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**Continuum thermodynamics of
chemically reacting fluid mixtures**

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ABSTRACT. We consider viscous and heat conducting mixtures of molecularly miscible chemical species forming a fluid in which the constituents can undergo chemical reactions. Assuming a common temperature for all components, a first main aim is the derivation of a closed system of partial mass and partial momentum balances plus a common balance of internal energy. This is achieved by careful exploitation of the entropy principle which, in particular, requires appropriate definitions of absolute temperature and chemical potentials based on an adequate definition of thermal energy that excludes diffusive contributions. The latter is crucial in order to obtain a closure framework for the interaction forces between the different species. The interaction forces split into a thermo-mechanical and a chemical part, where the former turns out to be symmetric if binary interactions are assumed. In the non-reactive case, this leads to a system of Navier-Stokes type sub-systems, coupled by inter-species friction forces. For chemically reacting systems and as a new result, the chemical interaction force is identified as a contribution which is non-symmetric, unless chemical equilibrium holds.

The theory also provides a rigorous derivation of the so-called generalized thermodynamic driving forces, avoiding the use of approximate solutions to the Boltzmann equations which is common in the engineering literature. Moreover, starting with a continuum thermodynamic field theory right away, local versions of fundamental relations known from thermodynamics of homogeneous systems, like the Gibbs-Duhem equation, are derived. Furthermore, using an appropriately extended version of the entropy principle and introducing cross-effects already before closure as entropy invariant couplings between principal dissipative mechanisms, the Onsager symmetry relations are a strict consequence. With a classification of the factors forming the binary products in the entropy production according to their parity instead of the classical distinction between so-called fluxes and driving forces, the apparent anti-symmetry of certain couplings is thereby also revealed.

If the diffusion velocities are small compared to the speed of sound, the well-known Maxwell-Stefan equations together with the so-called generalized thermodynamic driving forces follow in the special case without chemical reactions, thereby neglecting wave phenomena in the diffusive motion. This results in a reduced model having only the constituents' mass balances individually. In the reactive case, this approximation via a scale separation argument is no longer possible.

Instead, we first employ the partial mass and mixture internal energy balances, common to both model classes, to identify all constitutive quantities. Combined with the concept of entropy invariant model reduction, leaving the entropy production unchanged under the reduction from partial momentum balances to a single common mixture momentum balance, the chemical interactions yield an additional contribution to the transport coefficients, leading to an extension of the Maxwell-Stefan equations to chemically active mixtures. Within the considered model class for reactive fluid mixtures the new results are achieved for arbitrary free energy functions.

1. INTRODUCTION

We consider fluid systems being composed of N constituents, i.e. multicomponent mixtures of gases or liquids, typically containing additional dissolved chemical components. Main emphasis is put on chemically reacting mixtures, since the existing literature on fluid mixtures does not account for chemical processes in depth and, moreover, a thermodynamically consistent coupling between chemistry and fluid mechanics is often missing. This is especially true in case of highly concentrated mixtures for which cross-effects and non-idealities are to be included.

Our approach is based on continuum physics, where we strictly distinguish between universal laws and constitutive relations. We employ the field equations which follow from conservation laws for the extensive (i.e., mass additive) quantities *mass*, *momentum* and *energy*. This leads to unclosed sets of partial differential equations which need to be complemented by material dependent closure relations, so-called *constitutive equations*. Within *continuum thermodynamics*, the balance of *entropy* of the system is added to this set of differential equations together with the *second law of thermodynamics*. This severely restricts the closure relations admissible for the description of the constitutive functions appearing in these equations.

Let us start with some information about the different available continuum physics approaches, since our theory combines ideas from all these. The systematic theory of non-equilibrium thermodynamics for continuous matter was started in the year 1940 by C. Eckart who wrote the two basic papers [13, 14], entitled *The thermodynamics of irreversible processes I: The simple fluid* and *The thermodynamics of irreversible processes II: Fluid mixtures*. In the following years the theory was completed by J. Meixner. In the seminal paper [35], *Zur Thermodynamik der irreversiblen Prozesse in Gasen mit chemisch reagierenden, dissoziierenden and anregbaren Komponenten*, Meixner studied the phenomenological coefficients in detail and equipped these with Onsager-Casimir reciprocal relations. Finally in 1963, S.R. de Groot and P. Mazur reached a certain endpoint by putting everything together in the fundamental monograph *Non-equilibrium thermodynamics* ([19]). This theory is still in broad use under the labeling *Thermodynamics of irreversible processes*, TIP.

In 1962, W. Noll (cf. [55]) introduced new ideas to rationalize the mechanical theory of continua. In the following years the school around C. Truesdell applied these strategies to irreversible thermodynamics and established a variant of thermodynamics that has become very popular, at least for a certain time, under the name *Rational Thermodynamics*, RT. The first fundamental contribution from this school to mixture theory has been given by I. Müller in [37], correcting several erroneous contributions by other authors (see also [54]). Later, in [38], Müller introduced Lagrange multipliers for the exploitation of the entropy inequality. For a more complete presentation of rational thermodynamics of continuous media with Lagrange multipliers see [39]. An excellent overview on the initial difficulties in formulating rational continuum mixture theories has been provided by R.M. Bowen [5].

Both theories, TIP and RT, are not very different from each other. In particular, both split the laws of thermodynamics into universal laws, relying on balance equations, and characterizations of the material at hand via constitutive equations. Another agreement between TIP and RT is the fact that the description of diffusive transport processes leads to parabolic PDEs with infinite speed of propagation of disturbances. Since the latter apparently contradicts the fundamental physical principle that nothing should be faster than the speed of light, several researchers started a quest for a hyperbolic theory. This led to the invention of *Extended Thermodynamics*, ET, see [41]. Within ET, fluxes of the mentioned extensive quantities, like the heat flux in case of the energy balance, are themselves considered as governed by balance equations.

Our approach to the continuum thermodynamics of reacting fluid mixtures is a combination of elements of all three theories: We employ the partial balances of not only mass, indispensable for any mixture theory, but also momentum. This corresponds to an extended thermodynamics for the mass balances in which the time evolution of diffusion velocities is also monitored. Indeed, the contribution of chemical reactions to the diffusivities is similar as the contribution to the heat conductivity obtained in relativistic ET; cf. [41]. Actually we start also with partial energy balances in order to extract some structural information about the common energy balance on which the final modeling relies, where we only consider a single, common temperature.

We use an axiomatic approach guided by RT, including the principle of material frame indifference and also the strict separation into universal balance laws and material dependent constitutive relations. But we do not impose the principle of equipresence: we select the set of primitive thermodynamic variables when defining the form of the constitutive equation for the entropy. The dependence of all other quantities is then a consequence of their relations to the latter. Another important difference to RT lies in the entropy principle. In fact, in our theory—in agreement with W. Alt and I. Müller (see [1, 39])—the form of the entropy flux depends on the material at hand and comes as a result instead of being assumed via an axiom as in RT. Here we do not believe Gurtin's statement in [24] saying that the form of the entropy flux is "a matter of taste".

We consider the entropy principle by Alt and Müller as the prototype. However, we postulate an extended version by assuming further properties of the entropy production. The most important extension concerns its structure: Relying on classical TIP, we postulate it as a sum of binary products and exploit this structure to obtain closure relations which satisfy the entropy inequality. However, instead of the misleading notion of "fluxes" and "driving forces" as used in TIP, we build on Meixner [36] in introducing the parity of thermodynamic quantities and impose binary products of positive and negative parity factors. Incorporating a priori knowledge on the physics, we also predefine which dissipative mechanisms are to be included in the modeling. As compared to TIP, this allows for a strengthened version of the principle of detailed balance: Every dissipative mechanism alone has to fulfil the entropy inequality. Finally, we observed several forms of non-uniqueness of both the entropy flux and the entropy production, arising by addition of new terms to these quantities, but which sum up to zero in total. This way even new dissipative mechanisms can be introduced; cf. [11] for a non-trivial example.

All together, this enables a pragmatic evaluation of the entropy principle, yielding a particularly strong framework for the constitutive theory. This way, we obtain the following main results:

- 1 We provide various alternative forms of the energy balance and appropriately select the one which enables to obtain information about the inter-species interactions from the entropy principle.
- 2 We introduce a strengthened form of the entropy principle which includes a general version of the principle of detailed balance.
- 3 We employ the notion of parity to classify the co-factors in the binary products inside the entropy production and show that the parity of a physical quantity is directly related to its physical dimension.
- 4 We introduce a way to couple between different dissipative mechanisms by zero additions to the entropy production. This procedure of *entropy invariant mixing* describes cross-effects which automatically satisfy the Onsager symmetry. Hence the corresponding phenomenological cross-coefficients have arbitrary signs. Combined with the concept of parity, this way of introducing cross-effects also explains the appearance of the Onsager-Casimir relations, i.e. the apparent anti-symmetry of some cross-coupling coefficients.
- 5 We derive a consistent closed model for viscous, heat conducting and chemically reacting fluid mixtures, comprising N partial mass and N partial momentum balances. The model includes, in particular, a thermodynamically consistent closure for the interaction forces in the partial momentum balances and for the reaction rates as nonlinear functions of the affinities in the partial mass balances.
- 6 We introduce a new method for the reduction of a model with balances of partial momenta to a model where only the barycentric velocity in a common momentum balance appears. This derivation relies on identification of corresponding quantities in the partial mass and the mixture internal energy balance, since these are common to both model classes, combined with the invariance of the entropy production under this reduction process. Without chemistry, the derivation is also possible (and essentially known) via a scale-limit; but the latter is not rational in the choice of the approximation.
- 7 We extend the Maxwell-Stefan equations to the case of chemically reacting constituents, leading to a non-symmetric addition. We also take into account partial viscosities, leading to a stress-driven diffusion contribution.
- 8 We introduce a consistent general scheme to construct free energy functions for fluid mixtures. These *elastic mixtures* are obtained by combining information about the chemical potentials and the pressure-density relation at given composition.
- 9 Incompressibility of mixtures can be defined in different ways. We show the passage to incompressible limits based on appropriate equations of state for the mixture pressure, where

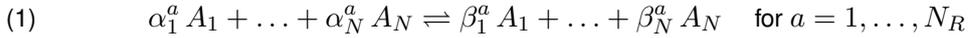
we consider several alternatives concerning the dependence on the constituents. We also revisit the apparent paradoxon concerning thermal expansion in an incompressible medium and explain how this is resolved.

To conclude this introduction, let us mention that there are also kinetic mixture theories available, the most famous one being the multi-species Boltzmann equations; cf. [15, 26]. While they provide a consistent derivation of a mixture theory, the admissible fluid mixtures contain only rather simple materials, viz. so-called simple mixtures (see Section 15 below) of monatomic gases. For more details on corresponding mixture models without partial momentum balances we refer to [15], kinetic models which account for partial momenta can be found in [25]. Let us note in passing that the Boltzmann equations can be motivated from first principles, but their rigorous derivation from the fundamental Liouville equation is still lacking; however, see [18]. Nevertheless, the multi-species Boltzmann equations provide a valuable micro-theory and we demand from our mixture theory that it contains the equations resulting from kinetic theory as a special case.

In our opinion, the strict separation into balance equations being rigorously valid within the continuum physics framework, and constitutive theory to model the material depend quantities, is the crucial factor for the success of TIP, RT and ET. There are other mixture continuum theories, relying on variational approaches, which do not have this clear distinction. Moreover, these theories are developed for specific classes of thermodynamic processes such as isentropic motions or isothermal systems. We refer to §231 in [17] for an assessment and only mention the classical d'Alembert/Lagrange theory; see, e.g., [21] for its extension to mixtures. In recent years, a further variant of the variational approach, called GENERIC ([23]), has emerged, where another disadvantage is that, up to now, this theory can only describe adiabatically isolated, closed systems.

2. BASIC QUANTITIES AND MODEL CLASSES

We consider fluid systems being composed of N constituents A_1, \dots, A_N , i.e. multicomponent mixtures of gases or liquids, typically containing additional dissolved chemical components. Special emphasis is put on chemically reacting mixtures, where we allow for N_R chemical reactions between the A_i according to



with stoichiometric coefficients $\alpha_i^a, \beta_i^a \in \mathbf{N}_0$.

The mixture occupies a region $\Omega \subset \mathbb{R}^3$. At any time $t \geq 0$, the thermodynamic state of the matter inside Ω is described by N partial mass densities ρ_1, \dots, ρ_N , by N partial velocities $\mathbf{v}_1, \dots, \mathbf{v}_N$ of the constituents and by the temperature T of the mixture. These quantities will be functions of time $t \geq 0$ and space $\mathbf{x} \in \mathbb{R}^3$. Partial mass densities and partial velocities are used to define the total mass density ρ and the barycentric velocity \mathbf{v} of the mixture according to

$$(2) \quad \rho := \sum_{i=1}^N \rho_i \quad \text{and} \quad \rho \mathbf{v} := \sum_{i=1}^N \rho_i \mathbf{v}_i.$$

The diffusion velocities \mathbf{u}_i and the corresponding diffusional mass fluxes \mathbf{j}_i are defined by

$$(3) \quad \mathbf{u}_i := \mathbf{v}_i - \mathbf{v} \quad \text{and} \quad \mathbf{j}_i := \rho_i \mathbf{u}_i \quad \text{with} \quad \sum_{i=1}^N \mathbf{j}_i = 0.$$

Finally, we introduce the molar concentrations and the molar fractions according to

$$(4) \quad c_i := \frac{\rho_i}{M_i} \quad \text{with molar mass } M_i, \quad x_i := \frac{c_i}{c} \quad \text{with} \quad c := \sum_{i=1}^N c_i.$$

Fluid mixtures can be modeled within three different levels of detail: class-I, class-II and class-III. Class-I considers as primitive variables the mass densities ρ_i of the constituents, the barycentric velocity \mathbf{v} and the temperature T of the mixture. The basic variables of class-II are the mass densities ρ_i , the velocities \mathbf{v}_i of the constituents and the temperature T of the mixture. Finally, in class-III one has the partial mass densities ρ_i , the partial velocities \mathbf{v}_i and partial temperatures T_i of the constituents. With this notion we follow [27].

There are several motivations for the more complex models, including in particular the following. For class-II model: (i) the different components can experience different boundary conditions for the partial velocities; (ii) the appearance of wave phenomena in the diffusive motion which are often ignored on a macroscopic scale; (iii) even for the derivation of class-I models, class-II models are important because they offer more information concerning the constitutive quantities. For class-III model: in plasma modeling, the constituents experience individual temperatures on time scales comparable to transport process times, hence separate energy balances are necessary and, in general, the individual species have different temperatures.

In the present study, we consider the model classes I and II. In particular, we derive consistent closures for class-II models of chemically reacting, heat conducting viscous fluid mixtures. Based on these, we derive improved class-I models which contain information from the class-II level within the constitutive relations. For example, due to the explicit structure of the thermal energy balance (27), certain cross-effects with Onsager symmetry can already be derived.

3. BALANCE EQUATIONS FOR CHEMICALLY REACTING FLUID MIXTURES

Partial Balances. The starting point of our modeling are the *partial balances of mass, momentum and energy*, which will later be complemented by the *entropy balance*. The local balances for the fluid components A_i read as

partial mass balance

$$(5) \quad \partial_t \rho_i + \operatorname{div}(\rho_i \mathbf{v}_i) = r_i,$$

partial momentum balance

$$(6) \quad \partial_t(\rho_i \mathbf{v}_i) + \operatorname{div}(\rho_i \mathbf{v}_i \otimes \mathbf{v}_i - \mathbf{S}_i) = \mathbf{f}_i + \rho_i \mathbf{b}_i,$$

partial energy balance

$$(7) \quad \partial_t(\rho_i e_i + \frac{\rho_i}{2} \mathbf{v}_i^2) + \operatorname{div}((\rho_i e_i + \frac{\rho_i}{2} \mathbf{v}_i^2) \mathbf{v}_i - \mathbf{v}_i \cdot \mathbf{S}_i + \mathbf{q}_i) = h_i + \rho_i \mathbf{b}_i \cdot \mathbf{v}_i.$$

In (5)-(7), the newly introduced quantities are: r_i - mass production due to chemical reactions, \mathbf{S}_i - partial stress, \mathbf{f}_i - momentum production, \mathbf{b}_i - body force acting on A_i , e_i - specific internal energy, \mathbf{q}_i - individual heat flux, h_i - internal energy production. Energy sources due to electromagnetic fields (i.e., radiation) are not considered here.

With these notations, the conservation laws for total mass, momentum and energy read

$$(8) \quad \sum_{i=1}^N r_i = 0, \quad \sum_{i=1}^N \mathbf{f}_i = 0, \quad \sum_{i=1}^N h_i = 0.$$

The mass productions r_i have the structure

$$(9) \quad r_i = \sum_{a=1}^{N_R} M_i \nu_i^a R_a,$$

where $R_a = R_a^f - R_a^b$ is the rate of reaction a , given by the rate R_a^f of the forward minus that of the backward path, and $\nu_i^a := \beta_i^a - \alpha_i^a$. Because mass is conserved in every single reaction, it holds that

$$(10) \quad \sum_{i=1}^N M_i \nu_i^a = 0 \quad \text{for all } a.$$

The reaction rates R_a as well as the interaction forces $\mathbf{f}_i - r_i \mathbf{v}_i$ are to be modeled. A constitutive model for the h_i is not required, since they do not appear in the common energy balance.

We define the *partial pressures* P_i and the traceless part \mathbf{S}_i° of the stresses \mathbf{S}_i by

$$(11) \quad P_i := -\frac{1}{3} \text{tr}(\mathbf{S}_i), \quad \mathbf{S}_i = -P_i \mathbf{I} + \mathbf{S}_i^\circ.$$

We further decompose the partial pressures according to

$$(12) \quad P_i = p_i + \Pi_i,$$

where the Π_i vanish in equilibrium. The pressure contribution p_i is often called *hydrostatic pressure* in which case Π_i is usually called *dynamic pressure*. For reasons which will become clear below, we call p_i the *partial thermodynamic pressure* and Π_i the *irreversible partial pressure contribution*. To economize notation, we use the abbreviation

$$(13) \quad \mathbf{S}_i^{\text{irr}} = -\Pi_i \mathbf{I} + \mathbf{S}_i^\circ$$

to denote the irreversible stress contribution. Consequently, $\mathbf{S}_i = -p_i \mathbf{I} + \mathbf{S}_i^{\text{irr}}$. Finally, the total pressure of the mixture is defined as $P := \sum_i P_i$. The latter is decomposed as $P = p + \Pi$ with $p := \sum_i p_i$ the total thermodynamic pressure. We also use the short hand notation $\mathbf{S}^{\text{irr}} = -\Pi \mathbf{I} + \mathbf{S}^\circ$ for the irreversible part of the mixture stress, where \mathbf{S}° is the traceless part of \mathbf{S} . Above, the short-hand notation \sum_i stands for the sum, where i runs from 1 to N . If nothing else is said, the same applies throughout the entire paper.

In the present work, we only consider *non-polar* fluid mixtures, i.e. there are no so-called surface or body couples and the fluid has vanishing spin density, which implies symmetry of stresses.

Mixture balances. We start by formulating the balances of total mass, momentum and energy, which follow by summation of the corresponding partial balances. Then appropriate further mixture quantities need to be defined, where the three meta-rules given by C. Truesdell (see [54]) provide a guidance:

- (I) All properties of the mixture must be mathematical properties of the constituents.
- (II) So as to describe the motion of a constituent, we may in imagination isolate it from the rest of the mixture, provided we allow properly for the actions of the other constituents upon it.
- (III) The motion of the mixture is governed by the same equations as is a single body.

Following this principle, we introduce the following additional quantities in order to obtain mixture balance equations which resemble the partial balances:

$$\rho \mathbf{b} := \sum_i \rho_i \mathbf{b}_i \quad (\text{total external force}),$$

$$\mathbf{S} := \sum_i (\mathbf{S}_i - \rho_i \mathbf{u}_i \otimes \mathbf{u}_i) \quad (\text{mixture stress tensor}),$$

$$\rho e_{\text{tot}} := \sum_i \rho_i (e_i + \frac{\mathbf{v}_i^2}{2}) = \rho \frac{\mathbf{v}^2}{2} + \sum_i \rho_i (e_i + \frac{\mathbf{u}_i^2}{2}) \quad (\text{total energy density}),$$

$$\mathbf{q}_{\text{tot}} := \sum_i (\mathbf{q}_i - \mathbf{u}_i \cdot \mathbf{S}_i + \rho_i (e_i + \frac{\mathbf{u}_i^2}{2}) \mathbf{u}_i) \quad (\text{total energy flux}),$$

$$\rho \pi := \sum_i \rho_i \mathbf{b}_i \cdot \mathbf{u}_i \quad (\text{power of body force due to diffusion}).$$

Summation of the partial balances now yields the balances for total mass, momentum and energy which read as

mass balance (continuity equation):

$$(14) \quad \partial_t \rho + \operatorname{div}(\rho \mathbf{v}) = 0,$$

momentum balance:

$$(15) \quad \partial_t(\rho \mathbf{v}) + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v} - \mathbf{S}) = \rho \mathbf{b},$$

energy balance:

$$(16) \quad \partial_t(\rho e_{\text{tot}}) + \operatorname{div}(\rho e_{\text{tot}} \mathbf{v} - \mathbf{v} \cdot \mathbf{S} + \mathbf{q}_{\text{tot}}) = \rho \mathbf{v} \cdot \mathbf{b} + \rho \pi.$$

For the constitutive modeling, in particular for exploitation of the entropy principle, we need a balance of internal energy instead of total energy. Here it is important to observe that different definitions of an internal part of the energy are possible. If partial energy balances are ignored, like in the case of standard TIP, the *internal energy* is (in the present context of non-polar fluids) that part of the total energy which cannot be eliminated by a Euclidean transformation, i.e. by a change to a different frame of reference. This leads to the definition of

$$(17) \quad \rho e_{\text{int}} := \rho e_{\text{tot}} - \frac{1}{2} \rho \mathbf{v}^2 \quad (\text{mixture internal energy}).$$

Subtracting the balance of kinetic energy due to barycentric motion from the balance of total energy, a straightforward computation yields the

mixture internal energy balance:

$$(18) \quad \partial_t(\rho e_{\text{int}}) + \operatorname{div}(\rho e_{\text{int}} \mathbf{v} + \mathbf{q}_{\text{tot}}) = \mathbf{S} : \nabla \mathbf{v} + \rho \pi.$$

As already noted in Chapter III, §4 of [19], the above defined internal energy contains kinetic energy of diffusion, while "the internal energy should only contain contributions from the thermal agitation and the short-range molecular interactions". In the present context of class-II modeling, this turns out to be even more relevant and we base our theory on the use of the *thermal part of the internal energy*, defined as

$$(19) \quad \rho e := \sum_i \rho_i e_i \quad (\text{thermal energy}).$$

Evidently, the link between the two quantities is given by

$$\rho e_{\text{int}} = \rho e + \frac{1}{2} \sum_i \rho_i \mathbf{u}_i^2.$$

To derive the balance of thermal energy, we start from the partial internal energy balance, obtained as usual by subtracting the (partial) kinetic energy balance from (7). This leads to the

partial balance of internal energy:

$$(20) \quad \partial_t(\rho_i e_i) + \operatorname{div}(\rho_i e_i \mathbf{v}_i + \mathbf{q}_i) = \mathbf{S}_i : \nabla \mathbf{v}_i + h_i - \mathbf{v}_i \cdot (\mathbf{f}_i - r_i \frac{\mathbf{v}_i}{2}).$$

Summation of (20) for all constituents yields a first version of the *thermal energy balance* which reads as

$$(21) \quad \partial_t(\rho e) + \operatorname{div}(\rho e \mathbf{v} + \tilde{\mathbf{q}}) = \sum_i \mathbf{S}_i : \nabla \mathbf{v}_i - \sum_i \mathbf{u}_i \cdot (\mathbf{f}_i - r_i \mathbf{v}_i + \frac{r_i}{2} \mathbf{u}_i),$$

where

$$(22) \quad \tilde{\mathbf{q}} := \sum_i (\mathbf{q}_i + \rho_i e_i \mathbf{u}_i).$$

The form (21) of the thermal energy balance will be used for exploitation of the entropy principle below. It will then turn out that another definition of the heat flux, containing the equilibrium part of the trace part of the stresses, is more convenient. Thus, for later use, observe that the identity

$$\sum_i \mathbf{S}_i : \nabla \mathbf{v}_i = \sum_i \mathbf{S}_i^{\text{irr}} : \nabla \mathbf{v}_i - p \operatorname{div} \mathbf{v} - \operatorname{div} (\sum_i p_i \mathbf{u}_i) + \sum_i \mathbf{u}_i \cdot \nabla p_i$$

generates a further useful alternative to represent the

thermal energy balance:

$$(23) \quad \partial_t(\rho e) + \operatorname{div}(\rho e \mathbf{v} + \mathbf{q}) = \sum_i \mathbf{S}_i^{\text{irr}} : \nabla \mathbf{v}_i - p \operatorname{div} \mathbf{v} - \sum_i \mathbf{u}_i \cdot (\mathbf{f}_i - r_i \mathbf{v}_i + \frac{r_i}{2} \mathbf{u}_i - \nabla p_i),$$

where the *heat flux* contains non-convective transport of heat and diffusive transport of the species enthalpy $\rho_i e_i + p_i$ and reads as

$$(24) \quad \mathbf{q} := \sum_i (\mathbf{q}_i + (\rho_i e_i + p_i) \mathbf{u}_i).$$

Later, we use the abbreviation $h_i := \rho_i e_i + p_i$. Since, from here on, we do not consider partial energy balances, this will not lead to confusion with the interspecies energy exchange rate.

As already mentioned, the balance equations given above are not closed. Together with the entropy principle below, they form the starting point of our constitutive theory.

4. FUNDAMENTALS OF CONSTITUTIVE MODELING

General Strategy. We consider the model classes I and II. Our strategy is to start with the closure procedure for class-II, followed by a reduction to a class-I model. Since the latter has to be thermodynamically consistent, we need to know the entropy production for both model classes. In the next sections, we focus on the model class II, although some considerations could be done for both classes simultaneously. The reason why we defer considerations on the class-I model to Section 13 is a subtle difference in the temperature definition. This will be explained in detail at the appropriate place below.

Recall the basic variables of the class-II model, which are ρ_i , \mathbf{v}_i and the common temperature T . The determination of these variables relies on the balance equations (5), (6) and (23). For convenience, we repeat them here, but with the momentum balance in its nonconservative form:

$$(25) \quad \partial_t \rho_i + \operatorname{div}(\rho_i \mathbf{v}_i) = r_i \quad \text{with} \quad r_i = \sum_{a=1}^{N_R} M_i \nu_i^a R_a,$$

$$(26) \quad \rho_i (\partial_t \mathbf{v}_i + (\mathbf{v}_i \cdot \nabla) \mathbf{v}_i) - \operatorname{div} \mathbf{S}_i = \mathbf{f}_i - r_i \mathbf{v}_i + \rho_i \mathbf{b}_i,$$

$$(27) \quad \partial_t(\rho e) + \operatorname{div}(\rho e \mathbf{v} + \mathbf{q}) = \sum_i \mathbf{S}_i^{\text{irr}} : \nabla \mathbf{v}_i - p \operatorname{div} \mathbf{v} - \sum_i \mathbf{u}_i \cdot (\mathbf{f}_i - r_i \mathbf{v}_i - \nabla p_i + \frac{r_i}{2} \mathbf{u}_i).$$

This system becomes a PDE-system for the basic variables, if these are related to the constitutive quantities

$$R_a, \quad p_i, \quad \Pi_i, \quad \mathbf{S}_i^{\circ}, \quad \mathbf{f}_i - r_i \mathbf{v}_i, \quad \rho e, \quad \mathbf{q}$$

in a material dependent manner.

Euclidean transformations. We consider the behavior of the involved quantities under coordinate transformations. The most general transformation between two Cartesian coordinate systems, with coordinates written as $(x_1, x_2, x_3) = (x_i)_{i=1,2,3}$ and $(x_1^*, x_2^*, x_3^*) = (x_i^*)_{i=1,2,3}$, respectively, is of the form (employing summation convention)

$$(28) \quad t^* = t + a, \quad x_i^* = O_{ij}(t) x_j + b_i(t), \quad \mathbf{O}(t) \mathbf{O}(t)^{\top} = \mathbf{I}.$$

These are called *Euclidean transformations*. We define the notion of *objective scalars, vectors and tensors (of rank two)* if their components transform according to

$$(29) \quad s^* = s \quad \text{for scalars,}$$

$$(30) \quad v_i^* = O_{ij}v_j \quad \text{for vectors,}$$

$$(31) \quad T_{ij}^* = O_{ik}O_{jl}T_{kl} \quad \text{for rank two tensors.}$$

Note that there are two different classes of quantities: those for which the transformation behavior can be derived are called *kinematic* quantities. Among them are the velocity, the velocity gradient, the acceleration and the diffusion velocities. The transformation properties of the remaining, non-kinematic quantities must be postulated, motivated by experimental experience. Important examples are the scalars mass densities and temperature, the vectors interaction forces and heat flux and the stress tensor. Note that a velocity is not an objective vector in the above sense, but diffusion velocities are, being the difference of two velocities.

Parity. To every physical quantity we introduce an associated parity, called *positive* (+1) or *negative* (-1), by simply assigning the factor -1 if the time unit "second" appears with an uneven power and +1 if it appears with even power. Here we assume SI base units. For example, this yields the parity of the densities of mass, momentum and internal energy according to

$$(32) \quad [\rho] = \frac{\text{kg}}{\text{m}^3} \rightarrow +1, \quad [\rho\mathbf{v}] = \frac{\text{kg}}{\text{m}^2\text{s}} \rightarrow -1, \quad [\rho e] = \frac{\text{kg}}{\text{m s}^2} \rightarrow +1.$$

Evidently, the time derivative of a quantity has the opposite parity, while spatial derivatives keep the parity unchanged.

Universal constitutive principles. The constitutive modeling of *fluids* needs to be consistent with, in particular, the following two universal principles; cf. [55], [39].

- (i) *The principle of material frame indifference* makes a statement on constitutive functions of objective quantities, saying that constitutive functions remain invariant under Euclidean transformation. As an example, consider the constitutive relation of an objective tensor \mathbf{T} , i.e. $T_{ij}^* = O_{ik}O_{jl}T_{kl}$, where we assume that \mathbf{T} is a function of $\nabla\mathbf{v}$. In two different Cartesian frames we have

$$(33) \quad T_{ij} = f_{ij}\left(\frac{\partial v_k}{\partial x_l}\right), \quad \text{respectively } T_{ij}^* = f_{ij}^*\left(\frac{\partial v_k^*}{\partial x_l^*}\right).$$

Then, with $v_i^* = O_{ij}(v_j - \dot{O}_{jl}O_{kl}(x_k^* - b_k) - \dot{b}_j)$, objectivity of \mathbf{T} requires

$$(34) \quad f^*(\mathbf{O}(t)\nabla\mathbf{v}\mathbf{O}(t)^\top + \dot{\mathbf{O}}(t)\mathbf{O}(t)^\top) = \mathbf{O}(t)f(\nabla\mathbf{v})\mathbf{O}(t)^\top.$$

Now the principle of material frame indifference states that $f^* = f$, hence – in this simple case – it implies that f is an *isotropic function*. Moreover, f can only depend on the symmetric part \mathbf{D} of $\nabla\mathbf{v}$ which follows from (34) by choosing $\mathbf{O} = \mathbf{I}$ and $\dot{\mathbf{O}} = -\mathbf{R}$, where \mathbf{R} is the anti-symmetric part of $\nabla\mathbf{v}$.

- (ii) *The entropy principle*, which consists of a certain set of axioms given below, further restricts the generality of the constitutive relations. This principle is also called the 2nd law of thermodynamics.

Formulation of the entropy principle. Any solution of the above system of partial differential equations, composed of the balance equations (25), (26), (27) for the different model classes, is called a *thermodynamic process*. Here, by a solution we just mean functions which satisfy the equations in a local sense. In particular, the value of a quantity and of its derivative can be chosen independently.

With this notion, the 2nd law of thermodynamics consists of the following axioms.

(I) There is an entropy/entropy-flux pair $(\rho s, \Phi)$ as a material dependent quantity, where ρs is an objective scalar and Φ is an objective vector.

(II) The pair $(\rho s, \Phi)$ satisfies the balance equation

$$(35) \quad \partial_t(\rho s) + \operatorname{div}(\rho s \mathbf{v} + \Phi) = \zeta.$$

(III) The entropy has the physical dimension $\text{J kg}^{-1} \text{K}^{-1} = \text{m}^2 \text{s}^{-2} \text{K}^{-1}$, hence is of positive parity. The entropy flux and the entropy production thus have negative parity.

(IV) Any admissible entropy flux is such that

(i) ζ consists of a sum of binary products according to

$$(36) \quad \zeta = \sum_m \mathcal{N}_m \mathcal{P}_m,$$

where the \mathcal{N}_m denote quantities of negative parity, while \mathcal{P}_m refers to positive parity.

(ii) Each binary product describes a dissipative mechanism which must be introduced in advance. Then, $\mathcal{N}_m \mathcal{P}_m \geq 0$ for all m and for every thermodynamic process.

(V) A thermodynamic process for which $\zeta = 0$ is said to be in thermodynamic equilibrium. This statement is to be understood in a pointwise sense; in particular, this must not hold everywhere, i.e. thermodynamic equilibrium can be attained locally.

A thermodynamic process is called reversible if $\zeta = 0$ everywhere.

In addition to these universal axioms, we impose two further ones which refer to the most general constitutive models we are interested in. These are:

(VI) There are the following *dissipative mechanisms* for the fluid mixtures under consideration: *mass diffusion, chemical reaction, viscous flow* (including bulk and shear viscosity) and *heat conduction*.

(VII) For the class of fluid mixtures under consideration, we restrict the dependence of the entropy according to

$$(37) \quad \rho s = \rho \tilde{s}(\rho e, \rho_1, \dots, \rho_N),$$

where $\rho \tilde{s}$ is a *strictly concave function* which satisfies the principle of material frame indifference. By means of this function, we define the (*absolute*) *temperature* T and *chemical potentials* μ_i according to

$$(38) \quad \frac{1}{T} := \frac{\partial \rho \tilde{s}}{\partial \rho e}, \quad -\frac{\mu_i}{T} := \frac{\partial \rho \tilde{s}}{\partial \rho_i}.$$

Remarks on the Entropy Principle. 1. Axioms (I) and (II) are identical to those versions given by Müller in [39] and Alt in [1].

2. Our concept of parity employed in axiom (III) and (IV-i) for generic quantities was stimulated by Meixner's paper [36]. In the present work this concept is simplified to the above rule on how to determine the parity of a given quantity. This concept of parity is crucial for a proper introduction of cross-couplings via entropy invariant mixing between dissipative mechanisms. This will be taken up in Section 6 below.

3. There is no axiom (IV-i) in the entropy principles of Müller in [39] or Alt in [1]. Instead, the versions of Müller and Alt rely on the *principle of equipresence* whereupon all constitutive quantities may depend on the same set of variables. For example, if the velocity gradient appears in the constitutive law of the stress tensor it should also appear in the constitutive law of the entropy density. The entropy

flux in their theories is completely determined by the principle of equipresence. Our version does not use this principle and thus is much simpler to exploit. In particular for advanced constitutive models the equipresence principle requires an enormous computational effort, cf. [33]. However, without equipresence, more preliminary knowledge is required.

4. Axiom (IV-ii) is a strengthened form of the principal of detailed balance, which essentially says that in equilibrium all individual dissipative mechanisms are themselves in equilibrium, i.e. zero entropy production implies that all binary products vanish. The latter property can be guaranteed if every binary product has non-negative entropy production for any thermodynamic process. This is precisely the content of axiom (IV-ii). The valid use of this strengthened form requires a careful choice of the decomposition of the entropy production into binary products such that each product contains a co-factor which can be varied independently of the others; cf. also the next remark and observe that the representation of the entropy production is not uniquely determined. For example, in the following we will show that chemical reactions contribute with two binary products to the entropy production. There is one product due to the generation of thermal energy and another one, which is new, that produces momentum.

5. The exploitation of Axiom (V) requires preliminary knowledge on equilibrium thermodynamics, where those quantities that vanish in thermodynamic equilibrium are to be identified. For example, we know by experience in advance that in thermodynamic equilibrium we must have

$$(39) \quad R_\alpha = 0, \quad \mathbf{u}_i = 0, \quad \nabla \mathbf{v}_i + \nabla \mathbf{v}_i^T = 0, \quad \nabla T = 0.$$

Correspondingly, these conditions motivate the constitutive axiom (VI), saying that the mechanisms that drive a body to equilibrium are: chemical reactions, mass diffusion, viscous flow and heat conduction. These mechanisms contribute with N_R , $N - 1$, N , respectively 1 binary product to the entropy production. Linear relations between the factors \mathcal{N}_m and \mathcal{P}_m with appropriate coefficients provide the simplest possibility to guarantee non-negativity of the entropy productions. However, note that this does not imply linearity with respect to the variables.

6. The assumptions on the constitutive functions function $\rho \tilde{s}$ in Axiom (VII) are crucial since they fix the class of fluid mixtures under consideration. In particular, the omission of density gradients in the list of variables for $\rho \tilde{s}$ excludes nonlocal effects, e.g. due to mesoscopic forces, which are required for so-called phase field models. Here, we consider single-phase fluid mixtures. The choice of ρe and the ρ_i as independent variables in (37) is generic, since these are the balanced quantities. A further dependence directly on the \mathbf{v}_i is not possible due to material frame indifference. But a dependence on the diffusion velocities \mathbf{u}_i is possible. Furthermore, a dependence on $\operatorname{div} \mathbf{v}$ and/or ∇T would also be consistent with the principle of material frame indifference. However, if we were to include such dependencies in the entropy function they will be ruled out by the exploitation of the entropy principle. The proof of this proposition is left to the reader.

7. The concavity postulate (VII) can be motivated as a generalization of a well-known result of equilibrium thermodynamics for homogeneous bodies. To this end we consider a fluid mixture in a container with time-dependent volume $V(t)$. The container is closed by a movable piston subjected to a constant pressure p_0 , and the outer surface of the whole device is at constant temperature T_0 . In this case the equations of balance for total energy E and total entropy S read

$$(40) \quad \frac{dE}{dt} + p_0 \frac{dV}{dt} = - \oint \mathbf{q} \cdot \mathbf{n} \, da \quad \text{and} \quad \frac{dS}{dt} + \frac{1}{T_0} \oint \mathbf{q} \cdot \mathbf{n} \, da \geq 0.$$

Elimination of the heat flux leads to the inequality

$$(41) \quad \frac{dA}{dt} \leq 0 \quad \text{with} \quad A = E - T_0 S + p_0 V.$$

Thus the quantity A , which is called available free energy, can only decrease and assumes its minimum in equilibrium.

Now we study for fixed external values T_0 and p_0 a homogeneous process inside the mixture which is characterized by the state $(T(t), p(t), m_1(t), \dots, m_N(t))$ and ask for its equilibrium state. Note that A is neither the Gibbs energy $G = E - TS + pV$ nor the Helmholtz free energy $\Psi = E - TS$. Rather, we have $A = G + (T - T_0)S + (p_0 - p)V$. Moreover, in a homogenous system we can write $\Psi = \rho\psi V$.

To keep this motivation short we only consider the non-reactive case, where the masses $m_i(t)$ are independent of time. Then the relevant variables of A are T and p and the minima follow from $\partial A/\partial T = 0$ and $\partial A/\partial p = 0$. The physically obvious result is that $T = T_0$ and $p = p_0$ give the necessary condition for equilibrium.

Its derivation makes use of three identities which are valid for homogenous systems, viz.

$$(42) \quad \frac{\partial G(T, p, m_1, \dots, m_N)}{\partial T} = -S, \quad \frac{\partial G(T, p, m_1, \dots, m_N)}{\partial p} = V, \quad \frac{\partial G(T, p, m_1, \dots, m_N)}{\partial m_i} = \mu_i.$$

The proof of these relations starts from $G(T, p, m_1, \dots, m_N) = V(\rho\hat{\psi}(T, \frac{m_1}{V}, \dots, \frac{m_N}{V}) + p)$ with $V = V(T, p, m_1, \dots, m_N)$. For example, we have

$$(43) \quad \frac{\partial G}{\partial m_i} = \frac{\partial V}{\partial m_i}(\rho\hat{\psi} + p) + \sum_{j=1}^N \frac{\partial \rho\hat{\psi}}{\partial \rho_j} \left(\frac{\delta_{ij}}{V} - \frac{m_j}{V^2} \frac{\partial V}{\partial m_i} \right) = \frac{\partial \rho\hat{\psi}}{\partial \rho_i} = \mu_i.$$

We proceed to characterize the equilibria. The sufficient conditions that A assumes a minimum at $T = T_0, p = p_0$ is the positive definiteness of the matrix of its second derivatives. We obtain, in the simple case with constant masses, the condition that

$$(44) \quad \begin{pmatrix} \frac{\partial S}{\partial T} & -\frac{\partial V}{\partial T} \\ \frac{\partial V}{\partial T} & \frac{\partial V}{\partial p} \end{pmatrix} \text{ is positive definite.}$$

If chemical reactions and, hence, time-dependent $m_i(t)$ are included above, the condition that the matrix

$$\left(\frac{\partial \mu_i}{\partial \rho_j} \right)_{i,j \in \{1, \dots, N\}} \text{ is positive definite}$$

is also derived as an additional part of the sufficient conditions for a minimum. We refrain from giving the details here.

These conditions coincide with corresponding inequalities which will be derived in the following section from the concavity postulate. But they will be more general in two aspects: They do not refer to homogeneous systems and they also hold in non-equilibrium.

8. The definition of temperature is accompanied by some subtleties. From a theoretical point of view there is a certain freedom how to define temperature. Because an object that we might call temperature does not explicitly appear in the equations of balance it cannot be introduced as a primitive quantity in thermodynamics. At first glance our definition (38)₁ seems natural, because it agrees with the corresponding definition of equilibrium thermodynamics. But the key point of the present approach is the choice of the total internal energy ρe according to (19) as a variable in (38)₁. Other choices are possible. Interestingly, de Groot and Mazur [19] mention our choice (19) but due to some unidentified reasons they finally prefer to choose ρe_{int} from (17) as a variable in the entropy function. Müller proceeds differently in [39]. He starts with an empirical temperature and after a chain of reasonings Müller obtains our definition (19) as a result. Let us also mention here the situation in Boltzmann's kinetic theory. Recall that the theory is restricted to monatomic ideal gases. Here the temperature is defined via p/ρ , where pressure and density are directly related to the distribution function. In equilibrium our choice obviously agrees with the kinetic definition, but in nonequilibrium there is a difference,

see [41] for more details. However, this fact does not generate any problem. One simply has to deal with two different temperature measures.

5. EXPLOITATION OF THE ENTROPY PRINCIPLE

Entropy inequality. Starting point for the evaluation of the 2nd law is the entropy balance, which we use in the form

$$\zeta = \partial_t(\rho s) + \mathbf{v} \cdot \nabla(\rho s) + \rho s \operatorname{div} \mathbf{v} + \operatorname{div} \Phi.$$

We insert $\rho s = \rho \tilde{s}(\rho e, \rho_1, \dots, \rho_N)$ into the first two terms and carry out the differentiations. Then we eliminate the resulting time derivatives by means of the balance equations (5) and (21). We introduce temperature and chemical potentials according to the definitions (38). Then, after straightforward computations, a first representation of the entropy production is

$$(45) \quad \zeta = \operatorname{div} \left(\Phi - \frac{\tilde{\mathbf{q}}}{T} + \sum_i \frac{\rho_i \mu_i \mathbf{u}_i}{T} \right) - \frac{1}{T} \left(\rho e - T \rho s - \sum_i \rho_i \mu_i \right) \operatorname{div} \mathbf{v} - \frac{1}{T} \sum_i P_i \operatorname{div} \mathbf{v}_i \\ - \frac{1}{T} \sum_i \mathbf{u}_i \cdot \left(\rho_i T \nabla \frac{\mu_i}{T} + \mathbf{f}_i - r_i \mathbf{v}_i + \frac{1}{2} r_i \mathbf{u}_i \right) - \frac{1}{T} \sum_{a=1}^{N_R} R_a \mathcal{A}_a + \frac{1}{T} \sum_i \mathbf{S}_i^\circ : \mathbf{D}_i^\circ + \tilde{\mathbf{q}} \cdot \nabla \frac{1}{T}.$$

In (45), we have rewritten the term $\sum_{i=1}^N r_i \mu_i$ as $\sum_{a=1}^{N_R} R_a \mathcal{A}_a$, introducing the so-called *affinities*

$$(46) \quad \mathcal{A}_a = \sum_{i=1}^N \nu_i^a M_i \mu_i.$$

This reflects the fact that every chemical reaction relates to a dissipative mechanism.

Now, for the derivation of the entropy production in the class-II model one has to account for the fact that, while for instance $\operatorname{div} \mathbf{u}_i$ can be chosen independently of \mathbf{u}_i in exploiting the entropy principle, the defining relations $\mathbf{u}_i = \mathbf{v}_i - \mathbf{v}$ lead to the constraints $\operatorname{div} \mathbf{u}_i = \operatorname{div} \mathbf{v}_i - \operatorname{div} \mathbf{v}$. These constraints are incorporated into the exploitation using Lagrange multipliers $\Lambda_i = \Lambda_i(T, \rho_1, \dots, \rho_N)$ and adding the terms

$$\sum_i \frac{\Lambda_i}{T} (\operatorname{div} \mathbf{v}_i - \operatorname{div} \mathbf{v} - \operatorname{div} \mathbf{u}_i)$$

to the entropy production; cf. Lemma 7.3.1 in [33] concerning a proof that the entropy inequality with this addition and without constraints is equivalent to the original inequality, but evaluated under the constraints. Finally, we introduce the *free energy density* $\rho \psi := \rho e - T \rho s$. Then, after rearrangement of terms, the entropy production for a class-II model reads as

$$(47) \quad \zeta = \operatorname{div} \left(\Phi - \frac{\tilde{\mathbf{q}}}{T} + \sum_i \frac{(\rho_i \mu_i - \Lambda_i) \mathbf{u}_i}{T} \right) - \frac{1}{T} \left(\rho \psi - \sum_i (\rho_i \mu_i - \Lambda_i) \right) \operatorname{div} \mathbf{v} \\ - \frac{1}{T} \sum_i (P_i - \Lambda_i) \operatorname{div} \mathbf{v}_i - \frac{1}{T} \sum_i \mathbf{u}_i \cdot \left(\rho_i T \nabla \frac{\mu_i}{T} + \mathbf{f}_i - r_i \mathbf{v}_i + \frac{1}{2} r_i \mathbf{u}_i - T \nabla \frac{\Lambda_i}{T} \right) \\ - \frac{1}{T} \sum_{a=1}^{N_R} R_a \mathcal{A}_a + \frac{1}{T} \sum_i \mathbf{S}_i^\circ : \mathbf{D}_i^\circ + \tilde{\mathbf{q}} \cdot \nabla \frac{1}{T}.$$

Now, we proceed as follows.

(a) To satisfy axiom (IV-i), we choose the entropy flux as

$$(48) \quad \Phi = \frac{\tilde{\mathbf{q}}}{T} - \sum_i \frac{(\rho_i \mu_i - \Lambda_i) \mathbf{u}_i}{T},$$

where the Λ_i will be determined below.

(b) The entropy production reduces to a sum of six binary products and we first choose

$$R_a = 0, \quad \nabla T = 0, \quad \mathbf{u}_i = 0, \quad \mathbf{D}_i^\circ = 0;$$

recall that $\text{tr}(\mathbf{D}_i) = \text{div} \mathbf{v}_i$ and $P_i = p_i + \Pi_i$, where $\Pi_i = 0$ in equilibrium. In this case the entropy inequality becomes

$$T\zeta = (\sum_i (\rho_i \mu_i - \Lambda_i) - \rho\psi) \text{div} \mathbf{v} + \sum_i (p_i - \Lambda_i) \text{div} \mathbf{v}_i - \sum_i \Pi_i \text{div} \mathbf{v}_i \geq 0,$$

where $\text{div} \mathbf{v}$ and all $\text{div} \mathbf{v}_i$ can be varied independently in the exploitation. For $\text{div} \mathbf{v} = \text{div} \mathbf{v}_i = 0$ the processes are in equilibrium, where the entropy production assumes a minimum. This implies

$$(49) \quad \rho\psi - \sum_i (\rho_i \mu_i - \Lambda_i) = 0, \quad p_i - \Lambda_i = 0 \quad \text{and} \quad - \sum_i \Pi_i \text{div} \mathbf{v}_i \geq 0.$$

Inserting $\Lambda_i = p_i$ from (49)₂ into (49)₁ yields

$$(50) \quad \rho\psi + p - \sum_i \rho_i \mu_i = 0.$$

Relation (50) is the *Gibbs-Duhem equation* which is well-known and also holds true for class-I models. Since it only involves equilibrium quantities, the Gibbs-Duhem equation also holds for general thermodynamic processes. Note that here an important result is the fact that only a *single* Gibbs-Duhem equation results.

Inserting $\Lambda_i = p_i$ from (49)₂ into (48) yields

$$(51) \quad \Phi = \frac{\mathbf{q}}{T} - \sum_i \frac{\rho_i \mu_i \mathbf{u}_i}{T},$$

if we define the *heat flux* for the class-II model as we already noted in (24), namely

$$\mathbf{q} := \sum_i (\mathbf{q}_i + (\rho_i e_i + p_i) \mathbf{u}_i).$$

The remaining part is the sum of four binary products which cause entropy production. These are the four postulated dissipative mechanisms, namely (i) mass diffusion, (ii) chemical reactions, (iii) viscous flow (bulk and shear viscosity) and (iv) heat conduction. The second law gives restrictions for constitutive equations of these dissipative mechanisms, where the axiom (VI-ii) requires all individual contributions to be non-negative.

With (a) and (b) above, the entropy production of the class-II model assumes its final form:

$$(52) \quad \begin{aligned} \zeta = & - \sum_i \mathbf{u}_i \cdot \left(\rho_i \nabla \frac{\mu_i}{T} + \frac{1}{T} (\mathbf{f}_i - r_i \mathbf{v}_i + \frac{1}{2} r_i \mathbf{u}_i - \nabla p_i) - (\rho_i e_i + p_i) \nabla \frac{1}{T} \right) \\ & - \frac{1}{T} \sum_{a=1}^{N_R} R_a \mathcal{A}_a + \frac{1}{T} \sum_i \mathbf{S}_i^{\text{irr}} : \mathbf{D}_i + \sum_i \mathbf{q}_i \cdot \nabla \frac{1}{T}. \end{aligned}$$

Remarks on the derivation of the entropy production. 1. The specific form of the intermediate representation (45) is not unique. Above, we employed the relation

$$\text{div}(\rho_i \mathbf{v}_i) = \mathbf{v} \cdot \nabla \rho_i + \mathbf{u}_i \cdot \nabla \rho_i + \text{div}(\rho_i \mathbf{u}_i)$$

to arrive at (45).

2. If the entropy balance is exploited with the thermal energy balance in the form (23) and if, furthermore, the term $\text{div} \mathbf{v}$ is eliminated using the relation

$$\text{div} \mathbf{v} = \sum_i y_i \text{div} \mathbf{v}_i + \sum_i \mathbf{u}_i \cdot \nabla y_i,$$

then no Lagrange multipliers are required. Apparently, this is the only form in which the interdependencies between the diverse velocity divergences are not interfering with the exploitation. Note that the Lagrange multipliers could still be used in which case $\Lambda_i = 0$ for all i .

We nevertheless preferred the derivation above with $\tilde{\mathbf{q}}$ instead of \mathbf{q} because the form of the heat flux according to (24) is not a priori clear. In fact, this definition for \mathbf{q} is only motivated by the final form which it implies for the entropy flux, i.e. (51), which resembles the classical one from TIP for mixtures.

3. It is interesting to observe that the entropy flux can be written as

$$\Phi = \sum_i \left(\frac{\mathbf{q}_i}{T} + \frac{\rho_i e_i + p_i - \rho_i \mu_i}{T} \mathbf{u}_i \right).$$

Let us note that in the case of so-called simple mixtures, introduced in detail in section 15 below, the quantity $(\rho_i e_i + p_i - \rho_i \mu_i)/T$ is nothing but the partial entropy $\rho_i s_i$. This nicely shows the two different contributions to the entropy flux in a class-II mixture. Note also that the total flux of entropy then attains the form

$$\rho s \mathbf{v} + \Phi = \sum_i \left(\rho_i s_i \mathbf{v}_i + \frac{\mathbf{q}_i}{T} \right),$$

thus being just the sum of the individual total entropy fluxes of the constituents, each having $\Phi_i = \mathbf{q}_i/T$ as the non-convective flux of partial entropy.

4. Note that in (52), the total heat flux according to (24) contributes with two terms: The first term involves heat transport due to conduction, while the second term describes diffusive heat transport and is proportional to the diffusion velocities. Therefore, in order to collect all co-factors of the \mathbf{u}_i which, hence, belong to the mechanism of diffusion, we shuffled those terms to the first binary product.

Based on the entropy production (52) we are going to derive mixture models for fluid mixtures of increasing physical complexity.

Helmholtz free energy and its derivatives. Recall that absolute temperature and chemical potentials are introduced according to the definitions (38). The specific (Helmholtz) free energy $\psi = e - Ts$ is useful if we change the variables from $\{\rho e, \rho_1, \dots, \rho_N\}$ to $\{T, \rho_1, \dots, \rho_N\}$ with $\rho e = \rho \hat{e}(T, \rho_1, \dots, \rho_N)$ by solving (38)₁ for ρe . Then, for $\psi = \hat{\psi}(T, \rho_1, \dots, \rho_N)$ we obtain from (38) the relations

$$(53) \quad \rho s = -\frac{\partial \rho \hat{\psi}}{\partial T}, \quad \mu_i = \frac{\partial \rho \hat{\psi}}{\partial \rho_i} \quad \text{implying} \quad e = -T^2 \frac{\partial}{\partial T} \left(\frac{\hat{\psi}}{T} \right).$$

The Gibbs-Duhem equation (50)₁ serves to determine the pressure p from the free energy density and for this reason we write

$$(54) \quad p = -\rho \psi + \sum_{i=1}^N \mu_i \rho_i.$$

Two further sets of variables are in common use. Using $\rho_i = \rho y_i$ we may change the variables from $\{T, \rho_1, \dots, \rho_N\}$ to $\{T, \rho, y_1, \dots, y_{N-1}\}$ and indicate this by writing, say,

$$(55) \quad \rho \psi = \rho \bar{\psi}(T, \rho, y_1, \dots, y_{N-1}).$$

The generic function $F(T, \rho, y_1, \dots, y_{N-1}) = \hat{F}(T, \rho_1, \dots, \rho_N)$ satisfies the simple rule $F_\rho = \sum_{j=1}^N y_j \hat{F}_{\rho_j}$ which is used to obtain from (54)

$$(56) \quad p = \bar{p}(T, \rho, y_1, \dots, y_{N-1}) = \rho^2 \frac{\partial \bar{\psi}}{\partial \rho}.$$

Next we solve (56) for $\rho = \rho(T, p, y_1, \dots, y_{N-1})$ and calculate from $e = \hat{e}(T, \rho, y_1, \dots, y_{N-1})$, obtained from (53)₃, the function $e = e(T, p, y_1, \dots, y_{N-1})$. Finally we introduce the specific heat at

constant densities, c_v , and the specific heat at constant pressure, c_p , by

$$(57) \quad c_v = \frac{\partial \hat{e}}{\partial T} \quad \text{and} \quad c_p = \frac{\partial e}{\partial T} + p \frac{\partial}{\partial T} \left(\frac{1}{\rho} \right).$$

The specific heat c_p is related to c_v by

$$(58) \quad c_p = c_v + T \frac{\partial(1/\bar{\rho})}{\partial T} \frac{\partial p}{\partial T} = c_v + \frac{T}{\rho^2} \left(\frac{\partial \bar{\rho}}{\partial T} \right)^2 \frac{\partial p}{\partial \rho},$$

The proof of (58)₁ starts from the two definitions of c_p and c_v and proceeds via $e = \psi + Ts$ and the relation $\partial_T s = 1/T \partial_T e + \partial_T(1/\rho) \partial_T \bar{p}$. Equation (58)₂ holds due to the identity $\partial_T \bar{p} = -\partial_T \rho / \partial_p \rho$.

Concavity of the entropy function. This paragraph addresses the exploitation of the concavity postulate. Here derivatives are indicated by indices, except in the main results. Moreover, note that two different representations of the entropy function will be used, viz.

$$(59) \quad \rho s = \rho \tilde{s}(\rho e, \rho_1, \rho_2, \dots, \rho_N) = \rho \hat{s}(T, \rho_1, \rho_2, \dots, \rho_N).$$

The entropy postulate (VII) states that the entropy function (59)₁ is strictly concave with respect to all variables. Thus the $(N+1) \times (N+1)$ matrix $-\mathbf{M}$ of its second derivatives has the property that

$$(60) \quad \mathbf{M} = - \begin{pmatrix} (\rho \tilde{s})_{\rho e \rho e} & (\rho \tilde{s})_{\rho e \rho_1} & \dots & (\rho \tilde{s})_{\rho e \rho_N} \\ (\rho \tilde{s})_{\rho_1 \rho e} & (\rho \tilde{s})_{\rho_1 \rho_1} & \dots & (\rho \tilde{s})_{\rho_1 \rho_N} \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ (\rho \tilde{s})_{\rho_N \rho e} & (\rho \tilde{s})_{\rho_N \rho_1} & \dots & (\rho \tilde{s})_{\rho_N \rho_N} \end{pmatrix} \quad \text{is positive definite,}$$

implying important inequalities. The positive definiteness of \mathbf{M} is exploited by Sylvester's criterion: All principal determinants must be positive, i.e.

$$(61) \quad -(\rho \tilde{s})_{\rho e \rho e} > 0, \quad -((\rho \tilde{s})_{\rho e \rho e} (\rho \tilde{s})_{\rho_1 \rho_1} - ((\rho \tilde{s})_{\rho e \rho_1})^2) > 0, \quad - \begin{vmatrix} (\rho \tilde{s})_{\rho e \rho e} & (\rho \tilde{s})_{\rho e \rho_1} & (\rho \tilde{s})_{\rho e \rho_2} \\ (\rho \tilde{s})_{\rho_1 \rho e} & (\rho \tilde{s})_{\rho_1 \rho_1} & (\rho \tilde{s})_{\rho_1 \rho_2} \\ (\rho \tilde{s})_{\rho_2 \rho e} & (\rho \tilde{s})_{\rho_2 \rho_1} & (\rho \tilde{s})_{\rho_2 \rho_2} \end{vmatrix} > 0,$$

and so on. These conditions are necessary and sufficient for the strict concavity of the entropy function. By means of (38) we can also write

$$(62) \quad -\left(\frac{1}{T}\right)_{\rho e} > 0, \quad \left(\frac{1}{T}\right)_{\rho e} \left(\frac{\hat{\mu}_1}{T}\right)_{\rho_1} - \left(\left(\frac{1}{T}\right)_{\rho_1}\right)^2 > 0, \quad \begin{vmatrix} \left(-\frac{1}{T}\right)_{\rho e} & \left(-\frac{1}{T}\right)_{\rho_1} & \left(-\frac{1}{T}\right)_{\rho_2} \\ \left(-\frac{1}{T}\right)_{\rho_1} & \left(\frac{\hat{\mu}_1}{T}\right)_{\rho_1} & \left(\frac{\hat{\mu}_1}{T}\right)_{\rho_2} \\ \left(-\frac{1}{T}\right)_{\rho_2} & \left(\frac{\hat{\mu}_1}{T}\right)_{\rho_2} & \left(\frac{\hat{\mu}_2}{T}\right)_{\rho_2} \end{vmatrix} > 0, \quad \dots$$

Next, we rewrite these inequalities in the variables $T, \rho_1, \rho_2, \dots, \rho_N$. To this end we consider a generic relation $\tilde{F}(\rho e, \rho_1, \rho_2, \dots, \rho_N) = \hat{F}(T, \rho_1, \rho_2, \dots, \rho_N)$ with $\rho e = \rho \hat{e}(T, \rho_1, \rho_2, \dots, \rho_N)$. The corresponding derivatives are related to each other by

$$(63) \quad \hat{F}_T = \tilde{F}_{\rho e}(\rho \hat{e})_T, \quad \hat{F}_{\rho_i} = \tilde{F}_{\rho e}(\rho \hat{e})_{\rho_i} + \tilde{F}_{\rho_i}.$$

We insert $(\rho \hat{e})_T = \rho \hat{e}_T = \rho c_v$ from (57)₁. Furthermore, using the identity $(\rho \hat{e})_{\rho_i} = \hat{\mu}_i - T \hat{\mu}_{iT}$ which follows by differentiation of (53), we obtain

$$(64) \quad \tilde{F}_{\rho e} = \frac{1}{\rho c_v} \hat{F}_T, \quad \tilde{F}_{\rho_i} = \hat{F}_{\rho_i} - (\hat{\mu}_i - T \hat{\mu}_{iT}) \hat{F}_T.$$

Choosing $\tilde{F} = -1/\tilde{T}$ and $\tilde{F} = \tilde{\mu}_i/\tilde{T}$, respectively, we derive

$$(65) \quad \left(-\frac{1}{\tilde{T}}\right)_{\rho e} = \frac{1}{\rho T^2 c_v}, \quad \left(-\frac{1}{\tilde{T}}\right)_{\rho i} = -\frac{\hat{\mu}_i - T \hat{\mu}_{iT}}{\rho T^2 c_v}, \quad \left(\frac{\tilde{\mu}_i}{\tilde{T}}\right)_{\rho j} = \frac{\hat{\mu}_{i\rho_j}}{T} + \frac{(\hat{\mu}_i - T \hat{\mu}_{iT})(\hat{\mu}_j - T \hat{\mu}_{jT})}{\rho T^2 c_v}.$$

Due to these representations we finally may rewrite the inequalities (62) as the simple statement

$$(66) \quad c_v > 0 \quad \text{and} \quad \left(\frac{\partial \hat{\mu}_i}{\partial \rho_j}\right)_{i,j \in \{1, \dots, N\}} \quad \text{is positive definite.}$$

From (66) we may derive further important inequalities concerning the constitutive functions for the specific thermal energy e and the pressure p . We again use $\rho_i = \rho y_i$ to change the variables from $\{T, \rho_1, \dots, \rho_N\}$ to $\{T, \rho, y_1, \dots, y_{N-1}\}$. Recall that the generic function $\bar{F}(T, \rho, y_1, \dots, y_{N-1}) = \hat{F}(T, \rho_1, \dots, \rho_N)$ satisfies the simple rule $\bar{F}_\rho = \sum_{j=1}^N y_j \hat{F}_{\rho_j}$ which is used to obtain from the Gibbs-Duhem equation (54) the relations

$$(67) \quad \bar{p}_\rho = -\bar{\psi} - \rho \bar{\psi}_\rho + \sum_{i=1}^N y_i \mu_i + \rho \sum_{i=1}^N y_i \mu_{i\rho} = \rho \sum_{i,j=1}^N y_i y_j \hat{\mu}_{i\rho_j}.$$

Furthermore we need here the relation , i.e.

$$(68) \quad c_p = c_v + \frac{T}{\rho^2} (\bar{\rho}_T)^2 p_\rho.$$

Employing the relations (58)₂ between the specific heats and (67)₂, we obtain from (66) the additional inequalities

$$(69) \quad \frac{\partial \bar{p}}{\partial \rho} > 0, \quad c_p > c_v \quad \text{and} \quad \left(\frac{\partial \rho}{\partial T}\right)^2 < \frac{c_p \rho^2}{T} \frac{\partial \rho}{\partial p}.$$

In particular the inequality (69)₃ plays an important role in the limiting case of incompressibility, which will be the subject of Section 16.

6. ENTROPY INVARIANT CROSS-COUPPLINGS AND THE ONSAGER RELATIONS.

By the above entropy principle, the entropy production has the form (36), i.e.

$$\zeta = \sum_m \mathcal{N}_m \mathcal{P}_m,$$

where the sum runs through all dissipative mechanisms and the factors $\mathcal{N}_m, \mathcal{P}_m$ have negative, respectively positive parity. But the precise form of this decomposition of the entropy production into binary products is by no means unique! Indeed, cross-effects between the dissipative mechanisms can be introduced by mixing inside the parity-groups. Such cross-effects leave both the parity structure (36) and the entropy production invariant. To be more specific, let us write the entropy production as a scalar product in an appropriate finite dimensional space, i.e.

$$(70) \quad \zeta = \langle \mathbf{N}, \mathbf{P} \rangle,$$

where all fluxes, respectively forces are placed inside the single vectors \mathbf{N} , respectively \mathbf{P} . Considering this representation, axiom (IV-ii) enforces a diagonal closure, corresponding to let

$$(71) \quad \mathbf{N} = \Lambda \mathbf{P} \quad \text{with} \quad \Lambda = \text{diag}(\lambda_k), \quad \lambda_k \geq 0.$$

Let us note in passing that we may want to impose several restrictions on the coefficients λ_k in (71) due to the assumption of isotropy; e.g., we assume the same coefficient for closing different Cartesian components of the same vector. However, for the subsequent explanation this does not play a role.

Now consider, instead of (70), the form

$$(72) \quad \zeta = \langle \tilde{\mathbf{N}}, \tilde{\mathbf{P}} \rangle \quad \text{with} \quad \tilde{\mathbf{N}} = A \mathbf{N}, \quad \tilde{\mathbf{P}} = B \mathbf{P},$$

where A and B are regular matrices. In order that, for arbitrary thermodynamic processes, the form ζ does not change we must have

$$(73) \quad \langle \mathbf{N}, \mathbf{P} \rangle = \langle \tilde{\mathbf{N}}, \tilde{\mathbf{P}} \rangle = \langle A \mathbf{N}, B \mathbf{P} \rangle \quad \text{for all } \mathbf{N}, \mathbf{P},$$

implying $A^T B = \mathbf{I}$. Axiom (IV-ii) also applies to this representation of ζ , i.e. $\tilde{N}_m \tilde{P}_m \geq 0$ for all m which again enforces a diagonal closure. This leads to the constitutive relations

$$(74) \quad \tilde{\mathbf{N}} = \tilde{\Lambda} \tilde{\mathbf{P}} \quad \text{hence} \quad \mathbf{N} = A^{-1} \tilde{\Lambda} B \mathbf{P} = B^T \tilde{\Lambda} B \mathbf{P}$$

with a diagonal matrix $\tilde{\Lambda}$ with non-negative entries. Hence

$$(75) \quad \mathbf{N} = L \mathbf{P} \quad \text{with } L \text{ being symmetric and positive semi-definite.}$$

Consequently, the entropy principle above, together with a linear (in non-equilibrium quantities) closure after entropy invariant mixing exactly leads to a full cross-coupling with a positive semi-definite and *symmetric* matrix of phenomenological coefficients. Hence the Onsager reciprocity relations are satisfied.

To arrive at (75), one does not need to start with a fully general regular matrix A . Indeed, recall from elementary matrix calculus that every regular matrix A allows for a decomposition of the type $A = LU$ with L a lower-triangular and U an upper triangular matrix, both being also quadratic and regular, such that also $U_{ii} = 1$, say, for all i . This follows for instance by applying the classical Gauss algorithm. Hence the entropy after mixing between mechanisms becomes

$$(76) \quad \zeta = \langle A \mathbf{N}, B \mathbf{P} \rangle = \langle U \mathbf{N}, L^T B \mathbf{P} \rangle = \langle U \mathbf{N}, U^{-T} \mathbf{P} \rangle,$$

since $B = A^{-T}$ because the entropy production is required to stay invariant. Consequently, it suffices to mix with an upper diagonal matrix U such that all $U_{ii} = 1$. For mixtures with few constituents, this fact allows for an easy cross-coupling "by hand".

The above observation leading to (75) is related to known considerations of the invariance of Onsager's relations under transformations of the system of fluxes and driving forces; cf. [19]. Note also that the entropy production invariance is to be understood for the form of the unclosed entropy production, not for the production rate in the final PDE-system. The considered cross-coupling via entropy neutral mixing between mechanisms is given above for fixed number of dissipative mechanisms. It is also possible to apply such a mixing in a more general way, also adding new dissipative mechanisms. This way, also the entropy flux will be altered. An example is provided below in Section 13, where we reduce our class-II model to obtain improved class-I closure relations. A totally different example can be found in [11].

In the classical literature on irreversible processes, the factors building the binary products in the entropy production are called *fluxes* and *driving forces*. This notion can be rather misleading in the context of cross-effects, since the assignment of the label "flux" to a quantity is usually guided by its appearance under a divergence, independently whether it has positive or negative parity. In fact this can lead to an apparent anti-symmetric coupling. To understand this, assume a second classification of the set of all factors appearing as components in \mathbf{N} and \mathbf{P} into fluxes and driving forces such that

$$\mathbf{N} = \begin{bmatrix} \mathbf{F}_1 \\ \mathbf{D}_2 \end{bmatrix}, \quad \mathbf{P} = \begin{bmatrix} \mathbf{D}_1 \\ \mathbf{F}_2 \end{bmatrix},$$

where the \mathbf{F}_i and \mathbf{D}_i are blocks entirely composed of fluxes or driving forces. Applying entropy invariant mixing and linear closure as above, we arrive at the constitutive relation

$$\begin{bmatrix} \mathbf{F}_1 \\ \mathbf{D}_2 \end{bmatrix} = L \begin{bmatrix} \mathbf{D}_1 \\ \mathbf{F}_2 \end{bmatrix} \quad \text{with } L = \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \geq 0, \quad L_{ii}^T = L_{ii}, \quad L_{12}^T = L_{21}.$$

Rewritten as a relation between fluxes and driving forces, this becomes

$$\begin{bmatrix} \mathbf{F}_1 \\ \mathbf{F}_2 \end{bmatrix} = \mathcal{L} \begin{bmatrix} \mathbf{D}_1 \\ \mathbf{D}_2 \end{bmatrix} \quad \text{with } \mathcal{L} = \begin{bmatrix} \mathcal{L}_{11} & \mathcal{L}_{12} \\ \mathcal{L}_{21} & \mathcal{L}_{22} \end{bmatrix},$$

where

$$\mathcal{L}_{11} = L_{11} - L_{12}L_{22}^{-1}L_{21}, \quad \mathcal{L}_{12} = L_{12}L_{22}^{-1} = -\mathcal{L}_{21}^\top, \quad \mathcal{L}_{22} = L_{22}.$$

Evidently, the matrix \mathcal{L} is not symmetric, but consists of symmetric blocks on the block-diagonal and skew-symmetric off-diagonal blocks. Note also that \mathcal{L} inherits the positive semi-definiteness of L ; in particular, the block $L_{11} - L_{12}L_{22}^{-1}L_{21}$ itself is positive semi-definite which follows from

$$\langle L_{11} x, x \rangle + \langle L_{12} y, x \rangle + \langle L_{21} x, y \rangle + \langle L_{22} y, y \rangle \geq 0 \quad \text{for all } x, y$$

applied with $y = -L_{22}^{-1}L_{21}x$.

The above considerations on the one hand show how to introduce cross-effects on the entropy production level. On the other hand, the replacement of the notions "flux / driving force" by "co-factors of positive and negative parity" resolves the apparent anti-symmetry of certain cross-coefficients. This will be taken up again in Section 11.

7. INVISCID, NON-REACTIVE FLUID MIXTURES

We are going to employ the entropy inequality for obtaining constitutive laws for the thermo-mechanical interactions, i.e. for the structure of the \mathbf{f}_i . Specialized to fluid mixtures without chemical reactions ($R_a = 0$) and with vanishing viscosity ($\mathbf{S}_i^\circ = 0, \Pi_i = 0$), the entropy production is reduced to the two dissipative mechanisms of diffusion and heat conduction and becomes

$$(77) \quad \zeta = - \sum_i \mathbf{u}_i \cdot \left(\rho_i \nabla \frac{\mu_i}{T} + \frac{1}{T} (\mathbf{f}_i - \nabla p_i - h_i T \nabla \frac{1}{T}) \right) + \sum_i \mathbf{q}_i \cdot \nabla \frac{1}{T}$$

with the partial enthalpies $h_i = \rho_i e_i + p_i$. For an efficient notation, we proceed to write (77) as

$$(78) \quad \zeta = \zeta_{\text{diff}} + \zeta_{\text{heat}} \quad \text{with} \quad \zeta_{\text{heat}} = \sum_i \mathbf{q}_i \cdot \nabla \frac{1}{T}.$$

We impose linear relations between the conjugate factors in the entropy production; but note that the resulting constitutive equations are of course nonlinear relations between the variables. For simplicity, we start with the case in which the two principal mechanisms are treated independently, without explicitly introducing an additional thermo-diffusion coupling. Full thermo-diffusion will be considered in Section 8 below.

We now exploit axiom (IV-ii). The term ζ_{heat} is non-negative if we assume *Fourier's law* for the thermal part $\sum_i \mathbf{q}_i$ of the heat flux \mathbf{q} from (24), i.e.

$$\sum_i \mathbf{q}_i = \alpha \nabla \frac{1}{T} \quad \text{with} \quad \alpha = \alpha(T, \rho_1, \dots, \rho_N) \geq 0.$$

In this case the heat flux itself is given by

$$(79) \quad \mathbf{q} = \sum_i \mathbf{q}_i + \sum_i h_i \mathbf{u}_i = \alpha \nabla \frac{1}{T} + \sum_i h_i \mathbf{u}_i.$$

Hence, despite the simple Fourier law, some cross-effects are already included in \mathbf{q} .

The remaining part ζ_{diff} is of the form

$$(80) \quad \zeta_{\text{diff}} = - \sum_i \mathbf{u}_i \cdot \left(\mathbf{B}_i + \frac{1}{T} \mathbf{f}_i \right) \quad \text{with} \quad \mathbf{B}_i := \rho_i \nabla \frac{\mu_i}{T} - \frac{1}{T} \nabla p_i - h_i \nabla \frac{1}{T}.$$

This shows a further advantage of the separation into the principal mechanisms, since now the \mathbf{B}_i turn out to sum up to zero which is basic for the exploitation of axiom (IV-ii) below. We indeed have

$$(81) \quad \sum_i \mathbf{B}_i = \frac{1}{T} \left(\sum_i \rho_i \nabla \mu_i - \nabla p \right) + \left(\sum_i \rho_i \mu_i - (\rho e + p) \right) \nabla \frac{1}{T}$$

and the Gibbs-Duhem equation (50) implies

$$\nabla p = \sum_{i=1}^N \rho_i \nabla \mu_i + \rho s \nabla T,$$

hence $\sum_i \mathbf{B}_i = 0$. Axiom (IV-ii) of the entropy principle now requires

$$(82) \quad - \sum_{i=1}^N \mathbf{u}_i \cdot \left(\mathbf{B}_i + \frac{1}{T} \mathbf{f}_i \right) \geq 0.$$

To incorporate the constraints

$$(83) \quad \sum_{i=1}^N \mathbf{B}_i = 0, \quad \sum_{i=1}^N \mathbf{f}_i = 0,$$

these are built into (82) by eliminating \mathbf{B}_N and \mathbf{f}_N . Thus, the necessary condition becomes

$$(84) \quad - \sum_{i=1}^{N-1} (\mathbf{u}_i - \mathbf{u}_N) \cdot \left(\mathbf{B}_i + \frac{1}{T} \mathbf{f}_i \right) \geq 0.$$

The corresponding linear Ansatz for $\mathbf{B}_i + \frac{1}{T} \mathbf{f}_i$, in order to guarantee (84), is

$$(85) \quad \mathbf{B}_i + \frac{1}{T} \mathbf{f}_i = - \sum_{j=1}^{N-1} \tau_{ij} (\mathbf{u}_j - \mathbf{u}_N) \quad (\text{for } i = 1, \dots, N-1)$$

with a positive definite $(N-1) \times (N-1)$ -matrix $[\tau_{ij}]$. This yields the constitutive laws for the momentum productions \mathbf{f}_i .

The representation (85) can be made symmetric with respect to the constituents by extending the *Maxwell-Stefan matrix* $[\tau_{ij}]$ to $N \times N$ -format according to

$$(86) \quad \tau_{Nj} = - \sum_{i=1}^{N-1} \tau_{ij} \quad (j = 1, \dots, N-1), \quad \tau_{iN} = - \sum_{j=1}^{N-1} \tau_{ij} \quad (i = 1, \dots, N).$$

Note that the definition of the τ_{Nj} is required to obtain

$$\mathbf{B}_i + \frac{1}{T} \mathbf{f}_i = - \sum_{j=1}^N \tau_{ij} (\mathbf{u}_j - \mathbf{u}_N) \quad \text{for } i = 1, \dots, N,$$

including $i = N$, while the definition of the τ_{iN} yields $\sum_{j=1}^N \tau_{ij} = 0$ for all i , hence \mathbf{u}_N above can be replaced by \mathbf{u}_i to attain the symmetric form

$$(87) \quad \mathbf{B}_i + \frac{1}{T} \mathbf{f}_i = \sum_{j=1}^N \tau_{ij} (\mathbf{u}_i - \mathbf{u}_j) \quad \text{for } i = 1, \dots, N.$$

The extended matrix will be positive semi-definite. We record this observation as

Proposition. The extended $N \times N$ -matrix $[\tau_{ij}]_1^N$ is positive semi-definite if the $(N-1) \times (N-1)$ -matrix $[\tau_{ij}]_1^{N-1}$ is positive (semi-)definite.

Proof. By the criterion of Sylvester, a quadratic matrix M is positive semi-definite iff the determinant of every upper left sub-matrix is non-negative. Here, we only need to check this for the determinant of the full matrix. The latter vanishes since, by definition, the N -th column is a linear combination of the first $N-1$ columns. \square

In the present case of *non-reactive* multicomponent fluids, we add the following assumption of **binary-type mechanical interactions**:

$$(88) \quad \tau_{ij} = \tau_{ij}(T, \rho_i, \rho_j) \rightarrow 0 \quad \text{if } \rho_i \rho_j \rightarrow 0+.$$

Let us emphasize that this assumption is not true for chemically reacting mixtures – this will become clear in section 9 below. Following Truesdell [53], binary-type interactions imply the symmetry of $[\tau_{ij}]$ as follows: evaluate $\sum_{i,j=1}^N \tau_{ij} (\mathbf{u}_i - \mathbf{u}_j) = 0$. In case $N = 2$, one obtains $(\tau_{12} - \tau_{21}) (\mathbf{u}_1 - \mathbf{u}_2) = 0$ for any thermodynamical process, hence $\tau_{12} = \tau_{21}$. Note that for $N = 2$ the system can only have binary interactions. In case $N = 3$, the summation gives

$$(\tau_{12} - \tau_{21}) (\mathbf{u}_1 - \mathbf{u}_2) + (\tau_{13} - \tau_{31}) (\mathbf{u}_1 - \mathbf{u}_3) + (\tau_{23} - \tau_{32}) (\mathbf{u}_2 - \mathbf{u}_3) = 0.$$

Exploitation of (88) yields:

$$\rho_3 \rightarrow 0+ \Rightarrow \tau_{12} = \tau_{21}; \quad \rho_2 \rightarrow 0+ \Rightarrow \tau_{13} = \tau_{31}; \quad \rho_1 \rightarrow 0+ \Rightarrow \tau_{23} = \tau_{32}.$$

The general case $N > 3$ follows in an analogous manner. Consequently, under the assumption (88), the full matrix $[\tau_{ij}]$ is symmetric and positive semi-definite. Let us note in passing, that this derivation of the symmetry of the mechanical interactions works exclusively in the considered case of binary (non-reactive) interactions and it exploits conservation of total momentum.

Exploiting the symmetry of $[\tau_{ij}]$ and using (87), the diffusive entropy production is

$$(89) \quad \zeta_{\text{diff}} = - \sum_{i=1}^N \mathbf{u}_i \cdot \left(\mathbf{B}_i + \frac{1}{T} \mathbf{f}_i \right) = - \frac{1}{2} \sum_{i,j=1}^N \tau_{ij} (\mathbf{u}_i - \mathbf{u}_j)^2,$$

showing that, necessarily,

$$\tau_{ij} \leq 0 \quad \text{for all } i \neq j.$$

Hence the natural Ansatz to incorporate both symmetry and binary-type interactions is

$$(90) \quad \tau_{ij} = - f_{ij} \rho_i \rho_j \quad \text{with } f_{ij} = f_{ji}, \quad f_{ij} = f_{ij}(T, \rho_i, \rho_j) \geq 0 \quad (i \neq j).$$

From a molecular dynamics viewpoint, the f_{ij} can be interpreted as "friction factors".

Thus, for class-II mixtures, we obtain

$$(91) \quad \mathbf{f}_i = -\rho_i T \nabla \frac{\mu_i}{T} + \nabla p_i + T h_i \nabla \frac{1}{T} - T \sum_j f_{ij} \rho_i \rho_j (\mathbf{v}_i - \mathbf{v}_j)$$

as the constitutive law for the thermo-mechanical interactions. Inserting this into the partial momentum balances, we obtain their final form in the case of inviscid, non-reactive fluid mixtures with binary-type interactions as

$$(92) \quad \rho_i (\partial_t \mathbf{v}_i + \mathbf{v}_i \cdot \nabla \mathbf{v}_i) = -\rho_i T \nabla \frac{\mu_i}{T} + T h_i \nabla \frac{1}{T} - T \sum_j f_{ij} \rho_i \rho_j (\mathbf{v}_i - \mathbf{v}_j) + \rho_i \mathbf{b}_i.$$

In the *isothermal case*, i.e. in the limit when the approach to thermal equilibrium is infinitely fast so that no temperature gradients persist, this simplifies according to

$$(93) \quad \rho_i (\partial_t \mathbf{v}_i + \mathbf{v}_i \cdot \nabla \mathbf{v}_i) = -\rho_i \nabla \mu_i - T \sum_j f_{ij} \rho_i \rho_j (\mathbf{v}_i - \mathbf{v}_j) + \rho_i \mathbf{b}_i.$$

In the non-isothermal case, the resulting class-II model for inviscid, non-reactive fluids with binary-type thermo-mechanical interactions in conservative form reads as

$$\text{mass} : \partial_t \rho_i + \text{div} (\rho_i \mathbf{v}_i) = 0$$

$$\text{mom.} : \partial_t (\rho_i \mathbf{v}_i) + \text{div} (\rho_i \mathbf{v}_i \otimes \mathbf{v}_i) = -\rho_i \nabla \mu_i + T (h_i - \rho_i \mu_i) \nabla \frac{1}{T} - T \sum_j f_{ij} \rho_i \rho_j (\mathbf{v}_i - \mathbf{v}_j) + \rho_i \mathbf{b}_i$$

$$\text{energy} : \partial_t (\rho e) + \text{div} (\rho e \mathbf{v} + \mathbf{q}) = -p \text{div} \mathbf{v} - \sum_i \mathbf{u}_i \cdot (\mathbf{f}_i - \nabla p_i)$$

with \mathbf{q} and \mathbf{f}_i from (79) and (91), respectively.

To derive a mixture heat equation as the temperature form of the energy balance, we choose the independent variables as $(T, \rho, y_1, \dots, y_{N-1})$. Relying on (53) and the Gibbs-Duhem equation (50), we obtain

$$(94) \quad \rho c_v \dot{T} + \text{div} \mathbf{q} = - \sum_{i=1}^N \mathbf{u}_i \cdot (\mathbf{f}_i - \nabla p_i) - \sum_{i=1}^N (\mu_i - \mu_N - T \frac{\partial(\mu_i - \mu_N)}{\partial T}) \rho \dot{y}_i - \frac{T}{\rho} \frac{\partial p}{\partial T} \dot{\rho}$$

with c_v the specific heat capacity at constant density from (57). Furthermore, the dot denotes the Lagrangean derivative w.r. to the barycentric velocity, e.g. $\dot{T} = \partial_t T + \mathbf{v} \cdot \nabla T$.

Let us briefly mention the special case of *simple mixtures* (cf. section 15 below for more details) for which

$$(95) \quad \rho \psi = \sum_{i=1}^N \rho_i \psi_i(T, \rho_i) \quad \text{and} \quad \rho_i \psi_i + p_i = \rho_i \mu_i.$$

In this case the constitutive law for the thermo-mechanical interactions (91) reduces to

$$(96) \quad \mathbf{f}_i = -T \sum_j f_{ij} \rho_i \rho_j (\mathbf{v}_i - \mathbf{v}_j),$$

hence the partial momentum balance simplifies to

$$(97) \quad \partial_t(\rho_i \mathbf{v}_i) + \operatorname{div}(\rho_i \mathbf{v}_i \otimes \mathbf{v}_i) = -\nabla p_i - T \sum_j f_{ij} \rho_i \rho_j (\mathbf{v}_i - \mathbf{v}_j) + \rho_i \mathbf{b}_i.$$

Note that the term $-\sum_i \mathbf{u}_i \cdot \mathbf{f}_i$ in the heat equation becomes $\frac{T}{2} \sum_j f_{ij} \rho_i \rho_j (\mathbf{v}_i - \mathbf{v}_j)^2$ in case of a simple mixture.

8. THERMO-DIFFUSION REVISITED

It is well known that temperature gradients can generate interaction forces and diffusion fluxes contribute to the heat flux. In class-I models, these phenomena are called Soret and Dufour effect, respectively. In fact there is a contribution to the heat flux in (79) that is proportional to the diffusion velocity and in (91) we observe the corresponding contribution $T h_i \nabla \frac{1}{T}$ to the interaction force. However, for simple mixtures the interaction forces becomes independent of the temperature gradient.

In order to prevent the disappearance of such phenomena, in particular for simple mixtures, we now apply the entropy invariant mixing. Usually, cross-effects are introduced into the thermo-fluid mechanical modeling via full coupling in the constitutive relations. Given M binary products in the entropy production, this leads to M^2 phenomenological coefficients. If linear constitutive relations are employed, symmetry between the phenomenological coefficients are assumed by postulating the Onsager reciprocity relations. We proceed in a different manner, employing the entropy invariant mixing from Section 6. The key point is the equivalent reformulation of the entropy production rate, which here can be simply based on a zero addition, introducing a mixing between the mechanisms "diffusion" and "heat conduction". For this purpose we rewrite ζ from (77) as

$$(98) \quad \zeta = -\sum_i \mathbf{u}_i \cdot \left(\mathbf{B}_i + \frac{1}{T} \mathbf{f}_i - d_i^T \nabla \frac{1}{T} \right) + \sum_i (\mathbf{q}_i - d_i^T \mathbf{u}_i) \cdot \nabla \frac{1}{T}.$$

Note that $\nabla \frac{1}{T}$ has been introduced as an additional driving mechanism for diffusion, while the new term is compensated by an appropriate change in the binary product involving the heat flux. The newly introduced phenomenological *thermal diffusivities* d_i^T are functions of $(T, \rho_1, \dots, \rho_N)$, they can attain positive or negative values. This fact is well-known in kinetic theories, cf. [15].

We now intend to repeat the arguments of Section 7, but $\sum_i (\mathbf{B}_i + \frac{1}{T} \mathbf{f}_i - d_i^T \nabla \frac{1}{T})$ need not be zero which was crucial in the derivation of the class-II model. This defect can be removed by introduction of a Lagrange multiplier. Indeed, given any $\lambda \in \mathbb{R}$, the entropy production equals

$$(99) \quad \zeta = -\sum_i \mathbf{u}_i \cdot \left(\mathbf{B}_i + \frac{1}{T} \mathbf{f}_i - (d_i^T - y_i \lambda) \nabla \frac{1}{T} \right) + \sum_i (\mathbf{q}_i - d_i^T \mathbf{u}_i) \cdot \nabla \frac{1}{T},$$

since $\sum_i y_i \mathbf{u}_i = 0$. With the choice of $\lambda = \sum_j d_j^T$, the co-factors of \mathbf{u}_i sum up to zero as before. Let $\delta_i^T = d_i^T - y_i \sum_j d_j^T$ and observe that the second binary product in (99) remains unchanged if d_i^T is replaced by δ_i^T . It is therefore no restriction to consider the entropy production given in (98) with the additional constraint

$$(100) \quad \sum_{i=1}^N d_i^T = 0.$$

Now, the arguments from Section 7 apply without changes and yield the closure relations

$$(101) \quad \mathbf{f}_i = -\rho_i T \nabla \frac{h_i}{T} + \nabla p_i + (h_i + d_i^T) T \nabla \frac{1}{T} - T \sum_j f_{ij} \rho_i \rho_j (\mathbf{v}_i - \mathbf{v}_j) =: \mathbf{f}_i^M,$$

$$(102) \quad \mathbf{q} = \sum_i \mathbf{q}_i + \sum_i h_i \mathbf{u}_i = \alpha \nabla \frac{1}{T} + \sum_i (h_i + d_i^T) \mathbf{u}_i.$$

Insertion of (101) into the momentum balance yields

$$(103) \quad \rho_i (\partial_t \mathbf{v}_i + \mathbf{v}_i \cdot \nabla \mathbf{v}_i) = -\rho_i \nabla \mu_i + T (h_i + d_i^T - \rho_i \mu_i) \nabla \frac{1}{T} - T \sum_j f_{ij} \rho_i \rho_j (\mathbf{v}_i - \mathbf{v}_j) + \rho_i \mathbf{b}_i,$$

which is complemented by the partial mass balances and the mixture internal energy balance to obtain the class-II model for an inviscid, non-reactive mixture with thermo-diffusion and diffusion-thermo effects. In case of simple mixtures, the partial momentum balances become

$$(104) \quad \rho_i (\partial_t \mathbf{v}_i + \mathbf{v}_i \cdot \nabla \mathbf{v}_i) = -\nabla p_i - d_i^T \nabla \ln T - T \sum_j f_{ij} \rho_i \rho_j (\mathbf{v}_i - \mathbf{v}_j) + \rho_i \mathbf{b}_i.$$

Note that now ∇T remains in the momentum balances even for simple mixtures.

Later on we will generate class-I models by a reduction procedure applied to class-II models. Then we will see that all cross-effects which are introduced by entropy invariant mixing in class-II automatically come with the usually postulated Onsager reciprocity relations into the class-I model. This is the true rationale behind the Onsager symmetry: We have Onsager reciprocity relations if the corresponding cross-effect does not generate further entropy production. Further examples of this statement are found in Section 11, where we take up the subject of entropy invariant mixing once more.

For subsequent sections, in which chemical reactions and viscous effects are to be included, it is helpful to observe the overall effect of thermo-diffusion: instead of the partial enthalpies h_i , one simply has to write $\mathcal{D}_i^T \equiv h_i + d_i^T$, where one may impose (100).

9. INVISCID, CHEMICALLY REACTIVE FLUID MIXTURES

Chemical reaction appear in the model with three contribution: (i) mass production in the partial mass balances, (ii) momentum production in the partial momentum balances and (iii) heat production in the energy balance. With chemical reactions, the entropy production reads as

$$(105) \quad \zeta = \sum_i (\mathbf{q}_i - d_i^T \mathbf{u}_i) \cdot \nabla \frac{1}{T} - \sum_i \mathbf{u}_i \cdot \left(\mathbf{B}_i - d_i^T \nabla \frac{1}{T} + \frac{1}{T} (\mathbf{f}_i - r_i \mathbf{v}_i + \frac{1}{2} r_i \mathbf{u}_i) \right) - \frac{1}{T} \sum_{a=1}^{N_R} R_a \mathcal{A}_a$$

with the affinities \mathcal{A}_a from (46) and the \mathbf{B}_i from (80). Recall that $\sum_i \mathbf{B}_i = 0$ and $\sum_i d_i^T = 0$.

Here we note another ambiguity in the decomposition of ζ into a sum of binary products. The term $\frac{1}{2} r_i \mathbf{u}_i$ appeared in the energy production because of chemical reactions via the mass balances. Similar to diffusive contributions to the heat flux in Section 7, we prefer to shuffle the term $\frac{1}{2} r_i \mathbf{u}_i$ to become a co-factor of \mathbf{u}_i in order to collect all terms related to the mechanism of diffusion. If we were to leave this term attached to the chemical reactions' entropy production, we then would have

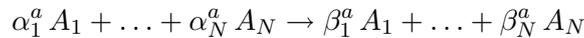
$$(106) \quad -\frac{1}{T} \sum_{a=1}^{N_R} R_a \sum_{n=1}^N M_i \nu_i^a (\mu_i + \frac{1}{2} \mathbf{u}_i^2).$$

While this change would not modify the value of ζ , it has tremendous implications after employing (linear) constitutive laws. In fact, the latter choice would contradict axiom (IV-ii) and a linear diagonal closure would result in a non-wellposed PDE-system. This subtle point will be taken up in more detail below.

We decompose the interaction force $\mathbf{f}_i - r_i \mathbf{v}_i$ according to

$$(107) \quad \mathbf{f}_i - r_i \mathbf{v}_i = \mathbf{f}_i^M + \mathbf{f}_i^C - r_i \mathbf{v}_i,$$

where we assume that the mechanical part \mathbf{f}_i^M has the same structure as for a non-reactive mixture; i.e., we model the \mathbf{f}_i^M according to (101). The chemical interaction part $\mathbf{f}_i^C - r_i \mathbf{v}_i$ corresponds to exchange of momentum because in a chemical reaction the reacting constituents inherit their momentum to the products. We now compute $\mathbf{f}_i^C - r_i \mathbf{v}_i$ via balancing of partial momenta. At first, for simplicity, we only consider the forward path, say, of the a^{th} chemical reaction, viz.



with rate R_a^f . The rate of change of momentum of constituent A_i is

$$-R_a^f \alpha_i^a M_i \mathbf{v}_i + R_a^f \beta_i^a M_i \mathbf{v}_i^{a,f}.$$

Here $\mathbf{v}_i^{a,f}$ denotes the average velocity of molecules of type A_i *after* they are formed in a reactive collision of the involved reactants, i.e. those for which $\beta_i^a > 0$. The only obstacle is that $\mathbf{v}_i^{a,f}$ is not known, but needs to be modeled based on a micro-theory. At this point it is helpful to notice that mass and momentum are conserved during chemical reactions, i.e.

$$(108) \quad \sum_{i=1}^N \alpha_i^a M_i = \sum_{i=1}^N \beta_i^a M_i \quad \text{and} \quad \sum_{i=1}^N \alpha_i^a M_i \mathbf{v}_i = \sum_{i=1}^N \beta_i^a M_i \mathbf{v}_i^{a,f}.$$

Now, if only one product is present in the a^{th} reaction, say A_k , this alone is sufficient to determine the velocity $\mathbf{v}_k^{a,f}$ from (108). In the more complicated general case it is sufficient to think of a reaction with only one reactant, i.e. the decomposition of A_k , say, into several parts. This is no restriction of generality, because any chemical reaction proceeds via a so-called transition complex where the interacting reactants form a (very short lived) intermediate species. An observer which follows this transition complex sees a stagnant particle which decomposes into several parts which then move away from the steady barycenter. In any new instance of this reaction, the products will move in different directions. But since we assume isotropic media in our theory, no direction is preferred. Consequently, the (ensemble) averaged velocity is zero. In other words, all products from one reaction path have *the same velocity* which coincides with the one of the transition complex, which in turn is nothing but the velocity of the center of mass of the reacting constituents.

Moreover, for the backward reaction the momentum conservation reads, by a similar reasoning, $\sum_{i=1}^N \alpha_i^a M_i \mathbf{v}_i^{b,f} = \sum_{i=1}^N \beta_i^a M_i \mathbf{v}_i$. Including also the analogous condition on $\mathbf{v}_i^{b,f}$ for the backward reactions, this leads to the following

fundamental assumption on reactive collisions:

$$(109) \quad \mathbf{v}_i^{a,f} = \mathbf{v}_a^f \quad \text{and} \quad \mathbf{v}_i^{a,b} = \mathbf{v}_a^b \quad \text{for forward and backward reactions, respectively.}$$

From the conservation of momentum in chemical reactions, we obtain

$$(110) \quad \mathbf{v}_a^f = \sum_i \alpha_i^a M_i \mathbf{v}_i / \sum_i \beta_i^a M_i \quad \text{as well as} \quad \mathbf{v}_a^b = \sum_i \beta_i^a M_i \mathbf{v}_i / \sum_i \alpha_i^a M_i.$$

In imposing this assumption, we follow Burgers [8] who used the same proposition for a study of the reactive Boltzmann equations.

Using the above assumptions and considerations, balancing of the chemical exchange of partial momentum leads to the representation

$$(111) \quad \mathbf{f}_i^C - r_i \mathbf{v}_i = - \sum_{j=1}^N C_{ij} (\mathbf{v}_i - \mathbf{v}_j),$$

where the *chemical interaction matrix* has the entries

$$(112) \quad C_{ij} = \sum_{a=1}^{N_R} \frac{M_i M_j}{\sum_k \alpha_k^a M_k} (R_a^f \beta_i^a \alpha_j^a + R_a^b \alpha_i^a \beta_j^a).$$

Note that the matrix $[C_{ij}]$ is, in general, *not* symmetric. But in the so-called detailed chemical equilibrium, i.e. in case $R_a^f = R_a^b$ for *all* reactions $a = 1, \dots, N_R$, it attains a symmetric form. Indeed, the anti-symmetric part of the chemical interaction matrix is

$$(113) \quad C_{ij} - C_{ji} = \sum_{a=1}^{N_R} R_a \frac{M_i M_j}{\sum_k \alpha_k^a M_k} (\beta_i^a \alpha_j^a - \alpha_i^a \beta_j^a).$$

Summation over i yields

$$(114) \quad \sum_{i=1}^N (C_{ij} - C_{ji}) = \sum_{a=1}^{N_R} R_a M_j (\alpha_j^a - \beta_j^a) = -r_j,$$

showing that $r_j = 0$ for all $j = 1, \dots, N$ is required for the symmetry of $[C_{ij}]$.

The decomposition into a chemical part and the mechanical interaction, the latter without changes compared to the non-reactive case, has to be justified by checking the thermodynamic consistency. At this point, insertion of $\mathbf{f}_i^M + \mathbf{f}_i^C - r_i \mathbf{v}_i$ into (105) leads to an interesting observation: if the term $\frac{1}{2} r_i \mathbf{u}_i$ were to remain in the binary product which corresponds to entropy production via chemical reactions in (105), the entropy production due to diffusion can, in general, become negative! As an example, in the simplest case $2A_1 \rightarrow A_2$, the contribution of $\mathbf{f}_i^C - r_i \mathbf{v}_i$ is $2R^f M_1 \mathbf{u}_2 (\mathbf{u}_2 - \mathbf{u}_1)$ which evidently can attain negative values; note that forward and backward reactions separately have to generate the right sign in the entropy production since no chemical equilibrium is assumed. For this reason we have shuffled the term $\frac{1}{2} r_i \mathbf{u}_i$ to the contribution corresponding to diffusive mass transport.

We proceed to check the fulfilment of the 2nd law, where we already know that the entropy production due to the mechanical part is non-negative. For the remainder, the contribution of the forward path, say, of the a^{th} reaction is

$$(115) \quad \zeta_{\text{diff}}^{a,f} = R_a^f \left(\sum_i M_i \frac{\alpha_i^a + \beta_i^a}{2} \mathbf{u}_i^2 - \sum_{i,j} \frac{M_i M_j \beta_i^a \alpha_j^a}{\sum_k \alpha_k^a M_k} \mathbf{u}_i \cdot \mathbf{u}_j \right).$$

Note that $\sum_k \alpha_k^a M_k = (\sum_k \alpha_k^a M_k)^{1/2} (\sum_k \beta_k^a M_k)^{1/2}$, hence the contribution $\zeta_{\text{diff}}^{a,f}$ to the entropy production is symmetric in α_i^a, β_i^a . This only holds if the term $\frac{1}{2} r_i \mathbf{u}_i^2$ is included in the diffusive contribution. Now, to see that the entropy inequality holds, we fix the reaction index a , abbreviate $M_i \alpha_i^a, M_i \beta_i^a$ as a_i, b_i and make use of the Cauchy-Schwarz inequality in the form

$$\sum_i a_i z_i = \sum_i a_i^{\frac{1}{2}} \cdot a_i^{\frac{1}{2}} z_i \leq \left(\sum_i a_i \right)^{\frac{1}{2}} \left(\sum_i a_i z_i^2 \right)^{\frac{1}{2}}.$$

Applying this to $\sum_{i,j} b_i a_j \mathbf{u}_{i,k} \mathbf{u}_{j,k}$, and summing over the velocity components $k = 1, 2, 3$, we obtain

$$\sum_{i,j} b_i a_j \mathbf{u}_i \cdot \mathbf{u}_j = \sum_i b_i \mathbf{u}_i \cdot \sum_i a_i \mathbf{u}_i \leq \left(\sum_i a_i \right)^{\frac{1}{2}} \left(\sum_i b_i \right)^{\frac{1}{2}} \left(\sum_i a_i \mathbf{u}_i^2 \right)^{\frac{1}{2}} \left(\sum_i b_i \mathbf{u}_i^2 \right)^{\frac{1}{2}}.$$

Employing mass conservation, this yields

$$\sum_{i,j} \frac{b_i a_j}{\sum_k a_k} \mathbf{u}_i \cdot \mathbf{u}_j \leq \left(\sum_i b_i \mathbf{u}_i^2 \right)^{\frac{1}{2}} \left(\sum_i a_i \mathbf{u}_i^2 \right)^{\frac{1}{2}} \leq \frac{1}{2} \sum_i (a_i + b_i) \mathbf{u}_i^2.$$

Consequently, $\zeta_{\text{diff}}^{a,f} \geq 0$ and, hence, the Ansatz (107) with \mathbf{f}_i^M according to (101) and $\mathbf{f}_i^C - r_i \mathbf{v}_i$ from (111) is consistent with the second law. Note that the above estimation only works due to the symmetric form of the sums in (115) and the latter only results if *precisely* the term $\frac{1}{2} r_i \mathbf{u}_i^2$ is shuffled within the entropy production.

To sum up, we obtained the closure law for the interaction force to read as

$$(116) \quad \mathbf{f}_i - r_i \mathbf{v}_i = -\rho_i T \nabla \frac{\mu_i}{T} + \nabla p_i + (h_i + d_i^T) T \nabla \frac{1}{T} - \sum_{j=1}^N (T f_{ij} \rho_i \rho_j + C_{ij}) (\mathbf{v}_i - \mathbf{v}_j)$$

with symmetric $f_{ij}(T, \rho_1, \dots, \rho_N) > 0$, and C_{ij} from (112).

Let us note in passing that the co-factors of the \mathbf{u}_i in (105) do not sum up to zero. As in Section 7, the latter can easily be achieved by addition of a Lagrange multiplier. But it is not needed for checking the entropy inequality, and this is all we had to do, since the closure relation for the mechanical part has already been obtained before (where it was important to employ a formulation in which the co-factors of \mathbf{u}_i sum up to zero) and the chemical part follows from the balance of momentum transfer in chemical reactions. But for the reduction to a class-I model below, the addition of a Lagrange multiplier will again be required.

Chemical Reaction Kinetics. It remains to close the mass production rates $R_a = R_a^f - R_a^b$ which have to respect the entropy inequality as well. The relevant reactive dissipation term is

$$\zeta_{\text{chem}} = -\frac{1}{T} \sum_{a=1}^{N_R} (R_a^f - R_a^b) \mathcal{A}_a \quad \text{with the affinities } \mathcal{A}_a = \sum_{i=1}^N \nu_i^a M_i \mu_i.$$

Since chemical reactions are often far from equilibrium, a linear (in the driving forces) closure for R_a is not appropriate. Guided by the proof of Boltzmann's H-theorem as well as by experimental knowledge on reaction kinetics, we use the nonlinear closure

$$(117) \quad \ln \frac{R_a^f}{R_a^b} = -\gamma_a \frac{\mathcal{A}_a}{RT} \quad \text{with } \gamma_a > 0$$

which implies

$$\zeta_{\text{chem}} = R \sum_{a=1}^{N_R} \frac{1}{\gamma_a} (R_a^f - R_a^b) (\ln R_a^f - \ln R_a^b) \geq 0,$$

since the logarithm is monotone increasing. Because of the strict monotonicity of $\ln x$, the reactive contribution to the entropy production only vanishes if *all reaction are separately in equilibrium*, i.e. all forward and corresponding backward rates coincide. This is an instance of the *principle of detailed balance*, called Wegscheider's condition in the context of chemical reaction kinetics. Notice that still one of the rates – either for the forward or the backward path – needs to be modeled, while the other one then follows from (117). Here, the approach via rigorous continuum thermodynamics fixes the set of variables on which the rates can depend. Note also that the factors γ_a in (117) are often set to 1, but a general $\gamma_a > 0$ is required in the Butler-Volmer equation in electrochemistry [12]. Note that the γ_a can also depend on the system's variables.

The standard closure for chemical reaction rates, used in so-called *elementary reactions* which do not involve intermediate steps, is referred to as *mass action kinetics*, where the rate for the forward reaction, say, is modeled as $R_a^f = k_a^f \prod_i x_i^{\alpha_i}$ with "rate constants" $k_a^f > 0$ which depend on temperature T and pressure p . To obtain the backward rate via (117), the chemical potentials need to be modeled by material functions since they appear in the affinities. For the important class of so-called *ideal mixtures*, the chemical potentials obey the relations

$$(118) \quad \mu_i(T, p, x_1, \dots, x_{N-1}) = g_i(T, p) + \frac{RT}{M_i} \log x_i \quad \text{for } i = 1, \dots, N \quad (\text{with } \sum_i x_i = 1),$$

where $g_i(T, p)$ is the Gibbs energy of the pure component A_i under the temperature and pressure of the mixture. In particular, (118) holds for a mixture of ideal gases, where g_i is explicitly given as a function of T, p . Define X_i for $i = 1, \dots, N$ such that $0 < X_i < 1$,

$$\prod_i X_i^{\nu_i^a} = \exp\left(-\frac{1}{RT} \sum_k M_k g_k(T, p) \nu_k^a\right) \quad \text{and} \quad \sum_i X_i = 1;$$

for details on the (nonempty) solution sets for this system see, e.g., section 2 in [6]. Then

$$R_a = R_a^f - R_a^b = R_a^f \left(1 - \prod_i \left(\frac{x_i}{X_i}\right)^{\nu_i^a}\right),$$

hence if the forward rate is modeled as $R_a^f = k_a^f \prod_i x_i^{\alpha_i}$, this yields

$$(119) \quad R_a = k_a^f \prod_i x_i^{\alpha_i} - k_a^b \prod_i x_i^{\beta_i} \quad \text{with } k_a^b = k_a^f / \prod_i X_i^{\nu_i^a}.$$

Note that the "rate constants" $k_a^f, k_a^b > 0$ are of course not constant but depend on the primitive variables. In practice, they especially depend strongly on the temperature. It is important to observe

that only one of k_a^f or k_a^b can be modeled in this manner, while the other one is then determined by (119). However, due to (118) the result (119) is restricted to the class of ideal mixtures.

In the case of non-ideal mixtures, the literature usually starts also from (119), but with activities instead of molar fractions; for a rather exhaustive review see [45]. In the context of our representation of the chemical reaction rates it is obvious that the corresponding chemical potentials are of the form

$$\mu_i(T, p, x_1, \dots, x_N) = g_i(T, p) + \frac{RT}{M_i} \log a_i \quad \text{for } i = 1, \dots, N,$$

where the so-called activities a_i of course depend on all primitive variables. Note that this just means replacing one unknown function by another one with the same set of variables; cf. also [44]. There is no advantage in this procedure, hence we prefer to employ (117), keeping the chemical potentials.

10. VISCOUS, CHEMICALLY REACTIVE FLUID MIXTURES

The next task is the closure of the viscous stresses $\mathbf{S}_i^{\text{irr}} = -\Pi_i \mathbf{I} + \mathbf{S}_i^\circ$. The viscous part of the entropy production in the class-II model is

$$(120) \quad \zeta_{\text{visc}} = \frac{1}{T} \sum_i (\mathbf{S}_i^\circ - \Pi_i \mathbf{I}) : (\mathbf{D}_i^\circ + \frac{1}{3} (\text{div } \mathbf{v}_i) \mathbf{I}) = \frac{1}{T} \sum_i \mathbf{S}_i^\circ : \mathbf{D}_i^\circ - \frac{1}{T} \sum_i \Pi_i \text{div } \mathbf{v}_i.$$

Employing linear constitutive theory, we obtain the constitutive relations

$$(121) \quad \mathbf{S}_i^\circ = \sum_j 2\eta_{ij} \mathbf{D}_j^\circ \quad \text{and} \quad \Pi_i = - \sum_j \lambda_{ij} \text{div } \mathbf{v}_j$$

with positive (semi-)definite matrices $[\eta_{ij}]$ and $[\lambda_{ij}]$, where the shear and bulk viscosities η_{ij} and λ_{ij} , respectively, are functions of the primitive thermodynamic variables.

Let us note in passing that in our theory, \mathbf{S}_i° is exclusively related to viscous mechanisms; this is in contrast to *Extended Thermodynamics* (cf. [41]), where \mathbf{S}_i° is itself a primitive variable for which a balance equation holds.

Inserting the constitutive relations derived in Sections 7, 9 and 10, we arrive at the following class-II model for a reactive, viscous mixture with binary type mechanical interactions.

Class-II model of a reactive, viscous fluid mixture:

(122)

$$\partial_t \rho_i + \text{div} (\rho_i \mathbf{v}_i) = \sum_a M_i \nu_i^a (R_a^f - R_a^b)$$

(123)

$$\rho_i (\partial_t \mathbf{v}_i + \mathbf{v}_i \cdot \nabla \mathbf{v}_i) = \text{div } \mathbf{S}_i^{\text{irr}} - \rho_i T \nabla \frac{\mu_i}{T} + \mathcal{D}_i^T T \nabla \frac{1}{T} - \sum_j (T f_{ij} \rho_i \rho_j + C_{ij}) (\mathbf{v}_i - \mathbf{v}_j) + \rho_i \mathbf{b}_i$$

$$\partial_t (\rho e) + \text{div} (\rho e \mathbf{v} + \alpha \nabla \frac{1}{T} + \sum_i \mathcal{D}_i^T (\mathbf{v}_i - \mathbf{v})) = -p \text{div } \mathbf{v} + \sum_i \mathbf{S}_i^{\text{irr}} : \nabla \mathbf{v}_i$$

(124)

$$- \sum_i (\mathbf{v}_i - \mathbf{v}) \cdot \left(\nabla p_i - \rho_i T \nabla \frac{\mu_i}{T} + \mathcal{D}_i^T T \nabla \frac{1}{T} - \sum_j (T f_{ij} \rho_i \rho_j + C_{ij}) (\mathbf{v}_i - \mathbf{v}_j) \right),$$

where the ratio of reaction rates and the chemical matrix are given by

$$R_a^f / R_a^b = \exp \left(- \frac{1}{RT} \sum_{k=1}^N \mu_k M_k \nu_k^a \right), \quad C_{ij} = \sum_{a=1}^{N_a} \frac{M_i M_j}{\sum_k \alpha_k^a M_k} (R_a^f \beta_i^a \alpha_j^a + R_a^b \alpha_i^a \beta_j^a),$$

and the irreversible stress parts $\mathbf{S}_i^{\text{irr}} = -\Pi_i \mathbf{I} + \mathbf{S}_i^\circ$ are determined by (121). Moreover, $\mathcal{D}_i^T = h_i + d_i^T$ with the thermo-diffusivities d_i^T from above.

This system becomes a closed PDE-system for the primitive variables, if the following constitutive functions are given: (i) the free energy function $\rho\psi(T, \rho_1, \dots, \rho_N)$ to calculate ρe and μ_i according to (53)_{2,3}; (ii) the partial energy $e_i(T, \rho_1, \dots, \rho_N)$ and partial pressure $p_i(T, \rho_1, \dots, \rho_N)$ such that the constraints $\rho e = \sum_i \rho_i e_i$ and $p = \sum_i p_i$ are satisfied, where p follows from (54); (iii) constitutive models for, say, the forward rates R_a^f .

The class-II model from above is new. In particular, the appearance of the chemical matrix for the reactive contribution to the interaction forces, as well as the nonlinear and thermodynamically consistent closure of the chemical reaction rates are, to the best of our knowledge, not present in the existing literature. Furthermore, our exploitation of the entropy principle based on $\text{div } \mathbf{v}_i$ instead of $\text{div } \mathbf{v}$ leads to the simple derivation of partial and cross viscosities in case of viscous fluid mixtures. Class-II models with partial and cross viscosities, but based on kinetic theory and without chemistry, can be found in [37] and in [28], [29]. More details concerning related work will be given in Section 12 for models including thermo-diffusion.

11. CROSS-EFFECTS REVISITED

We already considered several cross-effects, namely cross-diffusion and thermo-diffusion. In the present section we introduce additional couplings in which chemical reactions are involved. Before doing so, we first show how the cross-diffusion can also be derived as an entropy-invariant mixing between the individual diffusion mechanisms.

Cross-Diffusion. In Section 7, the symmetry of the phenomenological matrix $[\tau_{ij}]$ relies on the conservation law of barycentric momentum and on an assumption of pairwise interactions. Now we give a further proof that relies on the method of entropy invariant mixing. To this end we reconsider the entropy production (78) due to pure diffusion. To simplify the notation we abbreviate $\mathbf{U}_i = \mathbf{u}_i - \mathbf{u}_N$ and $\mathbf{F}_i = \mathbf{B}_i + \frac{1}{T}\mathbf{f}_i$ and may write

$$(125) \quad \zeta_{\text{diff}} = - \sum_{i=1}^{N-1} \mathbf{U}_i \cdot \mathbf{F}_i .$$

For illustration of the method we do not use the general abstract setting of Section 6, but introduce the mixing "by hand". For this purpose, we consider four constituents only and have $\zeta_{\text{diff}} = -(\mathbf{U}_1 \cdot \mathbf{F}_1 + \mathbf{U}_2 \cdot \mathbf{F}_2 + \mathbf{U}_3 \cdot \mathbf{F}_3)$. Here we introduce new terms without any effect on the entropy production, viz.

$$(126) \quad \zeta_{\text{diff}} = - \left((\mathbf{U}_1 + \lambda_{12}\mathbf{U}_2 + \lambda_{13}\mathbf{U}_3) \cdot \mathbf{F}_1 \right. \\ \left. + (\mathbf{U}_2 + \lambda_{23}\mathbf{U}_3) \cdot (\mathbf{F}_2 - \lambda_{12}\mathbf{F}_1) + \mathbf{U}_3 \cdot (\mathbf{F}_3 - \lambda_{13}\mathbf{F}_1 - \lambda_{23}\mathbf{F}_2 + \lambda_{23}\lambda_{12}\mathbf{F}_1) \right) .$$

According to Axiom (IV-ii), a diagonal closure is required. Thus with $\lambda_{11} \geq 0$, $\lambda_{22} \geq 0$ and $\lambda_{33} \geq 0$ we may let

$$(127) \quad \mathbf{F}_1 = -\lambda_{11}(\mathbf{U}_1 + \lambda_{12}\mathbf{U}_2 + \lambda_{13}\mathbf{U}_3), \quad \mathbf{F}_2 - \lambda_{12}\mathbf{F}_1 = -\lambda_{22}(\mathbf{U}_2 + \lambda_{23}\mathbf{U}_3), \\ \mathbf{F}_3 - \lambda_{13}\mathbf{F}_1 - \lambda_{23}\mathbf{F}_2 + \lambda_{12}\lambda_{23}\mathbf{F}_1 = -\lambda_{33}\mathbf{U}_3 .$$

This can be rewritten as $\mathbf{F}_i = - \sum_j \tau_{ij} \mathbf{U}_j$, where the matrix of coefficients is given by

$$(128) \quad [\tau_{ij}] = \begin{pmatrix} \lambda_{11} & \lambda_{11}\lambda_{12} & \lambda_{11}\lambda_{13} \\ \lambda_{11}\lambda_{12} & \lambda_{22} + \lambda_{11}\lambda_{12}^2 & \lambda_{11}\lambda_{12}\lambda_{13} + \lambda_{22}\lambda_{23} \\ \lambda_{11}\lambda_{13} & \lambda_{11}\lambda_{12}\lambda_{13} + \lambda_{22}\lambda_{23} & \lambda_{11}\lambda_{13}^2 + \lambda_{22}\lambda_{23}^2 + \lambda_{33} \end{pmatrix}$$

and is symmetric as well as positive definite.

Volume variation/chemical reaction cross-effect. The volume-variation/chemical reaction cross-effect refers to a possible coupling between the following binary products in (52):

$$(129) \quad \zeta_{\text{vol}} = -\frac{1}{T} \sum_{i=1}^N \Pi_i \operatorname{div} \mathbf{v}_i \quad \text{and} \quad \zeta_{\text{chem}} = -\frac{1}{T} \sum_{a=1}^{N_R} R_a \mathcal{A}_a.$$

The parity of the involved quantities are:

$$(130) \quad T \rightarrow +1, \quad \Pi_i \rightarrow 1, \quad \operatorname{div} \mathbf{v}_i \rightarrow -1, \quad R_a \rightarrow -1, \quad \mathcal{A}_a \rightarrow +1.$$

The mixing inside the parity-classes can most easily be introduced via a zero addition according to

$$(131) \quad \zeta_{\text{chem}} + \zeta_{\text{vol}} = -\frac{1}{T} \left(\sum_{a=1}^{N_R} (R_a + \sum_{i=1}^N l_{ai} \operatorname{div} \mathbf{v}_i) \mathcal{A}_a + \sum_{i=1}^N \operatorname{div} \mathbf{v}_i (\Pi_i - \sum_{a=1}^{N_R} l_{ai} \mathcal{A}_a) \right),$$

where the cross-coefficients l_{ai} have arbitrary signs. For simplicity we here rest content with linear constitutive laws. Axiom (IV-ii) and the procedure leading to (75) imply a closure with symmetry between the coefficients, resulting in

$$(132) \quad R_a + \sum_{i=1}^N l_{ai} \operatorname{div} \mathbf{v}_i = -\sum_{b=1}^{N_R} l_{ab} \mathcal{A}_b, \quad \operatorname{div} \mathbf{v}_i = -\sum_{j=1}^N \lambda_{ij}^{-1} (\Pi_j - \sum_{a=1}^{N_R} l_{aj} \mathcal{A}_a)$$

with positive (semi-)definite and symmetric matrices $[l_{ab}]$ and $[\lambda_{ij}^{-1}]$, where we assume the latter to be invertible with $[\lambda_{ij}^{-1}] = [\lambda_{ij}]^{-1}$. This finally leads to the closure

$$(133) \quad R_a = -\sum_{b=1}^{N_R} l_{ab} \mathcal{A}_b - \sum_{i=1}^N l_{ai} \operatorname{div} \mathbf{v}_i, \quad \Pi_i = -\sum_{j=1}^N \lambda_{ij} \operatorname{div} \mathbf{v}_j + \sum_{a=1}^{N_R} l_{ai} \mathcal{A}_a;$$

cf. also (162) and (163) below. Evidently, the mismatch between the standard "flux/driving force" notion and the parity-classes explains the apparent anti-symmetry of the volume variation/chemical reaction cross-effect in (133).

Cross-effects between chemical reaction with nonlinear closure. Let us finally show how to introduce cross-effects also between different chemical reactions with the much more appropriate nonlinear closure for the rate functions from (117). The original contribution in the entropy production corresponding to the chemical reaction rates is $\zeta_R = -\sum_a \mathcal{A}_a R_a$. After entropy neutral mixing between the different reactions, this becomes

$$(134) \quad \zeta_R = -\langle U \mathbf{A}, U^{-\top} \mathbf{R} \rangle \quad \text{with} \quad \mathbf{A} = (\mathcal{A}_1, \dots, \mathcal{A}_{N_R})^\top \quad \text{and} \quad \mathbf{R} = (R_1, \dots, R_{N_R})^\top.$$

Splitting \mathbf{R} according to

$$(135) \quad \mathbf{R} = \mathbf{R}^f - \mathbf{R}^b = (R_1^f - R_1^b, \dots, R_{N_R}^f - R_{N_R}^b)^\top,$$

we now perform the diagonal but nonlinear closure

$$(136) \quad (U \mathbf{A})_a = -\frac{1}{\beta_a} \ln \frac{(U^{-\top} \mathbf{R}^f)_a}{(U^{-\top} \mathbf{R}^b)_a} \quad \text{with} \quad \beta_a > 0.$$

In the equations above, U denotes an upper triangular $N_R \times N_R$ -matrix such that $U_{aa} = 1$ for all $a = 1, \dots, N_R$. This leads to the relation

$$(137) \quad \mathbf{R}^f = -U \Lambda U^{-\top} \mathbf{R}^b \quad \text{with} \quad \Lambda = \operatorname{diag} \{ \beta_a \exp((U \mathbf{A})_a) \}_{a=1, \dots, N_R},$$

hence

$$(138) \quad \mathbf{R} = \mathbf{R}^f - \mathbf{R}^b = (I - U \Lambda U^{-\top}) \mathbf{R}^b,$$

where the vector of backward rates \mathbf{R}^b still is to be modeled based on a micro-theory or on experimental experience.

12. COMPARISON WITH CLASS-II MODELS FROM THE LITERATURE

As early as in 1868, J. C. Maxwell in his paper [34] "On the dynamical theory of gases", building on and improving his own work, and three years later J. Stefan in the paper [50] "Über das Gleichgewicht und die Bewegung, insbesondere die Diffusion von Gasgemengen" were the first to formulate continuum mechanical partial momentum balances, i.e. they derived the first known class-II models. Maxwell considered binary gas mixtures and used kinetic theory to obtain the friction force between two different moving gas species. Since, as Stefan wrote*, the paper by Maxwell is not easy to digest, he himself gave a phenomenological derivation of essentially the same equations, but generalized to the case of N constituents. Written in our notation, his final partial momentum balances read as

$$(139) \quad \rho_i(\partial_t \mathbf{v}_i + (\mathbf{v}_i \cdot \nabla) \mathbf{v}_i) = -\nabla p_i + \rho_i \mathbf{b}_i - \sum_{j \neq i} f_{ij}(\mathbf{v}_i - \mathbf{v}_j).$$

He also derived a formula for the f_{ij} in the binary case and noted that these coefficients are symmetric, depend weakly on the temperature and are otherwise constant for given types of gases. Without rationale, he also used the symmetry for more than two constituents, thus implicitly assuming binary interactions. Stefan did not comment on equations of state for the partial pressures, but he successfully applied his model, in the stationary case and of course including partial mass balances, to describe experimental data for binary and also ternary systems which, as Stefan mentions in [50], had been obtained by Loschmidt and by Wretschko. So, at least for an isothermal mixture of ideal gases, one can say that J. Stefan in [34] obtained the first closed class-II model for a fluid mixture composed of N constituents.

Given these significant early contributions, it is somewhat surprising that further developments on class-II models for fluid mixtures are rarely found in the literature. Apparently, the next notable and in a sense very modern contribution was given by C. Truesdell in 1957 in [52]. In this and his later work [53] and [54], Truesdell made very important progress in uniting the continuum mechanical approach started by Stefan with thermodynamics, thus enabling a consistent derivation within a single theory. Moreover, Truesdell showed that the symmetry of f_{ij} is a consequence of the conservation of total momentum combined with binary interactions. This was developed considerably further by I. Müller in particular in [37]; see also [38]. Except for the momentum production due to chemical reactions, i.e. the appearance of the C_{ij} which is a central part of our model, Müller already obtained the right-hand side of (123), however, with a different arrangement of terms. At the same time, the phenomenological coefficients in this work are not related to those that are available from the experimental side. This might be the reason why this most important line of work, has been largely ignored especially in the engineering community - unfortunately, even until today. Let us note in passing that in this period quite some papers on rational thermodynamics of mixtures appeared, but some of those contained significant misconceptions; cf. the literature survey given in [5].

In the engineering science, more practical mixture models were developed, sometimes including partial momentum balances. An early example is [48], showing also the main problem in this line of research: Partial momentum balances are set up in a naive way, by adopting formulas from different theories to describe various force contributions and to insert them without a rationale behind. In particular, the Gibbs-Duhem relations are used in a non rigorous way. There are several more such contributions, but instead of quoting them individually we only cite the recent paper [9] which contains a nice overview of the literature on partial momentum balances. Unfortunately, this paper also employs the Gibbs-Duhem relation for isothermal systems in order to describe the force due to chemical potential gradients which is then assumed to hold in all situations.

* "Das Studium der Maxwell'schen Abhandlung ist nicht leicht." From [50], p. 72.

Still another line of research uses approximate solutions of the Boltzmann equations to obtain formulas describing the interspecies forces which are then represented in primitive variables of a continuum mechanical theory in which they are inserted. This approach is especially used for the derivation of multicomponent diffusion fluxes within a class-I framework and will thus be discussed further in Section 14 on the Maxwell-Stefan equations. A closed class-II model is derived in this way by Kerkhof in [28] and [29], where he introduces partial momentum balances of the form

$$\begin{aligned} \rho_i (\partial_t \mathbf{v}_i + \mathbf{v}_i \cdot \nabla \mathbf{v}_i) = & -c_i \nabla_T \mu_i^m - cRT \sum_{j \neq i} \frac{x_i x_j}{\mathfrak{D}_{ij}} (\mathbf{v}_i - \mathbf{v}_j) + \rho_i \mathbf{b}_i \\ & - cRT \sum_{j \neq i} \frac{x_i x_j}{\mathfrak{D}_{ij}} \left(\frac{D_i^T}{\rho_i} - \frac{D_j^T}{\rho_j} \right) \nabla \ln T. \end{aligned}$$

Here μ_i^m denotes the molar-based chemical potentials which satisfy $\mu_i^m = M_i \mu_i$, and ∇_T denotes the "gradient taken at constant T ". For a sound comparison, note first that the expression by Kerkhof is obtained from approximate solutions to the Boltzmann equations. It is well-known that the multi-species Boltzmann equations are a model for mixture of ideal gases, which represents a special simple mixture. In particular, if (T, p_i) are chosen as independent variables, then $c_i \nabla_T \mu_i^m = \rho_i \nabla_T \mu_i = \rho_i \frac{\partial \mu_i}{\partial p_i} \nabla p_i = \nabla p_i$. If we further let $\mathfrak{D}_{ij} = R/(cM_i M_j f_{ij})$, then the first three terms on the right-hand side coincide with those in (104). To compare the thermo-diffusion term, recall that any function $d_i^T(T, \rho_1, \dots, \rho_N)$ with $\sum_i d_i^T = 0$ is admissible in (103) or (104). In particular,

$$d_i^T = -cRT \sum_{j \neq i} \frac{x_i x_j}{\mathfrak{D}_{ij}} \left(\frac{D_i^T}{\rho_i} - \frac{D_j^T}{\rho_j} \right)$$

is a valid choice, hence the class-II momentum balances of Kerkhof above are consistent to our result, but specialized to the case of simple mixtures.

If the above form for the d_i^T is used, the two sums in the partial momentum balance can be combined and become

$$-cRT \sum_{j \neq i} \frac{x_i x_j}{\mathfrak{D}_{ij}} \left(\mathbf{v}_i + \frac{D_i^T}{\rho_i T} \nabla T - \left(\mathbf{v}_j + \frac{D_j^T}{\rho_j T} \nabla T \right) \right).$$

This form might call for a suggestive interpretation in the framework of a kinetic gas theory: two colliding molecules had their last collision at slightly different positions, hence at different temperatures. Indeed, the term $\mathbf{u}_i + \frac{D_i^T}{\rho_i} \nabla \log T$ can be viewed as a corrected diffusion velocity in case of an inhomogeneous temperature field. But an explanation of thermal diffusion along such a line of arguments is only possible if the temperature dependence of the collision frequencies is taken into account, i.e. it is a second-order transport effect. Instead of going into further details, we recommend Chapter 6 in [15] and the original literature mentioned there. A more thorough derivation via the Boltzmann equation gives the correct form and also leads to the above structure of the d_i^T . Note that, at this point and for the case of a simple mixture of ideal gases, the kinetic theory provides additional information not available in the pure phenomenological continuum thermodynamics. But also note that the Boltzmann equation only describes thermal diffusion if sufficiently realistic collision models are employed. The simple model of so-called *Maxwell molecules*, a favored choice since it allows for closed form computations of the collision integrals, does not include these effects, since then $d_i^T = 0$. For more details on the Boltzmann equation we again refer to [15] and, in the case of mixtures, however for Maxwell molecules, see [42].

One main achievement of the present work is the consistent and coherent derivation of closed class-II models within a continuum thermodynamical theory, including the proper extension to chemically reactive fluid mixtures. To the best of our knowledge, up to now no contribution treats the case of

chemically reacting fluid mixtures in such a way that the momentum change due to chemistry is appropriately accounted for. One of the very few papers which explicitly include a chemical contribution is [56], where the partial momentum balance reads as

$$(140) \quad \rho_i(\partial_t \mathbf{v}_i + \mathbf{v}_i \cdot \nabla \mathbf{v}_i) = \rho_i \mathbf{b}_i + \mathbf{S}_i + \sum_{j=1}^N \mathbf{P}_{ij} + r_i(\bar{\mathbf{v}}_i - \mathbf{v}_i).$$

Here \mathbf{P}_{ij} are the interaction forces between species A_i and A_j , assuming $\mathbf{P}_{ij} = -\mathbf{P}_{ji}$ without rationale, and $\bar{\mathbf{v}}_i$ is introduced to be the velocity of species A_i produced by chemical reaction. Later on, this velocity is not considered anymore. A similar case is [9], where $\bar{\mathbf{v}}_i$ is actually assumed to equal the partial bulk velocity \mathbf{v}_i such that the effect of chemical reactions is in fact eliminated. Note the difference to our modeling in which every chemical reaction is considered separately, since the (continuum averaged) velocity of A_i produced by reaction a depends on a , while for any particular reaction it is independent of the species!

13. CLASS-II \rightarrow CLASS-I MODEL REDUCTION

We introduce a new method for the derivation of the class-I model via reduction of the corresponding class-II versions, avoiding scale-separation arguments which are usually employed; cf. section 14 concerning the latter.

Reduction principle and its exploitation. Recall first that the basic variables of the class-I model are ρ_i , \mathbf{v} and T . The relevant balance equations of the class-I model rely on (5), (15) and (17). Here the inner structure of stress, energy density and heat flux are ignored, and they are considered as primitive quantities in the class-I setting. Exclusively the inner structure of the external body force $\rho \mathbf{b}$ and its internal power are taken into account. Thus the relevant balance equations read

$$(141) \quad \partial_t \rho_i + \operatorname{div}(\rho_i \mathbf{v} + \mathbf{j}_i^I) = \sum_{a=1}^{N_R} M_i \nu_i^a R_a^I,$$

$$(142) \quad \rho(\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) - \operatorname{div} \mathbf{S}^I = \sum_{i=1}^N \rho_i \mathbf{b}_i,$$

$$(143) \quad \partial_t(\rho e^I) + \operatorname{div}(\rho e^I \mathbf{v} + \mathbf{q}^I) = \mathbf{S}^I : \nabla \mathbf{v} + \sum_{i=1}^N \mathbf{j}_i^I \cdot \mathbf{b}_i.$$

Note the difference between (27) and (143). In particular, the external body forces do not explicitly occur in (27).

The constitutive quantities in the class-I model are

$$R_a^I, \quad p^I, \quad \mathbf{S}^{\text{irr},I} = -\Pi^I \mathbf{I} + \mathbf{S}^{\circ,I}, \quad \mathbf{j}_i^I, \quad \rho e^I, \quad \mathbf{q}^I,$$

and they must be related in a material dependent manner to the variables.

We now compare the equations (141)–(143) with the relevant equations of balance of the class-II model, viz.

$$(144) \quad \partial_t \rho_i + \operatorname{div}(\rho_i \mathbf{v} + \rho_i \mathbf{u}_i) = \sum_{a=1}^{N_R} M_i \nu_i^a R_a,$$

$$(145) \quad \rho_i(\partial_t \mathbf{v}_i + \mathbf{v}_i \cdot \nabla \mathbf{v}_i) - \operatorname{div} \mathbf{S}_i = \mathbf{f}_i - r_i \mathbf{v}_i + \rho_i \mathbf{b}_i,$$

$$(146) \quad \partial_t(\rho e) + \operatorname{div}(\rho e \mathbf{v} + \mathbf{q}) = \sum_i \mathbf{S}_i^{\text{irr}} : \nabla \mathbf{v}_i - p \operatorname{div} \mathbf{v} - \sum_i \mathbf{u}_i \cdot (\mathbf{f}_i - r_i \mathbf{v}_i - \nabla p_i + \frac{r_i}{2} \mathbf{u}_i).$$

The mass balances of the species and the energy balance of the mixture should be same in both models. Exclusively the partial momentum balances are ignored in class-I, where they are replaced by the momentum balance of the mixture.

Comparing the mass balances (141) and (144), we identify

$$(147) \quad \mathbf{j}_i^I = \rho_i \mathbf{u}_i \quad \text{and} \quad R_a^I = R_a.$$

To compare the energy balances (143) and (146), we substitute the first term on the right-hand side of (146) by the identity

$$(148) \quad \sum_i \mathbf{S}_i^{\text{irr}} : \nabla \mathbf{v}_i = \sum_i \mathbf{S}_i^{\text{irr}} : \mathbf{D} + \text{div} \left(\sum_i \mathbf{u}_i \cdot \mathbf{S}_i^{\text{irr}} \right) - \sum_i \mathbf{u}_i \cdot \text{div} (\mathbf{S}_i^{\text{irr}}).$$

Then we use (19) and (24) and identify energies, heat fluxes and stresses of both models:

$$(149) \quad \rho e^I = \sum_i \rho_i e_i, \quad \mathbf{q}^I = \sum_i (\mathbf{q}_i + (\rho_i e_i + p_i) \mathbf{u}_i - \mathbf{u}_i \cdot \mathbf{S}_i^{\text{irr}}), \quad \mathbf{S}^I = \sum_i \mathbf{S}_i.$$

Observe that \mathbf{S}^I does not equal the mixture stress \mathbf{S} obtained within class-II via Truesdell's meta-principle. Next, the equivalence of the energy balances (143) and (146) requires the relation

$$(150) \quad \rho_i \mathbf{b}_i = -\mathbf{f}_i + r_i \mathbf{v}_i - \frac{1}{2} r_i \mathbf{u}_i - \text{div} \mathbf{S}_i + \rho_i \lambda,$$

where the Lagrange parameter λ is introduced here to consider the constraints $\sum_i \mathbf{f}_i = 0$ and $\sum_i r_i = 0$ and is thus given by

$$(151) \quad \rho \lambda = \rho \mathbf{b} - \frac{1}{2} \sum_i r_i \mathbf{u}_i + \text{div} \sum_i \mathbf{S}_i.$$

We obtain

$$(152) \quad \mathbf{f}_i - r_i \mathbf{v}_i = -\frac{1}{2} (r_i \mathbf{u}_i + y_i \sum_k r_k \mathbf{u}_k) - \text{div} \mathbf{S}_i + y_i \text{div} \left(\sum_k \mathbf{S}_k \right) - \rho_i (\mathbf{b}_i - \mathbf{b}).$$

Below, this relation will serve to eliminate the momentum production \mathbf{f}_i in the class-II constitutive law (116) which then becomes a constitutive equation for the class-I diffusion flux \mathbf{j}_i^I .

Now we discuss the status of the class-I momentum balance (142). Recall at first that the mass balances of the species and the energy balance of the mixture occur in class-II and class-I as well. The essential difference of the two models concerns the momentum balances. While we consider the N partial momentum balances of the species in class-II, we only have a single momentum balance in class-I serving to determine the barycentric velocity of the mixture. It is thus natural to attain equivalent versions of the partial mass balances and the energy balance in the two models. However, then the equivalence of the barycentric momentum balance of the class-II model with the class-I momentum balance can only be reached in an approximative sense. If we were to have the relation $\mathbf{S}^I = \sum_i (\mathbf{S}_i - \rho_i \mathbf{u}_i \otimes \mathbf{u}_i)$, then (142) is a consequence of the class-II partial momentum balances (145). However, we have attained $\mathbf{S}^I = \sum_i \mathbf{S}_i$ from the equivalence of the energy balances. Thus our reduction class-II \rightarrow class-I leads to a class-I momentum balance that is an approximation because terms of order $|\mathbf{u}|^2$ are ignored from the class-II point of view.

Finally, we compare the entropy balances of both model classes. The class-I entropy principle can be exploited in an analogous manner to the above treatment in the model class-II. In particular, the class-I entropy balance

$$(153) \quad \partial_t (\rho s^I) + \text{div} (\rho s^I \mathbf{v} + \Phi^I) = \zeta^I$$

implies

$$(154) \quad \zeta^I = \operatorname{div} \left(\Phi^I - \frac{\mathbf{q}^I}{T} + \sum_i \frac{\mu_i \mathbf{j}_i^I}{T} \right) - \frac{1}{T} \left(\rho e - T \rho s^I + p - \sum_i \rho_i \mu_i \right) \operatorname{div} \mathbf{v} \\ - \sum_i \mathbf{j}_i^I \cdot \left(\nabla \frac{\mu_i}{T} - \frac{\mathbf{b}_i}{T} \right) - \frac{1}{T} \sum_{a=1}^{N_R} R_a^I \mathcal{A}_a + \frac{1}{T} \mathbf{S}^{I,\text{irr}} : \mathbf{D} + \mathbf{q}^I \cdot \nabla \frac{1}{T},$$

corresponding to the first representation of the class-II entropy production in (45). As in the class-II case, the second term on the right-hand side has to vanish, which again gives rise to the Gibbs-Duhem relation (50), now in the class-I context. Next, the above identifications according to (149) and (152) are used to compare with (45). This shows that the identity

$$(155) \quad \zeta^I - \operatorname{div} \Phi^I = \zeta^{\text{II}} - \operatorname{div} \Phi^{\text{II}}$$

is valid which implies that the desired final identification of the specific entropies, $s^I = s^{\text{II}}$, is consistent with those from above - a very satisfactory result, since it also yields $T^I = T^{\text{II}}$ as well as $\mu_i^I = \mu_i^{\text{II}}$. Note that we did not use different notations for the latter quantities in the different model classes, although their identification was not a priori possible.

Now we can start with the model reduction, based on all identifications and on relation (155). Before we continue, it is important to recall from the remarks on the entropy principle that the representation of the entropy production as a sum of binary products is not unique. Correspondingly, the choice of the entropy flux is not unique and can be modified due to a zero addition to ζ , adding also new dissipative mechanisms and changing co-factors in binary products which are already present. Actually, it is precisely this non-uniqueness which allows for improved class-I closure relations building on the additional knowledge from class-II. Moreover, since the system of axioms from our entropy principle applies also to the model class-I, the representation $\zeta^I = \zeta^{\text{II}} + \operatorname{div} (\Phi^I - \Phi^{\text{II}})$, as a consequence of (155), and the fact that the entropy flux Φ^I has to be chosen in such a way that ζ^I is a sum of binary products, yields the fundamental requirement

$$(156) \quad \zeta^I \equiv \zeta^{\text{II}} \quad \text{for any thermodynamic process.}$$

Hence the only consistent way for a class-II \rightarrow class-I model reduction is by means of an *entropy invariant model reduction*. Note also that the equality of the class-I and class-II entropy productions in particular guarantees that the reduced class-I model is thermodynamically consistent, i.e. the class-I closure relation obtained from the class-II constitutive laws always respect the class-I entropy inequality - this is by no means a trivial property.

Class-I constitutive model. For later comparison, let us start with a brief recap of the standard closure relations from classical TIP. Exploitation of (154), applying the axioms from the entropy principle in the class-I context and assuming as dissipative mechanisms the same as for the class-II model, except for using only a single viscous mechanism, one obtains the TIP-version of the entropy flux as

$$(157) \quad \Phi^{\text{TIP}} = \frac{\mathbf{q}^I}{T} - \frac{\sum_i \mu_i \mathbf{j}_i^I}{T},$$

and the corresponding entropy production as

$$(158) \quad \zeta^{\text{TIP}} = - \sum_i \mathbf{j}_i^I \cdot \left(\nabla \frac{\mu_i}{T} - \frac{1}{T} \mathbf{b}_i \right) - \frac{1}{T} \sum_{a=1}^{N_R} R_a^I \mathcal{A}_a + \frac{1}{T} \mathbf{S}^{I,\text{irr}} : \mathbf{D} + \mathbf{q}^I \cdot \nabla \frac{1}{T}.$$

Based on (158), the simplest closure relations for the constitutive quantities that vanish in equilibrium are obtained by assuming *linear relations* between so called fluxes and driving forces in the binary products of the entropy production. This yields Fourier's law for the heat flux, Fick's law for mass diffusion and Newton's law for the (deviatoric) stress in viscous fluids. It is known from experimental observations that cross-effects between the different dissipative mechanisms like the Soret effect

(thermal diffusion) and the Dufour (diffusion thermo) effect occur, such that—in principle—all possible couplings should be accounted for. This introduces a large number of so-called phenomenological coefficients which are often reduced by postulating the famous Onsager reciprocity (i.e. symmetry) relations (cf. [19]). For example, for isotropic fluid mixtures one has the well-known relations

$$(159) \quad \mathbf{j}_i^{\text{TIP}} = L_{i0} \nabla \frac{1}{T} - \sum_{j=1}^{N-1} L_{ij} \left(\nabla \left(\frac{\mu_j - \mu_N}{T} \right) - \frac{\mathbf{b}_j - \mathbf{b}_N}{T} \right),$$

$$(160) \quad \mathbf{q}^{\text{TIP}} = L_{00} \nabla \frac{1}{T} - \sum_{i=1}^{N-1} L_{0i} \left(\nabla \left(\frac{\mu_i - \mu_N}{T} \right) - \frac{\mathbf{b}_i - \mathbf{b}_N}{T} \right),$$

$$(161) \quad \mathbf{S}^{\text{TIP},\circ} = \eta \mathbf{D}^\circ.$$

$$(162) \quad \Pi^{\text{TIP}} = -l_{00} \operatorname{div} \mathbf{v} - \sum_{a=1}^{N_R} l_{0a} \mathcal{A}_a,$$

$$(163) \quad R_a^{\text{TIP}} = -l_{a0} \operatorname{div} \mathbf{v} - \sum_{b=1}^{N_R} l_{ab} \mathcal{A}_b.$$

Further couplings are possible like via a term $\nabla \frac{1}{T} \cdot \mathbf{D}$ with \mathbf{D} the symmetric part of the velocity gradient. However, those terms are excluded by assuming linearity between fluxes and driving forces. In the class-I setting within TIP this restriction is usually referred to as Curie's principle. The Onsager-Casimir reciprocity relations for (160)–(161) impose the following symmetry properties:

- symmetry of the mobilities $[L_{ij}]$, including $L_{0i} = L_{i0}$
- symmetry of the reaction cross-couplings $[l_{ab}]$ for $a, b \geq 1$
- anti-symmetry of the volume variation/chemical reaction coupling, i.e. $l_{0a} = -l_{a0}$

The last coupling with its apparently anti-symmetric character has caused quite some confusion, while this issue is fully clarified in our present theory. Note also that, according to [40], a convincing proof of the Onsager symmetry relations applied to transport phenomena is missing. Finally, the linear closure in (163) might be inappropriate for chemically reacting flows due to significant deviations from chemical equilibrium.

Class-I constitutive model via class-II \rightarrow class-I reduction. In the next sections we derive the class-I constitutive equations for the diffusion fluxes, heat fluxes, stresses and reaction rates that follow from the corresponding class-II equations.

We start with the two representations of the interaction forces $\mathbf{f}_i - r_i \mathbf{v}_i$. There is the class-II constitutive equation (116) and we have (152) which is among the conditions guaranteeing the equivalence of class-I and class-II energy balances. Eliminating $\mathbf{f}_i - r_i \mathbf{v}_i$ yields the constitutive equations for the diffusion fluxes of class-I. At first we obtain

$$(164) \quad \sum_{j=1}^N (T\tau_{ij} - C_{ij})(\mathbf{u}_i - \mathbf{u}_j) + \frac{1}{2}(r_i \mathbf{u}_i + y_i \sum_{j=1}^N r_j \mathbf{u}_j) = \mathbf{d}_i$$

with the abbreviation

$$(165) \quad \mathbf{d}_i := \rho_i T \nabla \frac{\mu_i}{T} - \rho_i (\mathbf{b}_i - \mathbf{b}) - T \mathcal{D}_i^T \nabla \frac{1}{T} - \operatorname{div} \mathbf{S}_i^{\text{irr}} + y_i \operatorname{div} \left(\sum_{j=1}^N \mathbf{S}_j^{\text{irr}} \right),$$

where $D_i^T := h_i + d_i^T$; recall also that $y_i = \rho_i/\rho$ are the mass fractions. Employing $\sum_{j=1}^N \tau_{ij} = 0$ from (86) and setting

$$(166) \quad \gamma_{ij} = -C_{ij} + \sum_{k=1}^N C_{ik} \delta_{ij} - \frac{1}{2} r_i \delta_{ij} - \frac{1}{2} y_i r_j, \quad F_{ij} = T \tau_{ij} + \gamma_{ij},$$

the system (164) simplifies to read

$$(167) \quad - \sum_{j=1}^N F_{ij} \mathbf{u}_j = \mathbf{d}_i.$$

Now note that $\sum_{i=1}^N \mathbf{d}_i = T \sum_{i=1}^N \mathbf{B}_i = 0$ and also $\sum_{i=1}^N F_{ij} = 0$ for all $j = 1, \dots, N$. In order to obtain the class-I diffusion fluxes $\mathbf{j}_i^I = \rho_i \mathbf{u}_i$, the system (167), together with the constraint $\sum_{i=1}^N y_i \mathbf{u}_i = 0$, has to be solved for \mathbf{u}_i , given $\mathbf{d}_1, \dots, \mathbf{d}_N$ with $\sum_{i=1}^N \mathbf{d}_i = 0$. There are essentially two ways to proceed: in the first variant, one keeps (167) and studies the linear map $\mathbf{F} : \{\mathbf{y}\}^\perp \rightarrow \{\mathbf{1}\}^\perp$ induced by the matrix $[F_{ij}]$, where $\mathbf{y} = (y_1, \dots, y_N)$ and $\mathbf{1} = (1, \dots, 1) \in \mathbb{R}^N$. The second variant, which will be employed here and leads to the Fickian form of the diffusion fluxes, eliminates \mathbf{u}_N in order to incorporate the constraint. In both approaches it is crucial to know that the new chemical interaction matrix $[\gamma_{ij}]$ is positive semi-definite on $\{\mathbf{y}\}^\perp$. The latter holds due to the estimates following equation (115); note that the positive semi-definiteness is only required on $\{\mathbf{y}\}^\perp$ and, on this set, the γ_{ij} can be replaced by

$$(168) \quad c_{ij} = -C_{ij} + \sum_{k=1}^N C_{ik} \delta_{ij} - \frac{1}{2} r_i \delta_{ij}.$$

Inserting the C_{ij} , it follows that

$$(169) \quad c_{ij} = \sum_{a=1}^{N_R} \left(R_a^f \left(\delta_{ij} \frac{M_j \beta_j + M_j \alpha_j}{2} - \frac{M_i \beta_i M_j \alpha_j}{\sum_k M_k \alpha_k} \right) + R_a^b \left(\delta_{ij} \frac{M_j \beta_j + M_j \alpha_j}{2} - \frac{M_j \beta_j M_i \alpha_i}{\sum_k M_k \alpha_k} \right) \right),$$

hence $[c_{ij}]$ is positive semi-definite. Consequently, the matrix $[F_{ij}]$ is positive definite on $\{\mathbf{y}\}^\perp$, given that the f_{ij} from (116) are strictly positive for all $i \neq j$. The matrix $[F_{ij}]$ plays a central role in the Maxwell-Stefan form of the multicomponent diffusion modeling; further information will be provided in Section 14 below.

Diffusion fluxes. To calculate the diffusion fluxes \mathbf{j}_i^I from (164), four steps are taken: (i) we introduce in (164) $\mathbf{j}_i^I = \rho_i \mathbf{u}_i$ and consider the constraint $\sum_i \mathbf{j}_i^I = 0$; (ii) we divide (164) by $\rho_i T$; (iii) we subtract the N^{th} equation; (iv) we define the inverse mobility matrix as

$$(170) \quad m_{ij}^{-1} = \tilde{F}_{ij} - \tilde{F}_{Nj} - \tilde{F}_{iN} + \tilde{F}_{NN} \quad \text{with} \quad \tilde{F}_{ij} = \frac{F_{ij}}{T \rho_i \rho_j}.$$

Evidently, the matrix $[\tilde{F}_{ij}]$ is positive definite on $\{\mathbf{y}\}^\perp$. Given $\mathbf{w} \in \mathbb{R}^{N-1}$ with $\mathbf{w} \neq 0$, a direct computation shows that

$$(171) \quad \sum_{i,j=1}^{N-1} m_{ij}^{-1} w_i w_j = \sum_{i,j=1}^N \tilde{F}_{ij} \tilde{w}_i \tilde{w}_j,$$

if we let $\tilde{w}_i = w_i$ for $i < N$ and $\tilde{w}_N = -\sum_{i < N} w_i$. Since $\tilde{\mathbf{w}} \perp \mathbf{y}$, the right-hand side in (171) is non-negative, hence $[m_{ij}^{-1}]$ is positive definite on \mathbb{R}^{N-1} . Thus we have for $i = 1, \dots, N-1$:

$$(172) \quad \mathbf{j}_i^I = - \sum_{j=1}^{N-1} m_{ij} \left(\nabla \frac{\mu_j - \mu_N}{T} - \frac{\mathbf{b}_j - \mathbf{b}_N}{T} - \left(\frac{\mathcal{D}_j^T}{\rho_j} - \frac{\mathcal{D}_N^T}{\rho_N} \right) \nabla \frac{1}{T} - \frac{\text{div}(\mathbf{S}_j^{\text{irr}})}{T \rho_j} + \frac{\text{div}(\mathbf{S}_N^{\text{irr}})}{T \rho_N} \right).$$

Comparison with the classical result (159) from TIP shows that the class-II \rightarrow class-I model reduction leads to a third driving force, viz. $\frac{1}{\rho_j} \operatorname{div}(\mathbf{S}_j^{\text{irr}}) - \frac{1}{\rho_N} \operatorname{div}(\mathbf{S}_N^{\text{irr}})$ due to the viscous stresses; cf. the next section for a comparison to the literature in the context of the Maxwell-Stefan equations. Furthermore, we may identify

$$(173) \quad L_{ij} = m_{ij} \quad \text{and} \quad L_{i0} = \sum_{j=1}^{N-1} m_{ij} \left(\frac{\mathcal{D}_j^T}{\rho_j} - \frac{\mathcal{D}_N^T}{\rho_N} \right).$$

Now observe that the m_{ij} are symmetric if and only if the c_{ij} are, i.e. precisely if all chemical reactions are in equilibrium ($R_a^f = R_a^b$ for all $a = 1, \dots, N_R$). In this situation, the Onsager symmetry of L_{ij} , which is introduced in the class-I model as a postulate, is implied by the class-II \rightarrow class-I reduction. We will take up this point again below when we discuss thermo-diffusion.

Note that the new driving force leads to a new and intricate PDE structure. Due to the class-II constitutive equations (121)_{1,2} for the viscous stresses, $\operatorname{div} \mathbf{j}_i^{\text{I}}$ will appear on the right-hand side of (172) and thus there is no algebraic representation of the diffusion fluxes. However, this phenomenon can be avoided by a specific assumption on the partial viscosities. A further, more detailed discussion will be carried out below.

Heat flux. The determination of the class-I heat flux \mathbf{q}^{I} starts from (149)₂, where we insert the class-II constitutive equations (102) for $\sum_i \mathbf{q}_i$ to arrive at

$$(174) \quad \mathbf{q}^{\text{I}} = \alpha \nabla \frac{1}{T} + \sum_{i=1}^{N-1} \left(\frac{\mathcal{D}_i^T}{\rho_i} - \frac{\mathcal{D}_N^T}{\rho_N} + \frac{\mathbf{S}_i^{\text{irr}}}{\rho_i} - \frac{\mathbf{S}_N^{\text{irr}}}{\rho_N} \right) \mathbf{j}_i^{\text{I}}.$$

Inserting the diffusion fluxes (172) and rearranging terms, we obtain

$$(175) \quad \begin{aligned} \mathbf{q}^{\text{I}} &= \left(\alpha + \sum_{i,j=1}^{N-1} m_{ij} \left(\frac{\mathcal{D}_i^T}{\rho_i} - \frac{\mathcal{D}_N^T}{\rho_N} + \frac{\mathbf{S}_i^{\text{irr}}}{\rho_i} - \frac{\mathbf{S}_N^{\text{irr}}}{\rho_N} \right) \left(\frac{\mathcal{D}_j^T}{\rho_j} - \frac{\mathcal{D}_N^T}{\rho_N} \right) \right) \nabla \frac{1}{T} \\ &- \sum_{i,j=1}^{N-1} m_{ij} \left(\frac{\mathcal{D}_i^T}{\rho_i} - \frac{\mathcal{D}_N^T}{\rho_N} + \frac{\mathbf{S}_i^{\text{irr}}}{\rho_i} - \frac{\mathbf{S}_N^{\text{irr}}}{\rho_N} \right) \left(\nabla \left(\frac{\mu_j - \mu_N}{T} \right) + \frac{\mathbf{b}_j - \mathbf{b}_N}{T} \right) \\ &- \sum_{i,j=1}^{N-1} m_{ij} \left(\frac{\mathcal{D}_i^T}{\rho_i} - \frac{\mathcal{D}_N^T}{\rho_N} + \frac{\mathbf{S}_i^{\text{irr}}}{\rho_i} - \frac{\mathbf{S}_N^{\text{irr}}}{\rho_N} \right) \left(\frac{\operatorname{div} \mathbf{S}_j^{\text{irr}}}{T \rho_j} - \frac{\operatorname{div} \mathbf{S}_N^{\text{irr}}}{T \rho_N} \right). \end{aligned}$$

Recall that both α and the m_{ij} are functions of T and all ρ_i . If we keep only linear terms of those quantities that vanish in equilibrium, we finally get

$$(176) \quad \begin{aligned} \mathbf{q}^{\text{I}} &= \left(\alpha + \sum_{i,j=1}^{N-1} m_{ij} \left(\frac{\mathcal{D}_i^T}{\rho_i} - \frac{\mathcal{D}_N^T}{\rho_N} \right) \left(\frac{\mathcal{D}_j^T}{\rho_j} - \frac{\mathcal{D}_N^T}{\rho_N} \right) \right) \nabla \frac{1}{T} \\ &- \sum_{i,j=1}^{N-1} m_{ij} \left(\frac{\mathcal{D}_i^T}{\rho_i} - \frac{\mathcal{D}_N^T}{\rho_N} \right) \left(\nabla \left(\frac{\mu_j - \mu_N}{T} \right) + \frac{\mathbf{b}_j - \mathbf{b}_N}{T} \right) \\ &- \sum_{i,j=1}^{N-1} m_{ij} \left(\frac{\mathcal{D}_i^T}{\rho_i} - \frac{\mathcal{D}_N^T}{\rho_N} \right) \left(\frac{\operatorname{div} \mathbf{S}_j^{\text{irr}}}{T \rho_j} - \frac{\operatorname{div} \mathbf{S}_N^{\text{irr}}}{T \rho_N} \right). \end{aligned}$$

This is the constitutive equation for the class-I heat flux derived by a class-II \rightarrow class-I reduction. By comparing (176) with (160) we again observe the further driving force $\frac{1}{\rho_j} \operatorname{div}(\mathbf{S}_j^{\text{irr}}) - \frac{1}{\rho_N} \operatorname{div}(\mathbf{S}_N^{\text{irr}})$ due to the viscous stresses.

Furthermore, we identify

$$(177) \quad L_{00} = \alpha + \sum_{i,j} m_{ij} \left(\frac{\mathcal{D}_i^T}{\rho_i} - \frac{\mathcal{D}_N^T}{\rho_N} \right) \left(\frac{\mathcal{D}_j^T}{\rho_j} - \frac{\mathcal{D}_N^T}{\rho_N} \right) \quad \text{and} \quad L_{0i} = \sum_j m_{ji} \left(\frac{\mathcal{D}_j^T}{\rho_j} - \frac{\mathcal{D}_N^T}{\rho_N} \right).$$

A comparison with (173) immediately implies that $L_{0i} = L_{i0}$ only if there is the symmetry of the mobility matrix $[m_{ij}]$. Recall its definition by (170) and (166) and observe that $m_{ij} = m_{ji}$ only holds if the chemical contribution to (166) is symmetric, i.e. $C_{ij} = C_{ji}$. However, according to (112) the latter symmetry only holds in the case of chemical equilibrium, i.e. $R_a^f = R_a^b$ for all $a = 1, \dots, N_R$. Thus if there are chemical reactions outside of equilibrium the Onsager reciprocity relations $L_{0i} = L_{i0}$ do not hold. Moreover, in this case the cross-effect of *thermo-diffusion* cannot be introduced by entropy neutral mixing.

Viscous stress and viscous pressure. We start from the identification of the class-I stress (149)₃. There we insert the class-II results (121) and use $\mathbf{v}_i = \mathbf{v} + \mathbf{j}_i^I/\rho_i$ to introduce the diffusion fluxes. Then we obtain

$$(178) \quad \mathbf{S}^{I,\circ} = \sum_{i,j=1}^N 2\eta_{ij} \left(\mathbf{D}^\circ + \frac{1}{2} (\nabla \mathbf{j}_j^I + (\nabla \mathbf{j}_j^I)^\top) \right), \quad \Pi^I = - \sum_{i,j=1}^N \lambda_{ij} (\operatorname{div} \mathbf{v} + \operatorname{div} \frac{\mathbf{j}_j^I}{\rho_j})$$

with the material parameters η_{ij} and λ_{ij} from the closure of the class-II model. This result implies a new and very intricate PDE structure. Due to (172) and (121), at least third-order derivatives of the velocities appear.

A first simplification of the model is achieved if we consider the special case in which the class-II viscosities in (121) and, hence, in (178) satisfy the relation

$$(179) \quad \eta_{ij} = y_i \eta_j \quad \text{and} \quad \lambda_{ij} = y_i \lambda_j.$$

The point is that this implies

$$(180) \quad \mathbf{S}_i^\circ = y_i \mathbf{S}^{I,\circ} \quad \text{and} \quad \Pi_i = y_i \Pi^I.$$

Consequently, the new driving force—which originates the intricate structure—simplifies in this case according to

$$(181) \quad \frac{1}{\rho_j} \operatorname{div} \mathbf{S}_j^{\text{irr}} - \frac{1}{\rho_N} \operatorname{div} \mathbf{S}_N^{\text{irr}} = \left(\frac{1}{\rho_j} \nabla y_j - \frac{1}{\rho_N} \nabla y_N \right) \mathbf{S}^{\text{irr}}.$$

Then the diffusion fluxes and the heat flux, (172) and (176), algebraically depend on $\mathbf{S}^{I,\circ}$ and the viscous pressure Π^I . But note that the stresses still depend on $\operatorname{div} (\mathbf{S}_j^{\text{irr}})$.

If the material parameters are further restricted to satisfy

$$(182) \quad \eta_{ij} = y_i \eta/N \quad \text{and} \quad \lambda_{ij} = y_i \lambda/N$$

with common functions $\eta \geq 0$ and $\lambda \geq 0$, we obtain

$$(183) \quad \mathbf{S}^\circ = 2\eta \mathbf{D}^\circ - \eta/N \sum_{j=1}^N \left(\nabla y_j \otimes \frac{\mathbf{j}_j^I}{\rho_j} + \frac{\mathbf{j}_j^I}{\rho_j} \otimes \nabla y_j \right), \quad \Pi = -\lambda \operatorname{div} \mathbf{v} + \frac{\lambda}{N} \operatorname{div} \left(\sum_{j=1}^N \frac{\mathbf{j}_j^I}{\rho_j} \right).$$

In this case the viscous stresses algebraically depend on the diffusion fluxes. But observe that insertion of these stresses into the class-I momentum balance still leads to a PDE of third order. Here it is important to note that the PDE-system has a triangular structure, where the mass densities, up to perturbations of lower order, can be solved prior to insertion into the constitutive stress relation. This allows to solve the system in a regularity setting, where the mass fluxes in the stress do not give rise to the leading order terms concerning the existence analysis.

Finally note that all new terms are formed by binary products of ∇y_i , $\mathbf{S}_i^{\text{irr}}$ and \mathbf{j}_i^{I} , respectively. Thus when $\nabla y_i = 0$ in equilibrium, which typically is the case in the setting of this model, we have nonlinear terms in driving forces and fluxes. However, those products are usually ignored in class-I models. In this case we have agreement with TIP and may identify $l_{00} = \lambda$ and $l_{0a} = 0$ according to (162). There results no cross-coupling with the chemical production rates in the class-II \rightarrow class-I reduction because we have not considered those couplings in the class-II setting.

Entropy flux. Let us finally compare the entropy fluxes. Inspection of (45), (154) and (156) shows that

$$(184) \quad \Phi^{\text{I}} = \frac{\mathbf{q}^{\text{I}}}{T} - \frac{\sum_i \mu_i \mathbf{j}_i^{\text{I}}}{T} + \frac{\sum_i \mathbf{u}_i \cdot \mathbf{S}_i^{\text{I}}}{T},$$

hence Φ^{I} does not coincide with the entropy flux from TIP, but

$$(185) \quad \Phi^{\text{I}} = \Phi^{\text{TIP}} + \frac{\sum_i \mathbf{u}_i \cdot \mathbf{S}_i^{\text{I}}}{T}.$$

Note, however, that $\Phi^{\text{I}} = \Phi^{\text{TIP}}$ does hold if the partial viscosities are restricted to satisfy (179). In total and compared to classical TIP, the modifications of the entropy flux and the constitutive relations obtained from the class-II \rightarrow class-I model reduction correspond to the addition of

$$(186) \quad 0 = \frac{1}{T} \sum_i \nabla \mathbf{u}_i : \mathbf{S}_i^{\text{irr}} + \frac{1}{T} \sum_i \mathbf{u}_i \cdot \text{div} \mathbf{S}_i^{\text{irr}} + \sum_i (\mathbf{u}_i \cdot \mathbf{S}_i^{\text{irr}}) \cdot \nabla \frac{1}{T} - \text{div} \left(\frac{\sum_i \mathbf{u}_i \cdot \mathbf{S}_i^{\text{I}}}{T} \right).$$

to ζ^{I} from (154). This corresponds to the addition of the new dissipative mechanism related to diffusion against partial stresses and this additional entropy producing term modifies the diffusion fluxes, the heat flux and the entropy flux.

14. THE MAXWELL-STEFAN EQUATIONS FOR REACTIVE FLUID MIXTURES

In the previous section, inversion of the system (167) has led to the Fickian form of the diffusivities according to (172), sometimes also referred to as the generalized Fick-Onsager form. Let us note that after insertion of particular forms of the chemical potentials, respectively the choice of a specific free energy function, the representation from (172) is usually written in terms of the partial mass densities or, equivalently, the molar concentrations. In simplest cases, this leads to relations of the form

$$(187) \quad \mathbf{j}_i = - \sum_j D_{ij} \nabla \rho_j$$

with so-called Fickian diffusivities D_{ij} . There are two disadvantages of the representation (172), respectively (187): (i) the symmetry between the different species A_i has been broken by eliminating one particular flux, namely \mathbf{j}_N ; (ii) the mobilities m_{ij} show complicated dependencies on, especially, the composition of the mixture. The first point is relevant for a mathematical analysis of the final PDE-system, where the symmetry of the system (167) in the \mathbf{u}_j is helpful. Besides binary mixtures, the Fickian form is appropriate in case the mixture is a solution with one major component (the solvent A_N , say) and several minor constituents (the solutes). Then, if the solution is dilute, i.e. if $y_i \ll 1$ for all $i \neq N$, the fluxes even reduce to the classical form of $\mathbf{j}_i = -D_i \nabla \rho_i$ as discovered by Adolf Fick; cf. [16]. The second point is much more severe, due to the following mathematical fact. A coupled system of diffusion equations of the form which results if (187) is inserted into the partial mass balances, say with $\mathbf{v} = 0$ for simplicity (which is irrelevant for the local-in-time existence properties), the solutions for positive initial values will in general not stay positive in case of constant diffusivities D_{ij} , even if the diffusion operator is elliptic. This underlines the fact that the diffusivities must depend on the composition and the form of this dependency is decisive concerning the well-posedness as well as qualitative properties of the system. Therefore, an alternative description which includes structural information on the diffusivities such that the final PDE-system becomes solvable

is strongly demanded. Of course, if such a description is given, the associated Fickian fluxes can, in principle, be calculated, since the different representations are equivalent. But let us also note in passing, that if the final form according to (187) is used, the D_{ij} are in general not even symmetric.

Motivated by the above facts, we provide the Maxwell-Stefan form of the multicomponent diffusion description which, essentially, corresponds to (164). This representation is, in the absence of chemical reaction, fully symmetric in the constituents and contains additional structural information which solves the problem above as will be explained below. Supported by statistical mechanics, it even turns out that the "friction coefficients" f_{ij} from (90) are only weakly dependent on the mixture composition. Furthermore, experiments have shown that this weak dependence can often be described via affine functions; cf. [51] where also further references are given.

Right from the beginning, there were two different derivations of what is now called the Maxwell-Stefan form. Maxwell in his classical paper [34] used kinetic theory of gases to derive a relation for the diffusion velocity of a binary mixture of simple gases. In order to be able to provide final results for the diffusion coefficient by analytical formulas, he assumed the dependence as r^{-5} of the intermolecular force fields, thus introducing the nowadays so-called Maxwellian molecules; recall that there is no thermo-diffusion in this case. Shortly after this, Stefan essentially gave a continuum mechanical derivation in [50], valid for a system of N constituents. He employed the assumption that[†] every particle of a gas, if it is moving, encounters a resistive force by every other gas, being proportional to the density of that gas and to the relative velocity between the two. As already noted above, he used this to formulate the partial momentum balance

$$\rho_i(\partial_t \mathbf{v}_i + (\mathbf{v}_i \cdot \nabla) \mathbf{v}_i) = -\nabla p_i + \rho_i \mathbf{b}_i - \sum_{j \neq i} f_{ij}(\mathbf{v}_i - \mathbf{v}_j).$$

He actually was also aware that, contrary to Maxwell's derivation, his force balance can be applied to liquid mixtures as well.

Later on, building on the work by Boltzmann and his famous equation, use of statistical mechanics gave rise to several types of approximate solutions to the multi-species Boltzmann equations. Hirschfelder, Curtiss, and Bird in particular obtained the so-called generalized driving forces \mathbf{d}_i which were to replace the partial pressure p_i in (139); see [26] and cf. also [4]. These have then been used to formulate the reduced force balances

$$(188) \quad - \sum_{j \neq i} f_{ij} \rho_i \rho_j (\mathbf{u}_i - \mathbf{u}_j) = \mathbf{d}_i,$$

or other equivalent versions thereof like

$$(189) \quad - \sum_{j \neq i} \frac{x_j \mathbf{J}_i - x_i \mathbf{J}_j}{c \mathfrak{D}_{ij}} = \mathbf{d}_i.$$

The latter form is found in most textbooks on multicomponent diffusion, where $c = \sum_i c_i$ with the molar concentrations $c_i = \rho_i/M_i$, $x_i = c_i/c$ are the molar fractions, $\mathbf{J}_i = c_i \mathbf{u}_i$ the molar mass diffusion fluxes and \mathfrak{D}_{ij} denote the so-called Maxwell-Stefan diffusivities. But neither a rigorous derivation of (188) by a time-scale separation argument—except for [56]—is given, nor a consistent derivation of the driving forces; the latter have been transferred to the continuum mechanical force balance from approximate solutions to the Boltzmann equations. Fortunately, it turned out that the resulting diffusive fluxes obey the second law of thermodynamics. While in the engineering literature this is often attributed to [49], it has already been shown much earlier by Truesdell in [53]. In the latter paper, it has also been shown that the Onsager relations of irreversible thermodynamics are in case of multicomponent diffusion processes nothing but the symmetry of the f_{ij} from above and that the

[†]"In einem Gemenge erfährt jedes einzelne Theilchen eines Gases, wenn es sich bewegt, von jedem anderen Gase einen Widerstand proportional der Dichte dieses Gases und der relativen Geschwindigkeit beider." From [50], p. 64.

latter rigorously follows in case of binary interactions from the total momentum balance. The system of type (188) or (189) is nowadays referred to as the Maxwell-Stefan equations.

Recall that the main advantage of the Maxwell-Stefan form (189) is its additional structural information and the fact that the \mathfrak{D}_{ij} turn out to depend only weakly on the composition. For binary systems, the MS-diffusivity \mathfrak{D}_{12} is actually independent of the composition (x_1, x_2) of the mixture; cf. [15]. Hence the same is true for the MS-diffusivities in a dilute mixture, since only binary interactions between each solute and the solvent occur.

We are now in position to briefly give three different derivations of the Maxwell-Stefan equations. This is helpful in order to place our new extension of the Maxwell-Stefan equations to the case of chemically reacting mixtures into the proper context.

Derivation of the Maxwell-Stefan equations within TIP. Once the two above-mentioned alternatives are present, it is observed that—at least in the isothermal case—one can indeed obtain the Maxwell-Stefan equations together with a set of thermodynamically consistent driving forces by means of the “resistance form” of the closure within TIP, as opposed to the standard “conductivity form”; cf. [30]. To briefly illustrate this, we rewrite the TIP entropy production from (158) for isothermal processes according to

$$(190) \quad \zeta_{\text{isotherm}}^{\text{TIP}} = - \sum_i \mathbf{u}_i \cdot \left(\rho_i \nabla \frac{\mu_i}{T} - \frac{\rho_i \mathbf{b}_i}{T} + y_i \lambda \right) - \frac{1}{T} \sum_{a=1}^{N_R} R_a \mathcal{A}_a + \frac{1}{T} \mathbf{S}^{\text{irr}} : \mathbf{D},$$

where we dropped the superscript indicating model class-I and introduced a Lagrange parameter λ . This parameter is now used to obtain

$$(191) \quad \zeta_{\text{isotherm}}^{\text{TIP}} = - \frac{1}{T} \sum_i \mathbf{u}_i \cdot \mathbf{d}_i - \frac{1}{T} \sum_{a=1}^{N_R} R_a \mathcal{A}_a + \frac{1}{T} \mathbf{S}^{\text{irr}} : \mathbf{D},$$

such that the driving forces \mathbf{d}_i satisfy $\sum_i \mathbf{d}_i = 0$. Employing the Gibbs-Duhem relation, the latter implies

$$(192) \quad \mathbf{d}_i = \rho_i T \nabla \frac{\mu_i}{T} - y_i \nabla p - \rho_i (\mathbf{b}_i - \mathbf{b}).$$

Incorporating the constraint on the \mathbf{d}_i , the entropy production becomes

$$(193) \quad \zeta_{\text{isotherm}}^{\text{TIP}} = - \frac{1}{T} \sum_{i=1}^{N-1} (\mathbf{u}_i - \mathbf{u}_N) \cdot \mathbf{d}_i - \frac{1}{T} \sum_{a=1}^{N_R} R_a \mathcal{A}_a + \frac{1}{T} \mathbf{S}^{\text{irr}} : \mathbf{D},$$

such that we may now repeat precisely the arguments from Section 7 to obtain

$$(194) \quad \mathbf{d}_i = \sum_{j \neq 1}^N \tau_{ij} (\mathbf{u}_i - \mathbf{u}_j),$$

where the matrix $[\tau_{ij}]$ has the same properties as the one in our derivation above. Exploiting Truesdell’s argument from Section 7 as before, the symmetry of $[\tau_{ij}]$ follows and the binary interaction assumption together with the positive definiteness again yields $\tau_{ij} = -f_{ij} \rho_i \rho_j$ with $f_{ij} = f_{ji} > 0$ for all $i \neq j$, hence the Maxwell-Stefan form in the isothermal case.

But note that this derivation does not imply anything on the dependence of the f_{ij} as functions of the primitive variables $(T, \rho_1, \dots, \rho_N)$. It also does not add to the understanding of the underlying mechanism as being a consequence of partial linear momentum exchange. Moreover, note that this only leads to the standard Maxwell-Stefan equations in which no information is contained about the diffusion directly related to momentum transfer during chemical reactions.

In the general, non-isothermal case, the \mathbf{d}_i from (192) get an additional term $y_i(\rho e + p)T\nabla\frac{1}{T}$ if the same derivation is used. This does not coincide with the generalized thermodynamic driving force from [26], [4], where the additional term is $h_i T \nabla \frac{1}{T}$ with the partial enthalpies h_i . The latter is precisely the form which we also get below, either in the diffusional approximation or via the entropy invariant model reduction. This defect of the above derivation within class-I can only be avoided if the full thermo-diffusive cross-coupling is employed.

Derivation of the Maxwell-Stefan equations via diffusional approximation. We use a scale-separation argument, but which is only applicable in the non-reactive case. To this end, we subtract the mass fraction weighted mixture momentum balance from the closed partial momentum balance (123) with $C_{ij} = 0$ in the absence of chemical reactions and, first, with $\mathcal{D}_i^T = 0$. The resulting equation is

$$(195) \quad \rho_i(\partial_t + \mathbf{v} \cdot \nabla)\mathbf{u}_i + \rho_i(\mathbf{u}_i \cdot \nabla)\mathbf{v}_i = y_i \nabla p - \rho_i \nabla \mu_i + \rho_i(\mathbf{b}_i - \mathbf{b}) \\ + T(h_i - \rho_i \mu_i) \nabla \frac{1}{T} + \text{div} \mathbf{S}_i^{\text{irr}} - y_i \text{div} (\sum_k \mathbf{S}_k^{\text{irr}}) - T \sum_j f_{ij} \rho_i \rho_j (\mathbf{u}_i - \mathbf{u}_j),$$

and our aim is to show that the terms on the left-hand side are negligible for the description on meso- and macroscopic time scales. To simplify the presentation, we do not consider the irreversible stress part in the intermediate computations; note that this term determines the order of the PDE, hence cannot be neglected anyhow. With this omission, we obtain the dimensionless formulation

$$(196) \quad \frac{U V}{C C} y_i (\partial_t^* \mathbf{u}_i^* + \mathbf{v}^* \cdot \nabla^* \mathbf{u}_i^* + \mathbf{u}_i^* \cdot \nabla^* \mathbf{v}_i^*) = y_i \frac{\nabla^* p^*}{\rho^*} - \frac{\rho_0 \mu_0}{p_0} y_i \nabla^* \mu_i^* \\ - \left(\frac{h_0 h_i^*}{p_0 \rho^*} - \frac{\rho_0 \mu_0}{p_0} y_i \mu_i^* \right) \nabla^* \ln T^* + \frac{\rho_0 B L}{p_0} y_i (\mathbf{b}_i^* - \mathbf{b}^*) - \frac{\rho_0^2 T_0 f_0 L}{p_0} \rho^* T^* \sum_j f_{ij}^* y_i y_j (\mathbf{u}_i^* - \mathbf{u}_j^*),$$

where dimensionless variables are labeled by an asterisk and the following reference quantities have been employed: reference diffusion velocity U , reference mixture velocity V , reference length L , reference mixture time scale $\tau := L/V$, reference mixture mass density ρ_0 , reference pressure p_0 , reference chemical potential μ_0 , reference enthalpy h_0 , reference temperature T_0 and reference friction coefficient f_0 . Furthermore, $C := \sqrt{p_0/\rho_0}$ is of the same order of magnitude as the sound speed. In many applications C is much larger than U , usually even significantly larger than V .

To proceed, we need to estimate the size of the thermo-mechanical interaction terms, i.e. the size of the "friction" coefficients f_{ij} , to obtain a reasonable reference value f_0 . For this purpose we first establish a relation between the f_{ij} and the so-called Maxwell-Stefan diffusivities \mathfrak{D}_{ij} , since quantitative information for the latter is available in the literature. At this point, consider a binary system under *isobaric* (i.e., constant pressure) and isothermal conditions. Neglecting in the above momentum balance the terms with a factor $U V/C^2$ yields

$$T f_{12} (y_2 \mathbf{j}_1 - y_1 \mathbf{j}_2) = T f_{12} \mathbf{j}_1 = -y_1 \nabla \mu_1.$$

Specializing to a dilute system with $y_1 \ll 1$, $y_2 \approx 1$, the chemical potential is given as

$$\mu_1 = \mu_1^0 + \frac{RT}{M_1} \ln x_1,$$

hence

$$T f_{12} \mathbf{j}_1 = -\frac{y_1 RT}{M_1 x_1} \nabla x_1 = -\frac{c RT}{\rho} \nabla x_1.$$

Using $\rho \approx M_2 c \equiv \text{const}$ with c the total molar concentration, this finally yields

$$\mathbf{j}_1 = -\frac{R}{c M_1 M_2 f_{12}} \nabla \rho_1,$$

which has the form of *Fick's law* with the binary diffusivity

$$\mathfrak{D}_{12} := \frac{R}{c M_1 M_2 f_{12}}.$$

Due to this relationship we further introduce a reference molar concentration c_0 and a reference diffusivity D . Letting $M := \rho_0/c_0$, $\mu_0 := RT_0/M$ and $\mathfrak{D}_{ij} := \frac{R}{cM_iM_jf_{ij}}$, the final form of the dimensionless partial momentum balance is

$$(197) \quad \frac{U}{C} \frac{V}{C} y_i (\partial_t^* \mathbf{u}_i^* + \mathbf{v}^* \cdot \nabla^* \mathbf{u}_i^* + \mathbf{u}_i^* \cdot \nabla^* \mathbf{v}_i^*) = y_i \frac{\nabla^* p^*}{\rho^*} - \frac{c_0 RT_0}{p_0} y_i \nabla^* \mu_i^* + \frac{\rho_0 BL}{p_0} y_i (\mathbf{b}_i^* - \mathbf{b}^*) \\ - \left(\frac{h_0}{p_0} \frac{h_i^*}{\rho^*} - \frac{c_0 RT_0}{p_0} y_i \mu_i^* \right) \nabla^* \ln T^* - \frac{c_0 RT_0}{p_0} \frac{UL}{D} \rho^* T^* \sum_j \frac{y_i y_j}{M_i^* M_j^* \mathfrak{D}_{ij}^*} (\mathbf{u}_i^* - \mathbf{u}_j^*).$$

Note that the above definition of \mathfrak{D}_{ij} is consistent with the relation between the friction factors f_{ij} and the Maxwell-Stefan diffusivities \mathfrak{D}_{ij} which was used in Section 12 for comparison with the engineering literature. Now, for multicomponent fluid mixtures not too far from standard conditions, the estimate

$$\frac{U}{C} \frac{V}{C} = 10^{-8} \dots 10^{-4}$$

is valid. The other dimensionless coefficients are of order one or above, for instance

$$\frac{c_0 RT_0}{p_0} = 10^0 \dots 10^3 \text{ (gas to liquid)}, \quad \frac{UL}{D} = 10^3 \dots 10^5.$$

Consequently, the desired simplification mentioned above yields an excellent approximation under such conditions. The resulting reduced form of the partial momentum balances reads as

$$(198) \quad - \sum_{j \neq i} \frac{y_j \mathbf{j}_i - y_i \mathbf{j}_j}{c M_i M_j \mathfrak{D}_{ij}} = \frac{y_i}{RT} \nabla \mu_i - \frac{y_i}{\rho RT} \nabla p - \frac{y_i}{RT} (\mathbf{b}_i - \mathbf{b}) \\ + \frac{\rho_i \mu_i - h_i}{\rho R} \nabla \frac{1}{T} + \frac{1}{\rho RT} (\operatorname{div} \mathbf{S}_i^{\text{irr}} - y_i \operatorname{div} (\sum_k \mathbf{S}_k^{\text{irr}})),$$

where we now also put back the irreversible stress parts. If full thermo-diffusion is added and put into the form mentioned in Section 12, we obtain

$$(199) \quad - \sum_{j \neq i} \frac{y_j \mathbf{j}_i - y_i \mathbf{j}_j}{c M_i M_j \mathfrak{D}_{ij}} - \sum_{j \neq i} \frac{\rho y_i y_j}{c M_i M_j \mathfrak{D}_{ij}} \left(\frac{D_i^T}{\rho_i} - \frac{D_j^T}{\rho_j} \right) \nabla \ln T = \frac{y_i}{RT} \nabla \mu_i - \frac{y_i}{\rho RT} \nabla p \\ - \frac{y_i}{RT} (\mathbf{b}_i - \mathbf{b}) + \frac{\rho_i \mu_i - h_i}{\rho R} \nabla \frac{1}{T} + \frac{1}{\rho RT} (\operatorname{div} \mathbf{S}_i^{\text{irr}} - y_i \operatorname{div} (\sum_k \mathbf{S}_k^{\text{irr}})).$$

Note that the above diffusional approximation ignores the acceleration of the relative (diffusional) motion. The cancelation removes sound waves due to diffusional motion, which are related to the so-called phenomenon of *second sound*; see, e.g., [39] for the later phenomenon. A somewhat similar order-of-magnitude analysis of the terms appearing in the partial momentum balances has been done in [56]. Let us also mention in passing that the appearance of stress induced diffusion has been investigated in [3] via an extended Chapman-Enskog theory.

In the Engineering literature on multicomponent diffusion, system (198) is often written using molar based quantities. With $x_i = c_i/c$, $\mathbf{J}_i = c_i \mathbf{u}_i$ and $\mu_i^m := M_i \mu_i$, one obtains

$$(200) \quad - \sum_{j \neq i} \frac{x_j \mathbf{J}_i - x_i \mathbf{J}_j}{c \mathfrak{D}_{ij}} = \frac{c_i}{RT} \nabla \mu_i^m - \frac{y_i}{RT} \nabla p + \frac{h_i - c_i \mu_i^m}{RT} \nabla \ln T - \frac{\rho_i}{RT} (\mathbf{b}_i - \mathbf{b}),$$

where we again omitted the irreversible stress part and only consider reduced thermo-diffusion for brevity. Observe that the \mathbf{J}_i do not sum to zero, but satisfy $\sum_i M_i \mathbf{J}_i = 0$. It is custom to apply the chain rule to separate different contributions from the gradient of the μ_i . This requires to fix the set of independent variables. With the common choice of $(T, p, x_i, \dots, x_{N-1})$, the notation is

$$\nabla \mu_i^m = \nabla_{p,T} \mu_i^m + \frac{\partial \mu_i^m}{\partial p} \nabla p + \frac{\partial \mu_i^m}{\partial T} \nabla T \quad \text{with} \quad \nabla_{p,T} \mu_i^m := \sum_{j=1}^{N-1} \frac{\partial \mu_i^m}{\partial x_j} \nabla x_j.$$

We then obtain

$$(201) \quad -RT \sum_{j \neq i} \frac{x_j \mathbf{j}_i - x_i \mathbf{j}_j}{c \mathfrak{D}_{ij}} = c_i \nabla_{p,T} \mu_i^m - (\phi_i - y_i) \nabla p + (h_i - c_i \mu_i^m + c_i T \frac{\partial \mu_i^m}{\partial T}) \nabla \ln T - \rho_i (\mathbf{b}_i - \mathbf{b}),$$

where ϕ_i denotes the partial molar volume of component A_i . The different contributions on the right-hand side correspond to, from left to right, concentration driven diffusion, pressure driven diffusion, thermo-diffusion and forced diffusion. Except for the contribution from the temperature gradient, the system (201) coincides with the models given in, e.g., [4], [51]. The additional term constitutes a driving force for thermal diffusion in non-simple mixtures. It is no surprise that this has been missed in the references cited above, since the standard derivation of the so-called generalized thermodynamic driving forces, going back to [26] employs approximate solutions to the multicomponent Boltzmann equations, hence inherently assumes a simple mixture. As explained already above, this contribution to the driving forces vanishes for simple mixtures.

The reactive extension of the Maxwell-Stefan equations. In the case of reacting mixtures, the scale reduction argument from above is not applicable, because for reactive flows the term

$$\rho_i (\partial_t + \mathbf{v} \cdot \nabla) \mathbf{u}_i + \rho_i (\mathbf{u}_i \cdot \nabla) \mathbf{v}_i,$$

which has been neglected in the non-reactive case, when summed over all constituents gives $\sum_i r_i \mathbf{u}_i$. While this might be small, it can not be neglected as it is crucial for the thermodynamic consistency. Instead, the Maxwell-Stefan form is derived by the above entropy invariant model reduction and was already given in a first form by (164) and (165). Brought into the notation of the present section, it reads

$$(202) \quad - \sum_{j=1}^N \frac{y_j \mathbf{j}_i - y_i \mathbf{j}_j}{c M_i M_j \mathfrak{D}_{ij}} - \sum_{j=1}^N \gamma_{ij} \left(\frac{\mathbf{j}_i}{\rho_i} - \frac{\mathbf{j}_j}{\rho_j} \right) - \sum_{j=1}^N \frac{\rho y_i y_j}{c M_i M_j \mathfrak{D}_{ij}} \left(\frac{D_i^T}{\rho_i} - \frac{D_j^T}{\rho_j} \right) \nabla \ln T =$$

$$\frac{1}{\rho RT} \left(\rho_i \nabla \mu_i - y_i \nabla p - \rho_i (\mathbf{b}_i - \mathbf{b}) + (h_i - \rho_i \mu_i) \nabla \ln T + \operatorname{div} \mathbf{S}_i^{\text{irr}} - y_i \operatorname{div} \left(\sum_{k=1}^N \mathbf{S}_k^{\text{irr}} \right) \right)$$

with γ_{ij} from (166). The second term on the left-hand side is new.

Let us close this section with a few remarks on mathematical properties of the resulting system of strongly coupled diffusion equations. A closer inspection of the definition of the γ_{ij} under the assumption that the forward reaction rates are modeled such that $R_a^f \rightarrow 0$ if $\rho_i \rightarrow 0$ for any i for which A_i is a reactand of this reaction, i.e. for which $\alpha_i^a > 0$, shows that (202) has the overall structure

$$(203) \quad \sum_{j \neq i} a_{ij} y_i y_j (\mathbf{u}_i - \mathbf{u}_j) = \mathbf{F}_i,$$

where the matrix $[a_{ij}]$ is positive definite (but, in general, not symmetric). Given the invertibility, the \mathbf{u}_i are bounded functions of the \mathbf{F}_i . As a direct consequence of (203), we then also have the relations

$$(204) \quad \mathbf{j}_i = \rho y_i \mathbf{u}_i = \frac{\rho}{\sum_{j \neq i} a_{ij} y_j} \mathbf{F}_i + y_i \frac{1}{\sum_{j \neq i} a_{ij} y_j} \sum_{j \neq i} a_{ij} \mathbf{j}_j.$$

This shows that the cross-effects vanish in case $y_i \rightarrow 0$. Therefore, the solution will retain non-negative values for all ρ_i if the \mathbf{F}_i are quasi-positive, i.e. such that $\mathbf{F}_i \geq 0$ whenever $\rho_i = 0$. An inspection of the corresponding terms in (202) shows that all of them contain the factor y_i , hence vanish in case $\rho_i = 0$, except for $\operatorname{div} \mathbf{S}_i^{\text{irr}}$. The latter also becomes harmless concerning positivity of solutions if $\mathbf{S}_i^{\text{irr}}$ contains a factor y_i . Recall that a particularly suitable choice was $\mathbf{S}_i^{\text{irr}} = y_i \sum_k \mathbf{S}_k^{\text{irr}}$ in which case the stress driven diffusion completely disappears.

For more information on inverting the non-reactive Maxwell-Stefan equations see [7]. Concerning criteria for the strong well-posedness of strongly coupled reaction-diffusion systems and positivity of solutions, the reader is referred in particular to [2].

15. SPECIAL FREE ENERGY DENSITIES FOR FLUID MIXTURES

General context. We discuss possible explicit free energy functions so that the various model schemes of the previous sections finally end up with a system of explicit PDEs for the variables. Recall that class-I models need to know the free energy function

$$(205) \quad \rho\psi = \rho\tilde{\psi}(T, \rho_1, \rho_2, \dots, \rho_N).$$

If this function were known we could calculate the specific energy e , the chemical potentials $(\mu_i)_{i \in \{1,2,\dots,N\}}$ and the pressure p according to

$$(206) \quad e = -T^2 \frac{\partial}{\partial T} \left(\frac{\tilde{\psi}}{T} \right), \quad \mu_i = \frac{\partial \rho_i \tilde{\psi}}{\partial \rho_i}, \quad p = -\rho\tilde{\psi} + \sum_{i=1}^N \rho_i \mu_i.$$

This is not sufficient for class-II models because here we additionally need to know constitutive functions for the partial specific energies $(e_i)_{i \in \{1,2,\dots,N\}}$ and the partial pressures $(p_i)_{i \in \{1,2,\dots,N\}}$, i.e.

$$(207) \quad e_i = \tilde{e}_i(T, \rho_1, \rho_2, \dots, \rho_N), \quad p_i = \tilde{p}_i(T, \rho_1, \rho_2, \dots, \rho_N).$$

Except in the special case of *simple mixtures* (cf. [39]), the functions in (207) cannot be derived from partial free energy densities in general.

Simple mixtures. If the functions in (207) are of the special form

$$(208) \quad e_i = \tilde{e}_i(T, \rho_i), \quad p_i = \tilde{p}_i(T, \rho_i),$$

they can be calculated from partial free energy densities $\psi_i = \tilde{\psi}_i(T, \rho_i)$ and the corresponding mixture is called *simple mixture*. In this case we have

$$(209) \quad e_i = -T^2 \frac{\partial}{\partial T} \left(\frac{\tilde{\psi}_i}{T} \right), \quad \mu_i = \frac{\partial \rho_i \tilde{\psi}_i}{\partial \rho_i}, \quad p_i = -\rho_i \tilde{\psi}_i + \rho_i \mu_i.$$

Mixtures of ideal gases. A special case of a simple mixture is a mixture of ideal gases. In the non-degenerate case ideal gases are characterized by the following constitutive functions for partial pressures, energies and entropies,

$$(210) \quad p_i = \rho_i \frac{k}{m_i} T, \quad e_i = z_i \frac{k}{m_i} (T - T^R) + e_i^R, \quad s_i = z_i \frac{k}{m_i} \ln \left(\frac{T}{T^R} \right) - \frac{k}{m_i} \ln \left(\frac{\rho_i}{\rho_i^R} \right) + s_i^R,$$

where $z_i = 3/2, 5/2$ or 3 for 1-atomic, 2-atomic and more-atomic constituents, respectively, the index R indicates a reference state and k is the Boltzmann constant, while m_i denotes the atomic mass of A_i . Usually, the specific entropy is written with p_i as a variable instead of ρ_i . Using $p = \sum_{i=1}^N p_i$, we may write

$$(211) \quad s_i(T, p_i) = (z_i + 1) \frac{k}{m_i} \ln \frac{T}{T^R} - \frac{k}{m_i} \ln \frac{p_i}{p_i^R} + s_i^R = s_i(T, p) - \frac{k}{m_i} \ln \frac{p_i}{p} = s_i(T, p) - \frac{k}{m_i} \ln x_i.$$

With $\psi_i = e_i - T s_i$, the total free energy density $\rho\psi = \sum_{i=1}^N \rho_i \psi_i$ can then be represented by

$$(212) \quad \rho\psi = \sum_{i=1}^N \rho_i \psi_i(T, p) + \sum_{i=1}^N \frac{kT}{m_i} \ln(x_i).$$

Ideal mixtures. The last expression has been calculated only for ideal gases. However, it was observed that there is a large class of mixtures that are appropriately described by (212)₂ with the last

term as it stands and with $\rho\psi(T, p)$ taken from data tables. Such mixtures are called *ideal mixtures*.

Elastic mixtures. We consider a further special fluid mixture that requires a different treatment. The following may also be considered as preliminary work to introduce the concept of incompressibility in the context of fluid mixtures.

Often one meets situations where the various contributions to the free energy originate from different sources. Let us describe a typical case. To this end we first transform the variables in the free energy function (205) from $T, \rho_1, \rho_2, \dots, \rho_N$ to $T, \rho, x_1, \dots, x_{N-1}$. We write

$$(213) \quad \rho\tilde{\psi}(T, \rho_1, \rho_2, \dots, \rho_N) = \rho\hat{\psi}(T, \rho, x_1, \dots, x_{N-1}) \quad \text{to calculate} \quad p = \rho^2 \frac{\partial \hat{\psi}}{\partial \rho}.$$

Abbreviating $x' = (x_1, x_2, \dots, x_{N-1})$, we now introduce a constitutive function $p = \hat{p}(T, \rho, x')$ for the total pressure of the mixture which is a response of variations of the total particle density n measuring the atomic distances. The available experimental data concern two kinds of variations of n : (i) variations of n at fixed composition and fixed temperature, that are called elastic deformations and (ii) non-elastic variations at fixed pressure due to changes of T and x' . To describe the elastic deformation we start from the state (T, ρ_*, x') and end up in the state (T, ρ, x') and define the mass density ρ_* by

$$(214) \quad \rho_* = \hat{\rho}_*(T, x') \quad \text{so that} \quad \hat{p}(T, \rho_*, x') = p^R \quad \text{for given} \quad p = \hat{p}(T, \rho, x').$$

A mixture that is characterized by (214) is called *elastic mixture* (cf. [10]).

In elastic mixtures we decompose the free energy into non-elastic and elastic contributions and define

$$(215) \quad \psi^{\text{th}} = \hat{\psi}(T, \rho_*, x') \quad \text{and} \quad \psi^{\text{el}} = \hat{\psi} - \psi^{\text{th}},$$

implying corresponding decompositions of the chemical potentials,

$$(216) \quad \mu_i^{\text{th}} = \hat{\mu}_i(T, \rho_*, x') \quad \text{and} \quad \mu_i^{\text{el}} = \hat{\mu}_i - \mu_i^{\text{th}}.$$

Thus we have achieved an additive decomposition of the free energy and the chemical potentials into elastic and non-elastic contributions. The latter are denoted here as thermal contribution.

In order to complete the determination of the free energy, we finally assume that, in addition to (214), also the thermal parts of the chemical potentials are given:

$$(217) \quad \mu_i^{\text{th}} = \hat{\mu}_i^{\text{th}}(T, x').$$

Then the procedure to determine the free energy function is as follows:

(i) Calculate

$$(218) \quad \psi^{\text{th}} = -\frac{p^R}{\rho_*} + \sum_{i=1}^N \frac{\rho_{*i}}{\rho_*} \mu_i^{\text{th}} \quad \text{with} \quad \frac{\rho_{*i}}{\rho_*} = \frac{m_i x_i}{\sum_{j=1}^N m_j x_j}.$$

(ii) Integrate

$$(219) \quad \frac{\partial \psi^{\text{el}}}{\partial \rho} = \frac{p(T, \rho, x')}{\rho^2} \quad \text{with} \quad \psi^{\text{el}}(T, \rho_*, x') = 0.$$

(iii) Form the total free energy density

$$(220) \quad \rho\psi = \rho\psi^{\text{el}} + \rho\psi^{\text{th}}.$$

(iv) Calculate μ_i from $\rho\psi$

$$(221) \quad \mu_i = \frac{\partial \rho\psi}{\partial \rho_i}(T, \rho_1, \rho_2, \dots, \rho_N).$$

(v) Calculate

$$(222) \quad \mu_i^{\text{el}} = \mu_i - \mu_i^{\text{th}}.$$

16. INCOMPRESSIBILITY IN THE CONTEXT OF FLUID MIXTURES

Definitions of incompressibility. The notion of incompressibility in a single fluid concerns the constitutive law for the pressure, which we write here as $p = \hat{\rho}(T, p)$. A single fluid is called incompressible if we have $\partial_p \hat{\rho} = 0$. There are reasons to prefer another definition: (i) incompressibility is a statement on atomic distances, which may be characterized by the mass density only in a single fluid. In a mixture, however, the particle densities are related to the atomic distances but not the total mass density; (ii) the inequality (69)₃, which is a consequence of the concavity postulate, reveals that the given definition of incompressibility implies $\partial_T \hat{\rho} = 0$, i.e. the mass density must be a constant if we only consider the limiting case $\partial_p \hat{\rho} = 0$ (cf. [39], [22]). Therefore we prefer to start with the compressible case and propose an elastic constitutive law for the pressure containing a bulk modulus K . After exploitation of the 2nd law of thermodynamics, we let $K \rightarrow \infty$. Two examples serve to illustrate the procedure.

Example 1. We consider the constitutive law

$$(223) \quad p = p^{\text{R}} + K \left(\frac{n}{n^{\text{R}}} - f(T, x) \right).$$

Here n^{R} denotes some reference value of the total particle density of the mixture, K is the bulk modulus and the function $f(T, x)$ characterizes a volumetric expansion due to a change of temperature and variations of the mole fractions. The volume expansion is measured at the reference pressure p^{R} where we have $n/n^{\text{R}} = f(T, x)$. To calculate the elastic part of the free energy according to (219), we write (223) in the form

$$(224) \quad p = p^{\text{R}} + K \left(\frac{M(x^{\text{R}})}{M(x)} \frac{\rho}{\rho^{\text{R}}} - f(T, x) \right) \quad \text{with} \quad M(x) = \sum_{i=1}^N M_i x_i.$$

Recall that the elastic transition concerns $\rho = M(x)n \Leftrightarrow \rho_* = M(x)f(T, x)n^{\text{R}}$. Integration of (219) leads to the elastic part of the free energy density,

$$(225) \quad \rho \hat{\psi}^{\text{el}}(T, \rho, x') = (p^{\text{R}} - K f(T, x)) \left(\frac{\rho}{\rho_*(T, x)} - 1 \right) + K f(T, x) \frac{\rho}{\rho_*(T, x)} \ln \left(\frac{\rho}{\rho_*(T, x)} \right).$$

The exploitation of the above scheme to determine μ_i^{el} gives in the limiting case $K \rightarrow \infty$:

$$(226) \quad n = n^{\text{R}} f(T, x), \quad \rho \psi^{\text{el}}(T, p, x') = 0 \quad \mu_i^{\text{el}} = \frac{p - p^{\text{R}}}{m_i n^{\text{R}} f(T, x)} \left(1 - \sum_{j=1}^N \frac{\partial \ln(f(T, x))}{\partial x_j} (\delta_{ij} - x_j) \right).$$

In the incompressible limit the particle density is no longer an independent variable because, due to (226)₁, it is now determined by the other variables. However, the number of independent variables has not changed. In (226)₃ the pressure still appears in the chemical potentials and must now be considered as a variable that substitutes the particle density as a variable.

The incompressible limit implies a constraint on $\text{div } \mathbf{v}$ that follows from the algebraic relation $\rho = M(x)n = n^{\text{R}} M(x) f(T, x)$. Differentiation with respect to time and application of the total mass balance yields

$$(227) \quad \text{div } \mathbf{v} = - \frac{\partial_t (M(x) f(T, x)) + \mathbf{v} \cdot \nabla (M(x) f(T, x))}{M(x) f(T, x)},$$

i.e. the evolution of $\text{div } \mathbf{v}$ is already given by the evolution of temperature and mole fractions.

Example 2. Here we discuss an alternative constitutive law for the pressure leading to a different constraint on $\operatorname{div} \mathbf{v}$ in the incompressible limit. We consider a solution and indicate the solvent by the index N and the dissolved substances by $i \in \{1, 2, \dots, N-1\}$. For simplicity, in this example we ignore volumetric changes, i.e. we set $f = 1$. We propose

$$(228) \quad p = p_N + \sum_{i=1}^{N-1} p_i \quad \text{with} \quad p_N = p_N^R + K \left(\frac{n_N}{n_N^R} - 1 \right), \quad p_i = \rho_i \frac{k}{m_i} T.$$

Thus we describe the solvent by an elastic liquid and the solutes as a mixture of ideal gases.

The determination of the free energy density and the chemical potentials runs along the same path as in Example 1. The density ρ_* for which we have $p = p^R$ is given by

$$(229) \quad \rho_* = \frac{p^R - p_N^R + K}{kT + \left(\frac{K}{n_N^R} - kT \right) x_N} M(x).$$

The elastic part of the free energy density now reads

$$(230) \quad \rho \psi^{\text{el}} = (p_N^R - K) \left(\frac{\rho}{\rho_*} - 1 \right) + \left(\frac{kT}{M(x)} + \left(\frac{K}{M(x)n_N^R} - \frac{kT}{M(x)} \right) x_N \right) \rho \ln \left(\frac{\rho}{\rho_*} \right).$$

The further results are exclusively given in the incompressible limit $K \rightarrow \infty$:

$$(231) \quad n_N = n_N^R, \quad \rho \psi^{\text{el}}(T, p, x') = 0, \quad (\mu_i^{\text{el}})_{i \in \{1, 2, \dots, N-1\}} = 0, \quad \mu_N^{\text{el}} = \frac{p - p^R}{m_N n_N^R}.$$

In order to compare the results of Example 2 with those of Example 1 we set $f = 1$ in (226). In this case we observe that (226)_{1,2} agrees with (231)_{1,2}, and the difference of the chemical potentials are also to be expected, because in Example 1 incompressibility concerns all atomic distances, while in Example 2 incompressibility is exclusively related to the distances between the particles of the solvent.

Accordingly, the resultant constraint refers to $\operatorname{div} \mathbf{v}_N$ and not to $\operatorname{div} \mathbf{v}$ as in Example 1, because the partial mass balance of constituent N now reduces to

$$(232) \quad \operatorname{div} \mathbf{v}_N = \frac{1}{m_N n_N^R} r_N.$$

Thus if there is no mass production of the solvent, which is the usual case, we have the simple constraint $\operatorname{div} \mathbf{v}_N = 0$.

Incompressibility as a limiting case. The classical literature frequently considers an incompressible limit where thermal expansion is still possible. This limiting case leads to two apparent inconsistencies, (cf. [39], [22]). One concerns the inequality (69)₃,

$$(233) \quad \left(\frac{\partial \rho}{\partial T} \right)^2 < \frac{c_p \rho^2}{T} \frac{\partial \rho}{\partial p},$$

and the other is related to the coupled systems of partial differential equations for the variables at hand. Here, we must show that $\operatorname{div} \mathbf{v} = 0$ is compatible with the variation of ρ , which seems to contradict the mass balance. In the following we show that an incompressible limit with thermal expansion is possible.

It is sufficient to discuss the problem in the context of a single fluid. The variables are then p , \mathbf{v} and T , the viscous stress is given by the Navier-Stokes stress and the heat flux is generated by Fourier's law. The mass density and the internal energy are calculated from the constitutive laws $\rho = \rho(T, p)$ and $e = e(T, p)$, respectively. In this case the relevant equations of balance for mass, momentum

and internal energy can be written as

$$(234) \quad \frac{\partial \rho}{\partial T} \dot{T} + \frac{\partial \rho}{\partial p} \dot{p} + \rho \operatorname{div} \mathbf{v} = 0,$$

$$(235) \quad \rho \dot{\mathbf{v}} + \nabla p - \operatorname{div} \mathbf{S}^{\text{irr}} = \rho \mathbf{g},$$

$$(236) \quad \rho c_p \dot{T} + \frac{T}{\rho} \frac{\partial \rho}{\partial T} \dot{p} + \operatorname{div} \mathbf{q} = \mathbf{S}^{\text{irr}} : \mathbf{D},$$

where $\dot{\psi} = \partial_t \psi + \mathbf{v} \cdot \nabla \psi$ indicates the material time derivative. Below, we let $g = \|\mathbf{g}\|$.

These equations embody four different phenomena whose importance may be characterized by four dimensionless numbers which are called Mach number, Reynolds number, Froude number and Fourier number, respectively. They are defined via

$$(237) \quad \text{Ma}^2 = \frac{v_0^2 \rho_R}{p_R}, \quad \text{Re} = \frac{\rho_R L_0 v_0}{\eta_R}, \quad \text{Fr}^2 = \frac{g t_0}{v_0}, \quad \text{Fo} = \frac{\kappa_R t_0}{\rho_R c_p^R L_0^2}.$$

After rewriting the equations (234)-(236) in a non-dimensional form, these numbers naturally appear. Let us introduce $t = t_0 t'$, $x = L_0 x'$, $p = p_R p'$, $\mathbf{v} = v_0 \mathbf{v}'$ with $v_0 := L_0/t_0$, $T = T_R T'$, $\mathbf{S}^{\text{irr}} = \sigma_0 \mathbf{S}'^{\text{irr}}$ with $\sigma_0 = \eta_R v_0 / L_0$ and $c_p = c_p^R c'_p$, where the quantities with a prime have no physical dimension. We set $c_p^R = p_R / \rho_R T_R$ and, dropping primes, obtain

$$(238) \quad \frac{\partial \rho}{\partial T} \dot{T} + \frac{\partial \rho}{\partial p} \dot{p} + \rho \operatorname{div} \mathbf{v} = 0,$$

$$(239) \quad \rho \dot{\mathbf{v}} + \frac{1}{\text{Ma}^2} \nabla p - \frac{1}{\text{Re}} \operatorname{div} \mathbf{S}^{\text{irr}} = \frac{1}{\text{Fr}^2} \rho \mathbf{e}_g,$$

$$(240) \quad \rho c_p \dot{T} + \frac{T}{\rho} \frac{\partial \rho}{\partial T} \dot{p} + \operatorname{div} \mathbf{q} = \frac{\text{Ma}^2}{\text{Re}} \mathbf{S}^{\text{irr}} : \mathbf{D},$$

where \mathbf{e}_g denotes the unit vector in direction of the gravity field \mathbf{g} . Our discussion starts with a simplified version of the explicit constitutive law (224) which we write in the form

$$(241) \quad \rho = 1 - \beta T_R (T - 1) + \frac{p_R}{K} (p - 1),$$

using the dimensionless variables. We consider water and choose $T_R = 293$ K, $\rho_R = 998$ kg/m³ and $p_R = 10^5$ Pa. In the neighborhood of this state we have a thermal expansion coefficient of $\beta = 2.07 \cdot 10^{-4}$ 1/K, a bulk modulus of $K = 2.18 \cdot 10^9$ Pa and a specific heat of $c_p = 4.18 \cdot 10^3$ J/kg/K. Moreover, we have $\eta_R = 10^{-3}$ Pa·s and $\kappa_R = 0.6$ W/K·m. Next, we introduce a small parameter $\varepsilon \ll 1$ and two parameter β_0, α_0 of order 1. In our example: $\varepsilon = 10^{-4}$, $\beta_0 = 6.07$, $\alpha_0 = 0.46$. Then (241) reads

$$(242) \quad \rho = 1 - \beta_0 (T - 1) \sqrt{\varepsilon} + \alpha_0 (p - 1) \varepsilon.$$

We conclude that the variation of ρ due to compressibility is about two orders of magnitude smaller than variation due to thermal expansion. In the limiting case $\varepsilon \rightarrow \infty$ the smallness parameter drops out from the inequality (233) and the remaining inequality reads as

$$(243) \quad \beta_0^2 < c'_p \alpha_0.$$

Note that $c'_p = 12247$ for the example above, hence the inequality (243) is satisfied.

Next we study the behavior of the equations (238)-(240) in the incompressible limit. We assume finite values of Re, Fo and consider the low Mach number limit $\text{Ma} = \sqrt{\varepsilon}$ with a fixed ratio $\gamma = \text{Fr}^2 / \text{Ma}$. In this regime we will obtain a consistent incompressible limit $\varepsilon \rightarrow \infty$.

To this end we formally expand the variables

$$(244) \quad p = p_0 + p_1 \text{Ma} + p_2 \text{Ma}^2 + \dots, \quad \mathbf{v} = \mathbf{v}_0 + \mathbf{v}_1 \text{Ma} + \dots, \quad T = T_0 + T_1 \text{Ma} + \dots$$

and correspondingly the constitutive functions. In the highest order, the equations (238)-(240) then reduce to

$$(245) \quad \operatorname{div} \mathbf{v}_0 = 0, \quad \dot{\mathbf{v}}_0 + \nabla p_2 - \frac{1}{\operatorname{Re}} \operatorname{div} \mathbf{S}_0^{\operatorname{irr}} = -\beta_0(T_0 - 1), \quad c_p \dot{T}_0 + \operatorname{Fo} \operatorname{div} \mathbf{q}_0 = 0.$$

Furthermore, we obtain $\nabla p_0 = 0$ and $\nabla p_1 = \frac{\operatorname{Ma}}{\operatorname{Fr}^2} \mathbf{e}_g$, but these equations are not needed to solve the coupled system (245). Observe that the higher order pressure p_2 becomes the Lagrange multiplier that guarantees the constraint (245)₁. Thus we have established a thermodynamically consistent limit describing incompressible behavior with thermal expansion. Some of the considerations about consistency of the incompressible limit above are closely related to those in [22].

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