

Kinetic approach to chemical reactions and inelastic transitions in a rarefied gas*

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A kinetic approach is presented for the analysis of a gas mixture with two kinds of nonconservative interactions. In a bimolecular chemical reaction, mass transfer and energy of chemical link arise, and in inelastic mechanical encounters, molecules get excited or de-excited due to their quantized structure. Molecules undergo transitions between energy levels also by absorption and emission of photons of the self-consistent radiation field. From the kinetic Boltzmann-type equations, the problem of equilibria and of their stability is addressed. A detailed balance principle is proved and a Lyapunov functional is constructed; mass action law and Planck's law of radiation are recovered.

1. Introduction

Kinetic approaches to the study of a gas mixture which can give rise to chemical reactions have been proposed in the literature starting from the sixties [12,14,16,20,21]. They are mainly concerned with derivation and calculation of macroscopic quantities for practical applications, but, also because of the complexity of the problem, results are still incomplete, especially from a theoretical point of view. On the other hand, mathematical questions related to kinetic equations for reacting gas mixtures have been investigated in [8]. In a recent paper [18] a detailed analysis of the kinetic equations, in the framework of phenomenological extended kinetic theory [7], has been presented for a mixture of four gases undergoing a reversible bimolecular chemical reaction plus elastic mechanical binary collisions. In particular, upon using and extending methods which are typical for the Boltzmann equation in kinetic theory [4], equilibria have been determined, the mass action law has been recovered, and a suitable generalization of the Boltzmann H-functional has been shown to be a Lyapunov functional for stability analysis.

The present work is aimed at generalizing the previous results to the case when the reacting species exhibit an internal structure, in the sense that a set of $N > 1$ discrete

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quantized energy levels are allowed to each of them. Indeed, this generalization is very important since a molecule is a mechanical system with translational, rotational, and vibrational degrees of freedom, but in several practical applications it is often sufficient to model it as a point mass having a sequence of internal states, which can be identified by a label assuming integral values, associated, in the simplest cases, to an internal energy characterizing the state. Therefore, one may think of a polyatomic gas as a mixture of monoatomic gases, and attach to each molecule, besides a continuous variable representing its center-of-mass velocity, a discrete variable representing the internal state.

In such a semiclassical scheme, a mechanical encounter may result in general in inelastic scattering (and in elastic scattering as a particular case). In this additional non-conservative process, there is no mass exchange, but kinetic energy is not conserved in a collision, since excitation or de-excitation occurs for the gas molecules. For the sake of generality, any energy level will be allowed to all participating species even when their interaction is a chemical reaction and, simultaneously, any final quantum state is permitted to each of the outgoing particles. Of course, the relative importance of the allowed processes between themselves is taken care of by the physical parameters to be introduced later. In any case, the gas will be considered as constituted formally by $4N$ different components, to be labelled according to a single index. Components are ordered in such a way that the s th chemical species, $s = 1, 2, 3, 4$, may be regarded as the equivalence class of the indices i which are congruent to s modulo 4 ($i \equiv s \pmod{4}$, or simply $i \equiv s$ when no confusion arises).

Moreover, transitions between different energy states of a single molecule may be due also to absorption or emission of photons with proper frequency, and therefore one is led to the field of radiation gas dynamics [2], where the interactions of gas particles with the photons of the self-consistent radiation are taken into account. Both inelastic scattering and radiation gas dynamics have experienced in the past kinetic approaches [3,5,6,13]. More recently, again in the frame of extended kinetic theory, a generalization of the detailed balance principle and of the H-theorem has been proved, and, accounting for photon stimulated emission, Planck's law of radiation has been consistently recovered [17,19].

The present paper will follow the line of the above kinetic approaches in the presence of both chemical reaction and inelastic transitions, under the usual simplifying assumptions of negligible Doppler broadening and photon momentum. One of the consequences of those assumptions is that only a discrete set of $2N(N-1)$ frequencies is allowed to photons, corresponding, via the Planck's constant h , to the $N(N-1)/2$ possible energy jumps for each species. In our approximation the particle phase space will thus be six-dimensional for gas molecules, and five-dimensional for photons (they travel at the speed of light c). We will be dealing then with a set of $2N(N+1)$ unknown distribution functions.

After writing down in section 2 the extended kinetic equations of the Boltzmann type for the distribution functions in terms of cross sections (encounters between gas molecules) and Einstein coefficients (gas-photon interactions), we investigate in sec-

tion 3 the main properties of the collision term, with particular attention to the derivation of collision invariants and to the construction of a Boltzmann-like inequality. This will be the starting point in order to achieve in section 4 a detailed balance principle, determining collision equilibria as a 7-parameter family of Gaussian distributions, and implying as a byproduct the Boltzmann factors of statistical mechanics, the mass action law for the chemical reaction, and Planck's law of radiation for each of the monochromatic photon fields. We study finally in section 5 stability under collisions of such equilibria by proving an analogous of the classical H-theorem by means of a suitable Lyapunov functional. It is shown in particular that, in space homogeneous conditions, there exists a unique equilibrium associated to any initial datum. Other points, related to macroscopic conservation laws, moment equations, and hydrodynamic limits will also be briefly discussed, even though their detailed analysis is left as future work.

2. Extended kinetic equations

Let A_i , $1 \leq i \leq 4N$, denote the general component of the gas mixture, and E_i the energy level corresponding to its state. Energies are monotonically increasing with their index in the frame of each species, namely, $E_i > E_j$ for $i \equiv j$, $i > j$, and may be normalized in such a way that $E_i \geq 0$, with equal sign only for one (or more) of the fundamental levels 1, 2, 3, 4. The chemical species s_i ($1 \leq s_i \leq 4$) of the i th component is given by $s_i = i - 4[i/4]$, where $[x]$ stands here for the largest integer strictly less than the real number x ($[x] = x - 1$ if x is integer). Given s , $1 \leq s \leq 4$, all molecules A_i with $i \equiv s$ share thus the same mass m_s , or, in other words, $m_i = m_j$ when $i \equiv j$. Since it is simply matter of ordering species, and the equal sign is of no practical relevance, we may take

$$\Delta E = E_3 + E_4 - E_1 - E_2 > 0, \quad (2.1)$$

where (1, 2) and (3, 4) are the two reacting pairs (either reactants or products), with then $m_1 + m_2 = m_3 + m_4$. The integer label of the energy level corresponding to A_i within its species is provided by $l_i = [(i + 4)/4]$, $1 \leq l_i \leq N$. Further symbols to be used later are ΔE_{ij}^{hk} for $E_h + E_k - (E_i + E_j)$, μ_{ij} for the reduced mass $m_i m_j / (m_i + m_j)$, and δ_{ij}^{hk} for $2\Delta E_{ij}^{hk} / \mu_{ij}$, which has physical dimensions of a quadratic speed, but is not necessarily positive. Moreover, ν_{ij} , with $i \equiv j$, $i < j$, will represent the photon frequency $(E_j - E_i)/h$ corresponding to a transition between the states A_i and A_j of a given species. No specific structure will be assumed in this paper for the sequence of energy levels in a species; the simple trend corresponding to a hydrogen atom would be

$$\frac{E_j - E_{s_j}}{E_i - E_{s_i}} = \frac{l_i^2(l_j^2 - 1)}{l_j^2(l_i^2 - 1)}, \quad j \equiv i, \quad i > s_i. \quad (2.2)$$

However, the discrete quantum states are introduced just to account for the fact that molecules do have rotational and vibrational degrees of freedom, and their specific

energy levels should then be used for practical purposes. No specific restrictions will be applied to the fundamental levels E_s , $s = 1, 2, 3, 4$, either. In order to avoid technical, but not substantial, complications due to degeneracy, it will only be assumed that all $2N(N - 1)$ allowed photon frequencies are distinct.

The general binary interaction between molecules is written as



and is described, under the same hypotheses underlying the Boltzmann equation [4], in terms of a cross section σ_{ij}^{hk} , relevant to the process in which particle i gets transformed into particle h , and particle j into particle k . If \mathbf{v} and \mathbf{w} denote the velocities of the impinging molecules A_i and A_j , and $g\mathbf{n}$, with $|\mathbf{n}| = 1$, the relative velocity $\mathbf{v} - \mathbf{w}$, σ_{ij}^{hk} turns out to be azimuthally symmetric, and to depend only on the relative speed $g = |\mathbf{v} - \mathbf{w}|$ and on $\mathbf{n} \cdot \mathbf{n}'$. A prime is used throughout to mean quantities relevant to the outgoing pair A_h and A_k , which have attained velocities \mathbf{v}' and \mathbf{w}' , respectively. Whenever it makes sense, cross sections have to satisfy the obvious indistinguishableness conditions:

$$\sigma_{ij}^{hk}(g, \mathbf{n} \cdot \mathbf{n}') = \sigma_{ji}^{hk}(g, -\mathbf{n} \cdot \mathbf{n}') = \sigma_{ij}^{kh}(g, -\mathbf{n} \cdot \mathbf{n}'). \quad (2.4)$$

In all encounters (2.3) mass, momentum, and total energy (kinetic plus internal) are conserved, and the cross section σ_{ij}^{ij} of the inverse collision is related to the cross section of the direct collision σ_{ij}^{hk} by the microreversibility condition [9]. Not all indices are allowed in the scheme (2.3), but only those corresponding to the following two classes of events:

- (a) the considered chemical reaction, with $i \neq j \neq h \neq k$, $i + j \equiv 3$, $h + k \equiv 3$;
- (b) mechanical collisions, with $i \equiv h$ and $j \equiv k$.

They differ in that mass transfer inside each pair takes place in the first case, but not in the second. Common features are conservation of center-of-mass velocity through the encounter, and variation ΔE_{ij}^{hk} of the global internal energy state for the pair. Such a variation might be positive, negative or, as a special case, zero, and results correspondingly in an opposite variation of kinetic energy. As discussed in [17,18], to which we refer the reader for technical details, this implies, contrary to classical kinetic theory, a variation of the relative speed through the collision, and a threshold effect on the endothermic interaction, that is prevented in case of insufficient impinging kinetic energy of the relative motion. Also the Jacobian of the transformation between quantities before and after collision is not unity any more. More precisely, with reference to the process $A_i + A_j \rightarrow A_h + A_k$, one ends up with

$$g' = g_{ij}^{hk} \stackrel{\text{def}}{=} \left[\frac{\mu_{ij}}{\mu_{hk}} (g^2 - \delta_{ij}^{hk}) \right]^{1/2}, \quad (2.5)$$

with a threshold $g^2 > \delta_{ij}^{hk}$ for $\delta_{ij}^{hk} > 0$. If $\delta_{ij}^{hk} < 0$, the threshold occurs for the inverse process, in which g' is given again by (2.5) upon interchanging i with h and j with k . In addition,

$$d\mathbf{v}' d\mathbf{w}' d\mathbf{n} = U(g^2 - \delta_{ij}^{hk}) \frac{\mu_{ij}}{\mu_{hk}} \frac{g_{ij}^{hk}}{g} d\mathbf{v} d\mathbf{w} d\mathbf{n}', \quad (2.6)$$

where the unit step function U accounts for the possible threshold. Setting $r_{ij} = m_i/(m_i + m_j)$, the velocities after collision turn out to be given by

$$\begin{aligned} \mathbf{v}' &= \mathbf{v}_{ij}^{hk} \stackrel{\text{def}}{=} r_{ij} \mathbf{v} + r_{ji} \mathbf{w} + r_{kh} g_{ij}^{hk} \mathbf{n}', \\ \mathbf{w}' &= \mathbf{w}_{ij}^{hk} \stackrel{\text{def}}{=} r_{ij} \mathbf{v} + r_{ji} \mathbf{w} - r_{kh} g_{ij}^{hk} \mathbf{n}', \end{aligned} \quad (2.7)$$

and are determined once \mathbf{n}' is given. Coming back to the bi-directional interaction (2.3), one can evaluate the total collision term (gain minus loss) for component i as

$$\begin{aligned} J_i^{ijhk} [f_i, f_j, f_h, f_k](\mathbf{v}) &= \iint U(g^2 - \delta_{ij}^{hk}) \left[\frac{\mu_{ij}}{\mu_{hk}} \frac{(g_{ij}^{hk})^2}{g} \sigma_{hk}^{ij}(g_{ij}^{hk}, \mathbf{n} \cdot \mathbf{n}') \right. \\ &\quad \left. \times f_h(\mathbf{v}_{ij}^{hk}) f_k(\mathbf{w}_{ij}^{hk}) - g \sigma_{ij}^{hk}(g, \mathbf{n} \cdot \mathbf{n}') f_i(\mathbf{v}) f_j(\mathbf{w}) \right] d\mathbf{w} d\mathbf{n}', \end{aligned} \quad (2.8)$$

where f_l is the general one-particle distribution function, and integration ranges over $\mathbb{R}^3 \times \mathbf{S}^2$. Collision terms for the other components j, h, k are obtained from (2.8) by proper permutation of indices. The present results include, as particular cases, those of [17,18] and introduce also a convenient rationale, which makes possible dealing with quite awkward expressions. The microreversibility condition

$$\mu_{ij}^2 g^2 \sigma_{ij}^{hk}(g, \mathbf{n} \cdot \mathbf{n}') = \mu_{hk}^2 (g_{ij}^{hk})^2 U(g^2 - \delta_{ij}^{hk}) \sigma_{hk}^{ij}(g_{ij}^{hk}, \mathbf{n} \cdot \mathbf{n}') \quad (2.9)$$

eliminates one of the cross sections, and yields, for instance,

$$\begin{aligned} J_i^{ijhk} &= \iint U(g^2 - \delta_{ij}^{hk}) g \sigma_{ij}^{hk}(g, \mathbf{n} \cdot \mathbf{n}') \\ &\quad \times \left[\left(\frac{\mu_{ij}}{\mu_{hk}} \right)^3 f_h(\mathbf{v}_{ij}^{hk}) f_k(\mathbf{w}_{ij}^{hk}) - f_i(\mathbf{v}) f_j(\mathbf{w}) \right] d\mathbf{w} d\mathbf{n}'. \end{aligned} \quad (2.10)$$

All equations (2.5) through (2.10) are in order for both events (a) and (b). In the latter case reduced mass μ_{ij} and μ_{hk} coincide, which yields a more symmetric form, closer to the classical Boltzmann equation, for (2.10). Still in case (b) one may recognize collisions between different species when $i \neq j$, and, for $i \equiv j$, standard elastic scattering when $h = i \wedge k = j$ or $h = j \wedge k = i$, or inelastic scattering otherwise. Occurrence of $\Delta E_{ij}^{hk} = 0$ for $i \neq j$ is unlikely in practice, but correctly accounted for in our model. Dependence on position \mathbf{x} and time t in distribution functions and collision integrals has been omitted in order to simplify notation.

We can now proceed to determining the total collision term for a general component due to particle-particle interactions in terms of the $4N$ -dimensional vector \vec{f} of

the single distribution functions. For a given A_i we may refer to (2.3) and let other indices vary in all allowed ways in such a manner that all contributions are included and repetitions are avoided. With the present definition of the cross section σ_{ij}^{hk} , a careful analysis shows that chemical contributions come from the $2N^3$ triplets of the set

$$D_i^C = \{(j, h, k), 1 \leq j, h, k \leq 4N, i \neq j \neq h \neq k, i + j \equiv 3, h + k \equiv 3\}, \quad (2.11)$$

whereas mechanical contributions are due to the $4N^3$ triplets of the set

$$D_i^M = \{(j, h, k), 1 \leq j, h, k \leq 4N, i \equiv h, j \equiv k\}. \quad (2.12)$$

In our scheme, in fact, chemical reactions described by the indices (i, j, h, k) and (i, j, k, h) , as well as mechanical encounters (i, j, i, k) and (i, k, i, j) have to be both counted. The total collision term for the i th component contributed by interactions between molecules is then

$$\bar{J}_i[\vec{f}] = \sum_{(j,h,k) \in D_i^C} J_i^{ijhk} [f_i, f_j, f_h, f_k] + \sum_{(j,h,k) \in D_i^M} J_i^{ijhk} [f_i, f_j, f_h, f_k]. \quad (2.13)$$

Consider now gas–radiation interaction. At a microscopic level we will consider, as typical in radiation gas dynamics [15], the following binary encounters between a molecule A and a photon p , each modeled according to the proper Einstein coefficient:

- (i) absorption $A_i + p_{ij} \rightarrow A_j$ (coefficient β_{ij});
- (ii) spontaneous emission $A_j \rightarrow A_i + p_{ij}$ (coefficient α_{ij});
- (iii) stimulated emission $A_j + p_{ij} \rightarrow A_i + 2p_{ij}$ (coefficient $\beta_{ji} = \beta_{ij}$).

In our hypothesis only $2N(N-1)$ monochromatic photons are present, and it is meant throughout that $i \equiv j$, $i < j$. In the last event (iii), which is a typical quantum effect, all photons share the same direction of motion, represented by a unit vector $\Omega \in \mathbf{S}^2$, which will constitute the kinetic variable for photons in the same way as the molecular velocity is the kinetic variable for gas particles. Radiation field is then described by an upper triangular matrix of photon distribution functions $\tilde{f}_{ij}(\mathbf{x}, \Omega, t)$, or rather, as it is customary, of radiation intensities $I_{ij} = ch\nu_{ij}\tilde{f}_{ij}$. Since photon momentum is disregarded, participating molecules A_i and A_j will in turn share the same velocity \mathbf{v} . The collision term for A_i and A_j in the radiative transition relevant to the pair (i, j) , $i \equiv j$, $i < j$, reads as

$$\begin{aligned} \tilde{J}_i^{ij} [f_i, f_j, I_{ij}] (\mathbf{v}) &= -\tilde{J}_j^{ij} [f_i, f_j, I_{ij}] (\mathbf{v}) \\ &= -f_i \int \beta_{ij} I_{ij} \, d\Omega + f_j \int (\alpha_{ij} + \beta_{ij} I_{ij}) \, d\Omega. \end{aligned} \quad (2.14)$$

Correspondingly, the collision term for p_{ij} in the same transition takes the form

$$\tilde{J}_{ij} [f_i, f_j, I_{ij}] (\Omega) = -\beta_{ij} I_{ij} \int f_i \, d\mathbf{v} + (\alpha_{ij} + \beta_{ij} I_{ij}) \int f_j \, d\mathbf{v}. \quad (2.15)$$

Due to the absence of degeneracy, this is the only collision contribution in the balance equation for p_{ij} . For a given molecule A_i , the total collision term contributed by radiative transitions involving upper and lower energy levels (in the same species, of course) is built up as

$$\tilde{J}_i[\vec{f}, \vec{I}] = \sum_{j \in D_i^+} \tilde{J}_i^{ij}[f_i, f_j, I_{ij}] + \sum_{j \in D_i^-} \tilde{J}_i^{ji}[f_j, f_i, I_{ji}], \quad (2.16)$$

where the sets D_i^\pm are defined by the condition $j \equiv i$, $l_j > l_i$ or $l_j < l_i$, respectively:

$$\begin{aligned} D_i^+ &= \{j, j \equiv i, i+4 \leq j \leq 4N-4+s_i\}, \\ D_i^- &= \{j, j \equiv i, s_i \leq j \leq i-4\}. \end{aligned} \quad (2.17)$$

At this point we are able to write down the $2N(N+1)$ kinetic equations governing the evolution of the distribution function of the whole system represented by the vector (\vec{f}, \vec{I}) :

$$\begin{aligned} \frac{\partial f_i}{\partial t} + \mathbf{v} \cdot \frac{\partial f_i}{\partial \mathbf{x}} &= \bar{J}_i[\vec{f}] + \tilde{J}_i[\vec{f}, \vec{I}], \quad 1 \leq i \leq 4N, \\ \frac{\partial I_{ij}}{\partial t} + c\mathbf{\Omega} \cdot \frac{\partial I_{ij}}{\partial \mathbf{x}} &= ch\nu_{ij} \tilde{J}_{ij}[f_i, f_j, I_{ij}], \quad (i, j) \in D_R, \end{aligned} \quad (2.18)$$

where

$$D_R = \{(i, j), 1 \leq i \leq 4N, j \in D_i^+\}. \quad (2.19)$$

System (2.18) constitutes a set of coupled nonlinear integrodifferential equations generalizing the Boltzmann equation to the present extended problem.

3. Collision invariants and Boltzmann inequality

Having in mind concepts and ideas from kinetic theory, let us introduce a $4N$ -dimensional vector $\vec{\varphi}$ of smooth functions $\varphi_i(\mathbf{v})$ and consider the functional

$$\begin{aligned} \bar{C}[\vec{\varphi}] &= \sum_{i=1}^{4N} \int \varphi_i(\mathbf{v}) \bar{J}_i[\vec{f}] \, d\mathbf{v} \\ &= \sum_{(i,j,h,k) \in D_G} \iiint \varphi_i(\mathbf{v}) K_i^{ijhk}[\vec{f}](\mathbf{v}, \mathbf{w}, \mathbf{n}') \, d\mathbf{v} \, d\mathbf{w} \, d\mathbf{n}', \end{aligned} \quad (3.1)$$

where $D_G = D_C \cup D_M$ with

$$\begin{aligned} D_C &= \{(i, j, h, k), 1 \leq i, j, h, k \leq 4N, i \not\equiv j \not\equiv h \not\equiv k, i+j \equiv 3, h+k \equiv 3\}, \\ D_M &= \{(i, j, h, k), 1 \leq i, j, h, k \leq 4N, i \equiv h, j \equiv k\}, \end{aligned} \quad (3.2)$$

and

$$K_i^{ijhk}[\vec{f}](\mathbf{v}, \mathbf{w}, \mathbf{n}') = U(g^2 - \delta_{ij}^{hk})g\sigma_{ij}^{hk}(g, \mathbf{n} \cdot \mathbf{n}') \\ \times \left[\left(\frac{\mu_{ij}}{\mu_{hk}} \right)^3 f_h(\mathbf{v}_{ij}^{hk}) f_k(\mathbf{w}_{ij}^{hk}) - f_i(\mathbf{v}) f_j(\mathbf{w}) \right]. \quad (3.3)$$

Interchanging \mathbf{v} with \mathbf{w} , \mathbf{n}' with $-\mathbf{n}'$, i with j , and h with k allows a different representation of $\overline{C}[\vec{\varphi}]$, which turns out to be exactly the same as (3.1), only with $\varphi_i(\mathbf{v})$ replaced by $\varphi_j(\mathbf{w})$. Analogously, on using \mathbf{v}_{ij}^{hk} , \mathbf{w}_{ij}^{hk} , and \mathbf{n} as independent variables in the integration, renaming them by \mathbf{v} , \mathbf{w} , and \mathbf{n}' , resorting to the Jacobian (2.6) and to the microreversibility condition (2.9), and interchanging i with h , and j with k , leads to a further representation of $\overline{C}[\vec{\varphi}]$ which differs from (3.1) only in that $\varphi_i(\mathbf{v})$ is replaced by $-\varphi_h(\mathbf{v}_{ij}^{hk})$. Finally, combination of the two transformations above yields a fourth representation of $\overline{C}[\vec{\varphi}]$, simply with $-\varphi_k(\mathbf{w}_{ij}^{hk})$ replacing $\varphi_i(\mathbf{v})$. Because of the above invariance properties, the functional \overline{C} may also be recast as

$$\overline{C}[\vec{\varphi}] = -\frac{1}{4} \sum_{(i,j,h,k) \in D_G} \iiint U(g^2 - \delta_{ij}^{hk})g\sigma_{ij}^{hk}(g, \mathbf{n} \cdot \mathbf{n}') \\ \times \left[\left(\frac{\mu_{ij}}{\mu_{hk}} \right)^3 f_h(\mathbf{v}_{ij}^{hk}) f_k(\mathbf{w}_{ij}^{hk}) - f_i(\mathbf{v}) f_j(\mathbf{w}) \right] \\ \times [\varphi_h(\mathbf{v}_{ij}^{hk}) + \varphi_k(\mathbf{w}_{ij}^{hk}) - \varphi_i(\mathbf{v}) - \varphi_j(\mathbf{w})] d\mathbf{v} d\mathbf{w} d\mathbf{n}'. \quad (3.4)$$

Analogously, introduce a $2N(N-1)$ -dimensional vector $\vec{\psi}$ obtained by suitable rearrangement of an upper triangular matrix of smooth functions $\psi_{ij}(\Omega)$, $1 \leq i \leq 4N-4$, $i+4 \leq j \leq 4N-4+s_i$, $j \equiv i$ (namely $(i,j) \in D_R$), and consider the functional

$$\tilde{C}[\vec{\varphi}, \vec{\psi}] = \sum_{i=1}^{4N} \int \varphi_i(\mathbf{v}) \tilde{J}_i[\vec{f}, \vec{I}](\mathbf{v}) d\mathbf{v} + \sum_{(i,j) \in D_R} \int \psi_{ij}(\Omega) \tilde{J}_{ij}[f_i, f_j, I_{ij}](\Omega) d\Omega. \quad (3.5)$$

It is not difficult to show, by recalling (2.15) and (2.16), and by interchanging i and j in a partial sum, that also this functional may be rewritten in the more symmetric form

$$\tilde{C}[\vec{\varphi}, \vec{\psi}] = - \sum_{(i,j) \in D_R} \iint \{ f_j(\mathbf{v}) [\alpha_{ij} + \beta_{ij} I_{ij}(\Omega)] - f_i(\mathbf{v}) \beta_{ij} I_{ij}(\Omega) \} \\ \times [\varphi_j(\mathbf{v}) - \varphi_i(\mathbf{v}) - \psi_{ij}(\Omega)] d\mathbf{v} d\Omega. \quad (3.6)$$

Consider the full collision production rate for a $2N(N+1)$ -dimensional vector $(\vec{\varphi}, \vec{\psi})$, expressed by the further functional

$$\begin{aligned} C[\vec{\varphi}, \vec{\psi}] &= \sum_{i=1}^{4N} \int \varphi_i (\bar{J}_i + \tilde{J}_i) d\mathbf{v} + \sum_{(i,j) \in D_R} \int \psi_{ij} \tilde{J}_{ij} d\Omega \\ &= \bar{C}[\vec{\varphi}] + \tilde{C}[\vec{\varphi}, \vec{\psi}]. \end{aligned} \quad (3.7)$$

From (3.4) and (3.6) it is immediately seen by inspection that $C[\vec{\varphi}, \vec{\psi}] = 0$, whatever \vec{f} and \vec{I} are, for the following five scalar quantities:

$$\begin{aligned} \varphi_i &= m_i, & 1 \leq i \leq 4N, & \quad \psi_{ij} = 0, & \quad (i, j) \in D_R, \\ \varphi_i &= m_i \mathbf{v}, & 1 \leq i \leq 4N, & \quad \psi_{ij} = \mathbf{0}, & \quad (i, j) \in D_R, \\ \varphi_i &= \frac{1}{2} m_i v^2 + E_i, & 1 \leq i \leq 4N, & \quad \psi_{ij} = h\nu_{ij}, & \quad (i, j) \in D_R, \end{aligned} \quad (3.8)$$

representing consistently mass, momentum, and total energy, respectively, for the whole system. More precisely, we can define as collision invariant any vector $(\vec{\varphi}, \vec{\psi})$ of continuous functions φ_i of \mathbf{v} and ψ_{ij} of Ω satisfying the requirements

$$\begin{aligned} \varphi_h(\mathbf{v}_{ij}^{hk}) + \varphi_k(\mathbf{w}_{ij}^{hk}) &= \varphi_i(\mathbf{v}) + \varphi_j(\mathbf{w}) \\ \forall (\mathbf{v}, \mathbf{w}, \mathbf{n}') \in \mathbb{R}^3 \times \mathbb{R}^3 \times \mathbf{S}^2, & \quad \forall (i, j, h, k) \in D_G, \\ \varphi_j(\mathbf{v}) - \varphi_i(\mathbf{v}) &= \psi_{ij}(\Omega) \quad \forall (\mathbf{v}, \Omega) \in \mathbb{R}^3 \times \mathbf{S}^2, & \quad \forall (i, j) \in D_R. \end{aligned} \quad (3.9)$$

It follows immediately that, if $(\vec{\varphi}, \vec{\psi})$ is a collision invariant, then

$$C[\vec{\varphi}, \vec{\psi}] = 0 \quad \forall (\vec{f}, \vec{I}). \quad (3.10)$$

It is remarkable that, like in standard kinetic theory, the set (3.9) may be explicitly solved, and all its solutions may be expressed analytically. If a solution exists, it must fulfil in particular the first of (3.9) with $i = j = h = k$ (elastic scattering between equal components), and thus, by a crucial theorem of [4], it has necessarily the form

$$\varphi_i(\mathbf{v}) = a_i + \mathbf{b}_i \cdot \mathbf{v} + c_i v^2, \quad 1 \leq i \leq 4N, \quad (3.11)$$

with $20N$ free coefficients a_i, \mathbf{b}_i, c_i . The option $j \neq i, h = i, k = j$ is also allowed in D_G (elastic scattering between different components), and the relevant equations from (3.9) may be specialized at $\mathbf{w} = -\mathbf{v}$ and $\mathbf{n}' = -\mathbf{v}/|\mathbf{v}|$, to yield a set of scalar equations to be satisfied $\forall \mathbf{v} \in \mathbb{R}^3, \mathbf{v} \neq \mathbf{0}$,

$$8(r_{ij} - r_{ji})(r_{ij}c_j - r_{ji}c_i)v^2 + 4(r_{ij}\mathbf{b}_j - r_{ji}\mathbf{b}_i) \cdot \mathbf{v} = 0. \quad (3.12)$$

It is then not difficult to deduce, when $j \neq i$, that

$$\frac{\mathbf{b}_i}{m_i} = \frac{\mathbf{b}_j}{m_j} \stackrel{\text{def}}{=} \mathbf{b}, \quad \frac{c_i}{m_i} = \frac{c_j}{m_j} \stackrel{\text{def}}{=} \frac{1}{2}c, \quad 1 \leq i, j \leq 4N. \quad (3.13)$$

When instead $j \equiv i$ the same result (3.13) can be achieved by a different choice of variables ($\mathbf{w} = \mathbf{0}, \mathbf{n}' = -\mathbf{v}/|\mathbf{v}|$). This leaves $4N + 4$ free parameters. Moreover,

(i, i, i, j) with $i \equiv j$ also belongs to D_G (simplest inelastic scattering), and then the first of (3.9) yields the further constraint

$$a_j - a_i = c(E_j - E_i), \quad 1 \leq i \leq 4N, \quad j \equiv i, \quad (3.14)$$

restricting coefficients to only eight: $a_1, a_2, a_3, a_4, \mathbf{b}, c$. Now, taking any $(i, j, h, k) \in D_C$, leads, on account of conservation laws, to the conditions

$$a_h + a_k - a_i - a_j = c\Delta E_{ij}^{hk} \quad (3.15)$$

among which only one is independent by (3.14), namely,

$$a_3 + a_4 - a_1 - a_2 = c\Delta E. \quad (3.16)$$

Finally, the second in (3.9) allows to evaluate all ψ_{ij} in terms of the φ_i , as

$$\psi_{ij}(\mathbf{\Omega}) = a_j - a_i = c(E_j - E_i), \quad (i, j) \in D_R. \quad (3.17)$$

So, any solution of (3.9) has necessarily the form determined above, depending on seven free parameters, and it is simply matter of some algebra to verify that they all indeed actually satisfy (3.9) for any choice of indices and independent variables. In conclusion, we have proved

Theorem 3.1. Collision invariants constitute a 7-dimensional linear space, whose general element may be written as

$$\varphi_i(\mathbf{v}) = a_i + \mathbf{b} \cdot m_i \mathbf{v} + c \frac{1}{2} m_i v^2, \quad \psi_{ij}(\mathbf{\Omega}) = c h \nu_{ij}, \quad (3.18)$$

with parameters a_i and c bound each other by (3.14) and (3.16).

We may single out, in several different ways, seven independent collision invariants: a possible choice is

$$\begin{aligned} \varphi_i &= \begin{cases} 1 & \text{if } i \equiv 1 \vee i \equiv 3, \\ 0 & \text{otherwise,} \end{cases} & \psi_{ij} &= 0, \\ & \text{corresponding to } a_1 = a_3, a_2 = a_4 = 0, \mathbf{b} = \mathbf{0}, c = 0, \\ \varphi_i &= \begin{cases} 1 & \text{if } i \equiv 1 \vee i \equiv 4, \\ 0 & \text{otherwise,} \end{cases} & \psi_{ij} &= 0, \\ & \text{corresponding to } a_1 = a_4, a_2 = a_3 = 0, \mathbf{b} = \mathbf{0}, c = 0, \\ \varphi_i &= \begin{cases} 1 & \text{if } i \equiv 2 \vee i \equiv 3, \\ 0 & \text{otherwise,} \end{cases} & \psi_{ij} &= 0, \\ & \text{corresponding to } a_2 = a_3, a_1 = a_4 = 0, \mathbf{b} = \mathbf{0}, c = 0, \\ \varphi_i &= m_i \mathbf{v}, & \psi_{ij} &= \mathbf{0}, \\ & \text{corresponding to } a_1 = a_2 = a_3 = a_4 = 0, c = 0, \\ \varphi_i &= \frac{1}{2} m_i v^2 + E_i, & \psi_{ij} &= h \nu_{ij}, \\ & \text{corresponding to } a_s = c E_s, s = 1, 2, 3, 4, \mathbf{b} = \mathbf{0}. \end{aligned} \quad (3.19)$$

The last two are the same as in (3.8) and correspond to momentum and total energy. The first three are related to the total number of particles in species 1 and 3, or 1 and 4, or 2 and 3, respectively, as implied by the chemical reaction. Summation of second and third yields an invariant that corresponds to total number of molecules; linear combination of the first three with coefficients $m_3 - m_2, m_4, m_2$ leads back to the mass, expressed by the first of (3.8).

A first consequence of theorem 3.1 is that seven independent equations of practical relevance, bearing no trace of complicated collision integrals, and describing physical conservations at a macroscopic scale, may be derived from (2.18). It is sufficient in fact to take seven independent collision invariants $(\vec{\varphi}, \vec{\psi})$, to multiply the first of (2.18) by φ_i and the second by $(1/(ch\nu_{ij}))\psi_{ij}$, to integrate with respect to the relevant kinetic variable, and to sum up over all admissible indices, in order to obtain $C[\vec{\varphi}, \vec{\psi}]$ at the right-hand side, which vanishes by definition (see (3.10)). Details will be omitted for brevity, and reference is made to the seven invariants (3.19). Macroscopic quantities are as usual suitable moments of the distribution functions, and are listed below. It is implicitly understood that $1 \leq i \leq 4N$, $1 \leq s \leq 4$, $(i, j) \in D_R$.

$$\begin{aligned}
 n_i &= \int f_i \, d\mathbf{v} && \text{number density of the } i\text{th component,} \\
 \mathbf{u}_i &= \frac{1}{n_i} \int \mathbf{v} f_i \, d\mathbf{v} && \text{drift velocity of the } i\text{th component,} \\
 N_s &= \sum_{i \equiv s} n_i && \text{number density of the } s\text{th species,} \\
 \mathbf{u}_s^\bullet &= \frac{1}{N_s} \sum_{i \equiv s} n_i \mathbf{u}_i && \text{drift velocity of the } s\text{th species,} \\
 n &= \sum_{i=1}^{4N} n_i = \sum_{s=1}^4 N_s && \text{total number density,} \\
 \rho &= \sum_{i=1}^{4N} m_i n_i = \sum_{s=1}^4 m_s N_s && \text{mass density,} \\
 \mathbf{u} &= \frac{1}{\rho} \sum_{i=1}^{4N} m_i n_i \mathbf{u}_i = \frac{1}{\rho} \sum_{s=1}^4 m_s N_s \mathbf{u}_s^\bullet && \text{mass velocity,} \\
 \mathbf{P} &= \sum_{i=1}^{4N} m_i \int (\mathbf{v} - \mathbf{u})(\mathbf{v} - \mathbf{u}) f_i \, d\mathbf{v} && \text{pressure tensor,} \\
 U &= \frac{1}{2} \text{tr} \mathbf{P} && \text{thermal energy density,} \\
 U^* &= \sum_{i=1}^{4N} E_i n_i && \text{excitation energy density,}
 \end{aligned}$$

$$\begin{aligned}
\mathbf{q} &= \frac{1}{2} \sum_{i=1}^{4N} m_i \int (\mathbf{v} - \mathbf{u})^2 (\mathbf{v} - \mathbf{u}) f_i \, d\mathbf{v} && \text{thermal heat flux,} \\
\mathbf{q}^* &= \sum_{i=1}^{4N} E_i \int (\mathbf{v} - \mathbf{u}) f_i \, d\mathbf{v} && \text{excitation heat flux,} \\
e_{ij} &= \frac{1}{c} \int I_{ij} \, d\Omega && \text{energy density of } (i, j)\text{-photons,} \\
\mathbf{u}_{ij} &= \frac{1}{e_{ij}} \int \Omega I_{ij} \, d\Omega && \text{drift velocity of } (i, j)\text{-photons,} \\
U_p &= \sum_{(i,j) \in D_R} e_{ij} && \text{radiation energy density,} \\
\mathbf{j}_p &= \sum_{(i,j) \in D_R} e_{ij} \mathbf{u}_{ij} && \text{radiation energy flux.}
\end{aligned}$$

Kinetic temperature T is defined, as usual, by $U = \frac{3}{2} n K_B T$, where K_B is the Boltzmann constant. The seven macroscopic conservation equations read as

$$\begin{aligned}
\frac{\partial}{\partial t} (N_1 + N_3) + \frac{\partial}{\partial \mathbf{x}} \cdot (N_1 \mathbf{u}_1^\bullet + N_3 \mathbf{u}_3^\bullet) &= 0, \\
\frac{\partial}{\partial t} (N_1 + N_4) + \frac{\partial}{\partial \mathbf{x}} \cdot (N_1 \mathbf{u}_1^\bullet + N_4 \mathbf{u}_4^\bullet) &= 0, \\
\frac{\partial}{\partial t} (N_2 + N_3) + \frac{\partial}{\partial \mathbf{x}} \cdot (N_2 \mathbf{u}_2^\bullet + N_3 \mathbf{u}_3^\bullet) &= 0, \\
\frac{\partial}{\partial t} (\rho \mathbf{u}) + \frac{\partial}{\partial \mathbf{x}} \cdot (\rho \mathbf{u} \mathbf{u} + \mathbf{P}) &= \mathbf{0}, \\
\frac{\partial}{\partial t} \left(\frac{1}{2} \rho u^2 + U + U^* + U_p \right) + \frac{\partial}{\partial \mathbf{x}} \cdot \left[\left(\frac{1}{2} \rho u^2 + U + U^* \right) \mathbf{u} \right] \\
+ \frac{\partial}{\partial \mathbf{x}} \cdot [\mathbf{P} \cdot \mathbf{u} + \mathbf{q} + \mathbf{q}^* + \mathbf{j}_p] &= 0,
\end{aligned} \tag{3.20}$$

and constitute of course an exact, but not closed, set of balance equations for macroscopic observables. The discussion on possible closure strategies is left as future work. Notice that a linear combination of the first three equations in (3.20), with coefficients $m_3 - m_2, m_4$, and m_2 , respectively, leads to the mass conservation equation

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \mathbf{x}} \cdot (\rho \mathbf{u}) = 0. \tag{3.21}$$

Analogously, the last two equations may be regarded as momentum and energy conservation equations. Momentum and energy are conserved for the system as a whole, whereas for molecules suitable conservations hold not only for the whole system, but also for some subsets of it.

Another consequence of theorem 3.1 concerns the functional

$$W[\vec{f}, \vec{I}] = \sum_{i=1}^{4N} \int \log \widehat{f}_i(\vec{J}_i + \vec{J}_i) d\mathbf{v} + \sum_{(i,j) \in D_R} \int \log \frac{\beta_{ij} I_{ij}}{\alpha_{ij} + \beta_{ij} I_{ij}} \vec{J}_{ij} d\Omega, \quad (3.22)$$

where $\widehat{f}_i = f_i/m_i^3$. It is clear that

$$W = C[\vec{\varphi}, \vec{\psi}], \quad \varphi_i = \log \widehat{f}_i, \quad \psi_{ij} = \log \frac{\beta_{ij} I_{ij}}{\alpha_{ij} + \beta_{ij} I_{ij}}. \quad (3.23)$$

Thus, in force of (3.7), (3.4) and (3.6) we may write, under standard positivity assumptions on cross sections, Einstein coefficients, and distribution functions

$$\begin{aligned} W = & -\frac{1}{4} \sum_{(i,j,h,k) \in D_G} \iiint U(g^2 - \delta_{ij}^{hk}) g \sigma_{ij}^{hk}(g, \mathbf{n} \cdot \mathbf{n}') m_i^3 m_j^3 \widehat{f}_i(\mathbf{v}) \widehat{f}_j(\mathbf{w}) \\ & \times \log \frac{\widehat{f}_h(\mathbf{v}_{ij}^{hk}) \widehat{f}_k(\mathbf{w}_{ij}^{hk})}{\widehat{f}_i(\mathbf{v}) \widehat{f}_j(\mathbf{w})} \left[\frac{\widehat{f}_h(\mathbf{v}_{ij}^{hk}) \widehat{f}_k(\mathbf{w}_{ij}^{hk})}{\widehat{f}_i(\mathbf{v}) \widehat{f}_j(\mathbf{w})} - 1 \right] d\mathbf{v} d\mathbf{w} d\mathbf{n}' \\ & - \sum_{(i,j) \in D_R} \iint \beta_{ij} I_{ij}(\Omega) f_i(\mathbf{v}) \log \frac{f_j(\mathbf{v})[\alpha_{ij} + \beta_{ij} I_{ij}(\Omega)]}{f_i(\mathbf{v}) \beta_{ij} I_{ij}(\Omega)} \\ & \times \left\{ \frac{[\alpha_{ij} + \beta_{ij} I_{ij}(\Omega)] f_j(\mathbf{v})}{\beta_{ij} I_{ij}(\Omega) f_i(\mathbf{v})} - 1 \right\} d\mathbf{v} d\Omega. \end{aligned} \quad (3.24)$$

Since, for $x > 0$, the convex function $(x - 1) \log x$ is non-negative, and vanishes only at $x = 1$, we easily realize that each of the several addends making up the right-hand side of (3.24) is non-negative, and vanishes if and only if the ratio appearing as argument of the log function equals unity, for all values of the relevant independent variables. A very strict conclusion may then be drawn from (3.24), which establishes the sign of W , and generalizes the classical Boltzmann inequality.

Theorem 3.2. The functional W defined by (3.22) is such that $W \leq 0 \forall (\vec{f}, \vec{I})$, and more precisely, $W = 0$ if and only if

$$\begin{aligned} & \widehat{f}_h(\mathbf{v}_{ij}^{hk}) \widehat{f}_k(\mathbf{w}_{ij}^{hk}) - \widehat{f}_i(\mathbf{v}) \widehat{f}_j(\mathbf{w}) = 0 \\ & \quad \forall (\mathbf{v}, \mathbf{w}, \mathbf{n}') \in \mathbb{R}^3 \times \mathbb{R}^3 \times \mathbf{S}^2, \quad \forall (i, j, h, k) \in D_G, \\ & [\alpha_{ij} + \beta_{ij} I_{ij}(\Omega)] f_j(\mathbf{v}) - \beta_{ij} I_{ij}(\Omega) f_i(\mathbf{v}) = 0 \\ & \quad \forall (\mathbf{v}, \Omega) \in \mathbb{R}^3 \times \mathbf{S}^2, \quad \forall (i, j) \in D_R. \end{aligned} \quad (3.25)$$

4. Collision equilibria

A collision equilibrium can be defined, like in [4], as any distribution function (\vec{f}, \vec{I}) for which

$$\begin{aligned}\bar{J}_i + \tilde{J}_i &= 0 \quad \forall \mathbf{v} \in \mathbb{R}^3 \quad \forall i = 1, \dots, 4N, \\ \tilde{J}_{ij} &= 0 \quad \forall \boldsymbol{\Omega} \in \mathbf{S}^2 \quad \forall (i, j) \in D_R.\end{aligned}\quad (4.1)$$

The following theorem can be proved:

Theorem 4.1. The pair (\vec{f}, \vec{I}) is a collision equilibrium if and only if satisfies conditions (3.25).

For the proof, it is first clear from (3.22) that any collision equilibrium makes the functional W vanish, and this implies, because of theorem 3.2, that the equilibrium distribution function (\vec{f}, \vec{I}) must fulfil (3.25). Conversely, notice that conditions (3.25) imply in turn equations (4.1), by virtue of (2.10) and (2.13)–(2.16) defining the total collision terms, so that the statement is proved.

The previous theorem represents the extended version of the detailed balance principle that is valid in the present context. It establishes that the net collision production rate for each gas component and photon frequency vanishes if and only if all single collision terms relevant to the allowed interactions vanish. In addition, conditions (3.25), recalling definition (3.9), may be read in turn in the following equivalent way: the vector $(\vec{\varphi}, \vec{\psi})$ defined by

$$\varphi_i = \log \hat{f}_i, \quad 1 \leq i \leq 4N, \quad \psi_{ij} = \log \frac{\beta_{ij} I_{ij}}{\alpha_{ij} + \beta_{ij} I_{ij}}, \quad (i, j) \in D_R, \quad (4.2)$$

is a collision invariant. Theorem 4.1 allows then explicit evaluation of all collision equilibria, since the requirement that vector (4.2) be a collision invariant implies, by theorem 3.1, that it must have the form prescribed by (3.18), which determines completely the subspace of equilibrium distributions as a 7-parameter family in the space of the admissible distribution functions. More specifically, the particle distribution functions may be written as

$$\hat{f}_i(\mathbf{v}) = \gamma_i \exp \left[\frac{1}{2} m_i c \left(\mathbf{v} + \frac{\mathbf{b}}{c} \right)^2 \right], \quad 1 \leq i \leq 4N, \quad (4.3)$$

with

$$\gamma_i = \exp \left(a_i - \frac{m_i \mathbf{b}^2}{2c} \right) > 0 \quad (4.4)$$

and $c < 0$ for existence of the macroscopic moments. Coefficients in (4.3), (4.4) are easily seen to be in a one-to-one relationship with physical observables as

$$\gamma_i = \frac{n_i}{(2\pi m_i K_B T)^{3/2}}, \quad \mathbf{b} = -c\mathbf{u}, \quad c = -\frac{1}{K_B T}, \quad (4.5)$$

and therefore we are led to the classical Maxwellian distributions

$$f_i^M(\mathbf{v}) = n_i \left(\frac{m_i}{2\pi K_B T} \right)^{3/2} \exp \left[-\frac{m_i}{2K_B T} (\mathbf{v} - \mathbf{u})^2 \right], \quad i = 1, \dots, 4N. \quad (4.6)$$

Number densities, because of (3.14), are in turn related by

$$n_j = n_i \exp \left(-\frac{E_j - E_i}{K_B T} \right), \quad 1 \leq i \leq 4N, \quad j \equiv i, \quad (4.7)$$

the well-known Boltzmann factors of statistical mechanics. Moreover, in force of (3.15), components relevant to different species are also related by

$$\frac{n_h n_k}{n_i n_j} = \left(\frac{m_h m_k}{m_i m_j} \right)^{3/2} \exp \left(-\frac{\Delta E_{ij}^{hk}}{K_B T} \right) \quad \forall (i, j, h, k) \in D_C, \quad (4.8)$$

which holds indeed $\forall (i, j, h, k) \in D_G$ by (4.7). Equation (4.8) represents the mass action law relevant to the chemical reaction associated to each of the several elements (i, j, h, k) in D_C . Combination of (4.7) and (4.8) (which, by the way, are compatible) determines uniquely all $4N$ number densities in terms of only 3 of them and of temperature, so that the Gaussian functions in (4.6) are determined up to 7 scalar parameters (including \mathbf{u}). Finally, in order to fulfil the detailed balance principle, ψ_{ij} in (4.2) must be equal to $-\hbar\nu_{ij}/K_B T$, that yields for radiation intensities at equilibrium

$$I_{ij}^M(\Omega) = \frac{\alpha_{ij}/\beta_{ij}}{\exp((\hbar\nu_{ij})/(K_B T)) - 1} \quad \forall (i, j) \in D_R, \quad (4.9)$$

reproducing the Planck's law of radiation for each of the $2N(N-1)$ monochromatic photons. Introducing the densities N_s for the 4 species, and the partition functions

$$Z_s(T) = \sum_{i \equiv s} \exp \left(-\frac{E_i - E_s}{K_B T} \right), \quad s = 1, 2, 3, 4, \quad (4.10)$$

the present conclusions on equilibria are summarized by the following proposition.

Theorem 4.2. The class of collision equilibria (\vec{f}, \vec{I}) is exhausted by the distribution functions defined by (4.6) and (4.9), with

$$n_i = \frac{N_{s_i}}{Z_{s_i}(T)} \exp \left(-\frac{E_i - E_{s_i}}{K_B T} \right), \quad i = 1, \dots, 4N; \quad (4.11)$$

they depend on 7 free parameters, which may be chosen as $N_1, N_2, N_3, N_4, \mathbf{u}$, and T , bound together by the mass action law

$$\frac{N_1 N_2}{N_3 N_4} = \left(\frac{m_1 m_2}{m_3 m_4} \right)^{3/2} \frac{Z_1(T) Z_2(T)}{Z_3(T) Z_4(T)} \exp \left(\frac{\Delta E}{K_B T} \right). \quad (4.12)$$

We conclude this section with some remarks on the equilibria above and the kinetic equations (2.18). Equilibria take that form even when several of the cross sections vanish, or, in other words, they are determined by the occurrence of a restricted number of crucial interactions. The proof of theorem 3.1 shows, for instance, that the same result can be achieved also when only the encounters described by the following sequences are active: (i, i, i, i) , (i, j, i, j) , (i, i, i, j) , and $(1, 2, 3, 4)$. Of course, distribution functions (4.6) and (4.9) are exact solutions of (2.18) when all parameters of theorem 4.2 are space and time independent. Otherwise, such distributions, depending on \mathbf{x} and t only via those parameters, simply make all collision terms vanish, and play the role of the local Maxwellians of the Boltzmann equation. For example, a typical assumption of local equilibrium would allow the simplest closure of the macroscopic equations (3.20). In fact, all moments different from the seven chosen as independent can be then explicitly expressed in terms of them, to yield a self-consistent (approximate) set of seven first-order nonlinear PDEs for the seven essential macroscopic fields. Another remark concerns the asymptotic analysis of equations (2.18) in terms of their typical collision relaxation times (both chemical and mechanical), and their interplay with the macroscopic space and time scales, which produces small parameters (Knudsen numbers) upon adimensionalization of the equations themselves. Hilbert and Chapman–Enskog expansions [4] would yield then the proper hydrodynamic equations for this extended problem. The hydrodynamic limit will depend of course on which collision terms exhibit the shortest relaxation time, and thus have to be considered as dominant in the process. The hydrodynamic space will follow by setting the proper collision terms equal to zero, and might then be larger than the space defined by theorem 4.2. This problem, which falls within a well-defined research line in transport theory (see, for instance, [1,10,11]), together with others, will be matter of future investigation.

5. Stability of equilibria

We study here Lyapunov stability of the absolute Maxwellians of theorem 4.2 as stationary solutions to the kinetic equations (2.18). As usual, we shall focus on the effects of collisions, and neglect for a moment spatial gradients and boundary conditions, which could be inserted in a second step [4]. Therefore, the space homogeneous version of (2.18) will be dealt with as a Cauchy problem with given initial conditions $f_i^\circ(\mathbf{v})$ and $I_{ij}^\circ(\Omega)$, and we can take advantage from the fact that a proper choice of the reference frame always allows to put $\mathbf{u} = \mathbf{0}$ in this case. So the dimension of the subspace of the collision equilibria, as well as the number of macroscopic conservation equations, collapses from 7 to 4. The present stability analysis is based on the construction of a suitable functional, which will bear the name H as generalization of the Boltzmann H-functional, to be shown to represent a Lyapunov functional for the problem, in the sense that $\dot{H} \leq 0$ and $H - H^M \geq 0$, with equal sign only at equilibria. Here and below superscript M will be used as a label of equilibrium. In other words, we shall prove here an extended version of the Boltzmann H-theorem.

First of all, notice that (3.20) immediately yields the first integrals

$$N_1 + N_3 = \text{constant}, \quad N_1 + N_4 = \text{constant}, \quad N_2 + N_3 = \text{constant}, \quad (5.1)$$

which also imply conservation of number density n and mass density ρ . The last equation in (3.20) corresponds to energy conservation, and reads as

$$\frac{3}{2}nK_{\text{B}}T + \sum_{i=1}^{4N} E_i n_i + \frac{1}{c} \sum_{(i,j) \in D_R} \int I_{ij} \, d\Omega = \text{constant} = \mathcal{E}^0. \quad (5.2)$$

Thus, the evolution of (\vec{f}, \vec{T}) in its admissible functional space, starting from $(\vec{f}^{\circ}, \vec{T}^{\circ})$, is confined to the subspace which is defined by conditions (5.1), (5.2), the constants being determined by the initial conditions themselves. We are led thus to consider the Maxwellian distributions which belong to such a subspace, namely to single out its intersection with the other subspace made up by collision equilibria. This means that equations (5.1), (5.2) have to be coupled to the equations relevant to equilibrium, in particular to (4.11), relating each n_i to N_{s_i} and T , to (4.9), expressing I_{ij} in terms of T , and to (4.12), binding together all N_s and T . There results a complicated nonlinear algebraic set of 5 equations for the 5 unknowns N_s^M and T^M , $s = 1, \dots, 4$, involving the initial values N_s° and T° . More precisely, we get from the first integrals (5.1)

$$N_1 - N_1^{\circ} = N_2 - N_2^{\circ} = -(N_3 - N_3^{\circ}) = -(N_4 - N_4^{\circ}) \quad (5.3)$$

and from energy conservation

$$\frac{3}{2}nK_{\text{B}}T^M + \sum_{s=1}^4 N_s^M \bar{E}_s(T^M) + U_p^M(T^M) = \mathcal{E}^0, \quad (5.4)$$

where

$$\begin{aligned} \bar{E}_s(T) &= \frac{1}{Z_s(T)} \sum_{i \equiv s} E_i \exp\left(-\frac{E_i - E_s}{K_{\text{B}}T}\right), \quad s = 1, \dots, 4, \\ U_p^M(T) &= \frac{4\pi}{c} \sum_{(i,j) \in D_R} \frac{\alpha_{ij}/\beta_{ij}}{\exp((E_j - E_i)/(K_{\text{B}}T)) - 1}. \end{aligned} \quad (5.5)$$

Notice that the average \bar{E}_s is monotone versus T , since

$$\bar{E}'_s(T) = \frac{e^{2E_s/(K_{\text{B}}T)}}{2K_{\text{B}}T^2 Z_s^2(T)} \sum_{i \equiv s} \sum_{j \equiv s} (E_i - E_j)^2 e^{-(E_i + E_j)/(K_{\text{B}}T)} > 0, \quad (5.6)$$

with $\bar{E}_s(0) = E_s$ and, with obvious notation, $\bar{E}_s(\infty) = \sum_{i \equiv s} E_i/N$. Inserting (5.3) at equilibrium into (5.4) leads to expressing equilibrium densities as

$$\begin{aligned} N_1^M &= N_1^{\circ} + X(T^M), & N_2^M &= N_2^{\circ} + X(T^M), \\ N_3^M &= N_3^{\circ} - X(T^M), & N_4^M &= N_4^{\circ} - X(T^M), \end{aligned} \quad (5.7)$$

where $X(T) = \chi(T)/Y(T)$, and the functions χ and Y are given by

$$\begin{aligned}\chi(T) &= \frac{3}{2}nK_B T + \sum_{s=1}^4 N_s^\circ \bar{E}_s(T) + U_p^M(T) - \mathcal{E}^0, \\ Y(T) &= \bar{E}_3(T) + \bar{E}_4(T) - \bar{E}_1(T) - \bar{E}_2(T).\end{aligned}\tag{5.8}$$

By positivity of number density for each species, the obvious constraint

$$\max(-N_1^\circ, -N_2^\circ) \leq X(T^M) \leq \min(N_3^\circ, N_4^\circ)\tag{5.9}$$

must be in order. It is not difficult to check that the continuous function $\chi(T)$ is monotonically increasing, with $\chi(0) < 0$ and $\chi(\infty) = \infty$, so that there exists a unique value $T = T^\#$ at which $\chi(T) = 0$. The trend of the average energy jump Y instead is not definite, and it might even vanish and become negative at some values of T for suitable, though probably unphysical, choices of the energy levels. At least, we can rely on the fact that $Y(0) = \Delta E > 0$, and that Y is bounded both from above and from below, due to the boundedness of all \bar{E}_s ; in addition, appropriate choices of levels, like for instance (2.2), can guarantee also $Y(\infty) > 0$, but we will not go deeper into this problem. At this point, everything is determined in terms of the only unknown T^M , for which the mass action law yields the transcendental equation

$$\xi(T^M) = \eta(T^M),\tag{5.10}$$

where

$$\begin{aligned}\xi(T) &= \frac{[N_1^\circ + X(T)][N_2^\circ + X(T)]}{[N_3^\circ - X(T)][N_4^\circ - X(T)]}, \\ \eta(T) &= \left(\frac{m_1 m_2}{m_3 m_4}\right)^{3/2} \frac{Z_1(T)Z_2(T)}{Z_3(T)Z_4(T)} \exp\left(\frac{\Delta E}{K_B T}\right).\end{aligned}\tag{5.11}$$

Any root T^M of (5.10) provides, via equations (5.7), (4.11), (4.6) and (4.9), a Maxwellian distribution (\bar{f}^M, \bar{I}^M) which shares the same values of all conserved quantities with the initial distribution $(\bar{f}^\circ, \bar{I}^\circ)$. As regards actual solvability of (5.10), we remark preliminarily that the trend of the positive function $\eta(T)$ is controlled by the result

$$\eta'(T) = -\frac{1}{K_B T^2} \eta(T) Y(T),\tag{5.12}$$

which implies its (at least piecewise) monotonicity, with additionally $\eta(0) = \infty$ and $\eta(\infty) = [m_1 m_2 / (m_3 m_4)]^{3/2}$. Now, owing to the continuity of all functions involved, the proof of existence of a solution to equation (5.10) can be performed, even though it turns out to be a little tedious and cumbersome.

Let first $Y(T^\#) \neq 0$. The search of T^M must be restricted to the values of T for which (5.9) is satisfied. There exists a maximal interval (T_1, T_2) for T^M , with $T^\#$ as internal point, where this occurs. From the divergence of $\chi(T)$ when $T \rightarrow \infty$

there follows necessarily $T_2 < +\infty$. In the closure of the interval, the function Y is different from zero with the same sign of $Y(T^\#)$. If $T_1 > 0$, then η is a bounded monotone continuous function in (T_1, T_2) (increasing or decreasing depending on the sign of Y), ranging between two positive values. Simultaneously, ξ is a continuous function ranging between 0 and $+\infty$, and approaching such values at the ends of the interval (T_1, T_2) (one or the other, depending again on the sign of Y). So, there exists at least one intersection point for $\xi(T)$ and $\eta(T)$ in the interval (T_1, T_2) . If $T_1 = 0$, as it may occur only for $Y(T^\#) > 0$, then η is monotonically decreasing from $+\infty$ (when $T \rightarrow 0$) to a positive value (when $T \rightarrow T_2$), whereas ξ takes on a non-negative value at $T = 0$, and diverges for $T \rightarrow T_2$, so that there exists again at least one solution in (T_1, T_2) . When, finally, $Y(T^\#) = 0$, the previous argument does not apply, but it is immediately seen that a Maxwellian state $(N_1^M, N_2^M, N_3^M, N_4^M, T^M)$ is obtained from the initial state by taking $T^M = T^\#$, and the N_s^M expressed by (5.7), but with $X(T^M)$ replaced by the root X^M of the algebraic equation

$$\frac{[N_1^\circ + X^M][N_2^\circ + X^M]}{[N_3^\circ - X^M][N_4^\circ - X^M]} = \eta(T^\#) \tag{5.13}$$

(the root is unique in the interval (5.9) by the monotonicity of the left-hand side with respect to X^M). In conclusion, the following existence result is proved.

Theorem 5.1. In space homogeneous conditions, to any initial distribution $(\vec{f}^\circ, \vec{I}^\circ)$ we can associate a Maxwellian (\vec{f}^M, \vec{I}^M) characterized by the same values of all macroscopic quantities which are conserved during the evolution.

Indeed, we expect also uniqueness for such a Maxwellian, like for the separate problems of chemical reaction alone [18], and of inelastic transitions only [17], but we were not able to prove it analytically by the previous analysis for an arbitrary choice of energy levels. However, it will be shown later how uniqueness can be easily ascertained by a different argument.

In order to study stability of an equilibrium (\vec{f}^M, \vec{I}^M) associated to a given initial condition as in theorem 5.1, consider the functional

$$H[\vec{f}, \vec{I}] = \sum_{i=1}^{4N} \int f_i \log \hat{f}_i \, d\mathbf{v} + \sum_{(i,j) \in D_R} \frac{1}{ch\nu_{ij}} \times \int \left[I_{ij} \log \frac{\beta_{ij} I_{ij}}{\alpha_{ij}} - \left(\frac{\alpha_{ij}}{\beta_{ij}} + I_{ij} \right) \log \left(1 + \frac{\beta_{ij} I_{ij}}{\alpha_{ij}} \right) \right] d\Omega. \tag{5.14}$$

Following a solution of the considered Cauchy problem, we can take the time derivative \dot{H} , get rid of time derivatives of f_i and I_{ij} via the kinetic equations, realize that \dot{H} is in turn a functional and, in particular, obtain

$$\dot{H}[\vec{f}, \vec{I}] = W[\vec{f}, \vec{I}]. \tag{5.15}$$

Therefore, bearing in mind theorem 3.2, the evolution of the distribution function (\vec{f}, \vec{I}) , starting from (\vec{f}^0, \vec{I}^0) , is such that $\dot{H} \leq 0 \forall t \geq 0$, with $\dot{H} = 0$ only at an equilibrium (\vec{f}^M, \vec{I}^M) compatible with the initial condition in the sense of theorem 5.1. We shall prove now that H has a local minimum at (\vec{f}^M, \vec{I}^M) , namely that the following H-theorem holds.

Theorem 5.2. The functional H in (5.14) is a strict Lyapunov functional in space homogeneous conditions for an equilibrium (\vec{f}^M, \vec{I}^M) defined by theorems 4.2 and 5.1.

We only need to prove that $H[\vec{f}, \vec{I}] - H[\vec{f}^M, \vec{I}^M] > 0$ for any $(\vec{f}, \vec{I}) \neq (\vec{f}^M, \vec{I}^M)$, at least in a neighborhood of (\vec{f}^M, \vec{I}^M) . We may write

$$H = \int \bar{\mathcal{H}} \, d\mathbf{v} + \int \tilde{\mathcal{H}} \, d\Omega, \quad \bar{\mathcal{H}} = \sum_{i=1}^{4N} m_i^3 \Phi(\hat{f}_i), \quad \tilde{\mathcal{H}} = \sum_{(i,j) \in D_R} \Psi_{ij}(I_{ij}),$$

$$\Phi(x) = x \log x,$$

$$\Psi_{ij}(x) = \frac{1}{ch\nu_{ij}} \left[x \log \frac{\beta_{ij}x}{\alpha_{ij}} - \left(\frac{\alpha_{ij}}{\beta_{ij}} + x \right) \log \left(1 + \frac{\beta_{ij}x}{\alpha_{ij}} \right) \right],$$
(5.16)

and easy calculations show that all Φ and Ψ_{ij} are strictly convex functions of their (positive) argument, i.e., $\Phi''(x) > 0$ and $\Psi''_{ij}(x) > 0$ for any $x > 0$. Define analogously

$$\mathcal{E}[\vec{f}, \vec{I}] = \int \bar{\mathcal{E}} \, d\mathbf{v} + \int \tilde{\mathcal{E}} \, d\Omega,$$

$$\bar{\mathcal{E}} = \sum_{i=1}^{4N} \left(\frac{1}{2} m_i v^2 + E_i \right) f_i(\mathbf{v}), \quad \tilde{\mathcal{E}} = \frac{1}{c} \sum_{(i,j) \in D_R} I_{ij}(\Omega),$$
(5.17)

which coincides with the energy density $\frac{3}{2}nK_B T + U^* + U_p$, constant during evolution. Resorting to (4.6) and (4.11) one can calculate

$$-K_B \left(\frac{\partial \bar{\mathcal{H}}}{\partial f_i} \right)^M = \frac{1}{T^M} \left(\frac{\partial \bar{\mathcal{E}}}{\partial f_i} \right)^M - K_B \left[1 - \frac{3}{2} \log(2\pi K_B T^M) + \frac{E_{s_i}}{K_B T^M} + \log \frac{N_{s_i}^M}{m_{s_i}^{3/2} Z_{s_i}(T^M)} \right],$$
(5.18)

from which

$$-K_B \sum_{i=1}^{4N} \int \left(\frac{\partial \bar{\mathcal{H}}}{\partial f_i} \right)^M (f_i - f_i^M) \, d\mathbf{v}$$

$$= \frac{1}{T^M} \sum_{i=1}^{4N} \int \left(\frac{\partial \bar{\mathcal{E}}}{\partial f_i} \right)^M (f_i - f_i^M) \, d\mathbf{v}$$

$$- K_B \left[\frac{1}{K_B T^M} \sum_{s=1}^4 E_s (N_s - N_s^M) + \sum_{s=1}^4 (N_s - N_s^M) \log \frac{N_s^M}{m_s^{3/2} Z_s(T^M)} \right].$$
(5.19)

But $N_1 - N_1^M = N_2 - N_2^M = -(N_3 - N_3^M) = -(N_4 - N_4^M)$, because of (5.3), and

$$\log \frac{N_1^M}{m_1^{3/2} Z_1^M} + \log \frac{N_2^M}{m_2^{3/2} Z_2^M} - \log \frac{N_3^M}{m_3^{3/2} Z_3^M} - \log \frac{N_4^M}{m_4^{3/2} Z_4^M} = \frac{\Delta E}{K_B T^M} \quad (5.20)$$

in force of the mass action law (4.12), so that the square bracket in (5.19) vanishes. On the other hand, from Planck's law (4.9)

$$-K_B \left(\frac{\partial \tilde{\mathcal{H}}}{\partial I_{ij}} \right)^M = -\frac{K_B}{ch\nu_{ij}} \left(-\frac{E_j - E_i}{K_B T^M} \right) = \frac{1}{T^M} \frac{1}{c} = \frac{1}{T^M} \left(\frac{\partial \tilde{\mathcal{E}}}{\partial I_{ij}} \right)^M. \quad (5.21)$$

Moreover, both $\bar{\mathcal{E}}$ and $\tilde{\mathcal{E}}$ are homogeneous functions of order 1 in their variables f_i and I_{ij} , so that

$$\mathcal{E}[\vec{f}, \vec{I}] = \sum_{i=1}^{4N} \int f_i \frac{\partial \bar{\mathcal{E}}}{\partial f_i} d\mathbf{v} + \sum_{(i,j) \in D_R} \int I_{ij} \frac{\partial \tilde{\mathcal{E}}}{\partial I_{ij}} d\Omega, \quad (5.22)$$

and, since \mathcal{E} is a first integral itself, $\mathcal{E}[\vec{f}, \vec{I}] = \mathcal{E}[\vec{f}^M, \vec{I}^M]$, or

$$\sum_{i=1}^{4N} \int \left(\frac{\partial \bar{\mathcal{E}}}{\partial f_i} \right)^M (f_i - f_i^M) d\mathbf{v} + \sum_{(i,j) \in D_R} \int \left(\frac{\partial \tilde{\mathcal{E}}}{\partial I_{ij}} \right)^M (I_{ij} - I_{ij}^M) d\Omega = 0. \quad (5.23)$$

Owing to (5.19) and (5.21), and recalling (5.16), we may write

$$\sum_{i=1}^{4N} m_i^3 \int \Phi'(\hat{f}_i^M) (\hat{f}_i - \hat{f}_i^M) d\mathbf{v} + \sum_{(i,j) \in D_R} \int \Psi'(I_{ij}^M) (I_{ij} - I_{ij}^M) d\Omega = 0. \quad (5.24)$$

Therefore, the difference

$$\begin{aligned} & H[\vec{f}, \vec{I}] - H[\vec{f}^M, \vec{I}^M] \\ &= \sum_{i=1}^{4N} m_i^3 \int [\Phi(\hat{f}_i) - \Phi(\hat{f}_i^M)] d\mathbf{v} + \sum_{(i,j) \in D_R} \int [\Psi_{ij}(I_{ij}) - \Psi_{ij}(I_{ij}^M)] d\Omega, \end{aligned} \quad (5.25)$$

may be recast as

$$\begin{aligned} & H[\vec{f}, \vec{I}] - H[\vec{f}^M, \vec{I}^M] \\ &= \sum_{i=1}^{4N} m_i^3 \int [\Phi(\hat{f}_i) - \Phi^L(\hat{f}_i)] d\mathbf{v} + \sum_{(i,j) \in D_R} \int [\Psi_{ij}(I_{ij}) - \Psi_{ij}^L(I_{ij})] d\Omega, \end{aligned} \quad (5.26)$$

where Φ^L and Ψ_{ij}^L denote the first-order Taylor polynomial of Φ and Ψ_{ij} , respectively, relevant to \hat{f}_i^M and I_{ij}^M ,

$$\begin{aligned} \Phi^L(\hat{f}_i) &= \Phi(\hat{f}_i^M) + \Phi'(\hat{f}_i^M) (\hat{f}_i - \hat{f}_i^M), \\ \Psi_{ij}^L(I_{ij}) &= \Psi_{ij}(I_{ij}^M) + \Psi'_{ij}(I_{ij}^M) (I_{ij} - I_{ij}^M). \end{aligned} \quad (5.27)$$

At this point convexity applies. Simply by Taylor's formula, each of the square brackets in (5.26) yields a non-negative function, positive on a set with nonzero measure, of its integration variable, unless the corresponding \widehat{f}_i or I_{ij} coincides with \widehat{f}_i^M or I_{ij}^M , in which case the integrand is identically zero. We may conclude that $H - H^M \geq 0$, with equal sign iff $(\vec{f}, \vec{I}) = (\vec{f}^M, \vec{I}^M)$, which completes the proof of the theorem.

The previous proof shows that the minimum property of $H[\vec{f}, \vec{I}]$ at (\vec{f}^M, \vec{I}^M) is not only local, but also global, i.e., it holds in the whole class of distribution functions which satisfy the required conservation equations. We have thus

Corollary 5.3. The equilibrium, which theorem 5.1 is about, is unique.

Suppose, in fact, that a second equilibrium exists. By applying twice theorem 5.2, we deduce that H at the second equilibrium must be simultaneously larger and smaller than H at the first equilibrium, which is evidently a contradiction.

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