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**STRUCTURE OF ENTROPIES IN
DISSIPATIVE MULTICOMPONENT FLUIDS**

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R.I. 759

Octobre 2012

Structure of Entropies in Dissipative Multicomponent Fluids

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Abstract

We investigate the structure of mathematical entropies for dissipative multicomponent fluid models derived from the kinetic theory of gases. The corresponding governing equations notably involve nonideal thermochemistry as well as diffusion fluxes driven by chemical potential gradients and temperature gradients. We obtain the general form of mathematical entropies compatible with the hyperbolic structure of the system of partial differential equations assuming a natural nondegeneracy condition. We next establish that entropies compatible with the hyperbolic-parabolic structure are unique up to an affine transform when they are independent on mass and heat diffusion parameters.

1 Introduction

Multicomponent fluids arise in many laboratory experiments and engineering applications such as reentry into earth atmosphere, chemical reactors, flames or atmospheric pollution [22]. On the other hand, mathematical entropies are an important tool for analyzing hyperbolic-parabolic systems of partial differential equations modeling fluids [33, 20, 55, 37, 49, 39, 9, 27, 22, 18, 28, 6, 52]. Mathematical entropies lead to symmetrized forms useful for existence theorems [55, 37, 54, 27, 28] as well as finite element formulations [35] and may also be used to derive a priori estimates. These are strong motivations for investigating the structure and properties of mathematical entropies for systems of partial differential equations modeling dissipative multicomponent fluids, higher order entropies [17, 23, 24, 25] laying beyond the scope of the present work.

The system of partial differential equations modeling dissipative multicomponent fluids derived from the kinetic theory of gases is first presented. We discuss conservation equations, thermodynamics, chemical production rates and transport fluxes. The mathematical structure of nonideal thermodynamics has recently been investigated [29] and the nonideal chemical production rates are directly expressed in terms of chemical potentials [44, 41, 31, 29]. These rates are compatible with the symmetric form of rates of progress derived from the kinetic theory of dilute reactive gases [16, 22]. The mass and heat diffusion fluxes, deduced from the kinetic theory of dilute or dense gases as well as from various macroscopic theories, are driven by chemical potential gradients and temperature gradients and viscous effects are also taken into account [45, 47, 10, 41, 3, 4, 43]. The resulting nonideal fluid model is shown to satisfy the second principle of thermodynamics, that is, physical entropy production due to transport fluxes and chemistry are both shown to be nonnegative.

The definition of an entropy function is adapted from Godunov [33] and Friedrichs and Lax [20] for the hyperbolic part, from Kawashima and Shizuta [37, 54, 38, 39] for the dissipative part, and from the structure of chemical sources [22, 28], Chen, Levermore and Liu [8] and Kawashima and Yong [40] for the source term. Mathematical entropies of the corresponding system of partial differential equations have thus to be compatible with the convective terms, the dissipative terms, and the chemical sources terms. The natural choice for such a mathematical entropy is $\sigma = -\mathcal{S}/R$ where \mathcal{S} denotes the physical entropy per unit volume and where the division by the gas constant R is introduced for convenience. For such nonideal fluids, however, the open sets where thermodynamics is admissible—in particular where the physical entropy Hessian is definite—are bounded by thermodynamically unstable states. As a consequence, even though the natural mathematical entropy σ and the corresponding symmetrizing variable $\mathbf{v} = (\partial_{\mathbf{u}}\sigma)^t$ are defined for all admissible states of the conservative variable

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\mathbf{u} , the map $\mathbf{u} \rightarrow \mathbf{v}$ is not globally one to one—unlike for ideal fluids—because of thermodynamic instabilities. The symmetrizing change of variable $\mathbf{u} \rightarrow \mathbf{v}$ is only *locally invertible* for such nonideal thermodynamics but still lead to global existence theorems around equilibrium states and asymptotic stability [30]. The corresponding natural local symmetrized form may also be evaluated in terms of the inverse of the Gibbs functions derivatives $\partial_{\rho_j} \mathcal{G}_i$, $i, j \in \mathfrak{S}$, where \mathcal{G}_i is the Gibbs function of the i th species per unit mass, ρ_j the partial density of the j th species, $\mathfrak{S} = \{1, \dots, n\}$ the species indexing set, and n the number of species [30]. This natural symmetrized form involves in particular the dissipation matrices $\tilde{\mathbf{B}}_{ij}$ relating the dissipative flux in the i th direction $\mathbf{F}_i^{\text{diss}} = -\sum_{j \in C} \tilde{\mathbf{B}}_{ij} \partial_j \mathbf{v}$ to the gradient of the natural symmetrizing variable $\partial_j \mathbf{v}$ in the j th direction, where $C = \{1, \dots, d\}$ denotes the spatial direction indexing set and d the spatial dimension.

We first investigate the structure of mathematical entropies in the absence of dissipation, i.e., for the multicomponent Euler equations, under a natural nondegeneracy assumption on the fluid thermodynamics. The nondegeneracy condition states that the volume per unit mass $\nu = \nu(p, y_1, \dots, y_n, s)$, written as a function of pressure p , species mass fractions y_1, \dots, y_n and entropy per unit mass s , is such that $\partial_{ps}^2 \nu \neq 0$. Under this assumption, mathematical entropies for multicomponent flows $\tilde{\sigma}$ compatible with the hyperbolic structure are found in the general form

$$\tilde{\sigma} = \varphi(\rho_1, \dots, \rho_n, \mathcal{S}) + \alpha_{\mathbf{v}} \cdot \rho \mathbf{v} + \alpha_{\mathcal{E}} (\mathcal{E} + \frac{1}{2} \rho |\mathbf{v}|^2) + \alpha_0, \quad (1.1)$$

where $\rho = \sum_{1 \leq i \leq n} \rho_i$ denotes the total mass per unit volume, \mathbf{v} the flow velocity, \mathcal{E} the energy per unit volume, φ a 1-homogeneous function of $\rho_1, \dots, \rho_n, \mathcal{S}$ and where $\alpha_{\mathbf{v}} \in \mathbb{R}^d$, $\alpha_{\mathcal{E}}, \alpha_0 \in \mathbb{R}$ are constants. The nontrivial term $\varphi(\rho_1, \dots, \rho_n, \mathcal{S})$ may equivalently be written $\rho \tilde{\varphi}(y_1, \dots, y_n, s)$ thanks to the relations $\rho_i = \rho y_i$ and $\mathcal{S} = \rho s$. When there is only one species $n = 1$, we recover that nontrivial entropies are in the form $\rho \tilde{\varphi}(s)$ [51, 56] and the multicomponent case is new to the authors's knowledge.

We then study the compatibility conditions with second order derivatives, which may be written as commutation type relations in the form $\tilde{\mathbf{B}}_{ij} \partial_{\mathbf{v}} \tilde{\nu} = (\partial_{\mathbf{v}} \tilde{\nu})^t \tilde{\mathbf{B}}_{ij}$, $i, j \in C$, between the dissipation matrices $\tilde{\mathbf{B}}_{ij}$ of the natural symmetrized form and the mathematical entropy derivative $\partial_{\mathbf{v}} \tilde{\nu}$ where $\tilde{\nu} = (\partial_{\mathbf{u}} \tilde{\sigma})^t$. We establish that when a mathematical entropy $\tilde{\sigma}$ is compatible with the hyperbolic structure of the governing equations, that is, with the multicomponent Euler equations, then $\tilde{\sigma}$ is *automatically* compatible with the dissipation matrices arising from viscous effects. Compatibility with dissipative effects is then reduced to the compatibility with a single mass and heat diffusion matrix $\tilde{\mathbf{B}}^L \partial_{\mathbf{v}} \tilde{\nu} = (\partial_{\mathbf{v}} \tilde{\nu})^t \tilde{\mathbf{B}}^L$ and this generalizes previous work by Hughes et al. [35] devoted to single component gases. We also address the compatibility with chemical source terms at chemical equilibrium points and establish that, for entropies $\tilde{\sigma}$ independent of chemical kinetic constants, the extended chemical reaction vectors are left eigenvectors of $\partial_{\mathbf{v}} \tilde{\nu}$.

In order to investigate the compatibility relations with diffusion matrices we first have to study in more details the mathematical structure of mass and heat diffusion fluxes derived from the kinetic theory of gases [57, 7, 19, 11, 15, 43]. We discuss diffusion velocities arising from Stefan-Maxwell type equations as well as quasi-diagonal diffusion matrix approximations. We also consider thermal diffusion cross effects generally termed Soret and Dufour effects. The resulting mass and heat diffusion matrices are then full matrices with intricate analytic expressions and their spectral properties cannot be determined, precluding the obtention of more information on mathematical entropy derivatives $\partial_{\mathbf{v}} \tilde{\nu}$ from the corresponding commutation type relations. As a consequence, in order to obtain more information from the compatibility relations with the mass and heat diffusion matrix $\tilde{\mathbf{B}}^L \partial_{\mathbf{v}} \tilde{\nu} = (\partial_{\mathbf{v}} \tilde{\nu})^t \tilde{\mathbf{B}}^L$, we investigate the subfamily of mathematical entropies $\tilde{\sigma}$ that are independent of the natural mass and heat diffusion parameters. In this natural situation, we establish that mathematical entropies $\tilde{\sigma}$ compatible with the hyperbolic-parabolic structure are in the form

$$\tilde{\sigma} = \alpha_{\mathcal{S}} \mathcal{S} + \sum_{i \in \mathfrak{S}} \alpha_i \rho_i + \alpha_{\mathbf{v}} \cdot \rho \mathbf{v} + \alpha_{\mathcal{E}} (\mathcal{E} + \frac{1}{2} \rho |\mathbf{v}|^2) + \alpha_0, \quad (1.2)$$

where $\alpha_{\mathcal{S}}, \alpha_i, i \in \mathfrak{S}, \alpha_{\mathbf{v}}, \alpha_{\mathcal{E}},$ and α_0 are constants so that $\tilde{\sigma}$ coincide with the natural entropy σ up to an affine transform, discarding trivial entropies proportional to conserved quantities. This contrasts with the multicomponent Euler system which admits many entropies (1.1) and these results generalize previous work by Hughes et al. [35] devoted to single component gases.

The system of partial differential equations modeling dissipative fluids is presented in Section 2. Mathematical entropies and symmetrized forms are investigated in Section 3. The hyperbolic situation is investigated in Section 4 as well as compatibility relations with dissipation matrices. Mass and heat diffusion fluxes are considered in more details in Section 5 and uniqueness of entropy up to an affine transform is discussed Section 6.

2 Nonideal mixtures of dissipative fluids

We present in this section the system of equations modeling dissipative multicomponent reactive fluids.

2.1 Governing equations

We denote by $\mathfrak{S} = \{1, \dots, n\}$ the species indexing set, n the number of species, ρ_i the mass density of the i th species, and m_i the molar mass of the i th species. The mass conservation equation for the i th species may be written

$$\partial_t \rho_i + \nabla \cdot (\rho_i \mathbf{v}) + \nabla \cdot \mathcal{F}_i = m_i \omega_i, \quad i \in \mathfrak{S}, \quad (2.1)$$

where \mathbf{v} denotes the velocity of the mixture, \mathcal{F}_i the mass diffusion flux and ω_i the molar production rate of the i th species. Bold symbols are used for vector or tensor quantities in the space \mathbb{R}^d where d is the dimension of the physical model under consideration so that for instance $\mathbf{v} = (v_1, \dots, v_d)^t$ and $\nabla = (\partial_1, \dots, \partial_d)^t$. The momentum conservation equation can be written in the form

$$\partial_t(\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v} + p \mathbb{I}_d) + \nabla \cdot \mathbf{\Pi} = 0, \quad (2.2)$$

where $\rho = \sum_{i \in \mathfrak{S}} \rho_i$ is the mass density of the mixture, p the pressure, \mathbb{I}_d the unit tensor in \mathbb{R}^d , and $\mathbf{\Pi}$ the viscous tensor. Finally, the energy conservation equation reads

$$\partial_t(\mathcal{E} + \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v}) + \nabla \cdot ((\mathcal{E} + \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} + p) \mathbf{v}) + \nabla \cdot (\mathcal{F}_e + \mathbf{\Pi} \cdot \mathbf{v}) = 0, \quad (2.3)$$

where \mathcal{E} is the internal energy per unit volume and \mathcal{F}_e the heat flux. These equations have to be completed by relations expressing the thermodynamic properties like \mathcal{E} and p , the chemical production rates ω_i , $i \in \mathfrak{S}$, and the transport fluxes \mathcal{F}_i , $i \in \mathfrak{S}$, $\mathbf{\Pi}$ and \mathcal{F}_e .

The equations governing fluid mixtures may generally be derived from the kinetic theory of dilute gases [7, 19, 22], the kinetic theory of dense gases [3, 4, 43], the thermodynamics of irreversible processes [45, 47, 10], from statistical mechanics [36, 2, 46] as well as statistical thermodynamics [41].

2.2 Thermodynamics

We denote by \mathcal{S} the entropy per unit volume, T the absolute temperature, and by $\mathbf{z} = (\rho_1, \dots, \rho_n, T)$, $\mathbf{u} = (\rho_1, \dots, \rho_n, \mathcal{E})^t$, and $\varrho = (\rho_1, \dots, \rho_n)^t$, the usual thermodynamic variables. We denote by $\tilde{\partial}$ the derivation operator with respect to the variable \mathbf{z} and the integer $\varkappa \in \mathbb{N}$, $\varkappa \geq 3$, denotes the regularity class of thermodynamic functions.

Definition 2.1. *Let \mathcal{E} , p , and \mathcal{S} be C^\varkappa functions of the variable $\mathbf{z} = (\rho_1, \dots, \rho_n, T)^t$ defined on a simply connected open set $\mathcal{O}_z \subset (0, \infty)^{n+1}$. These functions are said to define a thermodynamics when Properties (\mathcal{T}_1) - (\mathcal{T}_3) hold.*

(\mathcal{T}_1) *The map $\mathbf{z} \rightarrow \mathbf{u}$ is a C^\varkappa diffeomorphism from the set \mathcal{O}_z onto an open set \mathcal{O}_u .*

(\mathcal{T}_2) *For any $\mathbf{z} \in \mathcal{O}_z$, defining $\mathcal{G}_i = \tilde{\partial}_{\rho_i} \mathcal{E} - T \tilde{\partial}_{\rho_i} \mathcal{S}$, $i \in \mathfrak{S}$, we have the volumetric Gibbs' relation $T d\mathcal{S} = - \sum_{i \in \mathfrak{S}} \mathcal{G}_i d\rho_i + d\mathcal{E}$ and the constraint $\sum_{i \in \mathfrak{S}} \rho_i \mathcal{G}_i = \mathcal{E} + p - T\mathcal{S}$.*

(\mathcal{T}_3) *For any $\mathbf{z} \in \mathcal{O}_z$, the Hessian matrix $\partial_{uu}^2 \mathcal{S}$ is negative definite.*

Property (\mathcal{T}_1) is associated with the natural change of variables encountered in thermodynamics and temperature and species densities are assumed to be positive with $\mathcal{O}_z \subset (0, +\infty)^{n+1}$. Property (\mathcal{T}_2) is Gibbs' relation with a natural constraint since the variables are volumetric [29]. Property (\mathcal{T}_3) is the thermodynamic stability condition and the open set \mathcal{O}_z may have a complex shape because of thermodynamic instabilities [29]. Nonideal fluid thermodynamics are often built from equations of states and such a construction has been investigated mathematically [29]. Thermodynamic stability may not hold at high pressure and low temperature for nonideal fluids and may be characterized in terms of the derivatives of the species Gibbs functions \mathcal{G}_i , $i \in \mathfrak{S}$ [29].

Proposition 2.2. *Assume that (\mathcal{T}_1) - (\mathcal{T}_2) are satisfied and denote by Γ the matrix of size n with coefficients $\Gamma_{kl} = \rho \tilde{\partial}_{\rho_k} \mathcal{G}_l / T = \rho \tilde{\partial}_{\rho_l} \mathcal{G}_k / T$. Then, for any $\mathbf{z} \in \mathcal{O}_z$, the following statements are equivalent :*

(i) $\partial_{uu}^2 \mathcal{S}$ is negative definite.

(ii) $\tilde{\partial}_T \mathcal{E} > 0$ and Γ is positive definite.

Remark 2.3. *An interesting extra property of thermodynamics is the compatibility with perfect gases which will not be required in this work [29].*

2.3 Chemical production rates

We consider an arbitrary complex reaction mechanism with n^r reactions involving n species which may be written

$$\sum_{i \in \mathfrak{S}} \nu_{ij}^f \mathcal{M}_i \rightleftharpoons \sum_{i \in \mathfrak{S}} \nu_{ij}^b \mathcal{M}_i, \quad j \in \mathfrak{R}, \quad (2.4)$$

where ν_{ij}^f and ν_{ij}^b denote the forward and backward stoichiometric coefficients of the i th species in the j th reaction, \mathcal{M}_i the symbol of the molecule of the i th species, and $\mathfrak{R} = \{1, \dots, n^r\}$ the reaction indexing set. The forward and backward reaction vectors ν_j^f and ν_j^b of the j th reaction are defined by $\nu_j^f = (\nu_{1j}^f, \dots, \nu_{nj}^f)^t$ and $\nu_j^b = (\nu_{1j}^b, \dots, \nu_{nj}^b)^t$ and the global reaction vector by $\nu_j = \nu_j^b - \nu_j^f$. The species of the mixture are assumed to be constituted by atoms and we denote by \mathbf{a}_{il} the number of l th atom in the i th species, $\mathfrak{A} = \{1, \dots, n^a\}$ the set of atom indices, and $n^a \geq 1$ the number of atoms—or elements—in the mixture. The l th atomic vector is given by $\mathbf{a}_l = (\mathbf{a}_{1l}, \dots, \mathbf{a}_{nl})^t$ and the vector spaces spanned by reaction and atomic vectors are denoted by $\mathcal{R} = \text{span}\{\nu_i, i \in \mathfrak{R}\}$ and $\mathcal{A} = \text{span}\{\mathbf{a}_l, l \in \mathfrak{A}\}$ respectively. The unit vector is defined by $\mathbb{I} = (1, \dots, 1)^t$ and the reduced chemical potentials vector by $\mu = (\mu_1, \dots, \mu_n)^t$ where $\mu_i = m_i \mathcal{G}_i / RT$, $i \in \mathfrak{S}$. The Euclidean scalar product between $\mathbf{x}, \mathbf{y} \in \mathbb{R}^n$ is denoted by $\langle \mathbf{x}, \mathbf{y} \rangle$ and the orthogonal complement of a linear subspace $E \subset \mathbb{R}^n$ is denoted by E^\perp . The production vector ω is defined by $\omega = (\omega_1, \dots, \omega_n)^t$ and may be written

$$\omega = \sum_{j \in \mathfrak{R}} \tau_j \nu_j, \quad (2.5)$$

where τ_j denotes the rate of progress of the j th reaction. The proper form for the rate of progress of the j th reaction τ_j is deduced from statistical physics [44, 41]

$$\tau_j = \kappa_j^s (\exp\langle \mu, \nu_j^f \rangle - \exp\langle \mu, \nu_j^b \rangle), \quad (2.6)$$

where κ_j^s is the symmetric reaction constant of the j th reaction. These nonideal rates of progress have first been derived by Marcelin from chemical and statistical physics considerations [44] and rederived by Keizer in the framework of a nonequilibrium statistical thermodynamics [41]. These rates are compatible with traditional nonidealities used to estimate *equilibrium constants* [34] as well as with the symmetric forms of rates of progress derived from the kinetic theory of dilute reactive gases [22, 16, 31]. The mathematical assumptions associated with the chemical production rates are the following.

- (C₁) *The stoichiometric coefficients ν_{ij}^f and ν_{ij}^b , $i \in \mathfrak{S}$, $j \in \mathfrak{R}$, and the atomic coefficients \mathbf{a}_{il} , $i \in \mathfrak{S}$, $l \in \mathfrak{A}$, are nonnegative integers. The atomic vectors \mathbf{a}_l , $l \in \mathfrak{A}$, and the reaction vectors ν_j , $j \in \mathfrak{R}$, satisfy the atom conservation relations $\langle \nu_j^b, \mathbf{a}_l \rangle - \langle \nu_j^f, \mathbf{a}_l \rangle = \langle \nu_j, \mathbf{a}_l \rangle = 0$.*
- (C₂) *The atom masses \tilde{m}_l , $l \in \mathfrak{A}$, are positive constants, and the species molar masses m_i , $i \in \mathfrak{S}$, are given by $m_i = \sum_{l \in \mathfrak{A}} \tilde{m}_l \mathbf{a}_{il}$.*
- (C₃) *The symmetric rate constants κ_j^s , $j \in \mathfrak{R}$, are C^∞ positive functions of $T > 0$.*

For realistic complex chemistry networks, the number of chemical reactions is always much larger than the number of chemical species and one usually has $\mathcal{R} = \mathcal{A}^\perp$. From atom conservation and the definition of species masses, we now deduce the mass conservation property.

Lemma 2.4. *Denote by \mathbf{M} the diagonal matrix $\mathbf{M} = \text{diag}(m_1, \dots, m_n)$. Then the vector of chemical production rates ω is such that $\omega \in \mathcal{R}$ and $\mathbf{M}\omega \in \mathcal{M}\mathcal{R}$. Moreover, the unity vector satisfies $\mathbb{I} \in (\mathcal{M}\mathcal{R})^\perp$ so that we have the total mass conservation relation $\langle \mathbb{I}, \mathbf{M}\omega \rangle = \sum_{k \in \mathfrak{S}} m_k \omega_k = 0$.*

Proof. We deduce from (C₁)-(C₃) that $\mathbb{I} = \sum_{l \in \mathfrak{A}} \tilde{m}_l \mathbf{M}^{-1} \mathbf{a}_l$ so that $\mathbb{I} \in (\mathcal{M}\mathcal{R})^\perp$ since $\mathcal{A}^\perp \subset \mathcal{R}^\perp$. Moreover, $\omega \in \mathcal{R}$ since $\omega = \sum_{j \in \mathfrak{R}} \tau_j \nu_j$ and thus $\mathbf{M}\omega \in \mathcal{M}\mathcal{R}$ and finally $\langle \mathbf{M}\omega, \mathbb{I} \rangle = 0$. \square

The mathematical structure of chemical kinetics has been investigated—generally for homogeneous systems and kinetics of mass action type—by Aris [1], Wei [58], Shapiro and Shapley [50], Pousin [48], Krambeck [42], Giovangigli and Massot [22, 27, 28], and that of nonideal chemical production rates has been investigated by the authors [29].

2.4 Transport fluxes

The viscous tensor is in the form

$$\mathbf{\Pi} = -\kappa(\nabla \cdot \mathbf{v})\mathbb{I}_d - \eta(\nabla \mathbf{v} + (\nabla \mathbf{v})^t - \frac{2}{d}(\nabla \cdot \mathbf{v})\mathbb{I}_d), \quad (2.7)$$

where κ denotes the effective volume viscosity, η the shear viscosity, and \mathbb{I}_d the identity matrix in d dimensions. Actually, the coefficient $2/d$ in the viscous tensor (2.7) should be $2/3 = 2/d'$ where $d' = 3$ is the dimension of the velocity phase space of the associated kinetic model. However, we may consider the equations in \mathbb{R}^d with $d \leq d' = 3$ and the full size viscous tensor $\mathbf{\Pi}'$ is then a matrix of order $d' = 3$, with a coefficient $2/3$. If we denote then by $\mathbf{\Pi}$ the upper left block of size d of $\mathbf{\Pi}'$, that is, the useful part of $\mathbf{\Pi}'$, we may rewrite $\mathbf{\Pi}$ in the form (2.7) with $\kappa = \kappa' + (\frac{2}{d} - \frac{2}{3})\eta$ where κ' is the physical volume viscosity [25]. Note incidentally that the volume viscosity of polyatomic gases is positive and its impact on fast flows has been established in [5].

The mass and heat diffusion fluxes derived from the kinetic theory of dilute or the kinetic theory of dense gases may be written in the form [22, 31, 30]

$$\mathcal{F}_i = -\sum_{j \in \mathfrak{S}} \rho y_j D_{ij} (\mathbf{d}_j + \chi_j \nabla \ln T), \quad i \in \mathfrak{S}, \quad (2.8)$$

$$\mathcal{F}_e = \sum_{j \in \mathfrak{S}} \frac{RT}{m} \frac{\chi_j}{y_j} \mathcal{F}_j - \lambda \nabla T + \sum_{i \in \mathfrak{S}} h_i \mathcal{F}_i, \quad (2.9)$$

where $D = (D_{ij})_{i,j \in \mathfrak{S}}$ denotes the matrix of multicomponent diffusion coefficients, y_j the mass fraction of the j th species, χ_j the thermal diffusion ratio of the j th species, and λ the thermal conductivity. Denoting by $(\nabla \mu_j)_T$ the gradient at constant temperature of the reduced chemical potential $\mu_j = m_j \mathcal{G}_j / RT$, the generalized diffusion driving force of the j th species is given by $\mathbf{d}_j = x_j (\nabla \mu_j)_T$. The diffusion coefficients D_{ij} , $i, j \in \mathfrak{S}$ are symmetric and have been introduced by Waldman for dilute gases [57, 7] and Kurochkin [43] for dense gases. The diffusion coefficients and the thermal diffusion ratios satisfy the mass conservation constraints $Dy = 0$ and $\langle \mathbb{I}, \chi \rangle = 0$ where $y = (y_1, \dots, y_n)^t$ and $\chi = (\chi_1, \dots, \chi_n)^t$. Various extra mathematical properties of the transport coefficients are discussed in [21, 15, 27, 22]. Evaluating the transport coefficients generally requires solving transport linear systems derived from the kinetic theory of gases [11, 43, 53]. These coefficients may conveniently be evaluated from convergent series arising from iterative solution of the transport linear systems [11, 12, 13, 14, 15, 26, 31].

In order to express the heat and mass diffusion fluxes it is convenient to introduce the matrices \mathcal{L} and L defined by

$$\mathcal{L} = \begin{pmatrix} \mathcal{Y} & \frac{RT}{m} \chi + \mathcal{Y} h_\bullet \\ 0 & 1 \end{pmatrix}, \quad L = \rho m \mathcal{L}^t \begin{pmatrix} D & 0 \\ 0 & \frac{RT^2}{\rho m} \lambda \end{pmatrix} \mathcal{L}, \quad (2.10)$$

where $\mathcal{Y} = \text{diag}(y_1, \dots, y_n)$, $h_\bullet = (h_1, \dots, h_n)^t$, as well as the variable $\mathbf{v} = (\mathcal{G}_1, \dots, \mathcal{G}_n, -1)^t / RT$ so that we have

$$\mathcal{F}_i = -\sum_{i,j \in \mathfrak{S} \cup \{e\}} L_{ij} \nabla v_j, \quad i \in \mathfrak{S} \cup \{e\}. \quad (2.11)$$

The mathematical properties of the multicomponent transport matrix L are directly related to those of the diffusion matrix D , the thermal diffusion vector χ and the thermal conductivity λ [30].

Proposition 2.5. *Assume that Properties (\mathcal{T}_1) - (\mathcal{T}_3) hold, let $D \in \mathbb{R}^{n,n}$, $\chi \in \mathbb{R}^n$, and λ , and assume that L is given by (2.10). Then the following statements are equivalent*

- (i) *The matrix L is positive semi-definite with nullspace $N(L) = \mathbb{R}(\mathbb{I}, 0)^t$.*
- (ii) *The matrix D is symmetric positive semi-definite with nullspace $N(D) = \mathbb{R}y$ and $\lambda > 0$,*

The mathematical properties of the matrix L and of the viscosities κ and η that we will need are now the following.

(Tr₁) *The matrix L and the coefficients η and κ are C^∞ functions of $\mathbf{z} \in \mathcal{O}_z$.*

(Tr₂) *The matrix L is symmetric positive semi-definite and has nullspace $N(L) = \mathbb{R}(\mathbb{I}, 0)^t$, where $\mathbb{I} \in \mathbb{R}^n$ and $\mathbb{I} = (1, \dots, 1)^t$. The coefficient η is positive, the coefficient κ is nonnegative and is positive when $d = 1$.*

The following proposition shows that the physical entropy production due to macroscopic variable gradients and to chemical reactions are both nonnegative [16, 22, 30].

Lemma 2.6. *The physical entropy governing equation may be written in the form*

$$\partial_t \mathcal{S} + \nabla \cdot (\mathcal{S} \mathbf{v}) + \nabla \cdot \left(- \sum_{i \in \mathfrak{S}} \frac{\mathcal{G}_i}{T} \mathcal{F}_i + \frac{\mathcal{F}_e}{T} \right) = \mathbf{v}_{\nabla} + \mathbf{v}_{\omega}, \quad (2.12)$$

where the entropy production due to macroscopic gradients \mathbf{v}_{∇} and chemistry \mathbf{v}_{ω} are given by

$$\begin{aligned} \mathbf{v}_{\nabla} &= \sum_{i,j \in \mathfrak{S} \cup \{e\}} R L_{ij} \nabla v_i \cdot \nabla v_j + \frac{\kappa}{T} (\nabla \cdot \mathbf{v})^2 + \frac{\eta}{2T} |\nabla \mathbf{v} + \nabla \mathbf{v}^t - \frac{2}{d} \nabla \cdot \mathbf{v} \mathbb{I}_d|^2, \\ \mathbf{v}_{\omega} &= -R \langle \mu, \omega \rangle = \sum_{j \in \mathfrak{R}} R \kappa_j^s (\langle \mu, \nu_j^f \rangle - \langle \mu, \nu_j^b \rangle) (\exp \langle \mu, \nu_j^f \rangle - \exp \langle \mu, \nu_j^b \rangle). \end{aligned}$$

3 Mathematical entropies and symmetrization

We rewrite the system of partial differential equations modeling dissipative fluid in a quasilinear form and we investigate *local* symmetrization properties.

3.1 Vector notation

The conservative variable is defined by $\mathbf{u} = (\rho_1, \dots, \rho_n, \rho \mathbf{v}, \mathcal{E} + \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v})^t$ and the natural variable by $\mathbf{z} = (\rho_1, \dots, \rho_n, \mathbf{v}, T)^t$. The velocity components of vectors in $\mathbb{R}^{n+d+1} = \mathbb{R}^n \times \mathbb{R}^d \times \mathbb{R}$ are written as vectors of \mathbb{R}^d for convenience. Since the thermodynamic part of \mathbf{u} is $\mathbf{u} = (\rho_1, \dots, \rho_n, \mathcal{E})^t$ and the thermodynamic part of \mathbf{z} is $\mathbf{z} = (\rho_1, \dots, \rho_n, T)^t$ it is easily seen that \mathbf{u} is defined over the open set

$$\mathcal{O}_{\mathbf{u}} = \left\{ \mathbf{u} \in \mathbb{R}^{n+d+1} \quad \left(u_1, \dots, u_n, u_{n+d+1} - \frac{1}{2} \frac{u_{n+1}^2 + \dots + u_{n+d}^2}{\sum_{1 \leq i \leq n} u_i} \right)^t \in \mathcal{O}_{\mathbf{u}} \right\}, \quad (3.1)$$

and \mathbf{z} is defined over the open set

$$\mathcal{O}_{\mathbf{z}} = \{ \mathbf{z} \in \mathbb{R}^{n+d+1} \quad (z_1, \dots, z_n, z_{n+d+1})^t \in \mathcal{O}_{\mathbf{z}} \}. \quad (3.2)$$

Neither $\mathcal{O}_{\mathbf{u}}$ nor $\mathcal{O}_{\mathbf{z}}$ are likely to be convex in general due to the presence of thermodynamically unstable states [30] in contrast with ideal gas mixtures [27, 22]. In order to express the natural variable \mathbf{z} in terms of the conservative variable \mathbf{u} , we note the following property of the map $\mathbf{z} \rightarrow \mathbf{u}$ [30].

Proposition 3.1. *Assuming that (\mathcal{T}_1) - (\mathcal{T}_3) hold, the map $\mathbf{z} \mapsto \mathbf{u}$ is a C^∞ diffeomorphism from the open set $\mathcal{O}_{\mathbf{z}}$ onto the open set $\mathcal{O}_{\mathbf{u}}$.*

The equations modeling nonideal multicomponent reactive fluids may be written into the compact form $\partial_t \mathbf{u} + \sum_{i \in C} \partial_i \mathbf{F}_i + \sum_{i \in C} \partial_i \mathbf{F}_i^{\text{diss}} = \Omega$ where ∂_t is the time derivative operator, ∂_i the space derivative operator in the i th direction, \mathbf{F}_i the convective flux in the i th direction, $\mathbf{F}_i^{\text{diss}}$ the dissipative flux in the i th direction, Ω the source term, and $C = \{1, \dots, d\}$ the indexing set of spatial dimensions. The convective flux \mathbf{F}_i in the i th direction is given by

$$\mathbf{F}_i = (\rho_1 v_i, \dots, \rho_n v_i, \rho \mathbf{v} v_i + p \mathbf{e}^i, (\mathcal{E} + p + \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v}) v_i)^t, \quad (3.3)$$

where \mathbf{e}^i , $i \in C$, are the basis vectors of \mathbb{R}^d . The dissipative flux $\mathbf{F}_i^{\text{diss}}$ is given by

$$\mathbf{F}_i^{\text{diss}} = (\mathcal{F}_{1i}, \dots, \mathcal{F}_{ni}, \mathbf{\Pi}_{\bullet i}, \mathcal{F}_{ei}, + \sum_{j \in C} \Pi_{ij} v_j)^t, \quad (3.4)$$

where the spatial components of the transport fluxes have been written $\mathbf{\Pi} = (\Pi_{ij})_{i,j \in C}$, $\mathbf{\Pi}_{\bullet i} = (\Pi_{1i}, \dots, \Pi_{di})^t$, $\mathcal{F}_k = (\mathcal{F}_{k1}, \dots, \mathcal{F}_{kd})^t$, and $\mathcal{F}_e = (\mathcal{F}_{e1}, \dots, \mathcal{F}_{ed})^t$. Finally, the source term is given by

$$\Omega = (m_1 \omega_1, \dots, m_n \omega_n, \mathbf{0}, 0)^t, \quad (3.5)$$

where $\mathbf{0} = (0, \dots, 0)^t \in \mathbb{R}^d$. From the expressions of $\boldsymbol{\Pi}$ and \mathcal{F}_k , $k \in \mathfrak{S} \cup \{e\}$, the dissipative fluxes may be written in the form $F_i^{\text{diss}} = -\sum_{j \in C} \widehat{B}_{ij}(\mathbf{z}) \partial_j \mathbf{z}$, $i \in C$, where \widehat{B}_{ij} is the dissipative matrix relating the flux F_i^{diss} in the i th direction with the gradient of the natural variable in the j th direction $\partial_j \mathbf{z}$. Thanks to Proposition 3.1, we may then write that $F_i^{\text{diss}} = -\sum_{j \in C} B_{ij}(\mathbf{u}) \partial_j \mathbf{u}$, $i \in C$, where the dissipation matrices B_{ij} are defined as $B_{ij} = \widehat{B}_{ij} \partial_{\mathbf{u}} \mathbf{z}$, $i, j \in C$. Further introducing the Jacobian matrices $A_i = \partial_{\mathbf{u}} F_i$, $i \in C$, the governing equations are finally rewritten into the compact form

$$\partial_t \mathbf{u} + \sum_{i \in C} A_i(\mathbf{u}) \partial_i \mathbf{u} = \sum_{i, j \in C} \partial_i (B_{ij}(\mathbf{u}) \partial_j \mathbf{u}) + \Omega(\mathbf{u}). \quad (3.6)$$

In the next section, we discuss the properties of mathematical entropies for such a quasilinear system.

3.2 Mathematical entropy and symmetrization

The following definition of an entropy function [30] has been adapted from Godunov [33] and Friedrichs and Lax [20] for the hyperbolic part, from Kawashima and Shizuta [37, 54, 38, 39] for the dissipative part, and from the structure of chemical sources [22, 28], Chen, Levermore and Liu [8] and Kawashima and Yong [40] for the source term.

Definition 3.2. Consider a C^∞ function $\sigma(\mathbf{u})$ defined over the open domain $\mathcal{O}_{\mathbf{u}}$ assumed to be simply connected. The function σ is said to be an entropy function for the system (3.6) if the following properties hold.

- (E₁) The Hessian matrix $\partial_{\mathbf{u}}^2 \sigma(\mathbf{u})$ is positive definite over $\mathcal{O}_{\mathbf{u}}$.
- (E₂) There exists real-valued C^∞ functions $\mathbf{q}_i = \mathbf{q}_i(\mathbf{u})$ such that $\partial_{\mathbf{u}} \sigma(\mathbf{u}) A_i(\mathbf{u}) = \partial_{\mathbf{u}} \mathbf{q}_i(\mathbf{u})$ for any $\mathbf{u} \in \mathcal{O}_{\mathbf{u}}$ and $i \in C$.
- (E₃) We have $(\partial_{\mathbf{u}}^2 \sigma(\mathbf{u}))^{-1} (B_{ij}(\mathbf{u}))^t = B_{ji}(\mathbf{u}) (\partial_{\mathbf{u}}^2 \sigma(\mathbf{u}))^{-1}$ for any $\mathbf{u} \in \mathcal{O}_{\mathbf{u}}$ and $i, j \in C$.
- (E₄) The matrix $\widetilde{B}(\mathbf{u}, w) = \sum_{i, j \in C} B_{ij}(\mathbf{u}) (\partial_{\mathbf{u}}^2 \sigma(\mathbf{u}))^{-1} w_i w_j$ is symmetric positive semi-definite for any $\mathbf{u} \in \mathcal{O}_{\mathbf{u}}$ and $w \in \Sigma^{d-1}$.
- (E₅) There exists a vector space $\mathcal{E} \subset \mathbb{R}^{n+d+1}$ independent of \mathbf{u} such that for any $\mathbf{u} \in \mathcal{O}_{\mathbf{u}}$, we have $\Omega(\mathbf{u}) \in \mathcal{E}^\perp$, and $\Omega(\mathbf{u}) = 0$ if and only if $(\partial_{\mathbf{u}} \sigma(\mathbf{u}))^t \in \mathcal{E}$ and if and only if $\partial_{\mathbf{u}} \sigma(\mathbf{u}) \Omega(\mathbf{u}) = 0$.
- (E₆) For any $\mathbf{u} \in \mathcal{O}_{\mathbf{u}}$, if $\Omega(\mathbf{u}) = 0$, then $\partial_{\mathbf{u}} \Omega(\mathbf{u}) (\partial_{\mathbf{u}}^2 \sigma(\mathbf{u}))^{-1} = (\partial_{\mathbf{u}}^2 \sigma(\mathbf{u}))^{-1} (\partial_{\mathbf{u}} \Omega(\mathbf{u}))^t$ and moreover $N(\partial_{\mathbf{u}} \Omega (\partial_{\mathbf{u}}^2 \sigma(\mathbf{u}))^{-1}) = \mathcal{E}$.
- (E₇) For any $\mathbf{u} \in \mathcal{O}_{\mathbf{u}}$, we have $\partial_{\mathbf{u}} \sigma(\mathbf{u}) \Omega(\mathbf{u}) \leq 0$.

An important difficulty with nonideal fluids is the presence of thermodynamically unstable states associated with the loss of definiteness for entropy Hessian matrices. A consequence is the existence of distinct states which correspond to the same symmetrizing variable so that only *local* symmetrization may be obtained [30].

Definition 3.3. Consider a $C^{\infty-1}$ map $\mathbf{u} \rightarrow \mathbf{v}$ from $\subset \mathcal{O}_{\mathbf{u}}$ onto an open domain $\mathcal{O}_{\mathbf{v}}$. Assume that for any $\mathbf{u} \in \mathcal{O}_{\mathbf{u}}$ there exists subdomains $\mathcal{O}_{\mathbf{u}} \subset \mathcal{O}_{\mathbf{u}}$ and $\mathcal{O}_{\mathbf{v}} \subset \mathcal{O}_{\mathbf{v}}$ such that $\mathbf{u} \rightarrow \mathbf{v}$ is a $C^{\infty-1}$ diffeomorphism from $\mathcal{O}_{\mathbf{u}}$ onto $\mathcal{O}_{\mathbf{v}}$. Consider then the system in the \mathbf{v} variable

$$\widetilde{A}_0(\mathbf{v}) \partial_t \mathbf{v} + \sum_{i \in C} \widetilde{A}_i(\mathbf{v}) \partial_i \mathbf{v} = \sum_{i, j \in C} \partial_i (\widetilde{B}_{ij}(\mathbf{v}) \partial_j \mathbf{v}) + \widetilde{\Omega}(\mathbf{v}), \quad (3.7)$$

where $\widetilde{A}_0 = \partial_{\mathbf{v}} \mathbf{u}$, $\widetilde{A}_i = A_i \partial_{\mathbf{v}} \mathbf{u} = \partial_{\mathbf{v}} F_i$, $\widetilde{B}_{ij} = B_{ij} \partial_{\mathbf{v}} \mathbf{u}$, and $\widetilde{\Omega} = \Omega$. The system is said of the local symmetric form [30] if Properties (S₁)-(S₇) hold where $\mathcal{E} \subset \mathbb{R}^{n+d+1}$ denotes a vector space independent of $\mathbf{u} \in \mathcal{O}_{\mathbf{u}}$ and $\mathbf{v} \in \mathcal{O}_{\mathbf{v}}$.

- (S₁) The matrix $\widetilde{A}_0(\mathbf{v})$ is symmetric positive definite for $\mathbf{v} \in \mathcal{O}_{\mathbf{v}}$.
- (S₂) The matrices $\widetilde{A}_i(\mathbf{v})$, $i \in C$, are symmetric for $\mathbf{v} \in \mathcal{O}_{\mathbf{v}}$.

- (S₃) We have $\tilde{\mathbf{B}}_{ij}^t(\mathbf{v}) = \tilde{\mathbf{B}}_{ji}(\mathbf{v})$ for $i, j \in C$, and $\mathbf{v} \in \mathcal{O}_v$.
- (S₄) The matrix $\tilde{\mathbf{B}}(\mathbf{v}, w) = \sum_{i,j \in C} \tilde{\mathbf{B}}_{ij}(\mathbf{v}) w_i w_j$ is symmetric positive semi-definite, for $\mathbf{v} \in \mathcal{O}_v$, and $w \in \Sigma^{d-1}$, where Σ^{d-1} is the unit sphere in d dimensions.
- (S₅) There exists a vector space $\mathcal{E} \subset \mathbb{R}^{n+d+1}$ such that for any $\mathbf{v} \in \mathcal{O}_v$, we have $\Omega(\mathbf{v}) \in \mathcal{E}^\perp$. Moreover, we have $\Omega(\mathbf{v}) = 0$ if and only if $\mathbf{v} \in \mathcal{E}$ and if and only if $\langle \mathbf{v}, \Omega(\mathbf{v}) \rangle = 0$.
- (S₆) For any $\mathbf{v} \in \mathcal{O}_v$, if $\Omega(\mathbf{v}) = 0$, then $\partial_v \Omega(\mathbf{v}) = (\partial_v \Omega(\mathbf{v}))^t$ and $N(\partial_v \Omega(\mathbf{v})) = \mathcal{E}$.
- (S₇) For any $\mathbf{v} \in \mathcal{O}_v$, we have $\langle \mathbf{v}, \Omega(\mathbf{v}) \rangle \leq 0$.

The equivalence between symmetrization and entropy for hyperbolic systems of conservation laws, that is, the equivalence between (S₁)-(S₇) and (E₁)-(E₇), is obtained with $\mathbf{v} = (\partial_u \sigma)^t$.

Theorem 3.4. Assume that the system (3.6) admits an C^∞ entropy function σ defined over \mathcal{O}_u . Then, the system can be locally symmetrized around any point \mathbf{u} of \mathcal{O}_u with the symmetrizing variable $\mathbf{v} = (\partial_u \sigma)^t$. Conversely, assume that the system can be locally symmetrized with the $C^{\infty-1}$ map $\mathbf{u} \rightarrow \mathbf{v}$ in the neighborhood of any point \mathbf{u} of the simply connected open set \mathcal{O}_u . Then there exists a globally defined entropy over the open set \mathcal{O}_u such that $\mathbf{v} = (\partial_u \sigma)^t$.

Proof. We first directly establish the equivalence of (S₁)-(S₂) and (E₁)-(E₂) with $\mathbf{v} = (\partial_u \sigma)^t$. Indeed, if (S₁)-(S₂) holds, then $\tilde{\mathbf{A}}_0 = \partial_u \mathbf{v}$ is symmetric positive definite and so is $\partial_u \mathbf{v}$. From Poincaré Lemma, the symmetry of $\partial_u \mathbf{v}$, and the simple connectedness of \mathcal{O}_u , there exists σ with $\mathbf{v} = (\partial_u \sigma)^t$ and $\partial_u \mathbf{v} = \partial_u^2 \sigma$ is positive definite and we have established (E₁). Consider next the vector $\mathbf{p} = (\partial_u \sigma \partial_u F_i)^t$ which has its l th component given by $p_l = \sum_{1 \leq j \leq \bar{n}} \partial_{u_j} \sigma \partial_{u_l} F_{i,j}$ where $\bar{n} = n + d + 1$. The differential identity $\partial_{u_k} p_l = \sum_{1 \leq j \leq \bar{n}} \partial_{u_j u_k}^2 \sigma \partial_{u_l} F_{i,j} + \sum_{1 \leq j \leq \bar{n}} \partial_{u_j} \sigma \partial_{u_k u_l} F_{i,j}$ is then easily established. Since $\tilde{\mathbf{A}}_i = \mathbf{A}_i \partial_u \mathbf{u} = \partial_u F_i$ is symmetric from (S₂), we note that $(\partial_u \mathbf{v}) \tilde{\mathbf{A}}_i (\partial_u \mathbf{v}) = (\partial_u \mathbf{v}) \mathbf{A}_i = \partial_u^2 \sigma \mathbf{A}_i = \partial_u^2 \sigma \partial_u F_i$ is symmetric and this implies that $\partial_{u_k} p_l = \partial_{u_l} p_k$. By Poincaré Lemma and since \mathcal{O}_u is simply connected there exists \mathbf{q}_i such that $\partial_{u_l} \mathbf{q}_i = p_l$ and we have established (E₂).

Conversely, if (E₁)-(E₂) holds, then $\partial_u \mathbf{v} = \partial_u^2 \sigma$ is symmetric positive definite and so is $\tilde{\mathbf{A}}_0 = \partial_u \mathbf{v}$ and (S₁) is established. Moreover, the identity $\partial_{u_k u_l} \mathbf{q}_i = \sum_{1 \leq j \leq \bar{n}} \partial_{u_j u_k}^2 \sigma \partial_{u_l} F_{i,j} + \sum_{1 \leq j \leq \bar{n}} \partial_{u_j} \sigma \partial_{u_k u_l} F_{i,j}$ yields that $(\partial_u \mathbf{v}) \mathbf{A}_i$ is symmetric and so is $\tilde{\mathbf{A}}_i = (\partial_u \mathbf{v}) (\partial_u \mathbf{v} \mathbf{A}_i) (\partial_u \mathbf{v})$ and (S₂) is established.

Finally, it is next seen that each (S _{i}) is a reformulation of (E _{i}) for $3 \leq i \leq 7$ and conversely thanks to the relation $\mathbf{v} = (\partial_u \sigma)^t$. \square

3.3 Natural symmetric form

We evaluate in this section the natural symmetric form of the system of partial differential equations modeling nonideal fluids (2.1)–(2.3) using the essential mathematical entropy $\sigma = -S/R$ where the $1/R$ factor is introduced for convenience. It is reminded that the velocity components of all quantities in \mathbb{R}^{n+d+1} are denoted as vectors of \mathbb{R}^d for the sake of notational simplicity and the corresponding partitioning is also used for matrices.

Theorem 3.5. Assume that (T₁)-(T₃), (C₁)-(C₃), and (Tr₁)-(Tr₂) hold. Then the function $\sigma = -S/R$ is a mathematical entropy for the system (2.1)–(2.3) and the corresponding entropic variable is

$$\mathbf{v} = (\partial_u \sigma)^t = \frac{1}{RT} \left(\mathcal{G}_1 - \frac{1}{2} |\mathbf{v}|^2, \dots, \mathcal{G}_n - \frac{1}{2} |\mathbf{v}|^2, \mathbf{v}, -1 \right)^t. \quad (3.8)$$

For any $\mathbf{u} \in \mathcal{O}_u$ there exists open subdomains $\mathcal{O}_u \subset \mathcal{O}_u$ and $\mathcal{O}_v \subset \mathcal{O}_v$ such that the map $\mathbf{u} \rightarrow \mathbf{v}$ is a local $C^{\infty-1}$ diffeomorphism from \mathcal{O}_u onto \mathcal{O}_v . The system written in term of the entropic variable \mathbf{v} is

$$\tilde{\mathbf{A}}_0(\mathbf{v}) \partial_t \mathbf{v} + \sum_{i \in C} \tilde{\mathbf{A}}_i(\mathbf{v}) \partial_i \mathbf{v} = \sum_{i,j \in C} \partial_i (\tilde{\mathbf{B}}_{ij}(\mathbf{v}) \partial_j \mathbf{v}) + \tilde{\mathbf{\Omega}}(\mathbf{v}), \quad (3.9)$$

with $\tilde{\mathbf{A}}_0 = \partial_u \mathbf{v}$, $\tilde{\mathbf{A}}_i = \mathbf{A}_i \partial_u \mathbf{u}$, $\tilde{\mathbf{B}}_{ij} = \mathbf{B}_{ij} \partial_u \mathbf{u}$, and $\tilde{\mathbf{\Omega}} = \mathbf{\Omega}$, and is of the local symmetric form. The matrix $\tilde{\mathbf{A}}_0$ is given by

$$\tilde{\mathbf{A}}_0 = \begin{bmatrix} \Lambda & & Sym \\ \mathbf{v} \otimes \Lambda \mathbf{\Pi} & \langle \Lambda \mathbf{\Pi}, \mathbf{\Pi} \rangle \mathbf{v} \otimes \mathbf{v} + \rho RT \mathbf{\Pi}_d & \\ \Lambda \mathcal{G} & \langle \Lambda \mathcal{G}, \mathbf{\Pi} \rangle \mathbf{v}^t + \rho RT \mathbf{v}^t & \tilde{\mathbf{A}}_0^{T,T} \end{bmatrix}, \quad (3.10)$$

where $\Lambda = \rho R \Gamma^{-1}$, Γ^{-1} is the inverse of the matrix $\Gamma_{kl} = \rho \tilde{\partial}_{\rho_k} \mathcal{G}_l / T = \rho \tilde{\partial}_{\rho_l} \mathcal{G}_k / T$, $\mathcal{g}_i = \mathcal{G}_i - T \tilde{\partial}_T \mathcal{G}_i + \frac{1}{2} |\mathbf{v}|^2 = \tilde{\partial}_{\rho_i} \mathcal{E} + \frac{1}{2} |\mathbf{v}|^2$, $i \in \mathfrak{S}$, and $\tilde{\mathbf{A}}_0^{T,T} = \langle \Lambda \mathcal{g}, \mathcal{g} \rangle + \rho R T |\mathbf{v}|^2 + R T^2 \tilde{\partial}_T \mathcal{E}$. Since $\tilde{\mathbf{A}}_0$ is symmetric, we only give its left lower triangular part and write “Sym” in the upper triangular part. Denoting by $\boldsymbol{\xi} = (\xi_1, \dots, \xi_d)^t$ an arbitrary vector of \mathbb{R}^d and letting $\tilde{\mathbf{A}} = \sum_{i \in C} \xi_i \tilde{\mathbf{A}}_i$, we have

$$\tilde{\mathbf{A}} = \mathbf{v} \cdot \boldsymbol{\xi} \tilde{\mathbf{A}}_0 + R T \begin{bmatrix} 0 & & & \text{Sym} \\ \boldsymbol{\xi} \otimes \varrho & & \rho(\boldsymbol{\xi} \otimes \mathbf{v} + \mathbf{v} \otimes \boldsymbol{\xi}) & \\ \mathbf{v} \cdot \boldsymbol{\xi} \varrho^t & \mathbf{v} \cdot \boldsymbol{\xi} \rho \mathbf{v}^t + (\mathcal{E} + p + \frac{1}{2} \rho |\mathbf{v}|^2) \boldsymbol{\xi}^t & 2\mathbf{v} \cdot \boldsymbol{\xi} (\mathcal{E} + p + \frac{1}{2} \rho |\mathbf{v}|^2) & \end{bmatrix}. \quad (3.11)$$

Moreover, we have the decomposition

$$\tilde{\mathbf{B}}_{ij} = \tilde{\mathbf{B}}^L \delta_{ij} + \kappa R T \tilde{\mathbf{B}}_{ij}^\kappa + \eta R T \tilde{\mathbf{B}}_{ij}^\eta, \quad (3.12)$$

where

$$\tilde{\mathbf{B}}^L = \begin{bmatrix} L^{n,n} & & \text{Sym} \\ 0_{d,n} & 0_{d,d} & \\ L_{e\bullet} & 0_{1,d} & L_{e,e} \end{bmatrix}, \quad (3.13)$$

and denoting by $\boldsymbol{\xi} = (\xi_1, \dots, \xi_d)^t$ and $\boldsymbol{\zeta} = (\zeta_1, \dots, \zeta_d)^t$ arbitrary vectors of \mathbb{R}^d , the matrices $\tilde{\mathbf{B}}_{ij}^\kappa$ and $\tilde{\mathbf{B}}_{ij}^\eta$, $i, j \in C$, are given by

$$\sum_{i,j \in C} \xi_i \zeta_j \tilde{\mathbf{B}}_{ij}^\kappa = \begin{bmatrix} 0_{n,n} & 0_{n,d} & 0_{n,1} \\ 0_{d,n} & \boldsymbol{\xi} \otimes \boldsymbol{\zeta} & \mathbf{v} \cdot \boldsymbol{\zeta} \boldsymbol{\xi} \\ 0_{1,n} & \mathbf{v} \cdot \boldsymbol{\xi} \boldsymbol{\zeta}^t & \mathbf{v} \cdot \boldsymbol{\xi} \mathbf{v} \cdot \boldsymbol{\zeta} \end{bmatrix}, \quad (3.14)$$

$$\sum_{i,j \in C} \xi_i \zeta_j \tilde{\mathbf{B}}_{ij}^\eta = \begin{bmatrix} 0_{n,n} & 0_{n,d} & 0_{n,1} \\ 0_{d,n} & \boldsymbol{\xi} \cdot \boldsymbol{\zeta} \mathbb{I}_d + \boldsymbol{\zeta} \otimes \boldsymbol{\xi} - \frac{2}{d} \boldsymbol{\xi} \otimes \boldsymbol{\zeta} & \boldsymbol{\xi} \cdot \boldsymbol{\zeta} \mathbf{v} + \mathbf{v} \cdot \boldsymbol{\xi} \boldsymbol{\zeta} - \frac{2}{d} \mathbf{v} \cdot \boldsymbol{\zeta} \boldsymbol{\xi} \\ 0_{1,n} & \boldsymbol{\xi} \cdot \boldsymbol{\zeta} \mathbf{v}^t + \mathbf{v} \cdot \boldsymbol{\zeta} \boldsymbol{\xi}^t - \frac{2}{d} \mathbf{v} \cdot \boldsymbol{\xi} \boldsymbol{\zeta}^t & \boldsymbol{\xi} \cdot \boldsymbol{\zeta} \mathbf{v} \cdot \mathbf{v} + (1 - \frac{2}{d}) \mathbf{v} \cdot \boldsymbol{\xi} \mathbf{v} \cdot \boldsymbol{\zeta} \end{bmatrix}. \quad (3.15)$$

Finally, the equilibrium manifold is given by

$$\mathcal{E} = (\mathbf{M} \mathcal{R})^\perp \times \mathbb{R}^d \times \mathbb{R}, \quad (3.16)$$

where $\mathcal{R} = \text{span}\{v_i, i \in \mathfrak{R}\} \subset \mathbb{R}^n$ is spanned by the reaction vectors and $\mathbf{M} = \text{diag}(m_1, \dots, m_n)$.

For ideal fluids, the symmetrizing change of variable $\mathbf{u} \rightarrow \mathbf{v}$ is one to one and is thus a global change of variable [27, 22]. On the contrary, for nonideal fluid, even though the entropy σ is globally defined, a typical situation is that of distinct points \mathbf{u}^\sharp and \mathbf{u}^\flat such that $\mathbf{v}^\sharp = \mathbf{v}^\flat$. Indeed, we see from (3.8) that the equality $\mathbf{v}^\sharp = \mathbf{v}^\flat$ corresponds to the chemical equilibrium between the two stable phases \mathbf{u}^\sharp and \mathbf{u}^\flat with identical pressure, temperature and Gibbs functions, that may notably be observed for nonideal fluids [29].

4 Properties of mathematical entropies

We first discuss in this section the structure of mathematical entropies satisfying solely (\mathbf{E}_2) that is, entropies for the multicomponent Euler equations, under a natural nondegeneracy condition. We next discuss commutation relations (\mathbf{E}_3) between Jacobian matrices and dissipation matrices. We establish that such relations are automatically satisfied for dissipation matrices arising from viscous effects whenever the mathematical entropy is compatible with the hyperbolic structure. Compatibility with dissipation effects is then reduced to the compatibility with the mass and heat diffusion matrix L .

4.1 The hyperbolic case

We discuss functions of the conservative variable \mathbf{u} that solely satisfy (\mathbf{E}_2) . In other words, we investigate the structure of mathematical entropies in the absence of dissipation and source terms, that is, for the nonreactive multicomponent Euler equations. We assume that the thermodynamic structure is that of Properties (\mathcal{T}_1) - (\mathcal{T}_3) and an extra nondegeneracy assumption is required. This nondegeneracy condition is more easily written with the mass based variable $(p, y_1, \dots, y_n, s)^t$ where p denotes the pressure,

s the entropy per unit mass and y_i the mass fraction of the i th species. This variable may equally be used as a thermodynamic variable instead of the natural mass based variable $(\nu, y_1, \dots, y_n, T)^t$ where $\nu = 1/\rho$ denotes the volume per unit mass discussed in Appendix A. The natural non-degeneracy condition concerning thermodynamics is the following [51, 56].

(N) *The volume per unit mass $\nu = \nu(p, y_1, \dots, y_n, s)$ as a function of the variable (p, y_1, \dots, y_n, s) is such that $\partial_{ps}^2 \nu \neq 0$.*

This non-degeneracy condition also means that $\rho^2 c^2$ is not a function of p, y_1, \dots, y_n where c denotes the speed of sound [51, 56]. The structure of mathematical entropies for multicomponent flows satisfying (E₂) is given in the following theorem.

Theorem 4.1. *Assume that (T₁)-(T₃) and (N) hold and let $\tilde{\sigma}$ be a C^∞ function defined on the open set \mathcal{O}_u and satisfying (E₂). Then $\tilde{\sigma}$ is in the form*

$$\tilde{\sigma} = \varphi(\rho_1, \dots, \rho_n, \mathcal{S}) + \alpha_v \cdot \rho \mathbf{v} + \alpha_\mathcal{E}(\mathcal{E} + \frac{1}{2}\rho|\mathbf{v}|^2) + \alpha_0, \quad (4.1)$$

where φ is a 1-homogeneous C^∞ function of $\rho_1, \dots, \rho_n, \mathcal{S}$ and where $\alpha_v \in \mathbb{R}^d$, $\alpha_\mathcal{E}, \alpha_0 \in \mathbb{R}$ are constants.

The fact that φ is 1-homogeneous means that $\varphi(\rho_1, \dots, \rho_n, \mathcal{S}) = \rho f(y_1, \dots, y_n, s)$ for some C^∞ function. When there is only one species in the mixture $n = 1$, such a structure is established in the book of Denis Serre [51] in Lagrangian coordinates for the one dimensional case $d = 1$ and is also investigated by Vulkov in Eulerian coordinates for the two dimensional case $d = 2$ taking into account an eventual dependence on time [56]. To the authors's knowledge, the multicomponent case has not been previously investigated in the literature.

Proof. We establish that $\tilde{\sigma}$ is in the form $\tilde{\sigma} = \rho f(y_2, \dots, y_n, s) + \alpha_v \cdot \rho \mathbf{v} + \alpha_\mathcal{E} \rho (e + \frac{1}{2}|\mathbf{v}|^2) + \alpha_0$ where $\alpha_v, \alpha_\mathcal{E}, \alpha_0$ are constants. The decomposition (4.1) is then obtained upon letting $\varphi(\rho_1, \dots, \rho_n, \mathcal{S}) = \rho f(y_2, \dots, y_n, s)$ where $y_k = \rho_k/\rho$ for $k \in \mathfrak{S}$, $s = \mathcal{S}/\rho$, and $\rho = \sum_{k \in \mathfrak{S}} \rho_k$. We will use for convenience the variables $\mathbf{z}' = (\rho, y_2, \dots, y_n, \mathbf{v}, T)^t$ and $\mathbf{s} = (p, y_2, \dots, y_n, \mathbf{v}, s)^t$, denote by \mathfrak{S}' the corresponding species indexing set $\mathfrak{S}' = \{2, \dots, n\}$, and it is easily established that $\mathbf{z} \rightarrow \mathbf{z}'$ and $\mathbf{z} \rightarrow \mathbf{s}$ are C^∞ diffeomorphisms. We denote by $\tilde{\partial}'$ the derivation operator with respect to the variable $\mathbf{z}' = (\rho, y_2, \dots, y_n, \mathbf{v}, T)^t$, by $\bar{\partial}$ the derivation operator with respect to the variable $\mathbf{s} = (p, y_2, \dots, y_n, \mathbf{v}, s)^t$ and it is checked that the nondegeneracy condition reads $\bar{\partial}_{ps}^2 \nu \neq 0$.

The existence of fluxes $\tilde{\mathbf{q}}_i(\mathbf{u})$, $i \in C$, such that $\partial_u \tilde{\sigma} A_i = \partial_u \tilde{\mathbf{q}}_i$, $i \in C$, is equivalent to the existence of fluxes $\hat{\mathbf{q}}_i(\mathbf{z}')$, $i \in C$, such that $\partial_u \tilde{\sigma} \partial_{z'} F_i = \partial_{z'} \hat{\mathbf{q}}_i$, $i \in C$, since $A_i = \partial_u F_i$, and this property is equivalent to the compatibility relations $\tilde{\partial}'_{z'_k} (\partial_u \tilde{\sigma} \partial_{z'} F_i)_l = \tilde{\partial}'_{z'_l} (\partial_u \tilde{\sigma} \partial_{z'} F_i)_k$, for any $1 \leq k, l \leq n + d + 1$ since $\mathcal{O}_{z'}$ is simply connected. Upon writing the mathematical entropy $\tilde{\sigma}$ in the form $\tilde{\sigma} = \rho \bar{\varphi}(p, y_2, \dots, y_n, \mathbf{v}, s)$, the function $\bar{\varphi}$ is C^∞ over the open set \mathcal{O}_s since $\tilde{\sigma}$ is C^∞ over \mathcal{O}_u , and a lengthy calculation yields the vector $\mathbf{p}_i = \partial_u \tilde{\sigma} \partial_{z'} F_i$. Denoting its components in the form $\mathbf{p}_i = (\mathbf{p}_{i\rho}, \mathbf{p}_{iy_2}, \dots, \mathbf{p}_{iy_n}, \mathbf{p}_{i\mathbf{v}}, \mathbf{p}_{iT})^t$ with $\mathbf{p}_{i\mathbf{v}} = (\mathbf{p}_{iv_1}, \dots, \mathbf{p}_{iv_d})^t$ it is found that

$$\mathbf{p}_{i\rho} = v_i \bar{\varphi} + \rho v_i \bar{\partial}_p \bar{\varphi} \tilde{\partial}'_\rho p + \rho v_i \bar{\partial}_s \bar{\varphi} \tilde{\partial}'_\rho s + \bar{\partial}_{v_i} \bar{\varphi} \tilde{\partial}'_\rho p, \quad (4.2)$$

$$\mathbf{p}_{iy_k} = \rho v_i \bar{\partial}_p \bar{\varphi} \tilde{\partial}'_{y_k} p + \rho v_i \bar{\partial}_s \bar{\varphi} \tilde{\partial}'_{y_k} s + \rho v_i \bar{\partial}_{y_k} \bar{\varphi} + \bar{\partial}_{v_i} \bar{\varphi} \tilde{\partial}'_{y_k} p, \quad k \in \mathfrak{S}', \quad (4.3)$$

$$\mathbf{p}_{iv_j} = \rho v_i \bar{\partial}_{v_j} \bar{\varphi}, \quad j \in C, \quad j \neq i, \quad (4.4)$$

$$\mathbf{p}_{iv_i} = \rho \bar{\varphi} + \rho^2 c^2 \bar{\partial}_p \bar{\varphi} + \rho v_i \bar{\partial}_{v_i} \bar{\varphi}, \quad (4.5)$$

$$\mathbf{p}_{iT} = \bar{\partial}_{v_i} \bar{\varphi} \tilde{\partial}'_T p + \rho v_i \bar{\partial}_p \bar{\varphi} \tilde{\partial}'_T p + \rho v_i \bar{\partial}_s \bar{\varphi} \tilde{\partial}'_T s. \quad (4.6)$$

We have denoted here by

$$c^2 = \frac{1}{\bar{\partial}_p \rho} = \tilde{\partial}'_\rho p + \frac{T}{\rho^2} \frac{(\tilde{\partial}'_T p)^2}{\tilde{\partial}'_T e},$$

the square of the sound speed, and have also used the compatibility relations derived from Gibb's law $T \tilde{\partial}'_T s = \tilde{\partial}'_T e$, $\rho^2 \tilde{\partial}'_\rho e = p - T \tilde{\partial}'_T p$, $\rho^2 \tilde{\partial}'_\rho s = -\tilde{\partial}'_T p$, and one can establish that $\tilde{\partial}'_\rho p > 0$ from thermodynamic stability [29].

The compatibility relation $\tilde{\partial}'_\rho(\mathbf{p}_{iT}) = \tilde{\partial}'_T(\mathbf{p}_{i\rho})$ then yields—after lengthy algebra—the relations $\bar{\partial}_{v_i s}^2 \bar{\varphi} = 0$ making use of $\tilde{\partial}'_T s \tilde{\partial}'_\rho p - \tilde{\partial}'_T p \tilde{\partial}'_\rho s \neq 0$. Similarly, the compatibility relations $\tilde{\partial}'_\rho(\mathbf{p}_{iv_j}) = \tilde{\partial}'_{v_j}(\mathbf{p}_{i\rho})$

for $j \neq i$ yield that $\bar{\partial}_{v_i v_j}^2 \bar{\varphi} = 0$ for $i \neq j$, and the compatibility relations $\tilde{\partial}'_\rho(\mathbf{p}_{iy_k}) = \tilde{\partial}'_{y_k}(\mathbf{p}_{i\rho})$ then yields—after lengthy algebra—the relations $\bar{\partial}_{v_i y_k}^2 \bar{\varphi} = 0$, $k \in \mathfrak{S}'$, making use of $\bar{\partial}_{v_i s}^2 \bar{\varphi} = 0$ and $\tilde{\partial}'_\rho p > 0$.

From these relations $\bar{\partial}_{v_i s}^2 \bar{\varphi} = 0$, $i \in C$, $\bar{\partial}_{v_i y_k}^2 \bar{\varphi} = 0$, $k \in \mathfrak{S}'$, $i \in C$, and $\bar{\partial}_{v_i v_j}^2 \bar{\varphi} = 0$ for $i, j \in C$, $i \neq j$, defining $\bar{\varphi}_v$ by

$$\bar{\varphi}_v = \int_0^{v_1} \bar{\partial}_{v_1} \bar{\varphi} dv_1 + \cdots + \int_0^{v_d} \bar{\partial}_{v_d} \bar{\varphi} dv_d, \quad (4.7)$$

we deduce that $\bar{\varphi}$ may be written in the form

$$\bar{\varphi} = \bar{\varphi}_s(p, y_2, \dots, y_n, s) + \bar{\varphi}_v(p, \mathbf{v}). \quad (4.8)$$

It is then easily checked that both $\bar{\varphi}_s$ and $\bar{\varphi}_v$ are at least $C^{\kappa-1}$ over \mathcal{O}_s from the explicit expression of $\bar{\varphi}_v$ and the relation $\bar{\varphi} = \bar{\varphi}_s + \bar{\varphi}_v$, and we also have $\bar{\partial}_{v_i} \bar{\varphi} = \bar{\partial}_{v_i} \bar{\varphi}_v$ for any $i \in C$.

The compatibility relations $\tilde{\partial}'_\rho(\mathbf{p}_{iv_i}) = \tilde{\partial}'_{v_i}(\mathbf{p}_{i\rho})$, $\tilde{\partial}'_T(\mathbf{p}_{iv_i}) = \tilde{\partial}'_{v_i}(\mathbf{p}_{iT})$, and $\tilde{\partial}'_{y_k}(\mathbf{p}_{iv_i}) = \tilde{\partial}'_{v_i}(\mathbf{p}_{iy_k})$, then yields—after lengthy algebra—that for $i \in C$ and $k \in \mathfrak{S}'$

$$\bar{\partial}_{v_i}^2 \bar{\varphi} \tilde{\partial}'_\rho p = \tilde{\partial}'_\rho (\rho^2 c^2 \bar{\partial}_p \bar{\varphi}), \quad (4.9)$$

$$\bar{\partial}_{v_i}^2 \bar{\varphi} \tilde{\partial}'_T p = \tilde{\partial}'_T (\rho^2 c^2 \bar{\partial}_p \bar{\varphi}), \quad (4.10)$$

$$\bar{\partial}_{v_i}^2 \bar{\varphi} \tilde{\partial}'_{y_k} p = \tilde{\partial}'_{y_k} (\rho^2 c^2 \bar{\partial}_p \bar{\varphi}). \quad (4.11)$$

On the other hand, it is easily established that

$$\bar{\partial}_p \rho = \frac{1}{c^2}, \quad \bar{\partial}_s \rho = -\frac{T}{c^2} \frac{\tilde{\partial}'_T p}{\tilde{\partial}'_T e}, \quad (4.12)$$

$$\bar{\partial}_p T = \frac{T}{\rho^2 c^2} \frac{\tilde{\partial}'_T p}{\tilde{\partial}'_T e}, \quad \bar{\partial}_s T = \frac{T}{c^2} \frac{\tilde{\partial}'_\rho p}{\tilde{\partial}'_T e}, \quad (4.13)$$

and since $\bar{\partial}_s = (\bar{\partial}_s \rho) \tilde{\partial}'_\rho + (\bar{\partial}_s T) \tilde{\partial}'_T$ we obtain that $\bar{\partial}_s (\rho^2 c^2 \bar{\partial}_p \bar{\varphi}) = 0$. Since $\bar{\partial}_p \rho = \frac{1}{c^2}$ we also obtain that $\bar{\partial}_p \nu = -\frac{1}{\rho^2 c^2}$ so that from the nondegeneracy condition (\mathcal{N}) we deduce that $\bar{\partial}_s (\rho^2 c^2) \neq 0$. From the decomposition (4.8), $\bar{\partial}_s (\rho^2 c^2 \bar{\partial}_p \bar{\varphi}) = 0$, and $\bar{\partial}_s (\rho^2 c^2) \neq 0$ we now obtain that

$$-\bar{\partial}_p \bar{\varphi}_v = \bar{\partial}_p \bar{\varphi}_s + \frac{\rho^2 c^2 \bar{\partial}_{ps}^2 \bar{\varphi}_s}{\bar{\partial}_s (\rho^2 c^2)}.$$

This implies that $\bar{\partial}_p \bar{\varphi}_v$ is independent of \mathbf{v} and thus $\bar{\partial}_{pv_i}^2 \bar{\varphi}_v = 0$ for any $i \in C$. We now may use $\bar{\partial}_{v_i} \bar{\varphi}_v = \bar{\partial}_{v_i} \bar{\varphi}$ from (4.7) to obtain that $\bar{\partial}_{pv_i}^2 \bar{\varphi} = 0$. Since we already know that $\bar{\partial}_{sv_i}^2 \bar{\varphi} = 0$, $\bar{\partial}_{y_k v_i}^2 \bar{\varphi} = 0$, $k \in \mathfrak{S}'$, and $\bar{\partial}_{v_j v_i}^2 \bar{\varphi} = 0$, $j \in C$ for $i \neq j$, we conclude that $\bar{\partial}_{v_i} \bar{\varphi}$ only depends on v_i and from (4.7) we obtain that $\bar{\varphi}_v$ only depends on \mathbf{v} .

This now implies that $\bar{\partial}_p \bar{\varphi} = \bar{\partial}_p \bar{\varphi}_s$ and is thus independent of \mathbf{v} , and $\bar{\partial}_{v_i} (\rho^2 c^2 \bar{\partial}_p \bar{\varphi}) = 0$. Since we also have $\bar{\partial}_s (\rho^2 c^2 \bar{\partial}_p \bar{\varphi}) = 0$, we may write that $\rho^2 c^2 \bar{\partial}_p \bar{\varphi} = \psi(p, y_2, \dots, y_n)$ where ψ is $C^{\kappa-1}$. Next we use again the differential relation (4.9) to deduce that $\bar{\partial}_{v_i}^2 \bar{\varphi} \tilde{\partial}'_\rho p = \tilde{\partial}'_\rho (\rho^2 c^2 \bar{\partial}_p \bar{\varphi}) = \bar{\partial}_p \psi \tilde{\partial}'_\rho p$ and since $\tilde{\partial}'_\rho p > 0$ thank to thermodynamic stability, we deduce that $\bar{\partial}_p \psi(p, y_2, \dots, y_n) = \bar{\partial}_{v_i}^2 \bar{\varphi}(\mathbf{v})$ so that these functions are indeed a single constant independent of $i \in C$. From the differential relation (4.11) we also get that $\bar{\partial}_{y_k} \psi + \bar{\partial}_p \psi \tilde{\partial}'_{y_k} p = \bar{\partial}_{v_i}^2 \bar{\varphi} \tilde{\partial}'_{y_k} p$ so that $\bar{\partial}_{y_k} \psi = 0$, $k \in \mathfrak{S}'$, and ψ only depends on pressure. Since $\bar{\partial}_p \psi = \bar{\partial}_{v_i}^2 \bar{\varphi}$, $i \in C$, is a single constant $\alpha_\mathcal{E}$, we may thus write that there exists another constant α_0 such that $\psi(p) = -\alpha_0 + \alpha_\mathcal{E} p$ and we have established $\rho^2 c^2 \bar{\partial}_p \bar{\varphi} = -\alpha_0 + \alpha_\mathcal{E} p$.

From the relations (4.12) and (4.13) is established that $\bar{\partial}_p (1/\rho) = -\frac{1}{\rho^2 c^2}$ and $\bar{\partial}_p e = \frac{p}{\rho^2 c^2}$ so that

$$\bar{\partial}_p (\bar{\varphi}_s - \frac{\alpha_0}{\rho} - \alpha_\mathcal{E} e) = 0, \quad \bar{\partial}_{v_i}^2 \bar{\varphi}_v = \alpha_\mathcal{E}, \quad i \in C.$$

By direct integration we finally obtain

$$\rho \bar{\varphi}_s = \rho \mathfrak{f}(y_2, \dots, y_n, s) + \alpha_0 + \alpha_\mathcal{E} \rho e, \quad \rho \bar{\varphi}_v = \alpha_\mathcal{E} \frac{1}{2} \rho |\mathbf{v}|^2 + \alpha_v \cdot (\rho \mathbf{v}),$$

where \mathfrak{f} only depends on y_2, \dots, y_n, s and is C^κ since $\tilde{\sigma}$ is C^κ and since the remaining terms are C^∞ and the proof is complete. \square

From Theorem 4.1, discarding trivial entropies associated with momentum and total energy conservation, we may only consider the situation of entropies in the form $\tilde{\sigma} = \varphi(\rho_1, \dots, \rho_n, \mathcal{S})$ where φ is 1-homogeneous in its argument. This now constraints $\partial_z \tilde{\mathbf{v}}$ to have the following structure.

Lemma 4.2. *Let $\tilde{\sigma} = \varphi(\rho_1, \dots, \rho_n, \mathcal{S})$ be defined on \mathcal{O}_u where φ is 1-homogeneous. Letting $\tilde{\mathbf{v}} = \partial_u \tilde{\sigma}$, we then have the identity*

$$\partial_z \tilde{\mathbf{v}} = -R \partial_S \varphi \partial_z \mathbf{v} - R \mathbf{v} \otimes \partial_z (\partial_S \varphi) + \partial_z \mathcal{V}, \quad (4.14)$$

where

$$\mathcal{V} = \left(\partial_{\rho_1} \varphi, \dots, \partial_{\rho_n} \varphi, \mathbf{0}, 0 \right)^t. \quad (4.15)$$

Proof. The identity (4.14) is easily established after some algebra by deriving with respect to \mathbf{z} the relation (4.1) and by using the Euler relation $\sum_{i \in \mathcal{S}} \rho_i \partial_{\rho_i} \varphi + \mathcal{S} \partial_S \varphi = 0$. \square

Corollary 4.3. *Let $\tilde{\sigma}$ be a C^∞ function defined over \mathcal{O}_u and satisfying (E₁)(E₂). Then, discarding trivial entropies linearly proportional to the conserved quantities, $\tilde{\sigma}$ is in the form $\tilde{\sigma} = \varphi(\rho_1, \dots, \rho_n, \mathcal{S})$ where φ is 1-homogeneous and where $-R \partial_S \varphi \partial_u \mathbf{v} - R \mathbf{v} \otimes \partial_z (\partial_S \varphi) (\partial_z \mathbf{u})^{-1} + \partial_z \mathcal{V} (\partial_z \mathbf{u})^{-1}$ is positive definite.*

4.2 Compatibility with viscous dissipation matrices

We now consider the situation with nonzero dissipation matrices \mathbf{B}_{ij} , $i, j \in C$, and investigate commutation type relations associated with the compatibility condition (E₃). Denoting by $\tilde{\sigma}$ a mathematical entropy, the compatibility relations in (E₃) are in the form

$$(\partial_u^2 \tilde{\sigma})^{-1} \mathbf{B}_{ji}^t = \mathbf{B}_{ij} (\partial_u^2 \tilde{\sigma})^{-1}, \quad i, j \in C, \quad (4.16)$$

and may be written $(\partial_u \tilde{\mathbf{v}})^{-1} \mathbf{B}_{ji}^t = \mathbf{B}_{ij} (\partial_u \tilde{\mathbf{v}})^{-1}$, $i, j \in C$, where $\tilde{\mathbf{v}} = (\partial_u \tilde{\sigma})^t$. It is then more convenient to express the commutation relations (4.16) in terms of the matrices $\tilde{\mathbf{B}}_{ij} = \mathbf{B}_{ij} \partial_u \mathbf{v}$, $i, j \in C$. After some algebra we deduce that $(\partial_v \tilde{\mathbf{v}})^t \tilde{\mathbf{B}}_{ij} = \tilde{\mathbf{B}}_{ij} \partial_v \tilde{\mathbf{v}}$, $i, j \in C$, so that the compatibility relations may be rewritten

$$\tilde{\mathbf{B}}_{ij} \partial_v \tilde{\mathbf{v}} = (\partial_v \tilde{\mathbf{v}})^t \tilde{\mathbf{B}}_{ij}, \quad i, j \in C. \quad (4.17)$$

These relations show that richer dissipative processes yield more constraints on mathematical entropies. We may also combine these identities in order to obtain the following properties.

Proposition 4.4. *Let $\tilde{\sigma}$ be a C^∞ function defined on the open set \mathcal{O}_u satisfying (E₃) and such that $\partial_u^2 \tilde{\sigma}$ is invertible. Then letting $\tilde{\mathbf{v}} = (\partial_u \tilde{\sigma})^t$, we have the commutation relations*

$$(\tilde{\mathbf{A}}_0^{-1} \tilde{\mathbf{B}}_{ij}) \partial_v \tilde{\mathbf{v}} = \partial_v \tilde{\mathbf{v}} (\tilde{\mathbf{A}}_0^{-1} \tilde{\mathbf{B}}_{ij}), \quad i, j \in C, \quad (4.18)$$

$$(\tilde{\mathbf{A}}_0^{-1} \tilde{\mathbf{A}}_i) \partial_v \tilde{\mathbf{v}} = \partial_v \tilde{\mathbf{v}} (\tilde{\mathbf{A}}_0^{-1} \tilde{\mathbf{A}}_i), \quad i \in C. \quad (4.19)$$

Proof. From the symmetry of $\partial_u^2 \tilde{\sigma} = \partial_u \tilde{\mathbf{v}} = \partial_v \tilde{\mathbf{v}} \partial_u \mathbf{v}$, keeping in mind that $\tilde{\mathbf{A}}_0^{-1} = \partial_u \mathbf{v}$, we first deduce that $\tilde{\mathbf{A}}_0^{-1} (\partial_v \tilde{\mathbf{v}})^t = \partial_v \tilde{\mathbf{v}} \tilde{\mathbf{A}}_0^{-1}$. Moreover, using $\partial_u \tilde{\mathbf{v}} \mathbf{A}_i = \mathbf{A}_i^t \partial_u \tilde{\mathbf{v}}$, and $\mathbf{A}_i = \tilde{\mathbf{A}}_i \partial_u \mathbf{v}$, and proceeding as for the dissipation matrices, it is easily checked that $\tilde{\mathbf{A}}_i \partial_v \tilde{\mathbf{v}} = (\partial_v \tilde{\mathbf{v}})^t \tilde{\mathbf{A}}_i$ for $i \in C$.

We may now write that

$$(\tilde{\mathbf{A}}_0^{-1} \tilde{\mathbf{B}}_{ij}) \partial_v \tilde{\mathbf{v}} = \tilde{\mathbf{A}}_0^{-1} (\partial_v \tilde{\mathbf{v}})^t \tilde{\mathbf{B}}_{ij} = \partial_v \tilde{\mathbf{v}} (\tilde{\mathbf{A}}_0^{-1} \tilde{\mathbf{B}}_{ij}), \quad i, j \in C,$$

and similarly that

$$(\tilde{\mathbf{A}}_0^{-1} \tilde{\mathbf{A}}_i) \partial_v \tilde{\mathbf{v}} = \tilde{\mathbf{A}}_0^{-1} (\partial_v \tilde{\mathbf{v}})^t \tilde{\mathbf{A}}_i = \partial_v \tilde{\mathbf{v}} (\tilde{\mathbf{A}}_0^{-1} \tilde{\mathbf{A}}_i), \quad i \in C,$$

and this completes the proof of (4.18) and (4.19). \square

On the other hand, from Theorem 3.5, the matrices $\tilde{\mathbf{B}}_{ij}$ may be split in the form

$$\tilde{\mathbf{B}}_{ij} = \tilde{\mathbf{B}}^L \delta_{ij} + R T \kappa \tilde{\mathbf{B}}_{ij}^\kappa + R T \eta \tilde{\mathbf{B}}_{ij}^\eta,$$

and the corresponding relations (4.17) associated with $\tilde{\mathbf{B}}^L \delta_{ij}$, $\tilde{\mathbf{B}}_{ij}^\kappa$, and $\tilde{\mathbf{B}}_{ij}^\eta$ may be investigated separately. We discuss in this section the relations $\tilde{\mathbf{B}}_{ij}^\kappa \partial_v \tilde{\mathbf{v}} = (\partial_v \tilde{\mathbf{v}})^t \tilde{\mathbf{B}}_{ij}^\kappa$ and $\tilde{\mathbf{B}}_{ij}^\eta \partial_v \tilde{\mathbf{v}} = (\partial_v \tilde{\mathbf{v}})^t \tilde{\mathbf{B}}_{ij}^\eta$ which may be written in the compact form

$$\tilde{\mathbf{B}}^\kappa \partial_v \tilde{\mathbf{v}} = (\partial_v \tilde{\mathbf{v}})^t \tilde{\mathbf{B}}^\kappa, \quad (4.20)$$

$$\tilde{\mathbf{B}}^\eta \partial_v \tilde{\mathbf{v}} = (\partial_v \tilde{\mathbf{v}})^t \tilde{\mathbf{B}}^\eta, \quad (4.21)$$

where $\boldsymbol{\xi}, \boldsymbol{\zeta} \in \mathbb{R}^d$, $\boldsymbol{\xi} = (\xi_1, \dots, \xi_d)^t$, $\boldsymbol{\zeta} = (\zeta_1, \dots, \zeta_d)^t$, $\tilde{\mathbf{B}}^\kappa = \sum_{i,j \in C} \xi_i \zeta_j \tilde{\mathbf{B}}_{ij}^\kappa$ and $\tilde{\mathbf{B}}^\eta = \sum_{i,j \in C} \xi_i \zeta_j \tilde{\mathbf{B}}_{ij}^\eta$. It turns out that the relations (4.20) and (4.21) associated with viscous effects are automatically satisfied for entropies compatible with the hyperbolic structure.

Proposition 4.5. *Let M be a square matrix of size $n + d + 1$. Then Properties (i), (ii) and (iii) are equivalent for $d \geq 2$ whereas Properties (i) and (iii) are equivalent and $\tilde{\mathbf{B}}^\eta = 0$ for $d = 1$.*

(i) For any $\boldsymbol{\xi}, \boldsymbol{\zeta} \in \mathbb{R}^d$ we have $\tilde{\mathbf{B}}^\kappa(\boldsymbol{\xi}, \boldsymbol{\zeta})M = M^t \tilde{\mathbf{B}}^\kappa(\boldsymbol{\xi}, \boldsymbol{\zeta})$,

(ii) For any $\boldsymbol{\xi}, \boldsymbol{\zeta} \in \mathbb{R}^d$ we have $\tilde{\mathbf{B}}^\eta(\boldsymbol{\xi}, \boldsymbol{\zeta})M = M^t \tilde{\mathbf{B}}^\eta(\boldsymbol{\xi}, \boldsymbol{\zeta})$,

(iii) Writing $\mathbb{R}^{n+d+1} = \mathbb{R}^n \times \mathbb{R}^{d+1}$ and decomposing correspondingly M in the form

$$M = \begin{bmatrix} M^{e\varrho} & M^{ew} \\ M^{w\varrho} & M^{ww} \end{bmatrix},$$

there exist $\alpha \in \mathbb{R}$, $b \in \mathbb{R}^{d+1}$ and $b' \in \mathbb{R}^n$ such that

$$M^{ww} = \alpha \mathbb{I}_{d+1} + \begin{bmatrix} \mathbf{v} \\ -1 \end{bmatrix} \otimes b, \quad M^{w\varrho} = \begin{bmatrix} \mathbf{v} \\ -1 \end{bmatrix} \otimes b'.$$

Proof. We first note that

$$\tilde{\mathbf{B}}^\kappa(\boldsymbol{\xi}, \boldsymbol{\zeta}) = \begin{bmatrix} 0_{n,n} & 0_{n,d} & 0_{n,1} \\ 0_{d,n} & \mathbb{I}_d & 0_{d,1} \\ 0_{1,n} & \mathbf{v}^t & 0 \end{bmatrix} \begin{bmatrix} 0_{n,n} & 0_{n,d} & 0_{n,1} \\ 0_{d,n} & \boldsymbol{\xi} \otimes \boldsymbol{\zeta} & 0_{d,1} \\ 0_{1,n} & 0_{1,d} & 0 \end{bmatrix} \begin{bmatrix} 0_{n,n} & 0_{n,d} & 0_{n,1} \\ 0_{d,n} & \mathbb{I}_d & \mathbf{v} \\ 0_{1,n} & 0_{1,d} & 0 \end{bmatrix},$$

and

$$\tilde{\mathbf{B}}^\eta(\boldsymbol{\xi}, \boldsymbol{\zeta}) = \begin{bmatrix} 0_{n,n} & 0_{n,d} & 0_{n,1} \\ 0_{d,n} & \mathbb{I}_d & 0_{d,1} \\ 0_{1,n} & \mathbf{v}^t & 0 \end{bmatrix} \begin{bmatrix} 0_{n,n} & 0_{n,d} & 0_{n,1} \\ 0_{d,n} & \boldsymbol{\xi} \cdot \boldsymbol{\zeta} \mathbb{I}_d + \boldsymbol{\zeta} \otimes \boldsymbol{\xi} - \frac{2}{d} \boldsymbol{\xi} \otimes \boldsymbol{\zeta} & 0_{d,1} \\ 0_{1,n} & 0_{1,d} & 0 \end{bmatrix} \begin{bmatrix} 0_{n,n} & 0_{n,d} & 0_{n,1} \\ 0_{d,n} & \mathbb{I}_d & \mathbf{v} \\ 0_{1,n} & 0_{1,d} & 0 \end{bmatrix},$$

so that we have

$$\tilde{\mathbf{B}}^\eta(\boldsymbol{\xi}, \boldsymbol{\zeta}) = \boldsymbol{\xi} \cdot \boldsymbol{\zeta} (\tilde{\mathbf{B}}^\kappa(\mathbf{e}^1, \mathbf{e}^1) + \dots + \tilde{\mathbf{B}}^\kappa(\mathbf{e}^d, \mathbf{e}^d)) + \tilde{\mathbf{B}}^\kappa(\boldsymbol{\zeta}, \boldsymbol{\xi}) - \frac{2}{d} \tilde{\mathbf{B}}^\kappa(\boldsymbol{\xi}, \boldsymbol{\zeta}).$$

and (i) implies (ii). Moreover, it is straightforward to check that when $d \geq 2$

$$\tilde{\mathbf{B}}^\kappa(\boldsymbol{\zeta}, \boldsymbol{\xi}) - \frac{2}{d} \tilde{\mathbf{B}}^\kappa(\boldsymbol{\xi}, \boldsymbol{\zeta}) = \tilde{\mathbf{B}}^\eta(\boldsymbol{\xi}, \boldsymbol{\zeta}) - \boldsymbol{\xi} \cdot \boldsymbol{\zeta} \frac{d}{(d-1)(d+2)} (\tilde{\mathbf{B}}^\eta(\mathbf{e}^1, \mathbf{e}^1) + \dots + \tilde{\mathbf{B}}^\eta(\mathbf{e}^d, \mathbf{e}^d))$$

and the relation

$$\boldsymbol{\zeta} \otimes \boldsymbol{\xi} = \frac{d^2}{d^2+4} ((\boldsymbol{\zeta} \otimes \boldsymbol{\xi} - \frac{2}{d} \boldsymbol{\xi} \otimes \boldsymbol{\zeta}) + \frac{2}{d} (\boldsymbol{\xi} \otimes \boldsymbol{\zeta} - \frac{2}{d} \boldsymbol{\zeta} \otimes \boldsymbol{\xi})),$$

yields

$$\tilde{\mathbf{B}}^\kappa(\boldsymbol{\zeta}, \boldsymbol{\xi}) = \frac{d^2}{d^2+4} \left(\tilde{\mathbf{B}}^\kappa(\boldsymbol{\zeta}, \boldsymbol{\xi}) - \frac{2}{d} \tilde{\mathbf{B}}^\kappa(\boldsymbol{\xi}, \boldsymbol{\zeta}) \right) + \frac{2d}{d^2+4} \left(\tilde{\mathbf{B}}^\kappa(\boldsymbol{\xi}, \boldsymbol{\zeta}) - \frac{2}{d} \tilde{\mathbf{B}}^\kappa(\boldsymbol{\zeta}, \boldsymbol{\xi}) \right).$$

This implies that $\tilde{\mathbf{B}}^\kappa(\boldsymbol{\zeta}, \boldsymbol{\xi})$ is a linear combination of various particular values of $\tilde{\mathbf{B}}^\eta$ and (ii) implies (i) so that (i) and (ii) are equivalent when $d \geq 2$. In the situation $d = 1$, it is also seen that $\tilde{\mathbf{B}}^\eta(\boldsymbol{\xi}, \boldsymbol{\zeta}) = 0$ for any $\boldsymbol{\xi}, \boldsymbol{\zeta} \in \mathbb{R}^d$.

Decomposing next $\tilde{\mathbf{B}}^\kappa(\boldsymbol{\xi}, \boldsymbol{\zeta})$ in the form

$$\tilde{\mathbf{B}}^\kappa(\boldsymbol{\xi}, \boldsymbol{\zeta}) = \begin{bmatrix} 0_{n,n} & 0_{n,d+1} \\ 0_{d+1,n} & \tilde{\mathbf{B}}^{\kappa ww} \end{bmatrix} \quad (4.22)$$

where

$$\tilde{\mathbf{B}}^{\kappa ww}(\boldsymbol{\xi}, \boldsymbol{\zeta}) = \begin{bmatrix} \mathbb{I}_d & 0_{d,1} \\ \mathbf{v}^t & 0 \end{bmatrix} \begin{bmatrix} \boldsymbol{\xi} \otimes \boldsymbol{\zeta} & 0_{d,1} \\ 0_{1,d} & 0 \end{bmatrix} \begin{bmatrix} \mathbb{I}_d & \mathbf{v} \\ 0_{1,d} & 0 \end{bmatrix},$$

it is directly established that (i) holds if and only if we have the relations

$$\tilde{\mathbf{B}}^{\kappa ww} M^{ww} = (M^{ww})^t \tilde{\mathbf{B}}^{\kappa ww} \quad \tilde{\mathbf{B}}^{\kappa ww} M^{w\varrho} = 0. \quad (4.23)$$

Since only the vector $(\mathbf{v}, -1)^t$ lies in the nullspace of all possible $\tilde{\mathbf{B}}^{\kappa w w}$, for varying $\boldsymbol{\xi}$ and ζ , we obtain from $\tilde{\mathbf{B}}^{\kappa w w} M^{w\varrho} = 0$ that $M^{w\varrho}$ is in the form $M^{w\varrho} = (\mathbf{v}, -1)^t \otimes b'$ with $b' \in \mathbb{R}^n$. Conversely, when $M^{w\varrho}$ is in this form, then we trivially have $\tilde{\mathbf{B}}^{\kappa w w} M^{w\varrho} = 0$ for arbitrary $\boldsymbol{\xi}, \zeta \in \mathbb{R}^d$.

On the other hand, we may decompose $M^{w w}$ in the form

$$M^{w w} = \begin{bmatrix} M^{\mathbf{v}\mathbf{v}} & M^{\mathbf{v}T} \\ M^{T\mathbf{v}} & M^{TT} \end{bmatrix},$$

and the relation $\tilde{\mathbf{B}}^{\kappa w w} M^{w w} = (M^{w w})^t \tilde{\mathbf{B}}^{\kappa w w}$ is then equivalent to the three identities

$$\begin{aligned} \boldsymbol{\xi} \otimes (M^{\mathbf{v}\mathbf{v}})^t \zeta + \mathbf{v} \cdot \zeta \boldsymbol{\xi} \otimes (M^{T\mathbf{v}})^t &= (M^{\mathbf{v}\mathbf{v}})^t \boldsymbol{\xi} \otimes \zeta + \mathbf{v} \cdot \boldsymbol{\xi} (M^{T\mathbf{v}})^t \otimes \zeta, \\ \zeta \cdot M^{\mathbf{v}T} \boldsymbol{\xi} + \mathbf{v} \cdot \zeta M^{TT} \boldsymbol{\xi} &= \mathbf{v} \cdot \zeta (M^{\mathbf{v}\mathbf{v}})^t \boldsymbol{\xi} + \mathbf{v} \cdot \boldsymbol{\xi} \mathbf{v} \cdot \zeta (M^{T\mathbf{v}})^t, \\ \mathbf{v} \cdot \boldsymbol{\xi} \zeta \cdot M^{\mathbf{v}T} + \mathbf{v} \cdot \boldsymbol{\xi} \mathbf{v} \cdot \zeta M^{TT} &= \mathbf{v} \cdot \zeta \boldsymbol{\xi} \cdot M^{\mathbf{v}T} + \mathbf{v} \cdot \boldsymbol{\xi} \mathbf{v} \cdot \zeta M^{TT}. \end{aligned}$$

The last relation first yields that $\mathbf{v} \cdot \boldsymbol{\xi} \zeta \cdot M^{\mathbf{v}T} = \mathbf{v} \cdot \zeta \boldsymbol{\xi} \cdot M^{\mathbf{v}T}$ for any $\boldsymbol{\xi}, \zeta \in \mathbb{R}^d$ so that $M^{\mathbf{v}T}$ is proportional to \mathbf{v} . Letting $M^{\mathbf{v}T} = a\mathbf{v}$, after some algebra, it is obtained that all the remaining relations are equivalent to

$$(M^{\mathbf{v}\mathbf{v}})^t \boldsymbol{\xi} + \mathbf{v} \cdot \boldsymbol{\xi} (M^{T\mathbf{v}})^t = \alpha \boldsymbol{\xi},$$

and $a + M^{TT} = \alpha$, and we have established that (i) implies (iii) with $b = (-M^{T\mathbf{v}}, a)^t$. Conversely, it is easily checked that (iii) implies (i) and the proof is complete. \square

Corollary 4.6. *Assume that $\tilde{\sigma}$ is a mathematical entropy compatible with the hyperbolic structure of the system of partial differential equations so that (E₂) holds, $\partial_u^2 \tilde{\sigma}$ is invertible and let $\tilde{\mathbf{v}} = (\partial_u \tilde{\sigma})^t$. Then the commutation relations (4.20) and (4.21) automatically hold.*

Proof. Letting $\mathcal{J} = \partial_v \tilde{\mathbf{v}}$ we obtain from Lemma 4.2 that $\mathcal{J} = -R \partial_S \varphi \mathbb{I}_{n+d+1} - R \mathbf{v} \otimes \partial_z (\partial_S \varphi) (\partial_z \mathbf{v})^{-1} + \partial_z \mathcal{V} (\partial_z \mathbf{v})^{-1}$. Using now the partitioning introduced in (iii) of Proposition 4.5, we obtain from the definition of \mathbf{v} and \mathcal{V} that $\mathbf{v}^w = (\mathbf{v}, -1)^t / RT$ and $\mathcal{V}^w = 0$, so that $(\partial_z \mathcal{V})^{w\varrho} = 0$ and $(\partial_z \mathcal{V})^{w w} = 0$. Decomposing now \mathcal{J} in the form

$$\mathcal{J} = \begin{bmatrix} \mathcal{J}^{\varrho\varrho} & \mathcal{J}^{\varrho w} \\ \mathcal{J}^{w\varrho} & \mathcal{J}^{w w} \end{bmatrix},$$

and thanks to the special structure of \mathbf{v} and \mathcal{V} we directly obtain $\mathcal{J}^{w w} = -R \partial_S \varphi \mathbb{I}_{d+1} - R \mathbf{v}^w \otimes b$ and $\mathcal{J}^{w\varrho} = -R \mathbf{v}^w \otimes b'$ for some vectors b and b' , so Property (iii) of Proposition 4.5 holds and (4.20)(4.21) also hold from the same Proposition. \square

This corollary extend to the multicomponent case a previous result from Hughes, Franca and Mallet [35] about the compatibility with viscous dissipation matrices in single species mixtures.

4.3 Compatibility with diffusion dissipation matrices

We denote by $\tilde{\sigma}$ a mathematical entropy compatible with the hyperbolic structure and by $\tilde{\mathbf{v}} = (\partial_u \tilde{\sigma})^t$ the corresponding symmetrizing variable. We also denote by $\mathcal{J} = \partial_v \tilde{\mathbf{v}}$ the jacobian matrix and by Ξ the permutation that regroup the temperature with the species densities, that is, such that $\Xi \mathbf{z} = (\rho_1, \dots, \rho_n, T, \mathbf{v})^t$. From the structure of the matrix $\tilde{\mathbf{B}}^L$ we have the block decomposition

$$\Xi \tilde{\mathbf{B}}^L \Xi^t = \begin{bmatrix} L & 0_{n,d} \\ 0_{d,n} & 0_{d,d} \end{bmatrix}. \quad (4.24)$$

We also decompose $\Xi \mathcal{J} \Xi^t$ in the form

$$\Xi \mathcal{J} \Xi^t = \begin{bmatrix} \mathcal{J}^{zz} & \mathcal{J}^{zv} \\ \mathcal{J}^{vz} & \mathcal{J}^{vv} \end{bmatrix}. \quad (4.25)$$

Proposition 4.7. *Keeping the assumptions of Corollary 4.6, the following properties are equivalent*

- (i) *The entropy is compatible with the dissipative structure*

$$\tilde{\mathbf{B}}_{ij} \partial_v \tilde{\mathbf{v}} = (\partial_v \tilde{\mathbf{v}})^t \tilde{\mathbf{B}}_{ij}, \quad i, j \in C.$$

(ii) The entropy is compatible with the diffusion dissipation matrix $\tilde{\mathbf{B}}^L$

$$\tilde{\mathbf{B}}^L \partial_{\tilde{\mathbf{v}}} \tilde{\mathbf{v}} = (\partial_{\tilde{\mathbf{v}}} \tilde{\mathbf{v}})^t \tilde{\mathbf{B}}^L.$$

(iii) The partial jacobians \mathcal{J}^{zz} and \mathcal{J}^{zv} are compatible with the mass and heat diffusion matrix L

$$L\mathcal{J}^{zz} = (\mathcal{J}^{zz})^t L, \quad L\mathcal{J}^{zv} = 0. \quad (4.26)$$

Proof. The equivalence between (i) and (ii) is a direct consequence of Corollary 4.6 and of the structure $\tilde{\mathbf{B}}_{ij} = \tilde{\mathbf{B}}^L \delta_{ij} + RT\kappa\tilde{\mathbf{B}}_{ij}^\kappa + RT\eta\tilde{\mathbf{B}}_{ij}^\eta$ of dissipation matrices. Thanks to the structure of $\tilde{\mathbf{B}}^L$, it is then easily checked, after some block manipulations, that $\tilde{\mathbf{B}}^L \partial_{\tilde{\mathbf{v}}} \tilde{\mathbf{v}} = (\partial_{\tilde{\mathbf{v}}} \tilde{\mathbf{v}})^t \tilde{\mathbf{B}}^L$ is equivalent to (4.26) so that (ii) and (iii) are then equivalent. \square

On the other hand, the relations $\tilde{\mathbf{B}}_{ij} \partial_{\tilde{\mathbf{v}}} \tilde{\mathbf{v}} = (\partial_{\tilde{\mathbf{v}}} \tilde{\mathbf{v}})^t \tilde{\mathbf{B}}_{ij}$ and $(\tilde{\mathbf{A}}_0^{-1} \tilde{\mathbf{B}}_{ij}) \partial_{\tilde{\mathbf{v}}} \tilde{\mathbf{v}} = \partial_{\tilde{\mathbf{v}}} \tilde{\mathbf{v}} (\tilde{\mathbf{A}}_0^{-1} \tilde{\mathbf{B}}_{ij})$, $i, j \in C$ generally show that the compatibility with dissipation matrices yield constraints on the jacobian matrix $\partial_{\tilde{\mathbf{v}}} \tilde{\mathbf{v}}$ depending on their spectral properties. This is illustrated by the following abstract particular example.

Proposition 4.8. *Let $l \geq 1$ and consider the abstract system of partial differential equations in \mathbb{R}^d*

$$\partial_t \mathbf{u} - \mathcal{D} \Delta \mathbf{u} = 0, \quad (4.27)$$

where $\mathbf{u} = (u_1, \dots, u_l)^t$, $\Delta \mathbf{u} = (\Delta u_1, \dots, \Delta u_l)^t$, and $\mathcal{D} = \text{diag}(\delta_1, \dots, \delta_l)$, with $\delta_i > 0$, for $1 \leq i \leq l$. Letting $\sigma = \frac{1}{2} \langle \mathbf{u}, \mathbf{u} \rangle$, we have $\mathbf{u} = \mathbf{v}$, $\tilde{\mathbf{A}}_0 = \mathbb{I}_l$, $\mathbf{A}_i = \tilde{\mathbf{A}}_i = 0$, $i \in C$, and $\mathbf{B}_{ij} = \tilde{\mathbf{B}}_{ij} = \delta_{ij} \mathcal{D}$, $i, j \in C$. Then any strictly convex function $\tilde{\sigma}$ of \mathbf{u} satisfies $(\mathbf{E}_1)(\mathbf{E}_2)$ and $(\mathbf{S}_1)(\mathbf{S}_2)$ and the compatibility relations with the second order terms reduces to $\mathcal{D} \partial_{\tilde{\mathbf{v}}} \tilde{\mathbf{v}} = \partial_{\tilde{\mathbf{v}}} \tilde{\mathbf{v}} \mathcal{D}$.

Proof. It is easily checked that $\mathbf{u} = \mathbf{v}$, $\tilde{\mathbf{A}}_0 = \mathbb{I}_l$, $\mathbf{A}_i = \tilde{\mathbf{A}}_i = 0$, for $i \in C$, and $\mathbf{B}_{ij} = \tilde{\mathbf{B}}_{ij} = \delta_{ij} \mathcal{D}$, for $i, j \in C$. The compatibility condition with first order terms is thus trivial and any C^∞ function of \mathbf{u} such that $\partial_{\mathbf{u}}^2 \sigma$ is positive definite satisfies $(\mathbf{E}_1)(\mathbf{E}_2)$. The compatibility relations with the second order terms (4.17) then reduces to $\mathcal{D} \partial_{\tilde{\mathbf{v}}} \tilde{\mathbf{v}} = (\partial_{\tilde{\mathbf{v}}} \tilde{\mathbf{v}})^t \mathcal{D}$ but since $\mathbf{u} = \mathbf{v}$, the matrix $\partial_{\tilde{\mathbf{v}}} \tilde{\mathbf{v}} = \partial_{\mathbf{u}} \tilde{\mathbf{v}}$ is symmetric and we obtain $\mathcal{D} \partial_{\tilde{\mathbf{v}}} \tilde{\mathbf{v}} = \partial_{\mathbf{u}} \tilde{\mathbf{v}} \mathcal{D}$. \square

The structure of mathematical entropies compatible with the hyperbolic-parabolic structure of (4.27) then depends on the spectral properties of \mathcal{D} .

Proposition 4.9. *Keeping the assumptions of Proposition 4.8, the following properties hold.*

- (i) *When all the eigenvalues coincide $\delta_1 = \dots = \delta_l$ then any strictly convex function $\tilde{\sigma}$ of \mathbf{u} is compatible with the hyperbolic-parabolic structure of the system of partial differential equations (4.27).*
- (ii) *When $\delta_i \neq \delta_l$ for $i \neq l$, mathematical entropies $\tilde{\sigma}$ are constrained to be in the form $\tilde{\sigma} = \varphi(\mathbf{u}_1, \dots, \mathbf{u}_{l-1}) + \varphi_l(\mathbf{u}_l)$ where φ and φ_l are C^∞ strictly convex function of their argument.*
- (iii) *When all the eigenvalues are different $\delta_i \neq \delta_j$ for $i \neq j$, mathematical entropies $\tilde{\sigma}$ are constrained to be in the form $\tilde{\sigma} = \sum_{1 \leq i \leq l} \varphi_i(\mathbf{u}_i)$ where φ_i is a strictly convex function of \mathbf{u}_i .*

Proof. The compatibility relations $\mathcal{D} \partial_{\tilde{\mathbf{v}}} \tilde{\mathbf{v}} = \partial_{\mathbf{u}} \tilde{\mathbf{v}} \mathcal{D}$ are easily evaluated to be $(\delta_i - \delta_j) \partial_{\mathbf{u}_i} \tilde{\mathbf{v}}_j = 0$. When $\delta_i \neq \delta_l$ for $i \neq l$, we thus obtain $\partial_{\mathbf{u}_i} \tilde{\mathbf{v}}_l = 0$ if $i \neq l$ in such a way that the mathematical entropies are constrained to be in the form $\tilde{\sigma} = \varphi(\mathbf{u}_1, \dots, \mathbf{u}_{l-1}) + \varphi_l(\mathbf{u}_l)$. The partial Hessian matrices associated with φ and φ_l are then both positive definite since $\partial_{\mathbf{u}}^2 \tilde{\sigma}$ is positive definite. On the other hand when all the eigenvalues $\delta_1, \dots, \delta_l$ are different, i.e., $\delta_i \neq \delta_j$ for $i \neq j$, it is easily obtained that $\partial_{\mathbf{u}_i} \tilde{\mathbf{v}}_j = 0$ if $i \neq j$ in such a way that the mathematical entropies are constrained to be in the form $\tilde{\sigma} = \sum_{1 \leq i \leq l} \varphi_i(\mathbf{u}_i)$ and φ_i is a strictly convex function of \mathbf{u}_i from the definiteness of $\partial_{\mathbf{u}}^2 \tilde{\sigma}$. \square

In the absence of information of the spectra of \mathcal{D} , we may still obtain information on the structure of an entropy $\tilde{\sigma}$ if it is assumed that $\tilde{\sigma}$ is independent on some of the coefficients of the matrix \mathcal{D} .

Proposition 4.10. *Keep the assumptions of Proposition 4.8 and assume that $\tilde{\sigma}$ is independent of δ_l . Then the mathematical entropies are constrained to be in the form $\tilde{\sigma} = \varphi(\mathbf{u}_1, \dots, \mathbf{u}_{l-1}) + \varphi_l(\mathbf{u}_l)$ where φ and φ_l are strictly convex functions of their argument.*

Proof. If we assume that $\tilde{\sigma}$ is independent of δ_l , we may then differentiate $\mathcal{D} \partial_u \tilde{v} = \partial_u \tilde{v} \mathcal{D}$ with respect to δ_l and obtain that $\mathbf{e}^l \otimes \mathbf{e}^l \partial_u \tilde{v} = \partial_u \tilde{v} \mathbf{e}^l \otimes \mathbf{e}^l$ thanks to $\partial_{\delta_l} \mathcal{D} = \mathbf{e}^l \otimes \mathbf{e}^l$. The base vector \mathbf{e}^l is thus an eigenvector of $\partial_u \tilde{v} = (\partial_u \tilde{v})^t$ and we recover the relations $\partial_{u_i} \tilde{v}_l = 0$ if $i \neq l$ so that the mathematical entropies are again constrained to be in the form $\tilde{\sigma} = \varphi(u_1, \dots, u_{l-1}) + \varphi_l(u_l)$. \square

Turning back to the situation of multicomponent fluids, the independence of mathematical entropies $\tilde{\sigma}$ with respect to *some of the mass and heat diffusion parameters* may thus be seen as a practical method to constraint the mathematical entropies in the absence of information on the spectrum of the dissipation matrix $\tilde{\mathbf{B}}^L$. As a consequence, in the following we will make the assumption that mathematical entropies are independent on some of the mass and heat diffusion parameters. More specifically, we will write relations in the form

$$\partial_\mu L \mathcal{J}^{zz} = (\mathcal{J}^{zz})^t \partial_\mu L, \quad (4.28)$$

where μ are some relevant parameters associated with mass and heat diffusion phenomena.

4.4 Compatibility with source terms

We briefly address in this section the compatibility of mathematical entropies with source terms. In the following proposition, we obtain an analog of the commutation properties (4.18)–(4.19) of Proposition 4.4. Note that the linearized source terms $\mathbf{L} = -\partial_u \Omega$ or $\tilde{\mathbf{L}} = -\partial_v \Omega$ should not be confused with the mass and heat diffusion matrix L .

Proposition 4.11. *Let $\tilde{\sigma}$ be a C^∞ function defined on the open set \mathcal{O}_u satisfying (\mathbf{E}_6) and such that $\partial_u^2 \tilde{\sigma}$ is invertible and let $\tilde{\mathbf{L}} = -\partial_v \Omega(\mathbf{v})$ and $\tilde{\mathbf{v}} = (\partial_u \tilde{\sigma})^t$. Then, whenever \mathbf{v} is such that $\Omega(\mathbf{v}) = 0$, the matrix $\tilde{\mathbf{L}} \partial_v \tilde{\mathbf{v}}$ is symmetric positive semi-definite*

$$\tilde{\mathbf{L}} \partial_v \tilde{\mathbf{v}} = (\partial_v \tilde{\mathbf{v}})^t \tilde{\mathbf{L}}, \quad (4.29)$$

and we have the commutation relation

$$(\tilde{\mathbf{A}}_0^{-1} \tilde{\mathbf{L}}) \partial_v \tilde{\mathbf{v}} = \partial_v \tilde{\mathbf{v}} (\tilde{\mathbf{A}}_0^{-1} \tilde{\mathbf{L}}). \quad (4.30)$$

Moreover, we have

$$(\partial_v \tilde{\mathbf{v}}) \mathcal{E} \subset \mathcal{E}. \quad (4.31)$$

Proof. We first deduce from (\mathbf{S}_6) that at chemical equilibrium the matrix $\partial_v \Omega = -\tilde{\mathbf{L}} \partial_v \mathbf{v}$ so that $\tilde{\mathbf{L}} \partial_v \mathbf{v} = (\partial_v \mathbf{v})^t \tilde{\mathbf{L}}$ and multiplying of the right by $\partial_v \tilde{\mathbf{v}}$ and on the left by $(\partial_v \tilde{\mathbf{v}})^t$ yields (4.29). On the other hand, we have established in the proof of Proposition 4.4 that $\tilde{\mathbf{A}}_0^{-1} (\partial_v \tilde{\mathbf{v}})^t = \partial_v \tilde{\mathbf{v}} \tilde{\mathbf{A}}_0^{-1}$. We may then write that

$$(\tilde{\mathbf{A}}_0^{-1} \tilde{\mathbf{L}}) \partial_v \tilde{\mathbf{v}} = \tilde{\mathbf{A}}_0^{-1} (\partial_v \tilde{\mathbf{v}})^t \tilde{\mathbf{L}} = \partial_v \tilde{\mathbf{v}} (\tilde{\mathbf{A}}_0^{-1} \tilde{\mathbf{L}}),$$

and this is the commutation relation (4.30).

The fact that the image of \mathcal{E} is included in \mathcal{E} is then a consequence of (4.29) and of $N(\tilde{\mathbf{L}}) = \mathcal{E}$ at chemical equilibrium deduced from (\mathbf{S}_6) . \square

Remark 4.12. *Property (\mathbf{E}_7) also constraints the derivative of the entropy $\tilde{\mathbf{v}} = (\partial_u \tilde{\sigma})^t$ to be in the negative orthant defined by the vector Ω .*

The jacobian matrix of the source term $\partial_v \tilde{\Omega}$ at chemical equilibrium has been evaluated in [30]. Keeping in mind that ν_j is the reaction vector of the j th reaction and letting

$$(\mathbf{M} \nu_j)^* = (\mathbf{M} \nu_j, \mathbf{0}, 0)^t,$$

it has been established [27, 22] that at an equilibrium point \mathbf{v}^e , that is when $\Omega(\mathbf{v}^e) = 0$, we have

$$\tilde{\mathbf{L}}(\mathbf{v}^e) = \sum_{j \in \mathfrak{R}} \kappa_j^s \exp\langle (\mathbf{M} \nu_j^f)^*, \mathbf{v}^e \rangle (\mathbf{M} \nu_j)^* \otimes (\mathbf{M} \nu_j)^*. \quad (4.32)$$

We may now combine (4.29) and (4.32) in the following Corollary.

Corollary 4.13. *Keep the assumptions of Proposition 4.11 and assume that the mathematical entropy is independent of the chemistry kinetic constants κ_j^s , $j \in \mathfrak{R}$. Then all extended reaction vectors $(\mathbf{M}\nu_j)^*$, $j \in \mathfrak{R}$, are left eigenvectors of $\partial_{\mathbf{v}}\tilde{\mathbf{v}}$.*

Proof. We only have to differentiate the commutation relation with respect to the chemical reaction kinetic parameter κ_j^s in order to get that $(\mathbf{M}\nu_j)^* \otimes (\mathbf{M}\nu_j)^* \partial_{\mathbf{v}}\tilde{\mathbf{v}} = (\partial_{\mathbf{v}}\tilde{\mathbf{v}})^t (\mathbf{M}\nu_j)^* \otimes (\mathbf{M}\nu_j)^*$ and this implies that $(\mathbf{M}\nu_j)^*$ is a left eigenvector of $\partial_{\mathbf{v}}\tilde{\mathbf{v}}$. \square

Since $\mathcal{E}^\perp = \text{span}\{(\mathbf{M}\nu_j)^*, j \in \mathfrak{R}\}$, Corollary 4.13 may imply that the block \mathcal{J}^{ee} coincides with a scalar matrix over \mathcal{E}^\perp depending on the richness of the set of reaction vectors.

5 Mass and heat diffusion matrices

We present in this section the mathematical structure of typical multicomponent diffusion matrices derived from the kinetic theory of gases [15, 22]. In Section 5.1 we consider Stefan-Maxwell type equations whereas in Section 5.2 we study quasi-diagonal approximations. We then investigate the derivatives of the mass and heat diffusion matrix L with respect to the corresponding relevant transport parameters.

5.1 Stefan-Maxwell relations

We introduce the matrix Δ defined by

$$\begin{cases} \Delta_{kk} = \sum_{\substack{l \in \mathfrak{G} \\ l \neq k}} \frac{x_k x_l}{\mathcal{D}_{kl}^{\text{bin}}}, & k \in \mathfrak{G}, \\ \Delta_{kl} = -\frac{x_k x_l}{\mathcal{D}_{kl}^{\text{bin}}}, & k, l \in \mathfrak{G}, \quad k \neq l, \end{cases} \quad (5.1)$$

where $\mathcal{D}_{kl}^{\text{bin}}$ is the binary diffusion coefficient for the species pair (k, l) and x_k the mole fraction of the k th species. The kinetic theory of gases shows that, at first-order, the coefficients $\mathcal{D}_{kl}^{\text{bin}}$ only depends on pressure and temperature $\mathcal{D}_{kl}^{\text{bin}} = \mathcal{D}_{kl}^{\text{bin}}(T, p)$. More generally, for more accurate multicomponent diffusion coefficients, the quantities $\mathcal{D}_{kl}^{\text{bin}}$, $k, l \in \mathfrak{G}$, are Schur complements arising from transport linear systems of size larger than n , and are then functions of all state variables but have analogous properties [11, 26]. Similarly, with the kinetic theory of dense gases [43, 53], the binary diffusion coefficients are functions of the state variables $(\rho_1, \dots, \rho_n, T)^t$. In the following we denote by $y = (y_1, \dots, y_n)^t$ the vector of species mass fractions, by $\mathbb{1} = (1, \dots, 1)^t$ the vector with unity components, and we naturally assume that $y_i > 0$ for $i \in \mathfrak{G}$, and $\langle y, \mathbb{1} \rangle = 1$. The species mole fractions are defined by $x_j = my_j/m_j$ where $m = (\sum_{i \in \mathfrak{G}} y_i) / (\sum_{i \in \mathfrak{G}} y_i/m_i)$ is the molar mass of the mixture. The following properties of the matrix Δ are easily established [21, 22].

Proposition 5.1. *Assume that the coefficients $\mathcal{D}_{kl}^{\text{bin}}$, $k, l \in \mathfrak{G}$, $k \neq l$, are positive and symmetric, and that the species mass fractions are positive. Then Δ is symmetric positive semi-definite, $N(\Delta) = \mathbb{R}\mathbb{1}$, $R(\Delta) = \mathbb{1}^\perp$, Δ is irreducible and is a singular M -matrix.*

The multicomponent diffusion matrix D can then be defined as a generalized inverse of Δ [21, 22].

Proposition 5.2. *Keeping the assumptions of Proposition 5.1 there exists a unique generalized inverse D of Δ with prescribed range y^\perp and nullspace $\mathbb{R}y$, that is, a unique matrix D such that $D\Delta D = D$, $\Delta D \Delta = \Delta$, $R(D) = y^\perp$, and $N(D) = \mathbb{R}y$. This matrix D is positive semi-definite, we have $\Delta D = I - y \otimes \mathbb{1}$, $D \Delta = I - \mathbb{1} \otimes y$, and $D = (\Delta + ay \otimes y)^{-1} - b \mathbb{1} \otimes \mathbb{1}$ for any a, b positive with $ab = 1$. The coefficients of D are smooth functions of $z \in (0, \infty)^{n+1}$ provided that the binary diffusion coefficients are smooth functions of $z \in (0, \infty)^{n+1}$.*

Remark 5.3. *The Stefan-Maxwell relations for the diffusion matrix D may be written $\Delta D = \mathbb{I}_n - y \otimes \mathbb{1}$ and completed by the mass constraint $Dy = 0$. Denoting by \mathbf{v} the vector of diffusion velocities $\mathbf{v}_1, \dots, \mathbf{v}_n$ where $\mathcal{F}_i = \rho_i \mathbf{v}_i$ for $i \in \mathfrak{G}$, and $\mathbf{d} = (\mathbf{d}_1, \dots, \mathbf{d}_n)^t$ the vector of diffusion driving forces, we also have $\mathbf{v} = -D\mathbf{d}$ and the traditional Stefan-Maxwell relations $\Delta \mathbf{v} = -(\mathbf{d} - y \langle \mathbb{1}, \mathbf{d} \rangle)$ for the diffusion velocities are easily derived.*

The natural diffusion parameters at our disposal when the matrix D is evaluated from Stefan-Maxwell type equations are thus the binary diffusion coefficients $\mathcal{D}_{kl}^{\text{bin}}$ for $1 \leq k < l \leq n$, completed by the thermal conductivity λ and eventually the thermal diffusion ratios χ_i for $1 \leq i \leq n - 1$.

5.2 Quasi-diagonal approximation

We address in this section the situation of simplified diffusion models that are typically introduced in order to avoid the inversion of the Stefan Maxwell equations. We still assume that $y_i > 0$ for $i \in \mathfrak{S}$, and $\langle y, \mathbb{1} \rangle = 1$. In the following theorem, the diffusion matrix D defined in Proposition 5.2 and solution of the Stefan-Maxwell relations is expressed as a convergent matrix series. Upon truncating this series, approximated diffusion models are readily obtained [21, 12] and this procedure may be generalized to all transport coefficients [11, 13, 14, 15, 26].

Theorem 5.4. *Consider the Stefan-Maxwell matrix (5.1) and assume that the binary diffusion coefficients $\mathcal{D}_{kl}^{\text{bin}}$, $k, l \in \mathfrak{S}$, $k \neq l$, are positive and symmetric. Let M be a diagonal matrix such that $M_{kk} \geq \Delta_{kk}$, $k \in \mathfrak{S}$ and denote by P the projector $P = \mathbb{1} - \mathbb{1} \otimes y$. Consider the splitting $\Delta = M - W$ and denote by \mathcal{T} the iteration matrix $\mathcal{T} = M^{-1}W$. Then the spectral radius of the product $P\mathcal{T}$ is strictly lower than unity and the solution of the Stefan-Maxwell relations D may be expanded in the form*

$$D = \sum_{0 \leq j} (P\mathcal{T})^j P M^{-1} P^t, \quad (5.2)$$

and each partial sum $\sum_{0 \leq j \leq i} (P\mathcal{T})^j P M^{-1} P^t$ is symmetric, positive semi-definite with nullspace $\mathbb{R}y$.

It is interesting to note that the traditional series $\sum_{0 \leq j} \mathcal{T}^j$ associated with the splitting $\Delta = M - W$ is divergent since \mathcal{T} has the eigenvalue 1 associated with the singularity of Δ with $\mathcal{T}\mathbb{1} = \mathbb{1}$. The projector matrices used in Theorem 5.4 are required in order to obtain convergent series [21, 11, 15]. We consider in the following the often used one term approximation deduced from (5.2) and rewritten in the form

$$D \simeq P \mathcal{D}^m P^t, \quad (5.3)$$

where the matrix $\mathcal{D}^m = M^{-1}$ is a diagonal matrix

$$\mathcal{D}^m = \text{diag}(\mathcal{D}_1^m, \dots, \mathcal{D}_n^m). \quad (5.4)$$

This approximation of D may naturally be termed a quasi-diagonal approximation. We will not require a precise form for the coefficients \mathcal{D}_i^m in the following and will only assume that they are positive.

The natural diffusion parameters that are at our disposal are then the coefficients of the matrix \mathcal{D}_k^m for $1 \leq k \leq n$, completed by the thermal conductivity λ and eventually the thermal diffusion ratios χ_i for $1 \leq i \leq n - 1$.

Remark 5.5. *The positive coefficient $x_i \mathcal{D}_i^m$, $i \in \mathfrak{S}$ represent a diffusion coefficient of the i th species in the mixture where x_i is the mole fraction of the i th species. A very good approximation for such coefficients [21, 22] is the Hirschfelder-Curtiss approximation $\mathcal{D}_i^m = (1 - y_i)/\Delta_{ii}$.*

5.3 Assumptions on the diffusion coefficients

We introduce the strengthened assumptions concerning multicomponent transport (Tr'_2). These assumptions are required in order to investigate the uniqueness of entropy compatible with the hyperbolic-parabolic structure of the system of partial differential equations modeling multicomponent fluids.

- (Tr'₂)** (i) *The matrix L is given by the expression (2.10).*
(ii) *The matrix D is either obtained by solving Stefan-Maxwell type equations or from a quasi-diagonal approximation.*

In the first situation, the multicomponent diffusion matrix is given as in Proposition 5.2 with the Stefan-Maxwell matrix given by (5.1). The binary diffusion coefficients $\mathcal{D}_{ij}^{\text{bin}}$, $i, j \in \mathfrak{S}$, $i \neq j$, are positive smooth functions of $(\rho_1, \dots, \rho_n, T)$.

In the second situation, the multicomponent diffusion matrix is given by the quasi-diagonal approximation (5.3) with diagonal coefficients \mathcal{D}^m . The diagonal diffusion coefficients \mathcal{D}_k^m , $k \in \mathfrak{S}$, are positive smooth functions of $(\rho_1, \dots, \rho_n, T)$.

- (iii) *The thermal diffusion ratios χ_i , $i \in \mathfrak{S}$, are smooth functions of $(\rho_1, \dots, \rho_n, T)$ and satisfy the mass constraint $\langle \mathbb{1}, \chi \rangle = 0$.*
(iv) *The thermal conductivity λ , the shear viscosity η , the volume viscosity κ are smooth functions of $(\rho_1, \dots, \rho_n, T)$. These coefficients are such that $\lambda > 0$, $\eta > 0$, $\kappa \geq 0$, and $\kappa > 0$ when $d = 1$.*

- (v) The coefficients $\mathcal{D}_{ij}^{\text{bin}}$, $i, j \in \mathfrak{S}$, $i \neq j$, or \mathcal{D}_k^{m} , $k \in \mathfrak{S}$, (as depending on the transport model) the thermal conductivity λ , and the thermal diffusion ratios χ_i , $i \in \{1, \dots, n-1\}$, are independent and are independent of thermochemistry properties.

Property (i) simply corresponds to a convenient expression of L and Property (ii) introduce two typical expressions often used in the literature for the multicomponent matrix D . The Properties (iii) and (iv) are natural assumptions concerning the thermal diffusion ratios, the thermal conductivity, the shear viscosity and the bulk viscosity. The smoothness assumptions are typical consequences of the smoothness of collision integrals appearing in transport linear systems [11]. The independence of transport coefficients between them is a natural consequence of the independence of interaction potentials between pairs of molecules and of different moments. These coefficients are also assumed to be independent of thermodynamic properties which generally depend on the molecular structure of the molecule via partition functions.

5.4 Derivatives of the mass and heat diffusion matrix

We now investigate the derivatives of the matrix L with respect to the transport parameters. We first consider the situation where the multicomponent matrix is obtained from the Stefan-Maxwell relations. In this situation, the parameters that may be used in the differential commutation formula (4.28) are the binary diffusion coefficients $\mathcal{D}_{ij}^{\text{bin}}$, $1 \leq i < j \leq n$, the thermal conductivity λ , and eventually the thermal diffusion ratios χ_i , $1 \leq i \leq n-1$, if they are not assumed to identically vanish. We have to take into account the constraint $\langle \mathbb{1}, \chi \rangle = 0$ between the thermal diffusion ratios and there are only $n-1$ independent coefficients that are chosen to be the first $n-1$ coefficients $\chi_1, \dots, \chi_{n-1}$. The derivatives of L with respect to these parameters are given in the following lemma.

Lemma 5.6. *Keeping the assumptions of the Proposition 5.2, defining the matrix*

$$\tilde{\mathcal{L}} = \begin{pmatrix} D + \mathbb{1} \otimes \mathbb{1} & 0 \\ 0 & \frac{RT^2}{\rho m} \lambda \end{pmatrix} \mathcal{L}, \quad (5.5)$$

and denoting by $\mathbf{f}^1, \dots, \mathbf{f}^{n+1}$ the canonical basis vectors of \mathbb{R}^{n+1} , we have

$$\partial_{\mathcal{D}_{ij}^{\text{bin}}} L = \rho m \frac{x_i x_j}{(\mathcal{D}_{ij}^{\text{bin}})^2} \tilde{\mathcal{L}}^t \left((\mathbf{f}^i - \mathbf{f}^j) \otimes (\mathbf{f}^i - \mathbf{f}^j) \right) \tilde{\mathcal{L}}, \quad 1 \leq i < j \leq n. \quad (5.6)$$

$$\partial_{\chi_i} L = \frac{\rho^2 m}{T \lambda} \tilde{\mathcal{L}}^t \left((\mathbf{f}^i - \mathbf{f}^n) \otimes \mathbf{f}^{n+1} + \mathbf{f}^{n+1} \otimes (\mathbf{f}^i - \mathbf{f}^n) \right) \tilde{\mathcal{L}}, \quad 1 \leq i \leq n-1, \quad (5.7)$$

$$\partial_{\lambda} L = \frac{\rho^2 m^2}{RT^2 \lambda^2} \tilde{\mathcal{L}}^t \mathbf{f}^{n+1} \otimes \mathbf{f}^{n+1} \tilde{\mathcal{L}}, \quad (5.8)$$

Proof. These identities result from lengthy and tedious calculations. \square

It is interesting to observe that when the thermal diffusion ratios are taken into account, then the space spanned by the tangent matrices $\partial_{\mu} L$ for $\mu \in \{\mathcal{D}_{ij}^{\text{bin}}, 1 \leq i < j \leq n\} \cup \{\chi_i, 1 \leq i \leq n-1\} \cup \{\lambda\}$ has its maximal dimension $n(n+1)/2$. In this situation, it coincides with the set of symmetric matrices with nullspace containing $(\mathbb{1}, 0)^t$. On the other hand, when the matrix D is given by a quasi-diagonal approximation, the parameters that may be used in the differential commutation formula (4.28) are the diagonal coefficients \mathcal{D}_i^{m} , $1 \leq i \leq n$, the thermal conductivity λ , and eventually the thermal diffusion ratios χ_i , $1 \leq i \leq n-1$, if they are not assumed to identically vanish. The derivatives of L with respect to these parameters are given in the following lemma.

Lemma 5.7. *Keeping the assumptions and notation of Theorem 5.4, denoting $\mathbf{e}^1, \dots, \mathbf{e}^n$ the basis vectors of \mathbb{R}^n , $\mathbf{f}^1, \dots, \mathbf{f}^{n+1}$ and the basis vectors of \mathbb{R}^{n+1} , we have*

$$\partial_{\mathcal{D}_i^{\text{m}}} L = m \rho y_i^2 \mathbf{f}^i \otimes \mathbf{f}^i, \quad 1 \leq i < j \leq n. \quad (5.9)$$

$$\partial_{\chi_i} L = \rho RT \left(\mathbf{f}^i \otimes \mathbf{f}^{n+1} + \mathbf{f}^{n+1} \otimes \mathbf{f}^i \right), \quad 1 \leq i \leq n-1, \quad (5.10)$$

$$\partial_{\lambda} L = RT^2 \mathbf{f}^{n+1} \otimes \mathbf{f}^{n+1}, \quad (5.11)$$

where

$$\mathbf{f}^i = \begin{bmatrix} \mathbf{e}^i - y \\ h_i - h + \frac{RT}{m} \frac{\chi_i}{y_i} \end{bmatrix}, \quad 1 \leq i \leq n. \quad (5.12)$$

$$\mathbf{f}^{ni} = \begin{bmatrix} \mathcal{Y}D(\mathbf{e}^i - \mathbf{e}^n) \\ \langle D(\mathbf{e}^i - \mathbf{e}^n), \mathcal{Y}h_{\bullet} + RT \frac{\chi}{m} \rangle \end{bmatrix}, \quad 1 \leq i \leq n-1. \quad (5.13)$$

Proof. These identities result from lengthy and tedious calculations. \square

6 Uniqueness of entropy

We investigate uniqueness of mathematical entropies compatible with the hyperbolic-parabolic structure under the assumption that they are independent of the mass and heat transport parameters. These entropies are found to coincide up to an affine transform and are then compatible with source terms.

6.1 Constraints from diffusion matrices

We denote by $\tilde{\sigma}$ a mathematical entropy, $\tilde{\mathbf{v}} = (\partial_{\mathbf{u}} \tilde{\sigma})^t$ the corresponding symmetrizing variable, \mathcal{J} the matrix $\mathcal{J} = \partial_{\tilde{\mathbf{v}}} \tilde{\sigma}$ and by Ξ the permutation that regroup the temperature with the species densities, that is, such that $\Xi \mathbf{z} = (\rho_1, \dots, \rho_n, T, \mathbf{v})^t$. We have already investigated the properties of the permuted matrices $\Xi \tilde{\mathcal{B}}^L \Xi^t$ and $\Xi \mathcal{J} \Xi^t$ in Section 4.3. The dissipative compatibility relations for entropies already compatible with the hyperbolic structure have been shown to reduce to the relation (4.26). When the mathematical entropy is independent of transport parameters we may also use the differential relations (4.28) so that we have

$$L \mathcal{J}^{\mathbf{z}\mathbf{z}} = (\mathcal{J}^{\mathbf{z}\mathbf{z}})^t L, \quad L \mathcal{J}^{\mathbf{z}\mathbf{v}} = 0, \quad \partial_{\mu} L \mathcal{J}^{\mathbf{z}\mathbf{z}} = (\mathcal{J}^{\mathbf{z}\mathbf{z}})^t \partial_{\mu} L, \quad (6.1)$$

where μ denotes any relevant transport parameter. The structure of $\mathcal{J}^{\mathbf{z}\mathbf{z}}$ and $\mathcal{J}^{\mathbf{z}\mathbf{v}}$ is now investigated in the following propositions. We first consider the situation without thermal diffusion coefficients, that is, where $\chi_i = 0$, $i \in \mathfrak{S}$, and where we do not use any derivatives with respect to χ_i , $1 \leq i \leq n-1$,

Proposition 6.1. *Assume that $\tilde{\sigma}$ satisfies (E₃) and such that $\partial_{\mathbf{u}} \tilde{\mathbf{v}}$ is invertible. Assume also that $\tilde{\sigma}$ is independent of the mass and heat diffusion parameters. Then, in the absence of thermal diffusive effects, the matrices $\mathcal{J}^{\mathbf{z}\mathbf{z}}$ and $\mathcal{J}^{\mathbf{z}\mathbf{v}}$ are in the form*

$$\mathcal{J}^{\mathbf{z}\mathbf{z}} = \alpha \mathbb{I}_{n+1} + (\alpha - \alpha') \begin{bmatrix} h_{\bullet} \\ -1 \end{bmatrix} \otimes \mathbf{f}^{n+1} + \begin{bmatrix} \mathbb{I} \\ 0 \end{bmatrix} \otimes a, \quad \mathcal{J}^{\mathbf{z}\mathbf{v}} = \begin{bmatrix} \mathbb{I} \\ 0 \end{bmatrix} \otimes a', \quad (6.2)$$

where $a \in \mathbb{R}^{n+1}$ and $a' \in \mathbb{R}^d$ are vectors.

Proof. Since $N(L) = (\mathbb{I}, 0)^t$ we first obtain that $\mathcal{J}^{\mathbf{z}\mathbf{v}}$ is in the form $\mathcal{J}^{\mathbf{z}\mathbf{v}} = (\mathbb{I}, 0)^t \otimes a'$ for some vector $a' \in \mathbb{R}^d$. In order to investigate the structure of $\mathcal{J}^{\mathbf{z}\mathbf{z}}$ we then have to distinguish the two different possibilities for the multicomponent diffusion matrix.

Assume first that the diffusion matrix is obtained by solving the Stefan-Maxwell equations. It is then more convenient to work with the matrix $M = \tilde{\mathcal{L}} \mathcal{J}^{\mathbf{z}\mathbf{z}} \tilde{\mathcal{L}}^{-1}$ where $\tilde{\mathcal{L}}$ has been defined in Lemma 5.6. From the relations, $\partial_{\mu} L \mathcal{J}^{\mathbf{z}\mathbf{z}} = (\mathcal{J}^{\mathbf{z}\mathbf{z}})^t \partial_{\mu} L$ where μ is one of the parameters $\mathcal{D}_{ij}^{\text{bin}}$, $i, j \in \mathfrak{S}$, $i < j$, and λ , we obtain that $ZM = M^t Z$ for any Z in the form $\mathbf{f}^{n+1} \otimes \mathbf{f}^{n+1}$ or $(\mathbf{f}^i - \mathbf{f}^j) \otimes (\mathbf{f}^i - \mathbf{f}^j)$, $1 \leq i < j \leq n$. This implies in particular that there exist α_{ij} with $M^t (\mathbf{f}^i - \mathbf{f}^j) = \alpha_{ij} (\mathbf{f}^i - \mathbf{f}^j)$ for $1 \leq i < j \leq n$ and by forming the difference between two such relations, it is obtained that all the scalars α_{ij} are equal. Denoting by α this common value, we have $M^t \mathbf{f}^i - \alpha \mathbf{f}^i = a$ where a is a vector independent of $i \in \mathfrak{S}$. In addition, writing that $ZM = M^t Z$ for $Z = \mathbf{f}^{n+1} \otimes \mathbf{f}^{n+1}$ yields that $M^t \mathbf{f}^{n+1} = \alpha' \mathbf{f}^{n+1}$ and M is in the form

$$M = \begin{bmatrix} \alpha \mathbb{I}_n & 0_{n,1} \\ 0_{1,n} & \alpha' \end{bmatrix} + \begin{bmatrix} \mathbb{I} \\ 0 \end{bmatrix} \otimes a.$$

Therefore, $\mathcal{J}^{\mathbf{z}\mathbf{z}}$ is given by

$$\mathcal{J}^{\mathbf{z}\mathbf{z}} = \tilde{\mathcal{L}}^{-1} \left(\alpha \mathbb{I}_{n+1} + (\alpha' - \alpha) \mathbf{f}^{n+1} \otimes \mathbf{f}^{n+1} + \begin{bmatrix} \mathbb{I} \\ 0 \end{bmatrix} \otimes a \right) \tilde{\mathcal{L}},$$

and this yields that \mathcal{J}^{zz} is in the form (6.2).

In the situation where the multicomponent transport is given by a quasi-diagonal approximation, we may directly manipulate the matrix $M = \mathcal{J}^{zz}$. Since $ZM = M^t Z$ for any Z in the form $\mathbf{f}^{n+1} \otimes \mathbf{f}^{n+1}$ or $Z = \mathbf{f}^i \otimes \mathbf{f}^i$ for $1 \leq i \leq n$, we deduce that \mathbf{f}^{n+1} and \mathbf{f}^i for $1 \leq i \leq n$ are eigenvectors of M^t . We have in particular $M^t \mathbf{f}^i = \alpha_i \mathbf{f}^i$, for $1 \leq i \leq n$, and we also have the constraint $\sum_{i \in \mathfrak{S}} y_i \mathbf{f}^i = 0$. This implies that $\sum_{i \in \mathfrak{S}} \alpha_i y_i \mathbf{f}^i = 0$ and thus from (5.12) $\sum_{i \in \mathfrak{S}} \alpha_i y_i (\mathbf{e}^i - y) = 0$ so that $y_i \alpha_i = y_i \sum_{j \in \mathfrak{S}} y_j \alpha_j$ and that all the α_i are equal and we also have $M^t \mathbf{f}^{n+1} = \alpha' \mathbf{f}^{n+1}$ for some α' . From the structure of \mathbf{f}^i for $i \in \mathfrak{S}$, we next obtain that $M^t \mathbf{f}^i - \alpha \mathbf{f}^i - (\alpha - \alpha') h_i \mathbf{f}^{n+1}$ is a vector independent of $i \in \mathfrak{S}$. Proceeding as previously, we again deduce that \mathcal{J}^{zz} is in the form (6.2). \square

We now consider the situation where thermal diffusion effects are included in the model. This constraint more tightly the partial jacobian since the derivations with respect to the thermal diffusion coefficients may now be used.

Proposition 6.2. *Keeping the assumptions of Proposition 6.1 and further assuming that the thermal diffusion coefficients are taken into account, the matrices \mathcal{J}^{zz} and \mathcal{J}^{zv} are then in the form*

$$\mathcal{J}^{zz} = \alpha \mathbb{I}_{n+1} + \begin{bmatrix} \mathbb{1} \\ 0 \end{bmatrix} \otimes a, \quad \mathcal{J}^{zv} = \begin{bmatrix} \mathbb{1} \\ 0 \end{bmatrix} \otimes a', \quad (6.3)$$

where $a \in \mathbb{R}^{n+1}$ and $a' \in \mathbb{R}^d$ are vectors.

Proof. Assume first that the diffusion velocities are given by Stefan-Maxwell type equations. We may then consider again the transformed matrix $M = \tilde{\mathcal{L}} \mathcal{J}^{zz} \tilde{\mathcal{L}}^{-1}$ and from the beginning of the proof of Proposition 6.1 we obtain that M is in the form

$$M = \alpha \mathbb{I}_{n+1} + (\alpha - \alpha') \mathbf{f}^{n+1} \otimes \mathbf{f}^{n+1} + \begin{bmatrix} \mathbb{1} \\ 0 \end{bmatrix} \otimes a,$$

However, using now that $\partial_\mu L \mathcal{J}^{zz} = (\mathcal{J}^{zz})^t \partial_\mu L$ where μ is one χ_i , for $i \in \mathfrak{S}$, $i \neq n$, we obtain that $ZM = M^t Z$ for any Z in the form $\mathbf{f}^{n+1} \otimes (\mathbf{f}^i - \mathbf{f}^n) + (\mathbf{f}^i - \mathbf{f}^n) \otimes \mathbf{f}^{n+1}$, $1 \leq i \leq n-1$. After some algebra, noting that both $\mathbf{f}^i - \mathbf{f}^n$ and \mathbf{f}^{n+1} are orthogonal to $(\mathbb{1}, 0)^t$, it is obtained that

$$(\alpha' - \alpha) \left(\mathbf{f}^{n+1} \otimes (\mathbf{f}^i - \mathbf{f}^n) - (\mathbf{f}^i - \mathbf{f}^n) \otimes \mathbf{f}^{n+1} \right) = 0,$$

so that $\alpha = \alpha'$ and (6.3) is established.

When the quasi-diagonal approximation is used, the beginning of the proof is entirely similar to that of Proposition 6.1 and it is obtained that

$$\mathcal{J}^{zz} = \alpha \mathbb{I}_{n+1} + (\alpha - \alpha') \begin{bmatrix} b \\ -1 \end{bmatrix} \otimes \mathbf{f}^{n+1} + \begin{bmatrix} \mathbb{1} \\ 0 \end{bmatrix} \otimes a,$$

where $b \in \mathbb{R}^n$ has components $b_i = h_i + \frac{RT}{m} \frac{\chi_i}{y_i}$, $i \in \mathfrak{S}$, keeping in mind that the thermal diffusion factors in \mathcal{L} now do not vanish. Using the derivation with respect to the thermal diffusion ratios, we now obtain after some algebra that

$$(\alpha' - \alpha) \left(\mathbf{f}^{n+1} \otimes \mathbf{f}^{''i} - \mathbf{f}^{''i} \otimes \mathbf{f}^{n+1} \right) = 0,$$

and where we have used that both $\mathbf{f}^{''i}$ and \mathbf{f}^{n+1} are orthogonal to $(\mathbb{1}, 0)^t$ and that $\mathbf{f}^{''i}$ is orthogonal to $(b, -1)^t$. We thus conclude again that $\alpha' = \alpha$ and the proof is complete. \square

6.2 Uniqueness up to affine transforms

We investigate uniqueness up to affine transforms of mathematical entropies in the presence of thermal diffusion effects. It is assumed that Properties (\mathcal{T}_1) - (\mathcal{T}_3) , (\mathcal{N}) and (Tr_1) - (Tr'_2) hold.

Theorem 6.3. *Let $\tilde{\sigma}$ be a C^∞ function defined on the open set \mathcal{O}_u satisfying (E_2) - (E_3) and such that $\partial_u^2 \tilde{\sigma}$ is invertible and define $\tilde{v} = (\partial_u \tilde{\sigma})^t$. Assume that $\tilde{\sigma}$ is independent of the mass and heat diffusion parameters. Then $\tilde{\sigma}$ is in the form*

$$\tilde{\sigma} = \alpha_S \mathcal{S} + \sum_{i \in \mathfrak{S}} \alpha_i \rho_i + \alpha_v \rho v + \alpha_\varepsilon \left(\mathcal{E} + \frac{1}{2} \rho |v|^2 \right). \quad (6.4)$$

Proof. Let Ξ be the permutation matrix that regroups the temperature with the species densities, that is, such that $\Xi z = (\rho_1, \dots, \rho_n, T, \mathbf{v})^t$. We may partition $\Xi \mathcal{J} \Xi^t$ and $\Xi (\partial_z \tilde{\mathbf{v}}) \Xi^t$ in the form

$$\Xi \mathcal{J} \Xi^t = \begin{bmatrix} \mathcal{J}^{zz} & \mathcal{J}^{zv} \\ \mathcal{J}^{vz} & \mathcal{J}^{vv} \end{bmatrix}, \quad \Xi (\partial_z \tilde{\mathbf{v}}) \Xi^t = \begin{bmatrix} (\partial_z \tilde{\mathbf{v}})^{zz} & (\partial_z \tilde{\mathbf{v}})^{zv} \\ (\partial_z \tilde{\mathbf{v}})^{vz} & (\partial_z \tilde{\mathbf{v}})^{vv} \end{bmatrix}.$$

We also deduce from Proposition 6.2 that

$$\mathcal{J}^{zz} = (\partial_v \tilde{\mathbf{v}})^{zz} = \alpha \mathbb{I}_{n+1} + \begin{bmatrix} \mathbb{I} \\ 0 \end{bmatrix} \otimes a, \quad \mathcal{J}^{zv} = (\partial_v \tilde{\mathbf{v}})^{zv} = \begin{bmatrix} \mathbb{I} \\ 0 \end{bmatrix} \otimes a'. \quad (6.5)$$

From the matrix relation $\partial_z \tilde{\mathbf{v}} = \partial_v \tilde{\mathbf{v}} \partial_z \mathbf{v}$ we now obtain that

$$(\partial_z \tilde{\mathbf{v}})^{zz} = (\partial_v \tilde{\mathbf{v}})^{zz} (\partial_z \mathbf{v})^{zz} + (\partial_v \tilde{\mathbf{v}})^{zv} (\partial_z \mathbf{v})^{vz}.$$

From the structure of $\mathcal{J} = \partial_v \tilde{\mathbf{v}}$ obtained in Proposition 6.2, we further deduce that

$$(\partial_z \tilde{\mathbf{v}})^{zz} = \alpha \mathbb{I}_{n+1} (\partial_z \mathbf{v})^{zz} + \begin{bmatrix} \mathbb{I} \\ 0 \end{bmatrix} \otimes a'', \quad (6.6)$$

for some vector $a'' \in \mathbb{R}^{n+1}$.

On the other hand, from Theorem 4.1 we obtain that $\tilde{\sigma}$ has the structure (4.1) and from Lemma 4.2 we deduce that the matrix $\partial_z \tilde{\mathbf{v}}$ is in the form

$$\partial_z \tilde{\mathbf{v}} = -R \partial_S \varphi \partial_z \mathbf{v} - R \mathbf{v} \otimes \partial_z (\partial_S \varphi) + \partial_z \mathcal{V}. \quad (6.7)$$

Identifying both forms obtained for $(\partial_z \tilde{\mathbf{v}})^{zz}$, we deduce that $\tilde{\partial}_{\rho_k} (\partial_S \varphi) = 0$ for $k \in \mathfrak{S}$. A direct calculation shows that $\tilde{\partial}_{\rho_k} (\partial_S \varphi) = \partial_S^2 \varphi \tilde{\partial}_{\rho_k} \mathcal{S} + \partial_{\rho_k \mathcal{S}}^2 \varphi$ and we thus have

$$\partial_S^2 \varphi \tilde{\partial}_{\rho_k} \mathcal{S} + \partial_{\rho_k \mathcal{S}}^2 \varphi = 0, \quad k \in \mathfrak{S}. \quad (6.8)$$

Multiplying this identity by ρ_k and summing over $k \in \mathfrak{S}$ yields

$$\left(\sum_{k \in \mathfrak{S}} \rho_k \tilde{\partial}_{\rho_k} \mathcal{S} - \mathcal{S} \right) \partial_S^2 \varphi = 0,$$

since φ is 1-homogeneous and $\sum_{k \in \mathfrak{S}} \rho_k \partial_{\rho_k \mathcal{S}}^2 \varphi = -\mathcal{S} \partial_S^2 \varphi$. Using the identity

$$\sum_{k \in \mathfrak{S}} \rho_k \tilde{\partial}_{\rho_k} \mathcal{S} - \mathcal{S} = -\tilde{\partial}_T p,$$

we deduce that $\partial_S^2 \varphi = 0$ provided $\tilde{\partial}_T p$ is nonzero. However, $\tilde{\partial}_T p$ cannot vanish on any open set since otherwise we would obtain from (4.12) that $\tilde{\partial}_s \rho = 0$ and thus $\tilde{\partial}_s \nu = 0$ contradicting the nondegeneracy condition (\mathcal{N}) . We thus conclude that $\partial_S^2 \varphi = 0$ and from (6.8) we obtain that $\partial_{\rho_k \mathcal{S}}^2 \varphi = 0$ for any $k \in \mathfrak{S}$ so that $\partial_S \varphi$ is a constant. This implies the relation $\partial_z (\partial_S \varphi) = 0$ and the matrix identity

$$-R \partial_S \varphi (\partial_z \mathbf{v})^{zz} + (\partial_z \mathcal{V})^{zz} = \alpha \mathbb{I}_{n+1} (\partial_z \mathbf{v})^{zz} + \begin{bmatrix} \mathbb{I} \\ 0 \end{bmatrix} \otimes a''. \quad (6.9)$$

Since $\partial_S^2 \varphi = 0$ and $\partial_{\rho_k \mathcal{S}}^2 \varphi = 0$ for any $k \in \mathfrak{S}$ we also have $\tilde{\partial}_{\rho_k} \partial_{\rho_l} \varphi = \partial_{\rho_k \rho_l} \varphi$ in such a way that

$$(\partial_z \mathcal{V})^{zz} = \begin{bmatrix} \partial_{\rho_1 \rho_1} \varphi & \dots & \partial_{\rho_1 \rho_n} \varphi & 0 \\ \vdots & & \vdots & \vdots \\ \partial_{\rho_n \rho_1} \varphi & \dots & \partial_{\rho_n \rho_n} \varphi & 0 \\ 0 & \dots & 0 & 0 \end{bmatrix}. \quad (6.10)$$

Identifying the coefficient of the right lower corner in the relation (6.9), it is obtained that

$$-R \partial_S \varphi = \alpha,$$

so that finally

$$(\partial_z \mathcal{V})^{zz} = \begin{bmatrix} \mathbf{1} \\ 0 \end{bmatrix} \otimes a''.$$

By symmetry

$$(\partial_z \mathcal{V})^{zz} = \gamma \begin{bmatrix} \mathbf{1} \\ 0 \end{bmatrix} \otimes \begin{bmatrix} \mathbf{1} \\ 0 \end{bmatrix},$$

for some $\gamma \in \mathbb{R}$, and since φ is 1-homogeneous and $\partial_{\rho_k \mathcal{S}}^2 \varphi = 0$ for $k \in \mathfrak{S}$, we also have

$$(\partial_z \mathcal{V})^{zz} \begin{bmatrix} \rho \\ 0 \end{bmatrix} = 0.$$

This now implies that $\gamma \rho = 0$ so that $\gamma = 0$ and $(\partial_z \mathcal{V})^{zz} = 0$. Therefore, φ is an affine function of $\rho_1, \dots, \rho_n, \mathcal{S}$ and the proof is complete. \square

A direct consequence of this theorem is that after elimination of the trivial entropies $\alpha_i \rho_i$, $i \in \mathfrak{S}$, $\alpha_v \cdot \rho \mathbf{v}$, and $\alpha_{\mathcal{E}} (\mathcal{E} + \frac{1}{2} \rho |\mathbf{v}|^2)$ proportional to the components of \mathbf{u} , it only remains the classical entropy σ up to an affine transform. This strengthens the representation of Theorem for normal forms of multicomponent flows established in [30] since it then encompasses all possible normal forms constructed from entropies satisfying the assumptions of Theorem 6.3.

Remark 6.4. *A typical example where the nondegeneracy condition (\mathcal{N}) is not satisfied is that of barotropic fluids. In this situation the pressure is a function of ρ and it is easily established that $\bar{\partial}_{ps}^2 (1/\rho) = 0$. One may then check that there exists nontrivial families of mathematical entropies compatible with the hyperbolic-parabolic structure of the fluid system. This is notably the case for viscous sheets above fluid substrates as float glasses [32].*

6.3 Uniqueness without thermal diffusive effects

We investigate in this section uniqueness of mathematical entropies when $\chi_i = 0$, $i \in \mathfrak{S}$, that is, without thermal diffusive effects also termed the Soret and Dufour effects. The corresponding theorems apply in particular to the usual quasi-diagonal approximation for diffusion matrices. It is assumed that Properties (\mathcal{T}_1) - (\mathcal{T}_3) , (\mathcal{N}) and (Tr_1) - (Tr'_2) hold. The following extra assumption is also required and essentially means that the species molar masses are not identical as established by investigating the perfect gas limit.

(M) *The vectors $\tilde{\partial}_q p$ and $\mathbf{1}$ are linearly independent.*

Under this extra assumption, it is possible to extend the uniqueness theorem in the absence of thermal diffusion effects.

Theorem 6.5. *Let $\tilde{\sigma}$ be a C^∞ function defined on the open set \mathcal{O}_v satisfying (E_2) - (E_3) and such that $\partial_v^2 \tilde{\sigma}$ is invertible and define $\tilde{\mathbf{v}} = (\partial_v \tilde{\sigma})^t$. Assume that the mathematical entropy $\tilde{\sigma}$ is independent of the transport parameters. Then $\tilde{\sigma}$ is in the form (6.4).*

Proof. From Theorem 4.1 $\tilde{\sigma}$ is in the form (4.1) and from Lemma 4.2 the matrix $\partial_z \tilde{\mathbf{v}}$ is in the form

$$\partial_z \tilde{\mathbf{v}} = -R \partial_S \varphi \partial_z \mathbf{v} - R \mathbf{v} \otimes \partial_z (\partial_S \varphi) + \partial_z \mathcal{V}. \quad (6.11)$$

On the other hand, we deduce from Proposition 6.1 that

$$\mathcal{J}^{zz} = \alpha \mathbb{1}_{n+1} + (\alpha - \alpha') \begin{bmatrix} h_\bullet \\ -1 \end{bmatrix} \otimes \mathbf{f}^{n+1} + \begin{bmatrix} \mathbf{1} \\ 0 \end{bmatrix} \otimes a, \quad \mathcal{J}^{zv} = \begin{bmatrix} \mathbf{1} \\ 0 \end{bmatrix} \otimes a'. \quad (6.12)$$

We also note that

$$\begin{aligned} (\partial_z \mathbf{v})^{zz} &= \frac{1}{RT^2} \begin{bmatrix} \Gamma/\rho & |\mathbf{v}|^2 \mathbf{1} - \mathcal{G} \\ 0 & 1 \end{bmatrix}, & (\partial_z \mathbf{v})^{zv} &= -\frac{1}{RT} \begin{bmatrix} \mathbf{1} \\ 0 \end{bmatrix} \otimes \mathbf{v}, \\ (\partial_z \mathbf{v})^{vz} &= -\frac{1}{RT^2} \mathbf{v} \otimes \mathbf{f}^{n+1}, & (\partial_z \mathbf{v})^{vv} &= \frac{1}{RT} \mathbb{1}_d. \end{aligned}$$

Upon multiplying by \mathcal{J} and $\partial_z \mathbf{v}$ by blocs we obtain that

$$(\partial_z \tilde{\mathbf{v}})^{zz} = \alpha \mathbb{I}_{n+1} (\partial_z \mathbf{v})^{zz} + \frac{\alpha - \alpha'}{RT^2} \begin{bmatrix} h_\bullet \\ -1 \end{bmatrix} \otimes \mathbf{f}^{n+1} + \begin{bmatrix} \mathbb{I} \\ 0 \end{bmatrix} \otimes a''', \quad (6.13)$$

and where we have used that $((\partial_z \mathbf{v})^{zz})^t \mathbf{f}^{n+1} = \mathbf{f}^{n+1}/RT^2$. We thus deduce again that $\tilde{\partial}_{\rho_k} (\partial_S \varphi) = 0$ for $k \in \mathfrak{S}$, and as already established in the proof of Theorem 6.3 this implies that $\partial_{\mathfrak{S}}^2 \varphi = 0$ and $\partial_{\rho_k}^2 \varphi = 0$ for any $k \in \mathfrak{S}$ and $\partial_S \varphi$ is a constant.

We now identify the lower right coefficient of both identities (4.14) and (6.13) and after some algebra it yields that $\alpha' = -R\partial_S \varphi$. We then proceed to identify the left upper blocs of (4.14) and (6.13) and after some algebra, and thanks to the symmetry of $\partial_z \mathcal{V}$ from (6.10) it yields the matrix relation

$$(\alpha + R\partial_S \varphi)\Gamma + \rho RT^2 \partial_z \mathcal{V} = \mu \mathbb{I} \otimes \mathbb{I},$$

for some scalar μ . Multiplying on the right by the mass fraction vector $y = (y_1, \dots, y_n)^t$ we obtain that

$$(\alpha + R\partial_S \varphi)\Gamma y = \mu \mathbb{I},$$

since $\partial_z \mathcal{V} y = 0$ by homogeneity. However, we also have [30]

$$\Gamma y = \frac{\rho}{T} \partial_\rho p,$$

and since $\partial_\rho p$ and \mathbb{I} are not proportional from (\mathcal{M}) we conclude that $(\alpha + R\partial_S \varphi) = 0$. This now implies that $\alpha = \alpha'$ and the end of the proof is similar to that of Theorem 6.3. \square

7 Conclusion

We have investigated the mathematical structure of entropies for nonideal multicomponent flows involving nonideal thermochemistry as well as multicomponent diffusion driven by chemical potential gradients.

The general structure of entropies compatible with the hyperbolic structure has been obtained under a natural nond degeneracy condition and such entropies are automatically compatible with dissipation matrices associated with viscous effects.

Uniqueness of the mathematical entropy compatible with the hyperbolic-parabolic structure of the resulting system of partial differential equations has been obtained for the subfamily of entropies independent of the natural mass and heat diffusion parameters.

A The mass fraction variables

Thermodynamic functions in terms of the variables $(\rho_1, \dots, \rho_n, T)^t$ or $(\rho, y_2, \dots, y_n, T)^t$ do not have homogeneity properties. In order to have homogeneous functionals, it is necessary to use of the variable $(\nu, y_1, \dots, y_n, T)^t$ where $\nu = 1/\rho$ is the volume per unit mass, $\rho = \sum_{i \in \mathfrak{S}} \rho_i$, and $y_i = \rho_i/\rho$ is the mass fraction of the i th species. Assuming that the mass fractions are independent [29] and defining $e(\nu, y_1, \dots, y_n, T) = \nu \mathcal{E}\left(\frac{y_1}{\nu}, \dots, \frac{y_n}{\nu}, T\right)$, $p(\nu, y_1, \dots, y_n, T) = p\left(\frac{y_1}{\nu}, \dots, \frac{y_n}{\nu}, T\right)$, and $s(\nu, y_1, \dots, y_n, T) = \nu \mathcal{S}\left(\frac{y_1}{\nu}, \dots, \frac{y_n}{\nu}, T\right)$, then s and e are indeed 1-homogeneous and p is 0-homogeneous with respect to ν, y_1, \dots, y_n [29]. The mathematical structure of the corresponding mass based thermodynamic properties e , p , and s is fully described in [29] as well as the equivalence with (\mathcal{T}_1) - (\mathcal{T}_3) .

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