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MATHEMATICAL MODELING OF SUPERCRITICAL MULTICOMPONENT REACTIVE FLUIDS

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Mathematical Modeling of Supercritical Multicomponent Reactive Fluids

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Abstract

We investigate a system of partial differential equations modeling supercritical multicomponent reactive fluids. These equations involve nonideal fluid thermodynamics, nonideal chemistry as well as multicomponent diffusion fluxes driven by chemical potential gradients. Only local symmetrization of the resulting system of partial differential equations may be achieved because of thermodynamic instabilities even though the entropy function is globally defined. Local symmetrized forms are explicitly evaluated in terms of the inverse of the chemical potential Hessian and local normal forms lead to global existence and asymptotic stability of equilibrium states as well as decay estimates. We also discuss the deficiency of the resulting system of partial differential equations at thermodynamically unstable states typically associated with nonideal fluids.

1 Introduction

Supercritical reactive fluids arise in laboratory experiments and engineering applications like for instance Ariane's rocket engines [12, 46]. This is a strong motivation for investigating the mathematical structure of supercritical fluid models with chemical reactions. The mathematical structure of hyperbolic-parabolic symmetrizable systems of partial differential equations modeling single species fluids has already been investigated by many authors [44, 32, 82, 50, 71, 52, 18, 29, 9, 74]. Mathematical models for multicomponent ideal fluid mixtures with chemical kinetics of mass action type have also been analyzed in various frameworks [38, 34, 39, 30, 48, 57], but, to the authors' knowledge, the situation of supercritical reactive fluids is analyzed here for the first time.

The system of partial differential equations modeling supercritical multicomponent reactive fluids is first discussed. Governing equations for dense fluid mixtures may generally be derived from the thermodynamics of irreversible processes [61, 62, 67, 20], from statistical mechanics [49, 3, 63], from nonequilibrium statistical thermodynamics [54], as well as from the kinetic theory of dense gases [5, 6, 56]. The conservation equations, the thermodynamics, the chemical production rates and the transport fluxes are presented. Nonideal thermodynamics are often built from pressure laws by assuming a Gibbsian structure and compatibility with perfect gases at low densities and such a construction has recently been investigated mathematically [40]. The nonideal chemical production rates are deduced from statistical thermodynamics and are directly expressed in terms of chemical potentials [59, 60, 54, 43, 40]. These rates are compatible with the symmetric forms of rates of progress derived from the kinetic theory of dilute reactive gases [27, 34]. The transport fluxes are deduced from various macroscopic or molecular theories [62, 67, 20, 54, 5, 6, 56] and are driven by chemical potential gradients. Nonidealities in transport fluxes are notably important to prevent unphysical diffusion in dense cold fluids [43, 41]. The resulting nonideal fluid model is shown to satisfy the second principle of thermodynamics, that is, entropy production due to transport fluxes and chemistry are both shown to be nonnegative. As a typical exemple, the nonideal thermodynamics built from the Soave-Redlich-Kwong cubic equation of state, often used to model supercritical flames [70, 43], is discussed.

An important aspect of nonideal thermodynamics is the existence of thermodynamic instabilities which may be of thermal, mechanical, or chemical origin [40]. Instabilities of mechanical origin typically correspond to single species—or chemically frozen—liquid-vapor phase changes and are avoided at sufficiently high pressure. At supercritical pressure, one may indeed continuously transform a fluid

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from a liquid-like state into a gas-like state [43]. On the other hand, the instabilities of chemical origin correspond to phase separation at sufficiently—supercritical— high pressure and low temperature [43]. Mixtures of Hydrogen and Nitrogen may split for instance between two phases at temperatures below 100 K and pressures above 100 atm as established experimentally [81, 28], and these thermodynamic instabilities of chemical origin have been well reproduced computationally by using the Soave Redlich Kwong equation of state [40, 43]. From a mathematical point of view, these unstable points are associated with a change of sign of entropy Hessian eigenvalues.

We investigate symmetrized forms of the resulting system of partial differential equations. Existence of a symmetrized form is related to the existence of a mathematical entropy compatible with convective terms, dissipative terms and source terms. This mathematical entropy is taken to be the opposite of the physical entropy per unit volume. However, the open sets where thermodynamics is admissible—in particular where the entropy Hessian is definite—are bounded by thermodynamically unstable states for nonideal fluids. The set where the conservative variable may range is thus not anymore convex—like for perfect gases—and different states may correspond to the same entropic variable, i.e., to the same thermal variables and chemical potentials. As a consequence, even though there exists a mathematical entropy function σ and a symmetrizing variable $\mathsf{v} = (\partial_{\mathsf{u}}\sigma)^t$ defined for all admissible states of the conservative variable u, the corresponding map $\mathsf{u} \to \mathsf{v}$ is not anymore globally one to one—unlike for ideal fluids—because of thermodynamic instabilities. This symmetrizing change of variable is only *locally invertible* for such nonideal thermodynamics. Similarly, the normal change of variable are only locally invertible but this property is sufficient to rewrite locally the system into a normal form, that this, in the form of a symmetric hyperbolic-parabolic composite system.

The symmetrized forms associated with supercritical reactive fluids are evaluated in terms of the inverse of the Gibbs functions derivatives $\partial_{\rho_j}\mathcal{G}_i$, $1 \leqslant i, j \leqslant n$, where $\mathcal{G}_i$ is the Gibbs function of the ith species per unit mass and ρ_j the partial density of the jth species. We establish the dissipative structure of the linearized normal form around constant equilibrium states as well as stability conditions on the source term, i.e., the chemical entropy production is nonnegative and the source term lies in the range of its derivative at equilibrium. As a consequence, we obtain global existence results, asymptotic stability of stationary states and decay estimates towards the equilibrium states in all space dimensions for multicomponent dense fluid models including arbitrary complex chemistry as well as detailed nonideal transport fluxes. These results extends previous work associated with ideal gas mixtures and mass action type chemical kinetics [38] and apply in particular to metastable states such as undercooled vapor or superheated liquids.

We finally investigate how are transformed the mathematical properties of the system of partial differential equations at thermodynamic unstable states. We specifically consider a single fluid at a mechanical thermodynamic unstable point and a binary mixture at a chemical thermodynamic unstable point. In both situations, the normal forms degenerate whereas the *rescaled* normal forms remain hyperbolic and their dissipative subsystems remain symmetrizable and parabolic in the sense of Petrovsky. However, these rescaled normal forms are not anymore symmetrizable, and more fundamentally, the Shizuta-Kawashima condition does not hold anymore at thermodynamically unstable points so that they are not strictly dissipative. In other words, it is the global system structure which presents a deficiency at thermodynamically unstable states and pure compression waves remain undamped.

The system of partial differential equations modeling supercritical fluids is presented in Section 2. Symmetrization, existence of an entropy, and normal forms are investigated in Section 3 for an abstract system. These results are applied to supercritical reactive fluids in Section 4. Finally, the deficiency of the system of partial differential equations at thermodynamic unstable points is studied in Section 5.

2 Supercritical fluids

We present in this section the system of equations modeling supercritical multicomponent reactive fluids. We also discuss entropy production, thermodynamic instabilities as well a typical cubic equation of state often used for high pressure fluids.

2.1 Governing equations

2.1.1 Conservation laws

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

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

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

$$\partial_t(\rho \boldsymbol{v}) + \boldsymbol{\nabla}\cdot(\rho \boldsymbol{v}\otimes\boldsymbol{v} + \mathcal{P}\mathbb{I}_d) + \boldsymbol{\nabla}\cdot\boldsymbol{\Pi} = 0, \tag{2.2}$$

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

$$\partial_t(\mathcal{E} + \tfrac{1}{2}\rho \boldsymbol{v}\cdot\boldsymbol{v}) + \boldsymbol{\nabla}\cdot\big((\mathcal{E} + \tfrac{1}{2}\rho \boldsymbol{v}\cdot\boldsymbol{v} + \mathcal{P})\boldsymbol{v}\big) + \boldsymbol{\nabla}\cdot(\boldsymbol{Q} + \boldsymbol{\Pi}\cdot\boldsymbol{v}) = 0, \tag{2.3}$$

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

2.1.2 Historical derivation

The general equations governing nonideal gas mixtures with expressions for multicomponent fluxes in terms of chemical potential gradients and temperature gradients—with proper symmetry properties of the transport coefficients—have first been derived from the thermodynamic of irreversible processes by Meixner [61, 62] and Prigogine [67, 20]. The equations for dense fluids have then been obtained in the framework of statistical mechanics by Irwing and Kirkwood [49] and for dense fluid mixtures by Bearman and Kirkwood [3] and Mori [63]. The governing equations and the multicomponent fluxes have also been obtained by Keizer [54] from nonequilibrium statistical thermodynamics.

The kinetic theory of gases has been very well developed for dilute gas mixtures but the resulting equation of state is that of perfect gases [83, 80, 13, 31, 22]. A kinetic theory of dense gases has first been developed by Enskog for rigid spheres and extended by Thorne to binary mixtures [13, 31]. The advantage of the rigid sphere model is that collisions are instantaneous so that the probability of simultaneous multiple encounters is negligible. The principal transport mechanism in dense gases is then that of collisional transfer at variance with dilute gases where it is free molecular flow. However, it has been found by Bajaras et al. [2] that the results of the Enskog-Thorne theory—and of its straightforward extensions—are not compatible with the thermodynamics of irreversible processes. A modified form of Enskog equation has then been introduced by Van Beijeren and Ernst [5] and the resulting dense fluid gas mixture kinetic theory [6] has been shown to be compatible with the thermodynamics of irreversible processes. The corresponding Chapman-Enskog procedure has next been performed by Kurochkin et al. [56]. More general theories of dense gases have been based on multiple velocity distribution functions and on the BBGKY hierarchy of equations [13, 31]. Formal expressions have notably been derived for a single gas, assuming that the two-particle distribution function is time-independent [31]. To the authors' knowledge, however, a general kinetic theory of dense polyatomic reactive gas mixtures is still missing.

2.2 Thermodynamics

2.2.1 Dense fluid thermodynamics

We denote by $\mathcal{S}$ the entropy per unit volume, $\mathcal{E}$ the energy per unit volume, and $\mathcal{P}$ the pressure. The thermodynamic framework is presented by using the usual thermodynamic variables $z = (\rho_1, \dots, \rho_n, T)^t$ and $u = (\rho_1, \dots, \rho_n, \mathcal{E})^t$ where $\rho_1, \dots, \rho_n$ denotes the species mass per unit volume and T the absolute temperature. These variables z and u are essentially the thermodynamic components of the natural variable z and of the conservative variable u introduced later in Section 2.8. We denote by ∂ the derivation operator with respect to the variable u and by $\widetilde{\partial}$ the derivation operator with respect to the variable z. The integer $\varkappa \in \mathbb{N}$, $\varkappa \geqslant 3$, denotes the regularity class of thermodynamic functions.

Definition 2.1. *Let $\mathcal{E}$, $\mathcal{P}$, and $\mathcal{S}$ be $C^{\varkappa}$ functions of the variable $z = (\rho_1, \dots, \rho_n, T)^t$ 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 $(\mathcal{T}_1)$-$(\mathcal{T}_4)$ hold.*

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

($\mathcal{T}_2$) *For any $z \in \mathcal{O}_z$, defining $\mathcal{G}_i = \widetilde{\partial}_{\rho_i}\mathcal{E} - T\,\widetilde{\partial}_{\rho_i}\mathcal{S}$, $i \in \mathfrak{S}$, we have the volumetric Gibbs' relation*

$$T\mathrm{d}\mathcal{S} = -\sum_{i\in\mathfrak{S}} \mathcal{G}_i \mathrm{d}\rho_i + \mathrm{d}\mathcal{E}, \tag{2.4}$$

and the constraint $\sum_{i\in\mathfrak{S}} \rho_i\mathcal{G}_i = \mathcal{E} + \mathcal{P} - T\mathcal{S}$.

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

($\mathcal{T}_4$) *For any $(y_1, \dots, y_n, T) \in (0,\infty)^{n+1}$, such that $\sum_{i\in\mathfrak{S}} y_i = 1$, there exists $\rho_{\mathrm{m}} > 0$ such that $z_\rho = (\rho y_1, \dots, \rho y_n, T)^t \in \mathcal{O}_z$ for $0 < \rho < \rho_{\mathrm{m}}$. Moreover, we have the compatibility conditions*

$$\lim_{\rho\to 0} \frac{\mathcal{E}(z_\rho) - \mathcal{E}^{\mathrm{PG}}(z_\rho)}{\rho} = 0, \qquad \lim_{\rho\to 0} \frac{\mathcal{P}(z_\rho) - \mathcal{P}^{\mathrm{PG}}(z_\rho)}{\rho} = 0, \qquad \lim_{\rho\to 0} \frac{\mathcal{S}(z_\rho) - \mathcal{S}^{\mathrm{PG}}(z_\rho)}{\rho} = 0,$$

where the superscript $^{\mathrm{PG}}$ denotes the thermodynamics properties of perfect gas mixtures.

Property ($\mathcal{T}_1$) is associated with the natural change of variables traditionally encountered in thermodynamics and temperature as well as species densities are naturally assumed to be positive in the model with $\mathcal{O}_z \subset (0, +\infty)^{n+1}$. Property ($\mathcal{T}_2$) is Gibbs' relation in terms of volumetric densities with a simplified definition of the species Gibbs functions $\mathcal{G}_i$, $i \in \mathfrak{S}$. There is also a constraint associated with Gibbs' relation (2.4) in terms of $\mathcal{S}$, $\mathcal{E}$, and $\rho_1, \dots, \rho_n$, since these variables are volumetric [40]. Property ($\mathcal{T}_3$) is the natural thermodynamic stability condition since, from the second principle, the evolution of an isolated system tends to maximize its entropy. The entropy of a stable isolated system should thus be a concave function of its composition variables and internal energy. Whenever it is not the case, the system loses its homogeneity and splits between two or more phases in order to reach equilibrium. In particular, the open set $\mathcal{O}_z$ may have a complex shape because of real gas effects and thermodynamic instabilities at high pressure and low temperature. The open set $\mathcal{O}_u$ is also simply connected like $\mathcal{O}_z$ from ($\mathcal{T}_1$) allowing a unique determination of entropy. Property ($\mathcal{T}_4$) is finally the compatibility condition with perfect gases since for small ρ we must recover the perfect gas regime. Note that division by ρ is required since as $\rho \to 0$ all volumetric densities as well as both $\mathcal{P}$ and $\mathcal{P}^{\mathrm{PG}}$ go to zero. The compatibility with perfect gases *must naturally be written in term of densities* and it is mathematically absurd to formulate such compatibility it in terms of extensive absolute quantities.

Remark 2.2. *Since $z \to u$ is a diffeomorphism, we may equally define the thermodynamics with functions $T(u)$, $\mathcal{P}(u)$ and $\mathcal{S}(u)$ such that ($\mathcal{T}_1$)-($\mathcal{T}_4$) are satisfied.*

Supercritical fluid thermodynamics are generally built from equations of states and such a construction has been investigated mathematically [40]. In particular, unlike with classical fluid thermodynamics, the domain of validity is restricted by thermodynamic instabilities at low temperature and high pressure [43].

2.2.2 Perfect gases

The perfect gas pressure $\mathcal{P}^{\mathrm{PG}}$ associated with Property ($\mathcal{T}_4$) is given by

$$\mathcal{P}^{\mathrm{PG}} = RT\sum_{i\in\mathfrak{S}} \frac{\rho_i}{m_i}, \tag{2.5}$$

and the corresponding energy per unit volume $\mathcal{E}^{\mathrm{PG}}$ is in the form

$$\mathcal{E}^{\mathrm{PG}} = \sum_{i\in\mathfrak{S}} \rho_i e_i^{\mathrm{PG}}, \qquad e_i^{\mathrm{PG}} = e_i^{\mathrm{st}} + \int_{T^{\mathrm{st}}}^{T} c_{\mathrm{v}i}^{\mathrm{PG}}(\theta)\, d\theta, \tag{2.6}$$

where e_i^{PG} denotes the perfect gas internal energy per unit mass of the ith species, T^{st} the standard temperature, e_i^{st} the energy of formation at temperature T^{st} per unit mass of the ith species, and $c_{\mathrm{v}i}^{\mathrm{PG}}$ the perfect gas specific heat per unit mass of the ith species. The entropy per unit volume $\mathcal{S}^{\mathrm{PG}}$ in ($\mathcal{T}_4$) is given by

$$\mathcal{S}^{\mathrm{PG}} = \sum_{i\in\mathfrak{S}} \rho_i \mathcal{S}_i^{\mathrm{PG}}, \qquad \mathcal{S}_i^{\mathrm{PG}} = s_i^{\mathrm{st}} + \int_{T^{\mathrm{st}}}^{T} \frac{c_{\mathrm{v}i}^{\mathrm{PG}}(\theta)}{\theta}\, d\theta - \frac{RT}{m_i} \log \frac{\rho_i}{m_i\gamma^{\mathrm{st}}}, \tag{2.7}$$

where s_i^{st} is the formation entropy of the ith species at the standard temperature T^{st} and standard pressure p^{st}, and $\gamma^{\mathrm{st}} = p^{\mathrm{st}}/RT^{\mathrm{st}}$ is the standard concentration. The enthalpy $\mathcal{H}^{\mathrm{PG}} = \mathcal{E}^{\mathrm{PG}} + \mathcal{P}^{\mathrm{PG}}$, Gibbs function $\mathcal{G}^{\mathrm{PG}} = \mathcal{E}^{\mathrm{PG}} + \mathcal{P}^{\mathrm{PG}} - T\mathcal{S}^{\mathrm{PG}}$, and free energy $\mathcal{F}^{\mathrm{PG}} = \mathcal{E}^{\mathrm{PG}} - T\mathcal{S}^{\mathrm{PG}}$ are then easily evaluated. The assumptions required for perfect gases (PG) may be written [40, 34]

(PG) *The formation energies e_i^{st}, $i \in \mathfrak{S}$, and entropies s_i^{st}, $i \in \mathfrak{S}$, are real constants. The species mass per unit mole m_i, $i \in \mathfrak{S}$, and the gas constant R are positive constants. The species heat per unit mass $c_{\mathrm{v}i}^{\mathrm{PG}}$, $i \in \mathfrak{S}$, are C^∞ functions over $[0,\infty)$, and there exist constants $\underline{c}_{\mathrm{v}}$ and $\overline{c}_{\mathrm{v}}$ such that $0 < \underline{c}_{\mathrm{v}} \leqslant c_{\mathrm{v}i}^{\mathrm{PG}} \leqslant \overline{c}_{\mathrm{v}}$ for all $T \geqslant 0$ and $i \in \mathfrak{S}$.*

The extension up to zero temperature of specific heats, energies and enthalpies is commonly used in thermodynamics. The specific heats that are considered remain bounded away from zero since we consider perfect gases governed by Boltzmann statistics [34]. In the following proposition we investigate the mathematical properties of ideal gas mixture thermodynamics where of course ($\mathcal{T}_4$) is trivial.

Proposition 2.3. *The energy per unit volume $\mathcal{E}^{\mathrm{PG}}$, the pressure $\mathcal{P}^{\mathrm{PG}}$, and the entropy per unit volume $\mathcal{S}^{\mathrm{PG}}$, are C^∞ functions defined on the open set $\mathcal{O}_z^{\mathrm{PG}} = (0,\infty)^{n+1}$ which satisfy ($\mathcal{T}_1$)-($\mathcal{T}_4$). Moreover we have*

$$\mathcal{O}_u^{\mathrm{PG}} = \{u = (u_1, \dots, u_n, u_{\mathcal{E}})^t \text{ with } u_1 > 0, \dots, u_n > 0, u_{\mathcal{E}} > \sum_{i\in\mathfrak{S}} u_i e_i^0\},$$

where e_i^0 denotes the energy of the ith species at zero temperature $e_i^0 = e_i^{\mathrm{st}} - \int_0^{T^{\mathrm{st}}} c_{\mathrm{v}i}^{\mathrm{PG}}(\theta)\, d\theta$, $i \in \mathfrak{S}$.

Proof. The proof is straightforward and we refer to [34]. □

2.2.3 The mass fraction variables

Thermodynamic functionals 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 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 ith species. Assuming that the mass fractions are independent [40] and defining

$$e(\nu, y_1, \dots, y_n, T) = \nu\mathcal{E}\Big(\frac{y_1}{\nu}, \dots, \frac{y_n}{\nu}, T\Big),$$

$$p(\nu, y_1, \dots, y_n, T) = \mathcal{P}\Big(\frac{y_1}{\nu}, \dots, \frac{y_n}{\nu}, T\Big),$$

and

$$s(\nu, y_1, \dots, y_n, T) = \nu\mathcal{S}\Big(\frac{y_1}{\nu}, \dots, \frac{y_n}{\nu}, T\Big),$$

then s and e are indeed 1-homogeneous and p is 0-homogeneous with respect to $\nu, y_1, \dots, y_n$ [40]. With such independent mass fractions, the mass constraint $\sum_{k\in\mathfrak{S}} y_k = 1$ must be recovered from the governing equations and boundary conditions [34, 40]. The mathematical structure of the corresponding mass based thermodynamic properties e, p, and s is fully described in [40] as well as the equivalence with ($\mathcal{T}_1$)-($\mathcal{T}_4$).

2.3 Chemical production rates

We present in this section the mathematical structure of nonideal chemical production rates [40]. The mathematical structure of chemical kinetics has notably been investigated—generally for homogeneous systems and kinetics of mass action type—by Aris [1], Wei [84], Shapiro and Shapley [72], Pousin [68], Krambeck [55], Giovangigli and Massot [34, 38, 39], and that of nonideal chemical production rates has recently been investigated by the authors [40].

2.3.1 Nonideal rates

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

$$\sum_{i\in\mathfrak{S}} \nu_{ij}^{\mathrm{f}} \mathcal{M}_i \rightleftarrows \sum_{i\in\mathfrak{S}} \nu_{ij}^{\mathrm{b}} \mathcal{M}_i, \qquad j \in \mathfrak{R}, \tag{2.8}$$

where $\nu^{\rm f}_{ij}$ and $\nu^{\rm b}_{ij}$ denote the forward and backward stoichiometric coefficients of the ith species in the jth reaction, $\mathcal{M}_i$ the symbol of the molecule of the ith species, and $\mathfrak{R} = \{1, \dots, n^{\rm r}\}$ the reaction indexing set. All chemical reactions are reversible and the number of reactions $n^{\rm r} \geqslant 1$ is arbitrary. We are indeed interested in *elementary* chemical reactions which effectively take place in the fluid mixtures, and elementary reactions are always reversible [34].

The molar production rate of the ith species ω_i is given by [59, 60, 54]

$$\omega_i = \sum_{j\in\mathfrak{R}} (\nu^{\rm b}_{ij} - \nu^{\rm f}_{ij})\tau_j, \tag{2.9}$$

where τ_j denotes the rate of progress of the jth reaction. The proper form for the rate of progress of the jth reaction τ_j is deduced from statistical physics [59, 60, 54]

$$\tau_j = \kappa^{\rm s}_j \Big(\exp\Big(\sum_{i\in\mathfrak{S}} \nu^{\rm f}_{ij}\mu_i\Big) - \exp\Big(\sum_{i\in\mathfrak{S}} \nu^{\rm b}_{ij}\mu_i\Big)\Big), \tag{2.10}$$

where $\kappa^{\rm s}_j$ is the symmetric reaction constant of the jth reaction, $\mu_i = m_i\mathcal{G}_i/RT$ the reduced molar chemical potentials of the ith species, and $\mathcal{G}_i$ the Gibbs function per unit mass of the ith species.

These nonideal rates of progress have first been derived by Marcelin from chemical and statistical physics considerations [59, 60]. They have been rederived by Keizer in the framework of an extended statistical theory of nonequilibrium processes [54]. This form for rates of progress insures that entropy production due to chemical reactions is nonnegative and is compatible with traditional nonidealities used to estimate *equilibrium constants* [19, 45]. They are also compatible with the symmetric forms of rates of progress derived from the kinetic theory of dilute reactive gases [34, 27, 43]. Note that these rates are expressed in terms of chemical potentials, so that they are only defined where the corresponding thermodynamics is defined.

2.3.2 Mathematical structure

The species of the mixture are assumed to be constituted by atoms and we denote by $\mathfrak{a}_{il}$ the number of lth atom in the ith species, $\mathfrak{A} = \{1, \dots, n^{\rm a}\}$ the set of atom indices, and $n^{\rm a} \geqslant 1$ the number of atoms—or elements—in the mixture. It is convenient to introduce a vector notation in order to investigate the mathematical structure of the chemical production rates. The forward and backward reaction vectors $\nu^{\rm f}_j$ and $\nu^{\rm b}_j$ of the jth reaction are defined by $\nu^{\rm f}_j = (\nu^{\rm f}_{1j}, \dots, \nu^{\rm f}_{nj})^t$ and $\nu^{\rm b}_j = (\nu^{\rm b}_{1j}, \dots, \nu^{\rm b}_{nj})^t$, and the global reaction vector by $\nu_j = \nu^{\rm b}_j - \nu^{\rm f}_j$. The atomic vectors $\mathfrak{a}_l$, $l \in \mathfrak{A}$, are similarly given by $\mathfrak{a}_l = (\mathfrak{a}_{1l}, \dots, \mathfrak{a}_{nl})^t$, the unit vector by $\mathbb{1} = (1, \dots, 1)^t$, 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 $\mathsf{x}, \mathsf{y} \in \mathbb{R}^n$ is denoted by $\langle \mathsf{x}, \mathsf{y}\rangle$ 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 $\omega = (\omega_1, \dots, \omega_n)^t$ so that we have the vector relation $\omega = \sum_{j\in\mathfrak{R}} \tau_j\nu_j$ with $\tau_j = \kappa^{\rm s}_j\big(\exp\langle\mu, \nu^{\rm f}_j\rangle - \exp\langle\mu, \nu^{\rm b}_j\rangle\big)$, $j \in \mathfrak{R}$. The vector spaces spanned by the reaction vectors and the atomic vectors are denoted by $\mathcal{R}$ and $\mathcal{A}$, respectively

$$\mathcal{R} = \operatorname{span}\{\, \nu_i,\ i \in \mathfrak{R}\,\}, \qquad \mathcal{A} = \operatorname{span}\{\, \mathfrak{a}_l,\ l \in \mathfrak{A}\,\},$$

and we denote by M the diagonal matrix $\mathsf{M} = \operatorname{diag}(m_1, \dots, m_n)$. The mathematical assumptions associated with the chemical production rates are the following.

(C$_1$) *The stoichiometric coefficients $\nu^{\rm f}_{kj}$ and $\nu^{\rm b}_{kj}$, $k \in \mathfrak{S}$, $j \in \mathfrak{R}$, and the atomic coefficients $\mathfrak{a}_{kl}$, $k \in \mathfrak{S}$, $l \in \mathfrak{A}$, are nonnegative integers. The atomic vectors $\mathfrak{a}_l$, $l \in \mathfrak{A}$, and the reaction vectors ν_j, $j \in \mathfrak{R}$, satisfy the atom conservation relations*

$$\langle \nu^{\rm b}_j, \mathfrak{a}_l\rangle - \langle \nu^{\rm f}_j, \mathfrak{a}_l\rangle = \langle \nu_j, \mathfrak{a}_l\rangle = 0, \qquad j \in \mathfrak{R}, \quad l \in \mathfrak{A}.$$

(C$_2$) *The atom masses $\widetilde{m}_l$, $l \in \mathfrak{A}$, are positive constants, and the species molar masses m_k, $k \in \mathfrak{S}$, are given by*

$$m_k = \sum_{l\in\mathfrak{A}} \widetilde{m}_l\, \mathfrak{a}_{kl}, \qquad k \in \mathfrak{S}.$$

(C$_3$) *The symmetric rate constants $\kappa^{\rm s}_j$, $j \in \mathfrak{R}$, are C^∞ positive functions of $T > 0$.*

The reaction and atomic vector spaces are thus such that $\mathcal{R} \subset \mathcal{A}^\perp$ and $\mathcal{A} \subset \mathcal{R}^\perp$ from (C_1). For realistic complex chemistry networks, the number of chemical reactions is always much larger than the number of chemical species and one usually has $\mathcal{R} = \mathcal{A}^\perp$. In other words, in practical situations, the chemical reactions vectors ν_j, $j \in \mathfrak{R}$, are spanning the largest possible space. When this is not the case, one has simply to use the space $\mathcal{R}^\perp$ instead of $\mathcal{A}$ [55].

Remark 2.4. *The atoms vectors $\mathfrak{a}_l$, $l \in \mathfrak{A}$, may be assumed to be linearly independent. When this is not the case, it is first necessary to eliminate linearly dependent atomic vectors.*

Assuming that Properties $(\mathcal{T}_1)$-$(\mathcal{T}_4)$, (PG), and (C_1)-(C_3) hold, the resulting chemical production rates, which involve the chemical potentials μ_i, $i \in \mathfrak{S}$, are thus defined over the open set $\mathcal{O}_{\boldsymbol{z}}$. From atom conservation and the definition of species masses, we now deduce the mass conservation property.

Lemma 2.5. *The vector of chemical production rates ω is such that $\omega \in \mathcal{R}$ and $\mathsf{M}\,\omega \in \mathsf{M}\,\mathcal{R}$. Moreover, the unity vector satisfies $\mathbb{I} \in (\mathsf{M}\,\mathcal{R})^\perp$ so that we have the total mass conservation relation $\langle \mathbb{I}, \mathsf{M}\,\omega \rangle = \sum_{k\in\mathfrak{S}} m_k \omega_k = 0$.*

Proof. We deduce from (C_1)-(C_3) that $\mathbb{I} = \sum_{l\in\mathfrak{A}} \widetilde{m}_l \mathsf{M}^{-1} \mathfrak{a}_l$ so that $\mathbb{I} \in (\mathsf{M}\,\mathcal{R})^\perp$. Moreover, $\omega \in \mathcal{R}$ since $\omega = \sum_{j\in\mathfrak{R}} \tau_j \nu_j$ and thus $\mathsf{M}\,\omega \in \mathsf{M}\,\mathcal{R}$ and finally $\langle \mathsf{M}\,\omega, \mathbb{I} \rangle = 0$. ☐

2.4 Transport fluxes

2.4.1 General structure

A remarkable aspect of transport fluxes in nonideal gases is that they are directly expressed in terms of temperature gradients and chemical potential gradients. In the absence of forces acting on the species, the species mass and heat fluxes are in the form

$$
\begin{aligned}
\boldsymbol{\mathcal{F}}_i &= -\sum_{j\in\mathfrak{S}} L_{ij} \boldsymbol{\nabla}\Big(\frac{\mathcal{G}_j}{T}\Big) - L_{ie} \boldsymbol{\nabla}\Big(-\frac{1}{T}\Big), \qquad i \in \mathfrak{S}, && (2.11)\\
\boldsymbol{Q} &= -\sum_{j\in\mathfrak{S}} L_{ej} \boldsymbol{\nabla}\Big(\frac{\mathcal{G}_j}{T}\Big) - L_{ee} \boldsymbol{\nabla}\Big(-\frac{1}{T}\Big), && (2.12)
\end{aligned}
$$

where L_{ij}, $i,j \in \mathfrak{S}\cup\{e\}$, are the mass and heat transport coefficients which depend on the local state $\boldsymbol{z}$ of the fluid, $\mathcal{G}_j$ the Gibbs function of the jth species per unit mass and T the absolute temperature.

On the other hand, the viscous tensor is in the form

$$
\boldsymbol{\Pi} = -\kappa(\boldsymbol{\nabla}\cdot\boldsymbol{v})\mathbb{I}_d - \eta\big(\boldsymbol{\nabla}\boldsymbol{v} + (\boldsymbol{\nabla}\boldsymbol{v})^t - \tfrac{2}{d}(\boldsymbol{\nabla}\cdot\boldsymbol{v})\mathbb{I}_d\big), \tag{2.13}
$$

where κ denotes the effective volume viscosity, η the shear viscosity, and $\mathbb{I}_d$ the identity matrix in d dimensions. Actually, the full viscous tensor $\boldsymbol{\Pi}'$ is a matrix of dimension $d' = 3$ in the form $\boldsymbol{\Pi}' = -\kappa'\,\boldsymbol{\nabla}\cdot\boldsymbol{v}\,\mathbb{I}_3 - \eta\big(\boldsymbol{\nabla}\boldsymbol{v} + (\boldsymbol{\nabla}\boldsymbol{v})^t - \frac{2}{3}\boldsymbol{\nabla}\cdot v\,\mathbb{I}_3\big)$ involving the physical volume viscosity κ' and a coefficient $2/3$ instead of the coefficient $2/d$ in (2.13) since $d' = 3$ is the dimension of the velocity phase space of the corresponding kinetic model. However, we may assume that the spatial dimension of the model d has been reduced, that is, the equations are considered in $\mathbb{R}^d$ with $d \leq d' = 3$, independently from the kinetic velocity fluctuations which are always three dimensional. If we denote by $\boldsymbol{\Pi}$ the upper left block of size d of $\boldsymbol{\Pi}'$, that is, the useful part of $\boldsymbol{\Pi}'$, we may rewrite $\boldsymbol{\Pi}$ in the form [35]

$$
\boldsymbol{\Pi} = -\big(\kappa' + (\tfrac{2}{d} - \tfrac{2}{3})\eta\big)\,\boldsymbol{\nabla}\cdot\boldsymbol{v}\,\mathbb{I}_d - \eta\big(\boldsymbol{\nabla}\boldsymbol{v} + (\boldsymbol{\nabla}\boldsymbol{v})^t - \tfrac{2}{d}\boldsymbol{\nabla}\cdot v\,\mathbb{I}_d\big). \tag{2.14}
$$

Therefore, using a coeefficient $2/d$ instead of $2/3$ in the coefficient of the viscous tensor in (2.13) is equivalent to increasing the physical volume viscosity κ' by the amount $2\eta\,(d'-d)/d'd = 2\eta\,(3-d)/3d$. We have directly written the viscous tensor in the form (2.13) for convenience with the effective volume viscosity $\kappa = \kappa' + 2\eta\,(3-d)/3d$. We will assume in particular in the following that κ is positive when $d = 1$ keeping in mind that $\boldsymbol{\nabla}\boldsymbol{v} + (\boldsymbol{\nabla}\boldsymbol{v})^t - \frac{2}{d}\boldsymbol{\nabla}\cdot v\,\mathbb{I}_d$ then vanishes. Note incidentally that the volume viscosity of polyatomic gases is positive and its impact on fast flows has been established in [8].

The mathematical properties of the transport coefficients are the following.

(Tr_1) *The matrix L and the coefficients η and κ are $C^\varkappa$ functions of $\boldsymbol{z} \in \mathcal{O}_{\boldsymbol{z}}$.*

(Tr$_2$) *The matrix L defined by*

$$L = \begin{pmatrix} L_{11} & \cdots & L_{1n} & L_{1e} \\ \vdots & \ddots & \vdots & \vdots \\ L_{n1} & \cdots & L_{nn} & L_{ne} \\ L_{e1} & \cdots & L_{en} & L_{ee} \end{pmatrix}, \tag{2.15}$$

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

From an historical point of view, to the authors' knowledge, the expressions (2.11)(2.12) associated with nonideal gas mixtures—taking into account the symmetry of the transport matrix—have first been written in the framework of thermodynamics of irreversible processes by Meixner [61, 62] and later by Prigogine [67, 20]. Similar expressions had been written previously by Eckart [21] but only for ideal gas mixtures and without symmetry properties of the transport coefficients. The expressions (2.11)(2.12) have then been rederived in various frameworks, in particular by Bearman and Kirkwood [3] (only partially) and Mori [63] with statistical mechanics, by Keizer [54] in the framework of nonequilibrium statistical thermodynamics, and by Van Beijeren and Ernst [6] and Kurochkin et al. [56] in the framework of the kinetic theory of dense gases, thanks to a modified form of Enskog equation [5].

2.4.2 Heat and mass diffusion coefficients

The heat and mass diffusion fluxes $\boldsymbol{\mathcal{F}}_i$, $i \in \mathfrak{S}$, and $\boldsymbol{Q}$ may be rewritten in a more classical form than (2.11)(2.12) by defining high pressure multicomponent transport coefficients. To this aim, we first introduce the modified matrix $\widehat{L} = A^t L A$ where

$$\widehat{L} = \begin{pmatrix} \widehat{L}_{11} & \cdots & \widehat{L}_{1n} & \widehat{L}_{1e} \\ \vdots & \ddots & \vdots & \vdots \\ \widehat{L}_{n1} & \cdots & \widehat{L}_{nn} & \widehat{L}_{ne} \\ \widehat{L}_{e1} & \cdots & \widehat{L}_{en} & \widehat{L}_{ee} \end{pmatrix}, \qquad A = \begin{pmatrix} & & & -h_1 \\ & \mathbb{I}_n & & \vdots \\ & & & -h_n \\ 0 & \cdots & 0 & 1 \end{pmatrix}, \tag{2.16}$$

and $\mathbb{I}_n$ denotes the identity matrix in $\mathbb{R}^n$. The high pressure multicomponent diffusion coefficients D_{ij}, $i,j \in \mathfrak{S}$, thermal diffusion coefficients θ_i, $i \in \mathfrak{S}$, and partial thermal conductivity $\widehat{\lambda}$ are then defined by [56]

$$D_{ij}, = \frac{R\widehat{L}_{ij}}{\rho y_i y_j m}, \quad i,j \in \mathfrak{S}, \qquad \theta_i = \frac{\widehat{L}_{ie}}{\rho y_i T} = \frac{\widehat{L}_{ei}}{\rho y_i T}, \quad i \in \mathfrak{S}, \qquad \widehat{\lambda} = \frac{\widehat{L}_{ee}}{T^2}. \tag{2.17}$$

We may also introduce the gradient at constant temperature $(\boldsymbol{\nabla}\mu_j)_T$ of the reduced chemical potential $\mu_j = m_j \mathcal{G}_j / RT$ and the generalized diffusion driving force $\boldsymbol{d}_j = x_j (\boldsymbol{\nabla}\mu_j)_T$, so that

$$x_j \boldsymbol{\nabla}\mu_j = \boldsymbol{d}_j - \frac{x_j m_j h_j}{RT^2}\boldsymbol{\nabla}T, \qquad j \in \mathfrak{S}.$$

In these relations $x_j = m y_j / m_j$ is the mole fraction of the jth species and m the molar mass of the mixture $m = (\sum_{i\in\mathfrak{S}} y_i)/(\sum_{i\in\mathfrak{S}} y_i/m_i)$. Using the high pressure coefficients and the diffusion driving forces, the fluxes $\boldsymbol{\mathcal{F}}_i$, $i \in \mathfrak{S}$, and $\boldsymbol{Q}$ may be rewritten in the familiar form

$$\boldsymbol{\mathcal{F}}_i = -\sum_{j\in\mathfrak{S}} \rho y_i D_{ij} \boldsymbol{d}_j - \rho y_i \theta_i \boldsymbol{\nabla} \ln T, \qquad i \in \mathfrak{S}, \tag{2.18}$$

$$\boldsymbol{Q} = -\frac{\rho R T}{m} \sum_{j\in\mathfrak{S}} \theta_j \boldsymbol{d}_j - \widehat{\lambda}\boldsymbol{\nabla}T + \sum_{i\in\mathfrak{S}} h_i \boldsymbol{\mathcal{F}}_i. \tag{2.19}$$

The high pressure symmetric multicomponent diffusion coefficients D_{ij}, $i,j \in \mathfrak{S}$, introduced by Kurochkin [56], generalize the symmetric coefficients introduced for dilute gases by Waldmann [83, 80, 13]. On the contrary, Hirschfelder, Curtiss, and Bird have artificially destroyed the natural symmetries of transport models as discussed by Van de Ree [80].

The multicomponent diffusion matrix $D = (D_{ij})_{i,j\in\mathfrak{S}}$, the vector $\theta = (\theta_1,\dots,\theta_n)^t$ of thermal diffusion coefficients and the partial thermal conductivity $\widehat{\lambda}$ satisfy the following properties where we denote by $y = (y_1,\dots,y_n)^t$ the mass fraction vector.

Proposition 2.6. *Assume that Properties* $(\mathcal{T}_1)$-$(\mathcal{T}_4)$ *and* (PG) *hold and assume that* $L \in \mathbb{R}^{n+1,n+1}$ *is symmetric positive semi-definite with* $N(L) = \mathbb{R}\,(\mathbb{1},0)^t$. *Let* $\widehat{L} = A^t L A$ *where* A *is given by* (2.16) *and define the high pressure coefficients with* (2.17). *Then the matrix* D *is symmetric positive semi-definite with nullspace* $N(D) = \mathbb{R}y$, $\theta \in y^{\perp}$, *and* $\widehat{\lambda} > 0$.

Proof. Since $\widehat{L} = A^t L A$ and A is invertible we obtain that $\widehat{L}$ is symmetric positive semi-definite and that $N(\widehat{L}) = A^{-1}N(L)$. Since $(\mathbb{1},0)^t = A(\mathbb{1},0)^t$ we deduce that $N(\widehat{L}) = \mathbb{R}\,(\mathbb{1},0)^t$.

It is next easily established from (2.17) that

$$\widehat{L} = \frac{\rho m}{R}\begin{pmatrix} y_1^2 D_{11} & \cdots & y_1 y_n D_{1n} & \frac{RTy_1}{m}\theta_1 \\ \vdots & \ddots & \vdots & \vdots \\ y_n y_1 D_{n1} & \cdots & y_n^2 D_{nn} & \frac{RTy_n}{m}\theta_n \\ \frac{RTy_1}{m}\theta_1 & \cdots & \frac{RTy_n}{m}\theta_n & \frac{RT^2}{\rho m}\widehat{\lambda} \end{pmatrix}, \tag{2.20}$$

and since $\widehat{L}(\mathbb{1},0)^t = 0$ we obtain that $Dy = 0$ and $\langle \theta, y\rangle = 0$. From the symmetry of $\widehat{L}$ we also deduce that D is symmetric. In addition, for any $\mathsf{x}_\varrho = (\mathsf{x}_1,\dots,\mathsf{x}_n)^t \in \mathbb{R}^n$, letting $\mathcal{Y} = \operatorname{diag}(y_1,\dots,y_n)$ and $\widehat{\mathsf{x}} = (\mathcal{Y}^{-1}\mathsf{x}_\varrho, 0)^t$, we have $(\rho m/R)\langle \widehat{L}\widehat{\mathsf{x}}, \widehat{\mathsf{x}}\rangle = \langle D\mathsf{x}_\varrho, \mathsf{x}_\varrho\rangle$ so that D is positive semi-definite and $N(D) = \mathbb{R}y$ since $\mathcal{Y}^{-1}y = \mathbb{1}$. Finally, $\mathsf{f}^{n+1} = (0,\dots,0,1)^t$ is not in $N(\widehat{L})$ so that $\langle \widehat{L}\mathsf{f}^{n+1}, \mathsf{f}^{n+1}\rangle > 0$ and $\widehat{\lambda} > 0$. ☐

Various mathematical properties of the transport coefficients D, $\widehat{\lambda}$ and θ are discussed in [33, 26, 38, 34]. Evaluating the transport coefficients generally requires to solve transport linear systems derived from the kinetic theory of gases [22, 56, 78]. These coefficients may also conveniently be evaluated from convergent series arising from iterative solution of the transport linear systems [22, 23, 24, 25, 26, 36, 43].

2.4.3 Alternative formulation

An alternative form—similar to that of dilute gas mixtures—is also possible by introducing the high pressure thermal diffusion ratios χ_i, $i \in \mathfrak{S}$, and thermal conductivity λ [62, 56, 13]. The corresponding expressions of the mass and heat diffusion fluxes in terms of χ and λ are more practical from a mathematical point of view as well as a computational point of view than the corresponding expressions in terms of θ and $\widehat{\lambda}$ [23].

Definition 2.7. *Keep the assumptions of Proposition 2.6. There exists a unique vector of thermal diffusion ratios* χ *such that* $\theta = D\chi$ *and* $\langle \chi, \mathbb{1}\rangle = 0$. *The thermal conductivity is then defined by* $\lambda = \widehat{\lambda} - \frac{\rho R}{m}\langle D\chi, \chi\rangle$.

Proof. From Proposition 2.6 we know that D is symmetric positive semi-definite, $N(D) = \mathbb{R}y$, and that $\langle \theta, y\rangle = 0$. Since D is symmetric, we also obtain that $R(D) = y^{\perp}$ so that $\theta \in R(D)$ and there exists $\mathsf{x} \in \mathbb{R}^n$ such that $D\mathsf{x} = \theta$. We may next consider $\mathsf{x} + ty$ and there exists a unique t such that $\langle \mathsf{x} + ty, \mathbb{1}\rangle = 0$ since $\langle y, \mathbb{1}\rangle = 1$ and letting $\chi = \mathsf{x} + ty$ we have $D\chi = \theta$ and $\langle \chi, \mathbb{1}\rangle = 0$. Finally, if there are two such thermal diffusion vectors χ and χ', they satisfy $D(\chi - \chi') = 0$ and $\langle \mathbb{1}, \chi - \chi'\rangle = 0$ so that $\chi - \chi' \in N(D) \cap \mathbb{1}^{\perp} = \{0\}$ and $\chi' = \chi$. ☐

The transport fluxes may then be rewritten

$$\boldsymbol{\mathcal{F}}_i = -\sum_{j\in\mathfrak{S}} \rho y_i D_{ij}\big(\boldsymbol{d}_j + \chi_j \boldsymbol{\nabla}\ln T\big), \qquad i \in \mathfrak{S}, \tag{2.21}$$

$$\boldsymbol{Q} = \sum_{j\in\mathfrak{S}} \frac{RT}{m}\frac{\chi_j}{y_j}\boldsymbol{\mathcal{F}}_j - \lambda\boldsymbol{\nabla}T + \sum_{i\in\mathfrak{S}} h_i \boldsymbol{\mathcal{F}}_i. \tag{2.22}$$

It is then convenient to express the matrix $\widehat{L}$ directly in terms of the matrix D, the thermal diffusion ratios χ and the thermal conductivity λ.

Corollary 2.8. *Assume that the equivalent properties of Proposition 2.6 hold and define*

$$\widehat{\mathcal{L}} = \begin{pmatrix} \mathcal{Y} & \frac{RT}{m}\chi \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} \mathbb{I}_n & \frac{RT}{m}\chi \\ 0 & 1 \end{pmatrix}\begin{pmatrix} \mathcal{Y} & 0 \\ 0 & 1 \end{pmatrix}. \tag{2.23}$$

Then $\widehat{L}$ is given by

$$\widehat{L} = \frac{\rho m}{R}\widehat{\mathcal{L}}^t \begin{pmatrix} D & 0 \\ 0 & \frac{RT^2}{\rho m}\lambda \end{pmatrix} \widehat{\mathcal{L}}. \tag{2.24}$$

Proof. This results from direct calculations using (2.17), $\theta = D\chi$, and $\lambda = \widehat{\lambda} - \frac{\rho R}{m}\langle D\chi, \chi\rangle$. ☐

Remark 2.9. *It is also convenient to introduce the rescaled thermal diffusion ratio of the jth species $\widetilde{\chi}_j$ with $\widetilde{\chi}_j = \chi_j / x_j$. These coefficients remain smooth and bounded for zero mole fractions [22, 34].*

The mathematical properties of the multicomponent transport matrices L and $\widehat{L}$ are then directly related to those of the diffusion matrix D and the thermal conductivity λ.

Proposition 2.10. *Assume that Properties $(\mathcal{T}_1)$-$(\mathcal{T}_4)$ and (PG) hold. Let $L, \widehat{L} \in \mathbb{R}^{n+1,n+1}$ such that $\widehat{L} = A^t L A$ and let $D \in \mathbb{R}^{n,n}$, $\chi \in \mathbb{R}^n$, and $\lambda \in \mathbb{R}$ such that (2.24) holds. Then the following properties are equivalent*

(i) The matrix L is positive semi-definite with nullspace $N(L) = \mathbb{R}\,(\mathbb{I}, 0)^t$.

(ii) The matrix $\widehat{L}$ is positive semi-definite with nullspace $N(\widehat{L}) = \mathbb{R}\,(\mathbb{I}, 0)^t$.

(iii) The matrix D is symmetric positive semi-definite with nullspace $N(D) = \mathbb{R}y$ and $\lambda > 0$.

Proof. Since $\widehat{L} = A^t L A$ and A is invertible we first obtain that $\widehat{L}$ is symmetric positive semi-definite if and only if L is symmetric positive semi-definite and that $N(\widehat{L}) = A^{-1}N(L)$ and (i) and (ii) are equivalent since $(\mathbb{I}, 0)^t = A(\mathbb{I}, 0)^t$.

Assuming that these properties hold, we may use Proposition 2.7 and write $\widehat{L}$ in the form (2.24). Introducing $\mathsf{x}' = \big(\frac{RT}{m}\mathcal{Y}^{-1}\chi, -1\big)^t$ then $\mathsf{x}' \notin N(\widehat{L}) = \mathbb{R}(\mathbb{I}, 0)^t$ since its last component is nonzero so that $\langle \widehat{L}\mathsf{x}', \mathsf{x}'\rangle = \lambda T^2 > 0$ and $\lambda > 0$. We have thus established that (ii) implies (iii) since $D = D^t$ and $N(D) = \mathbb{R}y$ from Proposition 2.6.

Conversely, assume that (iii) holds. It is then readily obtained from (2.24) that $\widehat{L}$ is symmetric, and after some algebra, we obtain that for any $\mathsf{x} = (\mathsf{x}_1, \dots, \mathsf{x}_n, \mathsf{x}_\mathcal{E})^t \in \mathbb{R}^{n+1}$, letting $\mathsf{x}_\varrho = (\mathsf{x}_1, \dots, \mathsf{x}_n)^t$

$$\langle \widehat{L}\mathsf{x}, \mathsf{x}\rangle = \frac{\rho m}{R}\big\langle D(\mathcal{Y}\mathsf{x}_\varrho + \tfrac{RT}{m}\chi\mathsf{x}_\mathcal{E}), (\mathcal{Y}\mathsf{x}_\varrho + \tfrac{RT}{m}\chi\mathsf{x}_\mathcal{E})\big\rangle + \lambda T^2 \mathsf{x}_\mathcal{E}^2.$$

This in turn implies that $N(\widehat{L}) = \mathbb{R}\,(\mathbb{I}, 0)^t$ since $N(D) = \mathbb{R}\,y$, $\mathcal{Y}\mathbb{I} = y$ and $\lambda > 0$ and we have established that (iii) implies (ii). ☐

2.5 Entropy production

In this section, we investigate the entropy governing equation as well as the sign of entropy production. The entropy production term $\mathfrak{v}$ is decomposed into $\mathfrak{v} = \mathfrak{v}_\nabla + \mathfrak{v}_\omega$, where $\mathfrak{v}_\nabla$ denotes the variables' gradients contribution and $\mathfrak{v}_\omega$ the chemical reactions contribution.

Lemma 2.11. *The entropy governing equations may be written in the form*

$$\partial_t \mathcal{S} + \boldsymbol{\nabla}\cdot(\mathcal{S}\boldsymbol{v}) + \boldsymbol{\nabla}\cdot\Big(-\sum_{i\in\mathfrak{S}} \frac{\mathcal{G}_i}{T}\boldsymbol{\mathcal{F}}_i + \frac{\boldsymbol{Q}}{T}\Big) = \mathfrak{v}_\nabla + \mathfrak{v}_\omega, \tag{2.25}$$

where the entropy production due to macroscopic gradients $\mathfrak{v}_\nabla$ is in the form

$$\mathfrak{v}_\nabla = -\sum_{i\in\mathfrak{S}} \boldsymbol{\nabla}\Big(\frac{\mathcal{G}_i}{T}\Big)\cdot\boldsymbol{\mathcal{F}}_i + \boldsymbol{\nabla}\Big(\frac{1}{T}\Big)\cdot\boldsymbol{Q} - \frac{\boldsymbol{\Pi}:\boldsymbol{\nabla}\boldsymbol{v}}{T},$$

and the entropy production due to chemistry $\mathfrak{v}_\omega$ reads

$$\mathfrak{v}_\omega = -\frac{1}{T}\sum_{k\in\mathfrak{S}} \mathcal{G}_k m_k \omega_k = -R\langle \mu, \omega\rangle.$$

Proof. It is easily deduced from Gibbs relation $T\mathrm{d}\mathcal{S} = -\sum_{i\in\mathfrak{S}} \mathcal{G}_i \mathrm{d}\rho_i + \mathrm{d}\mathcal{E}$ that

$$T\big(\partial_t \mathcal{S} + \boldsymbol{v}\cdot\boldsymbol{\nabla}\mathcal{S}\big) = -\sum_{i\in\mathfrak{S}} \mathcal{G}_i\big(\partial_t\rho_i + \boldsymbol{v}\cdot\boldsymbol{\nabla}\rho_i\big) + \big(\partial_t\mathcal{E} + \boldsymbol{v}\cdot\boldsymbol{\nabla}\mathcal{E}\big). \tag{2.26}$$

On the other hand, upon multiplying the momentum conservation equation (2.2) by the velocity vector $\boldsymbol{v}$ we also obtain a governing equation for the kinetic energy $\frac{1}{2}\rho\boldsymbol{v}\cdot\boldsymbol{v}$ which can then be subtracted from the total energy conservation equation (2.3) to form the following governing equation for the internal energy $\mathcal{E}$

$$\partial_t\mathcal{E} + \boldsymbol{v}\cdot\boldsymbol{\nabla}\mathcal{E} = -\mathcal{E}\boldsymbol{\nabla}\cdot\boldsymbol{v} - \mathcal{P}\boldsymbol{\nabla}\cdot\boldsymbol{v} - \boldsymbol{\Pi}:\boldsymbol{\nabla}\boldsymbol{v} - \boldsymbol{\nabla}\cdot\boldsymbol{Q}. \tag{2.27}$$

Thanks to the internal energy governing equation (2.27) and the species (2.1) governing equations we obtain with (2.26) that

$$T\big(\partial_t\mathcal{S} + \boldsymbol{v}\cdot\boldsymbol{\nabla}\mathcal{S}\big) = -\sum_{i\in\mathfrak{S}} \mathcal{G}_i\big(-\rho_i\boldsymbol{\nabla}\cdot\boldsymbol{v} - \boldsymbol{\nabla}\cdot\boldsymbol{\mathcal{F}}_i + m_i\omega_i\big) - \mathcal{E}\boldsymbol{\nabla}\cdot\boldsymbol{v} - \mathcal{P}\boldsymbol{\nabla}\cdot\boldsymbol{v} - \boldsymbol{\Pi}:\boldsymbol{\nabla}\boldsymbol{v} - \boldsymbol{\nabla}\cdot\boldsymbol{Q}.$$

Regrouping all terms proportional to $\boldsymbol{\nabla}\cdot\boldsymbol{v}$ in the form $\big(\sum_{k\in\mathfrak{S}}\rho_k\mathcal{G}_k - \mathcal{E} - \mathcal{P}\big)\boldsymbol{\nabla}\cdot\boldsymbol{v} = -T\mathcal{S}\boldsymbol{\nabla}\cdot\boldsymbol{v}$ this equation is then rewritten

$$T\big(\partial_t\mathcal{S} + \boldsymbol{\nabla}\cdot(\mathcal{S}\boldsymbol{v})\big) = \sum_{i\in\mathfrak{S}} \mathcal{G}_i\boldsymbol{\nabla}\cdot\boldsymbol{\mathcal{F}}_i - \sum_{i\in\mathfrak{S}} \mathcal{G}_i m_i\omega_i - \boldsymbol{\Pi}:\boldsymbol{\nabla}\boldsymbol{v} - \boldsymbol{\nabla}\cdot\boldsymbol{Q}.$$

Using the identities

$$\frac{\mathcal{G}_i}{T}\boldsymbol{\nabla}\cdot\boldsymbol{\mathcal{F}}_i = \boldsymbol{\nabla}\cdot\Big(\frac{\mathcal{G}_i}{T}\boldsymbol{\mathcal{F}}_i\Big) - \boldsymbol{\mathcal{F}}_i\boldsymbol{\nabla}\cdot\Big(\frac{\mathcal{G}_i}{T}\Big), \qquad -\frac{1}{T}\boldsymbol{\nabla}\cdot\boldsymbol{Q} = -\boldsymbol{\nabla}\cdot\Big(\frac{\boldsymbol{Q}}{T}\Big) + \boldsymbol{Q}\boldsymbol{\nabla}\cdot\Big(\frac{1}{T}\Big),$$

we finally directly obtain the entropy conservation equation (2.25). □

We denote by $\mathcal{v}$ the variable

$$\mathcal{v} = \Big(\frac{\mathcal{G}_1}{T}, \dots, \frac{\mathcal{G}_n}{T}, -\frac{1}{T}\Big)^t, \tag{2.28}$$

which essentially represents the thermodynamic part of the entropic symmetrizing variables v investigated in Section 4.2.

Proposition 2.12. *The entropy production $\mathfrak{v}_{\triangledown}$ associated with the variables' gradients may be written*

$$\mathfrak{v}_{\triangledown} = \sum_{i,j\in\mathfrak{S}\cup\{e\}} L_{ij}\boldsymbol{\nabla}\mathcal{v}_i\cdot\boldsymbol{\nabla}\mathcal{v}_j + \frac{\kappa}{T}(\boldsymbol{\nabla}\cdot\boldsymbol{v})^2 + \frac{\eta}{2T}\big|\boldsymbol{\nabla}\boldsymbol{v} + \boldsymbol{\nabla}\boldsymbol{v}^t - \tfrac{2}{d}\boldsymbol{\nabla}\cdot\boldsymbol{v}\mathbb{I}_d\big|^2, \tag{2.29}$$

where, for any tensor $\mathsf{X} \in \mathbb{R}^{d,d}$, $|\mathsf{X}|^2$ denotes $|\mathsf{X}|^2 = \mathsf{X}:\mathsf{X} = \sum_{1\le i,j\le d}\mathsf{X}_{ij}^2$, and this entropy production $\mathfrak{v}_{\triangledown}$ is nonnegative.

Proof. The entropy production term associated with diffusion and heat conduction is directly rewritten with the help of the matrix L. Similarly, after some tensor manipulations, the term $-\boldsymbol{\Pi}:\boldsymbol{\nabla}\boldsymbol{v}$ is easily rewritten as $\kappa(\boldsymbol{\nabla}\cdot\boldsymbol{v})^2 + \frac{1}{2}\eta|\boldsymbol{\nabla}\boldsymbol{v} + \boldsymbol{\nabla}\boldsymbol{v}^t - \frac{2}{d}\boldsymbol{\nabla}\cdot\boldsymbol{v}\mathbb{I}_d|^2$. Since the matrix L is positive semi-definite, we conclude that entropy production associated with macroscopic gradients $\mathfrak{v}_{\triangledown}$ is nonnegative. □

In the following proposition—easily established—we discuss the situation where the entropy production associated with heat and mass transfer vanish.

Proposition 2.13. *Assume that* ($\mathcal{T}_1$)-($\mathcal{T}_4$), (PG), *and* (Tr_1)-(Tr_2) *hold and that $\kappa > 0$. Denote by $\widetilde{\boldsymbol{d}}_i$, $i \in \mathfrak{S}$, the linearly dependent diffusion driving forces $\widetilde{\boldsymbol{d}}_i = \boldsymbol{d}_i - y_i\sum_{j\in\mathfrak{S}}\boldsymbol{d}_j/\sum_{k\in\mathfrak{S}}y_k$, Then the following properties are equivalent.*

- *(i) The entropy production $\mathfrak{v}_{\triangledown}$ is zero.*
- *(ii) There exists $\mathbf{a} \in \mathbb{R}^d$ such that $\boldsymbol{d}_i = y_i\mathbf{a}$, $i \in \mathfrak{S}$, and $\boldsymbol{\nabla}\boldsymbol{v}$ is skew-symmetric.*
- *(iii) We have $\widetilde{\boldsymbol{d}}_i = 0$, $i \in \mathfrak{S}$, and $\boldsymbol{\nabla}\boldsymbol{v}$ is skew-symmetric.*

The most important property associated with the nonideal chemical production rates is that entropy production is guaranteed to be nonnegative as established in the following proposition. This property may be used in particular to establish the existence of chemical equilibrium points [40].

Proposition 2.14. *Assume that Properties* $(\mathcal{T}_1)$-$(\mathcal{T}_4)$, (PG), *and* (C_1)-(C_3) *hold and let* $z \in \mathcal{O}_z$. *The entropy production due to chemical reactions* $\mathfrak{v}_\omega$ *is nonnegative and can be written in the form*

$$\mathfrak{v}_\omega = -R\langle \mu, \omega \rangle = \sum_{j \in \mathfrak{R}} R\kappa_j^{\mathrm{s}} \big(\langle \mu, \nu_j^{\mathrm{f}} \rangle - \langle \mu, \nu_j^{\mathrm{b}} \rangle \big) \big(\exp\langle \mu, \nu_j^{\mathrm{f}} \rangle - \exp\langle \mu, \nu_j^{\mathrm{b}} \rangle \big). \tag{2.30}$$

Proof. Rewriting $\mathfrak{v}_\omega$ in the form $\mathfrak{v}_\omega = -\sum_{j\in\mathfrak{R}, i \in \mathfrak{S}} R\mu_i \nu_{ij} \tau_j = \sum_{j \in \mathfrak{R}} R\big\langle \mu, \nu_j^{\mathrm{f}} - \nu_j^{\mathrm{b}} \big\rangle \tau_j$ we directly obtain (2.30) from the expression (2.10) of the nonideal rates τ_j, $j \in \mathfrak{R}$ due to Marcelin [59, 60]. Finally the right hand side of (2.30) is always nonnegative thanks to (C_3) since the exponential map is increasing. ☐

2.6 Thermodynamic stability

Thermodynamic stability generally may not hold at high pressure and low temperature for nonideal fluids. In the following proposition, we characterize thermodynamic stability in terms of the derivatives of the species Gibbs functions $\mathcal{G}_i$, $i \in \mathfrak{S}$.

Proposition 2.15. *Assume that* $(\mathcal{T}_1)$-$(\mathcal{T}_2)$ *are satisfied and denote by* $\mathit{\Gamma}$ *the matrix of size n with coefficients* $\mathit{\Gamma}_{kl} = \rho \widetilde{\partial}_{\rho_k} \mathcal{G}_l / T = \rho \widetilde{\partial}_{\rho_l} \mathcal{G}_k / T$. *Then, for any* $z \in \mathcal{O}_z$, *the following statements are equivalent :*

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

(ii) $\widetilde{\partial}_T \mathcal{E} > 0$ *and* $\mathit{\Gamma}$ *is positive definite.*

Proof. From Gibbs' relation (2.4) we obtain that

$$\partial_{\mathcal{E}} \mathcal{S} = \frac{1}{T}, \qquad \partial_{\rho_k} \mathcal{S} = -\frac{\mathcal{G}_k}{T},$$

and this implies the compatibility relations

$$\partial_{\mathcal{E}} \big(\frac{-\mathcal{G}_k}{T} \big) = \partial_{\rho_k} \big(\frac{1}{T} \big). \tag{2.31}$$

Moreover, for any function f we have the differential relations

$$\partial_{\mathcal{E}} \mathsf{f} = \widetilde{\partial}_T \mathsf{f} \, \partial_{\mathcal{E}} T, \qquad \widetilde{\partial}_T \mathsf{f} = \partial_{\mathcal{E}} \mathsf{f} \, \widetilde{\partial}_T \mathcal{E}, \tag{2.32}$$

$$\partial_{\rho_k} \mathsf{f} = \widetilde{\partial}_{\rho_k} \mathsf{f} + \widetilde{\partial}_T \mathsf{f} \, \partial_{\rho_k} T, \qquad \widetilde{\partial}_{\rho_k} \mathsf{f} = \partial_{\rho_k} \mathsf{f} + \partial_{\mathcal{E}} \mathsf{f} \, \widetilde{\partial}_{\rho_k} \mathcal{E}. \tag{2.33}$$

We can now evaluate the volumetric entropy Hessian matrix. We first note that $\partial^2_{\mathcal{E}\mathcal{E}} \mathcal{S} = \partial_{\mathcal{E}}(\frac{1}{T})$ so that $\partial^2_{\mathcal{E}\mathcal{E}} \mathcal{S} = -\partial_{\mathcal{E}} T / T^2$. Similarly, we have $\partial^2_{\mathcal{E}\rho_k} \mathcal{S} = \partial_{\rho_k}(\frac{1}{T})$ so that $\partial^2_{\mathcal{E}\rho_k} \mathcal{S} = -\partial_{\rho_k} T / T^2$. Upon letting $\mathsf{f} = T$ in (2.33) we obtain that $\partial_{\rho_k} T = -\partial_{\mathcal{E}} T \, \widetilde{\partial}_{\rho_k} \mathcal{E}$ and we have established that $\partial^2_{\mathcal{E}\rho_k} \mathcal{S} = \partial_{\mathcal{E}} T \, \widetilde{\partial}_{\rho_k} \mathcal{E} / T^2$. Combining $\partial_{\rho_k} T = -\partial_{\mathcal{E}} T \, \widetilde{\partial}_{\rho_k} \mathcal{E}$ with (2.31) and (2.32), we also deduce that $\widetilde{\partial}_T(\frac{\mathcal{G}_k}{T}) = -\frac{\widetilde{\partial}_{\rho_k} \mathcal{E}}{T^2}$. In addition, from $\partial^2_{\rho_k \rho_l} \mathcal{S} = -\partial_{\rho_k}(\frac{\mathcal{G}_l}{T})$ and from (2.33) we deduce that $\partial^2_{\rho_k \rho_l} \mathcal{S} = -\widetilde{\partial}_{\rho_k}(\frac{\mathcal{G}_l}{T}) - \widetilde{\partial}_T(\frac{\mathcal{G}_l}{T}) \, \partial_{\rho_k} T$ so that $\partial^2_{\rho_k \rho_l} \mathcal{S} = -\frac{\widetilde{\partial}_{\rho_k} \mathcal{G}_l}{T} - \frac{\partial_{\mathcal{E}} T \, \widetilde{\partial}_{\rho_k} \mathcal{E} \, \widetilde{\partial}_{\rho_l} \mathcal{E}}{T^2}$, $k, l \in \mathfrak{S}$. We have thus established that

$$\partial^2_{\mathcal{E}\mathcal{E}} \mathcal{S} = -\frac{\partial_{\mathcal{E}} T}{T^2}, \qquad \partial^2_{\mathcal{E}\rho_k} \mathcal{S} = \frac{\partial_{\mathcal{E}} T \, \widetilde{\partial}_{\rho_k} \mathcal{E}}{T^2}, \quad k \in \mathfrak{S}, \tag{2.34}$$

$$\partial^2_{\rho_k \rho_l} \mathcal{S} = -\frac{\widetilde{\partial}_{\rho_k} \mathcal{G}_l}{T} - \frac{\partial_{\mathcal{E}} T \, \widetilde{\partial}_{\rho_k} \mathcal{E} \, \widetilde{\partial}_{\rho_l} \mathcal{E}}{T^2}, \quad k, l \in \mathfrak{S}. \tag{2.35}$$

Denoting $\mathfrak{f}^{\mathcal{E}} = (-\widetilde{\partial}_{\rho_1} \mathcal{E}, \dots, -\widetilde{\partial}_{\rho_n} \mathcal{E}, 1)^t$ we obtain that for any $\mathsf{x} = (\mathsf{x}_1, \dots, \mathsf{x}_n, \mathsf{x}_{\mathcal{E}})^t \in \mathbb{R}^{n+1}$

$$\big\langle (\partial^2_{uu} \mathcal{S}) \, \mathsf{x}, \mathsf{x} \big\rangle = -\frac{1}{\rho} \big\langle \mathit{\Gamma} \mathsf{x}_\varrho, \mathsf{x}_\varrho \big\rangle - \partial_{\mathcal{E}} T \frac{\langle \mathfrak{f}^{\mathcal{E}}, \mathsf{x} \rangle^2}{T^2}, \tag{2.36}$$

where $\mathit{\Gamma}_{kl} = \rho \widetilde{\partial}_{\rho_k} \mathcal{G}_l / T$, $k, l \in \mathfrak{S}$ and $\mathsf{x}_\varrho = (\mathsf{x}_1, \dots, \mathsf{x}_n)^t$.

Assume now that $\partial^2_{uu} \mathcal{S}$ is negative definite. Upon selecting first a vector x with $\mathsf{x}_{\mathcal{E}} = 1$ and $\mathsf{x}_\varrho = (0, \dots, 0)^t$ we obtain that $\partial_{\mathcal{E}} T > 0$ so that $\widetilde{\partial}_T \mathcal{E} = (1/\partial_{\mathcal{E}} T) > 0$. Similarly, selecting any nonzero $\mathsf{x}_\varrho = (\mathsf{x}_1, \dots, \mathsf{x}_n)^t$ and letting $\mathsf{x}_{\mathcal{E}} = \sum_{i \in \mathfrak{S}} \mathsf{x}_i \widetilde{\partial}_{\rho_i} \mathcal{E}$ we have $\langle \mathfrak{f}^{\mathcal{E}}, \mathsf{x} \rangle = 0$ and $\big\langle \mathit{\Gamma} \mathsf{x}_\varrho, \mathsf{x}_\varrho \big\rangle, = -\rho \big\langle (\partial^2_{uu} \mathcal{S}) \, \mathsf{x}, \mathsf{x} \big\rangle$ so that $\mathit{\Gamma}$ is positive definite. Finally, thanks to (2.36), the converse implications is straightforward. ☐

The inequality $\widetilde{\partial}_T\mathcal{E} > 0$ is usually termed the thermal stability condition. On the other hand, letting $\varrho = (\rho_1,\dots,\rho_n)^t$, the condition $\langle \varGamma\varrho, \varrho\rangle > 0$ is termed the mechanical stability condition. Indeed, introducing the variable $(\nu, y_1,\dots,y_n,T)$, where ν denotes the volume per unit mass and y_k the mass fraction of the kth species, and the corresponding derivation operator $\widetilde{\mathfrak{d}}$, it is easily established—after some differential algebra—that

$$\frac{\widetilde{\mathfrak{d}}_\nu p}{T} = -\sum_{ij\in\mathfrak{S}} \rho_i\rho_j \varGamma_{ij} = -\langle \varGamma\varrho, \varrho\rangle,$$

so that the stability condition $\langle \varGamma\varrho, \varrho\rangle > 0$ it is easily interpreted as $\widetilde{\mathfrak{d}}_\nu p < 0$ when p is considered as a function of $(\nu, y_1,\dots,y_n,T)$ [40]. The condition that $\varGamma - \varGamma\varrho\otimes\varGamma\varrho/\langle \varGamma\varrho, \varrho\rangle$ is positive semi-definite with nullspace $\mathbb{R}\varrho$ is also termed the chemical stability condition [40]. Combining these results and writting

$$\varGamma = \frac{\varGamma\varrho\otimes\varGamma\varrho}{\langle \varGamma\varrho, \varrho\rangle} + \Big(\varGamma - \frac{\varGamma\varrho\otimes\varGamma\varrho}{\langle \varGamma\varrho, \varrho\rangle}\Big),$$

the property that $\varGamma$ is positive definite encompasses both the mechanical and the chemical stability conditions [40]. Note that the mixture is globally stable on every convex set—with respect to the variable $\mathfrak{u}$—included in the stability domain where $\partial^2_{\mathfrak{u}\mathfrak{u}}\mathcal{S}$ is negative definite.

2.7 The SRK equation of state

We present in this section a typical equation of state often used to model mathematically high pressure fluids. This particular equation of state is only investigated to illustrate the preceding developments and will not be used outside Section 2.7.

2.7.1 Equation of state

Various equations of state have been introduced to represent the behavior of dense fluids [7, 76, 69, 77, 66]. The Benedict-Webb-Rubin equation of state [7] and its modified form by Soave [76] are notably accurate but are uneasy to handle. On the other hand, the Soave-Redlich-Kwong equation of state [69, 77] and the Peng-Robinson equation of state [66] allow an easier inversion by using Cardan's formula thanks to their cubic form. These cubic equations of state give accurate results over the range of pressures, temperatures and mixture states of interest for supercritical combustion [65, 64, 70, 43].

We discuss here the Soave-Redlich-Kwong equation of state [69, 77] which is in the form

$$\mathcal{P} = \sum_{i\in\mathfrak{S}} \frac{\rho_i}{m_i}\frac{RT}{1-\mathcal{B}} - \frac{\mathcal{A}}{1+\mathcal{B}}, \tag{2.37}$$

where $\mathcal{P}$ denotes the pressure, R the perfect gas constant, and $\mathcal{A}$ and $\mathcal{B}$ the attractive and repulsive parameters. These parameters $\mathcal{A}(\rho_1,\dots,\rho_n,T)$ and $\mathcal{B}(\rho_1,\dots,\rho_n)$ are evaluated with the Van der Waals mixing rules written here with a mass density formulation

$$\mathcal{A} = \sum_{i,j\in\mathfrak{S}} \rho_i\rho_j\alpha_i\alpha_j, \qquad \mathcal{B} = \sum_{i\in\mathfrak{S}} \rho_i\beta_i. \tag{2.38}$$

The pure-component parameters $\alpha_i(T)$ and β_i are deduced from the corresponding macroscopic fluid behavior for stable—or metastable—species and from interaction potentials for active radicals [40, 43]. The validity of this equation of state (2.37) and of the corresponding mixing rules (2.38) has been carefully studied by comparison with NIST data by Congiunti et al. [16] and with results of Monte Carlo simulations by Colonna and Silva [15] and Cañas-Marín et al. [10, 11]. This equation of state has been used in high pressure combustion models by Ribert et al. [70] and Giovangigli et al. [43].

From a mathematical point of view, we assume the following properties on the pure species coefficients $\alpha_i(T)$, and β_i, $i\in\mathfrak{S}$, where $\varkappa\in\mathbb{N}$ and $\varkappa \geqslant 3$.

(SRK) *For any* $i\in\mathfrak{S}$, $\alpha_i \in C^0[0,\infty)\cap C^{1+\varkappa}(0,\infty)$, $\alpha_i(0) > 0$, $\alpha_i \geqslant 0$, $\lim_{+\infty}\alpha_i = 0$, $\widetilde{\partial}_T\alpha_i \leqslant 0$ *and* $\widetilde{\partial}^2_{TT}\alpha_i \geqslant 0$ *over* $(0,\infty)$, *and the parameters* β_i, $i\in\mathfrak{S}$, *are positive constants.*

2.7.2 Construction of the thermodynamics

The thermodynamics associated with the SRK equation of state may then be constructed under the assumptions (SRK) and (PG) with the help of the Properties ($\mathcal{T}_1$)-($\mathcal{T}_4$), and such a construction has recently been investigated mathematically [40]. Some of the main results obtained in [40] are now summarized in terms of volumetric variables. Let the open set $\mathcal{O}'_z$ be given by

$$\mathcal{O}'_z = \{\ z = (\rho_1,\dots,\rho_n,T)^t,\ \rho_1>0,\dots,\rho_n>0,\ \sum_{i\in\mathfrak{S}} \rho_i\beta_i < 1\ \}, \tag{2.39}$$

and define the energy per unit volume $\mathcal{E}$ over $\mathcal{O}'_z$ by

$$\mathcal{E} = \sum_{i\in\mathfrak{S}} \rho_i e_i^{\mathrm{PG}} + \big(T\widetilde{\partial}_T\mathcal{A} - \mathcal{A}\big)\frac{\ln\big(1+\mathcal{B}\big)}{\mathcal{B}}, \tag{2.40}$$

where $e_i^{\mathrm{PG}} = e_i^{\mathrm{PG}}(T)$ is the perfect gas specific energy of the ith species. Further define the entropy per unit volume $\mathcal{S}$ over $\mathcal{O}'_z$ by

$$\mathcal{S} = \sum_{i\in\mathfrak{S}} \rho_i s_i^{\mathrm{PG}\star} - \sum_{i\in\mathfrak{S}} \frac{\rho_i R}{m_i}\ln\Big(\frac{\rho_i R T}{m_i(1-\mathcal{B})p^{\mathrm{st}}}\Big) + \widetilde{\partial}_T\mathcal{A}\,\frac{\ln\big(1+\mathcal{B}\big)}{\mathcal{B}}, \tag{2.41}$$

where $s_i^{\mathrm{PG}\star} = s_i^{\mathrm{PG}\star}(T)$ denotes the perfect gas specific entropy of the ith species at the standard pressure p^{st} [40].

Theorem 2.16. *Assuming that Properties* (SRK) *and* (PG) *hold, there exists a unique thermodynamics compatible with $\mathcal{P}$ which satisfies* ($\mathcal{T}_1$)-($\mathcal{T}_4$). *The corresponding energy and entropy per unit volume are given by* (2.40) *and* (2.41)*, respectively, and the open set $\mathcal{O}_z$ is given by*

$$\mathcal{O}_z = \{\ z \in \mathcal{O}'_z,\ \widetilde{\partial}_T\mathcal{E} > 0 \text{ and } \Gamma \text{ is positive definite }\}, \tag{2.42}$$

where Γ denotes the matrix defined over $\mathcal{O}'_z$ with coefficients $\Gamma_{ij} = \rho\widetilde{\partial}_{\rho_j}\mathcal{G}_i/T$, $i,j\in\mathfrak{S}$.

Proof. The proof is lengthy and we refer to [40]. ☐

2.7.3 Thermodynamic stability with SRK

The thermal stability condition $\widetilde{\partial}_T\mathcal{E} > 0$ is easily established as shown in the following proposition since we have $\mathcal{C}_{\mathrm{v}}^{\mathrm{PG}} > 0$ from (PG) and $\widetilde{\partial}^2_{TT}\mathcal{A} \geq 0$ from (SRK).

Proposition 2.17. *The heat capacity per unit mass at constant volume of the mixture $\widetilde{\partial}_T\mathcal{E} = \mathcal{C}_{\mathrm{v}}$ is given by*

$$\mathcal{C}_{\mathrm{v}} = \mathcal{C}_{\mathrm{v}}^{\mathrm{PG}} + T\widetilde{\partial}^2_{TT}\mathcal{A}\,\frac{\ln\big(1+\mathcal{B}\big)}{\mathcal{B}}, \tag{2.43}$$

where $\mathcal{C}_{\mathrm{v}}^{\mathrm{PG}} = \sum_{i\in\mathfrak{S}} \rho_i c_{\mathrm{v},i}^{\mathrm{PG}}$ so that (PG) *and* (SRK) *insure that thermal stability holds.*

The mechanical stability condition $\langle\Gamma\varrho,\varrho\rangle > 0$ for the SRK cubic equation of state is now discussed.

Proposition 2.18. *For any $\varrho = (\rho_1,\dots,\rho_n)^t \in (0,\infty)^n$ there exists a unique temperature $T^\star(\varrho) > 0$ such that $\langle\Gamma(T,\varrho)\varrho,\varrho\rangle = 0$, and we have*

$$\langle\Gamma\varrho,\varrho\rangle > 0 \iff T > T^\star(\varrho),$$

$$\lim_{\sum_{i\in\mathfrak{S}}\rho_i\beta_i\to 1} T^\star(\varrho) = 0, \qquad \lim_{\rho\to 0} T^\star(\varrho) = 0. \tag{2.44}$$

Proof. We refer the reader to [40] where the proposition is established in a mass based formulation. ☐

Defining then

$$\mathcal{P}^\star(\varrho) = \mathcal{P}\big(\varrho, T^\star(\varrho)\big),$$

and keeping in mind that $\mathcal{P}$ is a strictly increasing function of T, we deduce from Proposition 2.18 that $\langle\Gamma(\varrho,T)\varrho,\varrho\rangle > 0$ if and only if $\mathcal{P} > \mathcal{P}^\star(\varrho)$. Defining $\rho = \sum_{i\in\mathfrak{S}}\rho_i$, and letting

$$y_i = \frac{\rho_i}{\rho}, \qquad i\in\mathfrak{S}, \tag{2.45}$$

we next investigate the maximum of $T^\star$ and $\mathcal{P}^\star$ as ρ is varying with $y = (y_1, \dots, y_n)^t$ fixed. The following proposition is established in [40] is a mass based framework and is reformulated here in terms of volumetric variables.

Proposition 2.19. *For any $y \in (0,\infty)^n$ with $\langle y, \mathbb{1} \rangle = 1$, there exists a unique maximum positive value of $T^\star$ for $\rho \in (0, 1/\sum_{i\in\mathfrak{S}} y_i\beta_i)$ and this maximum is reached for $\rho = \rho^\star(y)$ where*

$$\rho^\star(y) = \frac{\sqrt[3]{2} - 1}{\sum_{i\in\mathfrak{S}} y_i\beta_i}.$$

Defining $T^{\star\star}$ and $\mathcal{P}^{\star\star}$ by

$$T^{\star\star}(y) = T^\star(\rho^\star(y)\,y), \qquad \mathcal{P}^{\star\star}(y) = \mathcal{P}^\star\big(\rho^\star(y)\,y\big) = \mathcal{P}\big(\rho^\star(y)\,y, T^\star(\rho^\star(y)\,y)\big), \tag{2.46}$$

then $T^{\star\star}(y)$ and $\mathcal{P}^{\star\star}(y)$ correspond to the critical temperature and pressure of the mixture with frozen mass fractions y. Moreover, for any ϱ, letting $\varrho = \rho y$ with $\langle y, \mathbb{1} \rangle = 1$, we always have the inequality

$$\mathcal{P}\big(\varrho, T^\star(\varrho)\big) \le \mathcal{P}^{\star\star}(y),$$

and

$$\mathcal{P}(\varrho, T) > \mathcal{P}^{\star\star}(y) \Longrightarrow \langle \Gamma\varrho, \varrho \rangle > 0,$$

Finally, since the set $\overline{\Sigma} = \{ y \in [0,\infty)^n;\ \langle y, \mathbb{1} \rangle = 1 \}$ is compact, there exists a maximum pressure $\max_{y\in\overline{\Sigma}} \mathcal{P}^{\star\star}(y)$.

When the condition $\mathcal{P} > \mathcal{P}^{\star\star}(y)$ is satisfied, the fluid is said to be in supercritical state. This shows that when the pressure $\mathcal{P}$ is large enough, the mechanical stability condition is automatically fulfilled for all possible mass fractions. On the other hand, it is generally not possible to investigate analytically the chemical stability conditions because of nonlinearities and furthermore *chemical stability may not hold at high pressure and low temperature.* As a typical exemple, mixtures of Hydrogen and Nitrogen may split into two phases at temperatures below 100 K and pressures higher that 100 atm as established experimentally [81, 28]. These chemical instabilities have been well reproduced computationally by using the Soave Redlich Kwong equation of state [40, 43]. In practice, the stability domain where the entropy is concave and where the mixture is stable must be determined numerically by investigating the eigenvalues of the matrix Γ. In the special situation of the SRK equation of state, the matrix Γ is given by the following proposition.

Proposition 2.20. *The coefficients of the matrix Γ, defined over $\mathcal{O}'_z$, are given by*

$$\begin{aligned}
\frac{\Gamma_{ij}}{\rho} =& \frac{R\delta_{ij}}{m_i\rho_i} + \frac{R}{1-\mathcal{B}}\Big(\frac{\beta_i}{m_j} + \frac{\beta_j}{m_i}\Big) + \sum_{k\in\mathfrak{S}} \frac{\rho_k}{m_k}\frac{R\,\beta_i\beta_j}{(1-\mathcal{B})^2} - \frac{2\alpha_i\alpha_j}{T}\frac{\ln(1+\mathcal{B})}{\mathcal{B}} \\
&+ \frac{2}{T}\sum_{k\in\mathfrak{S}} \rho_k\alpha_k\big(\alpha_i\beta_j + \alpha_j\beta_i\big)\Big(\frac{\ln(1+\mathcal{B})}{\mathcal{B}^2} - \frac{1}{\mathcal{B}(1+\mathcal{B})}\Big) \\
&+ \frac{\mathcal{A}\,\beta_i\beta_j}{T}\Big(-2\frac{\ln(1+\mathcal{B})}{\mathcal{B}^3} + \frac{2}{\mathcal{B}^2(1+\mathcal{B})} + \frac{1}{\mathcal{B}(1+\mathcal{B})^2}\Big), \qquad i,j \in \mathfrak{S}.
\end{aligned} \tag{2.47}$$

2.7.4 Rescaled Hessian matrices

The spectrum of the matrix Γ is more conveniently investigated by using rescaled matrices. Let us introduce the diagonal matrix $\Pi = \mathrm{diag}\big(\sqrt{m_1 y_1}, \dots, \sqrt{m_n y_n}\big)/\sqrt{R}$ as well as the rescaled matrices $\overline{\Gamma}$, $\widehat{\Gamma}_{\mathsf{r}}$, and $\widehat{\Gamma}_{\mathsf{l}}$, defined by

$$\overline{\Gamma} = \Pi\,\Gamma\,\Pi, \qquad \widehat{\Gamma}_{\mathsf{r}} = \Gamma\,\Pi^2, \qquad \widehat{\Gamma}_{\mathsf{l}} = \Pi^2\,\Gamma. \tag{2.48}$$

These matrices are $C^{\varkappa-1}$ function of $z \in \mathcal{O}'_z$ and their extension to zero mass fractions is investigated in the next proposition. When some species density vanishes, we assume for simplicity that for some $1 \leqslant n^+ < n$, the positive mass densities are the n^+ first components of ϱ. The general case is easily reduced to this situation upon introducing permutation matrices [22, 34]. We thus have $\rho_k > 0$ for $1 \leqslant k \leqslant n^+$ and $\rho_k = 0$ for $n^+ + 1 \leqslant k \leqslant n$. We denote by $n^0 = n - n^+$ the number of zero mass densities, ϱ^+ the vector of positive mass densities and ϱ^0 the vector of zero mass densities.

The indexing set of positive mass densities is also denoted by $\mathfrak{S}^+$ and that of zero mass densities by $\mathfrak{S}^0$. The decomposition $\mathbb{R}^n = \mathbb{R}^{n^+} \times \mathbb{R}^{n^0}$ induces a partitionning of vectors and any $\mathsf{x} \in \mathbb{R}^n$ can be written in the form $\mathsf{x} = (\mathsf{x}^+, \mathsf{x}^0)^t$ and we have for instance $\mathbb{I}^+ \in \mathbb{R}^{n^+}$ and $\mathbb{I}^+ = (1, \dots, 1)^t$. This partitionning of vectors induces a partitionning of matrices and for any matrix $A \in \mathbb{R}^{n,n}$, we denote by A^{++}, A^{+0}, A^{0+}, A^{00}, the corresponding blocks, in such a way that $(A\mathsf{x})^+ = A^{++}\mathsf{x}^+ + A^{+0}\mathsf{x}^0$, and $(A\mathsf{x})^0 = A^{0+}\mathsf{x}^+ + A^{00}\mathsf{x}^0$. Assuming that $\mathcal{S} - \mathcal{S}^{\mathrm{PG}}$ remains smooth for vanishing mass densities, only the blocks Γ^{++}, Γ^{+0}, and Γ^{0+} of the matrix Γ are defined for nonnegative mass fractions. This is in contrast with the matrices $\overline{\Gamma}$, $\widehat{\Gamma}_{\mathsf{r}}$, and $\widehat{\Gamma}_{\mathsf{l}}$, which are well defined for nonnegative mass fractions. In addition, the $++$ blocks are associated with the $\mathfrak{S}^+$ submixture, that is, would be obtained by solely considering the species subset indexed by $\mathfrak{S}^+$. For any diagonalizable matrix A with real eigenvalues, we denote by $\mathsf{d}^+(A)$, $\mathsf{d}^0(A)$, and $\mathsf{d}^-(A)$, the number of positive, zero and negative eigenvalues of A, respectively.

Proposition 2.21. *Assume that Properties* (SRK) *and* (PG) *hold, let Γ be defined as in Proposition 2.20, and $\overline{\Gamma}$, $\widehat{\Gamma}_{\mathsf{r}}$, and $\widehat{\Gamma}_{\mathsf{l}}$ be defined as in* (2.48)*. Then the matrix $\overline{\Gamma}$ admits a continuous extension to the set $\widetilde{\mathcal{O}}'_{\boldsymbol{z}}$ be given by*

$$\widetilde{\mathcal{O}}'_{\boldsymbol{z}} = \{\ \boldsymbol{z} = (\rho_1, \dots, \rho_n, T)^t,\ \rho_1 \geq 0, \dots, \rho_n \geq 0,\ \sum_{i \in \mathfrak{S}} \rho_i > 0\ \ \sum_{i \in \mathfrak{S}} \rho_i \beta_i < 1\ \}, \tag{2.49}$$

whereas $\widehat{\Gamma}_{\mathsf{r}}$ and $\widehat{\Gamma}_{\mathsf{l}}$ admit $C^{\varkappa-1}$ extensions to $\widetilde{\mathcal{O}}'_{\boldsymbol{z}}$. In addition, for any $\boldsymbol{z} \in \mathcal{O}'_{\boldsymbol{z}}$, we have $\mathsf{d}^+(\Gamma) = \mathsf{d}^+(\overline{\Gamma})$, $\mathsf{d}^0(\Gamma) = \mathsf{d}^0(\overline{\Gamma})$, $\mathsf{d}^-(\Gamma) = \mathsf{d}^-(\overline{\Gamma})$, and the matrices $\overline{\Gamma}$, $\widehat{\Gamma}^{\mathsf{r}}$, and $\widehat{\Gamma}_{\mathsf{l}}$, have the same spectrum.

When there are zero mass fractions, we have the block decompositions

$$\overline{\Gamma} = \begin{pmatrix} \overline{\Gamma}^{++} & 0_{n^+,n^0} \\ 0_{n^0,n^+} & \mathbb{I}_{n^0} \end{pmatrix}, \qquad \widehat{\Gamma}_{\mathsf{r}} = \begin{pmatrix} \widehat{\Gamma}_{\mathsf{r}}^{++} & 0_{n^+,n^0} \\ \widehat{\Gamma}_{\mathsf{r}}^{0+} & \mathbb{I}_{n^0} \end{pmatrix}, \qquad \widehat{\Gamma}_{\mathsf{l}} = \begin{pmatrix} \widehat{\Gamma}_{\mathsf{l}}^{++} & \widehat{\Gamma}_{\mathsf{l}}^{+0} \\ 0_{n^0,n^+} & \mathbb{I}_{n^0} \end{pmatrix},$$

so that $\overline{\Gamma}^{+0} = 0$, $\overline{\Gamma}^{0+} = 0$, $\widehat{\Gamma}_{\mathsf{r}}^{+0} = 0$, and $\widehat{\Gamma}_{\mathsf{l}}^{0+} = 0$. Moreover, we have $\overline{\Gamma}^{++} = \Pi^{++}\Gamma^{++}\Pi^{++}$, $\widehat{\Gamma}_{\mathsf{r}}^{++} = \Gamma^{++}(\Pi^{++})^2$, $\widehat{\Gamma}_{\mathsf{r}}^{0+} = \Gamma^{0+}(\Pi^{++})^2$, $\widehat{\Gamma}_{\mathsf{l}}^{++} = (\Pi^{++})^2\Gamma^{++}$, and $\widehat{\Gamma}_{\mathsf{l}}^{+0} = (\Pi^{++})^2\Gamma^{+0}$. In particular, we have $\mathsf{d}^+(\Gamma^{++}) = \mathsf{d}^+(\overline{\Gamma}^{++})$, $\mathsf{d}^0(\Gamma^{++}) = \mathsf{d}^0(\overline{\Gamma}^{++})$, and $\mathsf{d}^-(\Gamma^{++}) = \mathsf{d}^-(\overline{\Gamma}^{++})$, and the matrices $\overline{\Gamma}^{++}$, $\widehat{\Gamma}_{\mathsf{r}}^{++}$, and $\widehat{\Gamma}_{\mathsf{l}}^{++}$, have the same spectrum.

Proof. From Theorem 2.16, the thermodynamic functions are defined over $\mathcal{O}'_{\boldsymbol{z}}$ and the open set $\mathcal{O}_{\boldsymbol{z}}$ is given by (2.42). Therefore $\overline{\Gamma}$, as well as $\widehat{\Gamma}_{\mathsf{r}}$ and $\widehat{\Gamma}_{\mathsf{l}}$, is a $C^{\varkappa-1}$ function of $\boldsymbol{z} \in \mathcal{O}'_{\boldsymbol{z}}$, keeping in mind that the species mass densities remain positive when $\boldsymbol{z} \in \mathcal{O}'_{\boldsymbol{z}}$. Moreover, the coefficients of Γ are evaluated in Proposition 2.20 so $\Gamma_{ij} \simeq \delta_{ij}\rho_i^{-1}$ for vanishing mass densities. These expressions shows that the matrix $\overline{\Gamma}$ admits a continuous extension to $\widetilde{\mathcal{O}}'_{\boldsymbol{z}}$ and similarly that $\widehat{\Gamma}_{\mathsf{r}}$ and $\widehat{\Gamma}_{\mathsf{l}}$ admit $C^{\varkappa-1}$ extensions to $\widetilde{\mathcal{O}}'_{\boldsymbol{z}}$ since the $1/\rho_i$ singularity in Γ_{ii} is cancelled for $i \in \mathfrak{S}$.

Since the mass densities are positive if $\boldsymbol{z} \in \mathcal{O}'_{\boldsymbol{z}}$, the matrix Π is then invertible. From Sylvester's law of inertia we thus deduce that $\mathsf{d}^+(\Gamma) = \mathsf{d}^+(\overline{\Gamma})$, $\mathsf{d}^0(\Gamma) = \mathsf{d}^0(\overline{\Gamma})$, and $\mathsf{d}^-(\Gamma) = \mathsf{d}^-(\overline{\Gamma})$. Finally, we have $\Pi^{-1}\widehat{\Gamma}_{\mathsf{l}}\Pi = \overline{\Gamma}$ and $\Pi\widehat{\Gamma}_{\mathsf{r}}\Pi^{-1} = \overline{\Gamma}$ so that the matrices $\overline{\Gamma}$, $\widehat{\Gamma}_{\mathsf{r}}$, and $\widehat{\Gamma}_{\mathsf{l}}$, are similar and have the same spectrum. The properties when some mass fractions vanish are easily obtained from the assumption that $\mathcal{S} - \mathcal{S}^{\mathrm{PG}}$ remains smooth for vanishing mass fractions, from the explicit evaluation of Γ in Proposition 2.20 and from block manipulations. □

We deduce from Proposition 2.21 that $\mathsf{d}^+(\Gamma) = \mathsf{d}^+(\overline{\Gamma}) = \mathsf{d}^+(\widehat{\Gamma}_{\mathsf{r}}) = \mathsf{d}^+(\widehat{\Gamma}_{\mathsf{l}})$, $\mathsf{d}^0(\Gamma) = \mathsf{d}^0(\overline{\Gamma}) = \mathsf{d}^0(\widehat{\Gamma}_{\mathsf{r}}) = \mathsf{d}^0(\widehat{\Gamma}_{\mathsf{l}})$, and $\mathsf{d}^-(\Gamma) = \mathsf{d}^-(\overline{\Gamma}) = \mathsf{d}^-(\widehat{\Gamma}_{\mathsf{r}}) = \mathsf{d}^-(\widehat{\Gamma}_{\mathsf{l}})$, in such a way that any of the matrices Γ, $\overline{\Gamma}$, $\widehat{\Gamma}_{\mathsf{r}}$, or $\widehat{\Gamma}_{\mathsf{l}}$, may be used over $\mathcal{O}'_{\boldsymbol{z}}$ to determine the stability domain. An important consequence of Proposition 2.21 is that the stability of multicomponent mixtures can more conveniently be investigated with the help of the matrices $\widehat{\Gamma}_{\mathsf{r}}$ or $\widehat{\Gamma}_{\mathsf{l}}$ which behave smoothly for nonnegative mass fractions so that the whole stability diagram can be constructed over the set $\widetilde{\mathcal{O}}'_{\boldsymbol{z}}$ including automatically all mixture states with zero mass fractions. As a special case, we may also consider the limiting situation of pure species states. Denoting by $\mathsf{e}^1, \dots, \mathsf{e}^n$ the canonical base vectors of $\mathbb{R}^n$ and by $\boldsymbol{z}^i$ the state $\boldsymbol{z}^i = (\rho\mathsf{e}^i, T)^t$ for $y = \mathsf{e}^i$, we investigate thermodynamic stability in the neighborhood of $\boldsymbol{z}^i$.

Proposition 2.22. *Assume that for $\boldsymbol{z} = \boldsymbol{z}^i$ we have $\widetilde{\partial}_T\mathcal{E}(\boldsymbol{z}^i) = \mathcal{C}_{\mathrm{v}i} > 0$ and $\Gamma_{ii}(\boldsymbol{z}^i) > 0$ (or equivalently $\widetilde{\partial}_\nu p(\nu, \mathsf{e}^i, T) < 0$). Then thermodynamic stability holds in the neighborhood of $\boldsymbol{z}^i$.*

Proof. Since $\widetilde{\partial}_T\mathcal{E}(\boldsymbol{z}^i) > 0$ thermal stability holds in the neighborhood of $\boldsymbol{z}^i = (\rho\mathsf{e}^i, T)^t$. We thus only have to investigate the positive definiteness of the matrix $\mathit{\Gamma}$ and thus of the matrix $\overline{\mathit{\Gamma}}$. However, the pure state is a special case of Proposition 2.21 and we only have to check that the matrix $\overline{\mathit{\Gamma}}(\boldsymbol{z}^i)$ is positive definite. However, the limit value at $\boldsymbol{z}^i$ of $\overline{\mathit{\Gamma}}(\boldsymbol{z}^i)$ is the matrix $\mathrm{diag}(1, \dots, 1, \overline{\mathit{\Gamma}}_{ii}, 1, \dots, 1)$ where $\overline{\mathit{\Gamma}}_{ii} = m_i\mathit{\Gamma}_{ii}(\boldsymbol{z}^i)/R$ is positive so that $\overline{\mathit{\Gamma}}$ and $\mathit{\Gamma}$ are positive definite in the neighborhood of $\boldsymbol{z}^i$. ☐

In summary, thermal stability generally holds, mechanical stability holds when the mixture is supercritical, and chemical stability has to be investigated numerically at high pressure and low temperature by investigating the spectrum of the rescaled versions $\widehat{\mathit{\Gamma}}_{\mathsf{r}}$ or $\widehat{\mathit{\Gamma}}_{\mathsf{l}}$ of the matrix $\mathit{\Gamma}$, as for instance done for hydrogen/air mixtures [43, 40].

2.8 Quasilinear form

The conservative variable $\mathsf{u} \in \mathbb{R}^{n+d+1}$ associated with the equations (2.1)–(2.3) is defined by

$$\mathsf{u} = \big(\rho_1, \dots, \rho_n, \rho\boldsymbol{v}, \mathcal{E} + \tfrac{1}{2}\rho\boldsymbol{v}\cdot\boldsymbol{v}\big)^t, \tag{2.50}$$

where $\boldsymbol{v} = (v_1, \dots, v_d)^t \in \mathbb{R}^d$ and the natural variable $\mathsf{z} \in \mathbb{R}^{n+d+1}$ by

$$\mathsf{z} = \big(\rho_1, \dots, \rho_n, \boldsymbol{v}, T\big)^t. \tag{2.51}$$

Note that, for convenience, 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 $\mathbb{R}^d$. The components of u naturally appear as conserved quantities in the fluid system, and the components of the variable z are more practical to use in actual calculations of differential identities.

Since the thermodynamic part of u is $\boldsymbol{u} = (\rho_1, \dots, \rho_n, \mathcal{E})^t$ and the thermodynamic part of z is $\boldsymbol{z} = (\rho_1, \dots, \rho_n, T)^t$ it is easily seen that u is defined over the open set

$$\mathcal{O}_{\mathsf{u}} = \Big\{ \ \mathsf{u} \in \mathbb{R}^{n+d+1} \quad \Big(\mathsf{u}_1, \dots, \mathsf{u}_n, \mathsf{u}_{n+d+1} - \frac{1}{2}\frac{\mathsf{u}_{n+1}^2 + \cdots + \mathsf{u}_{n+d}^2}{\sum_{1\leq i\leq n}\mathsf{u}_i}\Big)^t \in \mathcal{O}_{\boldsymbol{u}} \ \Big\}, \tag{2.52}$$

and similarly z is defined over the open set

$$\mathcal{O}_{\mathsf{z}} = \{ \ \mathsf{z} \in \mathbb{R}^{n+d+1} \quad (\mathsf{z}_1, \dots, \mathsf{z}_n, \mathsf{z}_{n+d+1})^t \in \mathcal{O}_{\boldsymbol{z}} \ \}. \tag{2.53}$$

Of course, whenever $\boldsymbol{z} \in \mathcal{O}_{\boldsymbol{z}}$, the corresponding fluid variable z is naturally defined for all velocities $\boldsymbol{v} \in \mathbb{R}^d$. Moreover, it is easily checked that when the set $\mathcal{O}_{\mathsf{u}}$ is convex then $\mathcal{O}_{\boldsymbol{u}}$ is also convex. Therefore, since $\mathcal{O}_{\boldsymbol{u}}$ is generally not convex in the presence of thermodynamic unstable states, $\mathcal{O}_{\mathsf{u}}$ is not likely to be convex in general, in contrast with ideal gas mixtures [38, 34]. In order to express the natural variable z in terms of the conservative variable u, we investigate the map $\mathsf{z} \to \mathsf{u}$ and its range.

Proposition 2.23. *Assuming that* $(\mathcal{T}_1)$-$(\mathcal{T}_4)$ *and* (PG) *hold, the map* $\mathsf{z} \longmapsto \mathsf{u}$ *is a* $C^{\varkappa}$ *diffeomorphism from the open set* $\mathcal{O}_{\mathsf{z}}$ *onto the open set* $\mathcal{O}_{\mathsf{u}}$.

Proof. We first establish that the map $\mathsf{z} \longmapsto \mathsf{u}$ is one to one. Assuming that $\mathsf{u}(\mathsf{z}^\sharp) = \mathsf{u}(\mathsf{z}^\flat)$, then the corresponding mass densities coincide $\rho_k^\sharp = \rho_k^\flat$, $k \in \mathfrak{S}$, as well as the velocities $\boldsymbol{v}^\sharp = \boldsymbol{v}^\flat$ with straightforward notation. As a consequence, the energies $\mathcal{E}^\sharp$ and $\mathcal{E}^\flat$ also coincide, and we may then use the Property $(\mathcal{T}_1)$ or the monotonicity of $T \to \mathcal{E}(\rho_1, \dots, \rho_n, T)$ in order to conclude that $T^\sharp = T^\flat$ and the map is one to one. Moreover, the map $\mathsf{z} \longmapsto \mathsf{u}$ is $C^{\varkappa}$ over the open set $\mathcal{O}_{\mathsf{z}}$.

On the other hand, thanks to the triangular structure of the Jacobian matrix

$$\partial_{\mathsf{z}}\mathsf{u} = \begin{pmatrix} \mathbb{I}_n & 0 & 0 \\ \boldsymbol{v}\otimes\mathbb{1} & \rho\mathbb{I}_d & 0 \\ \widetilde{\partial}_{\boldsymbol{\rho}}\mathcal{E} + \frac{1}{2}|\boldsymbol{v}|^2 & \rho\boldsymbol{v}^t & \widetilde{\partial}_T\mathcal{E} \end{pmatrix},$$

where $\mathbb{I}_n$ is the identity tensor of size n, and since $\widetilde{\partial}_T\mathcal{E} > 0$ from Proposition 2.15 and $\rho > 0$ since $\mathcal{O}_{\boldsymbol{z}} \subset (0, \infty)^{n+1}$ we deduce that $\partial_{\mathsf{z}}\mathsf{u}$ is invertible. From the inverse function theorem, the $\mathsf{z} \longmapsto \mathsf{u}$ is a local $C^{\varkappa}$ diffeomorphism and the image is an open set. Finally, from the construction of u and $(\mathcal{T}_1)$, it is easily concluded that the range of $\mathsf{z} \to \mathsf{u}$ is the open set $\mathcal{O}_{\mathsf{u}}$ defined by (2.52). ☐

The equations modeling supercritical multicomponent reactive fluids may next be written into the compact form

$$\partial_t \mathsf{u} + \sum_{i\in C} \partial_i \mathsf{F}_i + \sum_{i\in C} \partial_i \mathsf{F}_i^{\mathrm{diss}} = \Omega, \tag{2.54}$$

where ∂_t is the time derivative operator, ∂_i the space derivative operator in the ith direction, F_i the convective flux in the ith direction, $\mathsf{F}_i^{\mathrm{diss}}$ the dissipative flux in the ith direction, Ω the source term, and $C = \{1, \dots, d\}$ the indexing set of spatial dimensions.

The convective flux F_i in the ith direction is given by

$$\mathsf{F}_i = \big(\rho_1 v_i, \dots, \rho_n v_i,\ \rho \boldsymbol{v} v_i + \mathcal{P} \boldsymbol{e}^i, (\mathcal{E} + \mathcal{P} + \tfrac{1}{2}\rho \boldsymbol{v}\cdot\boldsymbol{v}) v_i\big)^t, \tag{2.55}$$

where $\mathcal{P}$ is the pressure, $\boldsymbol{e}^i$, $i \in C$, the basis vectors of $\mathbb{R}^d$, and $\mathcal{E}$ the total energy per unit mass. The dissipative flux $\mathsf{F}_i^{\mathrm{diss}}$ is given by

$$\mathsf{F}_i^{\mathrm{diss}} = \big(\mathcal{F}_{1i}, \dots, \mathcal{F}_{ni},\ \boldsymbol{\mathit{\Pi}}_{\bullet i},\ Q_i + \sum_{j\in C} \mathit{\Pi}_{ij} v_j\big)^t, \tag{2.56}$$

where $\mathit{\Pi}_{ij}$, $i, j \in C$, are the components of the viscous tensor with $\boldsymbol{\mathit{\Pi}}_{\bullet i} = (\mathit{\Pi}_{1i}, \dots, \mathit{\Pi}_{di})^t$, $\mathcal{F}_{ki}$, $k \in \mathfrak{S}$, $i \in C$, the spatial components of the species mass fluxes $\boldsymbol{\mathcal{F}}_k = (\mathcal{F}_{k1}, \dots, \mathcal{F}_{kd})^t$, and Q_i, $i \in C$, the components of the heat flux vector $\boldsymbol{Q} = (Q_1, \dots, Q_d)^t$. Finally, the source term is given by

$$\Omega = \big(m_1 \omega_1, \dots, m_n \omega_n, \mathbf{0}, 0\big)^t, \tag{2.57}$$

where $\mathbf{0} = (0, \dots, 0)^t \in \mathbb{R}^d$. From the expressions of the species mass fluxes, the viscous tensor, and the heat flux, we deduce that the dissipative fluxes $\mathsf{F}_i^{\mathrm{diss}}$, $i \in C$, may be written in the form $\mathsf{F}_i^{\mathrm{diss}} = -\sum_{j\in C} \widehat{\mathsf{B}}_{ij}(\mathsf{z}) \partial_j \mathsf{z}$, $i \in C$, where $\widehat{\mathsf{B}}_{ij}$ denotes the dissipative matrix relating the flux $\mathsf{F}_i^{\mathrm{diss}}$ in the ith direction with the gradient of the natural variable $\partial_j \mathsf{z}$ in the jth direction. These matrices $\widehat{\mathsf{B}}_{ij}$ are square matrices of size $n + d + 1$ that are directly written in terms of the transport coefficients as well as the derivatives of the species chemical potentials μ_k, $k \in \mathfrak{S}$. Thanks to Proposition 2.23, we may then write that $\mathsf{F}_i^{\mathrm{diss}} = -\sum_{j\in C} \mathsf{B}_{ij}(\mathsf{u}) \partial_j \mathsf{u}$, $i \in C$, where the dissipative matrix B_{ij} is defined as $\mathsf{B}_{ij} = \widehat{\mathsf{B}}_{ij} \partial_{\mathsf{u}} \mathsf{z}$, $i, j \in C$. Further introducing the Jacobian matrices of the convective fluxes $\mathsf{A}_i = \partial_{\mathsf{u}} \mathsf{F}_i$, $i \in C$, the governing equations are finally rewritten in the compact form

$$\partial_t \mathsf{u} + \sum_{i\in C} \mathsf{A}_i(\mathsf{u}) \partial_i \mathsf{u} = \sum_{i,j\in C} \partial_i \big(\mathsf{B}_{ij}(\mathsf{u}) \partial_j \mathsf{u}\big) + \Omega(\mathsf{u}). \tag{2.58}$$

This is a quasilinear system in terms of the conservative variable u whose structure is discussed in an abstract framework in the next section.

3 Locally symmetrizable systems

We investigate in this section *local* symmetrization properties of a second-order quasilinear system of conservation laws with a source term.

3.1 Local symmetrization

3.1.1 Symmetric form

We consider an abstract second-order quasilinear system in the form

$$\partial_t \mathsf{u}^* + \sum_{i\in C^*} \mathsf{A}_i^*(\mathsf{u}^*) \partial_i \mathsf{u}^* = \sum_{i,j\in C^*} \partial_i \big(\mathsf{B}_{ij}^*(\mathsf{u}^*) \partial_j \mathsf{u}^*\big) + \Omega^*(\mathsf{u}^*), \tag{3.1}$$

where $\mathsf{u}^* \in \mathcal{O}_{\mathsf{u}^*}$, $\mathcal{O}_{\mathsf{u}^*}$ is an open set of $\mathbb{R}^{n^*}$, and $C^* = \{1, \dots, d\}$ denotes the set of direction indices of $\mathbb{R}^d$. The matrices A_i^* are the jacobian matrices of the convective fluxes denoted by F_i^* in such a way that $\mathsf{A}_i^* = \partial_{\mathsf{u}^*} \mathsf{F}_i^*$, $i \in C^*$. The superscript * is used to distinguish between the abstract second-order system (3.1) of size n^* in $\mathbb{R}^d$ and the particular system of partial differential equations (2.58) modeling supercritical reactive fluids of size $n + d + 1$ in $\mathbb{R}^d$. All quantities associated with the abstract system have the corresponding superscript *, so that, for instance, the unknown vector is u^*. We assume that the following smoothness properties hold for system (3.1).

(Pde_1) *The convective fluxes* F_i^*, $i \in C^*$, *dissipation matrices* B_{ij}^*, $i,j \in C^*$, *and source term* Ω^* *are* $C^\varkappa$ *functions of the variable* $\mathsf{u}^* \in \mathcal{O}_{\mathsf{u}^*}$ *and we have* $\mathsf{A}_i^* = \partial_{\mathsf{u}^*}\mathsf{F}_i^*$, $i \in C^*$.

It is not assumed that $\mathcal{O}_{\mathsf{u}^*}$ is convex since this is generally not the case for nonideal fluids, but it is still assumed that $\mathcal{O}_{\mathsf{u}^*}$ is simply connected since it is always the case in practical applications. A major difficulty with nonideal gases is the presence of thermodynamic unstable states associated with the loss of definiteness for entropy Hessian matrices. An important consequence is the existence of distinct states which correspond to the same symmetrizing variable. In order to take into account this situation, we use symmetryzing variables that are only *local* diffeomorphisms.

Definition 3.1. *Consider a* $C^\varkappa$ *map* $\mathsf{u}^* \to \mathsf{v}^*$ *from the open domain* $\mathcal{O}_{\mathsf{u}^*}$ *onto an open domain* $\mathcal{O}_{\mathsf{v}^*}$. *Assume that for any* $\mathsf{u} \in \mathcal{O}_{\mathsf{u}^*}$ *there exists subdomains* $\mathsf{o}_{\mathsf{u}^*} \subset \mathcal{O}_{\mathsf{u}^*}$ *and* $\mathsf{o}_{\mathsf{v}^*} \subset \mathcal{O}_{\mathsf{v}^*}$ *such that* $\mathsf{u}^* \to \mathsf{v}^*$ *is a* $C^\varkappa$ *diffeomorphism from* $\mathsf{o}_{\mathsf{u}^*}$ *onto* $\mathsf{o}_{\mathsf{v}^*}$ *and consider the corresponding system in the* v^* *variable*

$$\widetilde{\mathsf{A}}_0^*(\mathsf{v}^*)\partial_t \mathsf{v}^* + \sum_{i\in C^*} \widetilde{\mathsf{A}}_i^*(\mathsf{v}^*)\partial_i \mathsf{v}^* = \sum_{i,j\in C^*} \partial_i\big(\widetilde{\mathsf{B}}_{ij}^*(\mathsf{v}^*)\partial_j \mathsf{v}^*\big) + \widetilde{\Omega}^*(\mathsf{v}^*), \tag{3.2}$$

where $\widetilde{\mathsf{A}}_0^* = \partial_{\mathsf{v}^*}\mathsf{u}^*$, $\widetilde{\mathsf{A}}_i^* = \mathsf{A}_i^*\partial_{\mathsf{v}^*}\mathsf{u}^* = \partial_{\mathsf{v}^*}\mathsf{F}_i^*$, $\widetilde{\mathsf{B}}_{ij}^* = \mathsf{B}_{ij}^*\partial_{\mathsf{v}^*}\mathsf{u}^*$, $\widetilde{\Omega}^* = \Omega^*$. *The system is said of the local symmetric form if the matrices* $\widetilde{\mathsf{A}}_0^*$, $\widetilde{\mathsf{A}}_i^*$, $i \in C^*$, *and* $\widetilde{\mathsf{B}}_{ij}^*$, $i,j \in C^*$, *and the source term* $\widetilde{\Omega}$ *verify the following properties* (S_1)-(S_7) *where* $\mathcal{E}$ *is a vector space of* $\mathbb{R}^{n^*}$ *independent of* u^* *and* v^*.

(S_1) *The matrix* $\widetilde{\mathsf{A}}_0^*(\mathsf{v}^*)$ *is symmetric positive definite for* $\mathsf{v}^* \in \mathsf{o}_{\mathsf{v}^*}$.

(S_2) *The matrices* $\widetilde{\mathsf{A}}_i^*(\mathsf{v}^*)$, $i \in C^*$, *are symmetric for* $\mathsf{v}^* \in \mathsf{o}_{\mathsf{v}^*}$.

(S_3) *We have* $\widetilde{\mathsf{B}}_{ij}^*(\mathsf{v}^*)^t = \widetilde{\mathsf{B}}_{ji}^*(\mathsf{v}^*)$ *for* $i,j \in C^*$, *and* $\mathsf{v}^* \in \mathsf{o}_{\mathsf{v}^*}$.

(S_4) *The matrix* $\widetilde{\mathsf{B}}^*(\mathsf{v}^*, w) = \sum_{i,j\in C^*} \widetilde{\mathsf{B}}_{ij}^*(\mathsf{v}^*)w_i w_j$ *is symmetric positive semi-definite, for* $\mathsf{v}^* \in \mathsf{o}_{\mathsf{v}^*}$, *and* $w \in \Sigma^{d-1}$, *where* Σ^{d-1} *is the unit sphere in* d *dimensions.*

(S_5) *There exists a vector space* $\mathcal{E} \subset \mathbb{R}^{n^*}$ *such that for any* $\mathsf{v}^* \in \mathsf{o}_{\mathsf{v}^*}$, *we have* $\widetilde{\Omega}^*(\mathsf{v}^*) \in \mathcal{E}^\perp$. *Moreover, we have* $\widetilde{\Omega}^*(\mathsf{v}^*) = 0$ *if and only if* $\mathsf{v}^* \in \mathcal{E}$ *and if and only if* $\big\langle \mathsf{v}^*, \widetilde{\Omega}^*(\mathsf{v}^*)\big\rangle = 0$.

(S_6) *For any* $\mathsf{v}^* \in \mathsf{o}_{\mathsf{v}^*}$, *if* $\widetilde{\Omega}^*(\mathsf{v}^*) = 0$, *then* $\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*) = \big(\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*)\big)^t$ *and* $N\big(\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*)\big) = \mathcal{E}$.

(S_7) *For any* $\mathsf{v}^* \in \mathsf{o}_{\mathsf{v}^*}$, $\big\langle \mathsf{v}^*, \widetilde{\Omega}^*(\mathsf{v}^*)\big\rangle \leq 0$.

The symmetryzing properties (S_1)-(S_2) for hyperbolic systems of conservation laws have been introduced by Godunov [44] and Friedrichs and Lax [32], and are discussed in Dafermos [18] and Serre [73]. The properties associated with the dissipative part (S_3)-(S_4) have been introduced by Kawashima [50, 51], Umeda et al. [79], and Kawashima and Shizuta [75, 52]. The properties associated with the source terms (S_5)-(S_7) are adapted from the structure of chemical source and chemical equilibrium flows [34, 39], and from the structure of collisional invariants investigated by Chen, Levermore and Liu [14] and Kawashima and Yong [53]. In comparison with various definitions of symmetrizability [44, 32, 50, 51, 52, 38, 34], we have taken into account in (S_1)-(S_7) the second order dissipative terms, the source terms, the map $\mathsf{u}^* \to \mathsf{v}^*$ is only a local diffeomorphism, and the open domain $\mathsf{o}_{\mathsf{u}^*}$ may differ from $\mathcal{O}_{\mathsf{u}^*}$. Further properties of the jacobian matrix $\partial_{\mathsf{v}^*}\widetilde{\Omega}^*$ at equilibrium may be obtained from (S_5)-(S_7).

Proposition 3.2. *Keeping the notation of Definition 3.1 and assuming* (S_5)-(S_7), *then if* $\mathsf{v}^* \in \mathsf{o}_{\mathsf{v}^*}$ *is such that* $\widetilde{\Omega}^*(\mathsf{v}^*) = 0$, *the matrix* $\widetilde{\mathsf{L}}^* = -\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*)$ *is symmetric positive semi-definite. Moreover, in Property* (S_6), *we may replace* $N\big(\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*)\big) = \mathcal{E}$ *by* $R\big(\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*)\big) = \mathcal{E}^\perp$ *or equivalently by* $\mathrm{rank}\big(\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*)\big) = n^* - \dim(\mathcal{E})$.

Proof. Let us introduce the function of $\mathsf{v}^* \in \mathsf{o}_{\mathsf{v}^*}$ defined by $\psi(\mathsf{v}^*) = \big\langle \mathsf{v}^*, \widetilde{\Omega}^*(\mathsf{v}^*)\big\rangle = \mathsf{v}^{*t}\,\widetilde{\Omega}^*(\mathsf{v}^*)$. From ($\mathsf{S}_7$) we know that $\psi \leq 0$ in such a way that if $\mathsf{v}^* \in \mathsf{o}_{\mathsf{v}^*}$ satisfies $\widetilde{\Omega}^*(\mathsf{v}^*) = 0$, then ψ reaches its maximum at v^*. In this situation where $\widetilde{\Omega}^*(\mathsf{v}^*) = 0$, we thus have $\partial_{\mathsf{v}^*}\psi(\mathsf{v}^*) = 0$ and $\partial_{\mathsf{v}^*}^2\psi(\mathsf{v}^*)$ has to be symmetric negative semi-definite.

A direct calculation yields that

$$\partial_{\mathsf{v}_i^*}\psi = \widetilde{\Omega}_i^* + \sum_{1\leq k\leq n^*} \mathsf{v}_k^* \partial_{\mathsf{v}_i^*}\widetilde{\Omega}_k^*,$$

which is automatically zero when the source term vanish $\widetilde{\Omega}(\mathsf{v}^*) = 0$ since then $\mathsf{v}^* \in \mathcal{E}$ and we have $\partial_{\mathsf{v}_i^*}\widetilde{\Omega}^*(\mathsf{v}^*) \in \mathcal{E}^\perp$ from $\widetilde{\Omega}^* \in \mathcal{E}^\perp$. Similarly, $\partial^2_{\mathsf{v}^*}\psi = \partial_{\mathsf{v}^*}(\partial_{\mathsf{v}^*}\psi)^t$ is generally given by

$$\partial^2_{\mathsf{v}_i^*\mathsf{v}_j^*}\psi = \partial_{\mathsf{v}_i^*}\widetilde{\Omega}_j^* + \partial_{\mathsf{v}_j^*}\widetilde{\Omega}_i^* + \partial^2_{\mathsf{v}_i^*\mathsf{v}_j^*}\widetilde{\Omega}^{*t}\mathsf{v}^*,$$

but the last term vanishes when $\widetilde{\Omega}^*(\mathsf{v}^*) = 0$ thanks to $\partial^2_{\mathsf{v}_i^*\mathsf{v}_j^*}\widetilde{\Omega}^*(\mathsf{v}^*) \in \mathcal{E}^\perp$ since $\widetilde{\Omega}^* \in \mathcal{E}^\perp$, and $\mathsf{v}^* \in \mathcal{E}$. This shows that $\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*) + \big(\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*)\big)^t$ is symmetric negative semi-definite. Therefore, since $\widetilde{\mathsf{L}}^*(\mathsf{v}^*) = -\partial_{\mathsf{v}_i^*}\widetilde{\Omega}_j^*(\mathsf{v}^*)$ by construction and $\widetilde{\mathsf{L}}^*(\mathsf{v}^*) = \big(\widetilde{\mathsf{L}}^*(\mathsf{v}^*)\big)^t$ from (S_6) we deduce $\widetilde{\mathsf{L}}^*$ is symmetric positive semi-definite. In addition, since $\widetilde{\Omega}^*(\mathsf{v}'^*) \in \mathcal{E}^\perp$ for any $\mathsf{v}'^* \in \mathcal{O}_{\mathsf{v}^*}$, we also obtain that that $R\big(\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*)\big) \subset \mathcal{E}^\perp$ by construction.

On the other hand, since $\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*)$ is symmetric, we have $N\big(\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*)\big) = \mathcal{E}$ if and only if $R\big(\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*)\big) = \mathcal{E}^\perp$. In addition, if $R\big(\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*)\big) = \mathcal{E}^\perp$ then $\mathrm{rank}\big(\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*)\big) = n^* - \dim(\mathcal{E})$ whereas if $\mathrm{rank}\big(\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*)\big) = n^* - \dim(\mathcal{E})$ then $R\big(\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*)\big) = \mathcal{E}^\perp$ since we always have $R\big(\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{v}^*)\big) \subset \mathcal{E}^\perp$ from $\widetilde{\Omega}^* \in \mathcal{E}^\perp$ and the proof is complete. ☐

3.1.2 Mathematical entropy

The following definition of an entropy function is adapted from Godunov [44] and Friedrichs and Lax [32] for the hyperbolic part, from Kawashima and Shizuta [50, 51, 75, 52] for the dissipative part, from the structure of thermochemistry and chemical equilibrium flows [34, 39] and from Chen, Levermore and Liu [14] and Kawashima and Yong [53] for the source term.

Definition 3.3. *Consider a $C^{\varkappa}$ function $\sigma^*(\mathsf{u}^*)$ defined over the open domain $\mathcal{O}_{\mathsf{u}^*}$ assumed to be simply connected. The function σ^* is said to be an entropy function for the system* (3.1) *if the following properties hold.*

(E_1) *The Hessian matrix $\partial^2_{\mathsf{u}^*}\sigma^*(\mathsf{u}^*)$ is positive definite over $\mathcal{O}_{\mathsf{u}^*}$.*

(E_2) *There exists real-valued $C^{\varkappa}$ functions $\mathsf{q}_i^* = \mathsf{q}_i^*(\mathsf{u}^*)$ such that*

$$\big(\partial_{\mathsf{u}^*}\sigma^*(\mathsf{u}^*)\big)\,\mathsf{A}_i^*(\mathsf{u}^*) = \partial_{\mathsf{u}^*}\mathsf{q}_i^*(\mathsf{u}^*), \quad i \in C^*, \quad \mathsf{u}^* \in \mathcal{O}_{\mathsf{u}^*}.$$

(E_3) *For any $\mathsf{u}^* \in \mathcal{O}_{\mathsf{u}^*}$ we have*

$$\big(\partial^2_{\mathsf{u}^*}\sigma^*(\mathsf{u}^*)\big)^{-1}\big(\mathsf{B}_{ij}^*(\mathsf{u}^*)\big)^t = \mathsf{B}_{ji}^*(\mathsf{u}^*)\big(\partial^2_{\mathsf{u}^*}\sigma^*(\mathsf{u}^*)\big)^{-1}, \qquad i,j \in C^*.$$

(E_4) *The matrix*

$$\widetilde{\mathsf{B}}^*(\mathsf{u}^*, w) = \sum_{i,j\in C^*} \mathsf{B}_{ij}^*(\mathsf{u}^*)\,\big(\partial^2_{\mathsf{u}^*}\sigma^*(\mathsf{u}^*)\big)^{-1}\, w_i w_j,$$

is symmetric positive semi-definite for any $\mathsf{u}^* \in \mathcal{O}_{\mathsf{u}^*}$ and $w \in \Sigma^{d-1}$.

(E_5) *There exists a vector space $\mathcal{E} \subset \mathbb{R}^{n^*}$ such that for any $\mathsf{u}^* \in \mathcal{O}_{\mathsf{u}^*}$, $\Omega^*(\mathsf{u}^*) \in \mathcal{E}^\perp$. Moreover, $\Omega^*(\mathsf{u}^*) = 0$ if and only if $\big(\partial_{\mathsf{u}^*}\sigma^*(\mathsf{u}^*)\big)^t \in \mathcal{E}$ and if and only if $\big(\partial_{\mathsf{u}^*}\sigma^*(\mathsf{u}^*)\big)\Omega^*(\mathsf{u}^*) = 0$.*

(E_6) *For any $\mathsf{u}^* \in \mathcal{O}_{\mathsf{u}^*}$, if $\Omega^*(\mathsf{u}^*) = 0$, then $\partial_{\mathsf{u}^*}\Omega^*(\mathsf{u}^*)\,\big(\partial^2_{\mathsf{u}^*}\sigma^*(\mathsf{u}^*)\big)^{-1} = \big(\partial^2_{\mathsf{u}^*}\sigma^*(\mathsf{u}^*)\big)^{-1}\big(\partial_{\mathsf{u}^*}\Omega^*(\mathsf{u}^*)\,\big)^t$ and $N\big(\partial_{\mathsf{u}^*}\Omega^*(\mathsf{u}^*)\,\big(\partial^2_{\mathsf{u}^*}\sigma^*(\mathsf{u}^*)\big)^{-1}\big) = \mathcal{E}$.*

(E_7) *For any $\mathsf{u}^* \in \mathcal{O}_{\mathsf{u}^*}$, we have $\big(\partial_{\mathsf{u}^*}\sigma^*(\mathsf{u}^*)\big)\,\Omega^*(\mathsf{u}^*) \leq 0$.*

The fact that the entropy and the entropy fluxes may be defined uniquely over the domain $\mathcal{O}_{\mathsf{u}^*}$ is a consequence of its simple connectedness. The equivalence between symmetrization and entropy for hyperbolic systems of conservation laws, that is, the equivalence between (S_1)-(S_2) and (E_1)-(E_2), has been discussed by many authors and is obtained with $\mathsf{v}^* = (\partial_{\mathsf{u}^*}\sigma^*)^t$. The extension of the equivalence theorem to second-order systems of partial differential equations as well as to systems with source terms is then obtained since (S_3)-(S_7) is a reformulation of (E_3)-(E_7) and conversely. We clarify here the equivalence theorem in the particular situation of local symmetrizability including second-order terms as well as source terms [34].

Theorem 3.4. *Assume that the system* (3.1) *admits an entropy function σ^* defined over $\mathcal{O}_{\mathsf{u}^*}$. Then, the system can be locally symmetrized around any point u^* of $\mathcal{O}_{\mathsf{u}^*}$ with the symmetrizing variable $\mathsf{v}^* = (\partial_{\mathsf{u}^*}\sigma^*)^t$. Conversely, assume that the map $\mathsf{u}^* \to \mathsf{v}^*$ from $\mathcal{O}_{\mathsf{u}^*}$ onto an open set $\mathcal{O}_{\mathsf{v}^*}$ is a local diffeomorphism such that the system can be locally symmetrized in the neighborhood of any point u^* of the simply connected open set $\mathcal{O}_{\mathsf{u}^*}$. Then there exists a globally defined entropy over the open set $\mathcal{O}_{\mathsf{u}^*}$ such that $\mathsf{v}^* = (\partial_{\mathsf{u}^*}\sigma^*)^t$.*

Proof. Assume first that there exists an entropy σ^* as in Definition 3.3 and let $\mathsf{v}^* = \big(\partial_{\mathsf{u}^*}\sigma^*\big)^t$ be the symmetrizing variable. The map $\mathsf{u}^* \to \mathsf{v}^*$ is then a local diffeomorphism from (E_1) and we can define the functions

$$\mathfrak{s}^*(\mathsf{v}^*) = \langle \mathsf{u}^*, \mathsf{v}^* \rangle - \sigma^*(\mathsf{u}^*),$$

and

$$\mathfrak{q}_i^*(\mathsf{v}^*) = \langle F_i^*, \mathsf{v}^* \rangle - \mathsf{q}_i^*(\mathsf{u}^*), \qquad i \in C^*.$$

Differentiating these expressions then yields that $\big(\partial_{\mathsf{v}^*}\mathfrak{s}^*\big)^t = \mathsf{u}^*$ and $\big(\partial_{\mathsf{v}^*}\mathfrak{q}_i^*\big)^t = F_i^*$, making use of $\mathsf{v}^* = \big(\partial_{\mathsf{u}^*}\sigma^*\big)^t$ and Property (E_2). This implies that $\widetilde{\mathsf{A}}_0^* = \partial_{\mathsf{v}^*}\mathsf{u}^* = \partial^2_{\mathsf{v}^*}\mathfrak{s}^*$ and $\widetilde{\mathsf{A}}_i^* = \partial_{\mathsf{v}^*}F_i^* = \partial^2_{\mathsf{v}^*}\mathfrak{q}_i^*$, $i \in C^*$, so that these matrices are symmetric. It is next checked that (S_3)-(S_7) are direct consequences of (E_3)-(E_7).

Conversely, assume that the system is locally symmetrizable with the map $\mathsf{u}^* \to \mathsf{v}^*$ in the sense of Definition 3.1. It is mandatory then to look for gradients with respect to the conservative variable u^* and not with respect to the symmetric variable v^* as in traditional proofs since $\mathsf{u}^* \to \mathsf{v}^*$ is not globally invertible. To this aim, we observe that the matrices $\partial_{\mathsf{u}^*}\mathsf{v}^*$ and $\partial_{\mathsf{u}^*}\big((\mathsf{v}^*)^t\partial_{\mathsf{u}^*}\mathsf{F}_i^*\big)$ are symmetric. This is clear for $\partial_{\mathsf{u}^*}\mathsf{v}^*$ which is the inverse of the symmetric matrix $\widetilde{\mathsf{A}}_0^* = \partial_{\mathsf{v}^*}\mathsf{u}^*$ whereas denoting $\mathfrak{p}_k = \big((\mathsf{v}^*)^t\partial_{\mathsf{u}^*}\mathsf{F}_i^*\big)_k$ we have $\mathfrak{p}_k = \sum_{1\leq j\leq n^*} \mathsf{v}_j^*\partial_{\mathsf{u}_k^*}(\mathsf{F}_i)_j^*$ so that

$$\partial_{\mathsf{u}_l^*}\mathfrak{p}_k = \sum_{1\leq j\leq n^*} \partial_{\mathsf{u}_l^*}\mathsf{v}_j^*\partial_{\mathsf{u}_k^*}(\mathsf{F}_i)_j^* + \sum_{1\leq j\leq n^*} \mathsf{v}_j^*\partial^2_{\mathsf{u}_k^*\,\mathsf{u}_l^*}(\mathsf{F}_i)_j^*,$$

and is thus symmetric in (k,l) from the symmetry of second derivatives and the symmetry of the product

$$\big(\partial_{\mathsf{u}^*}\mathsf{v}^*\big)^t\partial_{\mathsf{u}^*}\mathsf{F}_i^* = \big(\partial_{\mathsf{u}^*}\mathsf{v}^*\big)^t\,\widetilde{\mathsf{A}}_i^*\;\partial_{\mathsf{u}^*}\mathsf{v}^*,$$

which a consequence of the symmetry of $\widetilde{\mathsf{A}}_i^* = \mathsf{A}_i^*\partial_{\mathsf{v}^*}\mathsf{u}^*$. Therefore, there exists σ^* and q_i^*, $i \in C^*$, defined over $\mathcal{O}_{\mathsf{u}^*}$, such that $\big(\partial_{\mathsf{u}^*}\sigma^*\big)^t = \mathsf{v}^*$ and $\big(\partial_{\mathsf{u}^*}\mathsf{q}_i^*\big)^t = \mathsf{F}_i^*$, $i \in C^*$ and (E_1)-(E_2) are established. It is then easily checked that (E_3)-(E_7) are direct consequences of (S_3)-(S_7). ☐

3.2 Local normal variable

We assume that the abstract quasilinear system (3.1) satisfies the following properties.

(Pde_2) *The system* (3.1) *admits an entropy function σ^* defined over the simply connected open set $\mathcal{O}_{\mathsf{u}^*}$.*

Introducing the symmetrizing variable $\mathsf{v}^* = (\partial_{\mathsf{u}^*}\sigma^*)^t$, the corresponding symmetric system (3.2) then locally satisfies Properties (S_1)-(S_7). The symmetric form (3.2) may be used in particular in order to obtain the classical entropic estimates [38]. However, depending on the range of the dissipation matrices $\widetilde{\mathsf{B}}_{ij}^*$, this system lies between the two limit cases of a hyperbolic system and a strongly parabolic system. In order to split the variables between hyperbolic and parabolic variables, we have to put the system into a normal form, that is, in the form of a symmetric hyperbolic–parabolic composite system.

Definition 3.5. *Consider a system locally symmetrizable as in Definition 3.1 and let* $\mathsf{u}^* \to \mathsf{w}^*$ *be a map from the open set* $\mathcal{O}_{\mathsf{u}^*}$ *onto an open set* $\mathcal{O}_{\mathsf{w}^*}$. *Assume that for any* $\mathsf{u}^* \in \mathcal{O}_{\mathsf{u}^*}$ *there exists* $\mathsf{o}_{\mathsf{u}^*} \subset \mathcal{O}_{\mathsf{u}^*}$ *and* $\mathsf{o}_{\mathsf{w}^*} \subset \mathcal{O}_{\mathsf{w}^*}$ *such that* $\mathsf{u}^* \to \mathsf{w}^*$ *is a diffeomorphism and assume that* $\mathsf{u}^* \to \mathsf{v}^*$, *from* $\mathsf{o}_{\mathsf{u}^*}$ *onto* $\mathsf{o}_{\mathsf{v}^*}$ *is also a diffeomorphism. Consider then the induced local diffeomorphism* $\mathsf{v}^* \to \mathsf{w}^*$ *from* $\mathsf{o}_{\mathsf{v}^*}$ *onto* $\mathsf{o}_{\mathsf{w}^*}$. *Letting* $\mathsf{v}^* = \mathsf{v}^*(\mathsf{w}^*)$ *in the symmetrized system* (3.2), *multiplying the conservative symmetric form* (3.2) *on the left side by the transpose of the matrix* $\partial_{\mathsf{w}^*}\mathsf{v}^*$, *we then get a new system in the variable* w^* *in the form*

$$\overline{\mathsf{A}}_0^*(\mathsf{w}^*)\partial_t \mathsf{w}^* + \sum_{i\in C^*} \overline{\mathsf{A}}_i^*(\mathsf{w}^*)\partial_i \mathsf{w}^* = \sum_{i,j\in C^*} \partial_i\big(\overline{\mathsf{B}}_{ij}^*(\mathsf{w}^*)\partial_j \mathsf{w}^*\big) + \overline{\mathcal{T}}^*(\mathsf{w}^*, \boldsymbol{\nabla}\mathsf{w}^*) + \overline{\Omega}^*(\mathsf{w}^*), \tag{3.3}$$

where $\overline{\mathsf{A}}_0^* = (\partial_{\mathsf{w}^*}\mathsf{v}^*)^t\, \widetilde{\mathsf{A}}_0^*\, (\partial_{\mathsf{w}^*}\mathsf{v}^*)$, $\overline{\mathsf{B}}_{ij}^* = (\partial_{\mathsf{w}^*}\mathsf{v}^*)^t\, \widetilde{\mathsf{B}}_{ij}^*\, (\partial_{\mathsf{w}^*}\mathsf{v}^*)$, $\overline{\mathsf{A}}_i^* = (\partial_{\mathsf{w}^*}\mathsf{v}^*)^t\, \widetilde{\mathsf{A}}_i^*\, (\partial_{\mathsf{w}^*}\mathsf{v}^*)$, *satisfies the properties* (S_1)-(S_4) *rewritten in terms of the overbar matrices and where* $\overline{\Omega}^* = (\partial_{\mathsf{w}^*}\mathsf{v}^*)^t\widetilde{\Omega}^*$ *and* $\overline{\mathcal{T}}^* = -\sum_{i,j\in C^*} \partial_i(\partial_{\mathsf{w}^*}\mathsf{v}^*)^t\, \widetilde{\mathsf{B}}_{ij}^*\, (\partial_{\mathsf{w}^*}\mathsf{v}^*)\partial_j \mathsf{w}^*$. *This system is then said to be of the local normal form if there exists a partition of* $\{1,\dots,n^*\}$ *into* $\mathrm{I} = \{1,\dots,n_0^*\}$ *and* $\mathrm{II} = \{n_0^*+1,\dots,n^*\}$ *such that the following properties hold.*

(Nor$_1$) *The matrices* $\overline{\mathsf{A}}_0^*$ *and* $\overline{\mathsf{B}}_{ij}^*$ *have the block structure*

$$\overline{\mathsf{A}}_0^* = \begin{pmatrix} \overline{\mathsf{A}}_0^{*\mathrm{I},\mathrm{I}} & 0 \\ 0 & \overline{\mathsf{A}}_0^{*\mathrm{II},\mathrm{II}} \end{pmatrix}, \qquad \overline{\mathsf{B}}_{ij}^* = \begin{pmatrix} 0 & 0 \\ 0 & \overline{\mathsf{B}}_{ij}^{*\mathrm{II},\mathrm{II}} \end{pmatrix}.$$

(Nor$_2$) *The matrix* $\overline{\mathsf{B}}^{*\mathrm{II},\mathrm{II}}(\mathsf{w}^*, w) = \sum_{i,j\in C^*} \overline{\mathsf{B}}_{ij}^{*\mathrm{II},\mathrm{II}}(\mathsf{w}^*)w_i w_j$ *is positive definite, for* $\mathsf{w}^* \in \mathsf{o}_{\mathsf{w}^*}$, *and* $w \in \Sigma^{d-1}$.

(Nor$_3$) *Denoting* $\partial_x = (\partial_1,\dots,\partial_d)^t$, *we have*

$$\overline{\mathcal{T}}^*(\mathsf{w}^*, \partial_x \mathsf{w}^*) = \Big(\overline{\mathcal{T}}_{\mathrm{I}}^*(\mathsf{w}^*, \partial_x \mathsf{w}_{\mathrm{II}}^*), \overline{\mathcal{T}}_{\mathrm{II}}^*(\mathsf{w}^*, \partial_x \mathsf{w}^*)\Big)^t,$$

where we have used the vector and matrix block structure induced by the partitioning of $\{1,\dots,n^*\}$ *into* $\mathrm{I} = \{1,\dots,n_0^*\}$ *and* $\mathrm{II} = \{n_0^*+1,\dots,n^*\}$, *so that we have* $\mathsf{w}^* = (\mathsf{w}_{\mathrm{I}}^*, \mathsf{w}_{\mathrm{II}}^*)^t$, *for instance.*

A sufficient condition for system (3.2) to be recast into a normal form is that the nullspace naturally associated with dissipation matrices is a fixed subspace of $\mathbb{R}^{n^*}$. This is Condition N introduced by Kawashima and Shizuta [52] which has been strengthened in [38] and which is assumed to hold.

(Pde$_3$) *The nullspace of the matrix*

$$\widetilde{\mathsf{B}}^*(\mathsf{v}^*, w) = \sum_{i,j\in C^*} \widetilde{\mathsf{B}}_{ij}^*(\mathsf{v}^*)w_i w_j,$$

does not depend on $\mathsf{v}^* \in \mathsf{o}_{\mathsf{v}^*}$ *and* $w \in \Sigma^{d-1}$ *and we have* $\widetilde{\mathsf{B}}_{ij}^*(\mathsf{v}^*)N(\widetilde{\mathsf{B}}^*) = 0$, $i,j \in C^*$.

We denote by $n_0^* = \dim\big(N(\widetilde{\mathsf{B}}^*)\big)$ the dimension of $N(\widetilde{\mathsf{B}}^*)$. We further consider an arbitrary constant nonsingular matrix P of dimension n^*, such that its first n_0^* columns span the nullspace $N(\widetilde{B}^*)$. More specifically, the matrix P is such that

$$\mathrm{span}\Big\{ (\mathsf{P}_{1j},\dots,\mathsf{P}_{nj})^t;\ 1 \le j \le n_0^* \Big\} = N(\widetilde{B}^*).$$

In order to characterize more easily normal forms for symmetric systems of conservation laws satisfying (Pde_1)-(Pde_3) we introduce the auxiliary variables [38, 34] $\mathsf{u}^{*\prime} = \mathsf{P}^t\mathsf{u}^*$ and $\mathsf{v}^{*\prime} = \mathsf{P}^{-1}\mathsf{v}^*$. The dissipation matrices corresponding to these auxiliary variables have nonzero coefficients only in the lower right block of size $n^* - n_0^*$, where $n_0^* = \dim\big(N(\widetilde{\mathsf{B}}^*)\big)$. Local normal symmetric forms are then equivalently—and more easily—obtained from the $\mathsf{v}^{*\prime}$ symmetric equation [38, 34]. A carefull examination of the proof in Giovangigli and Massot [38] reveals that the following theorem holds.

Theorem 3.6. *Consider a system of conservation laws* (3.2) *that is locally symmetric in the sense of Definition 3.1 and assume that the nullspace invariance property* (Pde_3) *is satisfied. Denoting by* $\mathsf{u}^{*\prime} = \mathsf{P}^t\mathsf{u}^*$ *and* $\mathsf{v}^{*\prime} = \mathsf{P}^{-1}\mathsf{v}^*$*, the usual auxiliary variable, any normal form of the system* (3.2) *is given by a local change of variable in the form*

$$\mathsf{w}^* = \big(\phi_{\mathrm{I}}(\mathsf{u}_{\mathrm{I}}^{*\prime}), \phi_{\mathrm{II}}(\mathsf{v}_{\mathrm{II}}^{*\prime})\big)^t,$$

where ϕ_{I} *and* ϕ_{II} *are two diffeomorphisms of* $\mathbb{R}^{n_0^*}$ *and* $\mathbb{R}^{n^*-n_0^*}$*, respectively, and we have*

$$\overline{\mathcal{T}}^*(\mathsf{w}^*, \partial_x \mathsf{w}^*) = \big(0,\, \overline{\mathcal{T}}_{\mathrm{II}}^*(\mathsf{w}^*, \partial_x \mathsf{w}_{\mathrm{II}}^*)\big)^t.$$

When the mathematical entropy σ^* is unique up to an affine transformation, as can be established for the Navier-Stokes-Fourier system of a single fluid [47, 34] and may be established for multicomponent nonideal fluids under the assumption that σ^* is independent of heat and mass diffusion transport parameters [42] then the symmetrizing variable v^* is unique up to a multiplicative constant, and Theorem 3.6 yields all the corresponding normal forms.

3.3 Dissipativity and asymptotic stability

3.3.1 Linearized normal form

We consider a system of conservation laws satisfying (Pde_1)-(Pde_3) and the additional property

(Pde_4) *The system* (3.1) *admits an equilibrium point* u^{*e}.

We denote by v^{*e} and w^{*e} the equilibrium point in the v^* and w^* variables respectively. If we linearize system (3.3) around the constant stationary state w^{*e}, we obtain a linear system in the variable $\widehat{\mathsf{w}}^* = \mathsf{w}^* - \mathsf{w}^{*e}$

$$\overline{\mathsf{A}}_0^*(\mathsf{w}^{*e})\partial_t\widehat{\mathsf{w}}^* + \sum_{i\in C^*}\overline{\mathsf{A}}_i^*(\mathsf{w}^{*e})\partial_i\widehat{\mathsf{w}}^* = \sum_{i,j\in C^*}\overline{\mathsf{B}}_{ij}^*(\mathsf{w}^{*e})\partial_i\partial_j\widehat{\mathsf{w}}^* - \overline{\mathsf{L}}^*(\mathsf{w}^{*e})\widehat{\mathsf{w}}^*, \tag{3.4}$$

where $\overline{\mathsf{L}}^*$ is defined by $\overline{\mathsf{L}}^* = -\partial_{\mathsf{w}^*}\overline{\Omega}^*$. The properties of the linearized source terms are established in the following lemma.

Lemma 3.7. *Assuming Properties* (Pde_1)-(Pde_4), (PG), *and* (S_1)-(S_7), *and letting* $\overline{\mathsf{L}}^* = -\partial_{\mathsf{w}^*}\overline{\Omega}^*$*, the matrix* $\overline{\mathsf{L}}^*(\mathsf{w}^{*e})$ *is symmetric positive semi-definite with maximal rank* $n^* - \dim(\mathcal{E})$.

Proof. This is a direct consequence of the identity $\overline{\mathsf{L}}^*(\mathsf{w}^{*e}) = -\big(\partial_{\mathsf{w}^*}\mathsf{v}^*(\mathsf{w}^{*e})\big)^t\partial_{\mathsf{v}^*}\widetilde{\Omega}^*(\mathsf{w}^{*e})\big(\partial_{\mathsf{w}^*}\mathsf{v}^*(\mathsf{w}^{*e})\big)$ and of Proposition 3.2. ☐

By Fourier transform, the spectral problem associated with the linear system of partial differential equations (3.4) reads

$$\lambda\overline{\mathsf{A}}_0^*(\mathsf{w}^{*e})\phi + \Big(\mathrm{i}\zeta\overline{\mathsf{A}}^*(\mathsf{w}^{*e}, w) + \zeta^2\overline{\mathsf{B}}^*(\mathsf{w}^{*e}, w) + \overline{\mathsf{L}}^*(\mathsf{w}^{*e})\Big)\phi = 0, \tag{3.5}$$

where $\zeta \in \mathbb{R}$, $\mathrm{i}^2 = -1$, $w \in \Sigma^{d-1}$, and

$$\overline{\mathsf{A}}^*(\mathsf{w}^{*e}, w) = \sum_{i\in C^*}\overline{\mathsf{A}}_i^*(\mathsf{w}^{*e})w_i, \qquad \overline{\mathsf{B}}^*(\mathsf{w}^{*e}, w) = \sum_{i,j\in C^*}\overline{\mathsf{B}}_{ij}(\mathsf{w}^{*e})w_iw_j.$$

We denote by $\mathcal{S}(\zeta, w)$ the set of complex numbers λ such that there exists $\phi \in \mathbb{C}^{n^*}$, $\phi \neq 0$, satisfying (3.5). The following result has been established by Shizuta and Kawashima [75] and Beauchard and Zuazua [4], and equivalent forms of the Kalman condition are also given by Beauchard and Zuazua [4] as well as Coron [17].

Theorem 3.8. *Assume that the matrix* $\overline{\mathsf{A}}_0^*(\mathsf{w}^{*e})$ *is symmetric positive definite, the matrices* $\overline{\mathsf{A}}_i^*(\mathsf{w}^{*e})$*,* $i \in C^*$*, are symmetric, the reciprocity relations* $\overline{\mathsf{B}}_{ij}^*(\mathsf{w}^{*e})^t = \overline{\mathsf{B}}_{ji}^*(\mathsf{w}^{*e})$*,* $i, j \in C^*$*, hold and that the matrix* $\overline{\mathsf{L}}^*(\mathsf{w}^{*e})$ *is symmetric positive semi-definite. Then the following properties are equivalent.*

(Spe_1) *There exists a compensating matrix K defined and C^∞ over Σ^{d-1}. That is, for any $w \in \Sigma^{d-1}$ the matrix $K(w)$ is real, the product $K(w)\overline{\mathsf{A}}_0^*(\mathsf{w}^{*e})$ is skew-symmetric, $K(-w) = -K(w)$, and the matrix*

$$K(w)\,\overline{\mathsf{A}}^*(\mathsf{w}^{*e}, w) + \overline{\mathsf{B}}^*(\mathsf{w}^{*e}, w) + \overline{\mathsf{L}}^*(\mathsf{w}^{*e}),$$

is positive definite.

(Spe_2) *For any $\zeta \in \mathbb{R}$, $\zeta \neq 0$, and any $w \in \Sigma^{d-1}$, the eigenvalues $\lambda \in \mathcal{S}(\zeta, w)$ have a negative real part.*

(Spe_3) *Let $\Psi \in \mathbb{R}^{n^*}\backslash\{0\}$ such that $\overline{\mathsf{B}}^*(\mathsf{w}^{*e}, w)\Psi = \overline{\mathsf{L}}^*(\mathsf{w}^{*e})\Psi = 0$ for some $w \in \Sigma^{d-1}$. Then we have $\zeta\overline{\mathsf{A}}_0^*(\mathsf{w}^{*e})\Psi + \overline{\mathsf{A}}^*(\mathsf{w}^{*e}, w)\Psi \neq 0$ for any $\zeta \in \mathbb{R}$.*

(Spe_4) *There exists $\delta > 0$ such that for any $\zeta \in \mathrm{i}\,\mathbb{R}$, $w \in \Sigma^{d-1}$ and any eigenvalue λ of $\mathcal{S}(\zeta, w)$, we have*

$$\Re(\lambda) \leq \delta \frac{|\zeta|^2}{1 + |\zeta|^2}.$$

(Spe_5) *Letting $\widehat{\mathsf{B}}^{*e} = \big(\overline{\mathsf{A}}_0(\mathsf{w}^{*e})\big)^{-1}\big(\overline{\mathsf{B}}^*(\mathsf{w}^{*e}, w) + \overline{\mathsf{L}}^*(\mathsf{w}^{*e})\big)$ and $\widehat{\mathsf{A}}^{*e} = \big(\overline{\mathsf{A}}_0(\mathsf{w}^{*e})\big)^{-1}\overline{\mathsf{A}}^*(\mathsf{w}^{*e}, w)$ the Kalman condition is satisfied*

$$\operatorname{rank}\big[\,\widehat{\mathsf{B}}^{*e}, \widehat{\mathsf{A}}^{*e}\,\widehat{\mathsf{B}}^{*e}, \ldots, (\widehat{\mathsf{A}}^{*e})^{n^*-1}\,\widehat{\mathsf{B}}^{*e}\,\big] = n^*.$$

The local dissipative properties (Spe_1)-(Spe_5) may also equivalently be formulated with *any* symmetric formulation, not necessarily in normal form. It may be formulated for instance in terms of the linearized natural symmetric form with $\widehat{\mathsf{v}}^* = \mathsf{v}^* - \mathsf{v}^{*e}$

$$\widetilde{\mathsf{A}}_0^*(\mathsf{v}^{*e})\partial_t\widehat{\mathsf{v}}^* + \sum_{i\in C^*} \widetilde{\mathsf{A}}_i^*(\mathsf{v}^{*e})\partial_i\widehat{\mathsf{v}}^* = \sum_{i,j\in C^*} \widetilde{\mathsf{B}}_{ij}^*(\mathsf{v}^{*e})\partial_i\partial_j\widehat{\mathsf{v}}^* - \widetilde{\mathsf{L}}^*(\mathsf{v}^{*e})\widehat{\mathsf{v}}^*. \tag{3.6}$$

Such an equivalence is a direct consequence from the relations at equilibrium $\overline{\mathsf{A}}_0 = (\partial_{\mathsf{w}}\mathsf{v})^t\, \widetilde{\mathsf{A}}_0\, (\partial_{\mathsf{w}}\mathsf{v})$, $\overline{\mathsf{B}}_{ij} = (\partial_{\mathsf{w}}\mathsf{v})^t\, \widetilde{\mathsf{B}}_{ij}^*\, (\partial_{\mathsf{w}}\mathsf{v})$, $\overline{\mathsf{A}}_i = (\partial_{\mathsf{w}}\mathsf{v})^t\, \widetilde{\mathsf{A}}_i^*\, (\partial_{\mathsf{w}}\mathsf{v})$, and $\overline{\mathsf{L}} = (\partial_{\mathsf{w}}\mathsf{v})^t\, \widetilde{\mathsf{L}}\, (\partial_{\mathsf{w}}\mathsf{v})$, which show in particular that (3.4) and (3.6) have the same spectrum $\mathcal{S}(\zeta, w)$.

A physical interpretation of the Shizuta-Kawashima condition may be obtained from (Spe_3) which means that all waves associated with the hyperbolic operator $\overline{\mathsf{A}}_0^*(\mathsf{w}^{*e})\partial_t + \sum_{i\in C^*} \overline{\mathsf{A}}_i^*(\mathsf{w}^{*e})\partial_i$ lead to dissipation, i.e., entropy production, since there are not in the nullspaces of $\overline{\mathsf{B}}^*$ and $\overline{\mathsf{L}}^*$. Finally, even if it is not known in general if the matrix $K(w)$ may be written $\sum_{j\in C^*} K^j w_j$, it is generally possible to obtain compensating matrices in this form in practical applications.

3.3.2 Global existence

We investigate the existence of solutions globally in time around equilibrium states. We assume that the system is strictly dissipative in the sense of Theorem 3.8.

(Pde_5) *The linearized system is strictly dissipative in the sense of Theorem 3.8.*

The following local properties of the source term required to obtain a priori estimates as well as decay estimates has been introduced by Giovangigli and Massot [38] and may be deduced from (S_1)-(S_7) as obsrved by Kawashima and Yong [53].

Proposition 3.9. *There exists a neighborhood of v^{*e} in $\mathsf{O}_{\mathsf{v}^*}$ and a positive constant $\delta > 0$ such that for any v^* in this neighborhood we have*

$$\delta\big|\widetilde{\Omega}^*(\mathsf{v}^*)\big|^2 \leq -\big\langle \mathsf{v}^* - \mathsf{v}^{*e}, \widetilde{\Omega}^*(\mathsf{v}^*)\big\rangle.$$

Proof. We introduce the decomposition $\mathbb{R}^{n^*} = \mathcal{E} \oplus \mathcal{E}^\perp$ and write for convenience $\mathsf{v}^* = (\mathsf{v}_{\mathrm{e}}^*, \mathsf{v}_{\mathrm{r}}^*)^t$. We then note that $\widetilde{\Omega}^* = (0, \widetilde{\Omega}_{\mathrm{r}}^*)^t$ or equivalently $\widetilde{\Omega}_{\mathrm{e}}^* = 0$ from (S_5), and that $\widetilde{\Omega}^*(\mathsf{v}_{\mathrm{e}}^*, 0) = 0$ since $\mathsf{v}^* \in \mathcal{E}$ implies that $\widetilde{\Omega}^* = 0$ also from (S_5). This yields in particular that $\widetilde{\Omega}_{\mathrm{r}}^*(\mathsf{v}_{\mathrm{e}}^*, \mathsf{v}_{\mathrm{r}}^*) = \widetilde{\Omega}_{\mathrm{r}}^*(\mathsf{v}_{\mathrm{e}}^*, \mathsf{v}_{\mathrm{r}}^*) - \widetilde{\Omega}_{\mathrm{r}}^*(\mathsf{v}_{\mathrm{e}}^*, 0)$ so that

$$\widetilde{\Omega}_{\mathrm{r}}^* = \int_0^1 \partial_{\mathsf{v}_{\mathrm{r}}^*}\widetilde{\Omega}_{\mathrm{r}}^*(\mathsf{v}_{\mathrm{e}}^*, \theta\mathsf{v}_{\mathrm{r}}^*)\,\mathrm{d}\theta\ \mathsf{v}_{\mathrm{r}}^*,$$

in such a way that

$$-\big\langle \mathsf{v}^* - \mathsf{v}^{*e}, \widetilde{\Omega}^*(\mathsf{v}^*)\big\rangle = -\big\langle \mathsf{v}^*, \widetilde{\Omega}^*(\mathsf{v}^*)\big\rangle = -\Big\langle \int_0^1 \partial_{\mathsf{v}_\mathrm{r}^*} \widetilde{\Omega}_\mathrm{r}^*(\mathsf{v}_\mathrm{e}^*, \theta \mathsf{v}_\mathrm{r}^*)\,\mathrm{d}\theta\ \mathsf{v}_\mathrm{r}^*, \mathsf{v}_\mathrm{r}^*\Big\rangle.$$

On the other hand, for $\mathsf{v}_\mathrm{e}^* = \mathsf{v}_\mathrm{e}^{*e}$ the matrix $-\partial_{\mathsf{v}_\mathrm{r}^*}\widetilde{\Omega}_\mathrm{r}^*(\mathsf{v}_\mathrm{e}^*, 0)$ is symmetric positive definite since it is of maximal rank which is the dimension of $\mathcal{E}^\perp$. We thus deduce that $\delta\|\mathsf{v}_\mathrm{r}^*\| \leq \|\widetilde{\Omega}^*\| \leq (1/\delta)\|\mathsf{v}_\mathrm{r}^*\|$ and $-\big\langle \mathsf{v}^* - \mathsf{v}^{*e}, \widetilde{\Omega}^*(\mathsf{v}^*)\big\rangle \geq \delta' \|\mathsf{v}_\mathrm{r}^*\|^2$ in the neighborhood of $\mathsf{v}^{*e} = (\mathsf{v}_\mathrm{e}^{*e}, 0)^t$ and the proof is complete. ☐

The following Theorem is established in [50, 38] under assumptions (Pde_1)-(Pde_5) and only *local* diffeomorphisms are required in the proof.

Theorem 3.10. *Let $d \geq 1$ and $l \geq [d/2] + 2$ be integers and consider the system* (3.3)*. Then there exists $b > 0$ small enough such that if w^{*0} satisfies $\|\mathsf{w}^{*0} - \mathsf{w}^{*e}\|_l < b$, there exists a unique global solution w^* to the Cauchy problem*

$$\overline{\mathsf{A}}_0^* \partial_t \mathsf{w}^* + \sum_{i \in C^*} \overline{\mathsf{A}}_i^* \partial_i \mathsf{w}^* = \sum_{i,j \in C^*} \partial_i(\overline{\mathsf{B}}_{ij}^* \partial_j \mathsf{w}^*) + \overline{\mathcal{T}}^* + \overline{\Omega}^*,$$

with initial condition

$$\mathsf{w}^*(0, x) = \mathsf{w}^{*0}(x),$$

such that

$$\begin{aligned} \mathsf{w}_\mathrm{I}^* - \mathsf{w}_\mathrm{I}^{*e} &\in C^0\big([0,\infty), W_2^l(\mathbb{R}^d)\big) \cap C^1\big([0,\infty), W_2^{l-1}(\mathbb{R}^d)\big), \\ \mathsf{w}_\mathrm{II}^* - \mathsf{w}_\mathrm{II}^{*e} &\in C^0\big([0,\infty), W_2^l(\mathbb{R}^d)\big) \cap C^1\big([0,\infty), W_2^{l-2}(\mathbb{R}^d)\big), \end{aligned}$$

and

$$\begin{aligned} \partial_x \mathsf{w}_\mathrm{I}^* &\in L^2\big((0,\infty), W_2^{l-1}(\mathbb{R}^d)\big), \\ \partial_x \mathsf{w}_\mathrm{II}^* &\in L^2\big((0,\infty), W_2^{l}(\mathbb{R}^d)\big). \end{aligned}$$

Furthermore, w^* satisfies the estimate

$$\|\mathsf{w}^*(t) - \mathsf{w}^{*e}\|_l^2 + \int_0^t \big(\|\partial_x \mathsf{w}_\mathrm{I}^*(\tau)\|_{l-1}^2 + \|\partial_x \mathsf{w}_\mathrm{II}^*(\tau)\|_l^2\big)\,\mathrm{d}\tau \leq C\|\mathsf{w}^{*0} - \mathsf{w}^{*e}\|_l^2,$$

where C is a positive constant and $\sup_{x\in\mathbb{R}^d} |\mathsf{w}^*(t) - \mathsf{w}^e|$ goes to zero as $t \to \infty$.

We may further investigate decay estimates under stronger assumptions [79, 50, 51, 38]. A general study of decay estimates for hyperbolic equations has recently been given by Beauchard and Zuazua [4].

Theorem 3.11. *Let $d \geq 1$, $l \geq [d/2] + 3$ and $\mathsf{w}^{*0}(x)$ be given, such that*

$$\mathsf{w}^{*0} - \mathsf{w}^{*e} \in W_2^l(\mathbb{R}^d) \cap L^p(\mathbb{R}^d),$$

with $p = 1$ if $d = 1$ and $p \in [1, 2)$ if $d \geq 2$. Then, if $\|\mathsf{w}^{*0} - \mathsf{w}^{*e}\|_l$ and $\|\mathsf{w}^{*0} - \mathsf{w}^{*e}\|_{L^p}$ are small enough, the unique global solution to the Cauchy problem satisfies the decay estimate

$$\|\mathsf{w}^*(t) - \mathsf{w}^{*e}\|_{l-2} \leq C(1+t)^{-\gamma}\left(\|\mathsf{w}^{*0} - \mathsf{w}^{*e}\|_{l-2} + \|\mathsf{w}^{*0} - \mathsf{w}^{*e}\|_{L^p}\right),$$

where C is a positive constant and $\gamma = d(1/2p - 1/4)$.

3.4 Dependence on a parameter

The asymptotic stability of equilibrium states for quasilinear systems of partial differential equations is by itself an important question. However, the coefficients of these systems often depend on parameters that are denoted by $\epsilon^* \in \mathbb{R}^{m^*}$ where $m^* \geq 1$ and the continuous dependence of solutions on these parameters is then a natural question.

We thus consider a system of partial differential equations in the form

$$\partial_t \mathsf{u}^* + \sum_{i\in C^*} \mathsf{A}_i^*(\mathsf{u}^*, \epsilon^*)\partial_i \mathsf{u}^* = \sum_{i,j\in C^*} \partial_i\big(\mathsf{B}_{ij}^*(\mathsf{u}^*, \epsilon^*)\partial_j \mathsf{u}^*\big) + \Omega^*(\mathsf{u}^*, \epsilon^*), \tag{3.7}$$

where $(\mathsf{u}^*, \epsilon^*) \in \mathsf{O}_{(\mathsf{u}^*,\epsilon^*)}$ and $\mathsf{O}_{(\mathsf{u}^*,\epsilon^*)}$ is an open set of $\mathbb{R}^{n^*} \times \mathbb{R}^{m^*}$. The continuous dependence of solutions with respect to the parameter $\epsilon^* \in \mathbb{R}^{m^*}$ has been investigated [37] and is summarized here.

It is first assumed that the system (3.1) admits an equilibrium point $\mathsf{u}^{*\mathrm{e}}$ independent of ϵ^* and that $\mathsf{O}_{(\mathsf{w}^*,\epsilon^*)}$ contains a subset in the form $\mathsf{O}_{\mathsf{w}^*} \times \mathsf{K}_{\epsilon^*}$, where $\mathsf{O}_{\mathsf{w}^*}$ is an open set of $\mathbb{R}^{n^*}$ independent of ϵ^* and K_{ϵ^*} a compact set of $\mathbb{R}^{m^*}$ independent of w^*. A main idea for local in time solutions is that all usual estimates can be made uniform with respect to the parameter ϵ^* since we are considering a compact set K_{ϵ^*}. Thanks to the local existence theorem and to *uniform stability estimates*, global solutions are next obtained for all $\epsilon^* \in \mathsf{K}_{\epsilon^*}$. Continuity with respect to the parameter ϵ^* is then a consequence of the continuity over finite time interval and of *uniform asymptotic stability* [37]. Similarly, decay estimates may also be established globally with respect to the parameter $\epsilon^* \in \mathbb{R}^{m^*}$ [37].

4 Asymptotic stability for supercritical fluids

The abstract results established in the previous section are now applied to the system of partial differential equations modeling supercritical reactive fluids. We first investigate the existence of constant equilibrium points and then evaluate symmetric forms of the system of partial differential equations. Local dissipativity and global existence results are then obtained and these results encompasses in particular the situations of undercooled vapors and superheated liquids.

4.1 Chemical equilibrium

4.1.1 Definition of chemical equilibrium

We discuss in this section chemical equilibrium points in atom conservation manifolds under the structural assumptions $(\mathcal{T}_1)$-$(\mathcal{T}_4)$, (PG), and (C_1)-(C_3).

Proposition 4.1. *Assume that Properties* $(\mathcal{T}_1)$-$(\mathcal{T}_4)$, (PG), *and* (C_1)-(C_3) *hold. Then for any* $z \in \mathcal{O}_z$, *the following statements are equivalent :*

(*i*) *The entropy production due to chemistry vanishes* $\mathfrak{v}_\omega = -\langle \mu, \omega \rangle = 0$.

(*ii*) *The reaction rates of progress vanish* $\tau_j = 0$, $j \in \mathfrak{R}$.

(*iii*) *The species production rates vanish* $\omega_k = 0$, $k \in \mathfrak{S}$.

(*iv*) *The vector* $\mu = (\mu_1, \dots, \mu_n)^t$ *belongs to* $\mathcal{R}^\perp$.

Proof. From (2.30) and (C_3) we obtain that $\mathfrak{v}_\omega = 0$ implies $\langle \mu, \nu_j \rangle = 0$, $j \in \mathfrak{R}$, and so $\tau_j = 0$, $j \in \mathfrak{R}$, and we have established that (*i*) implies (*ii*). The fact that (*ii*) implies (*iii*) is a consequence of the relations $\omega_k = \sum_{j \in \mathfrak{R}} \tau_j \nu_{kj}$, $k \in \mathfrak{S}$. We deduce from the definition $\mathfrak{v}_\omega = -\langle \mu, \omega \rangle$ that (*iii*) implies (*i*) so that the three statements (*i*), (*ii*), and (*iii*) are equivalent. Finally, it is easily established that (*iv*) is equivalent to $\langle \mu, \nu_j \rangle = 0$, $j \in \mathfrak{R}$, so that (*ii*) and (*iv*) are also equivalent and the proof is complete. ☐

Definition 4.2. *A point* $z^{\mathrm{e}} \in \mathcal{O}_z$ *which satisfies the equivalent properties of Proposition 4.1 is termed an equilibrium point.*

We are only interested here in positive equilibrium states with $\rho_i > 0$, $i \in \mathfrak{S}$, which are in the interior of the composition space. Spurious points with zero mass fractions where the source terms ω_k, $k \in \mathfrak{S}$, also vanish—termed ‘boundary equilibrium points’—are of a different nature [34]. Properly structured chemical kinetic mechanisms automatically exclude such spurious points unless some element is missing in the mixture [34].

4.1.2 Existence of equilibrium points

When defining chemical equilibrium states, it is necessary to use equations expressing the fact that atoms are neither created nor destroyed by chemical reactions. These atom conservation relations are typically in the form $\langle \varrho - \varrho^{\mathrm{f}}, \mathsf{M}^{-1}\mathfrak{a} \rangle = 0$, where $\mathfrak{a}$ is an atom vector and ϱ^{f} is a given state, and more generally in the form $\langle \varrho - \varrho^{\mathrm{f}}, \mathsf{x} \rangle = 0$, where $\mathsf{x} \in (\mathsf{M}\,\mathcal{R})^\perp$. As a consequence, equilibrium points have to be investigated in atom conservation affine manifolds in the form $\varrho^{\mathrm{f}} + \mathsf{M}\,\mathcal{R}$. Different equilibrium points may be obtained with various thermal properties kept fixed. We discuss in this section the existence of equilibrium points at fixed temperature and mass density. Existence of equilibrium states is generally obtained by extremalizing a thermodynamic functional over an atom conservation affine subspace and the following theorem is established in [40].

Theorem 4.3. *Assume that Properties* $(\mathcal{T}_1)$-$(\mathcal{T}_4)$, (PG), *and* (C_1)-(C_3) *hold. Let* $\varrho^{\mathrm{f}} = (\rho_1^{\mathrm{f}}, \dots, \rho_n^{\mathrm{f}})^t$ *with* $\rho_i^{\mathrm{f}} > 0$, $i \in \mathfrak{S}$, *and* $T^{\mathrm{e}} > 0$ *and assume that*

$$\forall \varrho \in (\varrho^{\mathrm{f}} + \mathsf{M}\,\mathcal{R}) \cap (0,\infty)^n \qquad (\rho_1, \dots, \rho_n, T^{\mathrm{e}})^t \in \mathcal{O}_z. \tag{4.1}$$

Further assume that $\mathcal{E} - \mathcal{E}^{\mathrm{PG}} - T(\mathcal{S} - \mathcal{S}^{\mathrm{PG}})$ *admits a smooth extension to the closure* $(\varrho^{\mathrm{f}} + \mathsf{M}\,\mathcal{R}) \cap [0,\infty)^n$ *of the reaction simplex. Then there exists a unique equilibrium state* ϱ^{e} *in the simplex* $(\varrho^{\mathrm{f}} + \mathsf{M}\,\mathcal{R}) \cap (0,\infty)^n$.

The thermodynamic functional to be maximized or minimized depends on which thermal properties are kept fixed and we refer to [34] for instance for equilibrium points with h and p fixed typical of laminar flames, in an ideal gas framework.

Remark 4.4. *In practical applications, the space* $\mathcal{R}$ *spanned by the reaction vectors* ν_j, $j \in \mathfrak{S}$, *is the maximum space* $\mathcal{R} = \mathcal{A}^\perp$ *so that equilibrium is achieved when* $\mu \in \mathcal{A}$. *Equilibrium points depend on the stoichiometric coefficients only through the vector space* $\mathcal{R}$ *spanned by the reaction vectors* ν_j, $j \in \mathfrak{R}$. *On the contrary, forward and backward reaction vectors* ν_j^{f}, *and* ν_j^{b}, $j \in \mathfrak{R}$, *are important for the production rates and in order to rule out 'boundary equilibrium points' [34].*

Remark 4.5. *Smoothness of equilibrium points as functions* T^{e} *and of the orthogonal projection of* ϱ^{f} *onto* $(\mathsf{M}\,\mathcal{R})^\perp$ *is easily obtained by using the implicit function theorem [55, 34].*

We now establish the existence of constant equilibrium states and the following result is a direct consequence of Theorem 4.3.

Corollary 4.6. *Keep the assumptions of Theorem 4.3 and let* $\boldsymbol{v}^{\mathrm{e}} \in \mathbb{R}^d$. *Then, denoting* $\mathsf{z}^{\mathrm{e}} = (\rho_1^{\mathrm{e}}, \dots, \rho_n^{\mathrm{e}}, \boldsymbol{v}^{\mathrm{e}}, T^{\mathrm{e}})^t$ *and letting* $\mathsf{u}^{\mathrm{e}} = \mathsf{u}^{\mathrm{e}}(\mathsf{z}^{\mathrm{e}}) = \big(\rho_1^{\mathrm{e}}, \dots, \rho_n^{\mathrm{e}}, \rho^{\mathrm{e}}\boldsymbol{v}^{\mathrm{e}}, \mathcal{E}^{\mathrm{e}} + \frac{1}{2}\rho^{\mathrm{e}}|\boldsymbol{v}^{\mathrm{e}}|^2\big)^t$ *the state* u^{e} *is an equilibrium state*

$$\Omega(\mathsf{u}^{\mathrm{e}}) = 0. \tag{4.2}$$

The equilibrium states for other variables will also be denoted with the superscript ^{e}. Thermodynamic stability holds for these equilibrium states in the sense that $\partial^2_{uu}\mathcal{S}$ is negative definite, from Definition 4.2.

4.2 Local symmetrization

We investigate in this section symmetric forms for the system of partial differential equations modeling nonideal fluids (2.1)–(2.3). We define the mathematical entropy σ by

$$\sigma = -\frac{\mathcal{S}}{R}, \tag{4.3}$$

where the $1/R$ factor is introduced for convenience. It is reminded that the velocity components of all quantities in $\mathbb{R}^{n+d+1} = \mathbb{R}^n \times \mathbb{R}^d \times \mathbb{R}$ are denoted as vectors of $\mathbb{R}^d$ for the sake of notational simplicity and the corresponding partitionning is also used for matrices. The following theorem generalizes the symmetric form for multicomponent flow previously obtained for ideal gas mixtures, ideal type diffusion, and chemical kinetics of mass action type [38].

Theorem 4.7. *Assume that* $(\mathcal{T}_1)$-$(\mathcal{T}_4)$, (PG), (C_1)-(C_3), *and* (Tr_1)-(Tr_2) *hold. The function* σ *is a mathematical entropy for the system* (2.1)–(2.3) *and the corresponding entropic variable is given by*

$$\mathsf{v} = (\partial_{\mathsf{u}}\sigma)^t = \frac{1}{RT}\Big(\mathcal{G}_1 - \tfrac{1}{2}|\boldsymbol{v}|^2, \dots, \mathcal{G}_n - \tfrac{1}{2}|\boldsymbol{v}|^2, \boldsymbol{v}, -1\Big)^t. \tag{4.4}$$

For any $\mathsf{u} \in \mathcal{O}_{\mathsf{u}}$ *there exists an open subdomain* $\mathsf{O}_{\mathsf{u}} \subset \mathcal{O}_{\mathsf{u}}$ *such that the map* $\mathsf{u} \to \mathsf{v}$ *is a local* $C^\varkappa$ *diffeomorphism from* O_{u} *onto an open set* O_{v}. *The system written in term of the entropic variable* v *is in the form*

$$\widetilde{\mathsf{A}}_0(\mathsf{v})\partial_t\mathsf{v} + \sum_{i\in C}\widetilde{\mathsf{A}}_i(\mathsf{v})\partial_i\mathsf{v} = \sum_{i,j\in C}\partial_i\big(\widetilde{\mathsf{B}}_{ij}(\mathsf{v})\partial_j\mathsf{v}\big) + \widetilde{\Omega}(\mathsf{v}), \tag{4.5}$$

with $\widetilde{\mathsf{A}}_0 = \partial_{\mathsf{v}}\mathsf{u}$, $\widetilde{\mathsf{A}}_i = \mathsf{A}_i\partial_{\mathsf{v}}\mathsf{u}$, $\widetilde{\mathsf{B}}_{ij} = \mathsf{B}_{ij}\partial_{\mathsf{v}}\mathsf{u}$, *and* $\widetilde{\Omega} = \Omega$, *is of the local symmetric form, that is,* (S_1)-(S_7) *hold. The matrix* $\widetilde{\mathsf{A}}_0$ *is given by*

$$\widetilde{\mathsf{A}}_0 = \begin{bmatrix} \Lambda & & \mathit{Sym} \\ \boldsymbol{v}\otimes\Lambda\mathbb{1} & \langle\Lambda\mathbb{1}, \mathbb{1}\rangle\boldsymbol{v}\otimes\boldsymbol{v} + \rho RT\mathbb{I}_d & \\ \Lambda\mathscr{g} & \langle\Lambda\mathscr{g}, \mathbb{1}\rangle\boldsymbol{v}^t + \rho RT\boldsymbol{v}^t & \widetilde{\mathsf{A}}_0^{T,T} \end{bmatrix}, \tag{4.6}$$

where $\Lambda = \rho R \mathit{\Gamma}^{-1}$ *and* $\mathit{\Gamma}^{-1}$ *is the inverse of the matrix* $\mathit{\Gamma}_{kl} = \rho\widetilde{\partial}_{\rho_k}\mathcal{G}_l/T = \rho\widetilde{\partial}_{\rho_l}\mathcal{G}_k/T$ *defined in Proposition 2.15 and where*

$$\mathscr{g}_i = \mathcal{G}_i - T\widetilde{\partial}_T\mathcal{G}_i + \tfrac{1}{2}|\boldsymbol{v}|^2 = \widetilde{\partial}_{\rho_i}\mathcal{E} + \tfrac{1}{2}|\boldsymbol{v}|^2, \qquad i \in \mathfrak{S},$$

$$\widetilde{\mathsf{A}}_0^{T,T} = \langle \Lambda\mathscr{g}\,,\mathscr{g}\,\rangle + \rho RT|\boldsymbol{v}|^2 + RT^2\widetilde{\partial}_T\mathcal{E}.$$

Since $\widetilde{\mathsf{A}}_0$ *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* $\widetilde{\mathsf{A}} = \sum_{i\in C}\xi_i\widetilde{\mathsf{A}}_i$ *the matrix* $\widetilde{\mathsf{A}}$ *is given by*

$$\widetilde{\mathsf{A}} = \boldsymbol{v}\cdot\boldsymbol{\xi}\,\widetilde{\mathsf{A}}_0 + RT\begin{bmatrix} 0 & & \mathit{Sym} \\ \boldsymbol{\xi}\otimes\varrho & \rho(\boldsymbol{\xi}\otimes\boldsymbol{v} + \boldsymbol{v}\otimes\boldsymbol{\xi}) & \\ \boldsymbol{v}\cdot\boldsymbol{\xi}\,\varrho^t & \boldsymbol{v}\cdot\boldsymbol{\xi}\,\rho\boldsymbol{v}^t + (\mathcal{E} + p + \tfrac{1}{2}\rho|\boldsymbol{v}|^2)\boldsymbol{\xi}^t & 2\boldsymbol{v}\cdot\boldsymbol{\xi}\,(\mathcal{E} + p + \tfrac{1}{2}\rho|\boldsymbol{v}|^2) \end{bmatrix}. \tag{4.7}$$

Moreover, we have the decomposition associated with (2.11), (2.12), *and* (2.13)

$$\widetilde{\mathsf{B}}_{ij} = RT\,\widetilde{\mathsf{B}}^L\delta_{ij} + \kappa RT\,\widetilde{\mathsf{B}}^\kappa_{ij} + \eta RT\,\widetilde{\mathsf{B}}^\eta_{ij}, \tag{4.8}$$

where

$$\widetilde{\mathsf{B}}^L = \frac{1}{T}\begin{bmatrix} L^{n,n} & & \mathit{Sym} \\ 0_{d,n} & 0_{d,d} & \\ L_{e\bullet} & 0_{1,d} & L_{e,e} \end{bmatrix}, \tag{4.9}$$

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* $\widetilde{\mathsf{B}}^\kappa_{ij}$ *and* $\widetilde{\mathsf{B}}^\eta_{ij}$*,* $i,j\in C$*, are given by*

$$\sum_{i,j\in C}\xi_i\zeta_j\widetilde{\mathsf{B}}^\kappa_{ij} = \begin{bmatrix} 0_{n,n} & 0_{n,d} & 0_{n,1} \\ 0_{d,n} & \boldsymbol{\xi}\otimes\boldsymbol{\zeta} & \boldsymbol{v}\cdot\boldsymbol{\zeta}\,\boldsymbol{\xi} \\ 0_{1,n} & \boldsymbol{v}\cdot\boldsymbol{\xi}\,\boldsymbol{\zeta}^t & \boldsymbol{v}\cdot\boldsymbol{\xi}\,\boldsymbol{v}\cdot\boldsymbol{\zeta} \end{bmatrix}, \tag{4.10}$$

$$\sum_{i,j\in C}\xi_i\zeta_j\widetilde{\mathsf{B}}^\eta_{ij} = \begin{bmatrix} 0_{n,n} & 0_{n,d} & 0_{n,1} \\ 0_{d,n} & \boldsymbol{\xi}\cdot\boldsymbol{\zeta}\mathbb{I}_d + \boldsymbol{\zeta}\otimes\boldsymbol{\xi} - \frac{2}{d}\boldsymbol{\xi}\otimes\boldsymbol{\zeta} & \boldsymbol{\xi}\cdot\boldsymbol{\zeta}\,\boldsymbol{v} + \boldsymbol{v}\cdot\boldsymbol{\xi}\,\boldsymbol{\zeta} - \frac{2}{d}\boldsymbol{v}\cdot\boldsymbol{\zeta}\,\boldsymbol{\xi} \\ 0_{1,n} & \boldsymbol{\xi}\cdot\boldsymbol{\zeta}\,\boldsymbol{v}^t + \boldsymbol{v}\cdot\boldsymbol{\zeta}\,\boldsymbol{\xi}^t - \frac{2}{d}\boldsymbol{v}\cdot\boldsymbol{\xi}\,\boldsymbol{\zeta}^t & \boldsymbol{\xi}\cdot\boldsymbol{\zeta}\,\boldsymbol{v}\cdot\boldsymbol{v} + (1-\frac{2}{d})\boldsymbol{v}\cdot\boldsymbol{\xi}\,\boldsymbol{v}\cdot\boldsymbol{\zeta} \end{bmatrix}. \tag{4.11}$$

Finally, the equilibrium manifold is given by

$$\mathscr{E} = (\mathsf{M}\,\mathcal{R})^\perp \times \mathbb{R}^d \times \mathbb{R}, \tag{4.12}$$

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

Proof. In order to establish that σ is an entropy we establish that properties (E_1)-(E_7) are satisfied. In order to establish that $\partial^2_{\mathsf{uu}}\sigma = \partial_{\mathsf{u}}(\partial_{\mathsf{u}}\sigma)^t$ is positive definite we can directly evaluate the differentials of $\partial^2_{\mathsf{uu}}\sigma$ in terms of that of $\partial^2_{uu}\mathcal{S}$. After lengthy but straightforward algebra it is established that for any $\mathsf{u}\in\mathcal{O}_{\mathsf{u}}$ and $\mathsf{x}\in\mathbb{R}^{n+d+1}$, and writting the components of u as $\mathsf{u} = \mathsf{u}(\mathsf{z})$, we have

$$-R\big\langle(\partial^2_{\mathsf{uu}}\sigma)\mathsf{x},\mathsf{x}\big\rangle = \big\langle(\partial^2_{uu}\mathcal{S})\mathsf{x}_u\,,\mathsf{x}_u\,\big\rangle - \frac{1}{\rho T}\big|\boldsymbol{v}\langle\mathbb{1},\mathsf{x}_\varrho\rangle - \mathbf{x}_{\boldsymbol{v}}\big|^2,$$

where $\mathsf{x} = \big(\mathsf{x}_1,\dots,\mathsf{x}_n,\mathbf{x}_{\boldsymbol{v}},\mathsf{x}_{\mathcal{E}}\big)^t$, $\mathbf{x}_{\boldsymbol{v}} = \big(\mathsf{x}_{n+1},\dots,\mathsf{x}_{n+d}\big)^t$, $\mathsf{x}_\varrho = \big(\mathsf{x}_1,\dots,\mathsf{x}_n\big)^t$, and $\mathsf{x}_u = \big(\mathsf{x}_1,\dots,\mathsf{x}_n,\mathsf{x}_{\mathcal{E}} + \frac{1}{2}\langle\mathsf{x}_\varrho,\mathbb{1}\rangle|\boldsymbol{v}|^2 - \boldsymbol{v}\cdot\mathbf{x}_{\boldsymbol{v}}\big)^t$. Since $\partial^2_{uu}\mathcal{S}$ is negative definite, $\rho > 0$, and $T > 0$, it is easily concluded that $\partial^2_{\mathsf{uu}}\sigma$ is positive definite and (E_1) is established. The entropy fluxes are then taken in the form $\mathsf{q}_i = \sigma v_i$, $i\in C$ and the relations $\partial_{\mathsf{u}}\sigma\partial_{\mathsf{u}}\mathsf{F}_i = \partial_{\mathsf{u}}\mathsf{q}$ are easily checked in the equivalent form $\partial_{\mathsf{u}}\sigma\partial_{\mathsf{z}}\mathsf{F}_i = \partial_{\mathsf{z}}\mathsf{q}$ after a little algebra so that (E_2) is established. Properties $(\mathsf{E}_3)(\mathsf{E}_4)$ are equivalent to $(\mathsf{S}_3)(\mathsf{S}_4)$ and are then established directly by inspecting the matrices $\widetilde{\mathsf{B}}_{ij}$, $i,j\in C$.

The matrices $\widetilde{\mathsf{A}}_0$, $\widetilde{\mathsf{A}}_i$, $i\in C$, and $\widetilde{\mathsf{B}}_{ij}$, $i,j\in C$, are easily evaluated by using the natural variable z after lengthy calculations that are omitted. The matrices matrices $\widetilde{\mathsf{A}}_0$, $\widetilde{\mathsf{A}}_i$, $i\in C$, are symmetric and $\widetilde{\mathsf{A}}_0$ is positive definite since the Hessian matrix $(\widetilde{\mathsf{A}}_0)^{-1} = \partial^2_{\mathsf{uu}}\sigma$ is positive definite. This may also be checked directly, letting $\mathsf{x} = (\mathsf{x}_1, \dots, \mathsf{x}_n, \mathsf{x}_{\boldsymbol{v}}, \mathsf{x}_{\mathcal{E}})^t$, $\boldsymbol{\mathsf{x}}_{\boldsymbol{v}} = (\mathsf{x}_{n+1}, \dots, \mathsf{x}_{n+d})^t$, and $\mathsf{x}_{\varrho} = (\mathsf{x}_1, \dots, \mathsf{x}_n)^t$, since a direct calculation yields

$$\langle \widetilde{\mathsf{A}}_0 \mathsf{x}, \mathsf{x} \rangle = \big\langle \Lambda(\mathsf{x}_{\varrho} + \boldsymbol{\mathsf{x}}_{\boldsymbol{v}} \cdot \boldsymbol{v} \mathbb{1} + \mathsf{x}_{\mathcal{E}} \boldsymbol{g}), (\mathsf{x}_{\varrho} + \boldsymbol{\mathsf{x}}_{\boldsymbol{v}} \cdot \boldsymbol{v} \mathbb{1} + \mathsf{x}_{\mathcal{E}} \boldsymbol{g}) \big\rangle + \rho RT (\boldsymbol{\mathsf{x}}_{\boldsymbol{v}} + \mathsf{x}_{\mathcal{E}} \boldsymbol{v}) \cdot (\boldsymbol{\mathsf{x}}_{\boldsymbol{v}} + \mathsf{x}_{\mathcal{E}} \boldsymbol{v}) + \mathsf{x}_{\mathcal{E}}^2 RT^2 \widetilde{\partial}_T \mathcal{E},$$

so that $\widetilde{\mathsf{A}}_0$ is positive definite from thermodynamic stability. Similarly we have (4.8) and the expressions of $\widetilde{\mathsf{B}}^L$, $\widetilde{\mathsf{B}}^{\kappa}_{ij}$, and $\widetilde{\mathsf{B}}^{\eta}_{ij}$ directly yields the reciprocity relations of Property (S_3). Finally, for any $\boldsymbol{\xi} \in \mathbb{R}^d$, the matrix $\sum_{i,j \in C} \xi_i \xi_j \delta_{ij} \widetilde{\mathsf{B}}^L = (\sum_{i \in C} \xi_i^2) \widetilde{\mathsf{B}}^L$ is positive semi-definite since L is positive semi-definite, whereas for any $\mathsf{x} = (\mathsf{x}_1, \dots, \mathsf{x}_n, \boldsymbol{\mathsf{x}}_{\boldsymbol{v}}, \mathsf{x}_{\mathcal{E}})^t$ we have

$$\Big\langle \Big(\sum_{i,j \in C} \xi_i \xi_j \widetilde{\mathsf{B}}^{\kappa}_{ij} \Big) \mathsf{x}, \mathsf{x} \Big\rangle = \big(\boldsymbol{\xi} \cdot (\boldsymbol{\mathsf{x}}_{\boldsymbol{v}} + \boldsymbol{v} \mathsf{x}_{\mathcal{E}}) \big)^2,$$

$$\Big\langle \Big(\sum_{i,j \in C} \xi_i \xi_j \widetilde{\mathsf{B}}^{\eta}_{ij} \Big) \mathsf{x}, \mathsf{x} \Big\rangle = \big(1 - \tfrac{2}{d}\big) \big(\boldsymbol{\xi} \cdot (\boldsymbol{\mathsf{x}}_{\boldsymbol{v}} + \boldsymbol{v} \mathsf{x}_{\mathcal{E}}) \big)^2 + |\boldsymbol{\xi}|^2 \big| \boldsymbol{\mathsf{x}}_{\boldsymbol{v}} + \boldsymbol{v} \mathsf{x}_{\mathcal{E}} \big|^2,$$

so that $\sum_{i,j \in C} \xi_i \xi_j \widetilde{\mathsf{B}}^{\kappa}_{ij}$ and $\sum_{i,j \in C} \xi_i \xi_j \widetilde{\mathsf{B}}^{\eta}_{ij}$ are positive semi-definite for any dimension $d \geq 1$ keeping in mind that $\sum_{i,j \in C} \xi_i \xi_j \widetilde{\mathsf{B}}^{\eta}_{ij} = 0$ when $d = 1$. Therefore, Properties $(\mathsf{S}_3)(\mathsf{S}_4)$ are established, and thus $(\mathsf{E}_3)(\mathsf{E}_4)$ are established.

We now investigate the structure and properties of the source term $\widetilde{\Omega} = (m_1 \omega_1, \dots, m_n \omega_n, \mathbf{0}, 0)^t$. We have defined the equilibrium manifold with (4.12) so that $\mathscr{E}^{\perp} = (\mathsf{M}\, \mathcal{R}) \times \{0\}^d \times \{0\}$ and thus by construction $\widetilde{\Omega} \in \mathscr{E}^{\perp}$. From Proposition 4.1, we obtain $\widetilde{\Omega} = 0$ if and only if $\mu \in \mathcal{R}^{\perp}$, and it is easy to check that $\mu \in \mathcal{R}^{\perp}$ if and only if $\mathsf{v} \in \mathscr{E}$. More specifically, if $\mu \in \mathcal{R}^{\perp}$, then $(\mathcal{G}_1, \dots, \mathcal{G}_n)^t \in \mathsf{M}^{-1} (\mathcal{R})^{\perp} = (\mathsf{M}\, \mathcal{R})^{\perp}$ since $\mathcal{G}_k = RT \mu_k / m_k$, and we know that $\mathbb{1} \in (\mathsf{M}\, \mathcal{R})^{\perp}$ from Lemma 2.5 so that $\mathsf{v} \in \mathscr{E}$ and the proof of the converse is similar. In addition, we know from Proposition 4.1, that $\widetilde{\Omega} = 0$ if and only if $\langle \mu, \omega \rangle = 0$. A straightforward calculation, however, yields that $\langle \mu, \omega \rangle = \langle \mathsf{v}, \widetilde{\Omega} \rangle$ and we have established that $\widetilde{\Omega} = 0$ if and only if $\mathsf{v} \in \mathscr{E}$ and if and only if $\langle \mathsf{v}, \widetilde{\Omega} \rangle = \langle \mathsf{v}, \Omega \rangle = 0$ and that (S_5) and (E_5) hold.

We now have to evaluate the jacobian matrix of the source term $\partial_{\mathsf{v}} \widetilde{\Omega}$ at equilibrium. To this aim, we define $(\mathsf{M}\, \nu_j^{\mathrm{f}})^{\star} = \big(\mathsf{M}\, \nu_j^{\mathrm{f}}, \mathbf{0}, 0 \big)^t$, $(\mathsf{M}\, \nu_j^{\mathrm{b}})^{\star} = \big(\mathsf{M}\, \nu_j^{\mathrm{b}}, \mathbf{0}, 0 \big)^t$, $(\mathsf{M}\, \nu_j)^{\star} = (\mathsf{M}\, \nu_j^{\mathrm{b}})^{\star} - (\mathsf{M}\, \nu_j^{\mathrm{f}})^{\star}$ so that

$$(\mathsf{M}\, \nu_j)^{\star} = \big(\mathsf{M}\, \nu_j, \mathbf{0}, 0 \big)^t,$$

and

$$\widetilde{\Omega} = \sum_{j \in \mathfrak{R}} (\mathsf{M}\, \nu_j^{\mathrm{f}})^{\star} \tau_j.$$

The nonideal rate of progress for the jth reaction may also be written in the form

$$\tau_j = \kappa_j^{\mathrm{s}} \Big(\exp \big\langle (\mathsf{M}\, \nu_j^{\mathrm{f}})^{\star}, \mathsf{v} \big\rangle - \exp \big\langle (\mathsf{M}\, \nu_j^{\mathrm{b}})^{\star}, \mathsf{v} \big\rangle \Big), \tag{4.13}$$

where κ_j^{s} is the symmetric reaction constant of the jth reaction. Noting v^e an equilibrium point where $\Omega(\mathsf{v}^e) = 0$, and thus where $\langle (\mathsf{M}\, \nu_j^{\mathrm{f}})^{\star}, \mathsf{v}^e \rangle = \langle (\mathsf{M}\, \nu_j^{\mathrm{b}})^{\star}, \mathsf{v}^e \rangle$ for $j \in \mathfrak{R}$, a direct calculation of $\partial_{\mathsf{v}} \widetilde{\Omega}$ yields that

$$\widetilde{L}(\mathsf{v}^e) = \sum_{j \in \mathfrak{R}} \kappa_j^{\mathrm{s}} \exp \big\langle (\mathsf{M}\, \nu_j^{\mathrm{f}})^{\star}, \mathsf{v}^e \big\rangle \; (\mathsf{M}\, \nu_j)^{\star} \otimes (\mathsf{M}\, \nu_j)^{\star}.$$

As a consequence, at equilibrium, $\widetilde{L}$ is symmetric positive semi-definite of rank $\dim(\mathscr{E}^{\perp}) = \dim(\mathcal{R})$ so that (S_6) and (E_6) are established. Finally, (S_7) and (E_7) are a direct consequence of Proposition 2.14 since $\langle \mu, \omega \rangle = \langle \mathsf{v}, \Omega \rangle$ and the proof is complete. ☐

For ideal fluids, the symmetrizing change of variable $\mathsf{u} \rightarrow \mathsf{v}$ is one to one and is thus a global change of variable [38, 34]. On the contrary, for nonideal fluid, even though the entropy σ is globally defined, the map $\mathsf{u} \rightarrow \mathsf{v}$ is only locally invertible and a typical situation is that of distinct points $\mathsf{u}^{\sharp}$ and $\mathsf{u}^{\flat}$ such that $\mathsf{v}^{\sharp} = \mathsf{v}^{\flat}$. Indeed, we see from (4.4) that the equality $\mathsf{v}^{\sharp} = \mathsf{v}^{\flat}$ corresponds to the chemical equilibrium between the two stable phases $\mathsf{u}^{\sharp}$ and $\mathsf{u}^{\flat}$ with identical pressure, temperature and chemical potentials, that may be observed once the entropy Hessian has lost its signature [40].

4.3 Local normal form

In this section we investigate local normal forms for the system (2.1)–(2.3) and first establish the nullspace invariance property.

Lemma 4.8. *The nullspace of the matrix*

$$\widetilde{\mathsf{B}}(\mathsf{v},\boldsymbol{\xi}) = \sum_{i,j\in C} \widetilde{\mathsf{B}}_{ij}(\mathsf{v})\xi_i\xi_j,$$

is independent of $\mathsf{v}\in\mathsf{O}_{\mathsf{v}}$ *and* $\boldsymbol{\xi}\in\Sigma^{d-1}$*, where* Σ^{d-1} *is the unit sphere in* d *dimensions. This nullspace is given by*

$$N(\widetilde{\mathsf{B}}) = \mathbb{R}(\mathbb{1},\mathbf{0},0)^t,$$

and we have $\widetilde{\mathsf{B}}_{ij}(\mathsf{v})N(\widetilde{\mathsf{B}}) = 0$*,* $i,j\in C$*, for* $\mathsf{v}\in\mathsf{O}_{\mathsf{v}}$*.*

Proof. From the proof of Theorem 4.7, letting $\mathsf{x} = \big(\mathsf{x}_1,\dots,\mathsf{x}_n,\mathbf{x}_{\boldsymbol{v}},\mathsf{x}_{\mathcal{E}}\big)^t$, with $\mathsf{x}^{\varrho} = \big(\mathsf{x}_1,\dots,\mathsf{x}_n\big)^t$, $\mathsf{x}_{\boldsymbol{v}} = \big(\mathsf{x}_{n+1},\dots,\mathsf{x}_{n+d}\big)^t$, we obtain that

$$\big\langle\widetilde{\mathsf{B}}\mathsf{x},\mathsf{x}\big\rangle = 2\tfrac{d-1}{d}\big(\boldsymbol{\xi}\cdot(\mathbf{x}_{\boldsymbol{v}}+\boldsymbol{v}\mathsf{x}_{\mathcal{E}})\big)^2 + |\boldsymbol{\xi}|^2\big|\mathbf{x}_{\boldsymbol{v}}+\boldsymbol{v}\mathsf{x}_{\mathcal{E}}\big|^2 + |\boldsymbol{\xi}|^2\big\langle\widetilde{\mathsf{B}}^L\mathsf{x},\mathsf{x}\big\rangle.$$

Assuming that $\big\langle\widetilde{\mathsf{B}}\mathsf{x},\mathsf{x}\big\rangle = 0$ and $|\boldsymbol{\xi}| = 1$ we thus obtain that $\big\langle\widetilde{\mathsf{B}}^L\mathsf{x},\mathsf{x}\big\rangle = 0$ and $\big|\mathbf{x}_{\boldsymbol{v}}+\boldsymbol{v}\mathsf{x}_{\mathcal{E}}\big| = 0$. From the structure of $\widetilde{\mathsf{B}}^L$ and since $N(L) = \mathbb{R}(\mathbb{1},0)^t$, we deduce that $\big(\mathsf{x}_1,\dots,\mathsf{x}_n,\mathsf{x}_{\mathcal{E}}\big)^t\in\mathbb{R}(\mathbb{1},0)^t$ so that $\mathsf{x}_{\mathcal{E}} = 0$ and $(\mathsf{x}_1,\dots,\mathsf{x}_n)^t\in\mathbb{R}\mathbb{1}$. Next from $\big|\mathbf{x}_{\boldsymbol{v}}+\boldsymbol{v}\mathsf{x}_{\mathcal{E}}\big| = 0$ we obtain that $\mathsf{x}_{n+i} = 0$ for $1\le i\le d$. We have thus established that $N(\widetilde{\mathsf{B}})$ is spanned by $(1,\dots,1,\mathbf{0},0)^t$ and it is easily checked that $\widetilde{\mathsf{B}}_{ij}(\mathsf{v})N(\widetilde{\mathsf{B}}) = 0$, $i,j\in C$, for $\mathsf{v}\in\mathsf{O}_{\mathsf{v}}$. ☐

Since $N(\widetilde{\mathsf{B}})$ is spanned by $(\mathbb{1},\mathbf{0},0)^t$, we define the matrix P by

$$\mathsf{P} = \begin{bmatrix} 1 & 0_{1,n-1} & 0_{1,d} & 0 \\ 1_{n-1,1} & \mathbb{I}_{n-1} & 0_{n-1,d} & 0_{n-1,1} \\ 0_{d,1} & 0_{d,n-1} & \mathbb{I}_d & 0_{d,1} \\ 0 & 0_{1,n-1} & 0_{1,d} & 1 \end{bmatrix}, \tag{4.14}$$

and we may introduce the auxiliary variable $\mathsf{u}' = \mathsf{P}\mathsf{u}$ and the corresponding entropic variable $\mathsf{v}' = \mathsf{P}^{-1}\mathsf{v}$ given by

$$\mathsf{u}' = \big(\rho,\rho_2,\dots,\rho_n,\rho\boldsymbol{v},\mathcal{E}+\tfrac12\rho|\boldsymbol{v}|^2\big)^t$$

and

$$\mathsf{v}' = \frac{1}{RT}\Big(\mathcal{G}_1-\tfrac12|\boldsymbol{v}|^2,\mathcal{G}_2-\mathcal{G}_1,\dots\mathcal{G}_n-\mathcal{G}_1,\boldsymbol{v},-1\Big)^t.$$

From Theorem 3.6, all normal variables are in the form $\mathsf{w} = \big(\phi_{\mathrm{I}}(\mathsf{u}'_{\mathrm{I}}),\phi_{\mathrm{II}}(\mathsf{v}'_{\mathrm{II}})\big)^t$ where u'_{I} is the first component of u' and $\mathsf{v}'_{\mathrm{II}}$ the last $n+d$ components of v'. For convenience, we choose the variable w given by

$$\mathsf{w} = \Big(\rho,\frac{\mathcal{G}_2-\mathcal{G}_1}{RT},\dots,\frac{\mathcal{G}_n-\mathcal{G}_1}{RT},\boldsymbol{v},T\Big)^t, \tag{4.15}$$

and we investigate the corresponding governing equations.

Theorem 4.9. *Assume that* $(\mathcal{T}_1)$*-*$(\mathcal{T}_4)$*,* (PG)*,* (C_1)*-*(C_3)*, and* (Tr_1)*-*(Tr_2) *hold. For any* $\mathsf{u}\in\mathcal{O}_{\mathsf{u}}$ *there exists a subdomain* $\mathsf{O}_{\mathsf{u}}\subset\mathcal{O}_{\mathsf{u}}$ *such that the map* $\mathsf{u}\to\mathsf{w}$ *is a* $C^{\varkappa}$ *diffeomorphism from the open set* O_{u} *onto an open set* O_{w} *and the map* $\mathsf{u}\to\mathsf{v}$ *is a* $C^{\varkappa}$ *diffeomorphism from the open set* O_{u} *onto an open set* O_{v}*. The induced diffeomorphism* $\mathsf{v}\to\mathsf{w}$ *is then a* $C^{\varkappa}$ *diffeomorphism from* O_{v} *onto* O_{w} *and the system written in the* w *variable is in the form*

$$\overline{\mathsf{A}}_0(\mathsf{w})\partial_t\mathsf{w} + \sum_{i\in C}\overline{\mathsf{A}}_i(\mathsf{w})\partial_i\mathsf{w} = \sum_{i,j\in C}\partial_i\big(\overline{\mathsf{B}}_{ij}(\mathsf{w})\partial_j\mathsf{w}\big) + \overline{\mathcal{T}}(\mathsf{w},\partial_x\mathsf{w}) + \overline{\Omega}(\mathsf{w}), \tag{4.16}$$

where $\overline{\mathsf{A}}_0 = \partial_{\mathsf{w}}\mathsf{v}^t\ \widetilde{\mathsf{A}}_0\ \partial_{\mathsf{w}}\mathsf{v}$*,* $\overline{\mathsf{A}}_i = \partial_{\mathsf{w}}\mathsf{v}^t\ \widetilde{\mathsf{A}}_i\ \partial_{\mathsf{w}}\mathsf{v}$*,* $i\in C$*,* $\overline{\mathsf{B}}_{ij} = \partial_{\mathsf{w}}\mathsf{v}^t\ \widetilde{\mathsf{B}}_{ij}\ \partial_{\mathsf{w}}\mathsf{v}$*,* $i,j\in C$*,* $\overline{\Omega} = \partial_{\mathsf{w}}\mathsf{v}^t\ \Omega$*, and* $\overline{\mathcal{T}} = -\sum_{i,j\in C}\partial_i\left(\partial_{\mathsf{w}}\mathsf{v}^t\right)\ \widetilde{\mathsf{B}}_{ij}\ \partial_{\mathsf{w}}\mathsf{v}\ \partial_j\mathsf{w}$*, and is in the local normal form. The matrix* $\overline{\mathsf{A}}_0$ *is given by*

$$\overline{\mathsf{A}}_0 = \begin{bmatrix} \overline{\mathsf{A}}_0^{\mathrm{I,I}} & Sym \\ 0_{n+d,1} & \overline{\mathsf{A}}_0^{\mathrm{II,II}} \end{bmatrix},$$

with

$$\overline{\mathsf{A}}_0^{\mathrm{I,I}} = \frac{1}{\langle \Lambda \mathbb{1}, \mathbb{1} \rangle} \qquad \overline{\mathsf{A}}_0^{\mathrm{II,II}} = \begin{bmatrix} \overline{\mathcal{A}}^{\mathrm{II,II}} & & \mathit{Sym} \\ 0_{d,n-1} & \frac{\rho}{RT}\mathbb{I}_d & \\ \frac{\overline{\mathsf{a}}^t}{RT^2} & 0_{1,d} & \overline{\mathsf{A}}_0^{T,T} \end{bmatrix},$$

and where $\overline{\mathcal{A}}^{\mathrm{II,II}}$ *is the square matrix of dimension* $n-1$ *with coefficients*

$$\overline{\mathcal{A}}_{kl}^{\mathrm{II,II}} = \Lambda_{kl} - \frac{(\Lambda \mathbb{1})_k (\Lambda \mathbb{1})_l}{\langle \Lambda \mathbb{1}, \mathbb{1} \rangle}, \quad 2 \le k, l \le n,$$

$\overline{\mathsf{a}}$ *is the vector of dimension* $n-1$ *with coefficients*

$$\overline{\mathsf{a}}_l = (\Lambda \mathscr{g})_l - (\Lambda \mathbb{1})_l \frac{\langle \Lambda \mathscr{g}, \mathbb{1} \rangle}{\langle \Lambda \mathbb{1}, \mathbb{1} \rangle}, \qquad 2 \le l \le n,$$

and $\overline{\mathsf{A}}_0^{T,T}$ *is given by*

$$\overline{\mathsf{A}}_0^{T,T} = \frac{1}{R^2T^4}\Big(\langle \Lambda \mathscr{g}, \mathscr{g} \rangle - \frac{\langle \Lambda \mathscr{g}, \mathbb{1} \rangle^2}{\langle \Lambda \mathbb{1}, \mathbb{1} \rangle} \Big) + \frac{1}{RT^2} \widetilde{\partial}_T \mathcal{E}.$$

Denoting by $\boldsymbol{\xi} = (\xi_1, \dots, \xi_d)^t$ *an arbitrary vector of* $\mathbb{R}^d$*, the matrices* $\overline{\mathsf{A}}_i$*,* $i \in C$*, are given by*

$$\sum_{i \in C} \xi_i \overline{\mathsf{A}}_i = \overline{\mathsf{A}}_0 \boldsymbol{v} \cdot \boldsymbol{\xi} + \begin{bmatrix} 0 & & & \mathit{Sym} \\ 0_{n-1,1} & 0_{n-1,n-1} & & \\ \frac{\rho}{\langle \Lambda \mathbb{1}, \mathbb{1} \rangle} \boldsymbol{\xi} & \boldsymbol{\xi} \otimes \overline{\mathsf{b}} & 0_{d,d} & \\ 0 & 0_{1,n-1} & \gamma \boldsymbol{\xi}^t & 0 \end{bmatrix},$$

where $\overline{\mathsf{b}}$ *is the vector of dimension* $n-1$ *with components*

$$\overline{\mathsf{b}}_l = \rho_l - \rho \frac{(\Lambda \mathbb{1})_l}{\langle \Lambda \mathbb{1}, \mathbb{1} \rangle}, \qquad 2 \le l \le n,$$

and

$$\gamma = \frac{1}{RT^2}\Big(\mathcal{E} + \tfrac{1}{2}\rho |\boldsymbol{v}|^2 + \mathcal{P} - \rho \frac{\langle \Lambda \mathscr{g}, \mathbb{1} \rangle}{\langle \Lambda \mathbb{1}, \mathbb{1} \rangle} \Big).$$

The matrices $\overline{\mathsf{B}}_{ij}$ *have the structure*

$$\overline{\mathsf{B}}_{ij} = \delta_{ij} RT \overline{\mathsf{B}}^L + RT\kappa \overline{\mathsf{B}}_{ij}^{\kappa} + RT\eta \overline{\mathsf{B}}_{ij}^{\eta},$$

where the matrix $\overline{\mathsf{B}}^L$ *is given by*

$$\overline{\mathsf{B}}^L = \frac{1}{T} \begin{bmatrix} 0 & & & \mathit{Sym} \\ 0_{n-1,1} & L^{n-1,n-1} & & \\ 0_{d,1} & 0_{d,n-1} & 0_{d,d} & \\ 0 & \frac{1}{RT^2} L_{e\bullet}^{n-1} & 0_{1,d} & \frac{1}{R^2T^4} L_{ee} \end{bmatrix}.$$

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* $\overline{\mathsf{B}}_{ij}^{\kappa}$*,* $\overline{\mathsf{B}}_{ij}^{\eta}$*,* $i, j \in C$*, are given by*

$$\sum_{i,j \in C} \xi_i \zeta_j \overline{\mathsf{B}}_{ij}^{\kappa} = \frac{1}{R^2T^2} \begin{bmatrix} 0_{n,n} & 0_{n,d} & 0_{n,1} \\ 0_{d,n} & \boldsymbol{\xi} \otimes \boldsymbol{\zeta} & 0_{d,1} \\ 0_{1,n} & 0_{1,d} & 0_{1,1} \end{bmatrix},$$

$$\sum_{i,j \in C} \xi_i \zeta_j \overline{\mathsf{B}}_{ij}^{\eta} = \frac{1}{R^2T^2} \begin{bmatrix} 0_{n,n} & 0_{n,d} & 0_{n,1} \\ 0_{d,n} & \boldsymbol{\xi} \cdot \boldsymbol{\zeta}\, \mathbb{I}_d + \boldsymbol{\zeta} \otimes \boldsymbol{\xi} - \frac{2}{d} \boldsymbol{\xi} \otimes \boldsymbol{\zeta} & 0_{d,1} \\ 0_{1,n} & 0_{1,d} & 0_{1,1} \end{bmatrix},$$

and finally

$$\overline{\Omega} = \Big(0, m_2\omega_2, \dots, m_n\omega_n, \mathbf{0}, 0 \Big)^t.$$

Proof. The proof is lengthy and tedious but presents no serious difficulties. □

4.4 Dissipativity and asymptotic stability

We consider the system (4.16) written in the $\mathsf{w} = (\mathsf{w}_{\rm I}, \mathsf{w}_{\rm II})^t$ variable, with the hyperbolic variable

$$\mathsf{w}_{\rm I} = \rho,$$

and the parabolic variable

$$\mathsf{w}_{\rm II} = \Big(\frac{\mathcal{G}_2 - \mathcal{G}_1}{RT}, \dots, \frac{\mathcal{G}_n - \mathcal{G}_1}{RT}, \boldsymbol{v}, T\Big)^t.$$

The mathematical structure of thermo-chemistry and multicomponent transport have been presented in Sections 2.2. The existence of constant equilibrium states has been established in Section 4.1. The equilibrium state in the variable w is denoted by w^e. We establish in the next proposition that the linearized system is strictly dissipative around constant equilibrium states.

Proposition 4.10. *Assume that* $(\mathcal{T}_1)$-$(\mathcal{T}_4)$, (PG), (C_1)-(C_3), *and* (Tr_1)-(Tr_2) *hold and consider a constant equilibrium state as in Proposition 4.6. Then the symmetric form of Theorem 4.4 linearized at* v^e *and the normal form of Theorem 4.9 linearized at* w^e *are strictly dissipative.*

Proof. Since strict dissipativity is equivalently established with the normal form as well as with the symmetrized form, we may use the later for convenience and use (Spe_3). We thus consider $\boldsymbol{\xi} \in \Sigma^{d-1}$ and assume that $\Psi \neq 0$ is such that $\widetilde{\mathsf{B}}(\mathsf{v}^e, \boldsymbol{\xi})\Psi = \widetilde{\mathsf{L}}(\mathsf{v}^e)\Psi = 0$ where $\widetilde{\mathsf{B}}(\mathsf{v}^e, \boldsymbol{\xi}) = \sum_{ij \in C} \widetilde{\mathsf{B}}_{ij}(\mathsf{v}^e)\xi_i\xi_j$ and $\widetilde{\mathsf{L}}(\mathsf{v}^e)$ is the opposite of the linearized source term at v^e.

We know then from Lemma 4.8 that $\Psi = \alpha(\mathbb{1}, \boldsymbol{0}, 0)^t$ for some $\alpha \neq 0$ and we must establish that for any $a \in \mathbb{R}$ we have $a\widetilde{\mathsf{A}}_0(\mathsf{v}^e)\Psi + \widetilde{\mathsf{A}}(\mathsf{v}^e, \boldsymbol{\xi})\Psi \neq 0$ where $\widetilde{\mathsf{A}}(\mathsf{v}^e, \boldsymbol{\xi}) = \sum_{i \in C} \widetilde{\mathsf{A}}_i(\mathsf{v}^e)\xi_i$.

However, a direct calculation using (4.6)(4.7) from Theorem 4.7—keeping the same notation—yields that

$$\frac{1}{\alpha}\Big(a\widetilde{\mathsf{A}}_0(\mathsf{v}^e)\Psi + \widetilde{\mathsf{A}}(\mathsf{v}^e, \boldsymbol{\xi})\Psi\Big) = (a + \boldsymbol{v}\cdot\boldsymbol{\xi}) \begin{bmatrix} \Lambda\mathbb{1} \\ \boldsymbol{v}\langle\Lambda\mathbb{1}, \mathbb{1}\rangle \\ \langle\Lambda\boldsymbol{g}, \mathbb{1}\rangle \end{bmatrix} + \begin{bmatrix} 0_{1,n} \\ \rho\boldsymbol{\xi} \\ \boldsymbol{v}\cdot\boldsymbol{\xi}\,\rho \end{bmatrix}.$$

If this vector is zero, then $a + \boldsymbol{v}\cdot\boldsymbol{\xi} = 0$ from the n first components since Λ is invertible and $\mathbb{1} \neq 0$. This then implies that $\rho = 0$ from the velocity components, since $\boldsymbol{\xi} \in \Sigma^{d-1}$, which is impossible so that (Spe_3) holds. □

The following theorems are now consequences of Theorem 3.10, Theorem 3.11, Proposition 4.10 and of the hyperbolic-parabolic structure of the system of partial differential equations modeling nonideal fluids in normal form established in Theorem 4.9.

Theorem 4.11. *Let* $d \geq 1$ *and* $l \geq [d/2] + 2$ *be integers and consider the system* (4.16)*. There exists* $b > 0$ *small enough such that if* $\|\mathsf{w}^0 - \mathsf{w}^e\|_l < b$, *there exists a unique global solution* w *to the Cauchy problem*

$$\overline{\mathsf{A}}_0(\mathsf{w})\partial_t\mathsf{w} + \sum_{i \in C}\overline{\mathsf{A}}_i(\mathsf{w})\partial_i\mathsf{w} = \sum_{i,j \in C}\partial_i\big(\overline{\mathsf{B}}_{ij}(\mathsf{w})\partial_j\mathsf{w}\big) + \overline{\mathcal{T}}(\mathsf{w}, \partial_x\mathsf{w}) + \overline{\Omega}(\mathsf{w}),$$

with initial condition

$$\mathsf{w}(0, x) = \mathsf{w}^0(x),$$

such that

$$\begin{aligned} \mathsf{w}_{\rm I} - \mathsf{w}_{\rm I}^{\rm e} &\in C^0\big([0,\infty), W_2^l(\mathbb{R}^d)\big) \cap C^1\big([0,\infty), W_2^{l-1}(\mathbb{R}^d)\big), \\ \mathsf{w}_{\rm II} - \mathsf{w}_{\rm II}^{\rm e} &\in C^0\big([0,\infty), W_2^l(\mathbb{R}^d)\big) \cap C^1\big([0,\infty), W_2^{l-2}(\mathbb{R}^d)\big), \end{aligned}$$

and

$$\begin{aligned} \boldsymbol{\nabla}\mathsf{w}_{\rm I} &\in L^2\big((0,\infty), W_2^{l-1}(\mathbb{R}^d)\big), \\ \boldsymbol{\nabla}\mathsf{w}_{\rm II} &\in L^2\big((0,\infty), W_2^{l}(\mathbb{R}^d)\big). \end{aligned}$$

Furthermore, w *satisfies the estimate*

$$\|\mathsf{w}(t) - \mathsf{w}^e\|_l^2 + \int_0^t \big(\|\boldsymbol{\nabla}\mathsf{w}_{\rm I}(\tau)\|_{l-1}^2 + \|\boldsymbol{\nabla}\mathsf{w}_{\rm II}\|_l^2\big)\,\mathrm{d}\tau \leq \ C\|\mathsf{w}^0 - \mathsf{w}^e\|_l^2,$$

where C *is a positive constant and* $\sup_{x \in \mathbb{R}^d}|\mathsf{w}(t) - \mathsf{w}^e|$ *goes to zero as* $t \to \infty$.

Theorem 4.12. *Let* $d \geq 2$*,* $l \geq [d/2] + 3$ *and* $\mathsf{w}^0(x)$ *be given, such that*

$$\mathsf{w}^0 - \mathsf{w}^e \in W_2^l(\mathbb{R}^d) \cap L^p(\mathbb{R}^d),$$

with $p \in [1, 2)$*. Then, if* $\|\mathsf{w}^0 - \mathsf{w}^e\|_l$ *and* $\|\mathsf{w}^0 - \mathsf{w}^e\|_{L^p}$ *are small enough, the unique global solution to the Cauchy problem satisfies the decay estimate*

$$\|\mathsf{w}(t) - \mathsf{w}^e\|_{l-2} \leq C(1+t)^{-\gamma} \left(\|\mathsf{w}^0 - \mathsf{w}^e\|_{l-2} + \|\mathsf{w}^0 - \mathsf{w}^e\|_{L^p} \right), \ t \in [0, +\infty),$$

uniformly in $\epsilon \in [0, \overline{\epsilon}]$ *where* C *is a positive constant and* $\gamma = d(1/2p - 1/4)$*.*

Emphasizing the dependence on physical parameters $\epsilon \in \mathsf{K}_\epsilon \subset \mathbb{R}^m$ and assuming structural properties discussed in Section 3.4 there is a continuous dependence of solutions with respect to the parameters ϵ [37]. Denoting by $\mathsf{w}(t, x, \epsilon)$ the solution obtained for $\epsilon \in \mathsf{K}_\epsilon$, we have for any $\alpha \in \mathsf{K}_\epsilon$

$$\lim_{\epsilon \to \alpha} \sup_{t \geq 0} \|\mathsf{w}(t, \cdot, \epsilon) - \mathsf{w}(t, \cdot, \alpha)\|_{C^{l-([d/2]+2)}} = 0.$$

The physical parameters may typically chosen to be some transport coefficients parameters as well as some thermochemistry constants.

5 Thermodynamically unstable points

We investigate in this section the deficiency of the system of partial differential equations modeling multicomponent nonideal fluids at thermodynamic unstable states. We first characterize hyperbolic and parabolic symmetric systems of conservation laws. We then specifically consider single component fluids at thermodynamic mechanical unstable points as well as binary mixtures fluids at thermodynamic chemical unstable points.

5.1 Hyperbolicity and parabolicity

We restate in this section various definitions of hyperbolicity and parabolicity keeping the notation of Section 3.2 for abstract systems of conservation laws.

5.1.1 Symmetric hyperbolic systems

Consider a first-order abstract system of partial differential equations written in the form

$$\overline{\mathsf{A}}_0^*(\mathsf{w}^*)\partial_t \mathsf{w}^* \ + \sum_{i \in C^*} \overline{\mathsf{A}}_i^*(\mathsf{w}^*)\partial_i \mathsf{w}^* = \overline{\Omega}^*(\mathsf{w}^*), \tag{5.1}$$

where $\overline{\mathsf{A}}_0^*$, $\overline{\mathsf{A}}_i^*$, $i \in C^*$, and $\overline{\Omega}^*$ are smooth functions of w^* over an open set $\mathsf{O}_{\mathsf{w}^*}$, $C^* = \{1, \dots, d\}$ the set of direction indices of $\mathbb{R}^d$, and where $\overline{\mathsf{A}}_0^*$ is assumed to be invertible. The following definition of hyperbolicity can be found in the book of Denis Serre [73].

Definition 5.1. *The system* (5.1) *is said to be hyperbolic at a given point* w^* *if*

$$\sup_{\boldsymbol{\xi} \in \mathbb{R}^d} \left\| \exp\bigl(-\mathrm{i}\bigl(\overline{\mathsf{A}}_0^*(\mathsf{w}^*)\bigr)^{-1} \overline{\mathsf{A}}^*(\mathsf{w}^*, \boldsymbol{\xi})\bigr) \right\| < \infty, \tag{5.2}$$

where for $\boldsymbol{\xi} \in \mathbb{R}^d$ *we have defined* $\overline{\mathsf{A}}^*(\mathsf{w}^*, \boldsymbol{\xi}) = \sum_{j \in C} \overline{\mathsf{A}}_i(\mathsf{w}^*)\xi_i$*.*

When the system (5.1) is hyperbolic, it is easily established that the matrix $\bigl(\overline{\mathsf{A}}_0^*\bigr)^{-1}\overline{\mathsf{A}}^*(\xi)$ is diagonalizable with real eigenvalues so that it is hyperbolic in the classical sense [18, 73]. We also have the following sufficient condition in terms of eigenvalues and eigenvector matrices established by Serre [73].

Proposition 5.2. *Assume that* $\bigl(\overline{\mathsf{A}}_0^*\bigr)^{-1}\overline{\mathsf{A}}^*(\mathsf{w}^*, \boldsymbol{\xi})$ *is diagonalizable at* w^* *for any* $\boldsymbol{\xi} \in \mathbb{R}^d$ *with real eigenvalues. Let* $P(\boldsymbol{\xi})$ *denote a matrix of eigenvectors and assume that*

$$\sup_{\boldsymbol{\xi} \in \mathbb{R}^d} \|P(\boldsymbol{\xi})\| \, \|P(\boldsymbol{\xi})^{-1}\| < \infty. \tag{5.3}$$

Then the system (5.1) *is also hyperbolic at* w^**.*

A fundamental property of Definition 5.1 is its invariance under a change of variable [73]. Moreover, when a first-order system is symmetrizable, the system (5.1) is hyperbolic [18, 73].

Definition 5.3. *The system* (5.1) *is said to be symmetric at a given point* w^* *when* $\overline{\mathsf{A}}_0^*(\mathsf{w}^*)$ *is positive definite and the matrices* $\overline{\mathsf{A}}_i^*(\mathsf{w}^*)$, $i \in C$, *are symmetric.*

Proposition 5.4. *A symmetric system of partial differential equation is hyperbolic.*

Since the existence of an entropy function also implies symmetrizability, it automatically implies hyperbolicity [18, 73].

5.1.2 Symmetric parabolic systems

Consider a second-order system in the form

$$\overline{\mathsf{A}}_0^*(\mathsf{w}^*)\partial_t \mathsf{w}^* \;=\; \sum_{i,j\in C^*} \overline{\mathsf{B}}_{ij}^*(\mathsf{w}^*)\partial_i\partial_j \mathsf{w}^* + \overline{\Omega}^*(\mathsf{w}^*, \partial_x \mathsf{w}^*), \tag{5.4}$$

where $\overline{\mathsf{A}}_0^*$, $\overline{\mathsf{B}}_{ij}^*$, $i, j \in C$, are smooth functions of w^* over an open set $\mathsf{O}_{\mathsf{w}^*}$, $\overline{\Omega}^*$ is a smooth function over $\mathsf{O}_{\mathsf{w}^*} \times \mathbb{R}^{dn^*}$, and where $\overline{\mathsf{A}}_0^*$ is invertible. We will generally consider second-order symmetric systems is the following sense.

Definition 5.5. *The system* (5.4) *is said to be symmetric at a given point* w^* *when* $\overline{\mathsf{A}}_0^*(\mathsf{w}^*)$ *is symmetric positive definite and* $\big(\overline{\mathsf{B}}_{ij}^*(\mathsf{w}^*)\big)^t = \overline{\mathsf{B}}_{ji}^*(\mathsf{w}^*)$, *for* $i, j \in C^*$.

We then have the following definition for strongly parabolic systems of second-order partial differential equations.

Definition 5.6. *Assume that the system* (5.4) *is symmetric at a given point* w^*. *This system is said to be strongly parabolic at* w^* *if there exists a positive constant* $\delta > 0$ *such that for any* $\boldsymbol{\xi} = (\xi_1, \dots, \xi_d)^t$ *and* $w = (w_1, \dots, w_{n^*})^t$ *we have*

$$\sum_{\substack{1\le i,j\le d\\ 1\le k,l\le n^*}} \big(\overline{\mathsf{B}}_{ij}^*\big)_{kl}\xi_i\xi_j w_k w_l \ge \delta |\boldsymbol{\xi}|^2 |w|^2. \tag{5.5}$$

Remark 5.7. *It is often the case that systems of partial differential equations of physical origin satisfy stronger properties than* (5.5) *at a given point* w^* *and are indeed such that*

$$\sum_{\substack{1\le i,j\le d\\ 1\le k,l\le n^*}} \big(\overline{\mathsf{B}}_{ij}^*\big)_{kl}\zeta_{ik}\zeta_{jl} \ge \delta |\zeta|^2, \tag{5.6}$$

for any $\zeta \in \mathbb{R}^{dn^*}$. *The condition* (5.5) *then simply corresponds to the situation where* ζ *is constrained to be a tensor product* $\zeta = \xi \otimes w$, *so that* $\zeta_{ik} = \xi_i w_k$, *for* $i \in \{1, \dots, d\}$, $k \in \{1, \dots, n^*\}$.

The definition of strong parabolicity is only given here for symmetric systems and will be applied to the symmetrized forms like (3.2) or (3.3), thereby naturally involving entropy Hessians. Indeed, the definition of strong parabolicity *in the usual sense*, which neither require symmetry properties nor entropy hessians, only has a meaning for *particular forms* of systems of partial differential equation under consideration which *need to be specified* as shown by the following counter example. Consider the system $\partial_t \mathsf{w}^* - \mathcal{D}\,\Delta \mathsf{w}^* = 0$ where $\mathsf{w}^* = (\mathsf{w}_1^*, \mathsf{w}_2^*)^t$, $\Delta \mathsf{w}^* = (\Delta \mathsf{w}_1^*, \Delta \mathsf{w}_2^*)^t$, and $\mathcal{D} = \mathrm{diag}(\delta_1, \delta_2)$, with $\delta_1 > 0$, $\delta_2 > 0$, and $\delta_1 \ne \delta_2$. In other words, consider two uncoupled heat equations which of course form a symmetric strongly parabolic system. Introduce next the modified variable $\mathsf{w}'^* = (\mathsf{w}_1^* + \mathsf{w}_2^*, \delta \mathsf{w}_2^*)^t$ where $\delta > 0$ is a positive parameter. We then have $\partial_t \mathsf{w}'^* - \mathcal{D}'\Delta \mathsf{w}'^* = 0$ with

$$\mathcal{D}' = \begin{bmatrix} \delta_1 & \frac{\delta_2 - \delta_1}{\delta} \\ 0 & \delta_2 \end{bmatrix},$$

so that if $0 < \delta < |\delta_2 - \delta_1|/(2\sqrt{\delta_1\delta_2})$ the quadratic form associated with $\mathcal{D}'$ is not positive definite and the system in the w'^* variable is not strongly parabolic *in the usual sense* even though it is obtained from a trivially strongly parabolic system.

Definition 5.8. *Denoting* $\overline{\mathsf{B}}^*(\mathsf{w}^*,\boldsymbol{\xi}) = \sum_{i,j\in C^*}\xi_i\xi_j\overline{\mathsf{B}}^*_{ij}(\mathsf{w}^*)$*, a system* (5.4) *is said to be parabolic in the sense of Petrovsky at a given point* w^* *if there exists a positive constant* δ *such that for any* $\boldsymbol{\xi}\in\mathbb{R}^d$*, the eigenvalues* λ *of* $\big(\overline{\mathsf{A}}^*_0(\mathsf{w}^*)\big)^{-1}\overline{\mathsf{B}}^*(\mathsf{w}^*,\boldsymbol{\xi})$*, are such that*

$$\Re(\lambda) \geq \delta|\boldsymbol{\xi}|^2. \tag{5.7}$$

Various other generalized definitions are discussed in the book of Ladyženskaja et al. [58], in particular that of Douglis and Nirenberg, Shirota, and Eĭdel'man, but these definitions coincide with that of Petrovsky for second-order systems [58].

Proposition 5.9. *Consider a second-order system in the form*

$$\overline{\mathsf{A}}^*_0(\mathsf{w}^*)\partial_t\mathsf{w}^* \;= \sum_{i,j\in C^*}\overline{\mathsf{B}}^*_{ij}(\mathsf{w}^*)\partial_i\partial_j\mathsf{w}^* + \overline{\Omega}^*,$$

and assume that the system is symmetric. Then the system is strongly parabolic at w^* *if and only if it is Petrovsky parabolic at* w^**.*

Proof. Assume that the system is parabolic in the sense of Petrovsky and let $\boldsymbol{\xi}\in\mathbb{R}^d$. Since the matrix $\big(\overline{\mathsf{A}}^*_0\big)^{-1}\overline{\mathsf{B}}^*$ is the product of a positive definite matrix $\big(\overline{\mathsf{A}}^*_0\big)^{-1}$ and of the symmetric matrix $\overline{\mathsf{B}}^*$, it is self-adjoint with respect to the scalar product $\langle\!\langle x,y\rangle\!\rangle = \langle\overline{\mathsf{A}}^*_0 x,y\rangle$ so that it is diagonalizable with real eigenvalues and admits a basis of eigenvectors orthonormal with respect to the scalar product $\langle\!\langle x,y\rangle\!\rangle$.

Denoting $f^1,\dots,f^{n^*}$ a basis of eigenvectors and $\lambda^1,\dots,\lambda^{n^*}$ the corresponding eigenvalues, we have $(\overline{\mathsf{A}}^*_0)^{-1}\overline{\mathsf{B}}^* f^i = \lambda_i f^i$ so that $\overline{\mathsf{B}}^* f^i = \lambda_i\overline{\mathsf{A}}^*_0 f^i$, for $1\leq i\leq n^*$. Since the eigenvector basis is orthonormal with respect to the scalar product $\langle\!\langle x,y\rangle\!\rangle$ we have $\langle\overline{\mathsf{A}}^*_0 f^i,f^j\rangle = 0$ when $i\neq j$. Upon forming $\lambda_i\langle\overline{\mathsf{A}}^*_0 f^i,f^j\rangle = \langle\overline{\mathsf{B}}^* f^i,f^j\rangle$ we deduce that $\langle\overline{\mathsf{B}}^* f^i,f^j\rangle = 0$ when $i\neq j$. From the relations $\lambda_j\langle\overline{\mathsf{A}}^*_0 f^i,f^j\rangle = \langle\overline{\mathsf{B}}^* f^i,f^j\rangle$ and the lower bound $\delta|\xi|^2\leq\lambda_j$, for $1\leq j\leq n^*$, we next obtain that

$$\delta|\xi|^2\langle\overline{\mathsf{A}}^*_0 x,x\rangle = \delta|\xi|^2\sum_{1\leq j\leq n^*}x_j^2\langle\overline{\mathsf{A}}^*_0 f^j,f^j\rangle \leq \sum_{1\leq j\leq n^*}\lambda_j x_j^2\langle\overline{\mathsf{A}}^*_0 f^j,f^j\rangle = \langle\overline{\mathsf{B}}^* x,x\rangle.$$

Since $\delta'\|x\|\leq\langle\overline{\mathsf{A}}^*_0 x,x\rangle$ for some positive constant δ' the system is strongly parabolic.

Conversely, assume that the system is strongly parabolic and let λ be an eigenvalue of $\big(\overline{\mathsf{A}}^*_0\big)^{-1}\overline{\mathsf{B}}^*$. We have then $\big(\overline{\mathsf{A}}^*_0\big)^{-1}\overline{\mathsf{B}}^* x = \lambda x$ for some $x\neq 0$ and we may write $\lambda\langle\overline{\mathsf{A}}^*_0 x,x\rangle = \langle\overline{\mathsf{B}}^* x,x\rangle$. This implies that $\lambda\langle\overline{\mathsf{A}}^*_0 x,x\rangle\geq\delta'|x||\boldsymbol{\xi}|$ since the system is strongly parabolic and we then obtain that $\lambda\geq\delta|\boldsymbol{\xi}|$ since $\langle\overline{\mathsf{A}}^*_0 x,x\rangle\leq C|x|$ for some constant C and the system is Petrovsky parabolic. □

From a practical point of view, for systems of partial differential equations derived from physics, thanks to the existence of a mathematical entropy, we can use symmetrized systems of partial differential equations and then rely of the classical definition of strongly parabolic systems.

In addition, strongly parabolicity is also invariant by a change of variable for symmetric systems, after multiplication of the left by the transpose of the jacobian matrix. Considering for instance the previous system $\partial_t\mathsf{w}^* - \mathcal{D}\,\Delta\mathsf{w}^* = 0$ where $\mathsf{w}^* = (\mathsf{w}^*_1,\mathsf{w}^*_2)^t$, $\Delta\mathsf{w}^* = (\Delta\mathsf{w}^*_1,\Delta\mathsf{w}^*_2)^t$, and $\mathcal{D} = \mathrm{diag}(\delta_1,\delta_2)$, with $\delta_1>0$, $\delta_2>0$, and letting $\mathsf{w}'^* = (\mathsf{w}^*_1+\mathsf{w}^*_2,\delta\mathsf{w}^*_2)^t$ where $\delta>0$ is a positive parameter and

$$\mathsf{P} = \begin{bmatrix}1 & 1\\ 0 & \delta\end{bmatrix}, \qquad \mathsf{Q} = \mathsf{P}^{-1},$$

we then have

$$\mathsf{Q}^t\mathsf{Q}\partial_t\mathsf{w}'^* - \mathsf{Q}^t\mathcal{D}\,\mathsf{Q}\Delta\mathsf{w}'^* = 0,$$

which remains symmetric strongly parabolic.

5.2 Mechanical unstable point for a single fluid

We investigate in this section the system of partial differential equation modeling a single fluid $n=1$ near a mechanical unstable point w^{u} where $\widetilde{\partial}_\rho p(\mathsf{w}^{\mathrm{u}}) = 0$. We assume that thermodynamic stability holds with $\widetilde{\partial}_\rho p>0$ in some neighborhood and we pass to the limit $\mathsf{w}\to\mathsf{w}^{\mathrm{u}}$ in the resulting system of partial differential equations.

We may use the calculations already made by using the normal variable $\mathsf{w} = (\rho,\boldsymbol{v},T)^t$ presented in Section 4.3. Note that the mass density ρ_1 is denoted by ρ since there is only one species. We may also use the relation $\widetilde{\partial}_\rho\mathcal{G}_1 = \widetilde{\partial}_\rho p/\rho$ where the index 1 is kept to distinguish between $\mathcal{G}_1$ and $\mathcal{G} = \rho_1\mathcal{G}_1$.

Proposition 5.10. *The system written in the* w *variable is in the form* (4.16) *and we have*

$$\overline{\mathsf{A}}_0 = \begin{bmatrix} \frac{\widetilde{\partial}_\rho p}{\rho RT} & 0_{1,d} & 0 \\ 0_{d,1} & \frac{\rho}{RT}\mathbb{I}_d & 0_{d,1} \\ 0 & 0_{1,d} & \frac{1}{RT^2}\widetilde{\partial}_T\mathcal{E} \end{bmatrix}.$$

Moreover, denoting by $\boldsymbol{\xi} = (\xi_1, \dots, \xi_d)^t$ *an arbitrary vector of* $\mathbb{R}^d$, *the matrices* $\overline{\mathsf{A}}_i$, $i \in C$, *are given by*

$$\sum_{i\in C} \xi_i \overline{\mathsf{A}}_i = \overline{\mathsf{A}}_0 \boldsymbol{v}\cdot\boldsymbol{\xi} + \begin{bmatrix} 0 & \frac{\widetilde{\partial}_\rho p}{RT}\boldsymbol{\xi}^t & 0 \\ \frac{\widetilde{\partial}_\rho p}{RT}\boldsymbol{\xi} & 0_{d,d} & \frac{\widetilde{\partial}_T p}{RT}\boldsymbol{\xi} \\ 0 & \frac{\widetilde{\partial}_T p}{RT}\boldsymbol{\xi}^t & 0 \end{bmatrix},$$

Finally, the dissipation matrices are left unchanged with respect to Theorem 4.9.

Proof. It is a particular case of Theorem 4.9. ☐

Assuming that we are in the neighborhood of the mechanical unstable point w^{u} and passing to the limit up to this point, we deduce from Proposition 5.10 that the normal form degenerates with lines of zero coefficients in the matrices $\overline{\mathsf{A}}_0(\mathsf{w}^{\mathrm{u}})$, $\overline{\mathsf{A}}_i(\mathsf{w}^{\mathrm{u}})$, $i \in C$, $\overline{\mathsf{B}}_{ij}(\mathsf{w}^{\mathrm{u}})$, $i, j \in C$, of the system of quasilinear partial differential equations as well as for the linearized source term in $\overline{\mathsf{L}}(\mathsf{w}^{\mathrm{u}})$ since then $\widetilde{\partial}_\rho p(\mathsf{w}^{\mathrm{u}}) = 0$. We also know that this is the case for *all normal forms* built from the representation Theorem 3.6.

It is thus mandatory to remove the singularity prior passing to the limit. This can be done by considering the rescaled system

$$\partial_t \mathsf{w} + \sum_{i\in C} (\overline{\mathsf{A}}_0)^{-1}\overline{\mathsf{A}}_i \partial_i \mathsf{w} = \sum_{i,j\in C} (\overline{\mathsf{A}}_0)^{-1}\overline{\mathsf{B}}_{ij}\partial_i\partial_j \mathsf{w} + \sum_{i,j\in C} (\overline{\mathsf{A}}_0)^{-1}\partial_i(\overline{\mathsf{B}}_{ij})\partial_j \mathsf{w} + (\overline{\mathsf{A}}_0)^{-1}\overline{\Omega}, \qquad (5.8)$$

and passing to the limit $\mathsf{w} \to \mathsf{w}^{\mathrm{u}}$ at a mechanical thermodynamically unstable point w^{u}. More specifically, since $\widetilde{\partial}_\rho p$ only appear in the upper left corner of $\overline{\mathsf{A}}_0$, it is easily checked that there is a cancellation of singularities in all the products $(\overline{\mathsf{A}}_0)^{-1}\overline{\mathsf{A}}_i$, $(\overline{\mathsf{A}}_0)^{-1}\overline{\mathsf{B}}_{ij}$, $(\overline{\mathsf{A}}_0)^{-1}\partial_i\overline{\mathcal{T}}$, and $(\overline{\mathsf{A}}_0)^{-1}\overline{\Omega}$. The limiting structure of the system of partial differential equations (5.8) is in the object of the following theorem.

Theorem 5.11. *At a mechanical thermodynamic unstable point* w^{u} *with* $\widetilde{\partial}_\rho p(\mathsf{w}^{\mathrm{u}}) = 0$ *and* $\widetilde{\partial}_T p(\mathsf{w}^{\mathrm{u}}) > 0$, *the limiting rescaled system of partial differential equations* (5.8) *remains hyperbolic in the sense of Definition 5.1 and the subsystem in the* w_{II} *variable remains symmetrizable and parabolic in the sense of Definition 5.8. The coupled system is not anymore symmetrizable, although its parabolic part still is. Finally, the Shizuta-Kawashima condition does not hold anymore and pure compression waves are undamped by viscosity and thermal conductivity.*

Proof. The products $(\overline{\mathsf{A}}_0)^{-1}\overline{\mathsf{A}}_i$ are easily evaluated in the form

$$(\overline{\mathsf{A}}_0)^{-1}\overline{\mathsf{A}}_i = \boldsymbol{v}\cdot\boldsymbol{\xi}\,\mathbb{I}_{n+d+1} + \begin{bmatrix} 0 & \rho\boldsymbol{\xi}^t & 0 \\ \frac{\widetilde{\partial}_\rho p}{\rho}\boldsymbol{\xi} & 0_{d,d} & \frac{\widetilde{\partial}_T p}{\rho}\boldsymbol{\xi} \\ 0 & \frac{T\widetilde{\partial}_T p}{\widetilde{\partial}_T\mathcal{E}}\boldsymbol{\xi}^t & 0 \end{bmatrix},$$

and there is a cancellation of singularities as $\widetilde{\partial}_\rho p$ goes to zero. The characteristic polynomial is easily evaluated as

$$\det\Big(X\mathbb{I} - (\overline{\mathsf{A}}_0)^{-1}\overline{\mathsf{A}}_i\Big) = (X - \boldsymbol{v}\cdot\boldsymbol{\xi})^d\Big((X - \boldsymbol{v}\cdot\boldsymbol{\xi})^2 - (\widetilde{\partial}_\rho p + \tfrac{T}{\rho}\tfrac{(\widetilde{\partial}_T p)^2}{\widetilde{\partial}_T\mathcal{E}})\Big).$$

All eigenvalues of $(\overline{\mathsf{A}}_0)^{-1}\overline{\mathsf{A}}_i$ thus remain real as $\widetilde{\partial}_\rho p \to 0$ and denoting by $P(\boldsymbol{\xi})$ a change of basis matrix between the canonical basis and a full system of eigenvectors, it is checked that $\|P(\boldsymbol{\xi})\|\ \|P(\boldsymbol{\xi})^{-1}\|$ remains bounded independently of ξ as $\widetilde{\partial}_\rho p \to 0$ so that the limiting system is hyperbolic.

On the other hand, the singularity in the matrices $\overline{\mathsf{A}}_0$ and $\overline{\mathsf{A}}_i$, $i \in C$, does not influence the equations associated with the parabolic variables so that the dissipative part remains symmetric strongly parabolic and the rescaled version remains Petrovsky parabolic.

Finally, the vector $(1, 0, \dots, 0)^t$ is an eigenvector of the limiting value of $(\overline{\mathsf{A}}_0)^{-1}\overline{\mathsf{A}}_i$ at a mechanically unstable point and is also in the nullspace of $\overline{\mathsf{B}}$ and $\overline{\mathsf{L}}$ so that (Spe_3) does not hold for the rescaled system. ☐

We conclude here that the Shizuta-Kawashima condition is of fundamental importance since it is the main indication that the state of the system is thermodynamically unstable.

5.3 Chemical unstable point for a binary mixture

We investigate in this section the system of partial differential equation modeling a binary fluid at a chemical thermodynamical unstable point. More specifically, we consider the situation of a two species mixture $n = 2$ near a point where the matrix

$$\mathit{\Gamma} = \frac{\rho}{T}\begin{bmatrix} \widetilde{\partial}_{\rho_1}\mathcal{G}_1 & \widetilde{\partial}_{\rho_2}\mathcal{G}_1 \\ \widetilde{\partial}_{\rho_1}\mathcal{G}_2 & \widetilde{\partial}_{\rho_2}\mathcal{G}_2 \end{bmatrix},$$

has one positive eigenvalue and one zero eigenvalue. We assume in all calculations that thermodynamic stability holds with $\mathit{\Gamma}$ positive definite and pass to the limit where the determinant vanish and the trace remains positive.

We may directly use in this situation the calculations already made using the normal variable $\mathsf{w} = \big(\rho, (\mathcal{G}_2 - \mathcal{G}_1)/RT, \boldsymbol{v}, T\big)^t$ presented in Section 4.3. To this aim, the matrix Λ is easily evaluated to be

$$\Lambda = \frac{RT}{\widetilde{\partial}_{\rho_1}\mathcal{G}_1\,\widetilde{\partial}_{\rho_2}\mathcal{G}_2 - \widetilde{\partial}_{\rho_1}\mathcal{G}_2\,\widetilde{\partial}_{\rho_2}\mathcal{G}_1}\begin{bmatrix} \widetilde{\partial}_{\rho_2}\mathcal{G}_2 & -\widetilde{\partial}_{\rho_2}\mathcal{G}_1 \\ -\widetilde{\partial}_{\rho_1}\mathcal{G}_2 & \widetilde{\partial}_{\rho_1}\mathcal{G}_1 \end{bmatrix}.$$

The normal form is investigated in the following proposition.

Proposition 5.12. *The system written in the* w *variable is in the form* (4.16) *and the coefficients of the matrix* $\overline{\mathsf{A}}_0$ *are the following. The coefficient* $\overline{\mathsf{A}}_0^{\mathrm{I,I}} = 1/\langle\Lambda\mathbb{1},\mathbb{1}\rangle$ *is given by*

$$\overline{\mathsf{A}}_0^{\mathrm{I,I}} = \frac{1}{RT}\frac{\widetilde{\partial}_{\rho_1}\mathcal{G}_1\,\widetilde{\partial}_{\rho_2}\mathcal{G}_2 - \widetilde{\partial}_{\rho_1}\mathcal{G}_2\,\widetilde{\partial}_{\rho_2}\mathcal{G}_1}{\widetilde{\partial}_{\rho_1}\mathcal{G}_1 + \widetilde{\partial}_{\rho_2}\mathcal{G}_2 - \widetilde{\partial}_{\rho_1}\mathcal{G}_2 - \widetilde{\partial}_{\rho_2}\mathcal{G}_1}.$$

On the other hand, the coefficient $\overline{\mathcal{A}}^{\mathrm{II,II}}$ *is easily evaluated after some algebra in the form*

$$\overline{\mathcal{A}}^{\mathrm{II,II}} = \frac{RT}{\widetilde{\partial}_{\rho_1}\mathcal{G}_1 + \widetilde{\partial}_{\rho_2}\mathcal{G}_2 - \widetilde{\partial}_{\rho_1}\mathcal{G}_2 - \widetilde{\partial}_{\rho_2}\mathcal{G}_1}.$$

The last coefficients are obtained after lengthy algebra in the form

$$\frac{\overline{\mathsf{a}}^t}{RT^2} = \frac{1}{T}\frac{\widetilde{\partial}_{\rho_2}\mathcal{E} - \widetilde{\partial}_{\rho_1}\mathcal{E}}{\widetilde{\partial}_{\rho_1}\mathcal{G}_1 + \widetilde{\partial}_{\rho_2}\mathcal{G}_2 - \widetilde{\partial}_{\rho_1}\mathcal{G}_2 - \widetilde{\partial}_{\rho_2}\mathcal{G}_1},$$

$$\overline{\mathsf{A}}_0^{TT} = \frac{1}{RT^3}\frac{(\widetilde{\partial}_{\rho_2}\mathcal{E} - \widetilde{\partial}_{\rho_1}\mathcal{E})^2}{\widetilde{\partial}_{\rho_1}\mathcal{G}_1 + \widetilde{\partial}_{\rho_2}\mathcal{G}_2 - \widetilde{\partial}_{\rho_1}\mathcal{G}_2 - \widetilde{\partial}_{\rho_2}\mathcal{G}_1} + \frac{1}{RT^2}\widetilde{\partial}_T\mathcal{E}.$$

From the expressions of the various matrices appearing in the normal form, it is again deduced, using the special form of the matrix $\overline{\mathsf{A}}_0$ that the rescaled form of the system of partial differential equation (5.8) pass to the limit at a chemical thermodynamically unstable point thanks to a cancellation of singularities. The limiting structure of the system of partial differential equations (5.8) for binary mixtures is in the object of the following theorem.

Theorem 5.13. *At a chemical thermodynamically unstable point* w^{u} *where the matrix* $\mathit{\Gamma}$ *is singular with* $\big(\widetilde{\partial}_{\rho_1}\mathcal{G}_1\,\widetilde{\partial}_{\rho_2}\mathcal{G}_2 - \widetilde{\partial}_{\rho_1}\mathcal{G}_2\,\widetilde{\partial}_{\rho_2}\mathcal{G}_1\big)(\mathsf{w}^{\mathrm{u}}) = 0$, $\big(\widetilde{\partial}_{\rho_1}\mathcal{G}_1 + \widetilde{\partial}_{\rho_2}\mathcal{G}_2 - \widetilde{\partial}_{\rho_1}\mathcal{G}_2 - \widetilde{\partial}_{\rho_2}\mathcal{G}_1\big)(\mathsf{w}^{\mathrm{u}}) > 0$ *and* $\widetilde{\partial}_T p(\mathsf{w}^{\mathrm{u}}) > 0$, *the limiting rescaled system of partial differential equations* (5.8) *remains hyperbolic in the sense of Definition 5.1 and the subsystem in the* w_{II} *variable remains symmetrizable and parabolic in the sense of Definition 5.8. The coupled system is not anymore symmetrizable, although its parabolic part still is. Finally, the Shizuta-Kawashima condition does not hold anymore and pure compression waves are undamped by viscosity and thermal conductivity.*

Proof. The proof is lengthy and tedious but similar to the previous situation of mechanically unstable points. □

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