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Entropy growth and entropy production rate in binary mixture shock waves

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Entropy growth and entropy production rate are analyzed in the stationary shock waves in a multitemperature model of a binary mixture of gases. The model is developed within the framework of extended thermodynamics. It is shown that the entropy density of the mixture increases monotonically through the shock profile, whereas the entropy densities of the constituents may not be monotonic. The analysis of entropy growth rate distinguished the contributions of momentum exchange (diffusion) and internal energy exchange between the constituents, and showed a substantially larger contribution of diffusion. At the same time, it is shown that the entropy production rates of the constituents may not be non-negative throughout the whole shock structure.

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I. INTRODUCTION

Entropy growth is a distinguishing feature of irreversible processes [1]. Once the system departs from the equilibrium state, it enters into an irreversible process and entropy growth may serve as a kind of measure of the "distance" between equilibrium and nonequilibrium state.

The local form of entropy inequality, as a physical law, has a distinguished role in modern continuum physics. The mathematical model of a thermodynamic process consists of physical balance laws, valid for any physical system, and constitutive relations that describe the response of the medium. The model is said to be thermodynamically consistent if the constitutive relations are chosen in such a way that the entropy inequality is satisfied for any thermodynamic process. The choice of the constitutive relations is dictated by the non-negativity of entropy production rate [1,2].

The status of entropy density is a bit different—its structure is subject to fundamental assumptions of the particular theoretical approach. An instructive review is given by Hutter [3]. Without any ambition to provide a comprehensive review of possible definitions of entropy, we shall stick only to those that are the most important to our study. Classical thermodynamics of irreversible processes is based upon the assumption of local thermodynamic equilibrium [1], thus implying that Gibbs' relation is locally valid. It results in the entropy density in the same form as classical equilibrium entropy. On the other hand, the kinetic theory of gases [4] leads to the entropy density defined through the velocity distribution function, which, in turn, for local Maxwellian distribution coincides with the equilibrium macroscopic entropy. A deeper insight into subtle relations between the macroscopic entropy density and statistical mechanics considerations is recently given by Goldstein and Lebowitz [5]. Nevertheless, other approaches to nonequilibrium processes emerged. Rational thermodynamics [6] provided a conceptual framework, whereas rational extended thermodynamics [7,8] led to quite general results by relaxing certain traditional assumptions. Namely, it assumed that entropy flux and entropy density are constitutive quantities determined through the closure process, rather than quantities whose structure is prescribed beforehand. This is achieved through the application of Liu's method of multipliers [9], which led to a more general form of entropy density comprising the quantities that vanish in (local) equilibrium. Although the above-mentioned approaches are the most important for our study, there are other ones as well that constitute the set of modern theory of nonequilibrium processes. They are presented by Maugin [10], Berezovski and Ván [11], and Öttinger [12]. Apart from these treatises, a nice overview of the exploitation of the entropy principle in modern nonequilibrium theories is given by Cimmelli *et al.* [13]. In the case of mixtures, a comprehensive analysis of entropy principle is made by Giovangigli [14], while an extended theory of mixtures is thoroughly discussed in [7,8,15].

The local form of the entropy balance law permits the flow, increase, or decrease of the entropy density, although the local entropy production rate is non-negative [6]. However, in certain irreversible processes the (non-)increase of entropy density is regarded as controversial. A typical example is the one-dimensional shock structure problem for the Navier-Stokes-Fourier model of a gas. Morduchow and Libby [16,17] showed that the entropy density profile is not monotonic within the continuous profile of the shock wave. In fact, it was proved by Serrin and Whang [18] that the nonmonotonic profile of the entropy density is consistent with the Navier-Stokes-Fourier model. As recently pointed out by Margolin *et al.* [19] and Margolin [20], this controversy may be attributed to the fact that Morduchow and Libby [17] computed

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the equilibrium entropy, in accordance with the assumption of local thermodynamic equilibrium, whereas shock waves are paradigmatic nonequilibrium processes. Since equilibrium entropy failed to obey the entropy growth condition pointwise, another definition of the entropy for nonequilibrium processes is sought for. The answer pled in [19,20], which leads to a monotonically increasing entropy density profile, is that the nonequilibrium entropy based upon the Boltzmann kinetic definition of entropy has to be used. For its computation one has to use the approximate velocity distribution function of Grad's type, in conjunction with appropriate constitutive relations. The results which have similar flavor were obtained by Zinner and Öttinger [21] in the analysis of 13 moment equations for the shock tube problem. It has to be noted that higher order entropies similar to the one used in [19,20], were exploited by Giovangigli [22] as kinetic entropy estimators for macroscopic models and by Torrilhon [23] for the derivation of the *H*-theorem for nonlinear regularized 13 moments equations.

The aim of this paper is to analyze the entropy growth and entropy production rate within the shock profiles in the multitemperature (MT) model of binary mixture developed within rational extended thermodynamics [7,24,25]. Three particular goals of the study are (1) to show that extended thermodynamics provides a proper definition of nonequilibrium entropy of the mixture whose growth is indisputable through the shock profile; (2) to analyze the entropy production rate within the profile; and (3) to analyze the entropy growth and entropy production rate from the point of view of constituents, and distinguish the mechanical (diffusion) and thermal (energy exchange) contributions in it. In this endeavor we shall rely on the huge database of shock profiles, presented partially by Madjarević *et al.* [26], to carefully analyze the entropy growth of the constituents and its correspondence to certain peculiar features of the MT shock profiles, such as temperature overshoot.

The paper is organized as follows. In Sec. II a brief overview of the basic principles of extended thermodynamics of mixtures will be given, along with the governing equations for the MT mixture. It will also contain the shock structure equations that will be solved numerically in a subsequent analysis. Section III is devoted to the entropy balance law in the MT mixture. The structure of the entropy balance law will be enlightened from the point of view described in Sec. II. Taking advantage of the structural properties of the MT model, we shall derive the entropy balance law for the mixture, as well as the entropy balance laws for the constituents. Section IV contains the main results—numerically computed profiles of the shock waves in a binary MT mixture—and their analysis. It is focused on two issues. First, it shows that the entropy density of the mixture grows monotonically within the shock profile. It may not be surprising if one takes into account that we are dealing with a mixture of Euler fluids, i.e., without internal dissipation of viscous or heat conducting type. However, profiles of the constituents' entropy densities are apparently nonmonotonic, which provides a new insight into analysis of the entropy growth. Second, the entropy production rate consists of two contributions—mechanical (momentum exchange due to diffusion) and thermal (energy exchange due to temperature difference)—and it will be shown that the mechanical one strongly prevails over the thermal one. It will also be shown that entropy production rates for the constituents may not be non-negative throughout the shock profile. The paper is concluded in Sec. V with a recap of the results and an indication of possible further steps in the analysis.

II. GOVERNING EQUATIONS OF MT MIXTURE

The basis for the multitemperature model of mixtures is laid within the framework of rational thermodynamics, through the metaphysical principles. This was exposed in detail in [6,24,25]. For conceptual reasons we shall give a brief overview of the model, and put it into a broader context. After that, the shock structure equations for a binary mixture will be given.

A. Balance laws for MT mixture

Mixtures are media with identifiable constituents. For each constituent, labeled $\alpha = 1, \ldots, n$, we may write the balance laws of mass, momentum, and energy, taking into account their mutual interaction through the source terms:

$$\begin{aligned}
&\frac{\partial \rho_\alpha}{\partial t} + \operatorname{div}(\rho_\alpha \mathbf{v}_\alpha) = \tau_\alpha,\\
&\frac{\partial}{\partial t}(\rho_\alpha \mathbf{v}_\alpha) + \operatorname{div}(\rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha - \mathbf{t}_\alpha) = \mathbf{m}_\alpha,\\
&\frac{\partial}{\partial t}\left(\frac{1}{2}\rho_\alpha v_\alpha^2 + \rho_\alpha \varepsilon_\alpha\right)\\
&\quad + \operatorname{div}\left\{\left(\frac{1}{2}\rho_\alpha v_\alpha^2 + \rho_\alpha \varepsilon_\alpha\right)\mathbf{v}_\alpha - \mathbf{t}_\alpha \mathbf{v}_\alpha + \mathbf{q}_\alpha\right\} = e_\alpha,
\end{aligned} \tag{1}$$

where standard notation for the field variables is used. On the other hand, the motion of the mixture is governed by the same equations as is a single body—conservation laws of mass, momentum, and energy. To that end, the source terms must obey the following restrictions:

$$\sum_{\alpha=1}^{n} \tau_\alpha = 0, \quad \sum_{\alpha=1}^{n} \mathbf{m}_\alpha = \mathbf{0}, \quad \sum_{\alpha=1}^{n} e_\alpha = 0. \tag{2}$$

The conservation laws for the whole mixture are then recovered by summation of the balance laws (1):

$$\begin{aligned}
&\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{v}) = 0,\\
&\frac{\partial}{\partial t}(\rho \mathbf{v}) + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v} - \mathbf{t}) = \mathbf{0},\\
&\frac{\partial}{\partial t}\left(\frac{1}{2}\rho v^2 + \rho\varepsilon\right) + \operatorname{div}\left\{\left(\frac{1}{2}\rho v^2 + \rho\varepsilon\right)\mathbf{v} - \mathbf{t}\mathbf{v} + \mathbf{q}\right\} = 0,
\end{aligned} \tag{3}$$

for the properly defined state variables and nonconvective fluxes:

$$\rho = \sum_{\alpha=1}^{n} \rho_\alpha, \quad \mathbf{v} = \frac{1}{\rho}\sum_{\alpha=1}^{n} \rho_\alpha \mathbf{v}_\alpha, \quad \mathbf{u}_\alpha = \mathbf{v}_\alpha - \mathbf{v},$$

$$\varepsilon_I = \frac{1}{\rho}\sum_{\alpha=1}^{n} \rho_\alpha \varepsilon_\alpha, \quad \varepsilon = \varepsilon_I + \frac{1}{2\rho}\sum_{\alpha=1}^{n} \rho_\alpha u_\alpha^2,$$

$$\mathbf{t} = \sum_{\alpha=1}^{n}(\mathbf{t}_\alpha - \rho_\alpha \mathbf{u}_\alpha \otimes \mathbf{u}_\alpha),$$

$$\mathbf{q} = \sum_{\alpha=1}^{n}\left\{\mathbf{q}_\alpha + \rho_\alpha\left(\varepsilon_\alpha + \frac{1}{2}u_\alpha^2\right)\mathbf{u}_\alpha - \mathbf{t}_\alpha\mathbf{u}_\alpha\right\}. \tag{4}$$

In the sequel, it will be assumed that constituents of the mixture are nonreacting Euler fluids, neither viscous, nor heat conducting:

$$\tau_\alpha = 0, \quad \mathbf{t}_\alpha = -p_\alpha\mathbf{I}, \quad \mathbf{q}_\alpha = \mathbf{0}. \tag{5}$$

Partial pressures p_α and specific internal energies ε_α are assumed to obey thermal and caloric equations of state of ideal gases:

$$p_\alpha = \rho_\alpha\frac{k_\mathrm{B}}{m_\alpha}T_\alpha, \quad \varepsilon_\alpha = \frac{k_\mathrm{B}T_\alpha}{m_\alpha(\gamma_\alpha - 1)} = c_{V_\alpha}T_\alpha. \tag{6}$$

Finally, the average temperature T is defined using the definition $(4)_4$ of the intrinsic specific internal energy in equilibrium [27] and caloric equations of state $(6)_2$:

$$\left(\sum_{\alpha=1}^{n}\rho_\alpha c_{V\alpha}\right)T = \sum_{\alpha=1}^{n}\rho_\alpha c_{V\alpha}T_\alpha. \tag{7}$$

The source terms are determined in accordance with fundamental principles of extended thermodynamics—Galilean invariance of governing equations and entropy principle. The former dictates the velocity dependence of the source terms:

$$\mathbf{m}_b = \hat{\mathbf{m}}_b; \quad e_b = \hat{e}_b + \hat{\mathbf{m}}_b\cdot\mathbf{v}, \quad b = 1,\ldots,n-1, \tag{8}$$

where $\hat{\mathbf{m}}_b$ and $\hat{e}_b$ are velocity-independent parts. Their structure is determined by the entropy principle:

$$\hat{\mathbf{m}}_b = -\sum_{c=1}^{n-1}\psi_{bc}(\mathbf{w})\left(\frac{\mathbf{u}_c}{T_c} - \frac{\mathbf{u}_n}{T_n}\right),$$

$$\hat{e}_b = -\sum_{c=1}^{n-1}\theta_{bc}(\mathbf{w})\left(-\frac{1}{T_c} + \frac{1}{T_n}\right), \tag{9}$$

where $\psi_{bc}(\mathbf{w})$ and $\theta_{bc}(\mathbf{w})$ are positive semidefinite matrix functions of objective quantities $\mathbf{w}$. For details of the analysis one may consult [24,25,28].

Since (1) and (3) constitute the system of equations whose number exceeds the number of field variables of an n-component mixture, it is common to choose the governing equations in the following way: (a) conservation laws (3) for the mixture and (b) balance laws (1) for $n-1$ constituents. Balance laws for one constituent, say n, are dropped from the list.

It is important to note that the nonequilibrium state of the MT mixture is characterized by the presence of diffusion velocities $\mathbf{u}_\alpha = \mathbf{v}_\alpha - \mathbf{v}$, and diffusion temperatures $\Theta_\alpha = T_\alpha - T$. Their analysis for processes in the neighborhood of the local equilibrium state was carefully performed in [27,29,30].

The final remark is about the definitions of state variables (4). They are based upon the mass fractions, but they are not unique. In fact, in diffusion problems studied in chemical engineering, as well as in numerical models, the use of volume or molar fractions is more frequent. Our choice was motivated by the standard definitions used in rational thermodynamics [6] and the kinetic theory of gases [4]. They are also common in the framework of extended thermodynamics [7] and facilitated the use of an extensive database of numerical simulations performed in our previous study [26]. For possible comparison with the results of other studies, we refer to [31], where different definitions of state variables were provided, along with transformation formulas.

B. Broader context and applicability of the model

At first sight, the MT model of mixtures may be regarded as quite unusual in the macroscopic setting, whereas in the kinetic theory of gases it appears as natural. Extended thermodynamics fills this space in between as a macroscopic theory that tends to bridge the gap between macro- and mesoscale, at which Boltzmann-like equations are valid (see [7,8]). In a recent study [32] the MT model was thoroughly studied from the kinetic theory point of view, and properly related to the MT equations obtained in the framework of extended thermodynamics. With this relation in mind, it is a natural intention to apply the MT model to highly nonequilibrium processes. To that end, it was successfully used in the analysis of shock structure in nonreacting mixtures [26,33], where the difference of the constituent's temperatures is attributed to the large discrepancy in atomic masses. Its applicability was also tested on a Zel'dovich-von Neumann-Döring (ZND) detonation wave [34], where the temperature difference appeared as a consequence of a large initial discrepancy in concentrations of reactants and products of chemical reaction. The MT approach is also applicable to nonequilibrium processes in a somewhat different setting—single polyatomic gas where rotational and vibrational temperatures are taken into account [35].

This brief review of possible applications of the MT model opens the perspective for its further contextualization, especially within chemically reacting mixtures. To that end, we would like to mention the possibility of its application to the ignition of reactive mixtures by the shock impingement. Being a proper nonequilibrium process, it would be of interest to discuss it from the MT point of view and to analyze the behavior of the entropy of the constituents in this context. Recent studies that treat the problem from theoretical [36], numerical [37], and experimental [38] viewpoints, provide a nice framework for possible extension by the use of MT assumption.

C. State variables in binary MT mixture

Thermodynamic processes in the MT model of binary gaseous mixture are governed by the conservation laws for the mixture and balance laws for one constituent, say 1. Therefore, it is natural to choose the density ρ, the velocity $\mathbf{v}$, and the temperature T of the mixture as field variables. However, for further analysis, instead of corresponding field variables ρ_1, $\mathbf{v}_1$, and T_1 for the constituent, it is more convenient to use the following state variables:

$$c = \frac{\rho_1}{\rho}; \quad \mathbf{J} = \rho_1\mathbf{u}_1 = -\rho_2\mathbf{u}_2; \quad \Theta = T_2 - T_1, \tag{10}$$

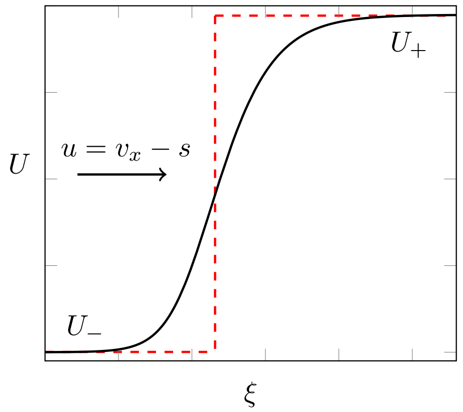

FIG. 1. Stationary shock structure: shock wave [red (dashed)] and shock structure [black (solid)]; U represents the generic state variable; U_- and U_+ are upstream and downstream equilibrium values; $u = v_x - s$ is the relative speed of the gas with respect to the stationary shock.

where c is the mass concentration, $\mathbf{J}$ is the diffusion flux, and Θ is the temperature difference. Furthermore, the analysis will be restricted to the mixture of monatomic gases, $\gamma_1 = \gamma_2 = \gamma = 5/3$. Consequently, the total pressure p and the intrinsic specific internal energy ε_I read

$$p = p_1 + p_2 = \rho \frac{k_B}{m} T; \quad \varepsilon_I = \frac{k_B}{m(\gamma - 1)} T, \tag{11}$$

where the average atomic mass $m = m(c)$ is introduced:

$$\frac{1}{m} = \frac{c}{m_1} + \frac{1-c}{m_2}. \tag{12}$$

Finally, starting from (7) and introducing the mass ratio μ,

$$\mu = \frac{m_1}{m_2}, \quad 0 < \mu \leqslant 1, \tag{13}$$

one may express the temperatures of the constituents in terms of T and Θ:

$$T_1 = T - f(c)\Theta; \quad T_2 = T + [1 - f(c)]\Theta, \tag{14}$$

where the auxiliary function $f(c)$ reads

$$f(c) = \frac{\mu(1-c)}{c + \mu(1-c)}.$$

D. The shock structure equations in binary MT mixture

One of the representative examples of strongly nonequilibrium processes with irreversible entropy production is the shock wave that propagates through a gas. Shock wave is a singular surface, traveling at speed s, on which jump of the state variables occurs. Values of the state variables in front of the shock and behind it are related to the shock speed through Rankine-Hugoniot relations. When the model inherits dissipation, shock wave is smoothed out and transformed into a continuous profile (Fig. 1). The shock structure is considered to be a plane traveling wave moving at the same speed s as a shock wave, and asymptotically connecting equilibrium states. Under these assumptions, equations which determine the structure of the shock wave can be derived from the governing equations using traveling wave ansatz, i.e., attaching the reference frame to the singular surface and assuming that field variables depend on a single independent variable $\xi = x - st$. Introducing the relative velocity $u = v_x - s$, where v_x is the x component of $\mathbf{v}$, and J and $\hat{m}_1$ as x components of the diffusion flux $\mathbf{J}$ and the source term $\hat{\mathbf{m}}_1$, respectively, governing equations for a binary mixture are reduced to the following set of ordinary differential equations:

$$\frac{d}{d\xi}(\rho u) = 0, \quad \frac{d}{d\xi}\left(\rho u^2 + p + \frac{J^2}{\rho c(1-c)}\right) = 0, \tag{15a}$$

$$\frac{d}{d\xi}\left\{\left(\frac{1}{2}\rho u^2 + \rho\varepsilon + p\right)u + \left(\frac{uJ}{\rho c(1-c)} + \frac{1}{\beta}\right)J\right\} = 0, \tag{15b}$$

$$\frac{d}{d\xi}(\rho c u + J) = 0, \tag{15c}$$

$$\frac{d}{d\xi}\left(\rho c u^2 + \frac{J^2}{\rho c} + 2uJ + p_1\right) = \hat{m}_1, \tag{15d}$$

$$\frac{d}{d\xi}\left\{\left(\frac{1}{2}\rho c\left(u + \frac{J}{\rho c}\right)^2 + \rho c\varepsilon_1 + p_1\right)\left(u + \frac{J}{\rho c}\right)\right\} = \hat{e}_1 + \hat{m}_1 u. \tag{15e}$$

In (15c), β represents the thermal inertia—reciprocal of the difference of dynamic enthalpies g_α:

$$\beta = \frac{1}{g_1 - g_2}, \quad g_\alpha = \varepsilon_\alpha + \frac{p_\alpha}{\rho_\alpha} + \frac{u_\alpha^2}{2}.$$

Source terms $\hat{m}_1$ and $\hat{e}_1$ can be, after straightforward transformations, put into the following forms:

$$\hat{m}_1 = -\psi_{11}\left(\frac{u_1}{T_1} - \frac{u_2}{T_2}\right) = -\psi_{11}\frac{cT_1 + (1-c)T_2}{c(1-c)T_1T_2}\frac{J}{\rho},$$

$$\hat{e}_1 = -\theta_{11}\left(-\frac{1}{T_1} + \frac{1}{T_2}\right) = \theta_{11}\frac{\Theta}{T_1T_2}. \tag{16}$$

Phenomenological coefficients ψ_{11} and θ_{11} can be expressed in terms of field variables and relaxation times for diffusion τ_D and temperature τ_T:

$$\psi_{11} = \frac{1}{\tau_D}\frac{\rho_1\rho_2}{\rho}T, \quad \theta_{11} = \frac{1}{\tau_T}\frac{\rho_1 c_{V_1}\rho_2 c_{V_2}}{\rho_1 c_{V_1} + \rho_2 c_{V_2}}T^2. \tag{17}$$

To determine the shock structure, Eqs. (15) must be adjoined with the following boundary conditions:

$$\lim_{\xi\to-\infty}\mathbf{U}(\xi) = \mathbf{U}_-, \quad \lim_{\xi\to+\infty}\mathbf{U}(\xi) = \mathbf{U}_+,$$

$$\lim_{\xi\to\pm\infty}\mathbf{U}'(\xi) = \mathbf{0}, \tag{18}$$

where $\mathbf{U} = (\rho, u, T, c, J, \Theta)^T$ is the column vector of field variables. The solution procedure for the shock structure problem in a binary mixture is explained in [26], whereas a comparison with available experimental data is provided in [33].

It is important to emphasize that [26,33], as well as the present study, are restricted to the continuous shock profiles. Being hyperbolic, our model is inherently limited when the shock structure is studied, since continuous shock profiles cease to exist when the shock speed is greater than the highest characteristic speed of the system. In other words, there exists an upper limit of the shock strength (i.e., Mach number) above which the continuous shock structure breaks down. This is peculiar for hyperbolic dissipative models, as explained in [7,39,40]. A detailed analysis of this limitation in a binary MT mixture is studied in [26]. However, discontinuous shock profiles, i.e., the profiles with so-called subshocks, were thoroughly studied in the context of rational extended thermodynamics. The conditions under which they occur, as well as their computation, are the subject of the series of papers [41–45].

III. ENTROPY BALANCE LAW IN MT MIXTURE

In modern continuum theories entropy inequality is treated as a constraint to physically admissible constitutive relations. Following this approach, it became one of the pillars of rational extended thermodynamics [7]; in conjunction with the objectivity principle, the entropy principle is used as a tool on which the closure procedure relies on. The main idea of the entropy principle in extended thermodynamics is to treat the entropy balance law as the main equation and the governing equations as constraints. In the same manner, it was exploited in the MT model of the mixture of Euler fluids to determine the structure of the source terms [24]. In this section we shall put it into another perspective, in accordance with the basic modeling assumptions of the mixture theory presented in Sec. II.

A. Entropy principle in extended thermodynamics

General features of the entropy principle and the method of multipliers will be summarized in the sequel. The system of balance laws which govern the thermodynamic process can be written in the form

$$\partial_t \mathbf{F}(\mathbf{U}) + \partial_i \mathbf{F}^i(\mathbf{U}) = \mathbf{P}(\mathbf{U}), \tag{19}$$

where $\mathbf{F}(\mathbf{U})$ is the vector of densities, $\mathbf{F}^i(\mathbf{U})$ are the components of fluxes, and $\mathbf{P}(\mathbf{U})$ is the vector of production (source) terms. It is assumed that densities, fluxes, and productions depend locally on field variables $\mathbf{U}$, i.e., they depend on values of field variables at the point, but not on their derivatives. Thus, (19) constitutes a hyperbolic system of balance laws, at least in a certain region of the state space.

Balance laws (19) are adjoined with an entropy balance law,

$$\partial_t h(\mathbf{U}) + \partial_i h^i(\mathbf{U}) = \sigma(\mathbf{U}) \geqslant 0, \tag{20}$$

where $h(\mathbf{U})$ is the entropy density, $h^i(\mathbf{U})$ are the components of the entropy flux, and $\sigma(\mathbf{U})$ is the entropy production rate. Local dependence is assumed in (20), as well as concavity of the entropy density. Since both the balance laws (19) and the entropy inequality (20) are quasilinear equations, Galilean invariance and entropy principle ensure the existence of the vector of Lagrange multipliers $\boldsymbol{\Lambda}(\mathbf{U})$ such that

$$\partial_t h + \partial_i h^i - \boldsymbol{\Lambda} \cdot (\partial_t \mathbf{F} + \partial_i \mathbf{F}^i - \mathbf{P}) \geqslant 0. \tag{21}$$

As a consequence, the following relations hold:

$$dh = \boldsymbol{\Lambda} \cdot d\mathbf{F}, \tag{22a}$$

$$dh^i = \boldsymbol{\Lambda} \cdot d\mathbf{F}^i, \tag{22b}$$

$$\sigma = \boldsymbol{\Lambda} \cdot \mathbf{P} \geqslant 0. \tag{22c}$$

From (22) one may expect several results. In principle, they determine the multipliers $\boldsymbol{\Lambda}$, unknown fluxes and entropy density h^0, and entropy flux h^i, which are regarded as constitutive quantities in extended thermodynamics. Moreover, once the multipliers are determined, the residual inequality (22c) provides a means for finding a proper form of the production $\mathbf{P}$. These are only the most important features of the entropy principle strictly connected to our study. Other interesting aspects are summarized in [46] and [7,8].

B. Entropy principle in MT mixtures

Exploitation of the entropy principle in MT mixtures of Euler fluids is demonstrated in [24]. It imposes restrictions on the structure of source terms, which determine their general form compatible with the residual inequality. In the case of a nonreacting mixture, the simplest possible way to satisfy the residual inequality, for any thermodynamic process, is to take the source terms in the forms (8) and (9). The aim of this section is to go through the application of the entropy principle to the MT mixture in a way a bit different than in [24]. The fact that the MT model consists of the blocks of Euler's gas dynamics equations with source terms will enable us to combine the basic principles upon which the mixture theory relies, with the application of the entropy principle by means of Liu's method of multipliers [9], also called the main field [47] in the context of extended thermodynamics. The outcome will be a deeper understanding of the structure of the entropy production rate.

First, we shall extend the application of Truesdell's metaphysical principles [6] to the entropy balance laws. Assume that the governing equations for the MT mixture of Euler fluids consist of the balance laws (1) for n constituents. In view of the assumptions about the constituents and the structure of balance laws (1), we shall assume that to each constituent we may ascribe the entropy balance law in the same form as if there were a single Euler gas, provided we introduce an appropriate entropy production rate for each constituent:

$$\frac{\partial}{\partial t}(\rho_\alpha S_\alpha) + \operatorname{div}(\rho_\alpha S_\alpha \mathbf{v}_\alpha) = \sigma_\alpha, \tag{23}$$

where S_α is the specific entropy and σ_α is the entropy production rate for the constituent α, $\alpha = 1, \ldots, n$. Since each constituent is an Euler fluid by assumption, and thus $\mathbf{q}_\alpha = \mathbf{0}$, it may me observed that the entropy flux contains only the convective part $\rho_\alpha S_\alpha \mathbf{v}_\alpha$. Moreover, at the level of constituents, entropy production rates σ_α may not have definite a sign; this will be confirmed *a posteriori* in the analysis of the shock structure in Sec. IV.

Following the same procedure as in the case of balance laws (1), entropy balance laws (23) may be summed up to obtain the entropy balance law for the mixture:

$$\frac{\partial}{\partial t}\left(\sum_{\alpha=1}^{n} \rho_\alpha S_\alpha\right) + \operatorname{div}\left(\sum_{\alpha=1}^{n} \rho_\alpha S_\alpha \mathbf{v}_\alpha\right) = \sum_{\alpha=1}^{n} \sigma_\alpha.$$

Using this equation, one may define the entropy density, entropy flux, and entropy production rate for the mixture:

$$\sum_{\alpha=1}^{n} \rho_\alpha S_\alpha = \rho S, \tag{24a}$$

$$\sum_{\alpha=1}^{n} \rho_\alpha S_\alpha \mathbf{v}_\alpha = \rho S \mathbf{v} + \sum_{\alpha=1}^{n} S_\alpha \mathbf{J}_\alpha, \tag{24b}$$

$$\sum_{\alpha=1}^{n} \sigma_\alpha = \sigma, \tag{24c}$$

where the definitions of diffusion velocities, $\mathbf{u}_\alpha = \mathbf{v}_\alpha - \mathbf{v}$, and diffusion fluxes, $\mathbf{J}_\alpha = \rho_\alpha \mathbf{u}_\alpha$, were used. Note that nonconvective entropy flux $\sum_{\alpha=1}^{n} S_\alpha \mathbf{J}_\alpha$ is caused by diffusion. The entropy balance law for the mixture then reads

$$\frac{\partial}{\partial t}(\rho S) + \operatorname{div}\left(\rho S \mathbf{v} + \sum_{\alpha=1}^{n} S_\alpha \mathbf{J}_\alpha\right) = \sigma \geqslant 0. \tag{25}$$

Turning now to the application of the method of multipliers, we may take them in the form $\boldsymbol{\Lambda} = (\Lambda^{\rho_\alpha}, \boldsymbol{\Lambda}^{\mathbf{v}_\alpha}, \Lambda^{\varepsilon_\alpha})$ corresponding to the balance laws (1). Their structure is easily determined [24]:

$$\Lambda^{\rho_\alpha} = -\frac{\mu_\alpha - \frac{1}{2}v_\alpha^2}{T_\alpha}, \quad \boldsymbol{\Lambda}^{\mathbf{v}_\alpha} = -\frac{\mathbf{v}_\alpha}{T_\alpha}, \quad \Lambda^{\varepsilon_\alpha} = \frac{1}{T_\alpha}, \tag{26}$$

where $\mu_\alpha = \varepsilon_\alpha - T_\alpha S_\alpha + p_\alpha/\rho_\alpha$ are the chemical potentials of the constituents. Following the procedure outlined above to each constituent, two important results are obtained: Gibbs' relations for the constituents:

$$T_\alpha dS_\alpha = d\varepsilon_\alpha - \frac{p_\alpha}{\rho_\alpha^2} d\rho_\alpha, \tag{27}$$

and the entropy production rates:

$$\sigma_\alpha = \frac{\hat{e}_\alpha}{T_\alpha} - \hat{\mathbf{m}}_\alpha \cdot \frac{\mathbf{u}_\alpha}{T_\alpha}, \tag{28}$$

where Galilean invariance (8) was used to obtain σ_α in a proper velocity-independent form. Using the definition (24c), and taking into account (28), as well as restrictions on the source terms (2), the entropy production rate for the mixture of nonreacting Euler fluids reads

$$\sigma = \sum_{b=1}^{n-1} \left(\frac{1}{T_b} - \frac{1}{T_n}\right) \hat{e}_b - \sum_{b=1}^{n-1} \left(\frac{\mathbf{u}_b}{T_b} - \frac{\mathbf{u}_n}{T_n}\right) \cdot \hat{\mathbf{m}}_b. \tag{29}$$

In such a way, the entropy production rate was recovered in the same form as in [24]. Finally, the entropy inequality $\sigma \geqslant 0$ is satisfied for the source terms in the form (9). Note also that constituents' entropy production rates (28) may not be explicitly determined unless the structure of the source terms $\hat{\mathbf{m}}_\alpha$ and $\hat{e}_\alpha$ is known.

This analysis of the entropy principle will be finalized with three observations about the structure of entropy density and entropy production rate that will be used in the sequel. First, it has to be emphasized that the present approach to the entropy principle is peculiar to rational extended thermodynamics of mixtures. This framework facilitates formal derivation of the entropy balance law (23) for each constituent. As a consequence, one may explicitly recognize the contribution of each constituent to the entropy production rate σ, through its partial entropy production rate σ_α, given by (28). Second, although the specific entropies of the constituents are determined by the Gibbs' relations (27), they do not have to be regarded as equilibrium entropies. Indeed, they depend on constituents' temperatures which inherit the information about the nonequilibrium state in which the system is. Third, since it is assumed that there are no chemical reactions between the constituents, there are no cross-effects in the entropy production rate (29) either. Therefore, it can be rewritten in the form

$$\sigma = \sigma_m + \sigma_e, \tag{30}$$

where σ_m is the entropy production rate due to mechanical diffusion (momentum exchange) and σ_e is the entropy production rate due to thermal diffusion (energy exchange):

$$\sigma_m = -\sum_{b=1}^{n-1} \left(\frac{\mathbf{u}_b}{T_b} - \frac{\mathbf{u}_n}{T_n}\right) \cdot \hat{\mathbf{m}}_b,$$

$$\sigma_e = \sum_{b=1}^{n-1} \left(\frac{1}{T_b} - \frac{1}{T_n}\right) \hat{e}_b. \tag{31}$$

Both aspects of the entropy production rate, i.e., componentwise entropy production and entropy production related to the dissipation mechanism, will be thoroughly analyzed in Sec. IV.

C. Entropy density in MT mixtures

Starting from Gibbs' relations for the constituents (27), and using thermal and caloric equations of state (6), one may determine the specific entropy of each constituent:

$$S_\alpha - S_{\alpha 0} = \frac{k_B}{m_\alpha(\gamma_\alpha - 1)} \log \frac{T_\alpha}{T_0} - \frac{k_B}{m_\alpha} \ln \frac{\rho_\alpha}{\rho_0},$$

where subscript 0 indicates the reference state. For further analysis it will be convenient to choose the reference state such that $S_\alpha = 0$ in it. Consequently, $S_{\alpha 0} = (k_B/m_\alpha)\log(\rho_{\alpha 0}/\rho_0)$, and introducing the reference concentrations $\rho_{\alpha 0}/\rho_0 = c_{\alpha 0}$ we obtain the following form of specific entropy for the constituents:

$$S_\alpha = \frac{k_\mathrm{B}}{m_\alpha(\gamma_\alpha - 1)}\left[\ln \frac{T_\alpha}{T_0} - (\gamma_\alpha - 1)\ln \frac{\rho_\alpha}{\rho_0}\right] + \frac{k_\mathrm{B}}{m_\alpha} \ln c_{\alpha 0}. \tag{32}$$

As a consequence, entropy density of the mixture $(24)_1$ now reads

$$\rho S = \sum_{\alpha=1}^{n} \rho_\alpha \frac{k_\mathrm{B}}{m_\alpha(\gamma_\alpha - 1)}\left[\ln \frac{T_\alpha}{T_0} - (\gamma_\alpha - 1)\ln \frac{\rho_\alpha}{\rho_0}\right] + \sum_{\alpha=1}^{n} \rho_\alpha \frac{k_\mathrm{B}}{m_\alpha} \ln c_{\alpha 0}. \tag{33}$$

It was shown in [27] that mixture entropy density reaches local maximum in equilibrium ($T_\alpha = T$, for all $\alpha = 1, \dots, n$), provided Gibbs' relations (27) hold.

D. Entropy inequality in the shock structure

In the shock structure problem in the binary MT mixture, described in Sec. II, the entropy balance law (25) is reduced to

$$\frac{d}{d\xi}[\rho S u + (S_1 - S_2)J] = \sigma \geqslant 0, \tag{34}$$

where we took into account $J_2 = -J_1 = -J$. When expressed in terms of proper state variables, the specific entropies S_1 and S_2 and the entropy density of the mixture ρS read

$$\begin{aligned} S_1 &= \frac{k_B}{m_1(\gamma-1)}\log\frac{T_1}{T_0} - \frac{k_B}{m_1}\log\frac{\rho c}{\rho_0 c_0}, \\ S_2 &= \frac{k_B}{m_2(\gamma-1)}\log\frac{T_2}{T_0} - \frac{k_B}{m_2}\log\frac{\rho(1-c)}{\rho_0(1-c_0)}, \\ \rho S &= \rho\left[c\frac{k_B}{m_1(\gamma-1)}\log\frac{T_1}{T_0} + (1-c)\frac{k_B}{m_2(\gamma-1)}\log\frac{T_2}{T_0}\right] \\ &\quad - \rho c\frac{k_B}{m_1}\log\frac{\rho c}{\rho_0 c_0} - \rho(1-c)\frac{k_B}{m_2}\log\frac{\rho(1-c)}{\rho_0(1-c_0)}, \end{aligned} \tag{35}$$

where T_1 and T_2 are determined by (14). It will be assumed in the sequel that the reference state is the equilibrium state in front of the shock, i.e., $\mathbf{U}_0 = \lim_{\xi\to-\infty}\mathbf{U}(\xi)$.

The entropy production rate (29) in the binary MT mixture reads

$$\sigma = \psi_{11}\left(\frac{cT_1 + (1-c)T_2}{c(1-c)T_1T_2}\right)^2\frac{J^2}{\rho^2} + \theta_{11}\frac{\Theta^2}{T_1^2T_2^2}, \tag{36}$$

where phenomenological coefficients are determined by (17). It can be decomposed and expressed in two ways. First, as a sum of mechanical σ_m and thermal σ_e dissipation contributions (30):

$$\begin{aligned} \sigma_m &= \psi_{11}\left(\frac{cT_1 + (1-c)T_2}{c(1-c)T_1T_2}\right)^2\frac{J^2}{\rho^2}, \\ \sigma_e &= \theta_{11}\frac{\Theta^2}{T_1^2T_2^2}, \end{aligned} \tag{37}$$

and second, as a sum of the entropy production rates of the constituents (28), $\sigma = \sigma_1 + \sigma_2$, where

$$\begin{aligned} \sigma_1 &= \theta_{11}\frac{1}{T_1}\frac{\Theta}{T_1T_2} + \psi_{11}\frac{cT_1 + (1-c)T_2}{c(1-c)T_1T_2}\frac{1}{cT_1}\frac{J^2}{\rho^2}, \\ \sigma_2 &= -\theta_{11}\frac{1}{T_2}\frac{\Theta}{T_1T_2} + \psi_{11}\frac{cT_1 + (1-c)T_2}{c(1-c)T_1T_2}\frac{1}{(1-c)T_2}\frac{J^2}{\rho^2}. \end{aligned} \tag{38}$$

IV. DISCUSSION

In this section the results of numerical analysis of the shock structure problem will be presented. Solutions depend on three parameters: the upstream Mach number M_0, the equilibrium concentration c_0, and the mass ratio μ. Out of the database that contains 4394 continuous shock profiles (see [26] for the detailed explanation), we have chosen four characteristic cases, determined by the parameters given in Table I, to illustrate the main features of the entropy density and the entropy production rate. The graphs of all the variables are given in dimensionless form, which is defined in the Appendix.

TABLE I. Values of the parameters in numerically computed profiles.

Cases	M_0	c_0	μ
(a)	1.20	0.35	0.05
(b)	1.60	0.21	0.10
(c)	1.30	0.11	0.10
(d)	2.00	0.09	0.02

A. Profiles of the field variables

To appreciate certain features of the shock structure that are important for the present study, we shall firstly analyze numerically computed profiles of the field variables.

Figure 2 shows that the velocity profiles of the mixture, as well as of the constituents, are monotonic. The lighter constituent (labeled 1) slows down faster than the heavier one. Inspection of these profiles indicates that the increase of the Mach number induces a larger discrepancy between the velocities [compare the cases (b) and (d) versus (a) and (c)].

Temperature profiles, given in Fig. 3, were the subject of an extensive analysis presented in [26]. That study was focused on the phenomenon of temperature overshoot. It was shown that it increases due to insufficient exchange of internal energy between the constituents, which in turn can be a consequence either of the large mass discrepancy, or of the large rarefaction of the flow. Nevertheless, temperature overshoot does not appear for any value of the parameters [see case (a)], and its magnitude increases with the increase of Mach number. Also, it is a common feature that the temperature of a heavier constituent initially lags behind the profile of average temperature in the upstream part, whereas in the downstream part it becomes larger. Consequently, there is a point within the profile at which the temperature profiles of the constituent intersect.

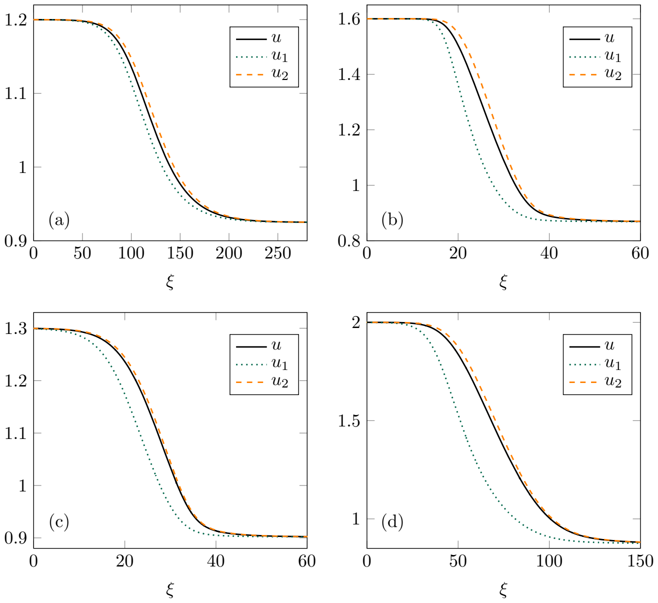

FIG. 2. Profiles of the velocities: (a) $M_0 = 1.20$, $c_0 = 0.35$, $\mu = 0.05$; (b) $M_0 = 1.60$, $c_0 = 0.21$, $\mu = 0.10$; (c) $M_0 = 1.30$, $c_0 = 0.11$, $\mu = 0.10$; (d) $M_0 = 2.00$, $c_0 = 0.09$, $\mu = 0.02$.

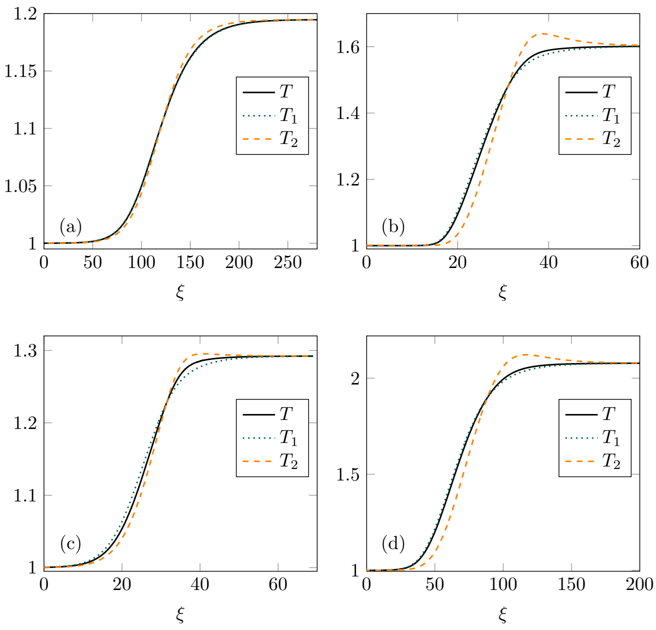

FIG. 3. Profiles of the temperatures: (a) $M_0 = 1.20,\ c_0 = 0.35,\ \mu = 0.05$; (b) $M_0 = 1.60,\ c_0 = 0.21,\ \mu = 0.10$; (c) $M_0 = 1.30,\ c_0 = 0.11,\ \mu = 0.10$; (d) $M_0 = 2.00,\ c_0 = 0.09,\ \mu = 0.02$.

Profiles of diffusion flux J and diffusion temperature Θ, presented in Fig. 4, visualize the behavior of nonequilibrium variables. They vanish in upstream and downstream equilibria, and have nonzero values within the shock structure. Their profiles reflect the behavior of the constituents' velocities and temperatures: diffusion flux J is of the same sign throughout the profile, while temperature difference Θ changes the sign since the temperature profiles intersect. It may be observed that the magnitude of nonequilibrium variables generally increases with the increase of the shock strength, i.e., Mach number.

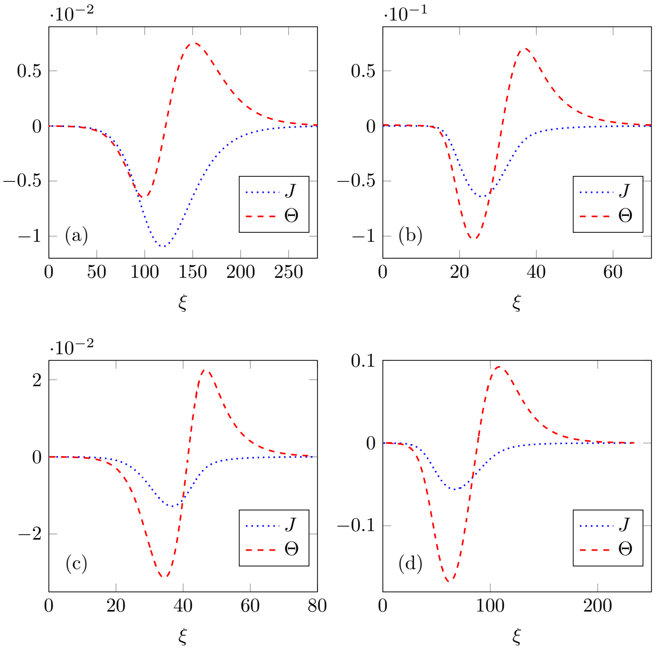

FIG. 4. Profiles of the diffusion flux and diffusion temperature: (a) $M_0 = 1.20,\ c_0 = 0.35,\ \mu = 0.05$; (b) $M_0 = 1.60,\ c_0 = 0.21,\ \mu = 0.10$; (c) $M_0 = 1.30,\ c_0 = 0.11,\ \mu = 0.10$; (d) $M_0 = 2.00,\ c_0 = 0.09,\ \mu = 0.02$.

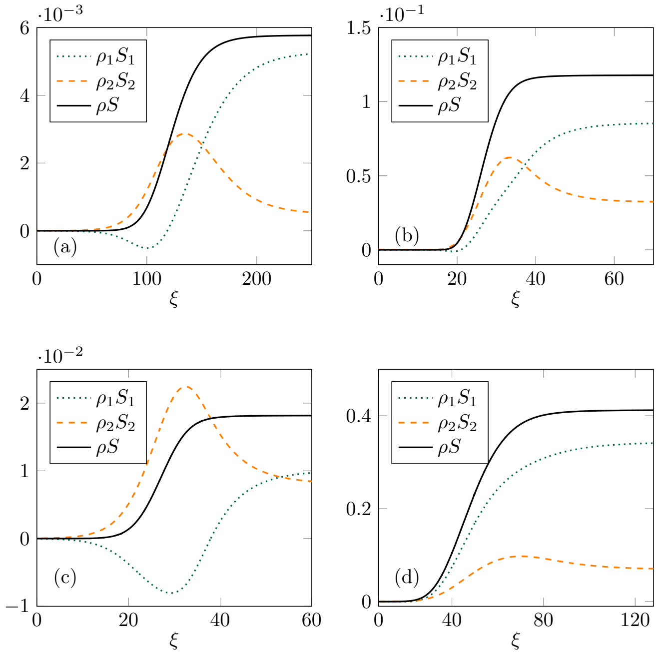

FIG. 5. Profiles of the entropy density: (a) $M_0 = 1.20,\ c_0 = 0.35,\ \mu = 0.05$; (b) $M_0 = 1.60,\ c_0 = 0.21,\ \mu = 0.10$; (c) $M_0 = 1.30,\ c_0 = 0.11,\ \mu = 0.10$; (d) $M_0 = 2.00,\ c_0 = 0.09,\ \mu = 0.02$.

B. Profiles of the entropy density and the entropy production rate

The main goal of this study is to prove that the entropy density (33), or equivalently (24a), increases monotonically within the shock profile, and that such an entropy density may be regarded as properly defined. Four representative cases, presented in Fig. 5, confirm our hypothesis. Moreover, the same conclusion was reached for all the continuous profiles in our database. Therefore, it may be concluded that the definition (33) of the entropy density is compatible with the requirement of the entropy growth through the shock structure.

The entropy density profiles, shown in Fig. 5, reveal more interesting features pertinent to mixtures. It is clear that the entropy density of a heavier constituent has a maximum within the shock profile; in case (c) it even overshoots the terminal value of the mixture entropy density. On the other hand, the entropy density profile of a lighter constituent has an "undershoot" [except in case (d)]: it decreases initially, attains local minimum, and then increases. Although the mixture entropy density grows monotonically, the entropy density profiles of the constituents are apparently nonmonotonic.

It is also interesting to note that the overall increase of the mixture entropy density [see Eq. (A12a) in the Appendix] depends on the Mach number only, and not on other parameters:

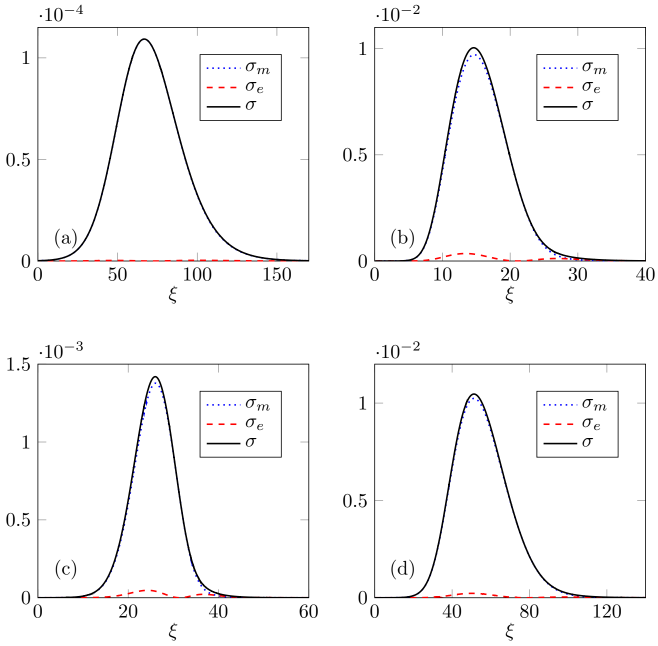

FIG. 6. Profiles of the entropy production—dissipation mechanism: (a) $M_0 = 1.20,\ c_0 = 0.35,\ \mu = 0.05$; (b) $M_0 = 1.60,\ c_0 = 0.21,\ \mu = 0.10$; (c) $M_0 = 1.30,\ c_0 = 0.11,\ \mu = 0.10$; (d) $M_0 = 2.00,\ c_0 = 0.09,\ \mu = 0.02$.

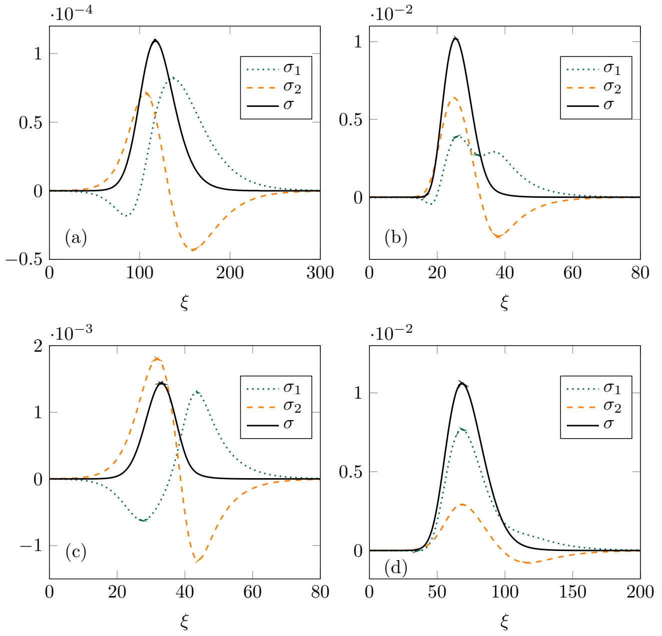

FIG. 7. Profiles of the entropy production—components: (a) $M_0 = 1.20,\ c_0 = 0.35,\ \mu = 0.05$; (b) $M_0 = 1.60,\ c_0 = 0.21,\ \mu = 0.10$; (c) $M_0 = 1.30,\ c_0 = 0.11,\ \mu = 0.10$; (d) $M_0 = 2.00,\ c_0 = 0.09,\ \mu = 0.02$.

it grows with the increase of M_0. Nevertheless, the relative contribution of terminal values of the constituents' entropy densities (A12b) and (A12c) are sensitive to equilibrium concentration c_0 and mass ratio μ.

Apart from the analysis of the entropy density, it is of interest to analyze the structure of the entropy production rate. First, it may be observed in Fig. 6 that the contribution of the entropy production rate σ_m due to mechanical diffusion (mechanical nonequilibrium) is substantially greater than the contribution of the entropy production rate σ_e due to thermal diffusion (thermal nonequilibrium). Thus, it may be concluded that even in the MT model the substantial part of the entropy production is of mechanical nature. Nevertheless, thermal nonequilibrium must not be ignored since it is related to the lack of energy exchange between the constituents, as indicated in [26].

Just as entropy density profiles exhibit unusual behavior within the shock structure, distribution of the entropy production rate possesses certain unexpected features. Namely, although the overall entropy production rate must be nonnegative, entropy production rates of the constituents may not be, as is obvious in Fig. 7. Furthermore, entropy production rate σ_2 of the heavier constituent has similar behavior in all cases: it is positive in the upstream part of the shock structure, and negative in the downstream one, thus having one local maximum and one local minimum. On the other hand, entropy production rate σ_1 of the lighter constituent has the opposite structure in cases (a) and (c): it is negative in the upstream part, and positive in the downstream one. However, the profiles in the other two cases are rather peculiar. In case (b), σ_1 has two local maxima in the downstream part of the profile; in case (d), apart from a narrow negative zone, the profile of σ_1 is positive with only one local maximum.

The present discussion shows certain features of entropy growth and entropy production rate within the shock profiles in the binary MT mixture. For a deeper insight, a systematic parametric analysis is needed. In particular, entropy growth is usually related to the strength of shock, i.e., the Mach number. Indeed, the jump of entropy density of the mixture (A12a) depends on the Mach number only, and not on other parameters (c_0 and μ). However, the transition zone—the shock profile—is influenced by all the parameters. When the Mach number decreases $M_0 \to 1$, keeping the values of other parameters fixed, the jump of the mixture entropy density decreases too. At the same time, a preliminary analysis showed that the profiles of constituents entropy densities remain highly nonmonotonic, reaching the amplitudes that are several times greater than the overall jump of mixture entropy density. On the other hand, the increase of Mach number, and the corresponding analysis of entropy growth, is limited by the model. As we already mentioned, continuous shock profiles cease to exist for sufficiently high values of the shock speed. Therefore, within the realm of the continuous shock structure problem we cannot determine the behavior of entropy and entropy production rate for high values of Mach number, e.g., in hypersonic flow. Furthermore, our previous studies (e.g., [26]) showed that the influence of the Mach number cannot be isolated from the influence of other parameters, equilibrium concentration c_0 and mass ratio μ. It is our intention to pursue the study in this direction in the future.

V. CONCLUSION

Our analysis extends the questions raised in [19,20] about the entropy growth and entropy production rate to the mixtures of Euler fluids. It was focused on a particular model that emerged within the framework of extended thermodynamics. The structure of the model captures nonequilibrium effects through the velocities and temperatures of the constituents, whose evolution is driven by the appropriate source terms. In addition to known results, presented in [8,24], we put the derivation of the entropy balance law into a different perspective by means of the formalism used for derivation of the conservation laws for the mixture.

Numerical analysis of the entropy growth within the shock wave in the binary MT mixture showed that the entropy density of the mixture grows monotonically, However, entropy densities of the constituents are not monotonic. Thus, monotonicity of the mixture entropy density is related to the complex dissipation mechanism which appears at the mixture level, rather than simple superposition of the dissipation effects exerted on the constituents. To that end, we reached our goal and proved that the entropy density (24) is properly defined.

At the same time, we also got a deeper insight into the entropy production rate. It turned out that the contribution of mechanical dissipation (due to diffusion) is considerably greater than the contribution of thermal dissipation (due to temperature difference). Moreover, our study revealed that the entropy production rates for the constituents need not be non-negative at all. This is in agreement with the results for the entropy density, explained above.

If we want to put these results in a broader context, we need a better understanding about what "properly defined entropy density" really means. To that end, a striking similarity may be observed in the construction of the entropy density in our study, and the one used in [19,20]. In both cases the entropy densities inherit all the relevant field variables that appear in a nonequilibrium process. In our case these are the temperatures and the concentrations of the constituents, whereas in the above-mentioned study those are normal stress and heat flux. In our study, entropy density is constructed in accordance with the level of approximation proposed from the outset. In [19,20], a two-step approximation is performed: first, Grad's 13 moments velocity distribution is used; then, constitutive relations of Navier-Stokes and Fourier were plugged into it to obtain the distribution akin to that obtained by the Chapman-Enskog method. In the classical approach, however, the equilibrium entropy density is used, that may be obtained from Boltzmann's kinetic entropy using local Maxwellian distribution, and which does not inherit any information upon nonequilibrium field variables. It may be noted that even in a recent study [48], where coupled constitutive relations were proposed by generalization of the entropy flux with the aim to extend the range of validity of Navier-Stokes-Fourier (NSF) equations, the equilibrium entropy density was retained and a nonmonotonic profile of entropy density was obtained within the shock structure.

In our opinion, if the governing equations of thermodynamic process are nonequilibrium ones, then proper entropy density should inherit this information through appropriate nonequilibrium contribution. Within extended thermodynamics and, to a certain extent, in thermodynamics with internal variables, this is achieved by construction. In the case of NSF equations, the contradiction faced in the classical approach may be overcome by the method proposed in [19,20], which resonates with the assertions of Ruggeri [49]—nonlocal constitutive relations may be regarded as approximations of proper balance laws. It is our intention to develop this idea and proceed in this spirit in the analysis of the proper choice of entropy density for nonequilibrium processes.

ACKNOWLEDGMENTS

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APPENDIX: DIMENSIONLESS QUANTITIES AND EQUATIONS

This Appendix contains the dimensionless equations needed for computation of the shock structure. To that end we need to express the relaxation times τ_D and τ_T in terms of measurable or computable quantities. In fact, the kinetic theory of gases relates them to the diffusivity D_{12} of a binary mixture of monatomic gases [4,50]:

$$\tau_D = \frac{cm_2 + (1-c)m_1}{k_B T} D_{12}, \qquad \tau_T = \frac{m_1 + m_2}{k_B T} D_{12}. \tag{A1}$$

The first relation comes from kinetic theory considerations, whereas the second one is a consequence of the ratio of relaxation times for monatomic gases [27,33,51]:

$$\frac{\tau_T}{\tau_D} = \frac{m_1 + m_2}{c\, m_2 + (1-c)\, m_1} > 1. \tag{A2}$$

The diffusivity of the binary mixture for the model of hard spheres reads [4,50]

$$D_{12} = \frac{3}{8nd_{12}^2}\left(\frac{k_B T}{2\pi}\frac{m_1 + m_2}{m_1 m_2}\right)^{1/2}, \tag{A3}$$

where $n = \rho/m$ is the mixture number density, $n = n_1 + n_2 = \rho_1/m_1 + \rho_2/m_2$, and $d_{12} = (d_1 + d_2)/2$ is the average atomic diameter of the mixture constituents whose diameters are d_1 and d_2.

Dimensionless variables will be introduced by scaling the state variables and the independent variable ξ with upstream equilibrium variables indicated by the subscript 0:

$$\tilde{\rho} = \frac{\rho}{\rho_0}, \quad \tilde{u} = \frac{u}{a_0}, \quad \tilde{T} = \frac{T}{T_0}, \quad M_0 = \frac{u_0}{a_0},$$
$$\tilde{J} = \frac{J}{\rho_0 a_0}, \quad \tilde{\Theta} = \frac{\Theta}{T_0}, \quad \tilde{\xi} = \frac{\xi}{l_0},$$
$$\tilde{S}_\alpha = \frac{S_\alpha}{S_0}, \quad \tilde{S} = \frac{S}{S_0}, \quad \tilde{\sigma}_\alpha = \frac{\sigma_\alpha l_0}{\rho_0 S_0 a_0}, \quad \tilde{\sigma} = \frac{\sigma l_0}{\rho_0 S_0 a_0}, \tag{A4}$$

where l_0 is the upstream reference length and $a_0 = \{\gamma(k_B/m_0)T_0\}^{1/2}$ is the upstream speed of sound; $m_0 = m(c_0)$

is the equilibrium average mass of the mixture; $S_0 = k_\mathrm{B}/[m_0(\gamma - 1)]$ is the reference specific entropy and M_0 is the upstream Mach number. For the sake of simplicity, the tilde will be dropped in the sequel. The upstream reference length l_0 will be taken as the average mean free path of the atoms in the mixture, and computed as follows:

$$\begin{aligned} l_0 &= \frac{n_1}{n}(l_1)_0 + \frac{n_2}{n}(l_2)_0, \\ (l_\alpha)_0 &= \frac{1}{\pi d_{12}^2}\left[n_1\left(1+\frac{m_\alpha}{m_1}\right)^{1/2} + n_2\left(1+\frac{m_\alpha}{m_2}\right)^{1/2}\right]^{-1}, \end{aligned} \tag{A5}$$

where n_α are number densities of the constituents, and $n = n_1 + n_2$ is the mixture number density.

Using the scaling described above, the shock structure equations (15) read

$$\begin{aligned} &\frac{d}{d\xi}(\rho u) = 0, \\ &\frac{d}{d\xi}\left(\rho u^2 + \frac{1}{\gamma}\frac{m_0}{m}\rho T + \frac{J^2}{\rho c(1-c)}\right) = 0, \\ &\frac{d}{d\xi}\left\{\left(\frac{1}{2}\rho u^2 + \frac{1}{\gamma - 1}\frac{m_0}{m}\rho T + \frac{J^2}{2\rho c(1-c)}\right)u \right. \\ &\qquad \left. + \left(\frac{uJ}{\rho c(1-c)} + \frac{1}{\beta}\right)J\right\} = 0, \\ &\frac{d}{d\xi}(\rho c u + J) = 0, \\ &\frac{d}{d\xi}\left\{\rho c u^2 + \frac{J^2}{\rho c} + 2uJ + \frac{1}{\gamma}\frac{m_0}{m_1}\rho c(T - f(c)\Theta)\right\} \\ &\quad = -\frac{l_0}{\tau_D a_0} m_\mu(T, c, \Theta)J, \\ &\frac{d}{d\xi}\left\{\left(\frac{1}{2}\rho c\left[u + \frac{J}{\rho c}\right]^2 + \frac{1}{\gamma - 1}\frac{m_0}{m_1}\rho c[T - f(c)\Theta]\right)\right. \\ &\qquad \left. \times \left(u + \frac{J}{\rho c}\right)\right\} = -\frac{l_0}{\tau_D a_0} m_\mu(T, c, \Theta)Ju \\ &\qquad + \frac{l_0}{\tau_T a_0} e_\mu(\rho, T, c, \Theta)\Theta. \end{aligned} \tag{A6}$$

Auxiliary functions m_μ and e_μ in source terms read

$$\begin{aligned} m_\mu(T, c, \Theta) &= \frac{T + [1 - c - f(c)]\Theta}{[T - f(c)\Theta]\{T + [1 - f(c)]\Theta\}}T, \\ e_\mu(\rho, T, c, \Theta) &= \frac{1}{\gamma(\gamma - 1)}\frac{m_0}{m_1}\frac{m}{m_2} \\ &\quad \times \frac{\rho c(1-c)T^2}{[T - f(c)\Theta]\{T + [1 - f(c)]\Theta\}}, \end{aligned}$$

mass ratios are expressed as

$$\begin{aligned} \frac{m_0}{m} &= \frac{c + \mu(1-c)}{c_0 + \mu(1 - c_0)}, \quad \frac{m_0}{m_1} = \frac{1}{c_0 + \mu(1 - c_0)}, \\ \frac{m}{m_2} &= \frac{\mu}{c + \mu(1-c)}, \end{aligned}$$

and $1/\beta$ stands for

$$\begin{aligned} \frac{1}{\beta} &= \frac{1}{\gamma - 1}\left[\frac{m_0}{m_1}(1-\mu)T - \frac{m_0}{m_1}\frac{m}{m_2}\Theta\right] \\ &\quad + \frac{J^2}{2\rho^2}\left[\frac{1}{c^2} - \frac{1}{(1-c)^2}\right]. \end{aligned}$$

For the sake of brevity, we shall not repeat the dimensionless form of specific entropies and mixture entropy density (35) since this is straightforward. Instead, we shall give the entropy production rate

$$\sigma = \gamma(\gamma - 1)\left[\frac{l_0}{\tau_D a_0}\frac{m_\mu^2}{\rho c(1-c)T}J^2 + \frac{l_0}{\tau_T a_0}e_\mu\frac{\Theta^2}{T_1 T_2}\right]. \tag{A7}$$

From this equation it is easy to distinguish mechanical and thermal contributions to the entropy production rate:

$$\begin{aligned} \sigma_m &= \gamma(\gamma - 1)\frac{l_0}{\tau_D a_0}\frac{m_\mu^2}{\rho c(1-c)T}J^2, \\ \sigma_e &= \gamma(\gamma - 1)\frac{l_0}{\tau_T a_0}e_\mu\frac{\Theta^2}{T_1 T_2}, \end{aligned} \tag{A8}$$

as well as the entropy production rates per constituent:

$$\begin{aligned} \sigma_1 &= \gamma(\gamma - 1)\left\{\frac{l_0}{\tau_D a_0}\frac{m_\mu}{\rho c T_1}J^2 + \frac{l_0}{\tau_T a_0}e_\mu\frac{\Theta}{T_1}\right\}, \\ \sigma_2 &= \gamma(\gamma - 1)\left\{\frac{l_0}{\tau_D a_0}\frac{m_\mu}{\rho(1-c)T_2}J^2 - \frac{l_0}{\tau_T a_0}e_\mu\frac{\Theta}{T_2}\right\}. \end{aligned} \tag{A9}$$

Dimensionless boundary conditions (18) are as follows:

$$\mathbf{U}_- = \begin{bmatrix} \rho_- \\ u_- \\ T_- \\ c_- \\ J_- \\ \Theta_- \end{bmatrix} = \begin{bmatrix} 1 \\ M_0 \\ 1 \\ c_0 \\ 0 \\ 0 \end{bmatrix}, \tag{A10}$$

$$\mathbf{U}_+ = \begin{bmatrix} \rho_+ \\ u_+ \\ T_+ \\ c_+ \\ J_+ \\ \Theta_+ \end{bmatrix} = \begin{bmatrix} \frac{4M_0^2}{3+M_0^2} \\ \frac{3+M_0^2}{4M_0} \\ \frac{1}{16}\left(14 - \frac{3}{M_0^2} + 5M_0^2\right) \\ c_0 \\ 0 \\ 0 \end{bmatrix}. \tag{A11}$$

Mixture state variables ρ_-, u_-, T_- in upstream equilibrium, and ρ_+, u_+, T_+ in downstream equilibrium represent the solution of Rankine-Hugoniot equations between the state variables at the shock wave for a single fluid. Constituent-related state variables c, J, and Θ have the same equilibrium values in front of and behind the shock. As proper nonequilibrium state variables, J and Θ vanish in equilibrium. A detailed description of the solution procedure for the shock structure equations, as well as the discussion of the existence of the continuous shock structure, the reader may find in [26].

Finally, overall jump across the shock wave of the entropy density of the mixture and the entropy densities of the constituents read

$$[\![\rho S]\!] = \rho_+ \ln \frac{T_+}{\rho_+^{\gamma-1}}, \tag{A12a}$$

$$[\![\rho_1 S_1]\!] = \rho_+ \frac{c_0}{c_0 + \mu(1 - c_0)} \ln \frac{T_+}{\rho_+^{\gamma-1}}, \tag{A12b}$$

$$[\![\rho_2 S_2]\!] = \rho_+ \frac{\mu(1 - c_0)}{c_0 + \mu(1 - c_0)} \ln \frac{T_+}{\rho_+^{\gamma-1}}. \tag{A12c}$$

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