^2 + \varepsilon_i(\zeta)$ . Again,  $\psi$  is a collision invariant, so that

$$(6.9) \quad \sum_{i=1}^N \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \mathcal{B}_{chem}(F(t, x, \cdot, \cdot), F(t, x, \cdot, \cdot))_i(v, \zeta) \psi_i(v, \zeta) dv d\mu_i(\zeta) = 0.$$

We recall (5.10), for any  $i \in \llbracket 1, N \rrbracket$ ,

$$(6.10) \quad \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} \mathcal{M}_i[n_i, \underline{u}, T](v, \zeta) \psi_i(v, \zeta) dv d\mu_i(\zeta) = \frac{1}{2} \rho_i |\underline{u}|^2 + n_i \frac{3 + \delta_i(T)}{2} k_B T + n_i \varepsilon_i^0.$$

On the other hand, again by a standard computation for the velocity-related term (see [17, Chapter 2]), for any  $i \in \llbracket 1, N \rrbracket$ ,

$$\begin{aligned} & \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} v \psi_i(v, \zeta) \mathcal{M}_i[n_i, \underline{u}, T](v, \zeta) dv d\mu_i(\zeta) \\ &= \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} v \frac{1}{2} m_i |v|^2 \mathcal{M}_i[n_i, \underline{u}, T](v, \zeta) dv d\mu_i(\zeta) + \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} v \varepsilon_i(\zeta) \mathcal{M}_i[n_i, \underline{u}, T](v, \zeta) dv d\mu_i(\zeta) \\ &= n_i \left( \frac{m_i}{2\pi k_B T} \right)^{3/2} \int_{\mathbb{R}^3} v \frac{1}{2} m_i |v|^2 \exp\left(-\frac{m_i |v - \underline{u}|^2}{2k_B T}\right) dv + n_i \left( \frac{\int_{\mathcal{E}_i} \varepsilon_i(\zeta) \exp\left(-\frac{\bar{\varepsilon}_i(\zeta)}{k_B T}\right) d\mu_i(\zeta)}{\int_{\mathcal{E}_i} \exp\left(-\frac{\bar{\varepsilon}_i(\zeta)}{k_B T}\right) d\mu_i(\zeta)} \right) \underline{u} \\ &= \frac{1}{2} \rho_i |\underline{u}|^2 \underline{u} + n_i k_B T \underline{u} + n_i \frac{3}{2} k_B T \underline{u} + n_i \left( \varepsilon_i^0 + \frac{\delta_i(T)}{2} k_B T \right) \underline{u}, \end{aligned}$$

therefore we get

$$(6.11) \quad \int_{\mathcal{E}_i} \int_{\mathbb{R}^3} v \psi_i(v, \zeta) \mathcal{M}_i[n_i, \underline{u}, T](v, \zeta) dv d\mu_i(\zeta) = \left( \frac{1}{2} \rho_i |\underline{u}|^2 + n_i k_B T + n_i \frac{3 + \delta_i(T)}{2} k_B T + n_i \varepsilon_i^0 \right) \underline{u}.$$

From the definition of  $\bar{\delta}$  given in (6.3) we note that it depends on  $(n_i)$  and  $T$ . Now notice that, for any  $i \in \llbracket 1, N \rrbracket$ ,

$$(6.12) \quad \partial_t (n_i \varepsilon_i^0) + \operatorname{div}_x (n_i \varepsilon_i^0 \underline{u}) = \varepsilon_i^0 (\partial_t n_i + \operatorname{div}_x (n_i \underline{u})) = \varepsilon_i^0 r_i.$$

Combining (6.7) and (6.9)–(6.12) while summing over  $i \in \llbracket 1, N \rrbracket$  yields

$$(6.13) \quad \partial_t \left( \frac{1}{2} \bar{\rho} |\underline{u}|^2 + \bar{n} \frac{3 + \bar{\delta}}{2} k_B T \right) + \operatorname{div}_x \left( \frac{1}{2} \bar{\rho} |\underline{u}|^2 \underline{u} + p \underline{u} + \bar{n} \frac{3 + \bar{\delta}}{2} k_B T \underline{u} \right) = - \sum_{i=1}^N \varepsilon_i^0 r_i.$$

Using the symmetry property of the rate constant, Lemma 13, we notice that

$$\sum_{i=1}^N \varepsilon_i^0 r_i = \sum_{i=1}^N \varepsilon_i^0 \sum_{\substack{j,k,l \\ \{(i,j) \rightarrow (k,l)\} \in \Omega_{chem}}} r_{ij}^{kl} = \sum_{\{(i,j) \rightarrow (k,l)\} \in \Omega_{chem}} \varepsilon_i^0 r_{ij}^{kl} = \sum_{\{(j,i) \rightarrow (l,k)\} \in \Omega_{chem}} \varepsilon_j^0 r_{ji}^{lk} = \sum_{\{(i,j) \rightarrow (k,l)\} \in \Omega_{chem}} \varepsilon_j^0 r_{ij}^{kl}$$

and similarly

$$\sum_{i=1}^N \varepsilon_i^0 r_i = - \sum_{\{(i,j) \rightarrow (k,l)\} \in \Omega_{chem}} \varepsilon_k^0 r_{ij}^{kl} = - \sum_{\{(i,j) \rightarrow (k,l)\} \in \Omega_{chem}} \varepsilon_l^0 r_{ij}^{kl}.$$

It follows from these symmetry arguments that

$$(6.14) \quad - \sum_{i=1}^N \varepsilon_i^0 r_i = \sum_{\{\{i,j\} \rightleftharpoons \{k,l\}\} \in \bar{\Omega}_{chem}} (\Delta \varepsilon^0)_{ij}^{kl} r_{ij}^{kl}.$$

Combining (6.13) with (6.14), we obtain (6.6).  $\square$

Notice that, since  $\bar{K}_{ij}^{kl}$ ,  $\delta_i$  and  $(\Delta \varepsilon^0)_{ij}^{kl}$  are known, the system (6.4)–(6.6) is composed of  $N$  [(6.4)] + 3 [(6.5)] + 1 [(6.6)] equations for  $N$   $[(n_i)_{1 \leq i \leq N}]$  + 3  $[\underline{u}]$  + 1  $[T]$  unknowns, hence it is a closed system.

## 7. EXAMPLE OF A COMPUTATION OF THE RATE OF REACTION

The purpose of this section is to show how to introduce the potential barriers  $\kappa_{ij}^{kl}$  (explained in Section 2) in the framework. Define  $E_a = \kappa_{ij}^{kl} - \varepsilon_i^0 - \varepsilon_j^0$  the activation energy of the reaction  $\{(i, j) \rightarrow (k, l)\}$ , and assume  $E_a > 0$ . We assume that the species  $i$  and  $j$  are monatomic, implying  $\mathcal{E}_i = \mathcal{E}_j = \{0\}$  and  $\bar{B}_{ij}^{kl}$  depends only on  $g \in \mathbb{R}^3$ . The quantities in this subsection are redundancy-free.

**Proposition 17.** *We consider the kernel used in [31, 32]. Let  $\beta > 0$ , define for any  $g \in \mathbb{R}^3$ ,*

$$(7.1) \quad \bar{B}_{ij}^{kl}(g) = \beta \left( 1 - \frac{E_a}{\frac{m_{ij}^*}{2}|g|^2} \right) \mathbf{1}_{\frac{m_{ij}^*}{2}|g|^2 \geq E_a}.$$

Then the rate constant is given, for any  $T > 0$ , by the formula

$$(7.2) \quad \mathbf{K}_{ij}^{kl}(T) = \frac{2\beta}{\sqrt{\pi}} \left[ \Gamma\left(\frac{3}{2}, \frac{E_a}{k_B T}\right) - \frac{E_a}{k_B T} \Gamma\left(\frac{1}{2}, \frac{E_a}{k_B T}\right) \right],$$

where  $\Gamma$  stands for the upper incomplete Gamma function.

The kernel (7.1), that takes into account that a reaction can occur only if the in-going kinetic energy is greater than the activation energy, does satisfy the assumptions of our framework because of how we took the transition state energy  $\kappa_{ij}^{kl}$  into account in (3.7). If we had not, the kernel would not have satisfied the positivity assumption 4 and could not have been considered.

*Proof.* We recall the definition (5.22) of the rate constant. Let  $\alpha > -3$ , we set, for  $g \in \mathbb{R}^3$ ,

$$\chi_\alpha(g) = |g|^\alpha \mathbf{1}_{\frac{m_{ij}^*}{2}|g|^2 \geq E_a}.$$

Then, for any  $T > 0$ ,

$$\begin{aligned} \mathbb{E}_{\lambda_T^{ij}}[\chi_\alpha] &= \left( \frac{m_{ij}^*}{2\pi k_B T} \right)^{3/2} \int_{\mathbb{R}^3} |g|^\alpha \mathbf{1}_{\frac{m_{ij}^*}{2}|g|^2 \geq E_a} e^{-\frac{m_{ij}^*|g|^2}{2k_B T}} dg \\ &= 4\pi \left( \frac{m_{ij}^*}{2\pi k_B T} \right)^{3/2} \int_{\mathbb{R}_+} z^\alpha \mathbf{1}_{\frac{m_{ij}^*}{2}z^2 \geq E_a} e^{-\frac{m_{ij}^*z^2}{2k_B T}} z^2 dz \\ &= \frac{2}{\sqrt{\pi}} \left( \frac{2k_B T}{m_{ij}^*} \right)^{\frac{\alpha}{2}} \int_{\frac{E_a}{k_B T}}^{\infty} x^{\frac{\alpha+3}{2}-1} e^{-x} dx. \end{aligned}$$

Denoting by  $\Gamma$  the upper incomplete Gamma function, defined as

$$\Gamma(\alpha, y) = \int_y^{\infty} x^{\alpha-1} e^{-x} dx,$$

we deduce that

$$\mathbb{E}_{\lambda_T^{ij}}[\chi_0] = \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \frac{E_a}{k_B T}\right), \quad \text{and} \quad \mathbb{E}_{\lambda_T^{ij}}[\chi_{-2}] = \frac{2}{\sqrt{\pi}} \left( \frac{m_{ij}^*}{2k_B T} \right) \Gamma\left(\frac{1}{2}, \frac{E_a}{k_B T}\right).$$

It comes that

$$\mathbf{K}_{ij}^{kl}(T) = \beta \mathbb{E}_{\lambda_T^{ij}} \left[ \chi_0 - \left( \frac{2E_a}{m_{ij}^*} \right) \chi_{-2} \right] = \frac{2\beta}{\sqrt{\pi}} \left[ \Gamma\left(\frac{3}{2}, \frac{E_a}{k_B T}\right) - \frac{E_a}{k_B T} \Gamma\left(\frac{1}{2}, \frac{E_a}{k_B T}\right) \right].$$

□



We plot  $\mathcal{K}_{ij}^{kl}$  given in (7.2) on Fig. 3, as well as the rate constant provided by Arrhenius' law  $\mathcal{K}_{Arr}(T) = \beta e^{-\frac{E_a}{k_B T}}$  as a matter of comparison. We observe that both provide similar trends. Since Arrhenius' law is empirical, Fig. 3 shows a good agreement of our theoretical result with respect to experimental ones.

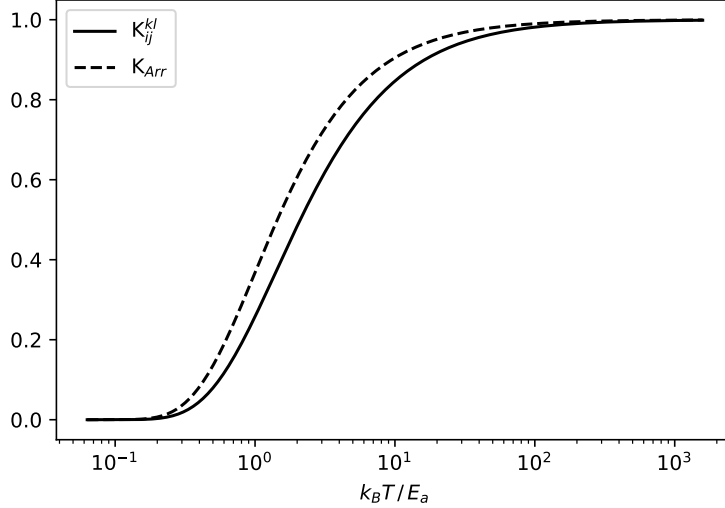


FIGURE 3. Plot of  $\mathcal{K}_{ij}^{kl}$  given in (7.2) and  $\mathcal{K}_{Arr}$  as functions of  $\frac{k_B T}{E_a}$ , with  $\beta = 1$ .

**Remark 1.** *The kernel (7.1) is energy-non-decreasing and non-constant. We verify on Fig. 3 that  $\mathcal{K}_{ij}^{kl}$  is indeed increasing with temperature, as stated in Proposition 14.*

## 8. REDUCED MODELS AND ENERGY OF REACTION

As explained in [15, Section 8] for a single polyatomic gas, to any state-based model it can be associated an energy-based one, corresponding typically to the Borgnakke-Larsen description with integration weight [14, 27, 28] when the initial description is not totally discrete [9, 35]. This kind of reduction may be extended also to inert or reactive gas mixtures. Let  $1 \leq i \leq N$ , we consider  $\mu_i^{\bar{\varepsilon}_i}$  the image measure on  $\mathbb{R}_+$  of  $\mu_i$  by  $\bar{\varepsilon}_i$ . Using the change of variables formula, one then easily concludes that the two following descriptions are equivalent in the kinetic framework:

- *State-based.* The molecule of the species  $i$  is described by its velocity  $v \in \mathbb{R}^3$  and internal state  $\zeta \in \mathcal{E}_i$ , where the space  $\mathcal{E}_i$  is endowed with the measure  $\mu_i$ . The associated energy of the molecule is  $\frac{1}{2}m_i|v|^2 + \varepsilon_i(\zeta)$ .
- *Energy-based.* The molecule of the species  $i$  is described by its velocity  $v \in \mathbb{R}^3$  and non-potential internal energy  $I \in \mathbb{R}_+$ , where the space  $\mathbb{R}_+$  is endowed with the measure  $\mu_i^{\bar{\varepsilon}_i}$ . The associated energy of the molecule is  $\frac{1}{2}m_i|v|^2 + I + \varepsilon_i^0$ . The quantity  $\varepsilon_i^0$  corresponds to the fundamental potential energy of configuration of the molecule.

Recall the law of conservation of energy (3.1) for a collision  $\{(i, j) \rightarrow (k, l)\}$

$$(8.1) \quad \frac{1}{2}m_i|v|^2 + \varepsilon_i(\zeta) + \frac{1}{2}m_j|v_*|^2 + \varepsilon_j(\zeta_*) = \frac{1}{2}m_k|v'|^2 + \varepsilon_k(\zeta') + \frac{1}{2}m_l|v'_*|^2 + \varepsilon_l(\zeta'_*).$$

Rewriting this equation with the reduced models gives

$$\frac{1}{2}m_i|v|^2 + I + \varepsilon_i^0 + \frac{1}{2}m_j|v_*|^2 + I_* + \varepsilon_j^0 = \frac{1}{2}m_k|v'|^2 + I' + \varepsilon_k^0 + \frac{1}{2}m_l|v'_*|^2 + I'_* + \varepsilon_l^0,$$

that is

$$(8.2) \quad \frac{1}{2}m_i|v|^2 + I + \frac{1}{2}m_j|v_*|^2 + I_* = \frac{1}{2}m_k|v'|^2 + I' + \frac{1}{2}m_l|v'_*|^2 + I'_* + (\Delta\varepsilon^0)_{ij}^{kl},$$

where  $(\Delta\varepsilon^0)_{ij}^{kl} = \varepsilon_k^0 + \varepsilon_l^0 - \varepsilon_i^0 - \varepsilon_j^0$  is thus interpreted as the energy consumed by the chemical reaction ( $(\Delta\varepsilon^0)_{ij}^{kl} = 0$  in the case of a mechanical collision). The formulation (8.2) coincides with the one considered in [28], and we highlight the fact that it is, from the reduction process, indeed equivalent to (8.1). Further details on the equivalence of these formulations for a single gas may be found in [15, Theorem 8.1].

However, the formulations (8.1) and (8.2) do differ on two aspects. First, (8.1) is completely microscopic, in the sense that it describes the system of the two colliding molecules as an isolated one, that is neither exchanging mass nor energy with its environment. On the other hand, in (8.2), some energy, namely  $(\Delta\varepsilon^0)_{ij}^{kl}$ , is exchanged with the environment. This means that the system of the two colliding molecules is not considered to be isolated, and this point of view is not completely microscopic. The second aspect is that (8.1) has the same form for both mechanical collisions and chemical reactions, which allows not to distinguish them for the main part of this work, while in the formulation (8.2), used in [28], one has to separate mechanical and reactive Boltzmann operators.

## 9. EXAMPLE OF A THREE SPECIES GAS MIXTURE UNDERGOING ONE CHEMICAL REACTION

This section has the purpose of explaining to the reader how a model may be built on a toy example in our general framework. We consider a gas composed of dihydrogen  $\text{H}_2$ , diiodine  $\text{I}_2$ , and hydrogen iodine  $\text{HI}$ , undergoing the reaction



**State-based model.** We choose, for this example, to describe those three molecules with a semi-classical model, with harmonic potential in the description of vibration. For the complete and detailed setting of this model, the authors refer the reader to [15, Subsection 7.3]. We report here, for completeness, some insights on its construction.

We assume the molecule to be a rigid rotor, that is, in the description of rotation we assume that no deformation is induced in the molecule. The rotation-related internal state we consider is thus the angular velocity of the molecule in a coordinate system attached to it. In general, this angular velocity lives in  $\mathbb{R}^3$ , however when the molecule is linear, being symmetric by rotation around its own axis, the contribution of the angular momentum's coordinate along this axis can be assumed to be 0. Since dihydrogen, diiodine and hydrogen iodine are diatomic (hence linear) molecules, we consider their angular velocities to live in  $\mathbb{R}^2$ , and there exists, for each  $A \in \{\text{H}_2, \text{I}_2, \text{HI}\}$ , a moment of inertia  $\mathcal{I}_A$  such that the kinetic energy of rotation associated to the molecule  $A$  with angular velocity  $z$  writes

$$\frac{1}{2}\mathcal{I}_A|z|^2.$$

Due again to the diatomic nature of the involved molecules, there is for each of them only one type of vibration, which we describe with the model of the quantum harmonic oscillator. Letting  $h$  be the Planck constant,  $c$  the speed of light and  $\nu_A$  the wavenumber associated to the molecule  $A \in \{\text{H}_2, \text{I}_2, \text{HI}\}$ , the energy associated to the mode of vibration  $l \in \mathbb{N}$  (the  $l^{\text{th}}$  energy level) writes

$$hc\nu_A \left( l + \frac{1}{2} \right).$$

We hence consider the internal state to be  $\zeta = (z, l)$ , so that each model writes, for  $A \in \{\text{H}_2, \text{I}_2, \text{HI}\}$ , as

$$(9.2) \quad (\mathcal{E}_A, \mathcal{A}_A, d\mu_A(\zeta)) = \left( \mathbb{R}^2 \times \mathbb{N}, \text{Bor}(\mathbb{R}^2) \otimes \mathcal{P}(\mathbb{N}), dz \times 1 \right),$$

$$\varepsilon_A(z, l) = \frac{1}{2} \mathcal{I}_A |z|^2 + hc \nu_A \left( l + \frac{1}{2} \right),$$

with  $dz \times 1$  denoting the tensor product of the Lebesgue measure on  $\mathbb{R}^2$  and the counting measure on  $\mathbb{N}$ .

**Corresponding energy-based model.** Applying the process of reduction explained above, that is computing the image measure  $\mu_A^{\varepsilon_A}$ , the energy-based model corresponding to (9.2) is the Borgnakke-Larsen model with weight  $\varphi_A$  and fundamental energy  $\frac{1}{2} hc \nu_A$ ,

$$(9.3) \quad (\mathbb{R}_+, \text{Bor}(\mathbb{R}_+), \varphi_A(I) dI), \quad I \mapsto I + \frac{1}{2} hc \nu_A,$$

with, for  $I \in \mathbb{R}_+$ ,

$$(9.4) \quad \varphi_A(I) = \frac{2\pi}{\mathcal{I}_A} \left\lceil \frac{I}{hc \nu_A} \right\rceil,$$

where  $\lceil \cdot \rceil$  is the ceiling function (upper integer part).

**Quantities of interest.** We immediately deduce from the model (9.2) that

$$\varepsilon_A^0 = \frac{1}{2} hc \nu_A,$$

implying that the energy consumed by the reaction  $\text{H}_2 + \text{I}_2 \rightarrow 2 \text{HI}$  is

$$\Delta\varepsilon^0 = 2\varepsilon_{\text{HI}}^0 - \varepsilon_{\text{H}_2}^0 - \varepsilon_{\text{I}_2}^0 = hc \left( \nu_{\text{HI}} - \frac{\nu_{\text{H}_2} + \nu_{\text{I}_2}}{2} \right).$$

The partition function of the species  $A \in \{\text{H}_2, \text{I}_2, \text{HI}\}$  writes, for any  $\beta > 0$ , as

$$(9.5) \quad Z_A(\beta) = \left( \int_{\mathbb{R}^2} e^{-\beta \frac{\mathcal{I}_A |z|^2}{2}} dz \right) \left( \sum_{l=0}^{\infty} e^{-\beta l hc \nu_A} \right) = \frac{2\pi}{\beta \mathcal{I}_A} \times \frac{1}{1 - e^{-\beta hc \nu_A}} = \frac{2\pi}{\mathcal{I}_A} \int_{\mathbb{R}_+} e^{-\beta I} \left\lceil \frac{I}{hc \nu_A} \right\rceil dI.$$

Also, one easily proves that, letting  $T_A^0 = hc \nu_A / k_B$ , the number of internal degrees of freedom writes, for any  $T > 0$ , as

$$\delta_A(T) = 2 + 2 \frac{T_A^0 / T}{\exp(T_A^0 / T) - 1}.$$

At mechanical equilibrium there exists  $n_{\text{H}_2}, n_{\text{I}_2}, n_{\text{HI}}, \underline{v}, T$  such that the state-based equilibrium distribution writes, for  $(v, z, l) \in \mathbb{R}^3 \times \mathbb{R}^2 \times \mathbb{N}$ , as

$$(9.6) \quad \mathcal{M}_A^{\text{state}}[n_A, \underline{v}, T](v, z, l) = n_A \left( \frac{m_A}{2\pi k_B T} \right)^{3/2} Z_A^{-1} \left( \frac{1}{k_B T} \right) \exp \left( -\frac{m_A |v - \underline{v}|^2}{2k_B T} - \frac{\frac{1}{2} \mathcal{I}_A |z|^2 + l hc \nu_A}{k_B T} \right),$$

for which the integrations are performed in the space  $(\mathbb{R}^3 \times \mathbb{R}^2 \times \mathbb{N}, dv dz \times 1)$ . On the other hand, the energy-based equilibrium distribution writes, for  $(v, I) \in \mathbb{R}^3 \times \mathbb{R}_+$ , as

$$(9.7) \quad \mathcal{M}_A^{\text{energy}}[n_A, \underline{v}, T](v, I) = n_A \left( \frac{m_A}{2\pi k_B T} \right)^{3/2} Z_A^{-1} \left( \frac{1}{k_B T} \right) \exp \left( -\frac{m_A |v - \underline{v}|^2}{2k_B T} - \frac{I}{k_B T} \right),$$

for which the integrations are performed in the space  $(\mathbb{R}^3 \times \mathbb{R}_+, d\nu \varphi_A(I) dI)$ . At chemical equilibrium, we obtain in this example the mass-action law

$$\begin{aligned}
 (9.8) \quad \frac{n_{\text{HI}}^2}{n_{\text{H}_2} n_{\text{I}_2}} &= \underbrace{\frac{m_{\text{HI}}^3}{m_{\text{H}_2}^{3/2} m_{\text{I}_2}^{3/2}}}_{\text{translation}} \times \underbrace{\frac{\mathcal{I}_{\text{H}_2} \mathcal{I}_{\text{I}_2}}{\mathcal{I}_{\text{HI}}^2}}_{\text{rotation}} \times \underbrace{\frac{\left(1 - e^{-\frac{hc\nu_{\text{H}_2}}{k_B T}}\right) \left(1 - e^{-\frac{hc\nu_{\text{I}_2}}{k_B T}}\right)}{\left(1 - e^{-\frac{hc\nu_{\text{HI}}}{k_B T}}\right)^2}}_{\text{vibration}} \times \underbrace{e^{-\frac{hc\left(\nu_{\text{HI}} - \frac{\nu_{\text{H}_2} + \nu_{\text{I}_2}}{2}\right)}{k_B T}}}_{\text{chemical}} \\
 &= \frac{m_{\text{HI}}^3}{m_{\text{H}_2}^{3/2} m_{\text{I}_2}^{3/2}} \times \frac{\mathcal{I}_{\text{H}_2} \mathcal{I}_{\text{I}_2}}{\mathcal{I}_{\text{HI}}^2} \times \frac{\sinh\left(\frac{hc\nu_{\text{H}_2}}{2k_B T}\right) \sinh\left(\frac{hc\nu_{\text{I}_2}}{2k_B T}\right)}{\sinh\left(\frac{hc\nu_{\text{HI}}}{2k_B T}\right)^2}.
 \end{aligned}$$

We notably remark that

$$\begin{aligned}
 (9.9) \quad \frac{n_{\text{HI}}^2}{n_{\text{H}_2} n_{\text{I}_2}} &\underset{T \rightarrow 0^+}{\sim} \frac{m_{\text{HI}}^3}{m_{\text{H}_2}^{3/2} m_{\text{I}_2}^{3/2}} \times \frac{\mathcal{I}_{\text{H}_2} \mathcal{I}_{\text{I}_2}}{\mathcal{I}_{\text{HI}}^2} \times e^{-\frac{hc\left(\nu_{\text{HI}} - \frac{\nu_{\text{H}_2} + \nu_{\text{I}_2}}{2}\right)}{k_B T}}, \\
 \frac{n_{\text{HI}}^2}{n_{\text{H}_2} n_{\text{I}_2}} &\underset{T \rightarrow \infty}{\rightarrow} \frac{m_{\text{HI}}^3}{m_{\text{H}_2}^{3/2} m_{\text{I}_2}^{3/2}} \times \frac{\mathcal{I}_{\text{H}_2} \mathcal{I}_{\text{I}_2}}{\mathcal{I}_{\text{HI}}^2} \times \frac{\nu_{\text{H}_2} \nu_{\text{I}_2}}{\nu_{\text{HI}}^2}.
 \end{aligned}$$

As expected from the fact that vibration activates with increasing temperature, we observe that, at low temperatures, the effect of vibration vanishes, whereas it does appear in the high temperature limit.

## 10. CONCLUSION

In this paper we extended the internal states general framework for polyatomic gases [15] to a mixture of monatomic or polyatomic gases, undergoing an arbitrary number of bimolecular chemical reactions. The proposed setting is general and it allows to describe the internal structure of each species of the mixture with its own adapted model, that may be monatomic, semi-classical, or any other model for the microscopic structure of a given molecule. In this way one is able to manage simultaneously monatomic gases, polyatomic constituents with a set of discrete energy levels or with continuous internal energy, polyatomic gases with two different internal variables to keep separate vibrational and rotational energies, and so on. The approach is completely microscopic, even when dealing with chemical reactions, and has been shown to be in complete agreement with previously known formulations, see Section 8. An important feature of our model is the inclusion in the general formulation of the notion of activation energy, which is of importance when studying the kinetics of chemical reactions, and for which an example is provided in Section 7.

We have defined the collision rules, Equations (3.1) and (3.8), studied the related collision invariants (Proposition 4 and Corollary 5), proved the H-Theorem (Theorem 1 and Corollary 6) and obtained the Maxwellian form related to the (mechanical) equilibrium, Equation (5.1), as well as mass action laws of chemical reactions, Theorem 2. As a hydrodynamic limit, we have formally recovered the Euler system of equations in presence of moderately slow chemical reactions, namely in an elastic dominated regime, Equations (6.4)–(6.6). We have derived a general formula for the rate constant of a given reaction, depending only on the global temperature of the gas and on the cross-section, see Equation (5.22), and proved it to be increasing with temperature whenever the latter increases with energy (Proposition 14).

The investigation of further mathematical properties of our system of Boltzmann equations could be an interesting and challenging future research line. At first, the compactness properties of linearized Boltzmann operators have gained much interest in recent literature, both for polyatomic gases [16] and for gas mixtures [18, 7], and it could be interesting to look for general conditions

(on the space of internal states and on its measure) guaranteeing such compactness results. An additional topic worth to be investigated, in view of applications to physical problems, is the consistent derivation from our kinetic system of hydrodynamic equations beyond the Euler level. Specifically, a suitable Chapman–Enskog asymptotic procedure should allow to establish the relationships between Boltzmann and Navier–Stokes equations, with transport coefficients depending also on suitable averages of the Boltzmann microscopic cross sections. Such coefficients could be made explicit in some specific situations, including the case of Maxwell molecules. A survey on the mathematical techniques for fluid–dynamic limits of kinetic models, with both formal and rigorous proofs, may be found in [30], and the formal Chapman–Enskog asymptotics for an inert mixture of monatomic and polyatomic gases, the latter ones having continuous internal energy, has been investigated in [6]. Analogous achievements for our general internal states Boltzmann framework, even in presence of chemical reactions, will be matter of future research.

#### APPENDIX A. AUXILIARY LEMMA

We prove here a technical lemma, needed in Proposition 14.

**Lemma 18.** *Let  $(\mathcal{X}, \mathcal{T}, \eta)$  be a measured space such that  $\eta(X) > 0$ . Let  $\psi, \varphi : \mathcal{X} \rightarrow \mathbb{R}_+$  measurable, in the sense of  $\mathcal{T}$  on  $\mathcal{X}$  and the Borelians on  $\mathbb{R}_+$ , such that  $\psi$  is non-constant  $\eta$ -a.e. and  $\varphi$  is  $\eta$ -non-constant, in the sense that*

$$(A.1) \quad \begin{aligned} \eta \otimes \eta (\{(x, x') \in \mathcal{X} \times \mathcal{X} \text{ s.t. } \psi(x) = \psi(x')\}) &= 0, \\ \eta \otimes \eta (\{(x, x') \in \mathcal{X} \times \mathcal{X} \text{ s.t. } \varphi(x) \neq \varphi(x')\}) &> 0. \end{aligned}$$

We assume that for any  $T > 0$ , defining  $\psi_T(x) = \frac{\psi(x)}{T}$ ,

$$(A.2) \quad \int_{\mathcal{X}} (1 + \varphi(x)) e^{-\psi_T(x)} d\eta(x) < \infty,$$

and for  $\eta$ -a.e.  $x, x' \in \mathcal{X}$ ,

$$(A.3) \quad \psi(x) \leq \psi(x') \implies \varphi(x) \leq \varphi(x').$$

Then the function  $K : \mathbb{R}_+^* \rightarrow \mathbb{R}_+$ , defined by

$$K(T) = \frac{\int_{\mathcal{X}} \varphi(x) e^{-\psi_T(x)} d\eta(x)}{\int_{\mathcal{X}} e^{-\psi_T(x)} d\eta(x)}, \quad T > 0,$$

is increasing on  $\mathbb{R}_+$ .

*Proof.* First, for  $\eta$ -a.e.  $x \in \mathcal{X}$ , we have

$$\frac{d}{dT} (e^{-\psi_T(x)}) = \frac{\psi(x)}{T^2} e^{-\psi_T(x)}.$$

From the integrability assumption (A.2), the bound  $ye^{-y} \leq 2e^{-y/2}$  for any  $y \geq 0$  and the Cauchy–Schwarz inequality,  $K$  is  $\mathcal{C}^1$  on  $\mathbb{R}_+^*$ , with

$$K'(T) = -\frac{1}{T^2} \frac{\left( \int_{\mathcal{X}} \psi(x) e^{-\psi_T(x)} d\eta(x) \right) \left( \int_{\mathcal{X}} \varphi(x) e^{-\psi_T(x)} d\eta(x) \right)}{\left( \int_{\mathcal{X}} e^{-\psi_T(x)} d\eta(x) \right)^2} + \frac{1}{T^2} \frac{\int_{\mathcal{X}} \varphi(x) \psi(x) e^{-\psi_T(x)} d\eta(x)}{\int_{\mathcal{X}} e^{-\psi_T(x)} d\eta(x)}.$$

We deduce that, for any  $T > 0$ ,

$$K'(T) > 0 \iff$$

$$\begin{aligned} \int_{\mathcal{X}} \int_{\mathcal{X}} \varphi(x) \psi(x) e^{-\psi_T(x)} e^{-\psi_T(x')} d\eta(x) d\eta(x') &> \int_{\mathcal{X}} \int_{\mathcal{X}} \psi(x) e^{-\psi_T(x)} \varphi(x') e^{-\psi_T(x')} d\eta(x) d\eta(x') \\ \iff \int_{\mathcal{X}} \int_{\mathcal{X}} (\varphi(x) - \varphi(x')) \psi(x) e^{-(\psi_T(x)+\psi_T(x'))} d\eta(x) d\eta(x') &> 0. \end{aligned}$$

We set

$$\mathcal{I} = \int_{\mathcal{X}} \int_{\mathcal{X}} (\varphi(x) - \varphi(x')) \psi(x) e^{-(\psi_T(x)+\psi_T(x'))} d\eta(x) d\eta(x').$$

Simply exchanging the indices, we have

$$\mathcal{I} = - \int_{\mathcal{X}} \int_{\mathcal{X}} (\varphi(x) - \varphi(x')) \psi(x') e^{-(\psi_T(x)+\psi_T(x'))} d\eta(x) d\eta(x'),$$

so that

$$\mathcal{I} = \frac{1}{2} \int_{\mathcal{X}} \int_{\mathcal{X}} (\varphi(x) - \varphi(x')) (\psi(x) - \psi(x')) e^{-(\psi_T(x)+\psi_T(x'))} d\eta(x) d\eta(x').$$

Hence, for any  $T > 0$ ,

$$K'(T) > 0 \iff \iint_{\mathcal{X}^2} (\varphi(x) - \varphi(x')) (\psi(x) - \psi(x')) e^{-(\psi_T(x)+\psi_T(x'))} d(\eta \otimes \eta)(x, x') > 0.$$

Assumptions (A.1) and (A.3) imply that the right-hand side integral is indeed positive for any  $T > 0$ , ending the proof.  $\square$

## APPENDIX B. PHYSICAL AND CHEMICAL QUANTITIES REMINDER

The purpose of this appendix is to sum up all the useful quantities defined in this paper, which have been collected in the following Tables 1, 2, 3.

|   |  |
|---|--|
| Fundamental energy of the species $i$   | $\varepsilon_i^0 = \inf \text{ess}_{\mu_i} \{\varepsilon_i\}$  |
| Grounded internal energy function of the species $i$                                      | $\bar{\varepsilon}_i = \varepsilon_i - \varepsilon_i^0 : \mathcal{E}_i \rightarrow \mathbb{R}_+$   |
| Energy law of the species $i$   | $\mu_i^{\bar{\varepsilon}_i} = \bar{\varepsilon}_i \# \mu_i$   |
| Partition function of the species $i$   | $Z_i(\beta) = \int_{\mathcal{E}_i} e^{-\beta \bar{\varepsilon}_i(\zeta)} d\mu_i(\zeta) = \int_{\mathbb{R}_+} e^{-\beta I} d\mu_i^{\bar{\varepsilon}_i}(I)$   |
| Gibbs measure on the space of internal states of the species $i$ at temperature $T > 0$   | $d\nu_T^i(\zeta) = Z \left( \frac{1}{k_B T} \right)^{-1} \exp \left( -\frac{\bar{\varepsilon}_i(\zeta)}{k_B T} \right) d\mu_i(\zeta)$  |
| Gibbs measure on the space of internal energies of the species $i$ at temperature $T > 0$ | $d\tilde{\nu}_T^i(I) = Z \left( \frac{1}{k_B T} \right)^{-1} \exp \left( -\frac{I}{k_B T} \right) d\mu_i^{\bar{\varepsilon}_i}(I)$   |
| Number of internal degrees of freedom of the species $i$ at temperature $T > 0$           | $\delta_i(T) = -\frac{2}{k_B T} (\log(Z_i))' \left( \frac{1}{k_B T} \right) = 2 \mathbb{E}_{\nu_T^i} \left[ \frac{\bar{\varepsilon}_i}{k_B T} \right]$   |
| Heat capacity at constant volume of the species $i$ at temperature $T > 0$                | $c_V^i(T) = \frac{3 + D_i(T)}{2},$<br>$D_i(T) = \frac{d(T\delta_i(T))}{dT} = \frac{2}{(k_B T)^2} (\log(Z_i))'' \left( \frac{1}{k_B T} \right) = 2 \text{Var}_{\nu_T^i} \left[ \frac{\bar{\varepsilon}_i}{k_B T} \right]$ |

TABLE 1. Quantities related to internal energy modelling of a single species

|  |   |
|--|---|
| Reduced and total mass of species $i$ and $j$                            | $m_{ij}^* = \frac{m_i m_j}{m_i + m_j}, \quad M_{ij} = m_i + m_j$  |
| Energy consumed by the chemical reaction $\{(i, j) \rightarrow (k, l)\}$ | $(\Delta \varepsilon^0)_{ij}^{kl} = \varepsilon_k^0 + \varepsilon_l^0 - \varepsilon_i^0 - \varepsilon_j^0$  |
| Activation energy of $\{(i, j) \rightarrow (k, l)\}$                     | $E_a = \kappa_{ij}^{kl} - \varepsilon_i^0 - \varepsilon_j^0$  |
| Averaged collision kernel  | $\bar{B}_{ij}^{kl}(g, \zeta, \zeta_*) = \iint_{\mathcal{E}_k \times \mathcal{E}_l} \int_{\mathbb{S}^2} \tilde{B}_{ij}^{kl}(g, \zeta, \zeta_*, \zeta', \zeta'_*, \omega) d\omega d\mu_k(\zeta') d\mu_l(\zeta'_*),$<br>$\tilde{B}_{ij}^{kl}(v - v_*, \zeta, \zeta_*, \zeta', \zeta'_*, \omega) = B_{ij}^{kl}(v, v_*, \zeta, \zeta_*, \zeta', \zeta'_*, \omega)$ |

TABLE 2. Fundamental quantities involved in interactions between different species

|   |   |
|---|---|
| Relative kinetic Gibbs probability measure on $\mathbb{R}^3$ , of the species $i$ and $j$ at temperature $T > 0$  | $d\lambda_T^{ij}(g) = \left( \frac{m_{ij}^*}{2\pi k_B T} \right)^{3/2} \exp\left( -\frac{m_{ij}^*  g ^2}{2k_B T} \right) dg$  |
| Rate constant of the chemical reaction $\{(i, j) \rightarrow (k, l)\}$ at temperature $T > 0$   | $\mathcal{K}_{ij}^{kl}(T) = \mathbb{E}_{\lambda_T^{ij} \otimes \nu_T^i \otimes \nu_T^j} [\bar{B}_{ij}^{kl}]$  |
| Rate of the chemical reaction $\{(i, j) \rightarrow (k, l)\}$ at temperature $T > 0$ and with respective densities $n_i, n_j, n_k$ and $n_l$                  | $r_{ij}^{kl} = \mathcal{K}_{kl}^{ij}(T) n_k n_l - \mathcal{K}_{ij}^{kl}(T) n_i n_j$   |
| Reaction rate of the species $i$  | $r_i = \sum_{\substack{j,k,l \\ \{(i,j) \rightarrow (k,l)\} \in \Omega_{chem}}} r_{ij}^{kl}$  |
| Equilibrium constant of the chemical reaction $\{(i, j) \rightarrow (k, l)\}$ at temperature $T > 0$ , with $\sigma_k = \sigma_l = -\sigma_i = -\sigma_j = 1$ | $\mathcal{K}_{ij}^{kl}(T) = \prod_{p \in \{i,j,k,l\}} \left\{ (2\pi m_p k_B T)^{3\sigma_p/2} Z_p \left( \frac{1}{k_B T} \right)^{\sigma_p} \right\} \exp\left( -\frac{(\Delta \varepsilon^0)_{ij}^{kl}}{k_B T} \right)$ |

TABLE 3. Quantities related to mechanical or global collision equilibrium



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M.B., M.G.: UNIVERSITÀ DEGLI STUDI DI PARMA, 43121 PARMA, ITALIA

*Email address:* `marzia.bisi@unipr.it`

*Email address:* `maria.groppi@unipr.it`

T.B.: SORBONNE UNIVERSITÉ, CNRS, UNIVERSITÉ PARIS CITÉ, LABORATOIRE JACQUES-LOUIS LIONS (LJLL), F-75005 PARIS, FRANCE

*Email address:* `thomas.borsoni@sorbonne-universite.fr`