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A THERMODYNAMICALLY CONSISTENT MODEL OF A LIQUID-VAPOR FLUID WITH A GAS

HÉLÈNE MATHIS

ABSTRACT. This work is devoted to the consistent modeling of a three-phase mixture of a gas, a liquid and its vapor. Since the gas and the vapor are miscible, the mixture is subjected to a non-symmetric constraint on the volume. Adopting the Gibbs formalism, the study of the extensive equilibrium entropy of the system allows to recover the Dalton's law between the two gaseous phases. In addition, we distinguish whether phase transition occurs or not between the liquid and its vapor. The thermodynamical equilibria are described both in extensive and intensive variables. In the latter case, we focus on the geometrical properties of equilibrium entropy. The consistent characterization of the thermodynamics of the three-phase mixture is used to introduce two Homogeneous Equilibrium Models (HEM) depending on mass transfer is taking into account or not. Hyperbolicity is investigated while analyzing the entropy structure of the systems. Finally we propose two Homogeneous Relaxation Models (HRM) for the three-phase mixtures with and without phase transition. Supplementary equations on mass, volume and energy fractions are considered with appropriate source terms which model the relaxation towards the thermodynamical equilibrium, in agreement with entropy growth criterion.

Key-words. Multiphase flows, entropy, thermodynamics of equilibrium, phase transition, homogeneous equilibrium model, hyperbolicity, homogeneous relaxation model.

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1. INTRODUCTION

The modelling of compressible multiphase flows is crucial for a wide range of applications, notably in the nuclear framework, for instance in vapor explosion of for fast transient situations [5, 35]. Within the two last decades, this topic has resulted in an abundant literature especially about two-phase flows, see for instance [3, 29, 16, 15, 11, 12]. More recently attention has been paid to the simulation of three-phase flows [23, 24, 33, 19], by means of relaxation models in the spirit of the two-fluid Baer and Nunziato model [3]. In all the latter references the mixture is assumed to be immiscible that is all the phases occupy different volumes. The thermodynamical equilibrium of the mixture is then depicted by the equality of the pressures and temperatures of the three phases (and also chemical potential as phase transition is considered). As the mixture dynamics is considered, each phase dynamic is depicted by an Euler type system which are coupled through non-conservative interfacial terms, additional advection equations of volume fractions and relaxation terms. The overall system enters the class of hyperbolic system of relaxation and admits good properties: hyperbolicity, well-understood wave structure, entropy inequality... For particular Equations of State (EoS), the Riemann problem is also well understood and has lead to the development of relevant numerical approximation (see again [23, 24, 33, 19] for three-fluid (perfectly immiscible) models). As immiscible mixture are considered, that is when the phases are intimate and share the same volume, one should refer to the works of Dellacherie [10, 9]. Since the phases are miscible, the model is in adequacy with the expected Dalton's law which states that the equilibrium mixture pressure is the sum of the pressures of each phases. We refer to [17] and [6] for fundamental Thermodynamics. The dynamic of the multicomponent fluid is again described by a Baer and Nunziato type of system, including relaxation terms and non-conservative interfacial terms. The authors also investigate the impact of the closure law on the hyperbolicity of the associated Homogeneous Equilibrium Model (HEM). These works complement the study proposed in [30] about the comparison of several closure laws applied to an HEM model in the case of a multicomponent immiscible mixture.

The purpose of the present work is to investigate the thermodynamics of a mixture which is not merely miscible or immiscible but of mix type. We focus on a three-phase compressible flows, composed of a liquid phase, its associated vapor phase and a gas. The gas is miscible with the vapor phase but no mass transfer can occur between either the gas and the vapor or the gas and the liquid. Besides phase transition can occur between the vapor and the liquid; in the whole paper we will distinguish whether phase transition between the liquid and the vapor occur or not. The core of the paper is the modelling of a rigorous thermodynamical model. It allows to construct reliable hyperbolic HEM models to depict the motion of the compressible three-phase mixture. We do not to address numerical aspects because of lack of relevant test cases.

First we aim at precisely give an accurate description of the thermodynamical equilibrium of the system. Adopting the Gibbs formalism, as done in [22, 31, 21], we intricate the extensive variables of the system. This description relies on the definition of the extensive equilibrium entropy of the system. The second law of Thermodynamics states that the thermodynamical equilibrium is attained as the mixture entropy reaches its maximum under some constraints. Depending on phase transition occurs or not between the liquid and its vapor, the set of

constraints changes, leading to different properties on the entropy function. The core issue is the volume constraint which reflects the non-symmetric immiscibility properties between the liquid and the gaseous phases. This constraint makes the whole modeling difficult since it prevents from using convenient tools of convex analysis such as sub-convolution and Legendre transform, see [31, 21]. At this stage, one recovers a consistent characterization of the thermodynamical equilibrium : the Dalton's law for the gaseous phases and the equality of the temperatures apply. Note that a similar description (in terms of extensive variables) has been proposed in [2] but the computations are restricted to particular equations of state (namely stiffened gas laws for the three phases). The present study is valid for any equations of state. Turning to the intensive variables, we analyse the specific equilibrium entropies in terms of optimization problems in the spirit of [22, 1, 31, 21, 14].

Section 3 addresses the construction of three-phase Euler systems at thermodynamical equilibrium called HEM models. Following the works of Dellacherie [10, 9], it consists in providing the correct closure laws to the three-phase Euler system in agreement with the optimization constraints presented in Section 2. We distinguish two cases depending on phase transition occurs or not between the vapor and the liquid phases. When phase transition is omitted, we prove that the resulting system is hyperbolic using a modified Godunov-Mock theorem in the spirit of [30]. When mass transfer is allowed, hyperbolicity is also proven. But the extension of the Godunov-Mock theorem is obsolete and one has to go back to the study the Jacobian matrix of the flux.

One difficulty when approximating solutions of HEM models is that the mixture pressure is often difficult to express analytically, even when the phases are depicted by simple EoS, see for instance the computations detailed in [2] for a three-phase mixture. Besides the mixture pressure law may present pathologies leading to the lack of convexity of the isentropes or slope discontinuities of the entropy, which result in the appearance of composite waves, see [32]. To overcome the problem, one could consider an approximate model by means of a relaxation procedure. One obtains a Homogeneous Relaxation model (HRM) where the relaxation towards the thermodynamical equilibrium is driven by source terms which comply with the entropy growth criterion. Section 4 presents two HRM models depending on whether phase transition occurs or not, following the construction proposed in [4] (see also refer to [26, 20, 27] for computational aspects).

2. A CONSISTENT THERMODYNAMICAL DESCRIPTION OF THE THREE PHASE SYSTEM

The purpose of this section is to give a proper description of the thermodynamical model. We begin by the determination of the extensive constraints on the state variables of the thermodynamical system. Because the gaseous phases are miscible with one another and immiscible with the liquid, the volume constraint is non-symmetric. According to the second principle, the mixture entropy achieves its maximum at thermodynamical equilibrium. We characterize two possible equilibria depending on phase transition occurs or not between the liquid and its vapor. One recovers the Dalton's law satisfied by the gaseous phases. Then we introduce the intensive formulation and study the equilibrium specific entropies for the models without and with phase transition. It turns out that they are concave, possibly with a saturation zone.

2.1. Single fluid thermodynamics: main definitions and assumptions.

Consider a fluid of mass $M \geq 0$ and internal energy $E \geq 0$ occupying a volume $V \geq 0$. As the fluid is homogeneous and at rest, its thermodynamical behaviour is described by its entropy function

$$\begin{aligned} S &: (\mathbb{R}^+)^3 \rightarrow \mathbb{R} \\ (M, V, E) &\mapsto S(M, V, E). \end{aligned}$$

This entropy function S is concave with respect to $W = (M, V, E) \in (\mathbb{R}^+)^3$. Then it is classical to extend it by $-\infty$ outside the close convex cone $(\mathbb{R}^+)^3$

$$S(W) = \begin{cases} S(W), & W \in (\mathbb{R}^+)^3, \\ -\infty, & \text{elsewhere.} \end{cases}$$

We adopt the assumptions stated in [6] and [13].

Assumption 1. Assume the entropy $S : (\mathbb{R}^+)^3 \rightarrow \mathbb{R} \cup \{-\infty\}$ is such that

- (i) the set of admissible states $C := \{W \in (\mathbb{R}^+)^3, S(W) > -\infty\}$ is a non-empty close convex domain,
- (ii) S is a concave function of W ,
- (iii) S is extensive or Positively Homogeneous of degree 1 (PH1), that is

$$\forall \lambda \in \mathbb{R}_*^+, \forall W \in C, \quad S(\lambda W) = \lambda S(W),$$

- (iv) S is upper semi-continuous that is

$$\forall W_0 \in C, \quad \lim_{W \rightarrow W_0} \sup S(W) \leq S(W_0),$$

- (v) S is of class \mathcal{C}^2 on C and its partial derivative with respect to the internal energy is strictly positive

$$\forall W \in C, \quad \frac{\partial S}{\partial E} > 0.$$

Assumptions (ii) and (iii) are equivalent to assume $(-S)$ sub-linear [34]. The existence and continuity assumption on the derivatives of S is quite strong even if it is common in literature. Observe that the extensive entropy S cannot be strictly concave since it is PH1.

The derivative of a PH1 function is PH0, said intensive. Therefore the smoothness assumption (v) allows to define intensive potentials:

- the temperature T

$$\frac{1}{T} = \frac{\partial S}{\partial E},$$

- the pressure P

$$\frac{P}{T} = \frac{\partial S}{\partial V},$$

- the chemical potential μ

$$\mu = -T \frac{\partial S}{\partial M}.$$

Hence one can state the extensive Gibbs relation

$$TdS = dE + PdV - \mu dM.$$

It is also common to define the specific entropy s by

$$Ms = S(M, V, E).$$

The extensive entropy S being PH1, s is PH0 (intensive) such that

$$(1) \quad s = S(1, V/M, E/M).$$

Hence s can be seen as a function of the specific volume $V/M =: \tau$ and the specific energy $E/M =: e$. Setting $M = 1$ in the extensive Gibbs relation gives the analogous intensive form

$$(2) \quad Tds = de + Pd\tau.$$

Since S is PH1, it satisfies the Euler's relation $\nabla S \cdot (M, V, E)^T = S$ which leads to another characterization of the chemical potential

$$(3) \quad \mu = -Ts + p\tau + e.$$

2.2. Extensive description of the three-phase model. We now consider a fluid system of fixed mass $M \geq 0$, volume $V \geq 0$ and internal energy $E \geq 0$, composed of a gas (indicated by the index g) and a pure body present under its liquid phase (with index l) and its vapor phase (with index v). We assume that no mass transfer arises between the gas and the others remaining phases but only mechanical and thermal exchanges. We use the (abusive) appellation *phase* to indicate either the liquid, the vapor or the gaseous component of the mixture.

We denote by $M_k \geq 0$, $V_k \geq 0$ and $E_k \geq 0$ the mass, the volume and the internal energy of the phase $k \in \{l, g, v\}$. We assume that each phase is entirely described by its entropy function S_k satisfying Assumptions 1 for an extensive state vector $W_k = (M_k, V_k, E_k)$ belonging to the close convex cone C_k defined in Assumption 1-(i).

We now state the constraints on the extensive variables. By the mass conservation, one has

$$(4) \quad M = M_l + M_g + M_v,$$

and the internal energy conservation leads to

$$(5) \quad E = E_l + E_v + E_g.$$

The vapor is miscible with the gas, that is these two phases form an intimate mixture occupying the same volume. On the other hand, the liquid phase is immiscible with the gas and the vapor, that is it occupies a different volume at a mesoscopic scale. One gets the following volumic constraints

$$(6) \quad \begin{cases} V = V_l + V_v, \\ V_g = V_v. \end{cases}$$

Note that we assume that no vacuum can occur (otherwise, one should consider $V \geq V_l + V_v$) and that the vapor and the gas are perfectly intimate. Unlike the mass or energy constraints, the volume constraint is not invariant over permutation of the indexes $k = l, g, v$. This feature induces difficulties to properly characterize the mixture equilibrium and the mixture entropy (both in extensive and intensive variables).

Remark 1. *If the vapor phase (resp. the gas) is absent, the system is made of the two remaining phases. To remove the vapor phase (resp. the gas), one has to impose $M_v = 0$ (resp. $M_g = 0$). Indeed setting $V_v = 0$ (resp. $V_g = 0$) is meaningless because the volume constraint (6) would impose the disappearance of*

both the vapor and the gas phases. On the other hand, if the liquid phase is absent, one has to set both $M_l = 0$ and $V_l = 0$.

Let us address the definition of the extensive equilibrium entropy of the mixture. Out of equilibrium, the entropy of the three-phase system is the sum of the phasic entropies. For $(W_l, W_g, W_v) \in C_l \times C_g \times C_v$, it reads

$$(7) \quad \Sigma(W_l, W_g, W_v) = S_l(W_l) + S_g(W_g) + S_v(W_v).$$

The second principle of Thermodynamics states that the system will evolve until the entropy Σ reaches a maximum. Depending on whether or not mass transfer arises between the vapor and the liquid phases, the maximization process relies on different set of constraints, namely Ω_{ext}^{NPT} (No Phase Transition) and Ω_{ext}^{PT} (Phase Transition), leading to two different mixture entropies. We recall that phase transition is not allowed between the gas and the other phases since it has a different molecular structure. Hence M_g is fixed.

Definition 1. Fix $M_g \geq 0$. Let $W = (M, V, E) \in (\mathbb{R}^+)^3$ be the state vector of the three-phase system. The equilibrium entropy of the mixture is:

- without phase transition: M_l and M_v are fixed satisfying the mass conservation (4) and

$$(8) \quad S_{NPT}(M, V, E, M_l, M_g) = \max_{(W_l, W_g, W_v) \in \Omega_{ext}^{NPT}} \Sigma(W_l, W_g, W_v),$$

where $\Omega_{ext}^{NPT} := \{W_k \in C_k, k = l, g, v \mid (5) \text{ and } (6) \text{ hold}\}$

- with phase transition:

$$(9) \quad S_{PT}(M, V, E, M_g) = \max_{(W_l, W_g, W_v) \in \Omega_{ext}^{PT}} \Sigma(W_l, W_g, W_v),$$

where $\Omega_{ext}^{PT} := \{W_k \in C_k, k = l, g, v \mid M - M_g = M_l + M_v, (5) \text{ and } (6) \text{ hold}\}$.

The constraint sets Ω_{ext}^{NPT} and Ω_{ext}^{PT} are closed bounded convex sets. According to Assumption 1-(iv) the entropies S_k are lower semi-continuous functions. Then the optimization problem is well posed [34, 25].

Proposition 1. The extensive equilibrium entropy S_{NPT} (resp. S_{PT}) of the three-phase mixture defined either by (8) (resp. (9)) is a PH1 concave function of its arguments.

Proof. The function $\Sigma(W_l, W_g, W_v)$ is a concave function on $C_l \times C_g \times C_v$ since it is a sum of concave functions. We now focus on the optimization problem (8) over the set of constraints Ω_{ext}^{NPT} that is without phase transition. The mass of gas M_g is fixed and the maximization is performed on the volume and the energy only. Hence we omit the dependency on M_l and M_g and get

$$\begin{aligned} S(M, V, E) &= \max_{\begin{cases} V = V_l + V_v \\ V_g = V_v \\ E = E_l + E_g + E_v \end{cases}} \Sigma(W_l, W_g, W_v), \\ &= \max_{\begin{cases} V = V_l + V_v \\ E = E_l + E_g + E_v \end{cases}} \Sigma(W_l, (M_g, V_v, E_g), W_v). \end{aligned}$$

Since the masses M and M_k , $k \in \{l, g, v\}$, are fixed, the problem can be written under the following form

$$\begin{aligned} S(W) &= (\mathbf{A}H)(V, E) \\ &= \max\{H(V_l, V_v, E_l, E_g, E_v) \mid \mathbf{A}(V_l, V_v, E_l, E_g, E_v)^t = (V, E)^t\}, \end{aligned}$$

where $H(V_l, V_g, E_l, E_g, E_v) = S_l(M_l, V_l, E_l) + S_g(M_g, V_g, E_g) + S_v(M_v, V_v, E_v)$ and $\mathbf{A} = \begin{pmatrix} 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 1 \end{pmatrix}$ is a linear mapping from $(\mathbb{R}^+)^5$ to $(\mathbb{R}^+)^2$ defining the constraints $V = V_l + V_v$ and $E = E_l + E_g + E_v$. Because the function H is concave with respect to $(V_l, V_v, E_l, E_g, E_v) \in (\mathbb{R}^+)^5$ (as the restriction of the concave function Σ) and \mathbf{A} is a linear transformation, the function $\mathbf{A}H$ is also concave with respect to (V, E) (see [34], Section 5). Then it follows that $S(W)$ is concave with respect to $W = (M, V, E) \in (\mathbb{R}^+)^3$. Similar arguments hold in the case of phase transition between the liquid and its vapor. \square

Remark 2. In [22] the authors provide a similar extensive definition of the mixture entropy for a two-phase mixture when considering phase transition between the two phases, indexed by $k = 1, 2$. They consider the mass and energy conservation that is $M = M_1 + M_2$ and $E = E_1 + E_2$. As the volume constraint is considered, they distinguish the immiscible and the miscible mixtures. When considering an immiscible mixture, their volume constraint is $V = V_1 + V_2$. Then the extensive entropy of the mixture satisfies an analogous formulation as (9), which turns to be an sup-convolution operation, namely

$$S(W) = S_1 \square S_2(W) = \max_{W_1 \in C_1} (S_1(W_1) + S_2(W - W_1)),$$

where the symbol \square is a notation for sup-convolution in convex analysis. When considering a miscible approach, their volume constraint is $V = V_1 = V_2$. Here again the extensive entropy of the mixture is a sup-convolution operation. The sup-convolution operation turns to have many interesting properties (especially linked to the Legendre transform). Such properties have been studied in [21] and [31], for the computation of admissible pressure laws for immiscible and miscible binary mixture.

In the present case, because the volume constraint (6) is simultaneously immiscible (between the liquid and the vapor and gas phases) and miscible (between the gas and the vapor), we cannot express the energy of the mixture as a sup-convolution procedure.

When the equilibrium entropy without phase transition is differentiable with respect to the volume V and the internal energy E , then one can define the temperature and the pressure of the mixture at equilibrium

$$(10) \quad \frac{1}{T} = \frac{\partial S_{NPT}}{\partial E}(M, V, E, M_l, M_g), \quad \frac{P}{T} = \frac{\partial S_{NPT}}{\partial V}(M, V, E, M_l, M_g).$$

The chemical potential and the potentials linked to the masses M_l and M_g are

$$\frac{\mu}{T} = -\frac{\partial S_{NPT}}{\partial M}(M, V, E, M_l, M_g), \quad \frac{\lambda_k}{T} = \frac{\partial S_{NPT}}{\partial M_k}(M, V, E, M_l, M_g), \quad k = l, g.$$

Hence one has the following relation

$$TdS_{NPT} = dE + pdV - \mu dM + \lambda_l dM_l + \lambda_g dM_g.$$

When phase transition is considered, one gets

$$TdS_{PT} = dE + pdV - \mu dM + \lambda_g dM_g.$$

When the maximum of the mixture entropy is reached in the interior of the set of constraints, the three phases are present and at thermodynamical equilibrium [22, 31].

Proposition 2. *The thermodynamical equilibrium corresponds to*

- *the equality of the temperatures*

$$(11) \quad T_l = T_g = T_v,$$

- *the Dalton's law on the pressures of the gas and the vapor phases*

$$(12) \quad p_l = p_g + p_v.$$

Moreover if phase transition is allowed between the liquid and its vapor then the equilibrium is also characterized by

$$(13) \quad \mu_l = \mu_v.$$

Proof. The optimization with respect to the energy and the volume are the same on the two sets of constraints Ω_{ext}^{NPT} and Ω_{ext}^{PT} . Let us fix the energy E_k of the phase $k \in \{l, g, v\}$. Then $E - E_k = E_{k'} + E_{k''}$, with $k' \neq k''$, $k, k' \in \{l, g, v\}$. Thus

$$\frac{\partial}{\partial E_{k'}} (S_k(M_k, V_k, E_k) + S_{k'}(M_{k'}, V_{k'}, E_{k'}) + S_{k''}(M_{k''}, V_{k''}, E_{k''})) = \frac{1}{T_{k'}} - \frac{1}{T_{k''}}.$$

Then the maximum is reached for $T_{k'} = T_{k''}$ for any $k' \neq k'' \in \{l, g, v\}$. Optimizing with respect to the volume under the volume constraint (6) gives

$$\frac{\partial}{\partial V_l} (S_l(M_l, V_l, E_l) + S_g(M_g, V - V_l, E_g) + S_v(M_v, V - V_l, E_g)) = \frac{p_l}{T_l} - \left(\frac{p_g}{T_g} + \frac{p_v}{T_v} \right).$$

Since the temperature are equal, it yields the Dalton's law on the pressures. We now focus on the case where phase transition occurs. In the case of phase transition, we then optimize with respect to the mass in the set of constraints Ω_{ext}^{PT} . Since the mass of the gas M_g is fixed, one has $M - M_g = M_l + M_v$. It yields

$$\frac{\partial}{\partial M_l} (S_l(M_l, V_l, E_l) + S_g(M_g, V_g, E_g) + S_v(M - M_g - M_l, V_v, E_v)) = \frac{\mu_l}{T_l} - \frac{\mu_v}{T_v}.$$

Because $T_l = T_v$, the chemical potentials of the liquid and vapor phases are also equal, the chemical potential of the gas μ_g being fixed. \square

One observe that the pressure relation (12), which contains the Dalton's law on the miscible vapor and gaseous phases, is a direct consequence of the maximization process under the volumic constraint (6).

As a consequence, at equilibrium, one may define the mixture temperature T and pressure p by

$$(14) \quad \begin{aligned} T &= T_l = T_g = T_v \\ p &= p_l = p_g + p_v. \end{aligned}$$

Nevertheless it is not possible de define a mixture chemical potential.

2.3. Intensive characterization of the entropies. We now turn to the definition of intensive quantities. The system is now entirely described by its intensive entropy s defined by (1) as a function of the specific volume $\tau = V/M > 0$ and the specific internal energy $e = E/M > 0$.

We introduce the mass fraction φ_k , the volume fraction α_k and the energy fraction z_k of the phase $k \in \{l, g, v\}$ defined respectively by

$$(15) \quad \varphi_k = M_k/M, \quad \alpha_k = V_k/V, \quad z_k = E_k/E,$$

which belong to $[0, 1]$. Each phase $k = l, g, v$ has a specific volume $\tau_k = V_k/M_k = \alpha_k \tau / \varphi_k$ and a specific internal energy $e_k = E_k/M_k = z_k e / \varphi_k$. The specific entropy s_k of the phase $k \in \{l, g, v\}$ is defined by

$$s_k(\tau_k, e_k) = S_k(1, \tau_k, e_k).$$

Moreover one can derive the intensive form of the Gibbs relation (2) for each phase $k \in \{l, g, v\}$

$$(16) \quad T_k ds_k = de_k + p_k d\tau_k.$$

We now turn to the intensive formulation of the extensive constraints. The extensive volume constraint (6) translates into

$$(17) \quad \begin{cases} 1 = \alpha_l + \alpha_v, \\ \alpha_g = \alpha_v. \end{cases}$$

The mass and energy conservations (4) and (5) read

$$(18) \quad 1 = \varphi_l + \varphi_g + \varphi_v,$$

$$(19) \quad 1 = z_l + z_g + z_v.$$

Out of equilibrium the intensive entropy of the three-phase system, expressed as a function of τ , e and the fractions φ_k, α_k, z_k , $k = l, g, v$, reads

$$(20) \quad \begin{aligned} & \sigma(\tau, e, (\varphi_k)_k, (\alpha_k)_k, (z_k)_k) \\ &= \varphi_l s_l \left(\frac{\alpha_l}{\varphi_l} \tau, \frac{z_l}{\varphi_l} e \right) + \varphi_g s_g \left(\frac{\alpha_g}{\varphi_g} \tau, \frac{z_g}{\varphi_g} e \right) + \varphi_v s_v \left(\frac{\alpha_v}{\varphi_v} \tau, \frac{z_v}{\varphi_v} e \right). \end{aligned}$$

At equilibrium and at fixed (τ, e) , the intensive entropy reaches its maximum. As in the extensive formulation, one has to define the set of constraints depending on whether phase transition occurs or not between the liquid and the vapor phase. Moreover since the gaseous phase does not exchange mass with the others phases, its mass fraction φ_g is fixed during the optimization process.

Proposition 3. Fix $\varphi_g \in [0, 1]$. Let $(\tau, e) \in (\mathbb{R}^+)^2$ be the specific state vector of the system. The equilibrium intensive entropy s of the mixture is:

- without phase transition: φ_l, φ_g are fixed according to (18) and

$$(21) \quad s_{NPT}(\tau, e, \varphi_l, \varphi_g) = \max_{((\alpha_k)_k, (z_k)_k) \in \Omega_{int}^{NPT}} \sigma(\tau, e, (\varphi_k)_k, (\alpha_k)_k, (z_k)_k),$$

where $\Omega_{int}^{NPT} := \{(\alpha_k, z_k), k = l, g, v \mid (17) \text{ and } (19) \text{ hold}\}$

- with phase transition:

$$(22) \quad s_{PT}(\tau, e, \varphi_g) = \max_{((\varphi_k)_k, (\alpha_k)_k, (z_k)_k) \in \Omega_{int}^{PT}} \sigma(\tau, e, (\varphi_k)_k, (\alpha_k)_k, (z_k)_k),$$

where $\Omega_{int}^{PT} := \{(\varphi_k, \alpha_k, z_k), k = l, g, v \mid 1 - \varphi_g = \varphi_l + \varphi_v, (17) \text{ and } (19) \text{ hold}\}$.

In both cases the equilibrium intensive entropy is a concave function of its arguments.

Proof. The characterization of the mixture intensive entropy is a direct consequence of the homogeneity of the extensive mixture entropies defined in (8) and (9), see Proposition 1. The relation (21) (resp. (22)) is achieved by dividing the optimization problem (8) on the set of constraints Ω_{ext}^{NPT} (resp. (9) on the set of constraints Ω_{ext}^{PT}) by the mass M . In the case without phase transition, the intensive entropy $s_{NPT}(\tau, e, \varphi_l, \varphi_g)$ is the restriction of the extensive entropy $S_{NPT}(M, V, E, M_l, M_g)$ on the affine convex subset $\{1\} \times (\mathbb{R}_+)^2 \times [0, 1]^2$. Since S_{NPT} is a concave function of (M, V, E) , s_{NPT} is a concave function of (τ, e) . The same holds in the case of phase transition. \square

We now focus on the intensive equilibrium entropy without phase transition s_{NPT} and prove that it is strictly convex with respect to (τ, ε) .

Proposition 4. *Assume that the mass fractions φ_k are fixed (no phase transition is allowed). Then the intensive equilibrium entropy (21)*

- depends only on (τ, e)
- is a strictly concave function of (τ, e)
- satisfies the relation : $Tds_{NPT} = de + pd\tau$, where T and p are the mixture temperature and pressure at equilibrium.

Proof. According to the definition (21), it is obvious that the equilibrium mixture entropy depends only on (τ, e) at fixed mass fractions φ_k , $k = l, g, v$. Then for any equilibrium state $(\tau, e) \in (\mathbb{R}^+)^2$, it exists (τ_k, e_k) such that

$$(23) \quad \begin{cases} e = \varphi_l e_l + \varphi_g e_g + \varphi_v e_v \\ \tau = \varphi_l \tau_l + \varphi_g \tau_g \\ \varphi_v \tau_v = \varphi_g \tau_g. \end{cases}$$

We now prove the Gibbs relation

$$Tds = de + pd\tau,$$

at fixed φ_k . The phasic entropies satisfy

$$Tds_k = de_k + p_k d\tau_k, \quad k = l, g, v.$$

Multiplying by φ_k and summing over $k = l, g, v$, give

$$Td\left(\sum_{k=l,g,v} \varphi_k s_k\right) = d\left(\sum_{k=l,g,v} \varphi_k e_k\right) + \sum_{k=l,g,v} \varphi_k p_k d\tau_k,$$

according to the equality of the temperatures. By (20) and (23) it yields

$$Tds_{NPT} = de + p_l d(\varphi_l \tau_l) + p_g d(\varphi_g \tau_g) + p_v d(\varphi_v \tau_v).$$

We now use miscibility of the vapor and gas phases $\varphi_g \tau_g = \varphi_v \tau_v$ to get

$$Tds_{NPT} = de + p_l d(\varphi_l \tau_l) + (p_g + p_v) d(\varphi_g \tau_g).$$

The characterization of the pressure equilibrium leads to conclusion.

We turn to the strict concavity of the s_{NPT} . Since the φ_k , $k = l, g, v$, are fixed, we denote $s_{NPT}(\tau, e) = s_{NPT}(\tau, e, (\varphi_k)_k)$. In order to prove that the entropy is

strictly concave, we show that for any equilibrium states (τ, e) and (τ', e') in $(\mathbb{R}^+)^2$, one has

$$s_{NPT}(\tau, e) < s_{NPT}(\tau', e') + \nabla_{(\tau, e)} s_{NPT}(\tau', e') \cdot \begin{pmatrix} \tau - \tau' \\ e - e' \end{pmatrix}.$$

Using formulation (20) one has

$$s_{NPT}(\tau, e) = \varphi_l s_l(\tau_l, e_l) + \varphi_g s_g(\tau_g, e_g) + \varphi_v s_v(\tau_v, e_v).$$

Since the phasic entropies are strictly concave functions of (τ_k, e_k) and differentiable, there exists (τ'_k, e'_k) such that

$$s_{NPT}(\tau, e) < \sum_{k=l, g, v} \varphi_k s_k(\tau'_k, e'_k) + \varphi_k \nabla s_k(\tau'_k, e'_k) \cdot \begin{pmatrix} \tau_k - \tau'_k \\ e_k - e'_k \end{pmatrix}.$$

Now one has $\nabla s_k(\tau'_k, e'_k) = \begin{pmatrix} 1/T_k(\tau'_k, e'_k) \\ p_k(\tau'_k, e'_k)/T_k(\tau'_k, e'_k) \end{pmatrix}$ with $T_k(\tau'_k, e'_k) = T$, $\forall k = l, g, v$, see Proposition 2. The definition of the equilibrium entropy, the equality of the temperature, and the constraints (18) lead to

$$s_{NPT}(\tau, e) < s_{NPT}(\tau', e') + \frac{1}{T}(e - e') + \frac{1}{T}(\varphi_l p_l(\tau_l - \tau'_l) + \varphi_g p_g(\tau_g - \tau'_g) + \varphi_v p_v(\tau_v - \tau'_v)).$$

Using the Dalton's law (14), one can express the mixture pressure as $p_l = p_v + p_g = p$. Then the volume constraints $\tau = \varphi_l \tau_l + \varphi_g \tau_g$ and $\tau = \varphi_l \tau_l + \varphi_v \tau_v$ give

$$s_{NPT}(\tau, e) < s_{NPT}(\tau', e') + \frac{1}{T_l}(e - e') + \frac{p}{T}(\tau - \tau').$$

According to the Gibbs relation, one has $\nabla_{(\tau, e)} s_{NPT} = \begin{pmatrix} 1/T \\ p/T \end{pmatrix}$ which leads to the conclusion. \square

As phase transition is considered between the liquid and its vapor, the mixture entropy is no longer strictly concave with respect to (τ, e) as φ_g is fixed.

Proposition 5. *Assume that the mass fraction φ_g is fixed. Then the intensive equilibrium entropy (22)*

- depends only on (τ, e)
- satisfies the relation : $T ds_{PT} = de + pd\tau$, where T and p are the mixture temperature and pressure at equilibrium.

The proof is similar to the proof of the Proposition 4.

Remark 3. *Note that we do not prove that the equilibrium entropy is a strictly concave function of (τ, e) . Actually this is not the case for binary (immiscible) mixture, see [28, 22, 21] for instance. One may find the computation of a three-phase mixture pressure law in [2] (with a mix type volume constraint like (6)). The authors consider that each phase is depicted by a stiffened gas but it is not possible to give an analytical formulation of the pressure. However computational results illustrate that a saturation zone exists, that is the mixture entropy is not strictly concave.*

3. EQUILIBRIUM THREE-COMPONENT EULER SYSTEMS

We now take into account the dynamic of the three-phase mixture, assuming that the three phases have the same velocity. The aim of this section is to provide an homogeneous equilibrium multicomponent Euler's system, called HEM model, with appropriate closure laws in agreement with the thermodynamical equilibria studied in Section 2.3. Two HEM models are presented corresponding to the cases with or without phase transition. The models have good properties: entropy structure and hyperbolicity.

3.1. Three-phase model without phase transition. At thermodynamical equilibrium the three phase flow is depicted by the multicomponent Euler system

$$(24) \quad \begin{cases} \partial_t(\varphi_l \rho) + \partial_x(\varphi_l \rho u) = 0, \\ \partial_t(\varphi_g \rho) + \partial_x(\varphi_g \rho u) = 0, \\ \partial_t \rho + \partial_x(\rho u) = 0, \\ \partial_t(\rho u) + \partial_x(\rho u^2 + p) = 0, \\ \partial_t(\rho E) + \partial_x((\rho E + p)u) = 0, \\ E = \frac{1}{2}u^2 + e, \\ \forall k \in \{l, g, v\} : p_k = p_k(\tau_k, e_k), \tau_k = \rho_k^{-1}, \\ \varphi_l + \varphi_g + \varphi_v = 1, \end{cases}$$

where the flow as a density ρ (we also define the specific volume $\tau = 1/\rho$), a velocity u , a pressure p , and an internal energy e , E being the total energy. The phase $k = l, g, v$ is depicted by its mass fraction, its pressure p_k , its specific volume τ_k and its specific internal energy e_k , see Section 2.3. All the phases evolve at the same velocity u and we recall that

$$(25) \quad \begin{cases} e = \varphi_l e_l + \varphi_v e_v + \varphi_g e_g, \\ \tau = \varphi_l \tau_l + \varphi_g \tau_g, \\ \varphi_v \tau_v = \varphi_g \tau_g. \end{cases}$$

The multicomponent Euler system admits ten equations and has seventeen unknowns which are

$$(\rho, u, E, p, e, (\varphi_k)_{k \in \{l, g, v\}}, (\tau_k)_{k \in \{l, g, v\}}, (e_k)_{k \in \{l, g, v\}}, (p_k)_{k \in \{l, g, v\}}).$$

Thus one has to provide seven closure laws. The first three closure laws are given by the constraints (25).

The 4 remaining closure laws are given by Proposition 2, that is

$$(26) \quad \begin{cases} T = T_l = T_g = T_v, \\ p = p_l = p_g + p_v, \end{cases}$$

where T and p are the thermodynamical temperature and pressure of the three phase flow and $p = p(1/\rho, e, \varphi_l, \varphi_g)$.

Proposition 6. *The intensive entropy $s_{NPT}(\tau, e, \varphi_l, \varphi_g)$ defined by (21) satisfies*

$$(27) \quad \partial_t s + u \partial_x s_{NPT} = 0.$$

Proof. Let $U = (\rho, \rho u, \rho E, \varphi_g \rho, \varphi_l \rho)$ is a smooth solution of the system (24), then one has

$$\begin{aligned}\partial_t \tau + u \partial_x \tau - \tau \partial_x u &= 0, \\ \partial_t u + u \partial_x u + \tau \partial_x p &= 0, \\ \partial_t e + u \partial_x e + p \tau \partial_x u &= 0, \\ \partial_t \varphi_k + u \partial_x \varphi_k &= 0, \quad k = l, g.\end{aligned}$$

Since s_{NPT} is function of $(\tau, e, \varphi_l, \varphi_g)$, it follows

$$\begin{aligned}\partial_t s_{NPT} &= \frac{\partial s_{NPT}}{\partial \tau} \partial_t \tau + \frac{\partial s_{NPT}}{\partial e} \partial_t e + \frac{\partial s_{NPT}}{\partial \varphi_l \tau} \partial_t \varphi_l + \frac{\partial s_{NPT}}{\partial \varphi_g} \partial_t \varphi_g \\ &= \partial_x u \left(\tau \frac{\partial s_{NPT}}{\partial \tau} - \tau p \frac{\partial s_{NPT}}{\partial e} \right) - u \partial_x s_{NPT}.\end{aligned}$$

Because the entropy s_{NPT} satisfies the relation $T ds_{NPT} = de + pd\tau$ (see Proposition 4), the first term of the right hand side is zero. Hence the entropy s_{NPT} satisfies a transport equation. \square

In order to study the hyperbolicity of the model (24), we adapt a result given in [30] which extends the Godunov-Mock theorem.

Lemma 1. *Let $w : \mathbb{R}^+ \times \mathbb{R} \rightarrow \mathbb{R}^n$ and $f : \mathbb{R}^n \rightarrow \mathbb{R}^n$ defining the system of conservation laws*

$$\partial_t w(t, x) + \partial_x f(w)(t, x) = 0,$$

where $w = (w_1, w_2)^t$ with $w_1 \in \mathbb{R}^l$ and $w_2 \in \mathbb{R}^{n-l}$ and $f = (0, f_2)^t$ with $f_2 \in \mathbb{R}^{n-l}$. Assume that $\eta(w)$ is a strictly convex function with respect to w_2 at fixed w_1 such that

$$\partial_t \eta(w) = 0,$$

and that $\nabla_{w_1} f_2(w) = 0$. Then the system is hyperbolic.

Proof. To prove the hyperbolicity we show that the system is symmetrizable that is there exists a symmetric positive-definite matrix P and a symmetric matrix Q such that

$$P(w) \partial_t w + Q(w) \partial_x w = 0.$$

We define the $n \times n$ symmetrization matrix $P(w)$ by

$$P(w) = \begin{pmatrix} \mathbf{I}_l & 0 \\ 0 & \nabla_{w_2}^2 \eta \end{pmatrix}.$$

The entropy η being strictly convex with respect to w_2 , the matrix $P(w)$ is symmetric positive-definite. The associated convection matrix is $Q(w) = P(w) \nabla_w f(w)$. Since $\nabla_{w_1} f_2(w) = 0$, the matrix Q is symmetric so that the system is symmetrizable. As a consequence the system is hyperbolic. \square

This lemma holds for any variables (t, x) as soon as the system is conservative. Besides we use it in Lagrangian coordinates to prove the following result.

Theorem 1. *The system (24) is hyperbolic.*

Proof. First the system (24) can be written in Lagrangian coordinates

$$\begin{cases} D_t \varphi_l = 0, \\ D_t \varphi_g = 0, \\ D_t \tau - D_m u = 0, \\ D_t u + D_m p = 0, \\ D_t E + D_m(pu) = 0, \end{cases}$$

where $D_t v = \partial_t v + u \partial_x v$ and $D_m v = \tau \partial_x v$. The associated flux reads $f = (0, 0, -u, p, pu)$. We introduce the function η

$$\eta : (\varphi_l, \varphi_g, \tau, u, E) \rightarrow -s_{NPT}(\tau, E - u^2/2, \varphi_l, \varphi_g).$$

According to Proposition 4, the function s_{NPT} is strictly concave with respect to (τ, e) and depends only on (τ, e) . Then η is strictly convex with respect to (τ, u, E) , see [8, 18]. Moreover s_{NPT} is solely advected by the system, since it satisfies (27), see Proposition 6. Hence it yields

$$\begin{aligned} D_t \eta(w) &= \partial_\tau D_t \tau + \partial_u D_t u + \partial_E D_t E \\ &= -\partial_\tau s_{NPT}(\tau, E - u^2/2, \varphi_l, \varphi_g) D_t \tau + \\ &\quad (u D_t u + D_t E) \partial_e s_{NPT}(\tau, E - u^2/2, \varphi_l, \varphi_g) \\ &= -\frac{p}{T} D_t \tau + \partial_e s_{NPT}(u D_t u - D_t E) = -\frac{p}{T} D_m u - \frac{u}{T} D_m p + \frac{1}{T} D_m(p) = 0. \end{aligned}$$

In addition the mixture pressure p , being a partial derivative of the entropy mixture s_{NPT} , does not depend on the fractions φ_l and φ_g . It implies that $\nabla_{\varphi_l, \varphi_g} f = 0$. Now Lemma 1 leads to the conclusion. \square

3.2. Three-phase model with phase transition. When phase transition occurs, the equilibrium multicomponent Euler system reads

$$(28) \quad \begin{cases} \partial_t(\varphi_g \rho) + \partial_x(\varphi_g \rho u) = 0, \\ \partial_t \rho + \partial_x(\rho u) = 0, \\ \partial_t(\rho u) + \partial_x(\rho u^2 + p) = 0, \\ \partial_t(\rho E) + \partial_x((\rho E + p)u) = 0, \\ E = \frac{1}{2} u^2 + e, \\ \forall k \in \{l, g, v\} : p_k = p_k(\tau_k, e_k), \tau_k = \rho_k^{-1}, \\ \varphi_l + \varphi_g + \varphi_v = 1. \end{cases}$$

The system admits nine equations and seventeen unknowns which are

$$(\rho, u, E, p, e, (\varphi_k)_{k \in \{l, g, v\}}, (\tau_k)_{k \in \{l, g, v\}}, (e_k)_{k \in \{l, g, v\}}, (p_k)_{k \in \{l, g, v\}}).$$

Thus one has to provide eight closure laws.

As in the previous case, three closure laws are given by the three intensive constraints (25)

$$\begin{cases} e &= \varphi_l e_l + \varphi_v e_v + \varphi_g e_g, \\ \tau &= \varphi_l \tau_l + \varphi_g \tau_g, \\ \varphi_v \tau_v &= \varphi_g \tau_g. \end{cases}$$

The five remaining closures are given by Proposition 2

$$(29) \quad \begin{cases} T = T_l = T_g = T_v, \\ p = p_l = p_g + p_v, \\ \mu_l = \mu_v. \end{cases}$$

where T and p are the thermodynamical temperature and pressure of the three phase flow and $p = p(1/\rho, e, \varphi_g)$.

Since the equilibrium entropy is not a strictly concave function of its arguments (see Remark 3), it is not possible to invoke the Godunov-Mock theorem or its extension Lemma 1 to prove the hyperbolicity of the system. However it is possible to prove the hyperbolicity by studying the eigenvalues of the system and the positivity of the mixture temperature.

Theorem 2. *The system (28) is hyperbolic.*

Proof. The quasilinear form of the system (28) reads

$$\partial_t \begin{pmatrix} \varphi_g \\ \rho \\ u \\ e \end{pmatrix} + \begin{pmatrix} u & 0 & 0 & 0 \\ 0 & u & \rho & 0 \\ \frac{1}{\rho} \frac{\partial p}{\partial \varphi_g} & \frac{1}{\rho} \frac{\partial p}{\partial \rho} & u & \frac{1}{\rho} \frac{\partial p}{\partial \rho} \\ 0 & 0 & p/\rho & u \end{pmatrix} \partial_x \begin{pmatrix} \varphi_g \\ \rho \\ u \\ e \end{pmatrix} = 0.$$

The Jacobian matrix of the flux has four eigenvalues $u - c$, u (double), $u + c$, where c is the speed of sound given by

$$(30) \quad c^2/\tau^2 = p \partial_e p - \partial_\tau p = -T(p^2 (s_{PT})_{ee} - 2p (s_{PT})_{\tau e} + (s_{PT})_{\tau\tau}).$$

According to Proposition 5, the entropy (s_{PT}) is a concave function which depends only on (τ, e) at fixed φ_g . Hence the right-hand side of (30) is non negative as soon as the temperature $T > 0$. This concludes the proof. \square

4. HOMOGENEOUS RELAXATION MODELS FOR THE THREE-PHASE FLOW

The equilibrium multicomponent Euler systems, presented in the previous section, are difficult to use for practical computations. Although they are proved to be hyperbolic, their pressure laws have no analytical expressions (even if p_k , $k = l, g, v$ are perfect gas laws). Moreover it is well known, see for instance [32, 28, 4], that such pressure laws present pathologies such that slope discontinuities, lack of convexity of the isentropes, leading to composite waves. To overcome this problem, some authors proposed [4, 22, 26, 20, 27] to approximate the equilibrium Euler system by a homogeneous relaxation model. It consists in adding convection equations on the fractions and to modify the pressure to make it depend on the fractions. In order to achieve the thermodynamical equilibrium, appropriate relaxation source terms complete the equations on the fractions. The numerical approximation of the relaxed model is easier. Traditionally it consists on a splitting approach. In a first step the convective part is treated with an approximate Riemann solver. During the second step the conservative variables are stored and the pressure is updated from the physical entropy maximization. By construction both steps are entropy satisfying.

We propose in this section to construct the HRM models associated to the HEM three-phase models studied in Section 3 while distinguishing the cases where phase transition occurs or not. First we focus on the model without phase transition and

adapt the construction of the HRM model introduced in [4]. The case with phase transition is treated as corollary.

4.1. HRM model without phase transition. Starting from the equilibrium three-phase model (24), we propose a non-homogeneous model in which the three phases are no longer at thermal and mechanical equilibrium (still without phase transition). To do so one introduces supplementary variables that are the volume fraction of liquid α_l and the energy fractions z_l and z_g defined in (15). Hence the pressure depends not only on $\rho, e, \varphi_l, \varphi_g$ but also on $Y = (\alpha_l, z_l, z_g)$. When no mass transfer occurs between the liquid and the gas, the fractions should be perfectly convected *i.e.*

$$(31) \quad \partial_t Y + u \partial_x Y = 0.$$

The mass conservation allows to write (31) under the conservative form

$$(32) \quad \partial_t(\rho Y) + \partial_x(\rho u Y) = 0.$$

Thus the resulting HRM model reads

$$(33) \quad \begin{cases} \partial_t(\varphi_k \rho) + \partial_x(\varphi_k \rho u) = 0, & k = l, g, \\ \partial_t(z_k \rho) + \partial_x(z_k \rho u) = 0, & k = l, g, \\ \partial_t(\alpha_l \rho) + \partial_x(\alpha_l \rho u) = 0, \\ \partial_t \rho + \partial_x(\rho u) = 0, \\ \partial_t(\rho u) + \partial_x(\rho u^2 + p) = 0, \\ \partial_t(\rho E) + \partial_x((\rho E + p)u) = 0, \end{cases}$$

with the closure pressure law

$$(34) \quad p = p(1/\rho, e, \varphi_l, \varphi_g, \alpha_l, z_l, z_g).$$

One should add an entropy criterion to the model. With $\rho = 1/\tau$ the concave function $\sigma(\tau, e, \varphi_l, \varphi_g, \alpha_l, z_l, z_g)$ defined in (20) would be an entropy function if it satisfies the first order PDE

$$(35) \quad \partial_\tau \sigma - p(1/\tau, e, \varphi_l, \varphi_g, \alpha_l, z_l, z_g) \partial_e \sigma = 0.$$

Setting $T = 1/\partial_e \sigma$, one recovers the relation

$$T d\sigma = de + p d\tau + \sum_{k=l,g} \partial_{\varphi_k} \sigma d\varphi_k + \partial_{\alpha_l} \sigma d\alpha_l + \sum_{k=l,g} \partial_{z_k} \sigma dz_k.$$

Weak solutions of (33)-(34) satisfy

$$(36) \quad \partial_t(\rho \sigma) + \partial_x(\rho u \sigma) \geq 0,$$

which becomes an equality as regular solutions are concerned. The concavity of σ with respect to $(\tau, e, \varphi_l, \varphi_g, \alpha_l, z_l, z_g)$ is equivalent to the convexity of $H = -\rho \sigma$ with respect to the conservative variables $(\rho, \rho u, \rho E, \varphi_l \rho, \varphi_g \rho, z_l \rho, z_g \rho, \alpha_l \rho)$, following [8, 18]. Hence $H = -\rho \sigma$ is a Lax entropy for (33).

In order to bring the system to thermodynamical equilibrium described in Proposition 3-(21), a source term has to be added to the fractions equations

$$\partial_t Y + u \partial_x Y = Q.$$

As relaxation towards the equilibrium is infinitely fast, one recovers the equilibrium fractions which satisfy

$$(37) \quad \begin{aligned} Y &= Y_{eq}^{NPT}(\tau, e, \varphi_l, \varphi_g) \\ &= \operatorname{argmax}_{(\alpha_l, z_l, z_g)} \sigma(\tau, e, \varphi_l, \varphi_g, \alpha_l, z_l, z_g). \end{aligned}$$

As a result the equilibrium pressure law is

$$(38) \quad p_{eq}^{NPT}(\tau, e, \varphi_l, \varphi_g) := p(\tau, e, \varphi_l, \varphi_g, Y_{eq}^{NPT}(\tau, e, \varphi_l, \varphi_g)),$$

defined by the Dalton's law (14). Following [7, 4, 27], a natural source term is

$$(39) \quad Q = \lambda(Y_{eq}^{NPT}(\tau, e, \varphi_l, \varphi_g) - Y)$$

where the parameter λ goes to $+\infty$ to achieve the thermodynamical equilibrium.

Moreover the source term Q complies with the entropy production criterion since

$$(40) \quad \begin{aligned} \partial_t \sigma + u \partial_x \sigma &= \nabla_Y \sigma \cdot (\partial_t Y + u \partial_x Y) \\ &= \lambda \nabla_Y \sigma \cdot (Y_{eq}^{NPT}(\tau, e, \varphi_l, \varphi_g) - Y) \\ &\geq \lambda (\sigma(\tau, e, \varphi_l, \varphi_g, Y_{eq}^{NPT}) - \sigma(\tau, e, \varphi_l, \varphi_g, \alpha_l, z_l, z_g)) \\ &\geq 0, \end{aligned}$$

by concavity of the entropy σ .

The drawback of the source term (39) is that the relaxation parameter λ is identical for all the fractions. Hence the relaxation times towards the mechanical and thermal equilibrium are the same, which has no particular physical meaning. An alternative which guarantees the entropy production is

$$(41) \quad \begin{aligned} Q &= \nabla_Y \sigma(\tau, e, \varphi_l, \varphi_g, Y), \\ &= \begin{pmatrix} \tau \left(\frac{p_l}{T_l} - \left(\frac{p_g}{T_g} + \frac{p_v}{T_v} \right) \right) \\ e \left(\frac{1}{T_l} - \frac{1}{T_v} \right) \\ e \left(\frac{1}{T_g} - \frac{1}{T_v} \right) \end{pmatrix}, \end{aligned}$$

since $\partial_t \sigma + u \partial_x \sigma = |\nabla_Y \sigma|^2 \geq 0$. This choice of source term enables to use different relaxation scales for mechanical and thermal equilibria.

4.2. HRM model with phase transition. Following the same methodology explained in Section 4.1, one obtains the HRM model taking into account phase transition between the liquid and the vapor. It reads

$$(42) \quad \begin{cases} \partial_t Y + u \partial_x Y = Q, \\ \partial_t(\varphi_g \rho) + \partial_x(\varphi_g \rho u) = 0, \\ \partial_t \rho + \partial_x(\rho u) = 0, \\ \partial_t(\rho u) + \partial_x(\rho u^2 + p) = 0, \\ \partial_t(\rho E) + \partial_x((\rho E + p)u) = 0, \end{cases}$$

where the fraction vector is $Y = (\varphi_l, \alpha_l, z_l, z_g)$ and the closure pressure law

$$(43) \quad p = p(1/\rho, e, \varphi_g, \varphi_l, \alpha_l, z_l, z_g).$$

Again the entropy $\sigma(\tau, e, \varphi_g, \varphi_l, \alpha_l, z_l, z_g)$ defined in (20) satisfy the entropy inequality (36) as soon as it complies with (35). The source term Q has to be chosen to recover the thermodynamical equilibrium described by the fractions

$$(44) \quad \begin{aligned} Y &= Y_{eq}^{PT}(\tau, e, \varphi_g) \\ &= \operatorname{argmax}_{(\varphi_l, \alpha_l, z_l, z_g)} \sigma(\tau, e, \varphi_l, \varphi_g, \alpha_l, z_l, z_g), \end{aligned}$$

leading to the equilibrium pressure law

$$(45) \quad p_{eq}^{PT}(\tau, e, \varphi_g) := p(\tau, e, \varphi_g, Y_{eq}^{PT}(\tau, e, \varphi_g)).$$

Again the source term Q could be either

$$(46) \quad Q = \lambda(Y_{eq}^{PT}(\tau, e, \varphi_g) - Y),$$

or

$$(47) \quad \begin{aligned} Q &= \lambda \nabla_Y \sigma(\tau, e, \varphi_g, Y_{eq}^{PT}(\tau, e, \varphi_g)) \\ &= \begin{pmatrix} s_l - \pi \frac{p_l}{T_l} - \frac{e_l}{T_l} - s_v + \tau_v \frac{p_v}{T_v} + \frac{e_v}{T_v} \\ \tau \left(\frac{p_l}{T_l} - \left(\frac{p_g}{T_g} + \frac{p_v}{T_v} \right) \right) \\ e \left(\frac{1}{T_l} - \frac{1}{T_v} \right) \\ e \left(\frac{1}{T_g} - \frac{1}{T_v} \right). \end{pmatrix} \end{aligned}$$

Using the characterization (3) of the chemical potential, the first component of Q boils down to

$$(48) \quad \partial_{\varphi_l} \sigma = -\frac{\mu_l}{T_l} + \frac{\mu_v}{T_v},$$

which reflects the mass transfer between the liquid and its vapor.

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