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THE MAXWELL-STEFAN DIFFUSION LIMIT FOR A KINETIC MODEL OF MIXTURES WITH GENERAL CROSS SECTIONS

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ABSTRACT. In this article, we derive the Maxwell-Stefan formalism from the Boltzmann equation for mixtures for general cross-sections. The derivation uses the Hilbert asymptotic method for systems at low Knudsen and Mach numbers. We also formally prove that the Maxwell-Stefan coefficients can be linked to the direct linearized Boltzmann operator for mixtures. That allows to compute the values of the Maxwell-Stefan diffusion coefficients with explicit and simple formulae with respect to the cross-sections. We also justify the specific ansatz we use thanks to the so-called moment method.

1. INTRODUCTION AND MOTIVATIONS

The study of mass transport in a gaseous mixture is one of the oldest topics investigated in mechanics and thermodynamics. The earliest contributions about mass transport by diffusion can be traced back to the nineteenth century: Graham [26], Fick [21], Maxwell [37], Stefan [44], to name a few, but probably the most celebrated ones. Later on, in 1968, Onsager's Nobel prize consecrated decisive works regarding thermodynamic aspects of such mass transport. An intrinsic difficulty consists in understanding the various diffusion laws previously introduced. In particular, the eagerness to identify both liquid and gas diffusions as a molecular mechanism can be interpreted as a mean to prove the existence of atoms as constitutive elements of matter. From this point of view, Perrin obtained his Nobel prize in 1926 for his early works [40] about the Brownian motion, hence clearly focused on diffusion, but awarded as a decisive contribution to the proof of matter discontinuity, linked to the discussion about atoms.

Diffusion is always a motion of a chemical species through something else, which can be either other chemical species, surrounding solvent particles, or solid systems. Consequently, diffusion phenomena for liquids and solids often distinguish from the gaseous ones. In the first case, the species of interest is not the dominant element: the solvent (water, for instance) or the solid matrix (crystallographic body) is the main matter inside which the transport takes place. As a consequence, in a liquid or a solid, there is in general no notion of spatial inhomogeneity (and hence no gradient of matter quantity) of the surrounding background. Hence, any phenomenological law for transport only takes into account the gradient of the transported species itself. This situation, which is specific to liquids or solids, is very different in the case of gaseous diffusion.

Since it models some kind of motion, gaseous diffusion needs to be linked to forces. This is not a simple problem, resulting from Newton's law for motion. Indeed, the difficulty mainly lies in the facts that it is sometimes difficult to define the systems of which the movement must be explained, and that the forces they undergo take place at the molecular level, where the deterministic viewpoint must be replaced by random and statistical considerations.

Among the most ancient problems regarding mass transport in mixtures lies the surprising debate between Fick and Maxwell-Stefan's laws tenants. Plenty of literature has been written on the topic, and we do not pretend to provide any kind of review regarding it in this article. The presentations of these laws are either essentially phenomenological (Maxwell-Stefan) or theoretically axiomatic (Fick, with Onsager's contributions). Let us just mention one example of the controversy: Duncan and

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Toor [20] investigate three-species gaseous mixtures, and point out the possibility of transport of a species when it has no initial gradient (of quantity of matter) *as an original phenomenon*, whereas it is quite clear that the Onsager theory allows it.

The striking formal analogy between Fick and Maxwell-Stefan formulations incites some authors to state that both approaches are the same one. They propose numerical methods to link the physical coefficients in both formulations, see for instance [23, 3]. But such a unification remains quite unclear: the physical reasons invoked to derive the regimes do not really match. Indeed, Fick deals with mass conservations and Maxwell-Stefan with momentum equations. Moreover, it is restricted to the computation of the Maxwell-Stefan coefficients from the Fick ones and not the converse, since, so far, up to our knowledge, no computation of the Maxwell-Stefan coefficients were available from the Boltzmann equation.

Our point of view is quite simple and constructive altogether: as far as dilute gases are concerned, any macroscopic transport phenomenon should be somehow derived from the Boltzmann equation for mixtures. Indeed, the Boltzmann equation can really take into account molecular interactions which qualitatively explain many diffusion processes. Roughly speaking, it has been proved, sometimes rigorously, for mono-species systems, that the Boltzmann equation allows to recover continuous transport processes in gases, and moreover to compute the involved physical coefficients, see [1, 2, 25, 38]. Continuing the work initiated in [7], we here show how it is possible to recover the Maxwell-Stefan formalism from the Boltzmann equation, as it is commonly known for Fick's law. A cornerstone of this work is the difference between the Chapman-Enskog development and the so-called rational extended thermodynamics, also known as the moment method. The first one leads to the Onsager/Fick formalism, and the second one to the Maxwell-Stefan theory.

The reason why one method should be preferentially used to the other also remains controversial. A key argument was given by Levermore [34] when explaining his moment closure hierarchy methodology:

> "More precisely, we seek models that properly capture the fluid dynamical regime when the mean free path is much smaller than the macroscopic length scales, while in the transition regime they give values for the momentum and energy fluxes (and other quantities) that are at least consistent with the nonnegativity of the particle density, and are thereby hopeful of the correct order of magnitude. By doing so, such models may provide a bridge over the transition regime that may be useful in the construction of hybrid fluid/kinetic simulations."

To state it by other means, the moment method, which, in our case, is also derived from the Hilbert expansion method, can be seen as a systematic way to reach gas dynamics which is neither at local equilibrium (Euler equations), nor very close to it (hydrodynamical regime which, in the mixture case, covers Fick's formalism). Such an assumption has received an important numerical agreement, as stated in [31, 32]: the moment method apparently produces equations which seem to fit an increasing rarefaction, whereas the Chapman-Enskog expansion and its continuations (Burnett) do not.

Let us discuss some more details about both diffusion theories. We must emphasize that both equations lie in the cross diffusion models, which first arose in population dynamics [43, 36, 35] and are currently widely studied from the mathematical viewpoint, see [14, 33, 18, 28] and the references therein. We deal with an ideal gas mixture constituted with $I \geq 2$ species $(\mathcal{A}_i)$. For each i, $1 \leq i \leq I$, we introduce n_i the number of molecules of $\mathcal{A}_i$, depending on time $t \in \mathbb{R}^+$ and position $x \in \mathbb{R}^3$. We also define the associated flux N_i of species $\mathcal{A}_i$. Let $\nu = \sum n_i$ be the total number of molecules in the mixture and set $\xi_i = n_i/\nu$ the mole fraction of species $\mathcal{A}_i$.

The Maxwell-Stefan equations give relationships between the fluxes and the mole fractions. They are written

$$(1) \qquad -\nu \, \nabla_x \xi_i = \sum_{j \neq i} \frac{\xi_j N_i - \xi_i N_j}{Ð_{ij}}, \quad 1 \leq i \leq I$$

where $Ð_{ij} > 0$ is the effective diffusion coefficient between species $\mathcal{A}_i$ and $\mathcal{A}_j$. For physical reasons, the diffusion coefficients are symmetric with respect to the particles exchange, *i.e.* $Ð_{ij} = Ð_{ji}$. Note that there are exactly $(I-1)$ independent equalities of type (1). The origin of (1) relies *force considerations* and stems from *momentum equations*. In fact, (1) translates, for species $\mathcal{A}_i$, the balance between the friction forces and the pressure ones. The main assumption of this model, which surely does not go by itself, is the fact that the different species have different *macroscopic velocities on macroscopic time scales*.

The thermodynamics of irreversible processes viewpoint is *apparently* very different from the Maxwell-Stefan description. It claims that the main reason for change in particle systems is not macroscopic mechanics (second Newton's law) but rather thermodynamics (principle of entropy minimization). Following this approach, a few quantities of interest (mass, momentum, energy, *etc.*) are transferred in systems because of the entropy organization. The main notion is then the one of *flux*, which usually differs from the notion of macroscopic mechanical movement). It enables the description of the spatial transfer rate. Close to equilibrium, linear considerations are invoked to model the fluxes as linear combinations of the so-called "generalized driving forces" (which actually do not have the physical dimension of a force). In general [24], fluxes are written as linear combinations of potential symmetrical gradient following

$$N_i = \sum_{j=1}^{I} \Lambda_{ij} : \nabla_x^{\mathrm{s}} \Pi_j,$$

where the symmetrical tensors N_i denote the fluxes and the symmetrized tensors $\nabla_x^{\mathrm{s}} \Pi_j$ are the potentials. The linear coefficients Λ_{ij} are, in fact, tensors, while the symbol : denotes the general tensor contraction product. The choice of fluxes and potentials is crucial, as well as the properties of the matrices Λ_{ij}. In non reactive mixtures, under isothermal conditions, the flux N_i of molecules of species $\mathcal{A}_i$ is usually written as

$$N_i = \sum_{j=1}^{I} \lambda_{ij} \nabla_x \left(\frac{\mu_j}{T} \right),$$

where μ_j are chemical potentials, and the λ_{ij} are the Onsager scalar coefficients. For ideal gases, under isothermal conditions (constant temperature T), the term $\nabla_x \left(\frac{\mu_j}{T} \right)$ reduces to $\nabla_x n_j / n_j$, and it comes

$$N_i = -\sum_{j=1}^{I} D_{ij} \nabla_x n_j,$$

where D_{ij} are the Fick coefficients. In order to enforce entropy decay, which is the main approach of the system, the Onsager scalar matrix λ_{ij} needs to be symmetrical and non positive. Finally, if we assume that the total number of molecules in the system, which is $\nu = \sum n_i$, does not depend on space and time, we can write (see also [16])

$$(2) \qquad N_i = -\nu \sum_{j=1}^{I} D_{ij} \nabla_x \xi_j,$$

with $D_{ij} = \lambda_{ij} / n_j > 0$.

Equations (1) and (2) look very similar, at least in the choice of the unknown functions. More precisely, in the Maxwell-Stefan system (1), the quantities $\nabla_x \xi_i$ are written as explicit linear combinations of the fluxes N_j, while in Fick's law (2), the fluxes N_i are explicit linear combinations

of the $\nabla_x \xi_j$. This analogy between Maxwell-Stefan and Fick formulations has conducted people to postulate a relation between the coefficients. The main reason to unify both formulations lies on microscopic considerations about colliding molecules. If we trust any of the above equations, they need to describe the same phenomena at the microscopic level. However, though formulations (1) and (2) are matricially inverse to each other, inversion does not go by itself [24, 3], and the question of the physical justification is often eluded. This can be explained by the fact that axiomatic macroscopic diffusion theories cannot provide enough information on the diffusion coefficients to deduce some relevant mathematical properties on the involved matrices of coefficients. Moreover, whereas Fick and Maxwell-Stefan's processes naturally originate from micro-collisions between molecules, they *do not belong to the same regime*. Note that [13, 4] provides a discussion about possible diffusion models in the lung, and that the Maxwell-Stefan equations were mathematically studied in [3, 6, 29], and eventually coupled with the Navier-Stokes equations [15], whereas Fick's law was investigated for instance in [24, 3] and many references therein.

In this article, we show how it is possible to derive the Maxwell-Stefan formalism from the Boltzmann equation modelling particles mixtures. The kinetic model, presented in various forms in [22, 19, 12, 7] and mathematically investigated in [5, 17, 11, 10], is first described in Section 2. The derivation is then performed in Section 3, by using the Hilbert asymptotic method for systems at low Knudsen and Mach numbers. We also formally prove that the Maxwell-Stefan coefficients can be straightforwardly linked to the direct linearized Boltzmann operator for mixtures. That allows us to provide the values of the Maxwell-Stefan coefficients with explicit and simple formulae with respect to the cross-sections. For the model derivation, we use a specific ansatz which we justify in Appendix A thanks to the moment method [34].

The present work is the natural continuation of [7], but with the notable fact that it completes the efficiency of the method to any kind of molecules interactions (with Grad's cutoff assumption) and not only Maxwellian molecules. Let us also mention the work in [27], where the authors choose a particular form of analytic cross sections, and perform explicit computations of the Maxwell-Stefan diffusion coefficients.

2. KINETIC MODEL FOR MONATOMIC GASEOUS MIXTURES

We first introduce the kinetic setting for monatomic gaseous mixtures. For each species $\mathcal{A}_i$ of molecular mass m_i, the unknown function is the number density function f_i. This function depends on space coordinates $x \in \mathbb{R}^3$ (or any subdomain of interest), time $t \geq 0$, and velocity $v \in \mathbb{R}^3$. More precisely, $f_i(t, x, v) \, \mathrm{d}x \, \mathrm{d}v$ is the number of molecules of species $\mathcal{A}_i$ in the mixture, at time t in an elementary volume of the space phase of size $\mathrm{d}x \, \mathrm{d}v$ centred at (x, v). The number density functions satisfy the Boltzmann equations, which read as follows, for any $i \in [\![1, I]\!]$,

$$(3) \qquad \partial_t f_i + v \cdot \nabla_x f_i = \sum_{j=1}^{I} Q_{ij}(f_i, f_j) \quad \text{on } \mathbb{R}^3 \times \mathbb{R}_+^* \times \mathbb{R}^3,$$

where the notation $[\![1, I]\!]$ denotes $[1, I] \cap \mathbb{N}$. These equations can also be written in a vector sense as

$$\partial_t f + v \cdot \nabla_x f = Q(f, f) \quad \text{on } \mathbb{R}^3 \times \mathbb{R}_+^* \times \mathbb{R}^3,$$

where $f = (f_1, \cdots, f_I)^\mathsf{T}$ and

$$Q(f, f) = \left(\sum_{j=1}^{I} Q_{1j}(f_1, f_j), \cdots, \sum_{j=1}^{I} Q_{Ij}(f_I, f_j) \right)^\mathsf{T}.$$

To specify the operator $Q(f, f)$, we first need to describe the collision mechanism between two molecules of species $\mathcal{A}_i$ and $\mathcal{A}_j$, $1 \leq i, j \leq I$, with respective pre-collisional velocities v', v'_*. After

a collision, their velocities are denoted by v and v_*. Since the collisions are supposed to be elastic, both momentum and kinetic energy are conserved, i.e.

$$(4) \qquad m_i v' + m_j v'_* = m_i v + m_j v_*, \qquad \frac{1}{2} m_i |v'|^2 + \frac{1}{2} m_j |v'_*|^2 = \frac{1}{2} m_i |v|^2 + \frac{1}{2} m_j |v_*|^2.$$

It is then standard, from (4), to write v' and v'_* as

$$(5) \quad v' = \frac{1}{m_i + m_j}(m_i v + m_j v_* + m_j |v - v_*| \sigma), \qquad v'_* = \frac{1}{m_i + m_j}(m_i v + m_j v_* - m_i |v - v_*| \sigma),$$

where $\sigma \in \mathbb{S}^2$ is a parameter taking into account both degrees of freedom allowed by (4). Denoting

$$\pi_{ij}(v, v_*, \sigma) := v' = \frac{1}{m_i + m_j}(m_i v + m_j v_* + m_j |v - v_*| \sigma),$$

it is straightforward to check that, for any vector $w \in \mathbb{R}^3$ and rotation $\Theta \in \mathrm{O}^+(\mathbb{R}^3)$,

$$(6) \quad \pi_{ij}(v + w, v_* + w, \sigma) = \pi_{ij}(v, v_*, \sigma) + w, \qquad \pi_{ij}(\Theta v, \Theta v_*, \Theta \sigma) = \Theta \pi_{ij}(v, v_*, \sigma), \qquad \forall v, v_*, \sigma,$$

where $\mathrm{O}^+(\mathbb{R}^3)$ denotes the three-dimensional rotation group. This observation will be useful in the sequel.

The microscopic equalities (5) are used in the expressions of the collision operators Q_{ij}, describing the interactions between molecules of species $\mathcal{A}_i$ and $\mathcal{A}_j$, $1 \leq i, j \leq I$. For any functions f, $g : \mathbb{R}^3 \to \mathbb{R}_+$, we define the following operator

$$(7) \qquad Q_{ij}(f, g)(v) = \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} B_{ij}(v, v_*, \sigma) \big[f(v') g(v'_*) - f(v) g(v_*) \big] \, d\sigma \, dv_*,$$

where v' and v'_*, are defined through (5), and the cross section B_{ij} satisfies the microreversibility assumptions $B_{ij}(v, v_*, \sigma) = B_{ji}(v_*, v, \sigma)$ and $B_{ij}(v, v_*, \sigma) = B_{ij}(v', v'_*, \sigma)$.

It is worthwhile noting that the operator describing the collisions of molecules of species $\mathcal{A}_j$ with molecules of species $\mathcal{A}_i$ is not defined using (5), but involving the symmetrical pre-collisional velocities w' and w'_* given by

$$w' = \frac{1}{m_i + m_j}(m_j v + m_i v_* + m_i |v - v_*| \sigma), \qquad w'_* = \frac{1}{m_i + m_j}(m_j v + m_i v_* - m_j |v - v_*| \sigma).$$

Consequently, we have

$$Q_{ji}(g, f)(v) = \int_{\mathbb{R}^3} \int_{\mathbb{S}^2} B_{ji}(v, v_*, \sigma) \big[g(w') f(w'_*) - g(v) f(v_*) \big] \, d\sigma \, dv_*.$$

Let us emphasize that the main difference of this work with [7] lies in the fact that we deal with general cross-sections with angular cut-off, instead of the simpler case of Maxwell molecules. The cross sections are only assumed to satisfy the standard Galilean invariance properties: for any i, j, vector $w \in \mathbb{R}^3$, and rotation $\Theta \in \mathrm{O}^+(\mathbb{R}^3)$, we have

$$(8) \qquad B_{ij}(v + w, v_* + w, \sigma) = B_{ij}(v, v_*, \sigma), \quad B_{ij}(\Theta v, \Theta v_*, \Theta \sigma) = B_{ij}(v, v_*, \sigma), \quad \forall v, v_*, \sigma.$$

Further notations are useful to write standard weak formulations of the collision operators. We set, for any g, $h \in L^2(\mathbb{R}^3)$,

$$(9) \qquad \langle g, h \rangle = \int_{\mathbb{R}^3} g(v) h(v) \, dv,$$

and, for any g, $h \in L^2(\mathbb{R}^3)^I$,

$$(10) \qquad \langle g, h \rangle_I = \sum_{i=1}^{I} \langle g_i, h_i \rangle.$$

Note that both previous notations can also be defined if h or its components take their values in the velocity space $\mathbb{R}^3$. They can also be extended, in a duality sense, whenever the products gh in (9) or $g_i h_i$ in (10) are in $L^1(\mathbb{R}^3)$. That allows to write, for any relevant test-function ψ, scalar or vector-valued,

$$(11) \qquad \langle Q_{ij}(f,g), \psi \rangle = \iiint B_{ij}\, f(v)\, g(v_*)\, \left[\psi(v') - \psi(v) \right]\, \mathrm{d}\sigma\, \mathrm{d}v_*\, \mathrm{d}v,$$

$$(12) \qquad \langle Q_{ij}(f,g), \psi \rangle = -\frac{1}{2} \iiint B_{ij}\, \left[f(v')\, g(v_*') - f(v)\, g(v_*) \right]\, \left[\psi(v') - \psi(v) \right]\, \mathrm{d}\sigma\, \mathrm{d}v_*\, \mathrm{d}v.$$

In particular, (11)–(12) imply that, for any i and j,

$$(13) \qquad \int_{\mathbb{R}^3} Q_{ij}(f,g)(v)\, \mathrm{d}v = 0,$$

$$(14) \qquad \int_{\mathbb{R}^3} Q_{ij}(f,g)(v)\, m_i\, v\, \mathrm{d}v + \int_{\mathbb{R}^3} Q_{ji}(g,f)(v)\, m_j\, v\, \mathrm{d}v = 0,$$

$$(15) \qquad \int_{\mathbb{R}^3} Q_{ij}(f,g)(v)\, \frac{1}{2}\, m_i\, |v|^2\, \mathrm{d}v + \int_{\mathbb{R}^3} Q_{ji}(g,f)(v)\, \frac{1}{2}\, m_j\, |v|^2\, \mathrm{d}v = 0.$$

Note that, if $i = j$, (14)–(15) reduce to the classical equalities for the Boltzmann collision operator, which are

$$(16) \qquad \int_{\mathbb{R}^3} Q_{ii}(f,g)(v)\, v\, \mathrm{d}v = 0, \qquad \int_{\mathbb{R}^3} Q_{ii}(f,g)(v)\, \frac{1}{2}\, |v|^2\, \mathrm{d}v = 0.$$

More details about the monatomic mixture model, including the weak forms of the collision operators, can be found, for instance, in [7].

Before introducing the associated macroscopic equations, we set, whenever it makes sense, for any real-valued function f,

$$\overline{f} = \int_{\mathbb{R}^3} f(v)\, \mathrm{d}v,$$

and, for any vector-valued function $f = (f_1, \cdots, f_I)$,

$$\overline{f} = \sum_{i=1}^{I} \overline{f_i}.$$

We define, for any i, the following macroscopic quantities as moments of the distribution function f_i, i.e.

$$n_i = \overline{f_i} = \int_{\mathbb{R}^3} f_i(v)\, \mathrm{d}v, \qquad n_i u_i = \overline{v f_i} = \int_{\mathbb{R}^3} v f_i(v)\, \mathrm{d}v,$$

where n_i is the number of molecules of species $\mathcal{A}_i$, and u_i is its associated macroscopic velocity. Then we denote by $\rho_i = m_i n_i$ the total mass of molecules of species $\mathcal{A}_i$, and define the total energy of the mixture

$$\mathcal{E} = \frac{1}{2} \sum_{i=1}^{I} m_i \overline{v^2 f_i} = \frac{1}{2} \sum_{i=1}^{I} \int_{\mathbb{R}^3} m_i v^2 f_i(v)\, \mathrm{d}v.$$

From these quantities, we introduce the total number of molecules $\nu = \sum n_i$, the total mass of the mixture $\rho = \sum \rho_i$, the molar bulk velocity $u = \sum n_i u_i / \nu$, and eventually the mixture temperature T thanks to the formula $\mathcal{E} = 1/2 \rho u^2 + 3/2 \nu k_B T$.

We can choose to write f_i as a local Maxwellian in the velocity variable, i.e. with the form
(17)
$$f_i(t,x,v) = n_i(t,x) \left(\frac{m_i}{2\pi k_B T(t,x)} \right)^{3/2} \exp\left(-\frac{m_i |v - u_i(t,x)|^2}{2 k_B T(t,x)} \right), \quad x \in \mathbb{R}^3, \quad t > 0, \quad v \in \mathbb{R}^3.$$

This corresponds to assuming small values of the Knudsen number. If we force the Boltzmann equations (3) with this family of functions, then, after integration over the kinetic functions for individual mass, individual velocity and total energy, it is straightforward to check that, for any i,

$$(18) \qquad \partial_t n_i + \nabla_x \cdot (n_i u_i) = 0,$$

$$(19) \qquad \partial_t(\rho_i u_i) + \nabla_x \cdot (\rho_i u_i \otimes u_i) + \nabla_x (k_B T n_i) = \sum_{j \neq i} \int_{\mathbb{R}^3} m_i v \, Q_{ij}(f_i, f_j)(v) \, \mathrm{d}v,$$

$$(20) \qquad \partial_t \mathcal{E} + \nabla_x \cdot ((\mathcal{E} + \nu k_B T) u) = 0,$$

where the term with $j = i$ vanishes in the right-hand side of (19) thanks to the conservation properties of the mono-species collision operators (16). The choice of Ansatz (17) and the computation of the above moment equations (18)–(20) are discussed in Section A and in Appendix A.2. The remaining question is the computation of the right-hand side term of (19), which is performed in the next section, in the limit of vanishing Mach numbers.

3. Computations of the Maxwell-Stefan diffusion coefficients

Let us now study the diffusion asymptotics of the Boltzmann equations for mixtures, which will allow to obtain expressions of the Maxwell-Stefan diffusion coefficients with respect to general cross-sections (B_{ij}) while recovering the symmetry feature and the nonnegativity of the $(Đ_{ij})$.

3.1. **Scaling the Boltzmann equations.** We use the mean free path $\varepsilon > 0$ as the asymptotic parameter to reach the classical diffusion limit (i.e. we perform the classical diffusive scaling in the Boltzmann equation $x = \tilde{x}/\varepsilon$, $t = \tilde{t}/\varepsilon^2$). In this setting, we also assume that both Knudsen and Mach numbers are of order ε.

If we denote $f^\varepsilon = (f_1^\varepsilon, \cdots, f_I^\varepsilon)$ the unknown function (the $\sim$ notations for x and t are then dropped), we can write

$$(21) \qquad \varepsilon \, \partial_t f_i^\varepsilon + v \cdot \nabla_x f_i^\varepsilon = \frac{1}{\varepsilon} \sum_{j=1}^I Q_{ij}(f_i^\varepsilon, f_j^\varepsilon), \quad \text{on } \mathbb{R}^3 \times \mathbb{R}_+^* \times \mathbb{R}^3, \qquad 1 \leq i \leq I.$$

The penalisation by $1/\varepsilon$ on the right-hand side term of (21) implies that f^ε is close to the global equilibrium. Following Ansatz (17), if we moreover consider small values of the Mach number, we can assume that

$$(22)$$
$$f_i^\varepsilon(t, x, v) = n_i^\varepsilon(t, x) \left(\frac{m_i}{2\pi k_B \, T^\varepsilon(t, x)} \right)^{3/2} e^{-m_i |v - \varepsilon u_i^\varepsilon(t,x)|^2 / 2k_B T^\varepsilon(t,x)}, \quad x \in \mathbb{R}^3, \quad t > 0, \quad v \in \mathbb{R}^3,$$

with $n_i^\varepsilon : \mathbb{R}^3 \times \mathbb{R}_+ \to \mathbb{R}_+$, $u_i^\varepsilon : \mathbb{R}^3 \times \mathbb{R}_+ \to \mathbb{R}^3$, for $1 \leq i \leq I$, and $T^\varepsilon : \mathbb{R}^3 \times \mathbb{R}_+ \to \mathbb{R}_+^*$. All macroscopic quantities defined above are of order 0 in ε. Consequently, functions satisfying (22) are close to the global equilibrium. It is the same framework as in [7].

In the same way as we got the moment equations (18)–(20) from Ansatz (17), we can obtain the following system from the scaled Ansatz (22). Note that, obviously, those moment equations can also be built from (18)–(20) with the classical diffusive scaling. Hence, in the same way as we defined f^ε from f, we add the dependence with respect to ε on all the notations defined at the end of Section 2 for the macroscopic quantities. Consequently, that allows us to write, for any i,

$$\varepsilon \partial_t n_i^\varepsilon + \varepsilon \nabla_x (n_i^\varepsilon u_i^\varepsilon) = 0,$$

$$\varepsilon^2 \partial_t(\rho_i^\varepsilon n_i^\varepsilon u_i^\varepsilon) + \nabla_x \cdot (\varepsilon^2 \rho_i^\varepsilon u_i^\varepsilon \otimes u_i^\varepsilon) + \nabla_x(k_B T^\varepsilon n_i^\varepsilon) = \frac{1}{\varepsilon} \sum_{j \neq i} \langle Q_{ij}(f_i^\varepsilon, f_j^\varepsilon), m_i v \rangle,$$

$$\varepsilon \partial_t(\varepsilon^2 \rho^\varepsilon u^{\varepsilon 2} + 3k_B T^\varepsilon \nu^\varepsilon) + \varepsilon \nabla_x \cdot [(\varepsilon^2 \rho^\varepsilon (u^\varepsilon)^2 + 5k_B T^\varepsilon \nu^\varepsilon) u^\varepsilon] = 0.$$

If we only keep the leading order in ε in the previous equations, we immediately get

$$(23) \qquad \partial_t n_i^\varepsilon + \nabla_x (n_i^\varepsilon u_i^\varepsilon) = 0,$$

$$(24) \qquad \nabla_x (k_B T^\varepsilon n_i^\varepsilon) = \frac{1}{\varepsilon} \sum_{j \neq i} \langle Q_{ij}(f_i^\varepsilon, f_j^\varepsilon), m_i v \rangle,$$

$$(25) \qquad \partial_t (3 k_B T^\varepsilon \nu^\varepsilon) + \nabla_x \cdot (5 k_B T^\varepsilon \nu^\varepsilon u^\varepsilon) = 0.$$

Then, summing over all indices i, we get, from (23)–(24) the mass and momentum equations for the whole mixture, i.e.

$$(26) \qquad \partial_t \nu^\varepsilon + \nabla_x \cdot (\nu^\varepsilon u^\varepsilon) \;=\; 0,$$

$$(27) \qquad \nabla_x (k_B T^\varepsilon \nu^\varepsilon) \;=\; 0,$$

where we used the momentum conservations for the collision operators (14) to write (27).

Let us now assume that the mixture temperature does not depend on space and time, and consequently on ε. Eqns. (25)–(27) then clearly implies that

$$\partial_t \nu^\varepsilon = 0, \qquad \nabla_x \nu^\varepsilon = 0, \qquad \nabla_x \cdot u^\varepsilon = 0,$$

which means that the total number of molecules ν does not depend on space and time, as the temperature itself, while the system is incompressible, and the total pressure $\nu k_B T$ is of course constant. This kind of physical setting is usually called *equimolar diffusion* [30].

Finally, with the isothermal assumption, (23)–(24) become, for any i,

$$(28) \qquad \partial_t n_i^\varepsilon + \nabla_x \cdot (n_i^\varepsilon u_i^\varepsilon) \;=\; 0,$$

$$(29) \qquad \nabla_x n_i^\varepsilon \;=\; \frac{1}{\varepsilon k_B T} \sum_{j \neq i} \int_{\mathbb{R}^3} m_i v \, Q_{ij}(f_i^\varepsilon, f_j^\varepsilon)(v) \, \mathrm{d}v.$$

3.2. Diffusion limit and diffusion coefficients.
Assume that, at least formally, for each i, n_i^ε, u_i^ε and $n_i^\varepsilon u_i^\varepsilon$ respectively converge towards n_i, u_i and N_i when ε goes to 0. We first recover the conservation law for the quantity of matter of each species by letting ε go to 0 in (28), to get

$$\partial_t n_i + \nabla_x \cdot N_i = 0.$$

The limit of (29) is more intricate. Indeed, the main difference with [7] is the computation of the limit of the collision term in the right hand side of (29), for which we do not have an explicit form of the cross section anymore. Let us set, for any i, j, with $i \neq j$,

$$F_{ij}^\varepsilon(\varepsilon u_i^\varepsilon, \varepsilon u_j^\varepsilon) = \int_{\mathbb{R}^3} m_i v \, Q_{ij}(f_i^\varepsilon, f_j^\varepsilon)(v) \, \mathrm{d}v.$$

In the sequel, we prove, at the formal level, that there exists $\alpha_{ij} \in \mathbb{R}$ such that

$$\lim_{\varepsilon \to 0} \frac{F_{ij}^\varepsilon(\varepsilon u_i^\varepsilon, \varepsilon u_j^\varepsilon)}{\varepsilon} = \alpha_{ij}(u_i - u_j).$$

This eventually ensures both the existence and the "explicit" expression of the Maxwell-Stefan diffusion coefficients $Đ_{ij}$ since, at the limit of vanishing ε, the momentum equations (29) take the classical form (1) of the Maxwell-Stefan equations.

The rest of this subsection is devoted to the computations of the limit, when ε goes to 0, of the quantity $F_{ij}^\varepsilon(\varepsilon u_i^\varepsilon, \varepsilon u_j^\varepsilon)/\varepsilon$. Two useful integral expressions of the Maxwell-Stefan diffusion coefficients are detailed in the following proposition.

Proposition 1. *The Maxwell-Stefan binary diffusion coefficients are given by*

$$\frac{1}{\nu Đ_{ij}} = \frac{1}{6(k_B T)^2} \left(\frac{m_i}{2\pi k_B T} \right)^{3/2} \left(\frac{m_j}{2\pi k_B T} \right)^{3/2}$$

$$(30) \qquad \iiint B_{ij}(v, v_*, \sigma) \exp\left[-\frac{m_i}{2k_B T}v^2 - \frac{m_j}{2k_B T}{v_*}^2\right] [m_i(v' - v)]^2 \, \mathrm{d}\sigma \, \mathrm{d}v_* \, \mathrm{d}v$$

$$= \frac{m_i m_j}{6(k_B T)^2 (m_i + m_j)} \left(\frac{m_i}{2\pi k_B T}\right)^{3/2} \left(\frac{m_j}{2\pi k_B T}\right)^{3/2}$$

$$(31) \qquad \iiint B_{ij}(v, v_*, \sigma) \exp\left[-\frac{m_i}{2k_B T}v^2 - \frac{m_j}{2k_B T}{v_*}^2\right] (v - v_* + |v - v_*|\sigma) \cdot (m_i v - m_j v_*) \, \mathrm{d}\sigma \, \mathrm{d}v_* \, \mathrm{d}v.$$

We must emphasize that (30) ensures the nonnegativity of the coefficients, while (31) allows to check their symmetry property.

Let us now focus on the formal proof of Proposition 1, with the study of $F_{ij}^\varepsilon(\varepsilon u_i^\varepsilon, \varepsilon u_j^\varepsilon)/\varepsilon$. Using Ansatz (22) and (11) with $\psi(v) = m_i v$, we can write

$$F_{ij}^\varepsilon(\varepsilon u_i^\varepsilon, \varepsilon u_j^\varepsilon) = \left(\frac{m_i}{2\pi k_B T}\right)^{3/2} \left(\frac{m_j}{2\pi k_B T}\right)^{3/2} n_i^\varepsilon n_j^\varepsilon$$

$$\iint_{\mathbb{R}^6} \int_{\mathbb{S}^2} B_{ij}(v, v_*, \sigma) \exp\left[-\frac{m_i}{2k_B T}(v - \varepsilon u_i^\varepsilon)^2\right] \exp\left[-\frac{m_j}{2k_B T}(v_* - \varepsilon u_j^\varepsilon)^2\right] m_i(v' - v) \, \mathrm{d}\sigma \, \mathrm{d}v_* \, \mathrm{d}v.$$

Let us first state some properties of F_{ij}^ε when ε is fixed, which are direct consequences of the Galilean invariance properties (8) of B_{ij}, and the properties (6) of v'.

Lemma 1. *For any $\tilde{u}_1$, $\tilde{u}_2$, $w \in \mathbb{R}^3$ and $\Theta \in \mathrm{O}^+(\mathbb{R}^3)$,*

$$(32) \qquad F_{ij}^\varepsilon(\varepsilon\tilde{u}_1 + w, \varepsilon\tilde{u}_2 + w) = F_{ij}^\varepsilon(\varepsilon\tilde{u}_1, \varepsilon\tilde{u}_2), \qquad F_{ij}^\varepsilon(\varepsilon\Theta\tilde{u}_1, \varepsilon\Theta\tilde{u}_2) = \Theta F_{ij}^\varepsilon(\varepsilon\tilde{u}_1, \varepsilon\tilde{u}_2).$$

Proof. This is proven by changing variables. In the first equation, we set $V = v - w$, $V_* = v_* - w$, then write

$$\int B_{ij}(v, v_*, \sigma) \exp\left[-\frac{m_i}{2k_B T}(v - \varepsilon\tilde{u}_1 - w)^2 - \frac{m_j}{2k_B T}(v_* - \varepsilon\tilde{u}_2 - w)^2\right] m_i\left(\pi_{ij}(v, v_*, \sigma) - v\right) \mathrm{d}v \, \mathrm{d}v_* \, \mathrm{d}\sigma$$

$$= \int B_{ij}(V + w, V_* + w, \sigma) \exp\left[-\frac{m_i}{2k_B T}(V - \varepsilon\tilde{u}_1)^2 - \frac{m_j}{2k_B T}(V_* - \varepsilon\tilde{u}_2)^2\right]$$

$$m_i\left(\pi_{ij}(V + w, V_* + w, \sigma) - V - w\right) \mathrm{d}V \, \mathrm{d}V_* \, \mathrm{d}\sigma,$$

and eventually use (6) and (8). In the second one, we write $\Theta V = v$, $\Theta V_* = v_*$, $\Theta\Sigma = \sigma$, then obtain

$$\int B_{ij}(v, v_*, \sigma) \exp\left[-\frac{m_i}{2k_B T}(v - \varepsilon\Theta\tilde{u}_1)^2 - \frac{m_j}{2k_B T}(v_* - \varepsilon\Theta\tilde{u}_2)^2\right] m_i\left(\pi_{ij}(v, v_*, \sigma) - v\right) \mathrm{d}V \, \mathrm{d}V_* \, \mathrm{d}\sigma$$

$$= \int B_{ij}(\Theta V, \Theta V_*, \Theta\Sigma) \exp\left[-\frac{m_i}{2k_B T}(\Theta V - \varepsilon\Theta\tilde{u}_1)^2 - \frac{m_j}{2k_B T}(\Theta V_* - \varepsilon\Theta\tilde{u}_2)^2\right]$$

$$m_i\left(\pi_{ij}(\Theta V, \Theta V_*, \Theta\Sigma) - \Theta V\right) \mathrm{d}V \, \mathrm{d}V_* \, \mathrm{d}\Sigma,$$

use (6) and (8) again, and the fact that Θ is an isometry. Note that, in both cases, the Jacobian of the changes of variables is 1. $\qquad\square$

Let us now deal with the asymptotic behaviour of $F_{ij}^\varepsilon(\varepsilon u_i^\varepsilon, \varepsilon u_j^\varepsilon)/\varepsilon$ when ε goes to 0. Because of (32), we deduce that

$$F_{ij}^\varepsilon(\varepsilon u_i^\varepsilon, \varepsilon u_j^\varepsilon) = F_{ij}^\varepsilon(\varepsilon u_i^\varepsilon - \varepsilon u_j^\varepsilon, 0) = F_{ij}^\varepsilon(0, \varepsilon u_j^\varepsilon - \varepsilon u_i^\varepsilon).$$

We are thus led to investigate the asymptotic behaviour of

$$H_{ij}^\varepsilon(u_{ij}^\varepsilon) = \frac{1}{2\varepsilon}\left(F_{ij}^\varepsilon(\varepsilon u_{ij}^\varepsilon, 0) + F_{ij}^\varepsilon(0, -\varepsilon u_{ij}^\varepsilon)\right) = \frac{1}{\varepsilon}F_{ij}^\varepsilon(\varepsilon u_{ij}^\varepsilon, 0) = \frac{1}{\varepsilon}F_{ij}^\varepsilon(0, -\varepsilon u_{ij}^\varepsilon),$$

where we set $u_{ij}^\varepsilon = u_i^\varepsilon - u_j^\varepsilon$. Note that the previous equality also allows to define H_{ij}^ε as an operator acting on any vector of $\mathbb{R}^3$.

Let n_i, n_j, u_i and u_j denote the respective formal limits of (n_i^ε), (n_j^ε), (u_i^ε) and (u_j^ε) when ε goes to 0. More precisely, we assume that each quantity depending on ε differs from its limit by $O(\varepsilon)$.

Lemma 2. *The following equality holds at the formal level:*

$$(33) \quad H_{ij}^\varepsilon(u_{ij}^\varepsilon) = -\frac{m_i^2}{2k_BT}\left(\frac{m_i}{2\pi k_BT}\right)^{3/2}\left(\frac{m_j}{2\pi k_BT}\right)^{3/2} n_i n_j$$

$$\left[\iiiint B_{ij}(v, v_*, \sigma)\exp\left[-\frac{m_i}{2k_BT}v^2 - \frac{m_j}{2k_BT}v_*{}^2\right][(v'-v)]\otimes^2 \,\mathrm{d}\sigma\,\mathrm{d}v_*\,\mathrm{d}v\right](u_i - u_j) + O(\varepsilon).$$

Proof. Using weak form (12), we can write, for any $\tilde{u} \in \mathbb{R}^3$,

$$(34) \quad H_{ij}^\varepsilon(\tilde{u}) = -\frac{1}{\varepsilon}\left(\frac{m_i}{2\pi k_BT}\right)^{3/2}\left(\frac{m_j}{2\pi k_BT}\right)^{3/2} n_i^\varepsilon n_j^\varepsilon \iiiint B_{ij}(v, v_*, \sigma)$$

$$\left(\exp\left[-\frac{m_i}{2k_BT}(v' - \varepsilon\tilde{u})^2\right]\exp\left[-\frac{m_j}{2k_BT}v_*'{}^2\right] - \exp\left[-\frac{m_i}{2k_BT}(v - \varepsilon\tilde{u})^2\right]\exp\left[-\frac{m_j}{2k_BT}v_*{}^2\right]\right)$$

$$m_i(v' - v)\,\mathrm{d}\sigma\,\mathrm{d}v_*\,\mathrm{d}v.$$

We first use the fact that

$$\exp\left[-\frac{m_i}{2k_BT}v'^2\right]\exp\left[-\frac{m_j}{2k_BT}v_*'{}^2\right] = \exp\left[-\frac{m_i}{2k_BT}v^2\right]\exp\left[-\frac{m_j}{2k_BT}v_*{}^2\right],$$

then use the following expansions with respect to ε:

$$\exp\left[-\frac{m_i}{2k_BT}\varepsilon^2\tilde{u}^2\right] = 1 + O(\varepsilon^2), \qquad \exp\left[\frac{m_i}{k_BT}\varepsilon v' \cdot \tilde{u}\right] = 1 + \varepsilon\frac{m_i}{k_BT}v' \cdot \tilde{u} + v'^2 O(\varepsilon^2),$$

as well as the similar ones for the other exponential term. Taking $\tilde{u} = u_{ij}^\varepsilon$ in (34) implies, after simplification by ε,

$$H_{ij}^\varepsilon(u_{ij}^\varepsilon) = -\left(\frac{m_i}{2\pi k_BT}\right)^{3/2}\left(\frac{m_j}{2\pi k_BT}\right)^{3/2}(n_i + O(\varepsilon))(n_j + O(\varepsilon))$$

$$\iiiint B_{ij}(v, v_*, \sigma)\exp\left[-\frac{m_i}{2k_BT}v^2\right]\exp\left[-\frac{m_j}{2k_BT}v_*{}^2\right]$$

$$\left[\frac{m_i}{k_BT}(v' - v)\cdot(u_i - u_j) + \left(1 + |v'| + |v| + v'^2 + v^2\right)O(\varepsilon)\right]m_i(v' - v)\,\mathrm{d}\sigma\,\mathrm{d}v_*\,\mathrm{d}v.$$

The term in $O(\varepsilon)$ in the previous integral remains integrable in both variables v and v_*, thanks to the collision rule (5) and the exponential functions, so that we eventually get (33). $\qquad\square$

Remark 1. *As we shall see in the next subsection, Proposition 2 is in fact directly linked to the nonnegativity of the linearized Boltzmann operator for mixtures, see also* [17].

Lemma 3. *The following equality holds at the formal level:*

$$(35) \quad H_{ij}^\varepsilon(u_{ij}^\varepsilon) = \frac{m_i}{2k_BT}\left(\frac{m_i}{2\pi k_BT}\right)^{3/2}\left(\frac{m_j}{2\pi k_BT}\right)^{3/2} n_i n_j$$

$$\left[\iiint B_{ij}(v, v_*, \sigma) \exp\left[-\frac{m_i}{2k_BT}v^2 - \frac{m_j}{2k_BT}v_*{}^2\right] (v_* - v + |v - v_*|\sigma) \otimes (m_iv - m_jv_*) \,\mathrm{d}\sigma\,\mathrm{d}v_*\,\mathrm{d}v\right] (u_i - u_j) + O(\varepsilon).$$

Proof. The proof principle is the same as in Lemma 2. Using weak form (11), we can write, for any $\tilde{u} \in \mathbb{R}^3$,

$$H_{ij}^\varepsilon(\tilde{u}) = \frac{m_im_j}{2\varepsilon(m_i + m_j)} \left(\frac{m_i}{2\pi k_BT}\right)^{3/2} \left(\frac{m_j}{2\pi k_BT}\right)^{3/2} n_i^\varepsilon n_j^\varepsilon$$

$$\iiint B_{ij}(v, v_*, \sigma) \left(\exp\left[-\frac{m_i}{2k_BT}(v - \varepsilon\tilde{u})^2\right] \exp\left[-\frac{m_j}{2k_BT}v_*{}^2\right]\right.$$

$$\left. - \exp\left[-\frac{m_i}{2k_BT}v^2\right] \exp\left[-\frac{m_j}{2k_BT}(v_* + \varepsilon\tilde{u})^2\right]\right) (v_* - v + |v - v_*|\sigma) \,\mathrm{d}\sigma\,\mathrm{d}v_*\,\mathrm{d}v.$$

In the same way as in the proof of Lemma 2, we use expansions of the exponential terms with respect to ε to obtain

$$H_{ij}^\varepsilon(u_{ij}^\varepsilon) = \frac{m_im_j}{2(m_i + m_j)} \left(\frac{m_i}{2\pi k_BT}\right)^{3/2} \left(\frac{m_j}{2\pi k_BT}\right)^{3/2} (n_i + O(\varepsilon))(n_j + O(\varepsilon))$$

$$\iiint B_{ij}(v, v_*, \sigma) \exp\left[-\frac{m_i}{2k_BT}v^2\right] \exp\left[-\frac{m_j}{2k_BT}v_*{}^2\right]$$

$$\left[\frac{1}{k_BT}(m_iv - m_jv_*) \cdot (u_i - u_j) + \left(1 + |v| + |v_*| + v^2 + v_*{}^2\right) O(\varepsilon)\right] (v_* - v + |v - v_*|\sigma) \,\mathrm{d}\sigma\,\mathrm{d}v_*\,\mathrm{d}v.$$

We conclude again in the same way to get (35). $\qquad\square$

Equations (33) and (35) allow to define a 3×3 matrix L_{ij} which acts on $(u_i - u_j)$. This matrix inherits the same kind of properties as (32). It can thus be considered as an endomorphism of $\mathbb{R}^3$ which commutes with all the elements of $\mathrm{O}^+(\mathbb{R}^3)$. Thanks to a standard result of linear algebra (which can also be seen as a corollary of Schur's lemma), there exists $\alpha_{ij} \in \mathbb{R}$ such that $L_{ij} = \alpha_{ij}\mathbb{I}_3$, where $\mathbb{I}_3$ denotes the identity matrix of $\mathbb{R}^{3\times3}$.

Thus the non-diagonal terms of the matrix L_{ij} are zero and the diagonal terms of L_{ij} are all equal to the same constant $\alpha_{ij} \in \mathbb{R}$. Lemmas 2–3 provide several expressions of this constant, for instance,

$$\alpha_{ij} = -\frac{1}{6k_BT} \left(\frac{m_i}{2\pi k_BT}\right)^{3/2} \left(\frac{m_j}{2\pi k_BT}\right)^{3/2} n_in_j$$

$$(36) \quad \iiint B_{ij}(v, v_*, \sigma) \exp\left[-\frac{m_i}{2k_BT}v^2 - \frac{m_j}{2k_BT}v_*{}^2\right] [m_i(v' - v)]^2 \,\mathrm{d}\sigma\,\mathrm{d}v_*\,\mathrm{d}v$$

$$= \frac{m_im_j}{6k_BT(m_i + m_j)} \left(\frac{m_i}{2\pi k_BT}\right)^{3/2} \left(\frac{m_j}{2\pi k_BT}\right)^{3/2} n_in_j$$

$$(37) \quad \iiint B_{ij}(v, v_*, \sigma) \exp\left[-\frac{m_i}{2k_BT}v^2 - \frac{m_j}{2k_BT}v_*{}^2\right] (v_* - v + |v - v_*|\sigma) \cdot (m_iv - m_jv_*) \,\mathrm{d}\sigma\,\mathrm{d}v_*\,\mathrm{d}v.$$

We observe that α_{ij} and n_in_j simultaneously vanish. Thus, it is possible to define α_{ij}/n_in_j as the proportionality coefficient. That ends the proof of Proposition 1.

Besides, it is straightforward to check from (36)–(37) that $\mathcal{D}_{ij} = -(k_BTn_in_j)/(\nu\alpha_{ij})$ does not depend on t or x and is nonnegative. It also satisfies the expected symmetry property with respect to i and j, thanks to the properties of the cross sections and the change of variables $(v, v_*) \mapsto (v_*, v)$, which also induces exchanging m_i and m_j. Eventually, let us recover the Maxwell-Stefan diffusion

equations by letting ε go to 0 in (29). We immediately get, for any i,

$$\nabla_x n_i = \frac{1}{\nu} \sum_{j \neq i} \frac{n_i n_j (u_i - u_j)}{\mathcal{D}_{ij}},$$

which yields (1).

Remark 2. *Noticing that the right-hand side of (29) converges, when ε vanishes, to*

$$\frac{1}{k_B T} \sum_{j \neq i} \alpha_{ij} (u_i - u_j),$$

it is quite natural to set, for any i,

(38) $$\alpha_{ii} = -\sum_{j \neq i} \alpha_{ij},$$

so that the limit term in the right-hand side of (29) reads

$$-\frac{1}{k_B T} \sum_{j=1}^{I} \alpha_{ij} u_j.$$

That allows to define the matrix $A = (\alpha_{ij})_{1 \leq i,j \leq I} \in \mathbb{R}^{I \times I}$, which depends on (n_i), and write the asymptotics of (29), for any i, under the usual matrix form [24]

$$\nabla_x n_i = -\frac{1}{k_B T} [AU]_i,$$

where U denotes the column vector $(u_1, \cdots, u_I)^\mathsf{T}$.

It is then clear that A is symmetric, negative semi-definite, and $\operatorname{rank} A = I - 1$. The symmetry is straightforwardly obtained from (37). Moreover, we can compute, for any $U \in \mathbb{R}^I$,

$$AU \cdot U = \sum_{i,j} \alpha_{ij} u_i u_j = \sum_i \sum_{j \neq i} \alpha_{ij} u_i (u_j - u_i) = -\frac{1}{2} \sum_{i,j} \alpha_{ij} (u_i - u_j)^2.$$

The previous equality, together with (36), ensures that A is negative semi-definite, and its nullspace is spanned, in $\mathbb{R}^I$, by $(1, \cdots, 1)^\mathsf{T}$. The value of $\operatorname{rank} A$ immediately follows.

Remark 3. *Of course, we can recover the expression of $\mathcal{D}_{ij}$ found in [7] for Maxwell molecules cross sections. In that case, each cross section B_{ij} depends on v, v_* and σ only through the cosine of the deviation angle $\theta \in [0, \pi]$ between $v - v_*$ and σ. Hence, for each (i,j) with $i \neq j$, we can write, under Grad's angular cutoff assumption,*

$$B_{ij}(v, v_*, \sigma) = b_{ij}(\cos \theta),$$

where $b_{ij} \in L^1(-1, 1)$ and $b_{ij} > 0$. Then (30) reduces to

$$\frac{1}{\mathcal{D}_{ij}} = \nu \left(\frac{m_i}{2\pi k_B T} \right)^{3/2} \left(\frac{m_j}{2\pi k_B T} \right)^{3/2} \frac{m_i m_j}{6(m_i + m_j)(k_B T)^2}$$
$$\|b_{ij}\|_{L^1} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \exp \left[-\frac{m_i}{2k_B T} v^2 - \frac{m_j}{2k_B T} v_*^2 \right] \left(m_i v^2 + m_j v_*^2 \right) \, \mathrm{d}v_* \, \mathrm{d}v.$$

Integration by parts on each coordinate of v and v_* allows to recover

$$\mathcal{D}_{ij} = \frac{(m_i + m_j) k_B T}{2\pi \, m_i m_j \nu \|b_{ij}\|_{L^1}}.$$

Besides, we can also recover the expression of $Đ_{ij}$ found in [27] for analytic factorized cross sections under Grad's angular cutoff assumption. In this case, the cross sections B_{ij} are supposed to be of the form

$$B_{ij}(v, v_*, \sigma) = \Phi(|v - v_*|) b_{ij}(\cos \theta),$$

where there exists a family $(a_n)_{n \in \mathbb{N}^*} \subset \mathbb{R}$ such that Φ can be written as a uniformly converging even power series:

$$\Phi(|v - v_*|) = \sum_{n \in \mathbb{N}^*} a_n |v - v_*|^{2n}.$$

Then the integrals in (31) can be more explicitly computed and lead to the coefficients given in [27, Theorem 2].

3.3. **Diffusion coefficients and linearized Boltzmann operator.** Eventually, we need a more convenient way to compare the Fick and Maxwell-Stefan coefficients. It is done by involving the linearized Boltzmann operator for mixtures. Whereas it is well-known that the Fick coefficients are related to the inverse operator, see [12] for instance, we show below how the Maxwell-Stefan coefficients depend on the direct operator.

Let us first recall a suitable definition of the linearized Boltzmann operator for mixtures in a L^2-setting. Consider given numbers of particles $n_1, \ldots, n_I$ of each species. Define the perturbation function $g = (g_1, \cdots, g_I)$ to the global equilibrium $(n_1 \mathcal{M}_1, \cdots, n_I \mathcal{M}_I)$ by

$$f_i = n_i \mathcal{M}_i + n_i \mathcal{M}_i^{1/2} g_i, \qquad 1 \leq i \leq I,$$

where we have denoted by $\mathcal{M}_i$ the normalized centred Maxwellian function related to species $\mathcal{A}_i$, i.e.

$$\mathcal{M}_i(v) = \left(\frac{m_i}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{m_i v^2}{2 k_B T} \right), \quad v \in \mathbb{R}^3.$$

Note that we obviously have $\sum_{j=1}^I Q_{ij}(n_i \mathcal{M}_i, n_j \mathcal{M}_j) = 0$ for any $1 \leq i \leq I$. The linearized Boltzmann operator $\mathcal{L}$ can then be defined as in [5, 8], so that $\mathcal{L}$ can be considered as an operator $L^2(\mathbb{R}^3)^I \to L^2(\mathbb{R}^3)^I$ with the standard Lebesgue product measure (without any weight). For any i, the ith component of $\mathcal{L}g$ writes

$$[\mathcal{L}g]_i = \sum_{j=1}^I n_i \, n_j \, \mathcal{M}_i^{-1/2} \left[Q_{ij}(g_i \mathcal{M}_i^{1/2}, \mathcal{M}_j) + Q_{ij}(\mathcal{M}_i, g_j \mathcal{M}_j^{1/2}) \right].$$

We can state the link between $\mathcal{L}$ and the diffusion coefficients $Đ_{ij}$, or, more precisely, with the coefficients $\alpha_{ij} = -(k_B T n_i n_j)/(\nu Đ_{ij})$.

Proposition 2. *Define, for any $i \in [\![1, I]\!]$ and $k \in \{1, 2, 3\}$,*

$$C_i^k : \mathbb{R}^3 \to \mathbb{R}^I, \ v \mapsto (0, \cdots, 0, m_i v_{(k)}, 0, \cdots, 0)^\mathsf{T},$$

where $v_{(k)}$ is the kth coordinate of v in $\mathbb{R}^3$. Then, for any i, $j \in [\![1, I]\!]$ with $i \neq j$, we have

$$(39) \qquad \qquad \alpha_{ij} = -\frac{1}{k_B T} \langle \mathcal{M}_i^{1/2} C_i^k, \mathcal{L}(\mathcal{M}_j^{1/2} C_j^k) \rangle_I, \qquad \forall k \in \{1, 2, 3\}.$$

Proof. Checking (39) is a simple verification. Let us choose $k = 1$ for instance, and fix i and j such that $j \neq i$. We first have

$$\langle \mathcal{M}_i^{1/2} C_i^1, \mathcal{L}(\mathcal{M}_j^{1/2} C_j^1) \rangle_I = \langle m_i v_{(1)} \mathcal{M}_i^{1/2}, [\mathcal{L}(\mathcal{M}_j^{1/2} C_j^1)]_i \rangle.$$

From the expression of $[\mathcal{L}g]_i$, we immediately get

$$\langle \mathcal{M}_i^{1/2} C_i^1, \mathcal{L}(\mathcal{M}_j^{1/2} C_j^1) \rangle_I$$

$$= \sum_{\ell=1}^{I} n_i n_\ell \langle m_i v_{(1)} \mathcal{M}_i^{1/2}, \mathcal{M}_i^{-1/2} \left(Q_{i\ell}(\mathcal{M}_i^{1/2} \mathcal{M}_j^{1/2} [C_j^1]_i, \mathcal{M}_\ell) + Q_{i\ell}(\mathcal{M}_i, \mathcal{M}_j^{1/2} \mathcal{M}_\ell^{1/2} [C_j^1]_\ell) \right) \rangle.$$

The term $[C_j^1]_i$ is of course zero because $i \neq j$, and the only nonzero term involving $[C_j^1]_\ell$ is the one for $\ell = j$. Consequently, we obtain

$$\langle \mathcal{M}_i^{1/2} C_i^1, \mathcal{L}(\mathcal{M}_j^{1/2} C_j^1) \rangle_I = n_i n_j \langle m_i v_{(1)}, Q_{ij}(\mathcal{M}_i, \mathcal{M}_j [C_j^1]_j) \rangle.$$

Thanks to the microscopic kinetic energy conservation in (4), we clearly have

$$\mathcal{M}_i(v') \mathcal{M}_j(v'_*) = \mathcal{M}_i(v) \mathcal{M}_j(v_*).$$

Together with the weak formulation (12) of Q_{ij} and the microscopic momentum conservation in (4), that eventually allows to write

$$\langle \mathcal{M}_i^{1/2} C_i^1, \mathcal{L}(\mathcal{M}_j^{1/2} C_j^1) \rangle_I = \frac{n_i n_j}{2} \iiint B_{ij} \left[m_i \left(v'_{(1)} - v_{(1)} \right) \right]^2 \mathcal{M}_i(v) \mathcal{M}_j(v_*) \, \mathrm{d}\sigma \, \mathrm{d}v_* \, \mathrm{d}v,$$

which yields (36). □

Remark 4. *The properties of A already mentioned in Remark 2 can also be recovered from Proposition 2 thanks to known results about $\mathcal{L}$. Indeed, the self-adjointness and nonposivity of $\mathcal{L}$, together with (39), clearly imply that A is symmetric and negative semi-definite.*

4. CONCLUSION AND PROSPECTS

Let us emphasize that the computations we perform in this article of the diffusion coefficients for a mixture of monatomic gases can surely be derived in the polyatomic case, with an equivalent of Ansatz (22). Indeed, they mostly rely on the Galilean invariance property. Even if the models for polyatomic gases are of course more complex [45, 9, 19], the Galilean invariance still holds. Consequently, there is no doubt we can quite straightforwardly recover expressions similar to (36)–(37) for polyatomic gases mixtures, but more intricate because of the other microscopic variables involved (internal energy, for instance).

The debate between Maxwell-Stefan's and Fick's equations for diffusion is an important question in the gaseous mixture case. At first, both were formulated as *axiomatic macroscopic considerations* for transport, but relying on apparently different postulates. The Fick approach was theorized later on by Onsager in the thermodynamics of irreversible processes framework, which itself was proven, for gaseous mixtures, to derive from the Boltzmann equation. This should have consecrated the Fick viewpoint over the Maxwell-Stefan one. Nevertheless, it was difficult for many people to let down the Maxwell-Stefan formulation, as it features formal conveniences compared to Fick, in particular concerning the issue of computing the diffusion coefficients. The apparent contradiction was then somehow solved by identifying the two processes: Fick and Maxwell-Stefan were the same, but formulated in different ways.

In this article, we perform further investigations on the Maxwell-Stefan equations thanks to the Boltzmann viewpoint. It is already known for long that a Chapman-Enskog expansion is a crucial tool to properly derive the Fick equations and compute the associated diffusion coefficients. We prove in this work that Maxwell-Stefan equations can also be derived, equivalently either using a Hilbert expansion or the moment method applied to the Boltzmann equation for mixtures. Using a former result by Le Tallec and Perlat, who proved that Levermore's 14-moment equations conveniently model a monatomic gas at moderate Knudsen number, we believe that the Maxwell-Stefan equations are likely to model moderately rarefied mixtures.

Then we come to a completely different picture of both models.

- Fick's law is needed to model a gas in the continuous regime. It models mass diffusion for mixtures and needs to be completed, if necessary by moment equations for mixture.

- Maxwell-Stefan's equations need to be invoked when moderate rarefaction occurs. They must be seen as momentum equations and need to be supplemented with equations for mass conservation.

As a consequence of this point of view, we conclude that there is no reason why there should be any link between Maxwell-Stefan and Fick coefficients. Besides, we have proven here that the Maxwell-Stefan coefficients are related to the direct linearized Boltzmann operator, whereas it is known that the Fick ones are computed with its inverse. Therefore, except for very few specific cases, which still need to be clarified, there is no chance, in a general way, that a simple link exists between the Maxwell-Stefan and Fick coefficients.

Appendix A. Moment method for the Boltzmann equation in the mixture case

This appendix aims to explain why the choice of Ansatz (17) is relevant, and why the Maxwell-Stefan formalism can also yield from general considerations on the entropic approximation for kinetic equations. We first introduce some notations, mainly related to tensor calculus. Then we briefly discuss Galerkin's approach for the moment method in a more general setting for kinetic equations, to eventually apply it for mixtures.

A.1. **Basics of tensor calculus.** What we explain in this subsection can be found in a more rigorous way in the reference book by Schwartz [42]. we provide it for the sake of completeness. For any d, $q \in \mathbb{N}^*$, an application $\mathsf{a} : [\![1,d]\!]^q \to \mathbb{R}$ is called a square tensor of size d and order q. The set of all square tensors of size d and order q is denote d by $\mathbb{T}(d,q)$. We extend the notation $\mathbb{T}(d,q)$ in the case when $q = 0$: an element of $\mathbb{T}(d,0)$ is just a real number. An entry of a tensor $\mathsf{a} \in \mathbb{T}(d,q)$ writes $\mathsf{a}[i_1, \cdots, i_q]$, where $i_p \in [\![1,d]\!]$ for all $p \in [\![1,q]\!]$.

For any d, q, $r \in \mathbb{N}^*$, we can define the outer product $\mathsf{a} \otimes \mathsf{b} \in \mathbb{T}(d, q+r)$ of two square tensors $\mathsf{a} \in \mathbb{T}(d,q)$ and $\mathsf{b} \in \mathbb{T}(d,r)$ by

$$(\mathsf{a} \otimes \mathsf{b})[i_1, \cdots, i_q, i_{q+1}, \cdots, i_{q+r}] = \mathsf{a}[i_1, \cdots, i_q]\, \mathsf{b}[i_{q+1}, \cdots, i_{q+r}], \quad 1 \le i_1, \cdots, i_{q+r} \le d,$$

and the contraction product $(\mathsf{a} : \mathsf{b}) \in \mathbb{T}(d,q)$ of two square tensors $\mathsf{a} \in \mathbb{T}(d, q+r)$ and $\mathsf{b} \in \mathbb{T}(d,r)$ by

$$(\mathsf{a} : \mathsf{b})[i_1, \cdots, i_q] = \sum_{j_1=1}^{d} \cdots \sum_{j_r=1}^{d} \mathsf{a}[i_1, \cdots, i_q, j_1, \cdots, j_r]\, \mathsf{b}[j_1, \cdots, j_r], \quad 1 \le i_1, \cdots, i_q, j_1, \cdots, j_r \le d.$$

Let us now recall the definition of the action of a square tensor on a tensor column. We already focus on the kinetic setting by considering so-called kinetic functions, i.e. functions of v. For given d, q, $r \in \mathbb{N}^*$, consider $I \ge 2$ tensor-valued kinetic functions, denoted by $\mathsf{t}_i(v) \in \mathbb{T}(d, q+r)$, for any i, and the associate tensor column $\mathsf{T}(v) = (\mathsf{t}_1(v), \cdots, \mathsf{t}_I(v))^\mathsf{T}$. The action of a tensor $\mathsf{a} \in \mathbb{T}(d,q)$ on $\mathsf{T}(v)$ is defined by the distribution of the contraction product on any line of $\mathsf{T}(v)$, i.e.

$$\mathsf{a} \cdot \mathsf{T}(v) := (\mathsf{t}_1(v) : \mathsf{a}, \cdots, \mathsf{t}_I(v) : \mathsf{a})^\mathsf{T} \in \mathbb{T}(d,r)^I.$$

Note that, if $r = 0$, $\mathsf{a} \cdot \mathsf{T}(v)$ is just a column vector (of size I) of kinetic functions. Moreover, for any $p \in \mathbb{N}$, if $\mathsf{A} = (\mathsf{a}_0, \cdots, \mathsf{a}_p)$ is a list of tensors in $\mathbb{T}(d,q)$, and $\underline{\mathsf{M}}(v) = (\mathsf{M}_0(v), \cdots, \mathsf{M}_p(v))$ is a list of tensor columns, i.e. each M_k lies in $\mathbb{T}(d,q)^I$, we set

$$\mathsf{A} \cdot \underline{\mathsf{M}}(v) = \sum_{j=0}^{p} \mathsf{a}_j \cdot \mathsf{M}_j(v) \in \mathbb{R}^I,$$

which is then also a column of real-valued kinetic functions.

Eventually, if $\mathsf{M}(v)$ is any list of tensors $(\mathsf{m}_1(v), \cdots, \mathsf{m}_I(v))$ such that $\mathsf{m}_i(v) \in \mathbb{T}(d,q)$ for all $i \in [\![1,I]\!]$, then we can compute

$$\langle \mathsf{M}, f \rangle_I = \sum_{i=1}^{I} \langle \mathsf{m}_i, f_i \rangle \in \mathbb{T}(d,q),$$

remembering the $\langle \cdot \rangle$ notations previously introduced in Section 2.

A.2. **Galerkin's approach for the moment method.** In this appendix, we briefly recall the Galerkin approach which allows to properly derive the moment method from a standard kinetic equation. In the next one, we apply the strategy to the mixture model. Let us then consider the following general collisional kinetic equation, whose unknown is a distribution function f : $\mathbb{R}^3 \times \mathbb{R}_+^* \times \mathbb{R}^3 \to \mathbb{R}^I$, with $I \geq 1$, i.e.

$$(40) \qquad \partial_t f + v \cdot \nabla_x f = K(f) \quad \text{on } \mathbb{R}^3 \times \mathbb{R}_+^* \times \mathbb{R}^3,$$

where K is some collision operator, whose domain is named $\mathcal{D}(K)$. We assume that (40) is endowed with a strictly convex entropy functional, namely, there exists a strictly convex function $\eta : \mathbb{R}^I \to \mathbb{R} \cup \{+\infty\}$, $y \mapsto \eta(y)$, such that the following entropy decay estimate holds for any $f \in \mathcal{D}(K)$:

$$(41) \qquad \langle K(f), \nabla_y \eta(f) \rangle_I \leq 0.$$

Then, in a very standard way, we denote by $\eta^* : \mathbb{R}^I \to \mathbb{R} \cup \{-\infty\}$, $z \mapsto \eta^*(z)$, its convex conjugate function. The collisional invariants associated to the collision operator K are defined as the kinetic (I-list of tensor-valued) functions $\mathsf{X}(v)$ such that, for any $f \in \mathcal{D}(K)$,

$$\langle \mathsf{X}, K(f) \rangle_I = 0,$$

and we denote by $\ker K$ the linear space of collision invariants. The most important feature of K is the *extended H-theorem*, which states, for any $f \in \mathcal{D}(K)$, that the following properties are equivalent:

  (i) $K(f) = 0$;
  (ii) $\langle \nabla_y \eta(f), K(f) \rangle_I = 0$;
  (iii) there exists $\phi \in \ker K$ such that $f = \nabla_z \eta^*(\phi)$.

In particular, joined to the entropy decay estimate (41), the previous properties mean that f should tend to a local equilibrium characterized by $K(f) = 0$ when there is no gradient. In practice, however, the transport term $v \cdot \nabla_x f$ and the collision one $K(f)$ compete, depending on the regime at stake. To exhibit the dominant term, let us recall that the gradient term behaves like the inverse of a typical length, denoted by $1/\ell$, and the Boltzmann collision term scales as the product of the density with the cross section, which is approximately the inverse of the mean free path $1/\lambda$. Then the value of the Knudsen number $\mathrm{Kn} = \lambda/\ell$ allows to characterize the regime.

At low Knudsen number, i.e. $\mathrm{Kn} \leq 10^{-3}$, collisions are much more important than any gradient and, following the extended H-theorem, *the zeroth-order* term (with respect to Kn) of any f satisfying the kinetic equation (40) should have the form $f^0(t, x, \cdot) = \nabla_z \eta^*(\phi_{x,t})$, where $\phi_{x,t} \in \ker K$ for any x and t. The remaining question is then the space and time equations satisfied by ϕ as a function of x and t. They can first be obtained by writing the hyperbolic conservation equation satisfied by the zeroth order moment of f. Subsequently, the first-order correction can be computed thanks to the Chapman-Enskog procedure and we get parabolic equations involving diffusive terms.

For higher (than 10^{-3}) Knudsen numbers, the collision process is not dominant any more, and the approximation of f^0 as a local equilibrium fails. Consequently, it is difficult to guess some a priori shape for the functions satisfying the kinetic equation, and this generally requires solving the full kinetic equation itself.

However, the case of significant deviation from the local equilibrium can still be computed using the moment point of view, if we consider that this method provides a practical and theoretical approach to compute Galerkin solutions to the kinetic equation itself [41]. More precisely, we say that f is a weak solution to the kinetic equation (40) when

$$(42) \qquad \langle \psi, \partial_t f \rangle_I + \langle \psi, v \cdot \nabla_x f \rangle_I = \langle \psi, K(f) \rangle_I,$$

for any relevant test-function ψ in the variable v. In particular, the space of relevant test-functions $\mathbb{M}$ must satisfy $\nabla_y \eta(f) \in \mathbb{M}$, so that, using $\nabla_y \eta(f)$ as a test-function in (42) and the entropy decay

for the collision term (41), the following estimate holds for the weak solution

$$\langle \nabla_y \eta(f), \partial_t f \rangle_I + \langle \nabla_y \eta(f), v \cdot \nabla_x f \rangle_I \leq 0.$$

The Galerkin method consists in considering an increasing sequence of subspaces $\ker K = \mathbb{M}_0 \subset \mathbb{M}_1 \subset \cdots$ such that $\mathrm{cl}(\cup \mathbb{M}_k) = \mathbb{M}$ (where cl stands for the closure topologic operator) and to take any of the finite dimensional subspaces $\mathbb{M}_k$, $k \in \mathbb{N}$, as the test-function space in (42), that is, for any $\psi \in \mathbb{M}_k$,

$$(43) \qquad \langle \psi, \partial_t f \rangle_I + \langle \psi, v \cdot \nabla_x f \rangle_I = \langle \psi, K(f) \rangle_I, \quad \text{with } \nabla_y \eta(f) \in \mathbb{M}_k.$$

We need to briefly recall the presentation performed in [34] to understand the method. The entropy condition for f implies that we can look for f under the form $f(t, x, v) = \nabla_z \eta^*(\varphi_k(v))$, where φ_k lies in $\mathbb{M}_k$. Let us then consider $\underline{\mathsf{M}}(v)$ be a basis of $\mathbb{M}_k$, that is $\underline{\mathsf{M}}(v) = (\mathsf{M}_1(v), \cdots, \mathsf{M}_p(v))$. An element of $\mathbb{M}_k$ can be written as $\mathsf{A} \cdot \underline{\mathsf{M}}(v)$. Looking for f is thus equivalent to look for the functions $\mathsf{A}(t, x)$ as the space-time component of the function $\nabla_y \eta(f)$ in the space $\mathbb{M}_k$. Alternatively, define the moment associated to f as

$$\mathsf{R}(t, x) = \langle \underline{\mathsf{M}}, f(t, x, \cdot) \rangle_I = (\langle \mathsf{M}_1, \nabla_z \eta^*(\mathsf{A}(t, x) \cdot \underline{\mathsf{M}}) \rangle_I, \cdots, \langle \mathsf{M}_p, \nabla_z \eta^*(\mathsf{A}(t, x) \cdot \underline{\mathsf{M}}) \rangle_I).$$

This is the so-called entropic change of variable: there is a one-to-one correspondence between $\mathsf{R}(t, x)$ and $\mathsf{A}(t, x)$. In order to help the reader with the thermodynamical interpretation of the unknowns R, A, let us emphasize that, in the context of the so-called thermodynamics of irreversible processes, when $\mathbb{M}_k = \mathbb{M}_0 = \ker K$, the following facts are standard.

- The unknown $\mathsf{R}^e(t, x)$ stores any of the extensive quantities which are conserved, which are not affected by the collision process.
- The unknown $\mathsf{A}^e(t, x)$ stores any of the so-called intensive conjugate conserved quantities.
- The unknown $\underline{\mathsf{M}}^e(v)$ stores the extensive kinetic functions associated to the conserved quantities.

The elements of the triplet $(\mathsf{R}^e, \mathsf{A}^e, \underline{\mathsf{M}}^e(v))$ are linked in a unique way thanks to the relationship

$$\mathsf{R}^e = \langle \underline{\mathsf{M}}^e, \nabla_z \eta^*(\mathsf{A}^e \cdot \underline{\mathsf{M}}^e) \rangle_I.$$

In the non-equilibrium context, we wish to keep the vocabulary of extensive moment (R) and intensive conjugate moment (A). The correspondence between extensive and conjugate intensive moments is established thanks to the study of the convex function

$$h(\mathsf{A}) = \langle \eta^*(\mathsf{A} \cdot \underline{\mathsf{M}}) \rangle_I,$$

for which we can also define the associated conjugate convex function h^*. For any moment $\mathsf{R} = (\mathsf{r}_1, \cdots, \mathsf{r}_p)$, we write

$$h^*(\mathsf{R}) = \sup_{\mathsf{A}} \left[\left(\sum_{k=1}^p \mathsf{a}_k : \mathsf{r}_k \right) - h(\mathsf{A}) \right], \quad \text{with } \mathsf{A} = (\mathsf{a}_1, \cdots, \mathsf{a}_p).$$

When things go round (in particular, h needs to be strictly convex), for any well-chosen R, there is a unique A such that $\mathsf{A} = \mathrm{Arg\,sup}(h^*(\mathsf{R}))$. It can be computed thanks to the Euler condition

$$(44) \qquad \mathsf{R} - \nabla_{\mathsf{A}} h(\mathsf{A}) = 0 \Leftrightarrow \mathsf{R} = \langle \underline{\mathsf{M}}, \nabla_z \eta^*(\mathsf{A} \cdot \underline{\mathsf{M}}) \rangle_I.$$

This establishes the one-to-one correspondence between R and A, which can be finally written using the functions h and h^*:

$$\mathsf{R}(\mathsf{A}) = \nabla_{\mathsf{A}} h(\mathsf{A}), \quad \mathsf{A}(\mathsf{R}) = \nabla_{\mathsf{R}} h^*(\mathsf{R}).$$

Hence, going back to our Galerkin problem, looking for the function f specified by both conditions from (43) leads us to eventually find the moments $\mathsf{R}(t, x)$ associated to f in the kinetic space $\mathbb{M}_k$. The moments can be searched by solving the moment equation associated to the Galerkin approximation.

Now, with [34], assume that f is a Galerkin approximation of the solution to the kinetic equation (40), that is we impose

$$f(t, x, \cdot) = \nabla_z \eta^*(\mathsf{A}(t, x) \cdot \underline{\mathsf{M}}).$$

The weak formulation for the Galerkin problem (43) now reads

$$\begin{aligned} \langle \underline{\mathsf{M}}, \partial_t f \rangle_I + \langle \underline{\mathsf{M}}, v \cdot \nabla_x f \rangle_I &= \langle \underline{\mathsf{M}}, K(f) \rangle_I, \\ f(t, x, \cdot) &= \nabla_z \eta^*(\mathsf{A}(t, x) \cdot \underline{\mathsf{M}}). \end{aligned}$$

If we introduce the notations

$$\mathsf{S}(\mathsf{A}) = \langle \underline{\mathsf{M}}, K(\nabla_z \eta^*(\mathsf{A} \cdot \underline{\mathsf{M}})) \rangle_I, \quad \mathsf{J}(\mathsf{A}) = \langle v \otimes \underline{\mathsf{M}} \cdot \mathsf{A}, \nabla_z \eta^*(\mathsf{A} \cdot \underline{\mathsf{M}}) \rangle_I,$$

we formally obtain

$$\partial_t \mathsf{R} + \nabla_x \cdot \mathsf{J}(\mathsf{A}) = \mathsf{S}(\mathsf{A}).$$

Using the one-to-one correspondence between A and R, thanks to the strictly convex functions h, h^*, the previous equation can be rewritten as

$$\partial_t \mathsf{R} + \nabla_\mathsf{A} \mathsf{J}(\nabla_\mathsf{R} h^*(\mathsf{R})) D^2_{\mathsf{RR}} h^*(\mathsf{R}) \nabla_x \mathsf{R} = \mathsf{S}(\nabla_\mathsf{R} h^*(\mathsf{R})).$$

Such an equation is known as the Friedrich-Lax form of the hyperbolic system, see [34]. Then, if this equation has a solution, the Galerkin problem also has a solution.

A.3. Application to the mixture case.
The Galerkin approach for the Boltzmann equation (3) was derived for a single monatomic gas, yielding (at the first level out of equilibrium) the so-called Levermore 14-moments. It has been computed with success [31, 32] as an alternative to the Navier-Stokes equations with slip boundary conditions or DSMC simulations in Couette flow at moderate Knudsen numbers. This seems to confirm the idea that the moment method enables to reach kinetic systems that tend to escape from local equilibrium. Up to our knowledge, the moment method has hardly been applied in the mixture case, see [39]. The method is roughly described in Appendix A.2 in a quite general setting. In order to apply the formalism in our situation, let us first write a few formal properties of the mixture kinetic model.

The entropy associated to the Boltzmann equations for mixtures (3) is given, for any $y \in \mathbb{R}^I$, by

$$(45) \qquad \eta(y) = \begin{cases} \displaystyle\sum_{i=1}^I y_i \ln(y_i) - y_i & \text{if } y \in (\mathbb{R}^*_+)^I, \\ +\infty & \text{in all other cases.} \end{cases}$$

We obviously have, for any $y \in (\mathbb{R}^*_+)^I$,

$$\nabla_y \eta(y) = (\ln(y_1), \cdots, \ln(y_I))^\mathsf{T}.$$

Besides, the associated conjugate convex function η^* satisfies, for any $z \in \mathbb{R}^I$,

$$\eta^*(z) = \sum_{i=1}^I e^{z_i},$$

which immediately implies that, for any $z \in \mathbb{R}^I$,

$$\nabla_z \eta^*(z) = (e^{z_1}, \cdots, e^{z_I})^\mathsf{T}.$$

Using the following notations, for any v,

$$\mathsf{N}_1(v) = \begin{bmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{bmatrix}, \cdots, \mathsf{N}_I(v) = \begin{bmatrix} 0 \\ \vdots \\ 0 \\ 1 \end{bmatrix},$$

$$\mathsf{C}_1(v) = \begin{bmatrix} m_1 v \\ 0 \\ \vdots \\ 0 \end{bmatrix}, \cdots, \mathsf{C}_I(v) = \begin{bmatrix} 0 \\ \vdots \\ 0 \\ m_I v \end{bmatrix}, \quad \mathsf{E}(v) = \frac{1}{2} \begin{bmatrix} m_1 v^2 \\ m_2 v^2 \\ \vdots \\ m_I v^2 \end{bmatrix},$$

the space $\mathbb{M}_0 = \ker Q$ for the mixture collision operator $Q(f,f)$ satisfies, as stated in [12],

$$(46) \qquad \mathbb{M}_0 = \mathrm{Span}(\mathsf{N}_1, \cdots, \mathsf{N}_I, \sum_i \mathsf{C}_i, \mathsf{E}).$$

Note that we already pointed out the importance of (C_i) in Proposition 2 to compute the Maxwell-Stefan diffusion coefficients. In the sequel, we also consider

$$(47) \qquad \mathbb{M}_1 = \mathrm{Span}(\mathsf{N}_1, \cdots, \mathsf{N}_I, \mathsf{C}_1, \cdots, \mathsf{C}_I, \mathsf{E}).$$

We clearly have $\mathbb{M}_0 \subset \mathbb{M}_1$.

Let us now consider the entropy density function $h : \mathbb{M}_1 \to \mathbb{R}$ given by

$$h(\mathsf{A}) = \overline{\eta^*(\mathsf{A} \cdot \underline{\mathsf{M}}(v))} = \sum_{i=1}^{I} \overline{\exp\left([\mathsf{A} \cdot \underline{\mathsf{M}}(v)]_i\right)},$$

where $\underline{\mathsf{M}}(v)$ is the tensorially formulated basis of $\mathbb{M}_1$ and where we have, as previously defined, for any i,

$$[\mathsf{A} \cdot \underline{\mathsf{M}}(v)]_i = \sum_{k=1}^{p} \mathsf{a}_k : [\mathsf{M}_k(v)]_i.$$

This function h takes its values in $\mathbb{R} \cup \{+\infty\}$, and its domain $\mathrm{dom}\, h$ is, by definition, the set of all A such that $h(\mathsf{A})$ is finite. That exactly requires that the intensive conjugate moment on the energy column tensor $\mathsf{E}(v)$ is negative. Moreover, thanks to the regularity of η^*, h is regular, and we can compute, at any point of the open set $\mathrm{dom}\, h$, the derivative of h, i.e., for any $\mathsf{A} \in \mathrm{dom}\, h$, and any $k \in [\![1, p]\!]$,

$$[\nabla_{\mathsf{A}} h(\mathsf{A})]_k = \sum_{i=1}^{I} \langle [\mathsf{M}_k(v)]_i, \nabla_z \eta^*([\mathsf{A} \cdot \underline{\mathsf{M}}(v)]_i) \rangle.$$

Thanks to the properties of η^*, h is a strictly convex function, and we have, for any A, and any indices k and ℓ,

$$(48) \qquad [D_{\mathsf{AA}}^2 h(\mathsf{A})]_{k\ell} = \sum_{i=1}^{I} \langle [\mathsf{M}_k(v)]_i \otimes [\mathsf{M}_\ell(v)]_i, D_{zz}^2 \eta^*([\mathsf{A} \cdot \underline{\mathsf{M}}(v)]_i) \rangle.$$

By strict convexity of η^*, $D_{zz}^2 \eta^*$ is a symmetrical positive bilinear form, and consequently, (48) implies that $D_{\mathsf{AA}}^2 h(\mathsf{A})$ is also a symmetrical positive bilinear form.

Consider now a so-called realizable moment $\underline{\mathsf{R}} = (\mathsf{R}_0, \cdots, \mathsf{R}_p)$. It means that there exists a vector-valued kinetic function $f = (f_1, \cdots, f_I)$, with nonnegative components, such that, for any $k \in [\![0, p]\!]$,

$$(49) \qquad \mathsf{R}_k = \langle \mathsf{M}_k(v), f \rangle_I = \sum_{i=1}^{I} \langle [\mathsf{M}_k(v)]_i, f_i \rangle.$$

Then it can be argued that the set of all realizable moments is included in the domain of h^*. Moreover, for any realizable moment R, the unique maximizer of $h^*(\mathsf{R})$ is obtained for A satisfying the Euler condition $\mathsf{R} = \nabla_{\mathsf{A}} h(\mathsf{A})$, which is recalled in (44) in Appendix A.2. As a consequence, we can compute a moment equation in $\mathbb{M}_1$ associated to the Boltzmann equation. Moreover, inverting, for any x and t, the extensive moment variable $\mathsf{R}(t, x)$ into the intensive conjugate variable $\mathsf{A}(t, x)$,

the quantity $\nabla_z \eta^*(A(t,x) \cdot \underline{M}(v))$ can be interpreted as a Galerkin approximation for the solution to the Boltzmann equation (3) in some regime which is not close to the equilibrium.

Let us now perform the computations to apply the Galerkin approximation in the extensive moment way. We define the moment R as

$$R = (n_1, \cdots, n_I, \ \rho_1 u_1, \cdots, \rho_I u_I, \ \mathcal{E}).$$

Such a moment is obtained from (49), choosing for $\underline{M}(v)$ the $\mathbb{M}_1$-tensor basis given in (47). It is usual to write the components of any function $f = \nabla_z \eta^*(A \cdot \underline{M}(v))$ under the form, for any i,

$$(50) \qquad f_i(v) = n_i \left(\frac{m_i}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{m_i (v - u_i)^2}{2k_B T} \right).$$

Note that the previous form is the one from (22) with $\varepsilon = 1$. From (50), we get, if necessary, the correspondence between R and A by applying $\nabla_y \eta(\cdot)$ to f. We have indeed, by definition,

$$A \cdot \underline{M}(v) = \nabla_y \eta(\nabla_z \eta^*(A \cdot \underline{M}(v))) = (\ln(f_1), \cdots, \ln(f_I))^\mathsf{T},$$

which lies in $\mathbb{R}^I$, and actually reads

$$(51) \qquad A \cdot \underline{M}(v) = \sum_{i=1}^{I} \left[\ln(n_i) + \frac{3}{2} \ln \left(\frac{m_i}{2\pi k_B T} \right) - \frac{m_i u_i^2}{2k_B T} \right] N_i(v) + \sum_{j=1}^{I} \frac{u_j}{k_B T} C_j(v) - \frac{1}{k_B T} E(v).$$

Observe that the one-to-one relationship between R and A is very nonlinear. The moment method then returns the equations (18)–(20). Its entropy structure can easily be recovered by noticing that, for any vector-valued f,

$$\langle \nabla_y \eta(f), Q(f,f) \rangle_I \leq 0.$$

Applying the previous estimate with $f = \nabla_z \eta^*(A \cdot \underline{M})$ immediately implies that

$$\langle A \cdot \underline{M}, Q(f,f) \rangle_I \leq 0.$$

Recalling that any of the N_i, $1 \leq i \leq I$, and E belong to $\ker Q$, we get from (51) the entropy estimate for (18)–(20), that is

$$\sum_{i=1}^{I} \frac{u_i}{k_B T} \langle C_i(v), Q(f,f) \rangle_I \leq 0 \quad \Longleftrightarrow \quad \sum_{i=1}^{I} \sum_{j=1}^{I} \frac{u_i}{k_B T} \langle m_i v, Q_{ij}(f_i, f_j) \rangle \leq 0.$$

Remark 5. *Recall that we have*

$$\frac{1}{\varepsilon} \langle m_i v, Q_{ij}(f_i^\varepsilon, f_j^\varepsilon) \rangle = \frac{1}{\varepsilon} F_{ij}^\varepsilon(\varepsilon u_i, \varepsilon u_j),$$

which converges, when ε goes to 0, towards $\alpha_{ij}(u_i - u_j)$. The previous entropy estimate allows to recover the nonpositivity of the matrix A defined in Remark 2.

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