ANALYSIS AND SIMULATION OF A NEW MULTI-COMPONENT TWO-PHASE FLOW MODEL WITH PHASE TRANSITIONS AND CHEMICAL REACTIONS

By

MAREN HANTKE (*Institut für Analysis und Numerik, Otto-von-Guericke-Universität Magdeburg, PSF 4120, D-39016 Magdeburg, Germany*)

AND

SIEGFRIED MÜLLER (*Institut für Geometrie und Praktische Mathematik, RWTH Aachen, Templergraben 55, 52056 Aachen, Germany*)

Abstract. A class-II-model for multi-component mixtures recently introduced in D. Bothe and W. Dreyer, *Continuum thermodynamics of chemically reacting fluid mixtures*, Acta Mech., 226 (2015), 1757–1805, is investigated for simple mixtures. Bothe and Dreyer were aiming at deriving physically admissible closure conditions. Here the focus is on mathematical properties of this model. In particular, hyperbolicity of the inviscid flux Jacobian is verified for non-resonance states. Although the eigenvalues cannot be determined explicitly but have to be computed numerically an eigenvector basis is constructed depending on the eigenvalues. This basis is helpful to apply standard numerical solvers for the discretization of the model. This is verified by numerical computations for two- and three-component mixtures with and without phase transition and chemical reactions.

1. Introduction. For the modeling and simulation of multi-phase flows Baer-Nunziato (B-N) type models [3] are frequently used. These can be derived from the ensemble averaging procedure of Drew [8]. A comprehensive introduction to these models can be found in the classical book of Drew and Passman [9]. In the literature there are simplified two-phase models available that can be derived from the above general model by assuming zero relaxation times; see [18]. A detailed discussion of these models is beyond the scope of this work. For this purpose the interested reader is referred to [23] and the references cited therein.

Typically B-N type models consist of balance equations for each constituent and further transport equations for their volume fractions. This ansatz leads to several problems: (i) A key problem is the thermodynamically correct closure of the artificial quantities such as interfacial velocity or interfacial pressure that cannot be closed from the entropy principle of thermodynamics; cf. [21]. (ii) The exchange of mass, momentum, and energy between the constituents is modeled usually by relaxation terms. Frequently, an equilibrium assumption is used; cf. [24]. This is a very restrictive assumption and is not applicable for all situations of interest. (iii) The models cannot be written in divergence form. Thus, the classical notion of a weak solution and the entropy solution cannot be applied; cf. [6]. Moreover, the discretization of non-conservative products leads to numerical difficulties; cf. [1]. (iv) The models do not conserve momentum and energy in the non-equilibrium case, thus, violating a classical physical principle. (v) The mixture model is conservative only when assuming velocity equilibrium.

The aforementioned disadvantages of B-N type models can be avoided by a new multi-component model introduced by Bothe and Dreyer [4]. This model can be employed to simulate chemically reacting flows as well as phase transitions. In particular, we apply this model to two phases where each phase is a simple multi-component mixture. Fluid mixtures can be modeled using different levels of details. The basic variables in our approach are the partial densities and the partial velocities of the constituents for each of the two phases and the temperature of the mixture. Accordingly the model under consideration is a so-called class-II-model that consists of balance laws for partial densities, partial momenta, and the total mixture energy. To close this system we have to provide equations of states for partial pressures and energies and reaction rates.

In the work of Bothe and Dreyer [4] the focus is on the derivation of a class-II-model that is thermodynamical consistent. They provide necessary and sufficient closure conditions but do not address solvability of the model and how to solve it numerically. The main objective of the present work is to verify that this model can be used in practice to simulate multi-component fluid flows with chemical reactions and two-phase flows with phase transitions.

To close the system of balance laws in a thermodynamically consistent manner Bothe and Dreyer [4] provide criteria for the (Helmholtz) free energy that ensure thermodynamical stability, i.e., the physical entropy is concave. Furthermore, by means of the entropy production terms they give thermodynamical admissible closures for the reaction rates. In the literature, typically no free energies are specified but calorical and thermal equations of states can be found. For this reason, we derive free energies for well-known equations of states, e.g., ideal gas, stiffened gas, van der Waals fluids, and verify the aforementioned criteria ensuring thermodynamical stability. In this context it turns out that the notions of partial pressures and densities are different from those used in B-N type models. For instance, the partial densities in our model correspond to the product of volume fractions and densities in the B-N type models. Thus, the equation of state is evaluated with respect to different densities. For a non-linear equation of state, e.g., stiffened gas, van der Waals, this leads to different pressures, energies, and temperature. As a consequence, model parameters have to be carefully chosen, in particular,

when performing comparisons between the models. Thus, not all equations of states are applicable to model total mass transfer of a component.

Furthermore, we consider phase transition and chemical reactions in more detail by means of special configurations. Here it turns out that the relaxation models used in the B-N context are related to the chemical reaction terms in the Bothe-Dreyer model. However, in our model we can choose the rate coefficient characterizing the reaction times. This coefficient is chosen typically as infinity in the B-N model and, thus, drives the fluid state to equilibrium restricting the range of applications. Appropriate rate coefficients can either be determined from experiments or, if available, can be looked up in the literature.

The available theory of conservation laws as well as numerical methods for these type of equations relies very much on the knowledge of eigenvalues and eigenvectors corresponding to the Jacobian of the inviscid fluxes. Therefore a key point in our work is related to determine these quantities for our Bothe-Dreyer model. Although we cannot explicitly compute the eigenvalues and eigenvectors except for the additional contact waves introduced in the multi-dimensional case, we can prove that all eigenvalues are real and a full set of linearly independent eigenvectors exists, i.e., the system is hyperbolic provided that a non-resonance condition holds and all eigenvalues corresponding to the acoustic waves are distinct. In particular, for a two-component mixture we can give sufficient criteria ensuring that all eigenvalues other than those corresponding to the additional contact discontinuities introduced in the multi-dimensional case are distinct for a given state. Finally we are able to give an upper bound for the spectral radius.

To perform numerical simulations we discretize the Bothe-Dreyer model by an adaptive DG solver. Since we are using an explicit time stepping, the time steps are restricted by a CFL constraint. Depending on the fluid state and the relaxation times either the characteristic velocities of the fluid or the chemical relaxation rates will be dominating the CFL number. Therefore, we investigate the stiffness of the system introduced by the chemical reactions. In particular, we determine the eigenvalues corresponding to the ODE system of the relaxation model incorporating mass conservation.

This work is structured as follows. First we introduce in Section 2 the model specifying the balance equations for chemically reacting fluids, the equation of states for simple mixtures derived from Helmholtz free energies and the reaction rates. This is concluded with a discussion on the entropy principle. Then in Section 3 we verify hyperbolicity of the model where we investigate the eigenvalues and eigenvectors of the Jacobian of the inviscid fluxes. In particular, we derive sufficient conditions. The stiffness of the chemical relaxation model is investigated in Section 4. Numerical results are presented in Section 5 where we consider a two-component flow with phase transition and a three-component flow with chemical reactions. We conclude with a summary of our findings and give an outlook on future work.

2. Model. Hutter and Jöhnk [17] describe a hierarchy of fluid mixture models with three different levels of detail, class-I-, class-II-, and class-III-models. The highest level of detail is considered in class III, where for all constituents balances of mass, momentum, and energy have to be formulated. In class II mass and momentum balances for all

components are formulated but only one energy balance for the mixture. The basic variables in that class are the mass densities, the velocities, and the mixture temperature. Finally, in class I beside the mass balances only one balance of momentum and one balance of energy are used. Here we consider a class-II-model for reacting fluid mixtures. This is a special case of a more general model derived by Bothe and Dreyer in [4].

2.1. *Balance equations for reacting fluid mixtures.* We consider fluid mixtures of N constituents $A_1, \ldots, A_N$, i.e., multi-component mixtures of liquids and/or gases. Each component i is described by its *partial mass density* ρ_i, its *partial velocity* $\boldsymbol{v}_i$, and the *mixture temperature* T. All these quantities are functions of time $t \geq 0$ and space $\boldsymbol{x} \in \mathbb{R}^d$. The partial mass densities and the partial velocities define the *total mass density* ρ and the *barycentric velocity* $\boldsymbol{v}$ of the mixture according to

$$\rho = \sum_{i=1}^{N} \rho_i \qquad \text{and} \qquad \rho\boldsymbol{v} = \sum_{i=1}^{N} \rho_i \boldsymbol{v}_i \,.$$

Using the notation of Bothe and Dreyer [4] we introduce the *diffusion velocities* $\boldsymbol{u}_i := \boldsymbol{v}_i - \boldsymbol{v}$ and the corresponding *diffusion mass fluxes* $\boldsymbol{j}_i := \rho_i \boldsymbol{u}_i$ with $\sum_{i=1}^{N} \boldsymbol{j}_i = 0$. Then the fluid mixture is described by

$$\partial_t(\rho_i) + \nabla \cdot (\rho_i \boldsymbol{v}_i) = r_i, \tag{2.1a}$$

$$\partial_t(\rho_i \boldsymbol{v}_i) + \nabla(\rho_i \boldsymbol{v}_i \otimes \boldsymbol{v}_i - \boldsymbol{S}_i) = \boldsymbol{f}_i + \rho_i \boldsymbol{b}_i, \tag{2.1b}$$

$$\partial_t(\rho e_{tot}) + \nabla \cdot (\rho e_{tot}\boldsymbol{v} + \boldsymbol{q}_{tot} - \boldsymbol{v} \cdot \boldsymbol{S}) = \rho\boldsymbol{v} \cdot \boldsymbol{b} + \rho\pi, \tag{2.1c}$$

with $i = 1, \ldots, N$. Here ρe_{tot} denotes the *total energy density* of the mixture which is related to the *specific internal energies* e_i of the components by

$$\rho e_{tot} = \sum_{i=1}^{N} \rho_i(e_i + \frac{1}{2}\boldsymbol{v}_i^2) = \rho e + \sum_{i=1}^{N} \frac{1}{2}\rho_i \boldsymbol{v}_i^2$$

with ρe the *thermal energy* of the mixture. The *stresses of a component* are given by

$$\boldsymbol{S}_i = -(p_i + \Pi_i)\boldsymbol{I} + \boldsymbol{S}_i^0 =: -p_i \boldsymbol{I} + \boldsymbol{S}_i^{irr} \tag{2.2}$$

with the identity matrix $\boldsymbol{I}$, the partial thermodynamic (hydrodynamic) pressure p_i, and Π_i the irreversible partial pressure contribution (dynamic pressure). Here $\boldsymbol{S}_i^0$ is the traceless part and $\boldsymbol{S}_i^{irr}$ the irreversible part of the stress $\boldsymbol{S}_i$. The *mixture stress* is then given by $\boldsymbol{S} = \sum_{i=1}^{N}(\boldsymbol{S}_i - \rho_i \boldsymbol{u}_i \otimes \boldsymbol{u}_i)$.

The *total energy flux* $\boldsymbol{q}_{tot}$ is related to the *individual heat fluxes* $\boldsymbol{q}_i$ via

$$\boldsymbol{q}_{tot} = \sum_{i=1}^{N}(\boldsymbol{q}_i - \boldsymbol{u}_i \cdot \boldsymbol{S}_i + \rho_i(e_i + \frac{1}{2}\boldsymbol{u}_i^2)\boldsymbol{u}_i) = \boldsymbol{q} + \frac{1}{2}\sum_{i=1}^{N} \rho_i \boldsymbol{u}_i^2 \boldsymbol{u}_i - \sum_{i=1}^{N} \boldsymbol{u}_i \cdot \boldsymbol{S}_i^{irr}, \tag{2.3}$$

where $\boldsymbol{q} = \sum_{i=1}^{N}(\boldsymbol{q}_i + (\rho_i e_i + p_i)\boldsymbol{u}_i)$ denotes the heat flux composed of non-convective transport of heat and diffusive transport of species enthalpy. Further quantities are the *mass productions due to chemical reactions* r_i, the *momentum productions* $\boldsymbol{f}_i$, the *body forces* $\boldsymbol{b}_i$ acting on constituent A_i with the corresponding *total external force* $\rho\boldsymbol{b} = \sum_{i=1}^{N} \rho_i \boldsymbol{b}_i$ and finally the *power of body force due to diffusion* $\rho\pi = \sum_{i=1}^{N} \rho_i \boldsymbol{b}_i \boldsymbol{u}_i$. With

this notation conservation of total mass and total momentum are ensured by the constraints

$$\sum_{i=1}^{N} r_i = 0 \qquad \text{and} \qquad \sum_{i=1}^{N} \boldsymbol{f}_i = \boldsymbol{0} \,. \tag{2.4}$$

To close system (2.1) we need to provide additional information on the equation of state and the chemical reaction rates. The remaining constitutive quantities are determined from the entropy principle of thermodynamics.

2.2. *Equation of state.* First of all an equation of state (EoS) is required to relate the partial pressures p_i and the thermal energy ρe to the partial densities ρ_i and the *mixture temperature T*. In order to derive a complete EoS; cf. [20] for a discussion on complete and incomplete EoS, we start with the mixture entropy ρs

$$\rho s = \rho \tilde{s}(\rho e, \rho_1, \ldots, \rho_N). \tag{2.5}$$

Obviously, the mixture temperature T and the *chemical potentials* μ_i are defined as follows:

$$\frac{1}{T} := \frac{\partial \rho \tilde{s}}{\partial \rho e} > 0 \qquad \text{and} \qquad -\frac{\mu_i}{T} := \frac{\partial \rho \tilde{s}}{\partial \rho_i} \,. \tag{2.6}$$

To perform the change of variables from $\{\rho e, \rho_1, \ldots, \rho_n\}$ to $\{T, \rho_1, \ldots, \rho_N\}$ it is useful to introduce the specific Helmholtz free energy

$$\Psi := e - Ts. \tag{2.7}$$

Then it follows from (2.6) with $\Psi = \hat{\Psi}(T, \rho_1, \ldots, \rho_N\}$

$$\rho s = -\frac{\partial \rho \hat{\Psi}}{\partial T}, \qquad \mu_i = \frac{\partial \rho \hat{\Psi}}{\partial \rho_i}, \qquad \text{and} \qquad e = -T^2 \frac{\partial}{\partial T} \left(\frac{\hat{\Psi}}{T} \right) \,. \tag{2.8}$$

Finally, the Gibbs-Duhem equation relates the mixture pressure p to the free energy via

$$p = -\rho \Psi + \sum_{i=1}^{N} \mu_i \rho_i \,. \tag{2.9}$$

Note that this is not sufficient to close the model. In addition one needs to know constitutive functions for the partial specific energies and the partial pressures or, alternatively, for the partial pressures and $\boldsymbol{q}$. Unfortunately, these are not given in [4, Section 15]. To avoid this problem we confine ourselves to simple mixtures defined by

DEFINITION 2.1 (Simple mixture). A mixture of N components is called a **simple mixture** if the partial pressures and the partial specific energies are of the form

$$e_i = e_i(T, \rho_i) \qquad \text{and} \qquad p_i = p_i(T, \rho_i) \,.$$

For simple mixtures the partial quantities can be calculated directly from the partial Helmholtz free energies $\Psi_i = \Psi_i(T, \rho_i)$ via

$$s_i = -\frac{1}{\rho_i} \frac{\partial \rho_i \Psi_i}{\partial T}, \quad e_i = -T^2 \frac{\partial}{\partial T} \left(\frac{\Psi_i}{T} \right), \quad \mu_i = \frac{\partial \rho_i \Psi_i}{\partial \rho_i}, \quad \text{and} \quad p_i = -\rho_i \Psi_i + \rho_i \mu_i \,. \tag{2.10}$$

From these the mixture quantities are determined as

$$\rho s = \sum_{i=1}^{N} \rho_i s_i, \quad \rho e = \sum_{i=1}^{N} \rho_i e_i, \quad \rho \Psi = \sum_{i=1}^{N} \rho_i \Psi_i, \quad \rho \nu = \sum_{i=1}^{N} \rho_i \nu_i, \quad p = \sum_{i=1}^{N} p_i. \quad (2.11)$$

Finally, the sound speed a_i of component i is defined by the slope of the isentropes in the pressure-density plane, i.e., $p_i = \check{p}_i(\rho_i, s_i)$, as

$$a_i^2 := \frac{\partial \check{p}_i(\rho_i, s_i)}{\partial \rho_i} = \frac{\partial p_i(\rho_i, T)}{\partial \rho_i} + T \left(\rho_i^2 \frac{\partial e_i(\rho_i, T)}{\partial T} \right)^{-1} \left(\frac{\partial p_i(\rho_i, T)}{\partial T} \right)^2. \quad (2.12)$$

Here we make use of the following thermodynamic identity (cf. [19]):

$$\left(p_i - \rho_i^2 \frac{\partial e_i}{\partial \rho_i} \right) = T \frac{\partial p_i}{\partial T}. \quad (2.13)$$

Introducing the specific heat capacity and the isothermal speed of sound

$$c_{vi} := \frac{\partial e_i(\rho_i, T)}{\partial T}, \quad \overline{a}_i^2 := \frac{\partial p_i(\rho_i, T)}{\partial \rho_i}, \quad (2.14)$$

then the sound speed can be written as

$$a_i^2 = \overline{a}_i^2 + \frac{T}{\rho_i^2 c_{vi}} \left(\frac{\partial p_i}{\partial T} \right)^2. \quad (2.15)$$

To ensure finite speeds of propagation, the sound speed a_i and $\overline{a}_i$ have to be real numbers, i.e.,

$$a_i^2 \geq 0 \quad \text{and} \quad \overline{a}_i^2 \geq 0. \quad (2.16)$$

Since this condition guarantees hyperbolicity of a single fluid system, we refer to it as the *hyperbolicity condition*. As will be proven in Theorem 3.3 below it is also a necessary condition for the multi-component system. Note that $a_i^2 \geq \overline{a}_i^2$ because of the positivity of the temperature (2.6) provided that $c_{vi} > 0$. The latter is a necessary condition to ensure the second law of thermodynamics; see Theorem 2.7 below.

For examples of simple mixtures we now consider mixtures of stiffened gases and van der Waals fluids, respectively.

2.2.1. *Mixture of stiffened gases.* Let the constant material parameters $c_{vi}, \gamma_i \pi_i$ and q_i denoting the specific heat capacity at constant volume, the adiabatic exponent, the minimal pressure and the heat of formation of component i, respectively, chosen such

that $c_{vi} > 0$, $\pi_i \geq 0$, q_i and $\gamma_i > 1$. Let further ρ_{i0} be some reference density at reference temperature T_0. Then by

$$\Psi_i(T, \rho_i) = -c_{vi} T \ln \frac{T}{T_0} + q_i \left(1 - \frac{T}{T_0} \right) + \frac{\pi_i}{\rho_i} + (\gamma_i - 1) c_{vi} T \ln \frac{\rho_i}{\rho_{i0}} + \frac{\pi_i}{\rho_i} \frac{T}{T_0}$$

the stiffened gas equation of state for component i is specified. From (2.10), (2.12), and (2.14) we conclude

$$e_i = c_{vi} T + \pi_i / \rho_i + q_i \,, \tag{2.17a}$$

$$\mu_i = -c_{vi} T \ln \frac{T}{T_0} + q_i \left(1 - \frac{T}{T_0} \right) + (\gamma_i - 1) c_{vi} T \ln \frac{\rho_i}{\rho_{i0}} + (\gamma_i - 1) c_{vi} T - \frac{\pi_i}{\rho_{i0}} \frac{T}{T_0} \,, \tag{2.17b}$$

$$p_i = \rho_i (\gamma_i - 1) c_{iv} T - \pi_i \,, \tag{2.17c}$$

$$s_i = c_{vi} + c_{ci} \ln \frac{T}{T_0} + q_i \frac{1}{T_0} - (\gamma_i - 1) c_{vi} \ln \frac{\rho_i}{\rho_{i0}} - \frac{\pi_i}{\rho_{i0}} \frac{1}{T_0} \,, \tag{2.17d}$$

$$a_i^2 = c_{vi} T (\gamma_i - 1) \gamma_i = \gamma_i \bar{a}_i^2 \,. \tag{2.17e}$$

For the mixture temperature we then deduce from (2.7) and (2.11)

$$T = \frac{\rho e - \pi - \rho q}{\rho c_v} \tag{2.18}$$

with

$$\rho q := \sum_{i=1}^{N} \rho_i q_i, \qquad \pi := \sum_{i=1}^{N} \pi_i, \qquad \text{and} \qquad \rho c_v := \sum_{i=1}^{N} \rho_i c_{vi} \,. \tag{2.19}$$

Obviously, the mixture temperature may become negative depending on the state of the internal energy. According to $(2.6)_a$ these states are not physically admissible.

REMARK 2.2. For $\pi_i = 0$ and $q_i = 0$ the stiffened gas equation of state reduces to the ideal gas equation.

REMARK 2.3. The hyperbolicity condition (2.16) reads

$$a_i^2 = \bar{a}_i^2 / \gamma_i > \bar{a}_i^2 = (\gamma_i - 1) c_{vi} T \geq 0. \tag{2.20}$$

This condition holds because of the constraints on the material parameters c_{vi} and γ_i and the positivity of the temperature (2.6).

2.2.2. *Mixtures of van der Waals fluids.* Let the constant material parameters c_{vi}, γ_i, M_i, b_{1i}, and b_{2i} denoting the specific heat capacity at constant volume, the adiabatic exponent and the molar mass of component i, the cohesion pressure and the covolume of component i, respectively, be chosen such that $c_{vi} > 0$, $b_{1i}, b_{2i} \geq 0$, $M_i > 0$, and $\gamma_i > 1$.

Let further ρ_{i0} be some reference density at reference temperature T_0. Then

$$\Psi_i(T, \rho_i) = -c_{vi}T \ln \frac{T}{T_0} - \frac{b_{1i}\rho_i}{M_i^2} + \frac{b_{1i}\rho_{i0}}{M_i^2} \frac{T}{T_0} + (\gamma_i - 1)c_{vi}T \ln \frac{\rho_i}{\rho_{i0}} - (\gamma_i - 1)c_{vi}T \ln \frac{M_i - b_{2i}\rho_i}{M_i - b_{2i}\rho_{i0}}$$

defines the van der Waals equation of state for component i. From (2.10), (2.12), and (2.14) we conclude

$$e_i = c_{vi}T - \frac{b_{1i}\rho_i}{M_i^2}, \tag{2.21a}$$

$$\mu_i = -c_{vi}T \ln \frac{T}{T_0} - 2\frac{b_{1i}\rho_i}{M_i^2} + \frac{b_{1i}\rho_{i0}}{M_i^2} \frac{T}{T_0} + (\gamma_i - 1)c_{vi}T \ln \frac{\rho_i}{\rho_{i0}} + (\gamma_i - 1)c_{vi}T \frac{M_i}{M_i - b_{2i}\rho_i} \tag{2.21b}$$

$$\quad - (\gamma_i - 1)c_{vi}T \ln \frac{M_i - b_{2i}\rho_i}{M_i - b_{2i}\rho_{i0}},$$

$$p_i = -\frac{b_{1i}\rho_i^2}{M_i^2} + \rho_i(\gamma_i - 1)c_{vi}T \frac{M_i}{M_i - b_{2i}\rho_i}, \tag{2.21c}$$

$$s_i = c_{vi} + c_{vi} \ln \frac{T}{T_0} - \frac{b_{1i}\rho_{i0}}{M_i^2} \frac{1}{T_0} - (\gamma_i - 1)c_{vi} \ln \frac{\rho_i}{\rho_{i0}} + (\gamma_i - 1)c_{vi} \ln \frac{M_i - b_{2i}\rho_i}{M_i - b_{2i}\rho_{i0}}, \tag{2.21d}$$

$$a_i^2 = -2\frac{b_{1i}\rho_i}{M_i^2} + c_{vi}T(\gamma_i - 1)\frac{M_i^2 \gamma_i}{(M_i - b_{2i}\rho_i)^2} = \bar{a}_i^2 + c_{vi}T \frac{M_i^2(\gamma_i - 1)^2}{(M_i - b_{2i}\rho_i)^2}. \tag{2.21e}$$

For the mixture temperature we then deduce from (2.7) and (2.11)

$$T = \left(\rho e + \sum_{i=1}^{N} \frac{b_{1i}\rho_i^2}{M_i^2}\right) / (\rho c_v) \tag{2.22}$$

with ρc_v defined in $(2.19)_c$.

REMARK 2.4. For $b_{1i} = 0$ and $b_{2i} = 0$ the van der Waals equation of state reduces to the ideal gas equation.

REMARK 2.5. The hyperbolicity condition (2.16) reads

$$a_i^2 = \bar{a}_i^2 + c_{vi}T \frac{M_i^2(\gamma_i - 1)^2}{(M_i - b_{2i}\rho_i)^2} > \bar{a}_i = -2\frac{b_{1i}\rho_i}{M_i^2} + c_{vi}T(\gamma_i - 1)\frac{M_i^2}{(M_i - b_{2i}\rho_i)^2} \geq 0. \tag{2.23}$$

REMARK 2.6. In the literature typically one will find formulae for e_i and p_i. To check whether these correspond to a thermodynamically consistent EoS one has to find a Helmholtz free energy Ψ_i such that the relations $(2.10)_a$ and $(2.10)_c$ hold true. By the following procedure it can be checked whether a pair of given EoS for e_i and p_i is thermodynamically consistent:

Step 1: Determine partial Helmholtz free energy Ψ_i by integration of $(2.10)_a$, i.e.,

$$\frac{\Psi_i(\rho_i, T)}{T} := c(\rho_i, T_0) - \int_{T_0}^{T} \frac{e_i(\rho_i, T)}{T^2} dT. \tag{2.24}$$

Step 2: Determine the integration constant $c(\rho_i, T_0)$ by plugging (2.24) into $(2.10)_c$ and integrating the resulting ODE

$$\frac{\partial c(\rho_i, T_0)}{\partial \rho_i} = \frac{p_i(\rho_i, T_0)}{\rho_i^2 T} + \int_{T_0}^{T} \frac{1}{T^2} \frac{\partial e_i(\rho_i, T)}{\partial \rho_i}, \quad c(\rho_{i0}, T_0) = c_0. \tag{2.25}$$

Step 3: Check whether the Helmholtz free energy Ψ_i satisfies $(2.10)_c$ for the given pressure p_i. In case of a stiffened gas EoS and a simple van der Waals EoS the above procedure verifies thermodynamical consistency.

2.2.3. *Material parameters.* Later on in Sections 4 and 5 we will investigate phase transition for water vapor and liquid water as well as a chemical reaction of hydrogen and oxygen. For all computations we will consider mixtures of stiffened gases using the parameters summarized in Table 1.

TABLE 1. Parameters for water, oxygen, and hydrogen

	γ	c_v $[J/kg/K]$	q $[J/kg]$	π $[Pa]$	ρ_0 $[kg/m^3]$	T_0 $[K]$	M $[kg]$
vapor	1.43	1040	$2.03 \cdot 10^6$	0	0.9	293	0.01802
liquid	2.35	1816	$-1.167 \cdot 10^6$	10^9	999	293	0.01802
oxygen	1.4	920	0	0	1.429	293	0.032
hydrogen	1.4	14304	0	0	0.09	293	0.00202

2.3. *Reaction rates.* In the model we consider N_R chemical reactions between the constituents A_i according to

$$\alpha_1^a A_1 + \ldots + \alpha_N^a A_N \rightleftharpoons \beta_1^a A_1 + \ldots + \beta_N^a A_N \qquad a = 1, \ldots, N_R \qquad (2.26)$$
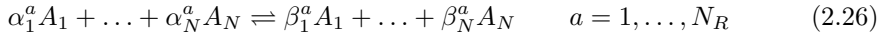
with *stoichiometric coefficients* α_i^a, $\beta_i^a \in \mathbb{N}_0$ and $\nu_i^a := \beta_i^a - \alpha_i^a$. The mass productions are of the form

$$r_i = \sum_{a=1}^{N_R} M_i \nu_i^a R_a \qquad (2.27)$$

with the *molar mass* M_i and R_a the *rate of reaction* a which is the difference of the rate of the forward and the backward path, $R_a = R_a^f - R_a^b$. Due to mass conservation in every single reaction it must hold that $\sum_{i=1}^N M_i \nu_i^a = 0$ for all a.

According to Bothe and Dreyer [4] the reaction rates of the forward and the backward path satisfy the relation

$$\frac{R_a^f}{R_a^b} = \exp\left(-\frac{1}{RT} \sum_{i=1}^N \nu_i^a M_i \mu_i\right) \qquad (2.28)$$

with R_a^f, $R_a^b > 0$. From this we determine for the difference of the forward and the backward path

$$R_a = R_a^f \left(1 - \exp\left(\frac{1}{RT} \sum_{i=1}^N \nu_i^a M_i \mu_i\right)\right). \qquad (2.29)$$

Usually the rates are not constant but depend on the state. For more details on this we refer to [4], [10], [12]. Note that only one of the rates R_a^f and R_a^b can be modeled, while the other one has to be determined by (2.28). For an example see [11].

2.4. *Entropy principle.* To derive thermodynamically consistent closure conditions for $\boldsymbol{f}_i$, $\boldsymbol{S}_i^0$, Π_i, and $\sum_{i=1}^{N} \boldsymbol{q}_i$, we first derive a balance law for the thermal energy. For this purpose we substitute the partial balances of the mass densities (2.1a) and the momentum (2.1b) and the definition of the mixture quantities in the balance of total energy (2.1c) to obtain

$$\partial_t(\rho e) + \nabla \cdot (\rho e \boldsymbol{v} + \boldsymbol{q}) = \sum_{i=1}^{N} \boldsymbol{S}_i^{irr} : \nabla \boldsymbol{v}_i - p \nabla \cdot \boldsymbol{v} - \sum_{i=1}^{N} \boldsymbol{u}_i \cdot (\boldsymbol{f}_i - r_i \boldsymbol{v}_i + \frac{1}{2} r_i \boldsymbol{u}_i - \nabla p_i). \quad (2.30)$$

According to Bothe and Dreyer [4] the interaction force

$$\boldsymbol{f}_i - r_i \boldsymbol{v}_i = \boldsymbol{f}_i^M + \boldsymbol{f}_i^C - r_i \boldsymbol{v}_i \quad (2.31)$$

is split into a mechanical part

$$\boldsymbol{f}_i^M = -T \sum_{j=1}^{N} f_{ij} \rho_i \rho_j (\boldsymbol{v}_i - \boldsymbol{v}_j) \quad \text{with} \quad (2.32a)$$

$$f_{ij} = f_{ij}(T, \rho_i, \rho_j) \geq 0, \quad f_{ij} = f_{ji}, \ i \neq j \quad (2.32b)$$

and a chemical part

$$\boldsymbol{f}_i^C - r_i \boldsymbol{v}_i = -\sum_{j=1}^{N} C_{ij} (\boldsymbol{v}_i - \boldsymbol{v}_j) \quad \text{with} \quad (2.33a)$$

$$C_{ij} = \sum_{a=1}^{N_R} \frac{M_i M_j}{\sum_{k=1}^{N} \alpha_k^a M_k} (R_a^f \beta_i^a \alpha_j^a + R_a^b \alpha_i^a \beta_j^a). \quad (2.33b)$$

We emphasize that (2.32) differs from [4] due to the assumption of a simple mixture.

It remains to verify that this approach is in agreement with the second law of thermodynamics. For this purpose we derive from the equation of state (2.5) the entropy balance

$$\partial_t(\rho s) + \nabla \cdot (\rho s \boldsymbol{v} + \boldsymbol{\Phi}) = \zeta, \quad (2.34)$$

where we employ the evolution equations for the partial densities (2.1a) and the thermal energy (2.30). Here the entropy flux $\boldsymbol{\Phi}$ is given by

$$\boldsymbol{\Phi} := \frac{1}{T} \left(\boldsymbol{q} - \sum_{i=1}^{N} \rho_i \mu_i \boldsymbol{u}_i \right). \quad (2.35)$$

According to Bothe and Dreyer [4] the entropy production ζ is composed of the following additive contributions:

$$\zeta := \zeta_{heat} + \zeta_{dif,nonreact} + \zeta_{dif,react} + \zeta_{chem} + \zeta_{visc} \quad (2.36)$$

corresponding to heat flux, diffusion flux with respect to non-reacting and reacting mixtures, chemical reaction kinetics and viscosity, respectively. These are

$$\zeta_{heat} := \sum_{i=1}^{N} \boldsymbol{q}_i \cdot \nabla \frac{1}{T}, \tag{2.37a}$$

$$\zeta_{dif,nonreact} := -\frac{1}{T} \sum_{i=1}^{N} \boldsymbol{u}_i \cdot \boldsymbol{f}_i^M, \tag{2.37b}$$

$$\zeta_{dif,react} := -\sum_{i=1}^{N} \boldsymbol{u}_i \cdot \frac{1}{T} \left(\boldsymbol{f}_i^C - r_i \boldsymbol{v}_i + \frac{1}{2} r_i \boldsymbol{u}_i \right), \tag{2.37c}$$

$$\zeta_{chem} := -\frac{1}{T} \sum_{a=1}^{N_R} R_a \mathcal{A}_a = -\frac{1}{T} \sum_{i=1}^{N} r_i \mu_i, \tag{2.37d}$$

$$\zeta_{visc} := \frac{1}{T} \sum_{i=1}^{N} \boldsymbol{S}_i^{irr} : \boldsymbol{D}_i, \qquad \boldsymbol{D}_i := \frac{1}{2} \left(\nabla \boldsymbol{v}_i + \nabla \boldsymbol{v}_i^T \right). \tag{2.37e}$$

Note that the body forces do not cause a production of energy. To ensure non-negativity of the entropy production terms (2.37) we have to make some assumptions. The following ansatz:

$$\sum_{i=1}^{N} \boldsymbol{q}_i = \kappa \nabla \frac{1}{T} \quad \text{with} \quad \kappa = \kappa(T, \rho_1, \ldots, \rho_N) \geq 0 \tag{2.38}$$

guarantees

$$\zeta_{heat} = \alpha \nabla \frac{1}{T} \cdot \nabla \frac{1}{T} \geq 0. \tag{2.39}$$

Using the closure condition (2.32) we deduce

$$\zeta_{dif,nonreact} = \frac{1}{2} \sum_{i,j=1}^{N} f_{ij} \rho_i \rho_j (\boldsymbol{v}_i - \boldsymbol{v}_j)^2 \geq 0. \tag{2.40}$$

Further, employing the definition of the coefficients C_{ij} defined by (2.33b) the entropy production corresponding to the diffusion flux with respect to reacting mixtures can be rewritten as

$$\zeta_{dif,react} = \sum_{a=1}^{N_R} \left(\zeta_{dif}^{a,f} + \zeta_{dif}^{a,b} \right) \tag{2.41}$$

with

$$\zeta_{dif}^{a,f} := \frac{R_a^f}{T} \left(\sum_{i=1}^{N} \frac{M_i}{2} (\alpha_i^a + \beta_i^a) \boldsymbol{u}_i^2 - \sum_{i,j=1}^{N} \frac{M_i M_j}{\sum_{k=1}^{N} \alpha_k^a M_k} \beta_i^a \alpha_j^a \boldsymbol{u}_i \boldsymbol{u}_j \right), \tag{2.42a}$$

$$\zeta_{dif}^{a,b} := \frac{R_a^b}{T} \left(\sum_{i=1}^{N} \frac{M_i}{2} (\alpha_i^a + \beta_i^a) \boldsymbol{u}_i^2 - \sum_{i,j=1}^{N} \frac{M_i M_j}{\sum_{k=1}^{N} \alpha_k^a M_k} \alpha_i^a \beta_j^a \boldsymbol{u}_i \boldsymbol{u}_j \right). \tag{2.42b}$$

By means of the Cauchy-Schwarz inequality and positivity of the temperature (2.6) it follows

$$\zeta_{dif}^{a,f} \geq 0, \quad \zeta_{dif}^{a,b} \geq 0. \tag{2.43}$$

Moreover, from the closure condition (2.28) and monotonicity of the logarithm we deduce

$$\zeta_{chem} = R \sum_{a=1}^{N_R} (R_a^f - R_a^b)(\ln(R_a^f) - \ln(R_a^b)) \geq 0. \tag{2.44}$$

Furthermore, using the closure conditions

$$\boldsymbol{S}_i^0 = \sum_{j=1}^N 2\eta_{ij} \boldsymbol{D}_j^0, \quad \Pi_i = -\sum_{j=1}^N \lambda_{ij} \nabla \cdot \boldsymbol{v}_j \quad \text{with} \tag{2.45a}$$

$$\boldsymbol{\eta} = (\eta_{ij})_{i,j=1,\ldots d} \text{ (shear viscosity)}, \tag{2.45b}$$

$$\boldsymbol{\lambda} = (\lambda_{ij})_{i,j=1,\ldots d} \text{ (bulk viscosity) positive semi-definite} \tag{2.45c}$$

we conclude that the entropy production due to viscosity is non-negative, i.e.,

$$\zeta_{visc} = \frac{1}{T} \sum_{i=1}^N (\boldsymbol{S}_i^0 - \Pi_i \boldsymbol{I}) : (\boldsymbol{D}_i^0 + \frac{1}{d}(\nabla \cdot \boldsymbol{v}_i)\boldsymbol{I}) = \frac{1}{T} \sum_{i=1}^N \boldsymbol{S}_i^0 : \boldsymbol{D}_i^0 - \frac{1}{T} \sum_{i=1}^N \Pi_i \nabla \cdot \boldsymbol{v}_i \geq 0. \tag{2.46}$$

Here $\boldsymbol{D}_i^0$ denotes the traceless part of $\boldsymbol{D}_i$.

Finally, we verify that the entropy is a strictly concave function. Since the temperature introduced in (2.6) is positive, i.e., $\rho\tilde{s}$ is strongly monotone in ρe, we can perform a variable transformation exchanging ρe and T, i.e.,

$$\rho e = \rho\hat{e}(T, \rho_1, \ldots, \rho_N). \tag{2.47}$$

Plugging this into the definition of the Helmholtz free energy (2.7) we obtain

$$\rho\hat{\Psi}(T, \rho_1, \ldots, \rho_N) = \rho\hat{e}(T, \rho_1, \ldots, \rho_N) - T\rho\tilde{s}(\rho\hat{e}(T, \rho_1, \ldots, \rho_N), \rho_1, \ldots, \rho_N). \tag{2.48}$$

From this we derive

$$\frac{\partial \rho\hat{\Psi}}{\partial T} = -\rho\tilde{s}, \quad \frac{\partial \rho\hat{\Psi}}{\partial \rho_i} = \mu_i, \quad e = -T^2 \frac{\partial}{\partial T}\left(\frac{\hat{\Psi}}{T}\right). \tag{2.49}$$

Then Bothe and Dreyer give a criterion for the entropy that can easily be checked.

THEOREM 2.7 (Bothe-Dreyer [4]). The entropy $\rho\tilde{s}$ is a strictly concave function and $-\rho\tilde{s}$ is a strictly convex function in $(\rho e, \rho_1, \ldots, \rho_N)$, respectively, if and only if

$$c_v := \frac{\partial \hat{e}}{\partial T} > 0 \text{ and } \left(\frac{\partial \hat{\mu}_i}{\partial \rho_j}\right)_{i,j=1,\ldots N} \text{ is positive definite .} \tag{2.50}$$

REMARK 2.8. In case of a stiffened gas the thermodynamic stability condition (2.50) reads

$$\frac{\partial \hat{e}_i}{\partial T} = c_{vi} > 0, \quad \frac{\partial \hat{\mu}_i}{\partial \rho_i} = (\gamma_i - 1)c_{vi}T\frac{1}{\rho_i} = \frac{\overline{a}_i^2}{\rho_i} > 0. \tag{2.51}$$

For a van der Waals fluid the thermodynamic stability condition (2.50) becomes

$$\frac{\partial e_i}{\partial T} = c_{vi} > 0, \quad \frac{\partial \mu_i}{\partial \rho_i} = (\gamma_i - 1)c_{vi}T\frac{M_i^2}{\rho_i(M_i - b_{2i}\rho_i)^2} - 2\frac{b_{1i}}{M_i^2} = \frac{\overline{a}_i^2}{\rho_i} > 0. \tag{2.52}$$

Obviously, if the hyperbolicity condition (2.16) holds strictly, i.e., $\overline{a}_i^2 > 0$, then it implies thermodynamical consistency provided the specific heat capacity at constant volume is positive.

Note that in general for B-N type models the entropy is not a *strict* convex function; cf. [21].

3. Hyperbolicity. Neglecting viscosity and heat conduction as well as relaxation processes and external forces in the fluid equations (2.1) the model reduces to a first order system describing transport effects only. In the following we investigate for which states the inviscid system is hyperbolic, i.e., all eigenvalues of the Jacobian of the inviscid flux in any direction are real and there exists a basis of right (left) eigenvectors that spans the state space. Then all wave speeds are finite and the system may be locally decoupled. From a mathematical point of view, this property is helpful in the construction of numerical fluxes, in particular, Riemann solvers, reconstruction polynomials and limiters based on characteristic decomposition. Therefore we need to determine the eigenvalues and eigenvectors as well as the corresponding characteristic fields.

3.1. *Primitive variables.* To determine the eigenvalues and eigenvectors it is convenient to consider the system of equations for the primitive variables: mass densities, velocities and temperature. For this purpose we first derive from the balances of momentum and mass densities (2.1b) and (2.1a), respectively, the balances of partial velocities

$$\partial_t \boldsymbol{v}_i + (\boldsymbol{v}_i \cdot \nabla)\boldsymbol{v}_i - \rho_i^{-1}\nabla \cdot \boldsymbol{S}_i = \rho_i^{-1}(\mathbf{i} - \mathbf{r_i}\boldsymbol{v_i}) + \boldsymbol{b_i}. \tag{3.1}$$

Furthermore, we rewrite the balance of total energy (2.1c) in terms of the mixture temperature and obtain

$$\partial_t T + \sum_{i=1}^{N}\left(\frac{\partial \rho e}{\partial T}\right)^{-1}\left(h_i - \rho_i\frac{\partial \rho e}{\partial \rho_i}\right)\nabla \cdot \boldsymbol{v}_i + \sum_{i=1}^{N}\left(\frac{\partial \rho e}{\partial T}\right)^{-1}\frac{\partial e_i}{\partial T}\rho_i\boldsymbol{v}_i \cdot \nabla T = 0. \tag{3.2}$$

This balance law can be derived computing the time derivative of the relation (2.47) and then employing the balance laws for the mass densities (2.1a) and the thermal energy (2.1c) for a non-reacting and inviscid mixture. The balance equations of partial densities (2.1a), partial velocities (3.1) and (3.2) form a quasi-conservative system

$$\partial_t \boldsymbol{w} + \sum_{k=1}^{d} \boldsymbol{B}_k(\boldsymbol{w})\partial_{x_k}\boldsymbol{w} = \boldsymbol{0} \tag{3.3}$$

for the primitive variables $\boldsymbol{w} := ((\rho_1, \boldsymbol{v}_1^T), \ldots, (\rho_N, \boldsymbol{v}_N^T), T)^T$ with $\boldsymbol{B}_k$ being block matrices

$$\boldsymbol{B}_k = \begin{pmatrix} \boldsymbol{B}_{1,k} & & & \boldsymbol{b}_{1,k} \\ & \ddots & & \vdots \\ & & \boldsymbol{B}_{N,k} & \boldsymbol{b}_{N,k} \\ \boldsymbol{c}_{1,k}^T & \cdots & \boldsymbol{c}_{N,k}^T & c_k \end{pmatrix}$$

with

$$\boldsymbol{B}_{i,k} = \begin{pmatrix} v_{ik} & \rho_i \boldsymbol{e}_k^T \\ \frac{\partial_{\rho_i} p_i}{\rho_i} \boldsymbol{e}_k & v_{ik} \boldsymbol{I} \end{pmatrix}, \; \boldsymbol{b}_{i,k} = \begin{pmatrix} 0 \\ \frac{\partial_T p_i}{\rho_i} \boldsymbol{e}_k \end{pmatrix}, \; \boldsymbol{c}_{i,k} = \begin{pmatrix} 0 \\ \frac{T \partial_T p_i}{\rho c_v} \boldsymbol{e}_k \end{pmatrix}, \; c_k = \sum_{i=1}^N \frac{\rho_i \partial_T e_i}{\rho c_v} v_{ik}.$$

Here $\boldsymbol{e}_k$ and $\boldsymbol{I}$ denote the k-th unit vector in $\mathbb{R}^d$ and the unit matrix in $\mathbb{R}^d$, respectively. To verify hyperbolicity we have to check that for any direction $\boldsymbol{n} \in \mathbb{R}^d$, $|\boldsymbol{n}| = 1$, the projected matrix

$$\boldsymbol{B}_n = \sum_{k=1}^d \boldsymbol{B}_k n_k \tag{3.4}$$

has real eigenvalues and the corresponding eigenvectors form a basis for $\mathbb{R}^{2N+1}$. Introducing the normal velocity $v_{in} = \sum_{k=1}^d v_{ik} n_k$ and the orthogonal block diagonal matrix $\boldsymbol{R}_n = \text{diag}(\boldsymbol{Q}_1, \ldots, \boldsymbol{Q}_n, 1)$, with $\boldsymbol{Q}_n = \text{diag}(1, \boldsymbol{O}_n)$ and orthogonal matrix $\boldsymbol{O}_n = (\boldsymbol{n}, \boldsymbol{t}_1, \ldots, \boldsymbol{t}_{d-1})$ we can rewrite $\boldsymbol{B}_n$ as

$$\tilde{\boldsymbol{B}}_n := \boldsymbol{R}_n^T \boldsymbol{B}_n \boldsymbol{R}_n = \begin{pmatrix} \tilde{\boldsymbol{B}}_{1,n} & & & \tilde{\boldsymbol{b}}_{1,n} \\ & \ddots & & \vdots \\ & & \tilde{\boldsymbol{B}}_{N,n} & \tilde{\boldsymbol{b}}_{N,n} \\ \tilde{\boldsymbol{c}}_{1,n}^T & \cdots & \tilde{\boldsymbol{c}}_{N,n}^T & c_n \end{pmatrix} \tag{3.5}$$

with entries

$$\tilde{\boldsymbol{B}}_{i,n} = \begin{pmatrix} v_{in} & \rho_i \boldsymbol{e}_1^T \\ \frac{\partial_{\rho_i} p_i}{\rho_i} \boldsymbol{e}_1 & v_{in} \boldsymbol{I} \end{pmatrix}, \; \tilde{\boldsymbol{b}}_{i,n} = \begin{pmatrix} 0 \\ \frac{\partial_T p_i}{\rho_i} \boldsymbol{e}_1 \end{pmatrix}, \; \tilde{\boldsymbol{c}}_{i,n} = \begin{pmatrix} 0 \\ \frac{T \partial_T p_i}{\rho c_v} \boldsymbol{e}_1 \end{pmatrix}, \; c_n = \sum_{i=1}^N \frac{\rho_i \partial_T e_i}{\rho c_v} v_{in}. \tag{3.6}$$

3.2. *Existence of real eigenvalues.* A straightforward calculation gives

$$\det(\tilde{\boldsymbol{B}}_n - \lambda \boldsymbol{I}) = \det(\boldsymbol{R}_n^T \boldsymbol{B}_n \boldsymbol{R}_n - \lambda \boldsymbol{I}) = (\rho c_v)^{-1} \prod_{i=1}^N (v_{in} - \lambda)^{d-1} p_N(\lambda) \tag{3.7}$$

with the polynomial p_N of degree $2N + 1$ defined as

$$p_N(\lambda) = \sum_{i=1}^N \rho_i c_{vi} (v_{in} - \lambda)((v_{in} - \lambda)^2 - a_i^2) \prod_{j=1, j \neq i}^N ((v_{jn} - \lambda)^2 - \overline{a}_j^2), \tag{3.8}$$

where the partial sound speed a_i and $\overline{a}_i^2$ are defined by (2.12) and (2.14), respectively. Obviously, there are N eigenvalues $\lambda = v_{in}$, $i = 1, \ldots, N$, with multiplicity $d - 1$. The other $2N + 1$ eigenvalues are determined by the roots of the polynomial p_N. In slight abuse of notion we call p_N the characteristic polynomial that is only correct in the one-dimensional case.

REMARK 3.1. In case of a single-component fluid, i.e., $N = 1$, the roots of p_N are given by

$$\lambda = v_{in}, \quad \lambda_{i,\pm} = v_{in} \pm a_i, \qquad i = 1. \tag{3.9}$$

These coincide with the well-known eigenvalues of the Euler equations.

REMARK 3.2. In case of a mixture of stiffened gases the sound speed a_i tends to $\overline{a}_i$ for $T \to 0$ and $\gamma_i \to 1$. In the limit the roots of p_N are given by

$$\lambda_i = \sum_{i=1}^{N} \frac{\rho_i c_{vi}}{\rho c_v} v_{in}, \quad \lambda_{i,\pm} = v_{in} \pm a_i. \tag{3.10}$$

In general, it is hard, if not impossible, to determine explicitly all roots of the characteristic polynomial p_N, and thus, it is not obvious that all eigenvalues are real. However, this follows directly if the matrix $\boldsymbol{B}_n$ can be symmetrized using similarity transformations.

THEOREM 3.3 (Existence of real eigenvalues). Let ρ_i, ρc_v, $\partial_T p_i \neq 0$ (non-isothermal). If the state satisfies the condition

$$\rho_i \frac{T}{\rho c_v} > 0, \quad \partial_{\rho_i} p_i \frac{T}{\rho c_v} \equiv \overline{a}_i^2 \frac{T}{\rho c_v} > 0, \quad i = 1, \dots, N, \tag{3.11}$$

then all eigenvalues of $\tilde{\boldsymbol{B}}_n$ are real.

Proof. The basic idea is to symmetrize $\tilde{\boldsymbol{B}}$ using a similarity transformation. For this purpose, we multiply $\tilde{\boldsymbol{B}}_n$ by the block diagonal matrix $\boldsymbol{D} := \operatorname{diag}(\boldsymbol{D}_1, \dots, \boldsymbol{D}_N, 1)$ with $\boldsymbol{D}_i := \operatorname{diag}(\alpha_i, \boldsymbol{1} + (\beta_i - 1)\boldsymbol{e}_1)$ and its inverse $\boldsymbol{D}^{-1}$ from the left and the right, respectively. Here we assume that the parameters α_i and β_i are non-zero. This results in the matrix

$$\check{\boldsymbol{B}}_n := \boldsymbol{D}\tilde{\boldsymbol{B}}_n\boldsymbol{D}^{-1} = \begin{pmatrix} \boldsymbol{D}_1\tilde{\boldsymbol{B}}_{1,n}\boldsymbol{D}_1^{-1} & & & \boldsymbol{D}_1\tilde{\boldsymbol{b}}_{1,n} \\ & \ddots & & \vdots \\ & & \boldsymbol{D}_N\tilde{\boldsymbol{B}}_{N,n}\boldsymbol{D}_N^{-1} & \boldsymbol{D}_N\tilde{\boldsymbol{b}}_{N,n} \\ \tilde{\boldsymbol{c}}_{1,n}^T\boldsymbol{D}_1^{-1} & \dots & \tilde{\boldsymbol{c}}_{N,n}^T\boldsymbol{D}_N^{-1} & c_n \end{pmatrix}. \tag{3.12}$$

Obviously, this matrix is symmetric if

$$\boldsymbol{D}_i\tilde{\boldsymbol{B}}_{i,n}\boldsymbol{D}_i^{-1} = (\boldsymbol{D}_i\tilde{\boldsymbol{B}}_{i,n}\boldsymbol{D}_i^{-1})^T, \quad \tilde{\boldsymbol{c}}_{i,n}\boldsymbol{D}_i^{-1} = \boldsymbol{D}_i\tilde{\boldsymbol{b}}_{i,n}, \quad i = 1, \dots, N,$$

or, equivalently,

$$\alpha_i^2 \rho_i^2 = \beta_i^2 \partial_{\rho_i} p_i, \quad \beta_i^{-1}\frac{T\partial_T p_i}{\rho c_v} = \beta_i\frac{\partial_T p_i}{\rho_i}, \quad i = 1, \dots, N.$$

According to the assumptions (3.11) there exist non-vanishing real parameters α_i and β_i. Since a symmetric matrix has only real eigenvalues and these are invariant under the similarity transformation (3.12) the assertion follows. $\qquad\square$

REMARK 3.4. Obviously, the symmetrization condition (3.11) holds because of the positivity of the temperature (2.6), the hyperbolicity condition (2.16), and the stability condition (2.50). In particular, in case of a stiffened gas the symmetrization condition (3.11) reads

$$\alpha_i^2 = \frac{T}{\rho c_v}\frac{c_{vi}(\gamma_i - 1)T}{\rho_i} > 0, \quad \beta_i^2 = \frac{\rho_i T}{\rho c_v} > 0. \tag{3.13}$$

For a van der Waals fluid the symmetrization condition (3.11) becomes

$$\alpha_i^2 = \frac{T}{\rho c_v} \left(\frac{R_i T}{1/\rho_i - b_i} \frac{1}{\rho_i^2} - 2\rho_i a_i \right) > 0, \quad \beta_i^2 = \frac{\rho_i T}{\rho c_v} > 0. \tag{3.14}$$

3.3. *Eigenvectors.* Since now we know that all roots of the characteristic polynomial (3.7) are real, we determine the corresponding left and right eigenvectors. The following result is obvious and is given only for sake of completeness.

PROPOSITION 1. There exist $(d-1)$-multiple eigenvalues $\lambda_{i,0} = v_{in}$, $i = 1, \ldots, N$ with corresponding left and right eigenvectors $\boldsymbol{l}_{i,0}^k$ and $\boldsymbol{r}_{i,0}^k$ determined by

$$\boldsymbol{l}_{i,0}^k = \boldsymbol{r}_{i,0}^k = (\underbrace{\boldsymbol{0}, \ldots, \boldsymbol{0}}_{i-1}, (0, \boldsymbol{t}_k^T), \underbrace{\boldsymbol{0}, \ldots, \boldsymbol{0}}_{N-i}, 0)^T, \quad k = 1, \ldots, d-1. \tag{3.15}$$

In particular,

$$\nabla_{\boldsymbol{w}} \lambda_{i,0} \cdot \boldsymbol{r}_{i,0}^k = 0, \tag{3.16}$$

i.e., the corresponding characteristic fields are linearly degenerated.

The eigenvectors determined in Proposition 1 correspond to the multi-dimensional case. The remaining eigenvectors can be determined from the one-dimensional case. For this reason we introduce the matrix $\tilde{\boldsymbol{B}}_{i,n}^{(1)}$ and the vectors $\tilde{\boldsymbol{b}}_{i,n}^{(1)}$ and $\tilde{\boldsymbol{c}}_{i,n}^{(1)}$ which are the one-dimensional counterparts to $\tilde{\boldsymbol{B}}_{i,n}$, $\tilde{\boldsymbol{b}}_{i,n}$ and $\tilde{\boldsymbol{c}}_{i,n}$ defined in (3.6). In particular,

$$\tilde{\boldsymbol{B}}_{i,n} = \begin{pmatrix} \tilde{\boldsymbol{B}}_{i,n}^{(1)} & \boldsymbol{0}_{d-1}^T \\ \boldsymbol{0}_{d-1} & v_{in}\boldsymbol{I}_{d-1} \end{pmatrix}, \ \tilde{\boldsymbol{b}}_{i,n} = \begin{pmatrix} \tilde{\boldsymbol{b}}_{i,n}^{(1)} \\ \boldsymbol{0}_{d-1} \end{pmatrix}, \ \tilde{\boldsymbol{c}}_{i,n} = \begin{pmatrix} \tilde{\boldsymbol{c}}_{i,n}^{(1)} \\ \boldsymbol{0}_{d-1} \end{pmatrix}. \tag{3.17}$$

To determine the remaining eigenvectors we verify two lemmata. First of all, we determine the eigenvalues and eigenvectors of the matrix $\tilde{\boldsymbol{B}}_{i,n}^{(1)}$ that are subject to the non-resonance condition.

DEFINITION 3.5. Let $\lambda \in \mathbb{R}$. Then λ is considered to be in **non-resonance** if

$$\sigma_k^n(\lambda) := (\delta_k^n(\lambda))^2 - \overline{a}_k^2 \neq 0 \quad \forall k = 1, \ldots, N \tag{3.18}$$

with $\delta_k^n(\lambda) := v_{kn} - \lambda$.

LEMMA 3.6. The eigenvalues and corresponding eigenvectors of the matrices $\tilde{\boldsymbol{B}}_{k,n}^{(1)}$ are determined by

$$\lambda_{\pm}^k = v_{kn} \pm \overline{a}_k, \tag{3.19}$$

$$\boldsymbol{r}_{\pm}^k = (\pm \rho_k/\overline{a}_k, 1)^T. \tag{3.20}$$

If the *non-resonance condition* (3.18) holds, i.e., λ is not an eigenvalue of $\tilde{\boldsymbol{B}}_{k,n}^{(1)}$, then the inverse $\tilde{\boldsymbol{B}}_{k,n}^{(1)} - \lambda\boldsymbol{I}$ exists and is given by

$$(\tilde{\boldsymbol{B}}_{k,n}^{(1)} - \lambda\boldsymbol{I})^{-1} = \frac{1}{\sigma_k^n(\lambda)} \begin{pmatrix} \delta_k^n(\lambda) & -\rho_k \\ -\overline{a}_k^2/\rho_k & \delta_k^n(\lambda) \end{pmatrix}. \tag{3.21}$$

The non-resonance condition essentially indicates that the eigenvalues of the matrices $\tilde{\boldsymbol{B}}_{k,n}^{(1)}$, $k = 1, \ldots, N$ are no roots of the characteristic polynomial p_N defined by (3.8). Because of Remark 3.2 this may happen for a mixture of stiffened gases if $a_k = \overline{a}_k$. The

latter only holds true for isothermal fluids, i.e., $p_k = p_k(\rho_k)$, that are of no interest here; cf. equation (2.15).

Furthermore, we need the following identity.

LEMMA 3.7. Let $\lambda \in \mathbb{R}$ be such that the non-resonance condition (3.18) holds. Then the following relation is true:

$$c_n - \lambda - \sum_{k=1}^{N}(\tilde{\boldsymbol{c}}_{k,n}^{(1)})^T(\tilde{\boldsymbol{B}}_{k,n}^{(1)} - \lambda\boldsymbol{I}_2)^{-1}\tilde{\boldsymbol{b}}_{k,n}^{(1)} = \frac{p_N(\lambda)}{\kappa_0(\lambda)\rho c_v} \tag{3.22}$$

with

$$\kappa_0(\lambda) := \prod_{k=1}^{N}\sigma_k^n(\lambda) \neq 0. \tag{3.23}$$

Proof. First of all, the non-resonance condition (3.18) implies $\sigma_k^n(\lambda) \neq 0$ and, thus, $\kappa_0 \neq 0$. Then by definition of $\tilde{\boldsymbol{b}}_{k,n}^{(1)}$ and $\tilde{\boldsymbol{c}}_{k,n}^{(1)}$, see equations (3.6) and (3.17), as well as Lemma 3.6 and the inverse (3.21) and using (2.11) it follows

$$(\tilde{\boldsymbol{c}}_{k,n}^{(1)})^T(\tilde{\boldsymbol{B}}_{k,n}^{(1)} - \lambda\boldsymbol{I}_2)^{-1}\tilde{\boldsymbol{b}}_{k,n}^{(1)} = (\rho c_v)^{-1}\frac{T(\partial_T p_k)^2}{\rho_k}\frac{\delta_k^n(\lambda)}{\sigma_k^n(\lambda)} = (\rho c_v)^{-1}\rho_k c_{vk}(a_k^2 - \overline{a}_k^2)\frac{\delta_k^n(\lambda)}{\sigma_k^n(\lambda)}. \tag{3.24}$$

Finally, the assertion follows by definition of c_n and the polynomial p_N; see equations (3.6) and (3.8), respectively. $\qquad\square$

Now we can determine the right eigenvectors to the roots of the polynomial p_N.

PROPOSITION 2. Let $\lambda \in \mathbb{R}$ be one of the existing $2N + 1$ roots of the characteristic polynomial (3.8), i.e., $p_N(\lambda) = 0$, and let the non-resonance condition (3.18) hold true. Then the corresponding right eigenvector is determined by

$$\boldsymbol{r}_\lambda^T = (\boldsymbol{r}_{\lambda,1}^T, \ldots, \boldsymbol{r}_{\lambda,N}^T, 1) \tag{3.25}$$

with

$$\boldsymbol{r}_{\lambda,k}^T = \frac{1}{\sigma_k^n(\lambda)\rho_k}\partial_T p_k(\rho_k, -\delta_k^n(\lambda)\boldsymbol{n}^T)^T. \tag{3.26}$$

Proof. First of all, we determine the right eigenvectors to the matrix $\tilde{\boldsymbol{B}}_n$ where we consider the following splitting in sub-vectors:

$$\tilde{\boldsymbol{r}}_\lambda^T = (\tilde{\boldsymbol{r}}_{\lambda,1}^T, \ldots, \tilde{\boldsymbol{r}}_{\lambda,N}^T, r_\lambda) \quad \text{with} \quad \tilde{\boldsymbol{r}}_{\lambda,k} = \begin{pmatrix} \tilde{\boldsymbol{r}}_{\lambda,k}^{(1)} \\ \boldsymbol{0}_{d-1} \end{pmatrix} \in \mathbb{R}^{d+1}, \; r_\lambda \in \mathbb{R}. \tag{3.27}$$

For the right eigenvalues it must hold that $(\tilde{\boldsymbol{B}}_n - \lambda\boldsymbol{I})\tilde{\boldsymbol{r}}_\lambda = 0$. Using (3.5), (3.17), and (3.27) this is equivalent to

$$(\tilde{\boldsymbol{B}}_{k,n}^{(1)} - \lambda\boldsymbol{I}_2)\tilde{\boldsymbol{r}}_{\lambda,k}^{(1)} + \tilde{\boldsymbol{b}}_{k,n}^{(1)}r_\lambda = \boldsymbol{0}, \quad k = 1, \ldots, N, \tag{3.28a}$$

$$\sum_{k=1}^{N}(\tilde{\boldsymbol{c}}_{k,n}^{(1)})^T\tilde{\boldsymbol{r}}_{\lambda,k}^{(1)} + (c_n - \lambda)r_\lambda = 0. \tag{3.28b}$$

Because of the non-resonance condition λ is not an eigenvalue of the matrices $\tilde{\boldsymbol{B}}_{k,n}^{(1)}$. Thus, we can make the following ansatz for the vectors $\tilde{\boldsymbol{r}}_{\lambda,k}^{(1)}$:

$$\tilde{\boldsymbol{r}}_{\lambda,k}^{(1)} = -(\tilde{\boldsymbol{B}}_{k,n}^{(1)} - \lambda\boldsymbol{I}_2)^{-1}\tilde{\boldsymbol{b}}_{k,n}^{(1)}r_\lambda. \tag{3.29}$$

We now plug (3.29) into (3.28b) to determine r_λ as

$$\left(c_n - \lambda - \sum_{k=1}^{N}(\tilde{\boldsymbol{c}}_{k,n}^{(1)})^T(\tilde{\boldsymbol{B}}_{k,n}^{(1)} - \lambda\boldsymbol{I}_2)^{-1}\tilde{\boldsymbol{b}}_{k,n}^{(1)}\right)r_\lambda = 0. \tag{3.30}$$

According to Lemma 3.7 the factor on the left-hand side of (3.30) can be written as

$$c_n - \lambda - \sum_{k=1}^{N}(\tilde{\boldsymbol{c}}_{k,n}^{(1)})^T(\tilde{\boldsymbol{B}}_{k,n}^{(1)} - \lambda\boldsymbol{I}_2)^{-1}\tilde{\boldsymbol{b}}_{k,n}^{(1)} = \frac{p_N(\lambda)}{\kappa_0(\lambda)\rho c_v}. \tag{3.31}$$

Note that $\kappa_0(\lambda) \neq 0$ because of the non-resonance condition. Since by assumption $p_N(\lambda) = 0$, we are free to choose a non-vanishing value $r_\lambda \neq 0$. We now may simplify (3.29). By definition (3.17) of $\tilde{\boldsymbol{b}}_{k,n}^{(1)}$ as the one-dimensional counterpart of $\tilde{\boldsymbol{b}}_{k,n}$ defined by (3.6) as well as Lemma 3.6 and the inverse (3.21) we obtain

$$\tilde{\boldsymbol{r}}_{\lambda,k}^{(1)} = r_\lambda \frac{1}{\sigma_k^n(\lambda)\rho_k}\partial_T p_k(\rho_k, -\delta_k^n(\lambda))^T. \tag{3.32}$$

Finally, the right eigenvector to $\boldsymbol{B}_n$ can be determined by multiplication with the matrix $\boldsymbol{R}_n$ from the left

$$\boldsymbol{r}_\lambda^T := (\boldsymbol{R}_n\tilde{\boldsymbol{r}}_\lambda)^T = \left(\boldsymbol{r}_{\lambda,1}^T, \ldots, \boldsymbol{r}_{\lambda,N}^T, r_\lambda\right) \tag{3.33}$$

with

$$\boldsymbol{r}_{\lambda,k}^T := \boldsymbol{Q}_n\tilde{\boldsymbol{r}}_{\lambda,k}^T = r_\lambda\frac{1}{\sigma_k^n(\lambda)\rho_k}\partial_T p_k(\rho_k, -\delta_k^n(\lambda)\boldsymbol{n}^T)^T. \tag{3.34}$$

From this the assertion follows with $r_\lambda = 1$. $\square$

Similarly, the corresponding left eigenvectors can be determined.

PROPOSITION 3. Let $\lambda \in \mathbb{R}$ be one of the existing $2N + 1$ roots of the characteristic polynomial (3.8), i.e., $p_N(\lambda) = 0$, and let the non-resonance condition (3.18) hold true. Then the corresponding left eigenvector is determined by

$$\boldsymbol{l}_\lambda^T = \left(\boldsymbol{l}_{\lambda,1}^T, \ldots, \boldsymbol{l}_{\lambda,N}^T, 1\right) \tag{3.35}$$

with

$$\boldsymbol{l}_{\lambda,k}^T = l_\lambda\frac{\partial_T p_k}{\rho c_v \, \sigma_k^n(\lambda)}T(\overline{a}_k^2/\rho_k, -\delta_k^n(\lambda)\boldsymbol{n}^T)^T. \tag{3.36}$$

Choosing the scaling factor

$$l_\lambda^{-1} = 1 + \sum_{k=1}^{N}\frac{\rho_k c_{vk}}{\rho c_v}\frac{1}{(\sigma_k^n(\lambda))^2}(a_k^2 - \overline{a}_k^2)(\overline{a}_k^2 + (\delta_k^n(\lambda))^2) > 0, \tag{3.37}$$

then $\boldsymbol{l}_{\lambda,k}^T\boldsymbol{r}_{\lambda,k} = 1$, where $\boldsymbol{r}_{\lambda,k}$ is the corresponding right eigenvector.

Proof. Again, we first determine the left eigenvectors to the matrix $\tilde{\boldsymbol{B}}_n$ where we consider the following splitting in sub-vectors:

$$\tilde{\boldsymbol{l}}_\lambda^T = \left(\tilde{\boldsymbol{l}}_{\lambda,1}^T, \ldots, \tilde{\boldsymbol{l}}_{\lambda,N}^T, l_\lambda\right) \quad \text{with} \quad \tilde{\boldsymbol{l}}_{\lambda,k} = \begin{pmatrix} \tilde{\boldsymbol{l}}_{\lambda,k}^{(1)} \\ \boldsymbol{0}_{d-1} \end{pmatrix} \in \mathbb{R}^{d+1}, \; l_\lambda \in \mathbb{R}. \tag{3.38}$$

For the left eigenvalues it must hold that $\tilde{\boldsymbol{l}}_\lambda^T(\tilde{\boldsymbol{B}}_n - \lambda\boldsymbol{I}) = \boldsymbol{0}^T$ or, equivalently, $(\tilde{\boldsymbol{B}}_n - \lambda\boldsymbol{I})^T\tilde{\boldsymbol{l}}_\lambda = \boldsymbol{0}$. Using (3.5), (3.17), and (3.38) this is equivalent to

$$(\tilde{\boldsymbol{B}}_{k,n}^{(1)} - \lambda\boldsymbol{I}_2)^T\tilde{\boldsymbol{l}}_{\lambda,k}^{(1)} + \tilde{\boldsymbol{c}}_{k,n}^{(1)}l_\lambda = \boldsymbol{0}, \quad k = 1,\ldots,N, \tag{3.39a}$$

$$\sum_{k=1}^N (\tilde{\boldsymbol{b}}_{k,n}^{(1)})^T\tilde{\boldsymbol{l}}_{\lambda,k}^{(1)} + (c_n - \lambda)l_\lambda = 0. \tag{3.39b}$$

Because of the non-resonance condition λ is not an eigenvalue of the matrices $\tilde{\boldsymbol{B}}_{k,n}$ and, thus, we can make the following ansatz for the vectors $\tilde{\boldsymbol{l}}_{\lambda,k}$:

$$\tilde{\boldsymbol{l}}_{\lambda,k}^{(1)} = -(\tilde{\boldsymbol{B}}_{k,n}^{(1)} - \lambda\boldsymbol{I}_2)^{-T}\tilde{\boldsymbol{c}}_{k,n}^{(1)}l_\lambda. \tag{3.40}$$

Then we plug (3.40) into (3.39b) to determine l_λ as

$$\left(c_n - \lambda - \sum_{k=1}^N \tilde{\boldsymbol{b}}_{k,n}^T(\tilde{\boldsymbol{B}}_{k,n} - \lambda\boldsymbol{I})^{-T}\tilde{\boldsymbol{c}}_{k,n}\right)l_\lambda = 0. \tag{3.41}$$

According to Lemma 3.7 the factor on the left-hand side of (3.30) can be written as

$$c_n - \lambda - \sum_{k=1}^N (\tilde{\boldsymbol{b}}_{k,n}^{(1)})^T(\tilde{\boldsymbol{B}}_{k,n}^{(1)} - \lambda\boldsymbol{I}_2)^{-T}\tilde{\boldsymbol{c}}_{k,n}^{(1)}$$

$$= c_n - \lambda - \sum_{k=1}^N (\tilde{\boldsymbol{c}}_{k,n}^{(1)})^T(\tilde{\boldsymbol{B}}_{k,n}^{(1)} - \lambda\boldsymbol{I}_2)^{-1}\tilde{\boldsymbol{b}}_{k,n}^{(1)} \tag{3.42}$$

$$= \frac{p_K(\lambda)}{\kappa_0(\lambda)\rho c_v}.$$

Note that $\kappa_0(\lambda) \neq 0$ because of the non-resonance condition. Since by assumption $p_N(\lambda) = 0$, we are free to choose a non-vanishing value $l_\lambda \neq 0$. By definition (3.17) of $\tilde{\boldsymbol{c}}_{k,n}^{(1)}$ as the one-dimensional counterpart of $\tilde{\boldsymbol{c}}_{k,n}$ defined by (3.6) as well as Lemma 3.6 and the inverse (3.21) we obtain

$$\tilde{\boldsymbol{l}}_{\lambda,k}^{(1)} = l_\lambda \frac{T\partial_T p_k}{\sigma_k^n(\lambda)}(\overline{a}_k^2/\rho_k, -\delta_k^n(\lambda), \boldsymbol{0}_{d-1})^T. \tag{3.43}$$

From the orthogonality condition $\boldsymbol{l}_{\lambda,k}^T\boldsymbol{r}_{\lambda,k} = 1$ and (3.32) we conclude (3.37). In particular, we make use of the identity (2.13). Finally, the left eigenvector to $\boldsymbol{B}_n$ can be determined by multiplication with the matrix $\boldsymbol{R}_n^T$ from the left:

$$\boldsymbol{l}_\lambda^T := (\boldsymbol{R}_n\tilde{\boldsymbol{l}}_\lambda)^T = \left(\boldsymbol{l}_{\lambda,1}^T, \ldots, \boldsymbol{l}_{\lambda,N}^T, l_\lambda\right) \tag{3.44}$$

with

$$\boldsymbol{l}_{\lambda,k}^T := (\boldsymbol{Q}_n\tilde{\boldsymbol{l}}_{\lambda,k})^T = l_\lambda \frac{T\partial_T p_k}{\rho c_v \, \sigma_k^n(\lambda)}(\overline{a}_k^2/\rho_k, -\delta_k^n(\lambda)\boldsymbol{n}^T)^T. \tag{3.45}$$

From this the assertion follows. $\qquad\square$

3.4. *Existence of an eigenvector basis.* It remains to verify that the eigenvectors are linearly independent. Since the eigenvectors $\boldsymbol{r}_\lambda$ and $\boldsymbol{l}_\lambda$ in (3.25) and (3.35), respectively, depend on the eigenvalues, this can only hold true when the roots of the polynomial p_N are simple and are at non-resonance. Then we can prove the following result.

THEOREM 3.8 (Existence of an eigenvector basis). Let there be $2N+1$ simple roots λ_i, $i = 1, \ldots, 2N + 1$, of the characteristic polynomial (3.8) satisfying the non-resonance condition (3.18). Then the corresponding left eigenvectors $\boldsymbol{l}_{\lambda_i}$, $i = 1, \ldots, 2N + 1$, and $\boldsymbol{l}_{i,0}^k$, $i = 1, \ldots, N$, $k = 1, \ldots, d - 1$, given by (3.35) and (3.15), respectively, and right eigenvectors $\boldsymbol{r}_{\lambda_i}$, $i = 1, \ldots, 2N + 1$, and $\boldsymbol{r}_{i,0}^k$, $i = 1, \ldots, N$, $k = 1, \ldots, d - 1$ given by (3.25) and (3.15), respectively, are orthogonal to each other.

Proof. First of all, we rewrite the left and right eigenvectors in block matrices $\boldsymbol{L}$ and $\boldsymbol{R}$ with rows and columns containing the left and right eigenvectors, respectively:

$$
\boldsymbol{L} = \begin{pmatrix} \boldsymbol{L}_1 & \cdots & \boldsymbol{L}_N & \boldsymbol{l} \\ \boldsymbol{L}_1^d & & & \\ & \ddots & & \\ & & \boldsymbol{L}_N^d & \end{pmatrix}, \ \boldsymbol{R} = \begin{pmatrix} \boldsymbol{R}_1 & \boldsymbol{R}_1^d & & \\ \vdots & & \ddots & \\ \boldsymbol{R}_N & & & \boldsymbol{R}_N^d \\ \boldsymbol{r}^T & & & \end{pmatrix} \tag{3.46}
$$

with block matrices $\boldsymbol{R}_k \overset{(3.25)}{=} (\boldsymbol{r}_{\lambda_1,k}, \ldots, \boldsymbol{r}_{\lambda_{2N+1},k}) \in \mathbb{R}^{(d+1)\times(2N+1)}$, $\boldsymbol{R}_k^d \in \mathbb{R}^{(d+1)\times(d-1)}$, $\boldsymbol{r} \in \mathbb{R}^{2N+1}$ as well as $\boldsymbol{L}_k^T \overset{(3.35)}{=} (\boldsymbol{l}_{\lambda_1,k}, \ldots, \boldsymbol{l}_{\lambda_{2N+1},k})$ $\boldsymbol{L}_k^d \in \mathbb{R}^{(d-1)\times(d+1)}$, $\boldsymbol{l} \in \mathbb{R}^{2N+1}$ for $k = 1 \ldots, N$. In particular, we obtain by Propositions 1, 2, and 3

$$
\boldsymbol{R}_k \overset{(3.25)}{=} \partial_T p_k \begin{pmatrix} \frac{1}{\sigma_k^n(\lambda_1)} & \cdots & \frac{1}{\sigma_k^n(\lambda_{2N+1})} \\ \frac{-\delta_k^n(\lambda_1)}{(\sigma_k^n(\lambda_1)\rho_k)}\boldsymbol{n} & \cdots & \frac{-\delta_k^n(\lambda_{2N+1})}{(\sigma_k^n(\lambda_{2N+1})\rho_k)}\boldsymbol{n} \end{pmatrix},
$$

$$
\boldsymbol{R}_k^d \overset{(3.15)}{=} \begin{pmatrix} 0 & \cdots & 0 \\ \boldsymbol{t}_1 & \cdots & \boldsymbol{t}_{d-1} \end{pmatrix},
$$

$$
\boldsymbol{r} \overset{(3.25)}{=} \boldsymbol{1}_{2N+1},
$$

$$
\boldsymbol{L}_k^T \overset{(3.35)}{=} \frac{T\partial_T p_k}{\rho c_v} \begin{pmatrix} l_{\lambda_1} \frac{\overline{a}_k^2}{\sigma_k^n(\lambda_1)\rho_k} & \cdots & l_{\lambda_{2K+1}} \frac{\overline{a}_k^2}{\sigma_k^n(\lambda_{2K+1})\rho_k} \\ l_{\lambda_1} \frac{-\delta_k^n(\lambda_1)}{\sigma_k^n(\lambda_1)}\boldsymbol{n} & \cdots & l_{\lambda_{2N+1}} \frac{-\delta_k^n(\lambda_{2N+1})}{\sigma_k^n(\lambda_{2N+1})}\boldsymbol{n} \end{pmatrix},
$$

$$
\boldsymbol{L}_k^d \overset{(3.15)}{=} (\boldsymbol{R}_k^d)^T, \ \boldsymbol{l}^T \overset{(3.37)}{=} \begin{pmatrix} l_{\lambda_1} \\ \vdots \\ l_{\lambda_{2N+1}} \end{pmatrix}.
$$

For $k = 1, \ldots, N$ the vectors $\boldsymbol{r}_{i,0}^k$, $i = 1, \ldots, d - 1$, are $d - 1$ linearly independent right eigenvectors to the $(d - 1)$-multiple eigenvalue v_{kn} of the matrix $\boldsymbol{B}_n$. Since by assumption all roots λ_i, $i = 1, \ldots, 2N + 1$, of the characteristic polynomial p_N defined by (3.8) are distinct, then the vectors $\boldsymbol{r}_{\lambda_i}$ are linearly independent right eigenvectors of the matrix $\boldsymbol{B}_n$. Note that these eigenvectors coincide for multiple roots. Furthermore, the eigenvectors $\boldsymbol{r}_{i,0}^k$ and $\boldsymbol{r}_{\lambda_i}$ are linearly independent as can be directly concluded from the matrices $\boldsymbol{R}_k$ and $\boldsymbol{R}_k^d$. Thus, the vectors $\boldsymbol{r}_{i,0}^k$ and $\boldsymbol{r}_{\lambda_i}$ form a right eigenvector basis to the

matrix $\boldsymbol{B}_n$, i.e., the matrix $\boldsymbol{R}$ is invertible. Then the matrix $\boldsymbol{L}$ must coincide with the inverse $\boldsymbol{R}^{-1}$ except for a scaling of the rows, i.e., $\boldsymbol{L} = \boldsymbol{SR}$ with $\boldsymbol{S} = \mathrm{diag}(\boldsymbol{s}^\lambda, \boldsymbol{s}^1, \ldots, \boldsymbol{s}^N)$, $\boldsymbol{s}^\lambda = (s_{\lambda_1}, \ldots, s_{\lambda_{2N+1}})$, $\boldsymbol{s}^i = (s^i_{1,0}, \ldots, s^i_{d-1,0})$. The scaling factors are determined by the orthogonality conditions $s_{\lambda_i} := \boldsymbol{r}_{\lambda_i} \cdot \boldsymbol{l}_{\lambda_i}$ and $s^k_{i,0} := \boldsymbol{r}^k_{i,0} \cdot \boldsymbol{l}^k_{i,0}$. By definition of the left and right eigenvectors it can be verified that $\boldsymbol{S} = \boldsymbol{I}$. Thus we conclude $\boldsymbol{LR} = \boldsymbol{I}$, i.e., the assertion holds. $\qquad\square$

Finally we conclude from Theorems 3.3 and 3.8

CONCLUSION 1 (Hyperbolicity). Let the assumptions of Theorems 3.3 and 3.8 hold true. Then the non-reacting, inviscid class-II-model (2.1) without external forces is hyperbolic.

So far, it is open whether the assumptions in Theorem 3.8 on the roots of the polynomial (3.8) always hold. In particular, we cannot yet conclude from the non-resonance condition (3.18) that all roots of p_N are simple. However, for subsonic mixtures at non-resonance we can verify that all roots of p_N are simple.

THEOREM 3.9 (Sufficient condition for simple roots). Consider a subsonic simple mixture, i.e.,

$$|v_{in}| < \bar{a}_i \qquad \text{and} \qquad |v_{in} - v_{jn}| < \min(\bar{a}_i, \bar{a}_j) \qquad i,j = 1, \ldots, N, \qquad (3.47)$$

at non-resonance. Then the roots of the characteristic polynomial p_N defined in (3.8) are simple.

Proof. First of all, we note that the non-resonance condition is equivalent to

$$v_{j_1 n} - \bar{a}_{j_1} < v_{j_2 n} - \bar{a}_{j_2} < \cdots < v_{j_N n} - \bar{a}_{j_N} \qquad (3.48\text{a})$$

$$v_{k_1 n} + \bar{a}_{k_1} < v_{k_2 n} + \bar{a}_{k_2} < \cdots < v_{k_N n} + \bar{a}_{k_N n}. \qquad (3.48\text{b})$$

Thus, we may reorder the terms in the characteristic polynomial (3.8) as follows:

$$p_N(\lambda) = \sum_{l=1}^N \rho_{i_l} c_{vi_l}(v_{i_l n} - \lambda)((v_{i_l n} - \lambda)^2 - a^2_{i_l}) \prod_{j=1, j \neq l}^N (v_{i_j n} - \lambda - \bar{a}_{i_j}) \prod_{j=1, k_j \neq i_l}^N (v_{k_j n} - \lambda + \bar{a}_{k_j}).$$

Then a simple calculation using the assumptions (3.47) and (3.48) gives

$$\mathrm{sign}(p_N(v_{j_l n} - \bar{a}_{j_l})) = (-1)^l \quad \text{and} \quad \mathrm{sign}(p_N(v_{k_l n} + \bar{a}_{k_l})) = (-1)^{N+l} \qquad (3.49)$$

for $l = 1, \ldots, N$. In addition,

$$p_N(\lambda) \to \pm\infty \qquad \text{for} \quad \lambda \to \mp\infty.$$

Thus, there exist $2N + 1$ intervals where the polynomial p_N of degree $2N + 1$ changes its sign. Obviously, the roots cannot be at resonance, i.e., coincide with some $v_{jn} \pm \bar{a}_j$ because of (3.49). This proves the above statement. $\qquad\square$

From Theorem 3.9 we conclude on an upper bound for the maximum of the absolute values of the characteristic speed, i.e., the spectral radius of the flux Jacobian.

CONCLUSION 2. For a subsonic simple mixture we define

$$v_{\min} := \min\{v_1 - \bar{a}_1, \ldots, v_N - \bar{a}_N\} \qquad \text{and} \qquad v_{\max} := \max\{v_1 + \bar{a}_1, \ldots, v_N + \bar{a}_N\}.$$

Then for the roots of the characteristic polynomial p_N defined in (3.8),

$$v_{\min} \leq \lambda_{\min} < 0 \qquad \text{and} \qquad 0 < \lambda_{\max} \leq v_{\max}.$$

This result can be used in numerical calculations to determine appropriate time steps.

3.5. *Characteristic fields.* For the construction of a Riemann solver it is important to determine the characteristic field corresponding to an eigenvalue. This is characterized by the sign of the product $\nabla_{\boldsymbol{w}}\lambda(\boldsymbol{w}) \cdot \boldsymbol{r}_\lambda(\boldsymbol{w})$. Although we do not yet know explicitly the eigenvalues in general we nevertheless may determine their derivatives with respect to the state in phase space.

LEMMA 3.10. Let $\lambda = \lambda(\boldsymbol{w})$ be an eigenvalue to some state $\boldsymbol{w}$ of primitive variables satisfying the non-resonance condition (3.18). If $\boldsymbol{w} \to \lambda(\boldsymbol{w})$ is a differentiable function in a local neighborhood of $\boldsymbol{w}$, then the derivative of the eigenvalues are given by

$$\frac{\partial\,\lambda(\boldsymbol{w})}{\partial\,w_l} = \frac{A_{w_l}(\lambda(\boldsymbol{w}))}{B(\lambda(\boldsymbol{w}))}$$

with

$$A_{w_l} := \sum_{i=1}^{N} \left(\frac{\partial\,\rho_i c_{vi}}{\partial\,w_l}(v_{in} - \lambda) + \rho_i c_{vi} \frac{\partial\,v_{in}}{\partial\,w_l} \right) \frac{\tilde{\sigma}_i^n(\lambda)}{\sigma_i^n(\lambda)} \qquad (3.50a)$$

$$+ \sum_{i=1}^{N} \rho_i c_{vi} \frac{2(v_{in} - \lambda)}{(\sigma_i^n(\lambda))^2}$$

$$\times \left((v_{in} - \lambda)\frac{\partial\,v_{in}}{\partial\,w_l}(\sigma_i^n(\lambda) - \tilde{\sigma}_i^n(\lambda)) - \left(a_i \frac{\partial\,a_i}{\partial\,w_l}\sigma_i^n(\lambda) - \overline{a}_i \frac{\partial\,\overline{a}_i}{\partial\,w_l}\tilde{\sigma}_i^n(\lambda) \right) \right),$$

$$B(\lambda) := \sum_{i=1}^{N} \rho_i c_{vi} \left(1 + 2(v_{in} - \lambda)^2 \left(\frac{1}{\tilde{\sigma}_i^n(\lambda)} - \frac{1}{\sigma_i^n(\lambda)} \right) \right) \frac{\tilde{\sigma}_i^n(\lambda)}{\sigma_i^n(\lambda)}. \qquad (3.50b)$$

provided that $B(\lambda(\boldsymbol{w})) \neq 0$.

Proof. First of all, we note that for any λ satisfying the non-resonance condition (3.18) we may rewrite the characteristic polynomial (3.8) as $p_N(\lambda) = \kappa_0(\lambda)r_N(\lambda)$ with polynomial κ_0 introduced in Lemma 3.7. The rational function r_N is defined as

$$r_N(\lambda) := \sum_{i=1}^{N} \rho_i c_{vi}(v_{in} - \lambda)\frac{\tilde{\sigma}_i^n(\lambda)}{\sigma_i^n(\lambda)},$$

where $\sigma_i^n(\lambda)$ is defined by (3.18) and, similarly, $\tilde{\sigma}_i^n(\lambda) := (v_{in} - \lambda)^2 - a_i^2$. If λ is a root of the polynomial p_N satisfying the non-resonance condition, then it is also a root of the rational function r_N.

By assumption $\lambda = \lambda(\boldsymbol{w})$ is an eigenvalue at non-resonance corresponding to the state $\boldsymbol{w}$ in the phase space spanned by the primitive variables $\boldsymbol{w}$; see equation (3.3). Since the eigenvalues depend continuously on the coefficients of the characteristic polynomial p_N, the function $\boldsymbol{w} \to \sigma_i^n(\lambda(\boldsymbol{w}))$ is continuous. Thus there exists a small neighborhood of $\boldsymbol{w}$ in phase space where the corresponding eigenvalues are also at non-resonance. Then the derivatives of the function $\boldsymbol{w} \to r_N(\lambda(\boldsymbol{w}))$ can be determined as

$$\frac{\partial\,r_N(\lambda(\boldsymbol{w}))}{\partial\,w_l} = A_{w_l}(\lambda(\boldsymbol{w})) - \frac{\partial\,\lambda(\boldsymbol{w})}{\partial\,w_l}B(\lambda(\boldsymbol{w}))$$

with A_{w_l} and B defined by (3.50). Note that $\sigma_i^n(\lambda) - \tilde{\sigma}_i^n(\lambda) = \overline{a}_i^2 - a_i^2$. Finally, the assertion follows because for any eigenvalue, i.e., root of the characteristic polynomial p_N, at non-resonance $r_N(\lambda(\boldsymbol{w})) = 0$. $\square$

By means of the derivatives of the eigenvalues and the right eigenvectors, see Lemma 3.10 and Proposition 2, respectively, we may now investigate the characteristic field.

PROPOSITION 4. Under the assumptions of Lemma 3.10 the characteristic field is determined by

$$B(\lambda(\boldsymbol{w}))\nabla_{\boldsymbol{w}}\lambda(\boldsymbol{w}) \cdot \boldsymbol{r}_\lambda(\boldsymbol{w})$$

$$= \sum_{l=1}^N \rho_l(v_{ln} - \lambda)\frac{\sigma_l^n(\lambda) + \overline{a}_l^2 - a_l^2}{(\sigma_l^n(\lambda))^2}\left(\frac{\partial c_{vl}}{\partial \rho_l}\frac{\partial p_l}{\partial T} + \sigma_l^n(\lambda)\frac{\partial c_{vl}}{\partial T}\right)$$

$$+ \sum_{l=1}^N \rho_l c_{vl}(v_{ln} - \lambda)\frac{\partial p_l}{\partial T}\frac{1}{(\sigma_l^n(\lambda))^3}\left(\frac{\partial (\overline{a}_l^2 - a_l^2)}{\partial \rho_l}\sigma_l^n(\lambda) + \frac{\partial \overline{a}_l^2}{\partial \rho_l}(\overline{a}_l^2 - a_l^2)\right)$$

$$+ 2\sum_{l=1}^N c_{vl}(v_{ln} - \lambda)^3\frac{\partial p_l}{\partial T}\frac{(\overline{a}_l^2 - a_l^2)}{(\sigma_l^n(\lambda))^3}$$

$$+ \sum_{l=1}^N \rho_l c_{vl}(v_{ln} - \lambda)\frac{1}{(\sigma_l^n(\lambda))^2}\left(\frac{\partial (\overline{a}_l^2 - a_l^2)}{\partial T}\sigma_l^n(\lambda) + \frac{\partial \overline{a}_l^2}{\partial T}(\overline{a}_l^2 - a_l^2)\right). \quad (3.51)$$

Proof. Since we are dealing with simple mixtures, see Section 2.2, the terms A_{w_l} simplify:

$$A_{\rho_l} = (v_{ln} - \lambda)\left(c_{vl} + \rho_l\frac{\partial c_{vl}}{\partial \rho_l} - 2\rho_l c_{vl}\left(\frac{a_l}{\tilde{\sigma}_l^n(\lambda)}\frac{\partial a_l}{\partial \rho_l} - \frac{\overline{a}_l}{\sigma_l^n(\lambda)}\frac{\partial \overline{a}_l}{\partial \rho_l}\right)\right)\frac{\tilde{\sigma}_l^n(\lambda)}{\sigma_l^n(\lambda)}, \quad (3.52a)$$

$$A_{v_{l,k}} = \rho_l c_{vl}\left(1 + 2(v_{ln} - \lambda)^2\left(\frac{1}{\tilde{\sigma}_l^n(\lambda)} - \frac{1}{\sigma_l^n(\lambda)}\right)\right)\frac{\tilde{\sigma}_l^n(\lambda)}{\sigma_l^n(\lambda)}n_k, \quad (3.52b)$$

$$A_T = \sum_{i=1}^N \rho_i(v_{in} - \lambda)\left(\frac{\partial c_{vi}}{\partial T} - 2c_{vi}\left(\frac{a_i}{\tilde{\sigma}_i^n(\lambda)}\frac{\partial a_i}{\partial T} - \frac{\overline{a}_i}{\sigma_i^n(\lambda)}\frac{\partial \overline{a}_i}{\partial T}\right)\right)\frac{\tilde{\sigma}_i^n(\lambda)}{\sigma_i^n(\lambda)}. \quad (3.52c)$$

By (3.25) we then compute for the characteristic field corresponding to the eigenvalue λ

$$B(\lambda(\boldsymbol{w}))\nabla_{\boldsymbol{w}}\lambda(\boldsymbol{w}) \cdot \boldsymbol{r}_\lambda(\boldsymbol{w}) = \sum_{l=1}^N (A_{\rho_l}, A_{v_{l,1}}, \dots, A_{v_{l,d}})\boldsymbol{r}_{\lambda,l} + A_T.$$

From the definition of $\sigma_l^n(\lambda)$, $\tilde{\sigma}_l^n(\lambda)$ and the sound speed (2.15) we deduce

$$\sigma_l^n(\lambda) - \tilde{\sigma}_l^n(\lambda) = a_l^2 - \overline{a}_l^2,$$

$$a_l\frac{\partial a_l}{\partial *}\sigma_n^l(\lambda) - \overline{a}_l\frac{\partial \overline{a}_l}{\partial *}\tilde{\sigma}_l^n(\lambda) = \frac{1}{2}\left(\frac{\partial (a_l^2 - \overline{a}_l^2)}{\partial *}\sigma_l^n(\lambda) + \frac{\partial \overline{a}_l^2}{\partial *}(a_l^2 - \overline{a}_l^2)\right), \quad * \in \{\rho_l, T\}.$$

Then after some further calculus we obtain (3.51). $\square$

Although the formula (3.51) is not very handy it might be helpful for a particular choice of fluids to determine the characteristic fields to a given eigenvalue, for instance in case of velocity equilibrium.

3.6. *Velocity equilibrium.* Of particular interest are states at velocity equilibrium, i.e.,

$$v_{in} = v \quad \forall\, i = 1, \ldots, N.$$

For these states we are able to determine the eigenvalues explicitly and determine the corresponding characteristic fields at least for a two-component mixture.

PROPOSITION 5. In case of velocity equilibrium and $N = 2$ there exist $2N + 1$ distinct roots of the characteristic polynomial (3.8) determined by

$$\lambda_0 = v, \; \lambda_{\pm,\pm} = v \pm \sqrt{-\frac{p}{2} \pm \sqrt{\left(\frac{p}{2}\right)^2 - q}} \tag{3.53}$$

with

$$p = -(\rho c_v)^{-1}(\rho_1 c_{v1}(a_1^2 + \overline{a}_2^2) + \rho_2 c_{v2}(a_2^2 + \overline{a}_1^2)), \; q = (\rho c_v)^{-1}(\rho_1 c_{v1} a_1^2 \overline{a}_2^2 + \rho_2 c_{v2} a_2^2 \overline{a}_1^2) \tag{3.54}$$

provided that

$$a_i^2 > \overline{a}_i^2 > 0 \quad \text{and} \quad c_{vi} > 0 \quad \forall\, i = 1, \ldots, N. \tag{3.55}$$

In particular, the roots (3.53) satisfy the non-resonance condition (3.18) if and only if the conditions (3.55) and $\overline{a}_1^2 \neq \overline{a}_2^2$ hold.

Proof. For a state in velocity equilibrium the characteristic polynomial (3.8) reduces to

$$p_N(\lambda) = \sum_{i=1}^{N} \rho_i c_{vi}(v - \lambda)((v - \lambda)^2 - a_i^2) \prod_{j=1, j \neq i}^{N} ((v - \lambda)^2 - \overline{a}_j^2). \tag{3.56}$$

Obviously, $\lambda = v$ is always a root. In case of $N = 2$ the remaining polynomial reduces to a polynomial of degree 4 that due to symmetry reduces to a quadratic polynomial for $\overline{\lambda} = (v - \lambda)^2$. From this the roots (3.53) can be determined. It remains to verify that both the discriminants are positive. For this purpose we check that

$$p^2 - 4q = (\rho c_v)^{-2} \left(\left(\rho_1 c_{v1}(a_1^2 - \overline{a}_2^2) - \rho_2 c_{v2}(a_2^2 - \overline{a}_1^2)\right)^2 + 4\rho_1 c_{v1} \rho_2 c_{v2}(a_1^2 - \overline{a}_1^2)(a_2^2 - \overline{a}_2^2) \right)$$
$$> 0.$$

Finally we have to verify that $-p - \sqrt{p^2 - 4q} > 0$. Since $p < 0$, this is equivalent to verify

$$q = (\rho c_v)^{-1} \left(\rho_1 c_{v1} a_1^2 \overline{a}_2^2 + \rho_2 c_{v2} a_2^2 \overline{a}_1^2\right) > 0.$$

This holds by assumption.

To verify the non-resonance condition (3.18) we first note that in the equilibrium case it reads $\sigma_k(\lambda) := (v - \lambda)^2 - \overline{a}_k^2$, $k = 1, \ldots, N$. Obviously, $\sigma_k(\lambda_0) \neq 0$ if $\overline{a}_k^2 \neq 0$ holds true. For the other roots, we observe that $\sigma_k(\lambda_{\pm,\pm}) = 0$ is equivalent to $\overline{a}_k^4 + \overline{a}_k^2 p + q = 0$. Rearranging terms we can rewrite this as $(-1)^k \rho_k c_{vk}(a_k^2 - \overline{a}_k^2)(\overline{a}_1^2 - \overline{a}_2^2)$. From this the assertion follows immediately. $\square$

Probably, this result can be extended to $N = 3$ proceeding similarly but determining the roots of a cubic polynomial for $\overline{\lambda} = (v - \lambda)^2$ that are known to be real. For the general case we easily conclude from (3.56)

PROPOSITION 6. In case of velocity equilibrium $\lambda_0 = v$ is a simple root and is at non-resonance. The remaining $2N$ roots of the polynomial p_N take the form $\lambda_{i,\pm} = v \pm \sqrt{z_i}$, $i = 1, \ldots, N$, for some $z_i > 0$ provided the hyperbolicity condition (2.16) holds.

To determine the corresponding characteristic fields we make the following observation.

REMARK 3.11. For λ_0 we obtain the estimate

$$B(\lambda_0) = \sum_{i=1}^{N} \rho_i c_{vi} \frac{a_i^2}{\overline{a}_i^2} > \sum_{i=1}^{N} \rho_i c_{vi} = \rho c_v > 0.$$

If all the roots $\lambda_{k,\pm}$, $k = 1, \ldots, N$, are at non-resonance, i.e., $z_i \neq \overline{a}_i^2$, then we obtain

$$B(\lambda_{k,\pm}) = \left((v - \lambda_{k,\pm}) \prod_{j=1}^{N} \sigma_j^n(\lambda_{k,\pm}) \right)^{-1} p_N(\lambda_{k,\pm}) + 2(v - \lambda_{k,\pm})^2 \sum_{i=1}^{N} \rho_i c_{vi} \frac{a_i^2 - \overline{a}_i^2}{(\sigma_i^n(\lambda_{k,\pm}))^2}$$
$$> 0,$$

because $p_N(\lambda_{k,\pm}) = 0$ and $a_i^2 > \overline{a}_i^2$. Hence, condition (3.50b) is satisfied in case of velocity equilibrium.

Finally, we conclude from Remark 3.11, Proposition 4, and Lemma 3.10 the following result.

PROPOSITION 7. Let the fluid be a mixture of stiffened gases. In case of velocity equilibrium the eigenvalue $\lambda_0 = v$ corresponds to a linearly degenerated field. The remaining eigenvectors $\lambda_{i,\pm} = v \pm \sqrt{z_i}$, $i = 1, \ldots, N$, are assumed to be at non-resonance. Then the corresponding characteristic fields are genuinely non-linear if

$$\sum_{l=1}^{N} \rho_l c_{vl}^2 (\gamma_l - 1)^2 \frac{(v - \lambda_{k,\pm})^4 - \overline{a}_l^4}{((v - \lambda_{k,\pm})^2 - \overline{a}_l^2)^4} \neq 0 \quad \forall \, k = 1, \ldots, N. \tag{3.57}$$

Proof. For a mixture of stiffened gases equation (3.51) simplifies to

$$B(\lambda(\boldsymbol{w})) \nabla_{\boldsymbol{w}} \lambda(\boldsymbol{w}) \cdot \boldsymbol{r}_\lambda(\boldsymbol{w}) = - \sum_{l=1}^{N} \rho_l c_{vl}^2 (\gamma_l - 1)^2 \frac{(v_{ln} - \lambda(\boldsymbol{w}))^3}{((v_{ln} - \lambda(\boldsymbol{w}))^2 - \overline{a}_l^2)^3} ((v_{ln} - \lambda(\boldsymbol{w}))^2 + \overline{a}_l^2).$$

For an equilibrium state $\boldsymbol{w}$ with $\lambda(\boldsymbol{w}) = \lambda_0$ or $\lambda(\boldsymbol{w}) = \lambda_{k,\pm}$ it holds that $B(\lambda(\boldsymbol{w})) \neq 0$ by assumption and Remark 3.11. Obviously, the right-hand side vanishes in case of $\lambda(\boldsymbol{w}) = \lambda_0$ whereas it is non-zero for $\lambda(\boldsymbol{w}) = \lambda_{k,\pm}$ because of (3.57). $\qquad \square$

4. Stiffness of chemical relaxation model. In a numerical calculation the time step size is restricted due to transport and the stiffness introduced by the chemical reactions. To investigate the latter we perform an operator splitting where we separate the fluid motion and the chemical reactions. Then the relaxation process is described by the ODE

$$\frac{d \rho_i}{d t} = \overline{r}_i(\bar{T}, \rho_1 \ldots, \rho_N), \quad \frac{d \rho_i \boldsymbol{v}_i}{d t} = \mathbf{0}, \quad \frac{d \rho e_{tot}}{d t} = \mathbf{0}, \tag{4.1}$$

or, in short form

$$\frac{d\,\boldsymbol{u}}{d\,t} = \boldsymbol{f}(\boldsymbol{u}) \tag{4.2}$$

with $\boldsymbol{u} = (\rho_1, \ldots, \rho_N, \rho_1\boldsymbol{v}_1^T, \ldots, \rho_N\boldsymbol{v}_N^T, \rho e_{tot})^T$, $\boldsymbol{f} = (\bar{r}_1, \ldots, \bar{r}_N, \boldsymbol{0}^T, 0)^T$, $\bar{r}_i = r_i(\boldsymbol{u})$, $\bar{T} = T(\boldsymbol{u})$.

The constraint of the time discretization is characterized by the largest absolute eigenvalue of the Jacobian $\partial\boldsymbol{f}/\partial\boldsymbol{u}$ that coincides with the largest eigenvalue of the matrix $\boldsymbol{R} := (d\bar{r}_i/d\rho_j)_{ij}$. Because of the conservation property (2.4) this matrix is a rank-1 matrix, and thus has one eigenvalue 0. In case of a single reaction the Jacobian exhibits at most one non-trivial eigenvalue; cf. (4.3) and (4.4). For two components the non-trivial eigenvalue is determined by $d\bar{r}_1/d\rho_1 - d\bar{r}_1/d\rho_2$. This eigenvalue is unchanged if there are other additional inert components, i.e., $\bar{r}_i = 0$, $i > 2$.

It remains to calculate the required derivatives. Assuming a single reaction and starting with

$$\bar{r}_i = \nu_i M_i R^f \left(1 - \exp\sum_{k=1}^{N}\left(\frac{\nu_k M_k}{R}\right)\left(\frac{\mu_k(\rho_k, \bar{T})}{\bar{T}}\right)\right) \tag{4.3}$$

we obtain for constant rate R^f

$$\frac{d\bar{r}_i}{d\rho_j} = (r_i - \nu_i R^f M_i)\sum_{k=1}^{N}\left(\frac{\nu_k M_k}{R}\right)\frac{d}{d\rho_j}\left(\frac{\mu_k(\rho_k, \bar{T})}{\bar{T}}\right). \tag{4.4}$$

Using the relations (2.10) a straightforward calculation gives

$$\frac{d}{d\rho_j}\left(\frac{\mu_k(\rho_k, \bar{T})}{\bar{T}}\right) = \begin{cases} -\frac{1}{T^2}\left(e_k + \frac{p_k}{\rho_k} - \frac{T}{\rho_k}\frac{\partial}{\partial T}p_k(\rho_k, T)\right)\frac{\partial\bar{T}}{\partial\rho_j}, & k \neq j, \\ \frac{1}{T\rho_j}\frac{\partial}{\partial\rho_j}p_j(\rho_j, T) - \frac{1}{T^2}\left(e_j + \frac{p_j}{\rho_j} - \frac{T}{\rho_j}\frac{\partial}{\partial T}p_j(\rho_j, T)\right)\frac{\partial\bar{T}}{\partial\rho_j}, & k = j. \end{cases}$$

Finally we obtain

$$\frac{d\bar{r}_i}{d\rho_j} = (r_i - \nu_i R^f M_i)$$

$$\times\left(\frac{\nu_j M_j}{R}\frac{1}{T\rho_j}\frac{\partial p_j(\rho_j, T)}{\partial\rho_j} - \frac{1}{T^2}\sum_{k=1}^{N}\frac{\nu_k M_k}{R}\left(e_k + \frac{p_k}{\rho_k} - \frac{T}{\rho_k}\frac{\partial}{\partial T}p_k(\rho_k, T)\right)\frac{\partial\bar{T}}{\partial\rho_j}\right).$$

For stiffened gases this expression simplifies to

$$\frac{d\bar{r}_i}{d\rho_j} = (r_i - \nu_i R^f M_i)\left(\frac{\nu_j M_j}{R}\frac{(\gamma_j - 1)c_j}{\rho_j} + \frac{1}{T^2}\sum_{k=1}^{N}\frac{\nu_k M_k}{R}\frac{(q_k + c_{vk}T)(q_j - \frac{1}{2}\boldsymbol{v}_j^2 + c_{vj}T)}{\rho c_v}\right).$$

REMARK 4.1. The rate R^f may depend on the states of the substances under consideration, e.g., on concentrations, on partial pressures, or on the temperature. There is some literature available on how to determine such rates; see for instance [2, Chapter 21] or [22]. Nevertheless, the computations are complicated and one needs to know

reaction constants, specific activation energies, etc. This is beyond the scope of this paper. Therefore for simplicity we choose different constant rates in our numerical examples.

For an example, we first consider a mixture of a water vapor and liquid water. The material parameters are chosen as in [23]; see Table 1. The exchange of mass between the phases correlates to a phase transition, where condensation is assumed to be the forward reaction

$$1(H_2O)_{vapor} \rightleftharpoons 1(H_2O)_{liquid}. \tag{4.5}$$
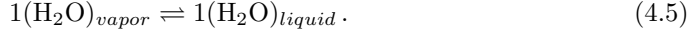
Accordingly we have $\nu_{vapor} = -1$ and $\nu_{liquid} = 1$. The initial state is chosen at rest with $p_{vapor} = 2 \cdot 10^5$ Pa, $p_{liquid} = 10^5$ Pa and $T = 298$ K. Because phase transition is a slow process we use a small forward reaction rate $R^f = 10^2$. We solve system (4.1) numerically using a fourth order Runge-Kutta scheme and obtain the results presented in Figure 1.

It can be observed that the density of liquid water increases whereas the density of water vapor decreases, i.e., vapor condensates, resulting in a temperature increase. The pressures of the fluids show a similar behavior as the densities. From a numerical point of view it is important to note that the stiffness of the relaxation system increases moderately by a factor of about 5 until the equilibrium state is reached.
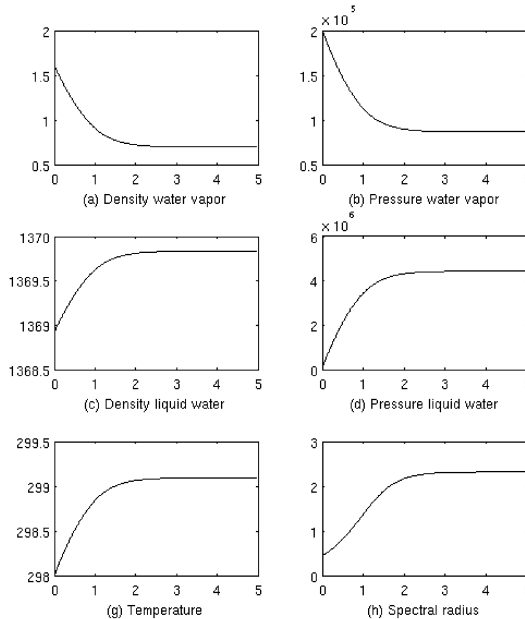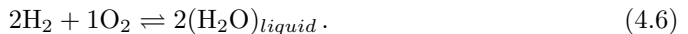

FIG. 1. Relaxation process 1 - Liquid-vapor phase transition

As a second example we consider a mixture of three components. The material parameters chosen are related to liquid water, oxygen, and hydrogen; see Table 1. The corresponding chemical reaction is the so-called oxyhydrogen reaction

$$2H_2 + 1O_2 \rightleftharpoons 2(H_2O)_{liquid}. \tag{4.6}$$

We observe that $\nu_{\mathrm{H_2}} = -2$, $\nu_{\mathrm{O_2}} = -1$, and $\nu_{\mathrm{H_2O}} = 2$. As before we choose an initial state at rest with $p_{\mathrm{H_2}} = 2 \cdot 10^5$ Pa, $p_{\mathrm{O_2}} = 10^5$ Pa, $p_{\mathrm{H_2O}} = 10^4$ Pa and $T = 298$ K. Since the process is a very fast chemical reaction, a large forward reaction rate $R^f = 10^5$ is used. The results are shown in Figure 2.
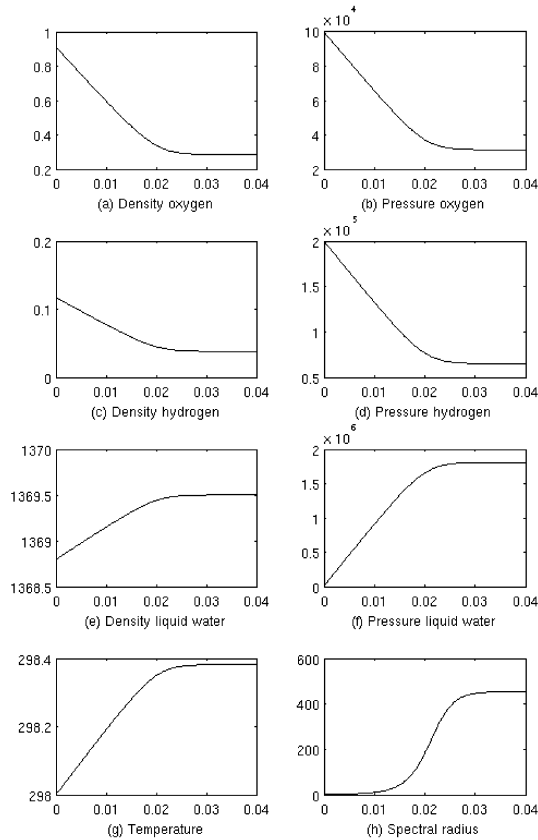

FIG. 2. Relaxation process 2 - Oxyhydrogen reaction

We observe that the density of liquid water increases whereas the density of oxygen and hydrogen decrease due to the recombination reaction resulting in a slight temperature increase. Again, the pressures of the fluids show a similar behavior as the densities. Obviously, the stiffness of the relaxation system increases significantly by a factor of about 500 until the equilibrium state is reached.

Both, the condensation process as well as the chemical reaction relax into an equilibrium state. Obviously the equilibrium state is achieved much faster for the oxyhydrogen reaction. This effect is mostly induced by the higher reaction rate R^f. As a consequence the Jacobian of (4.2) for this reaction exhibits a significantly larger spectral radius. This introduces a severe stiffness into the system and can lead to an additional time step restriction of the coupled system besides the CFL constraint.

5. Numerical results. In order to solve model (2.1) we apply a third order Runge-Kutta discontinuous Galerkin (RK-DG) method [5] to the inviscid system

$$\partial_t \boldsymbol{u} + \sum_{k=1}^{d} \partial_{x_k} \boldsymbol{F}_k(\boldsymbol{u}) = \boldsymbol{Q}(\boldsymbol{u}) \tag{5.1}$$

with conserved quantities $\boldsymbol{u}$, fluxes $\boldsymbol{F}_k$ and source $\boldsymbol{Q}$

$$\boldsymbol{u} = ((\rho_1, \rho_1 \boldsymbol{v}_1^T), \ldots, (\rho_N, \rho_N \boldsymbol{v}_N^T), \rho e_{tot})^T,$$
$$\boldsymbol{F}_k = (\boldsymbol{F}_{k,1}^T, \ldots, \boldsymbol{F}_{k,N}^T, F_{\rho e_{tot}})^T, \quad k = 1, \ldots, d,$$
$$\boldsymbol{Q} = (\boldsymbol{Q}_1^T, \ldots, \boldsymbol{Q}_N^T, 0)^T,$$

and partial fluxes and sources

$$\boldsymbol{F}_{k,i} = (\rho_i v_{k,i}, \rho_i v_{k,i} \boldsymbol{v}_i^T + p_i \boldsymbol{e}_k^T)^T, \quad i = 1, \ldots, N,$$
$$F_{\rho e_{tot}} = \sum_{i=1}^{N} \rho_i v_{i,k}(e_i + p_i/\rho_i + 0.5\boldsymbol{v}_i^2),$$
$$\boldsymbol{Q}_i = (r_i, \boldsymbol{f}_i^T)^T, \quad i = 1, \ldots, N.$$

We use polynomial elements of order $p = 3$ and a third order SSP-Runge-Kutta method with three stages for the time discretization. For the numerical flux and the limiter, we choose the local Lax-Friedrichs flux and the minmod limiter from [5], respectively. The time stepping is controlled by the CFL number. The performance of this RK-DG solver is enhanced by local multi-resolution based grid adaptation; see [16]. Details on the adaptive solver can be found in [13, 14].

The limiter is applied to the local characteristic variables. For this purpose we need to compute the left and right eigenvectors of the Jacobian of the projected flux $\boldsymbol{F}_n = \sum_{k=1}^{d} \boldsymbol{F}_k n_k$ in direction $\boldsymbol{n} \in \mathbb{R}^d$, $|\boldsymbol{n}| = 1$. Since the eigenvalues are not explicitly known we proceed as follows:

(1) Determine the eigenvalues of the *symmetric* matrix $\check{\boldsymbol{B}}_n = \boldsymbol{D}\tilde{\boldsymbol{B}}_n\boldsymbol{D}^{-1}$ defined in (3.12) with appropriate coefficients α_i and β_i by means of a numerical eigenvalue solver. Because of similarity transformations these coincide with the eigenvalues of the matrices $\boldsymbol{B}_n$ and $\tilde{\boldsymbol{B}}_n$ defined by (3.4) and (3.5), respectively. Note that in the multi-dimensional case ($d > 1$) the matrix $\boldsymbol{M}$ decouples, i.e., there exists a permutation matrix $\boldsymbol{P}$ such that

$$\boldsymbol{P}\check{\boldsymbol{B}}_n\boldsymbol{P}^{-1} = \begin{pmatrix} \check{\boldsymbol{B}}_R & & & \\ & v_{1n}\boldsymbol{I}_{d-1} & & \\ & & \ddots & \\ & & & v_{Nn}\boldsymbol{I}_{d-1} \end{pmatrix}.$$

Thus it suffices to determine the eigenvalues of the reduced matrix $\check{\boldsymbol{B}}_R$ coinciding with the roots of the characteristic polynomial (3.8). The reduced matrix can be determined from $\check{\boldsymbol{B}}_n$ by deleting the $((i-1)(d+1)+2+j)$-th column and row for $j = 1, \ldots, d-1$ and $i = 1, \ldots, N$.

(2) Check whether the eigenvalues of $\check{\boldsymbol{B}}_R$ are all simple roots and the non-resonance condition (3.18) holds. Then the left and right eigenvectors $\boldsymbol{l}$ and $\boldsymbol{r}$ of the matrix $\boldsymbol{B}_n$ can be computed according to (3.15), (3.25), and (3.35). Otherwise an iterative solver has to be applied to $\check{\boldsymbol{B}}_R$ to compute the eigenvectors numerically.

(3) Since by the variable transformation $\boldsymbol{u} = \boldsymbol{u}(\boldsymbol{w})$,

$$\boldsymbol{A}_n \equiv \frac{\partial \boldsymbol{F}_n(\boldsymbol{u})}{\partial \boldsymbol{u}} = \frac{\partial \boldsymbol{u}}{\partial \boldsymbol{w}} \boldsymbol{B}(\boldsymbol{u}(\boldsymbol{w})) \left(\frac{\partial \boldsymbol{u}}{\partial \boldsymbol{w}}\right)^{-1}$$

the left and right eigenvectors of the matrix $\boldsymbol{A}_n$ are determined as $\left(\frac{\partial \boldsymbol{u}}{\partial \boldsymbol{w}}\right)^{-T} \boldsymbol{l}$ and $\frac{\partial \boldsymbol{u}}{\partial \boldsymbol{w}} \boldsymbol{r}$, respectively.

For the computations we consider different Riemann problems for two- and three-component flows with and without phase transition or chemical reaction. The discontinuity in the initial data is located in the middle of the domain. The computational domain is given by $\Omega = [-1, 1]$ discretized by 10 cells on the coarsest level and using $L = 10$ levels of refinement. For the time discretization we choose a fixed CFL number of 0.1. Since we cannot construct explicitly the solution of the Riemann problem, we choose the discretization fine enough to ensure grid converged solutions.

5.1. *Example 1: Two-phase flow with phase transition.* First we consider a Riemann problem for a mixture of a water vapor and liquid water. The material parameters are chosen as in [23]; see Table 1. The exchange of mass between the phases correlates to a phase transition, where condensation is assumed to be the forward reaction (4.5). Since phase transition is a slow process we use a small value for the forward reaction rate: $R^f = 100$. The initial data are given in Table 2.

TABLE 2. Initial for data Example 1

	p_L [Pa]	v_L [m/s]	T_L [K]	p_R [Pa]	v_R [m/s]	T_R [K]
vapor	5×10^3	2	293	10^4	3	298
liquid	10^5	3	–	10^5	2	–

In Figure 3 we show the results for both computations with and without relaxation. We can distinguish five different waves: four waves move at approximately sound speed and one with flow velocity, probably corresponding to four acoustic waves and one contact wave as in case of a B-N model. The acoustic waves split in two pairs where the slow moving pair and the fast moving pair are only visible in the vapor phase and the liquid phase, respectively.

Taking into account phase transition does not change the wave structure but due to the reaction the states of the mixture are affected. Due to vaporization the density and the pressure in the vapor phase increase significantly whereas the respective quantities

in the liquid decrease slightly. Note that a change in the density of the liquid is hardly visible because it is about 4–5 orders of magnitude larger than the density of the vapor, i.e., a small amount of vaporizing liquid increases the amount of vapor significantly. Correspondingly, the vapor velocity decreases when the acoustic wave has passed whereas the liquid velocity is hardly affected.
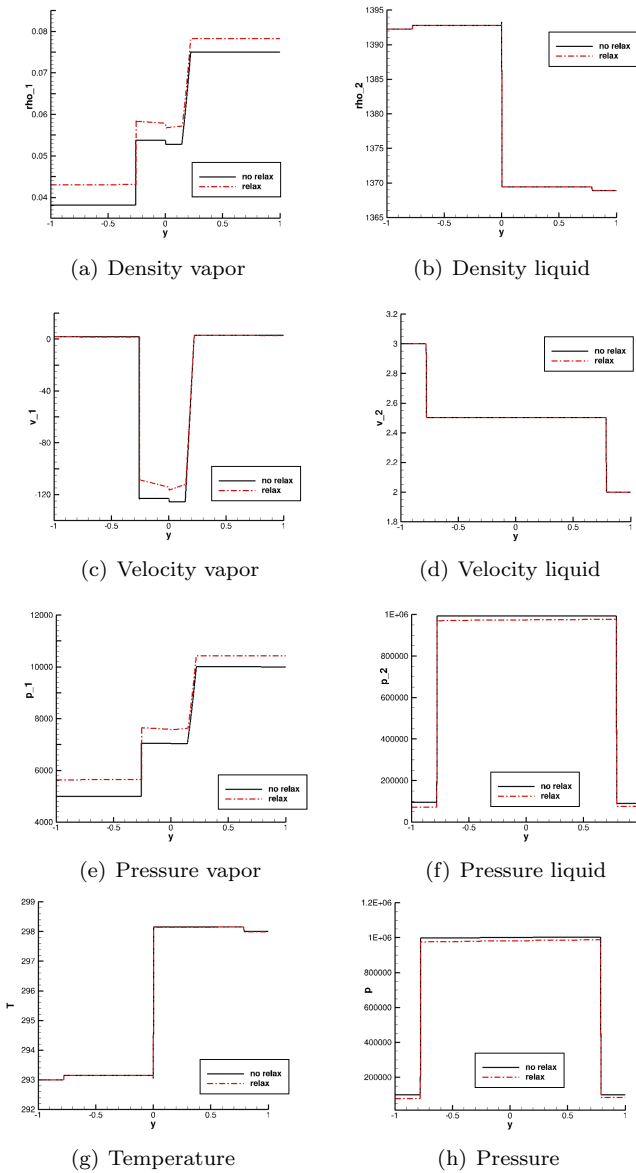

(a) Density vapor

(b) Density liquid

(c) Velocity vapor

(d) Velocity liquid

(e) Pressure vapor

(f) Pressure liquid

(g) Temperature

(h) Pressure

FIG. 3. Example 1 - two-phase flow with (black, solid) and without (red, dash-dot) phase transition, $t = 6 \times 10^{-4}s$.

These results meet the expectations due to the fact that water is a liquid at atmospheric pressure in the present temperature regime.

5.2. *Example* 2: *Three-phase flow with chemical reaction.* Next we consider a mixture of three components. The material parameters chosen are related to liquid water, oxygen and hydrogen; see Table 1. The corresponding chemical reaction is the so-called
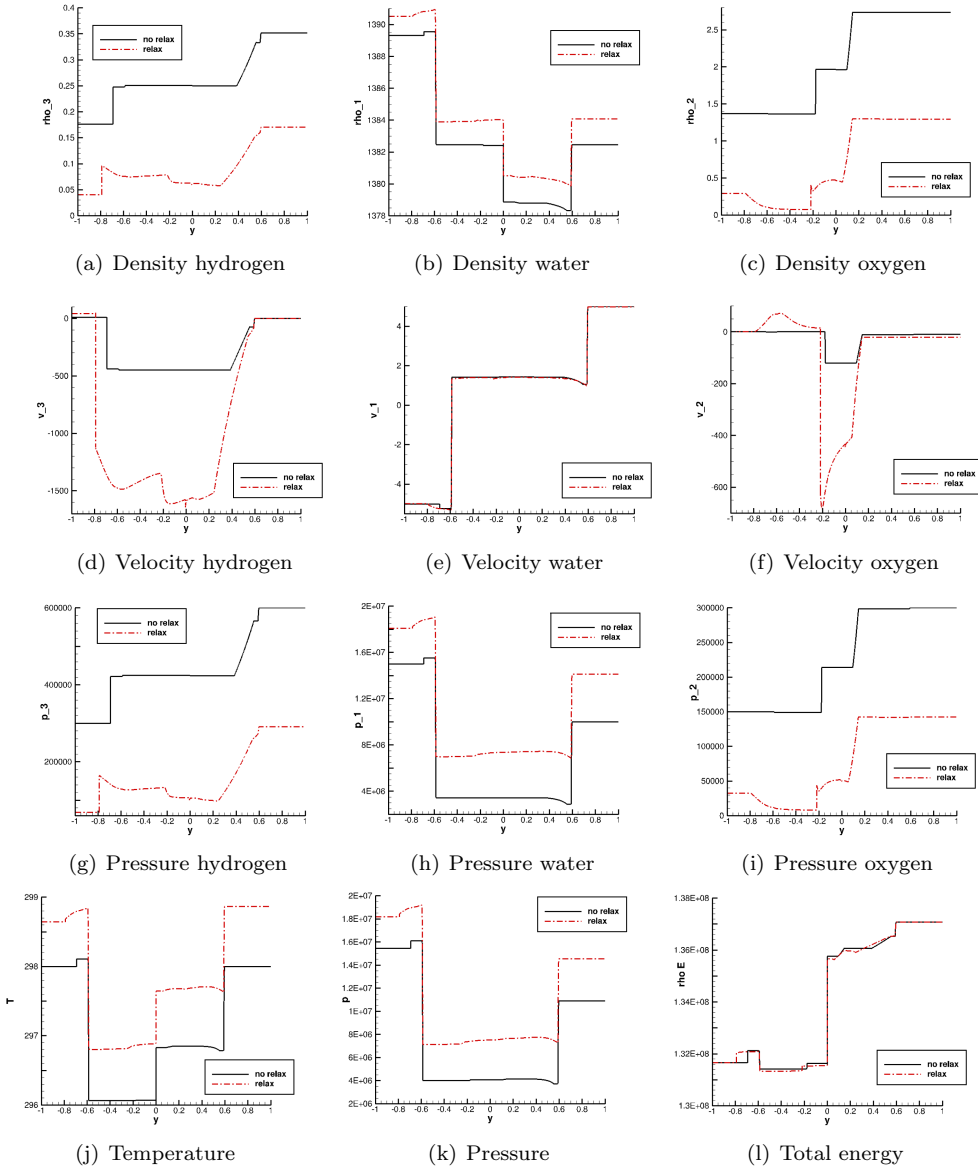

(a) Density hydrogen   (b) Density water   (c) Density oxygen

(d) Velocity hydrogen   (e) Velocity water   (f) Velocity oxygen

(g) Pressure hydrogen   (h) Pressure water   (i) Pressure oxygen

(j) Temperature   (k) Pressure   (l) Total energy

FIG. 4. Example 2 - three-component flow with (black, solid) and without (red, dash-dot) chemical reaction, $t = 4.5 \times 10^{-4} s$.

oxyhydrogen reaction (4.6). Since this is a very fast chemical reaction, we choose a large reaction rate: $R^f = 10^5$. The Riemann initial data are summarized in Table 3.

TABLE 3. Initial data for Example 2

	p_L [Pa]	v_L [m/s]	T_L [K]	p_R [Pa]	v_R [m/s]	T_R [K]
oxygen	1.5×10^5	0	298	3×10^5	-10	298
hydrogen	3×10^5	10	–	6×10^5	0	–
water	1.5×10^7	-5	–	10^7	5	–

In Figure 4 we show the results for both computations with and without relaxation. We can distinguish seven different waves, see the total energy of the mixture: six waves move at approximately sound speed and one with flow velocity, probably corresponding to six acoustic waves and one contact wave as in case of a B-N model. Again, not all waves are present in each component.

Taking into account phase transition does not change the wave structure but due to the fast reaction the states of the mixture are strongly affected. Due to the forward reaction the density and the pressure for oxygen and hydrogen decrease whereas the density of water increases. On the other hand, the oxygen and hydrogen are significantly accelerated when the fastest of the acoustic waves has passed whereas the water velocity is hardly affected.

6. Conclusion. We investigated the class-II-type recently introduced by Bothe and Dreyer in [4]. Here we confine ourselves to simple mixtures. This model has several advantages in comparison to classical Baer-Nunziato type models: (i) Each component can undergo a phase transition or a chemical reaction. In the Bothe-Dreyer approach phase transitions are modeled as a chemical reaction, where the exchange terms are modeled by stoichiometric relations. (ii) Due to the algebraic nature of the exchange terms for simple mixtures the system can be rewritten in divergence form and it is conservative. Thus, there exists an entropy-entropy flux pair and the system can be symmetrized according to Godlewski and Raviart [15]. (iii) Volume fractions or artificial interfacial quantities have not yet been introduced. (iv) The modeling of source terms starts from thermodynamics. Thus, it is ensured by construction that the model is thermodynamically consistent, i.e., the second law of thermodynamics is satisfied. All closure conditions can be derived from the entropy principle of thermodynamics; cf. [4]. (v) The extension of the model to more constituents or the allowance of further reactions is an easy task. This is a notable difference to B-N type models; cf. [21]. In particular, the system is also well defined for vanishing constituents.

In the focus of the present work has been the investigation of hyperbolicity of the model. Although we cannot give explicitly the eigenvalues of the flux Jacobian, we constructed an eigenvector basis where the eigenvalues enter as parameters provided the non-resonance condition holds. The eigenvalues can be computed numerically for a given

state. This is very useful in numerical schemes to locally decouple the system and is used for instance, to perform flux vector splitting, limiting, reconstruction, etc. Thus, a classical DG discretization could be applied to our model and computations for two- and three-component flows with and without phase transition have been performed.

Since we do not *explicitly* know the eigenvalues nor the corresponding right eigenvectors, we cannot investigate the characteristic fields. We only can characterize the fields to a given state once the eigenvalue has been computed either by numerical tools or is known. Thus, we cannot conclude that there exists a unique solution of the Riemann problem. Also classical results known for single component fluids could not be confirmed for multi-component fluids: (i) For a single component fluid it is known that the pressure is a Riemann invariant across a contact discontinuity. In our model, it turned out that in general neither the mixture pressure nor the partial pressures are invariants. (ii) The same holds true for the mixture velocity and the partial velocities. (iii) Similarly, one can verify that neither the partial entropy nor the mixture entropy are invariants. Note that in the single component case the entropy is an invariant across a rarefaction wave. (iv) For multiple eigenvalues we could prove that the mixture temperature is a Riemann invariant across the corresponding fields in our model.

Our current results open several interesting perspectives for future investigations:

- Since our class-II-model exhibits severe problems in the calculation of the eigenvalues and eigenvectors, we want to consider also the reduced class-I-model composed of balance laws for partial densities, mixture momentum, and mixture energy. Here we hope to find the eigenvalues and eigenvectors explicitly because for a two-component model the characteristic polynomial is of degree 4.
- In the literature numerous models are available to model two-phase or multi-component flows. However, a thorough comparison of different model classes is missing. Therefore we would like to compare our class-II-model with a reduced B-N model composed of balance laws for volume fractions, partial densities, partial momenta, and a total mixture energy.
- Our model has been embedded in a parallel, adaptive, multi-dimensional DG solver. This allows us to investigate more complex applications also in several space dimensions.
- In contrast to B-N type models where relaxation times are typically assumed to be infinite, the choice of the relaxation time is a free parameter in our model related to the forward reaction rates. For our computations we used constant rates. Further investigations are needed to derive realistic reaction rates depending on the state.

References

[1] R. Abgrall and S. Karni, *A comment on the computation of non-conservative products*, J. Comput. Phys. **229** (2010), no. 8, 2759–2763. MR2595792
[2] P. Atkins and J. de Paula, *Physical Chemistry*, OUP Oxford, 2014.
[3] M. R. Baer and J. W. Nunziato, *A two-phase mixture theory for the deflagration-to-detonation transition (DDT) in reactive granular materials*, Int. J. Multiphase Flows, **12** (1986), pp. 861–889.
[4] D. Bothe and W. Dreyer, *Continuum thermodynamics of chemically reacting fluid mixtures*, Acta Mech. **226** (2015), no. 6, 1757–1805. MR3347503

[5] B. Cockburn and C.-W. Shu, *The Runge-Kutta discontinuous Galerkin method for conservation laws. V. Multidimensional systems*, J. Comput. Phys. **141** (1998), no. 2, 199–224. MR1619652

[6] G. Dal Maso, P. G. Lefloch, and F. Murat, *Definition and weak stability of nonconservative products*, J. Math. Pures Appl. (9) **74** (1995), no. 6, 483–548. MR1365258

[7] P. Deuflhard and A. Hohmann, *Numerische Mathematik* (German), de Gruyter Lehrbuch. [de Gruyter Textbook], Walter de Gruyter & Co., Berlin, 1991. Eine algorithmisch orientierte Einführung. [An algorithmically oriented introduction]. MR1197354

[8] D. Drew, *Mathematical modeling of two-phase flow*, Ann. Rev. Fluid Mech., 15 (1983), pp. 261–291.

[9] D. A. Drew and S. L. Passman, *Theory of multicomponent fluids*, Applied Mathematical Sciences, vol. 135, Springer-Verlag, New York, 1999. MR1654261

[10] W. Dreyer and F. Duderstadt, *Towards the thermodynamic modeling of nucleation and growth of liquid droplets in single crystals*, Free boundary problems (Trento, 2002), Internat. Ser. Numer. Math., vol. 147, Birkhäuser, Basel, 2004, pp. 113–130. MR2044568

[11] W. Dreyer, F. Duderstadt, M. Hantke, and G. Warnecke, *Bubbles in liquids with phase transition. Part 1. On phase change of a single vapor bubble in liquid water*, Contin. Mech. Thermodyn. **24** (2012), no. 4-6, 461–483. MR2992847

[12] W. Dreyer, C. Guhlke, and R. Müller, *A new perspective on the electron transfer: Recovering the Butler–Volmer equation in non-equilibrium thermodynamics*, WIAS preprint 2204.

[13] N. Gerhard, F. Iacono, G. May, S. Müller, and R. Schäfer, *A high-order discontinuous Galerkin discretization with multiwavelet-based grid adaptation for compressible flows*, J. Sci. Comput. **62** (2015), no. 1, 25–52. MR3295028

[14] N. Gerhard and S. Müller, *Adaptive multiresolution discontinuous Galerkin schemes for conservation laws: multi-dimensional case*, Comput. Appl. Math. **35** (2016), no. 2, 321–349. MR3514813

[15] E. Godlewski and P.-A. Raviart, *Numerical approximation of hyperbolic systems of conservation laws*, Applied Mathematical Sciences, vol. 118, Springer-Verlag, New York, 1996. MR1410987

[16] N. Hovhannisyan, S. Müller, and R. Schäfer, *Adaptive multiresolution discontinuous Galerkin schemes for conservation laws*, Math. Comp. **83** (2014), no. 285, 113–151. MR3120584

[17] K. Hutter and K. Jöhnk, *Continuum methods of physical modeling*, Springer-Verlag, Berlin, 2004. Continuum mechanics, dimensional analysis, turbulence. MR2060165

[18] A. Kapila, R. Menikoff, J. Bdzil, S. Son, and D. Stewart, *Two-phase modelling of DDT in granular materials: Reduced equations*, Phys. Fluid **13** (2001), 3002–3024.

[19] L. D. Landau and E. M. Lifshitz, *Statistical physics*, Course of Theoretical Physics. Vol. 5. Translated from the Russian by E. Peierls and R. F. Peierls, Pergamon Press Ltd., London-Paris; Addison-Wesley Publishing Company, Inc., Reading, Mass., 1958. MR0136378

[20] R. Menikoff and B. J. Plohr, *The Riemann problem for fluid flow of real materials*, Rev. Modern Phys. **61** (1989), no. 1, 75–130. MR977944

[21] S. Müller, M. Hantke, and P. Richter, *Closure conditions for non-equilibrium multi-component models*, Contin. Mech. Thermodyn. **28** (2016), no. 4, 1157–1189. MR3513192

[22] M. J. Pilling and P. W. Seakins, *Reaction Kinetics*. Oxford Science Publications, 1999.

[23] A. Zein, *Numerical methods for multiphase mixture conservation laws with phase transition*, Ph.D. thesis, Otto-von-Guericke University, Magdeburg, 2010.

[24] A. Zein, M. Hantke, and G. Warnecke, *Modeling phase transition for compressible two-phase flows applied to metastable liquids*, J. Comput. Phys. **229** (2010), no. 8, 2964–2998. MR2595804