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

Hélène Mathis[1,*]

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.

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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 loss of coolant accident in pressurized water reactors or in vapor explosions in steel industry [5, 45]. Erosion due to cavitation may also involve three-phase models. Indeed it has been shown in [43] that the collapse and rebound of a cavitation bubble of vapor immersed in water are influenced by the amount of non-condensable gas present inside the bubble before its collapse. Within the two last decades, modelling compressible multiphase flows has resulted in an abundant literature especially about two-phase flows, see for instance [3,12,13,16,17,33]. More recently attention has been paid to the simulation of three-phase flows [20,25,26,39,41], 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

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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, etc. For particular Equations of State (EoS), the Riemann problem is also well understood and has led to the development of relevant numerical approximation (see again [20, 25, 26, 39] 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 and Rency [10, 11]. Since the phases are miscible, Dellacherie and coauthor state that the equilibrium mixture pressure is the sum of the pressures of each phases. This expected result is known as the Dalton's law, see [18] 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. In [10,11], 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 [34] about the comparison of several closure laws applied to a 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 occurs or not. The core of the paper is the modelling of a rigorous thermodynamical model. It allows to construct a hyperbolic HEM model to depict the motion of the compressible three-phase mixture which possesses a mathematical entropy structure in adequacy with the thermodynamics of the mixture. We do not address numerical aspects and focus on the thermodynamical modelling and the entropy structure of the HEM we built. The numerical approximation of the three-phase HEM and Homogeneous Relaxation Models (HRM) is a huge topic in itself, in particular as regards the relaxation towards the thermodynamical equilibrium. We refer to [30] for the approximation of (immiscible) three-phase HRM models and to [20, 25, 39, 41] for the approximation of (immiscible) three-phase three-pressure models.

First we aim at precisely give an accurate description of the thermodynamical equilibrium of the system. Adopting the Gibbs formalism, as done in [23, 24, 36], 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 wether 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. Namely we consider that the vapor (occupying the volume V_{v}) and the gas (with volume V_{g}) are perfectly intimate and behave like ideal gases while an interface separates the liquid (with volume V_{l}) and these gaseous phases. The constraint reads

$$\begin{cases} V = V_{\mathrm{l}} + V_{\mathrm{g}}, \\ V_{\mathrm{g}} = V_{\mathrm{v}}. \end{cases}$$

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 relative works in [23, 36]. At this stage, the maximization of the mixture entropy allows to recover a consistent characterization of the thermodynamical equilibrium: the Dalton's law for the gaseous phases and the equality of the temperatures apply. We recall that the Dalton's law states that the mixture pressure of two ideal gases has to be the sum of the partial pressures, see [38].

Actually we have used the same thermodynamical model in [2] to model the rebound and collapse of a bubble of air and vapor surrounded by liquid. In this preliminary work, each phase follows a stiffened gas law. Following [4], rather than maximizing the mixture entropy, one imposes directly the thermodynamical

equilibrium. It allows to compute the mass fraction of the vapor and then deduces the other quantities, notably the mixture pressure as a function of the mean specific volume, the mean internal energy and the mass fraction of gas. Note that the mixture pressure is not analytical and the computation of the mass and volume fractions require to solve nonlinear problems. Then the mixture pressure law is coupled to a HEM model for the fluid dynamic. One provides numerical results obtained by a finite volume scheme with relaxation. The computational effort due to the computation of the mixture pressure law is significantly reduced using local grid refinement and parallelization. Numerical results present some pressure jumps in the cavitation region. Understanding these phenomena has motivated the present work, which can be seen as an extension of [2]. In the sequel we do not restrict ourselves to a particular equation of state but consider general equations satisfying classical assumptions of smoothness and concavity, see [6]. In order to investigate the question of the origine of the pressure jumps highlighted in [2], the idea is to analyze the specific equilibrium entropies in terms of optimization problems in the spirit of [1, 15, 23, 24, 36]. We specially focus on the (strict) concavity property of the mixture entropy. This study allows then to address the construction of three-phase Euler systems at thermodynamical equilibrium with a coherent entropy structure. We focus on the stability of the systems and prove their hyperbolicity.

Section 3 addresses the construction of three-phase Euler systems at thermodynamical equilibrium called HEM models. Following the works of Dellacherie and Rency [10, 11], 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 wether 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 [34]. 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 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 detailled in [2] for a three-phase mixture (see also Rem. 2.10). Besides phase transition leads to a lack of convexity of the isentropes or slope discontinuities of the entropy, which result in the appearance of composite waves, see [37, 40, 44]. 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 [21, 28, 29] 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. It begins by the thermodynamical modelling of a single fluid. We assume that it is characterized by a set of extensive variables, namely its mass, volume and energy and that its thermodynamical behaviour is entirely described by its extensive entropy function. We make several classical assumptions about the smoothness of this entropy [6]: strict concavity, upper semi-continuity and differentiability. Then we turn to the modelling of the three-phase mixture. We assume that each phase is depicted by an extensive entropy function with similar properties. These assumptions are mandatory to address the thermodynamical description of the mixture. Indeed, according to the second principle, at thermodynamical equilibrium, the mixture entropy results from the maximization of the sum of the phasic entropies. The existence of the maximum is ensured by the semi-continuity assumptions on the phasic entropies. The key point of the modelling is 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. We characterize two possible equilibria depending on whether 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

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

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 [14].

Assumption 2.1. *Assume the entropy $S : (\mathbb{R}^+)^3 \to \mathbb{R} \cup \{-\infty\}$ 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

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

(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 [42]. 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
$$P := T\frac{\partial S}{\partial V},$$
- the chemical potential μ
$$\mu := -T\frac{\partial S}{\partial M}.$$

Hence one can state the extensive Gibbs relation

$$T\mathrm{d}S = \mathrm{d}E + P\mathrm{d}V - \mu\mathrm{d}M.$$

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

$$s = S(1, V/M, E/M). \tag{2.1}$$

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

$$T\mathrm{d}s = \mathrm{d}e + P\mathrm{d}\tau. \tag{2.2}$$

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

$$\mu = -Ts + p\tau + e. \tag{2.3}$$

Since S is a PH1 concave function of class $\mathcal{C}^2$ on the convex domain C, one can prove that $(\tau, e) \mapsto s(\tau, e)$ is strictly concave on the convex set $\{(\tau, e),\ (1, \tau, e) \in C\}$. This result, proven in [9] and [32], is based on the study of the Hessian matrix of S and its signature on the interior of C.

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 $k \in \{\mathrm{l}, \mathrm{g}, \mathrm{v}\}$. We assume that each phase is entirely described by its entropy function S_k satisfying Assumption 2.1 for an extensive state vector $W_k = (M_k, V_k, E_k)$ belonging to the close convex cone C_k defined in Assumption 2.1-(i).

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

$$M = M_\mathrm{l} + M_\mathrm{g} + M_\mathrm{v}, \tag{2.4}$$

and the internal energy conservation leads to

$$E = E_\mathrm{l} + E_\mathrm{v} + E_\mathrm{g}. \tag{2.5}$$

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 volume constraints

$$\begin{cases} V = V_\mathrm{l} + V_\mathrm{v}, \\ V_\mathrm{g} = V_\mathrm{v}. \end{cases} \tag{2.6}$$

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

Remark 2.2 (Absence of one phase)**.** 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 $M_{\rm v} = 0$ (resp. $M_{\rm g} = 0$). Indeed setting $V_{\rm v} = 0$ (resp. $V_{\rm g} = 0$) is meaningless because the volume constraint (2.6) 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 $M_{\rm l} = 0$ and $V_{\rm l} = 0$.

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 $(W_{\rm l}, W_{\rm g}, W_{\rm v}) \in C_{\rm l} \times C_{\rm g} \times C_{\rm v}$, it reads

$$\Sigma(W_{\rm l}, W_{\rm g}, W_{\rm v}) = S_{\rm l}(W_{\rm l}) + S_{\rm g}(W_{\rm g}) + S_{\rm v}(W_{\rm v}). \tag{2.7}$$

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 $\Omega_{\rm ext}^{\rm NPT}$ (No Phase Transition) and $\Omega_{\rm ext}^{\rm PT}$ (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 $M_{\rm g}$ is fixed.

Definition 2.3. Fix $M_{\rm g} \geq 0$. 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: $M_{\rm l}$ and $M_{\rm v}$ are fixed satisfying the mass conservation (2.4) and

$$S_{\rm NPT}(M, V, E, M_{\rm l}, M_{\rm g}) = \max_{(W_{\rm l}, W_{\rm g}, W_{\rm v}) \in \Omega_{\rm ext}^{\rm NPT}} \Sigma(W_{\rm l}, W_{\rm g}, W_{\rm v}), \tag{2.8}$$

  where $\Omega_{\rm ext}^{\rm NPT} := \{W_k \in C_k,\ k = {\rm l}, {\rm g}, {\rm v}\ |(2.5) \text{ and } (2.6) \text{ hold}\}$
- with phase transition:

$$S_{\rm PT}(M, V, E, M_{\rm g}) = \max_{(W_{\rm l}, W_{\rm g}, W_{\rm v}) \in \Omega_{\rm ext}^{\rm PT}} \Sigma(W_{\rm l}, W_{\rm g}, W_{\rm v}), \tag{2.9}$$

  where $\Omega_{\rm ext}^{\rm PT} := \{W_k \in C_k,\ k = {\rm l}, {\rm g}, {\rm v}\ |M - M_{\rm g} = M_{\rm l} + M_{\rm v}, (2.5) \text{ and } (2.6) \text{ hold}\}$.

The existence of the mixture entropies $S_{\rm NPT}$ and $S_{\rm PT}$ is ensured as soon as the phasic entropies S_k, $k = {\rm l}, {\rm g}, {\rm v}$, satisfy Assumption 2.1. Indeed the constraint sets $\Omega_{\rm ext}^{\rm NPT}$ and $\Omega_{ext}^{ext} by \Omega_{ext}^{PT}$ are non-empty closed bounded convex sets (see Assumption 2.1-(i)). According to Assumption 2.1-(iv) the entropies S_k are upper semi-continuous functions, therefore Σ is also upper semi-continuous. This semi-continuity assumption guarantees that the maximum is reached [27, 42]. Note that the maximum may not be reached on a unique point but the maximal value is unique.

Proposition 2.4. *The extensive equilibrium entropy $S_{\rm NPT}$ (resp. $S_{\rm PT}$) of the three-phase mixture defined either by (2.8) (resp. (2.9)) is a PH1 concave function of its arguments.*

Proof. The function $\Sigma(W_{\rm l}, W_{\rm g}, W_{\rm v})$ is a concave function on $C_{\rm l} \times C_{\rm g} \times C_{\rm v}$ since it is a sum of concave functions. We now focus on the optimization problem (2.8) over the set of constraints $\Omega_{\rm ext}^{\rm NPT}$ that is without phase transition. The mass of gas $M_{\rm g}$ is fixed and the maximization is performed on the volume and the energy only. Hence we omit the dependency on $M_{\rm l}$ and $M_{\rm g}$ and get

$$\begin{aligned} S(M, V, E) = & \max_{\begin{cases} V = V_{\rm l} + V_{\rm v} \\ V_{\rm g} = V_{\rm v} \\ E = E_{\rm l} + E_{\rm g} + E_{\rm v} \end{cases}} \Sigma(W_{\rm l}, W_{\rm g}, W_{\rm v}), \\ = & \max_{\begin{cases} V = V_{\rm l} + V_{\rm v} \\ E = E_{\rm l} + E_{\rm g} + E_{\rm v} \end{cases}} \Sigma(W_{\rm l}, (M_{\rm g}, V_{\rm v}, E_{\rm g}), W_{\rm v}). \end{aligned}$$

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

$$\begin{aligned} S(W) &= (\mathbf{A}H)(V,E) \\ &= \max\{H(V_\mathrm{l}, V_\mathrm{v}, E_\mathrm{l}, E_\mathrm{g}, E_\mathrm{v}) |\ \mathbf{A}(V_\mathrm{l}, V_\mathrm{v}, E_\mathrm{l}, E_\mathrm{g}, E_\mathrm{v})^t = (V,E)^t\}, \end{aligned}$$

where $H(V_\mathrm{l}, V_\mathrm{g}, E_\mathrm{l}, E_\mathrm{g}, E_\mathrm{v}) = S_\mathrm{l}(M_\mathrm{l}, V_\mathrm{l}, E_\mathrm{l}) + S_\mathrm{g}(M_\mathrm{g}, V_\mathrm{v}, E_\mathrm{g}) + S_\mathrm{v}(M_\mathrm{v}, V_\mathrm{v}, E_\mathrm{v})$ 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 $V = V_\mathrm{l} + V_\mathrm{v}$ and $E = E_\mathrm{l} + E_\mathrm{g} + E_\mathrm{v}$. Because the function H is concave with respect to $(V_\mathrm{l}, V_\mathrm{v}, E_\mathrm{l}, E_\mathrm{g}, E_\mathrm{v}) \in (R^+)^5$ (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 [42], Sect. 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. □

Remark 2.5. In [24] 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 (2.9), which turns to be a 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 [23] and [36], for the computation of admissible pressure laws for immiscible and miscible binary mixture.

In the present case, because the volume constraint (2.6) 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

$$\frac{1}{T} = \frac{\partial S_\mathrm{NPT}}{\partial E}(M,V,E,M_\mathrm{l},M_\mathrm{g}), \quad \frac{P}{T} = \frac{\partial S_\mathrm{NPT}}{\partial V}(M,V,E,M_\mathrm{l},M_\mathrm{g}). \tag{2.10}$$

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

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

The notations λ_k may be also found in [32]. Hence one has the following relation

$$T\mathrm{d}S_\mathrm{NPT} = \mathrm{d}E + p\mathrm{d}V - \mu\mathrm{d}M + \lambda_\mathrm{l}\mathrm{d}M_\mathrm{l} + \lambda_\mathrm{g}\mathrm{d}M_\mathrm{g}. \tag{2.11}$$

When phase transition is considered, one gets

$$T\mathrm{d}S_\mathrm{PT} = \mathrm{d}E + p\mathrm{d}V - \mu\mathrm{d}M + \lambda_\mathrm{g}\mathrm{d}M_\mathrm{g}. \tag{2.12}$$

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 [24, 36].

Proposition 2.6. *The thermodynamical equilibrium corresponds to*

- *the equality of the temperatures*

$$T_{\rm l} = T_{\rm g} = T_{\rm v}, \tag{2.13}$$

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

$$p_{\rm l} = p_{\rm g} + p_{\rm v}. \tag{2.14}$$

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

$$\mu_{\rm l} = \mu_{\rm v}. \tag{2.15}$$

Proof. The optimization with respect to the energy and the volume are the same on the two sets of constraints $\Omega_{\rm ext}^{\rm NPT}$ and $\Omega_{\rm ext}^{\rm PT}$. Let us fix the energy E_k of the phase $k \in \{\rm l, g, v\}$. Then $E - E_k = E_{k'} + E_{k''}$, with $k' \neq k''$, $k, k' \in \{\rm l, g, v\}$. 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 $k' \neq k'' \in \{\rm l, g, v\}$. Optimizing with respect to the volume under the volume constraint (2.6) gives

$$\frac{\partial}{\partial V_{\rm l}}(S_{\rm l}(M_{\rm l}, V_{\rm l}, E_{\rm l}) + S_{\rm g}(M_{\rm g}, V - V_{\rm l}, E_{\rm g}) + S_{\rm v}(M_{\rm v}, V - V_{\rm l}, E_{\rm g})) = \frac{p_{\rm l}}{T_{\rm l}} - \left(\frac{p_{\rm g}}{T_{\rm g}} + \frac{p_{\rm v}}{T_{\rm v}}\right).$$

Since the temperatures 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 $\Omega_{\rm ext}^{\rm PT}$. Since the mass of the gas $M_{\rm g}$ is fixed, one has $M - M_{\rm g} = M_{\rm l} + M_{\rm v}$. It yields

$$\frac{\partial}{\partial M_{\rm l}}(S_{\rm l}(M_{\rm l}, V_{\rm l}, E_{\rm l}) + S_{\rm g}(M_{\rm g}, V_{\rm g}, E_{\rm g}) + S_{\rm v}(M - M_{\rm g} - M_{\rm l}, V_{\rm v}, E_{\rm v})) = \frac{\mu_{\rm l}}{T_{\rm l}} - \frac{\mu_{\rm v}}{T_{\rm v}}.$$

Because $T_{\rm l} = T_{\rm v}$, the chemical potentials of the liquid and vapor phases are also equal, the chemical potential of the gas $\mu_{\rm g}$ being fixed. □

One observes that the pressure relation (2.14), 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 (2.6).

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

$$\begin{aligned} T &= T_{\rm l} = T_{\rm g} = T_{\rm v} \\ p &= p_{\rm l} = p_{\rm g} + p_{\rm v}. \end{aligned} \tag{2.16}$$

Nevertheless it is not possible to 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 (2.1) 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 $k \in \{\rm l, g, v\}$ defined respectively by

$$\varphi_k = M_k/M, \quad \alpha_k = V_k/V, \quad z_k = E_k/E, \tag{2.17}$$

which belong to $[0,1]$. Each phase $k=\mathrm{l},\mathrm{g},\mathrm{v}$ has a specific volume $\tau_k = V_k/M_k = \alpha_k\tau/\varphi_k$ and a specific internal energy $e_k = E_k/M_k = z_k e/\varepsilon_k$. The specific entropy s_k of the phase $k\in\{\mathrm{l},\mathrm{g},\mathrm{v}\}$ 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 (2.2) for each phase $k\in\{\mathrm{l},\mathrm{g},\mathrm{v}\}$

$$T_k \mathrm{d}s_k = \mathrm{d}e_k + p_k \mathrm{d}\tau_k. \tag{2.18}$$

We now turn to the intensive formulation of the extensive constraints. The extensive volume constraint (2.6) translates into

$$\begin{cases} 1 = \alpha_\mathrm{l} + \alpha_\mathrm{v}, \\ \alpha_\mathrm{g} = \alpha_\mathrm{v}. \end{cases} \tag{2.19}$$

The mass and energy conservations (2.4) and (2.5) read

$$1 = \varphi_\mathrm{l} + \varphi_\mathrm{g} + \varphi_\mathrm{v}, \tag{2.20}$$

$$1 = z_\mathrm{l} + z_\mathrm{g} + z_\mathrm{v}. \tag{2.21}$$

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, $k=\mathrm{l},\mathrm{g},\mathrm{v}$, reads

$$\begin{aligned} &\sigma(\tau,e,(\varphi_k)_k,(\alpha_k)_k,(z_k)_k) \\ &= \varphi_l s_\mathrm{l}\left(\frac{\alpha_\mathrm{l}}{\varphi_\mathrm{l}}\tau, \frac{z_\mathrm{l}}{\varphi_\mathrm{l}}e\right) + \varphi_\mathrm{g} s_\mathrm{g}\left(\frac{\alpha_\mathrm{g}}{\varphi_\mathrm{g}}\tau, \frac{z_\mathrm{g}}{\varphi_\mathrm{g}}e\right) + \varphi_\mathrm{v} s_\mathrm{v}\left(\frac{\alpha_\mathrm{v}}{\varphi_\mathrm{v}}\tau, \frac{z_\mathrm{v}}{\varphi_\mathrm{v}}e\right). \end{aligned} \tag{2.22}$$

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 2.7. *Fix $\varphi_\mathrm{g}\in[0,1]$. 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 (2.20) and*

$$s_{\mathrm{NPT}}(\tau,e,\varphi_\mathrm{l},\varphi_\mathrm{g}) = \max_{((\alpha_k)_k,(z_k)_k)\in\Omega_{\mathrm{int}}^{\mathrm{NPT}}} \sigma(\tau,e,(\varphi_k)_k,(\alpha_k)_k,(z_k)_k), \tag{2.23}$$

  where $\Omega_{\mathrm{int}}^{\mathrm{NPT}} := \{(\alpha_k,z_k),\ k=\mathrm{l},\mathrm{g},\mathrm{v} |$ (2.19) and (2.21) hold$\}$
- *with phase transition:*

$$s_{\mathrm{PT}}(\tau,e,\varphi_\mathrm{g}) = \max_{((\varphi_k)_k,(\alpha_k)_k,(z_k)_k)\in\Omega_{\mathrm{int}}^{\mathrm{PT}}} \sigma(\tau,e,(\varphi_k)_k,(\alpha_k)_k,(z_k)_k), \tag{2.24}$$

  where $\Omega_{\mathrm{int}}^{\mathrm{PT}} := \{(\varphi_k,\alpha_k,z_k),\ k=\mathrm{l},\mathrm{g},\mathrm{v} | 1-\varphi_\mathrm{g} = \varphi_\mathrm{l}+\varphi_\mathrm{v},$ (2.19) and (2.21) 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 (2.8) and (2.9), see Proposition 2.4. The relation (2.23) (resp. (2.24)) is achieved by dividing the optimization problem (2.8) on the set of constraints $\Omega_{\mathrm{ext}}^{\mathrm{NPT}}$ (resp. (2.9) on the set of constraints $\Omega_{\mathrm{ext}}^{\mathrm{PT}}$) by the mass M. In the case without phase transition, the intensive entropy $s_{\mathrm{NPT}}(\tau,e,\varphi_\mathrm{l},\varphi_\mathrm{g})$ is the restriction of the extensive entropy $S_{\mathrm{NPT}}(M,V,E,M_\mathrm{l},M_\mathrm{g})$ 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. □

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 2.8. *Assume that the mass fractions φ_k are fixed (no phase transition is allowed). Then the intensive equilibrium entropy* (2.23)

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

Proof. According to the definition (2.23), it is obvious that the equilibrium mixture entropy depends only on (τ, e) at fixed mass fractions φ_k, $k = \mathrm{l}, \mathrm{g}, \mathrm{v}$. Then for any equilibrium state $(\tau, e) \in (\mathbb{R}^+)^2$, it exists (τ_k, e_k) such that

$$\begin{cases} e = \varphi_{\mathrm{l}} e_{\mathrm{l}} + \varphi_{\mathrm{g}} e_{\mathrm{g}} + \varphi_{\mathrm{v}} e_{\mathrm{v}} \\ \tau = \varphi_{\mathrm{l}} \tau_{\mathrm{l}} + \varphi_{\mathrm{g}} \tau_{\mathrm{g}} \\ \varphi_{\mathrm{v}} \tau_{\mathrm{v}} = \varphi_{\mathrm{g}} \tau_{\mathrm{g}}. \end{cases} \tag{2.25}$$

We now prove the Gibbs relation

$$T\mathrm{d}s = \mathrm{d}e + p\mathrm{d}\tau,$$

at fixed φ_k. The phasic entropies satisfy

$$T\mathrm{d}s_k = \mathrm{d}e_k + p_k \mathrm{d}\tau_k, \quad k = \mathrm{l}, \mathrm{g}, \mathrm{v}.$$

Multiplying by φ_k and summing over $k = \mathrm{l}, \mathrm{g}, \mathrm{v}$, gives

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

according to the equality of the temperatures. By (2.22) and (2.25) it yields

$$T\mathrm{d}s_{\mathrm{NPT}} = \mathrm{d}e + p_{\mathrm{l}}\mathrm{d}(\varphi_{\mathrm{l}}\tau_{\mathrm{l}}) + p_{\mathrm{g}}\mathrm{d}(\varphi_{\mathrm{g}}\tau_{\mathrm{g}}) + p_{\mathrm{v}}\mathrm{d}(\varphi_{\mathrm{v}}\tau_{\mathrm{v}}).$$

We now use miscibility of the vapor and gas phases $\varphi_{\mathrm{g}}\tau_{\mathrm{g}} = \varphi_{\mathrm{v}}\tau_{\mathrm{v}}$ to get

$$T\mathrm{d}s_{\mathrm{NPT}} = \mathrm{d}e + p_{\mathrm{l}}\mathrm{d}(\varphi_{\mathrm{l}}\tau_{\mathrm{l}}) + (p_{\mathrm{g}} + p_{\mathrm{v}})\mathrm{d}(\varphi_{\mathrm{g}}\tau_{\mathrm{g}}).$$

The characterization of the pressure equilibrium leads to the conclusion.

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

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

Using formulation (2.22) one has

$$s_{\mathrm{NPT}}(\tau, e) = \varphi_{\mathrm{l}} s_{\mathrm{l}}(\tau_{\mathrm{l}}, e_{\mathrm{l}}) + \varphi_{\mathrm{g}} s_{\mathrm{g}}(\tau_{\mathrm{g}}, e_{\mathrm{g}}) + \varphi_{\mathrm{v}} s_{\mathrm{v}}(\tau_{\mathrm{v}}, e_{\mathrm{v}}).$$

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

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

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 $T_k(\tau'_k, e'_k) = T$, $\forall k = \mathrm{l}, \mathrm{g}, \mathrm{v}$, see Proposition 2.6. The definition of the equilibrium entropy, the equality of the temperature, and the constraints (2.20) lead to

$$s_{\mathrm{NPT}}(\tau, e) < s_{\mathrm{NPT}}(\tau', e') + \frac{1}{T}(e - e') + \frac{1}{T}\left(\varphi_{\mathrm{l}} p_{\mathrm{l}}(\tau_{\mathrm{l}} - \tau'_{\mathrm{l}}) + \varphi_{\mathrm{g}} p_{\mathrm{g}}(\tau_{\mathrm{g}} - \tau'_{\mathrm{g}}) + \varphi_v p_{\mathrm{v}}(\tau_{\mathrm{v}} - \tau'_{\mathrm{v}})\right).$$

Using Dalton's law (2.16), one can express the mixture pressure as $p_{\mathrm{l}} = p_{\mathrm{v}} + p_{\mathrm{g}} = p$. Then the volume constraints $\tau = \varphi_{\mathrm{l}}\tau_{\mathrm{l}} + \varphi_{\mathrm{g}}\tau_{\mathrm{g}}$ and $\tau = \varphi_{\mathrm{l}}\tau_{\mathrm{l}} + \varphi_{\mathrm{v}}\tau_{\mathrm{v}}$ give

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

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

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 2.9. *Assume that the mass fraction φ_{g} is fixed. Then the intensive equilibrium entropy* (2.24)

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

The proof is similar to the proof of Proposition 2.8.

Remark 2.10. 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 [23, 24, 31] for instance. As three-phase mixture is considered, we refer to [2]. This work relies on the same extensive constraints as in the present model: conservation of the mass (2.4), of the energy (2.5) and a mix-type constraint on the volume (2.6). The maximization procedure of Section 2, leading to the characterization of the mixture entropy s_{PT} (with phase transition), actually coincides with the procedure given in [2] for stiffened gases. A stiffened gas is depicted by the specific entropy:

$$s_k(\tau_k, e_k) = C_k \ln\left((e_k - Q_k - \pi_k\tau_k)\tau_k^{\gamma_k - 1}\right) + s_k^0,$$

where γ_k is the polytropic coefficient, C_k is the specific heat at constant volume, Q_k is the heat of formation, π_k is a reference pressure and s_k^0 a reference entropy. The phasic temperature, pressure and chemical potential read:

$$\begin{aligned} C_k T_k &= e_k - Q_k - \pi_k\tau_k, \\ p_k + \pi_k &= (\gamma_k - 1)\rho_k C_k T_k, \\ \mu_k &= Q_k + \gamma_k C_k T_k - T_k\left(C_k \ln\left(C_k T_k \tau_k^{\gamma_k - 1} + S_k^0\right)\right), \end{aligned}$$

where the phasic specific volume and internal energy can be expressed as:

$$\tau_k = \frac{\alpha_k}{\varphi_k}\tau, \quad e_k = \frac{z_k}{\varphi_k}e. \tag{2.26}$$

In [2], one uses the characterization of the thermodynamical equilibrium given in Proposition 2.6 to express the mixture pressure as a function of the mean specific volume τ, the mean internal energy e and the volume fraction of gas φ_{g}. For sake of completness we recall the process of construction of the mixture pressure law for a stiffened gas mixture.

The determination of the mixture pressure law is a three-step process. First one imposes the equality of the temperatures (2.13). Using the intensive volume constraint (2.19), one obtains

$$p = \sum_{k=\mathrm{l,g,v}} \alpha_k p_k = (\gamma - 1)\rho(e - Q) - \gamma\pi, \tag{2.27}$$

with

$$\gamma = \frac{\sum_{k=\mathrm{l,g,v}} \varphi_k \gamma_k C_k}{\sum_{k=\mathrm{l,g,v}} \varphi_k C_k}, \quad \pi = \sum_{k=\mathrm{l,g,v}} \alpha_k \pi_k, \quad Q = \sum_{k=\mathrm{l,g,v}} \varphi_k Q_k. \tag{2.28}$$

Note that one gets rid of the energy fractions. At this stage the mixture pressure law writes again as a stiffened gas law, this has been highlighted in [4]. Then setting the mechanical equilibrium (2.14) with (2.27) gives a second order equation in α_v. One can prove that it admits one single root α_v in $(0,1)$. Thus α_v can be written as a function of the mass fraction φ_v. One may find the analytical expression of $\alpha_\mathrm{v}(\varphi_\mathrm{v})$ in formula (2.11) of [2]. At this stage all the fractions have been eliminated, except the mass fraction of vapor φ_v. If phase transition does not occur between the liquid and the vapor, one can then determine the mixture pressure law $p = p(\tau, e, \varphi_\mathrm{l}, \varphi_\mathrm{g})$. This mixture pressure is thus explicit (but quite complicated, see again formula (2.11) of [2]). If phase transition is allowed (like in [2]), then one eliminates φ_v by imposing the chemical equilibrium between the liquid and its vapor:

$$\mu_\mathrm{v}(\varphi_\mathrm{v}) = \mu_\mathrm{l}(\varphi_\mathrm{v}).$$

Doing so fixes the mass fraction of vapor such that $0 < \varphi_\mathrm{v} < 1 - \varphi_\mathrm{g}$. Note that this step requires to solve a nonlinear equation.
Finally using φ_v in (2.28) and (2.27) gives the mixture pressure $p = p(\tau, e, \varphi_\mathrm{g})$.
The question of concavity of the mixture entropy is not adressed in [2]. However it is possible to couple the mixture pressure law to a fluid model. Taking advantage of the stiffened gas law form of the mixture pressure, one uses a finite volume scheme with relaxation method (as in [4]) with local grid refinement. The computational results illustrate the existence of a saturation zone, that is the mixture entropy is not strictly concave.

Remark 2.11. (Saturation of a constraint and restriction to two-phase models). We focus in Proposition 2.6 on a maximum reached in the interior of the set of constraints $\Omega_{\mathrm{ext}}^{\mathrm{NPT}}$ and $\Omega_{\mathrm{ext}}^{\mathrm{PT}}$. Of course it may be reached on the boundary of the set of constraints, leading to saturation of (at least) one of the extensive constraints. Then the equality of the temperatures and the partial Dalton's law are not necessarily valid and the optimum is characterized by inequalities. As an example, we study the saturation for the liquid phase.
Let $\bar{W} = ((\bar{M}, \bar{V}, \bar{E})_\mathrm{l}, (\bar{M}, \bar{V}, \bar{E})_\mathrm{g}, (\bar{M}, \bar{V}, \bar{E})_\mathrm{v})$ be the maximizer of the mixture entropy Σ on the boundary of the set of constraints $\Omega_{\mathrm{ext}}^{\mathrm{PT}}$. By concavity of Σ, for any state $W = ((M, V, E)_\mathrm{l}, (M, V, E)_\mathrm{g}, (M, V, E)_\mathrm{v}) \in \Omega_{\mathrm{ext}}^{\mathrm{PT}}$, one has

$$\nabla_W \Sigma(W) \cdot (W - \bar{W}) \leq 0.$$

If the energy constraint is saturated, it reads

$$\left(\frac{1}{T_\mathrm{l}} - \frac{1}{T_k}\right) \cdot (E_\mathrm{l} - \bar{E}_\mathrm{l}) \leq 0, \quad k = \mathrm{g}, \mathrm{v}.$$

If $\bar{E}_\mathrm{l} = 0$ then $\dfrac{1}{T_\mathrm{l}} - \dfrac{1}{T_\mathrm{g}} \leq 0$ and $\dfrac{1}{T_\mathrm{l}} - \dfrac{1}{T_\mathrm{v}} \leq 0$. Conversely $\bar{E}_\mathrm{l} = E$ leads to $\dfrac{1}{T_\mathrm{l}} - \dfrac{1}{T_\mathrm{g}} \geq 0$ and $\dfrac{1}{T_\mathrm{l}} - \dfrac{1}{T_\mathrm{v}} \geq 0$. The saturation of the volume constraint yields

$$\left(\frac{p_\mathrm{l}}{T_\mathrm{l}} - \left(\frac{p_\mathrm{g}}{T_\mathrm{g}} + \frac{p_\mathrm{v}}{T_\mathrm{v}}\right)\right) \cdot (V_\mathrm{l} - \bar{V}_\mathrm{l}) \leq 0.$$

If $\bar{V}_\mathrm{l} = V$ (resp. $\bar{V}_\mathrm{l} = 0$) then $\frac{p_\mathrm{l}}{T_\mathrm{l}} \geq \frac{p_\mathrm{g}}{T_\mathrm{g}} + \frac{p_\mathrm{v}}{T_\mathrm{v}}$ (resp. $\frac{p_\mathrm{l}}{T_\mathrm{l}} \leq \frac{p_\mathrm{g}}{T_\mathrm{g}} + \frac{p_\mathrm{v}}{T_\mathrm{v}}$). Finally as phase transition occurs between the liquid and the vapor, the mass constraint is saturated and gives

$$\left(\frac{\mu_\mathrm{l}}{T_\mathrm{l}} - \frac{\mu_\mathrm{v}}{T_\mathrm{v}}\right) \cdot (M_\mathrm{l} - \bar{M}_\mathrm{l}) \leq 0.$$

If $\bar{M}_\mathrm{l} = M - M_\mathrm{g}$ (since the mass of gas is fixed), it gives $\frac{\mu_\mathrm{l}}{T_\mathrm{l}} \geq \frac{\mu_\mathrm{v}}{T_\mathrm{v}}$. Conversely $\bar{M}_\mathrm{l} = 0$ yields $\frac{\mu_\mathrm{l}}{T_\mathrm{l}} \leq \frac{\mu_\mathrm{v}}{T_\mathrm{v}}$.
Moroever the model is valid when only two phases are present but the set of constraints has to be modified.

- If the vapor phase is absent, there remains the liquid and the gas phases which form an immiscible mixture without mass transfer. The set of extensive constraints is then $(M, V, E) = (M_\mathrm{l}, V_\mathrm{l}, E_\mathrm{l}) + (M_\mathrm{g}, V_\mathrm{g}, E_\mathrm{g})$, where M_g is fixed. This two-phase model has been investigated by Jung in [22, 32] for stiffened gas laws. The thermodynamical equilibrium (when it is reached in the interior of the set of constraints) is characterized by the equality of the phasic temperatures and the equality of the phasic pressures.
- If the gas is absent, the mixture is immiscible, composed of the liquid and its vapor. The extensive constraints are $(M, V, E) = (M_\mathrm{l}, V_\mathrm{l}, E_\mathrm{l}) + (M_\mathrm{v}, V_\mathrm{v}, E_\mathrm{v})$. If phase transition is not taking into account, one ends up with the model of Jung [32]. Conversely, the case with phase transition has been widely studied, see for instance [31] for perfect gas law and [15] for more general equations of state. One can prove that the corresponding intensive mixture entropy is not strictly convex. Actually it corresponds to the concave hull of the maximum of the phasic entropies (see [15] for a geometrical proof in [23] for a proof based on Legendre transform). The thermodynamical equilibrium is characterized by the equality of the temperatures, pressures and chemical potentials of both phases.
- If only the vapor and the gas are present, the extensive constraints are

$$\begin{cases} V = V_\mathrm{g} = V_\mathrm{v}, \\ (M, E) = (M_\mathrm{g}, E_\mathrm{g}) + (M_\mathrm{v}, E_\mathrm{v}). \end{cases}$$

  This case has been studied in [23]. The intensive mixture entropy is strictly concave because (it is actually a sub-convolution of the phasic entropies). The thermodynamical equilibrium is given by the equality of the phasic temperatures and Dalton's law on the phasic pressures.

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 a 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

$$\begin{cases} \partial_t(\varphi_\mathrm{l}\rho) + \partial_x(\varphi_\mathrm{l}\rho u) = 0, \\ \partial_t(\varphi_\mathrm{g}\rho) + \partial_x(\varphi_\mathrm{g}\rho u) = 0, \\ \partial_t\rho + \partial_x(\rho u) = 0, \\ \partial_t(\rho u) + \partial_x(\rho u^2 + p) = 0, \\ \partial_t(\rho\mathcal{E}) + \partial_x((\rho\mathcal{E} + p)u) = 0, \\ \mathcal{E} = \dfrac{1}{2}u^2 + e, \\ \forall k \in \{\mathrm{l}, \mathrm{g}, \mathrm{v}\} : \ p_k = p_k(\tau_k, e_k), \ \tau_k = \rho_k^{-1}, \\ \varphi_\mathrm{l} + \varphi_\mathrm{g} + \varphi_\mathrm{v} = 1, \end{cases} \tag{3.1}$$

where the flow has 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 $k = \mathrm{l}, \mathrm{g}, \mathrm{v}$ 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

$$\begin{cases} e = \varphi_\mathrm{l} e_\mathrm{l} + \varphi_\mathrm{v} e_\mathrm{v} + \varphi_\mathrm{g} e_\mathrm{g}, \\ \tau = \varphi_\mathrm{l} \tau_\mathrm{l} + \varphi_\mathrm{g} \tau_\mathrm{g}, \\ \varphi_\mathrm{v} \tau_\mathrm{v} = \varphi_\mathrm{g} \tau_\mathrm{g}. \end{cases} \tag{3.2}$$

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

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

Thus one has to provide seven closure laws. The first three closure laws are given by the constraints (3.2).

The 4 remaining closure laws are given by Proposition 2.6, that is

$$\begin{cases} T = T_\mathrm{l} = T_\mathrm{g} = T_\mathrm{v}, \\ p = p_\mathrm{l} = p_\mathrm{g} + p_\mathrm{v}, \end{cases} \tag{3.3}$$

where T and p are the thermodynamical temperature and pressure of the three phase flow and $p = p(1/\rho, e, \varphi_\mathrm{l}, \varphi_\mathrm{g})$.

We recall that the computation of the mixture pressure $p = p(1/\rho, e, \varphi_\mathrm{l}, \varphi_\mathrm{g})$ may be not explicit depending on the phasic equation of states. In order to determine the mixture pressure, one should impose the thermodynamical equilibrium characterized by the temperature equilibrium (2.13), the partial Dalton's law (2.14) and the chemical equilibrium (2.15) (when mass transfer occurs). Remark 2.10 contains some hints of computations in the case of a stiffened gas law. In that case, without phase transition, the mixture pressure is explicit.

Proposition 3.1. *The intensive entropy $s_{\mathrm{NPT}}(\tau, e, \varphi_\mathrm{l}, \varphi_\mathrm{g})$ defined by (2.23) satisfies*

$$\partial_t s + u \partial_x s_{\mathrm{NPT}} = 0. \tag{3.4}$$

Proof. Let $U = (\rho, \rho u, \rho\mathcal{E}, \varphi_\mathrm{g}\rho, \varphi_\mathrm{l}\rho)$ is a smooth solution of the system (3.1), then one has

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

Since s_{NPT} is a function of $(\tau, e, \varphi_\mathrm{l}, \varphi_\mathrm{g})$, it follows

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

Because the entropy s_{NPT} satisfies the relation $T \mathrm{d}s_{\mathrm{NPT}} = \mathrm{d}e + p\mathrm{d}\tau$ (see Prop. 2.8), the first term of the right hand side is zero. Hence the entropy s_{NPT} satisfies the transport equation (3.4). □

In order to study the hyperbolicity of the model (3.1), we adapt a result given in [34] which extends the Godunov–Mock theorem.

Lemma 3.2. *Let $w : \mathbb{R}^+ \times \mathbb{R} \to \mathbb{R}^n$ and $f : \mathbb{R}^n \to \mathbb{R}^n$ 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

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

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. □

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 3.3. *The system (3.1) is hyperbolic.*

Proof. First the system (3.1) can be written in Lagrangian coordinates

$$\begin{cases} D_t\varphi_{\mathrm{l}} = 0, \\ D_t\varphi_{\mathrm{g}} = 0, \\ D_t\tau - D_m u = 0, \\ D_t u + D_m p = 0, \\ D_t\mathcal{E} + D_m(pu) = 0, \end{cases}$$

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

$$\eta : (\varphi_{\mathrm{l}}, \varphi_{\mathrm{g}}, \tau, u, \mathcal{E}) \to -s_{\mathrm{NPT}}(\tau, \mathcal{E} - u^2/2, \varphi_{\mathrm{l}}, \varphi_{\mathrm{g}}).$$

According to Proposition 2.8, 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 $(\tau, u, \mathcal{E})$, see [9, 19]. Moreover s_{NPT} is solely advected by the system, since it satisfies (3.4), see Proposition 3.1. Hence it yields

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

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 $\nabla_{\varphi_{\mathrm{l}}, \varphi_{\mathrm{g}}} f = 0$. Now Lemma 3.2 leads to the conclusion. □

3.2. Three-phase model with phase transition

When phase transition occurs, the equilibrium multicomponent Euler system reads

$$\begin{cases} \partial_t(\varphi_{\mathrm{g}}\rho) + \partial_x(\varphi_{\mathrm{g}}\rho u) = 0, \\ \partial_t\rho + \partial_x(\rho u) = 0, \\ \partial_t(\rho u) + \partial_x(\rho u^2 + p) = 0, \\ \partial_t(\rho\mathcal{E}) + \partial_x((\rho\mathcal{E} + p)u) = 0, \\ \mathcal{E} = \dfrac{1}{2}u^2 + e, \\ \forall k \in \{\mathrm{l},\mathrm{g},\mathrm{v}\} : \ p_k = p_k(\tau_k, e_k), \ \tau_k = \rho_k^{-1}, \\ \varphi_{\mathrm{l}} + \varphi_{\mathrm{g}} + \varphi_{\mathrm{v}} = 1. \end{cases} \tag{3.5}$$

The system consists of nine equations and seventeen unknowns which are

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

Thus one has to provide eight closure laws.

As in the previous case, three closure laws are given by the three intensive constraints (3.2)

$$\begin{cases} e & = \varphi_{\mathrm{l}}e_{\mathrm{l}} + \varphi_{\mathrm{v}}e_{\mathrm{v}} + \varphi_{\mathrm{g}}eg, \\ \tau & = \varphi_{\mathrm{l}}\tau_{\mathrm{l}} + \varphi_{\mathrm{g}}\tau_{\mathrm{g}}, \\ \varphi_{\mathrm{v}}\tau_{\mathrm{v}} & = \varphi_{\mathrm{g}}\tau_{\mathrm{g}}. \end{cases}$$

The five remaining closures are given by Proposition 2.6

$$\begin{cases} T = T_{\mathrm{l}} = T_{\mathrm{g}} = T_{\mathrm{v}}, \\ p = p_{\mathrm{l}} = p_{\mathrm{g}} + p_{\mathrm{v}}, \\ \mu_{\mathrm{l}} = \mu_{\mathrm{v}}, \end{cases} \tag{3.6}$$

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

Since the equilibrium entropy is not a strictly concave function of its arguments (see Rem. 2.10), it is not possible to invocate the Godunov–Mock theorem or its extension Lemma 3.2 to prove the hyperbolicity of the system. However it is possible to check the hyperbolicity by studying the eigenvalues of the system and proving that the mixture speed of sound is real. The proof mimics the one provided in [15] Theorem 5.1 and (see [1] Thm. 2.4 for a shortened version).

Theorem 3.4. *The system* (3.5) *is hyperbolic.*

Proof. The quasilinear form of the system (3.5) reads

$$\partial_t \begin{pmatrix} \varphi_{\mathrm{g}} \\ \rho \\ u \\ e \end{pmatrix} + \begin{pmatrix} u & 0 & 0 & 0 \\ 0 & u & \rho & 0 \\ \dfrac{1}{\rho}\dfrac{\partial p}{\partial \varphi_{\mathrm{g}}} & \dfrac{1}{\rho}\dfrac{\partial p}{\partial \rho} & u & \dfrac{1}{\rho}\dfrac{\partial p}{\partial e} \\ 0 & 0 & p/\rho & u \end{pmatrix} \partial_x \begin{pmatrix} \varphi_{\mathrm{g}} \\ \rho \\ u \\ e \end{pmatrix} = 0.$$

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

$$\begin{aligned} c^2/\tau^2 &= p\partial_e p - \partial_\tau p \\ &= -T(p^2\partial_{ee}s_{\mathrm{PT}} - 2p\partial_{\tau e}s_{\mathrm{PT}} + \partial_{\tau\tau}s_{\mathrm{PT}}). \end{aligned} \tag{3.7}$$

According to Proposition 2.9 and Remark 2.10, the entropy ($s_{\rm PT}$) is a concave but not strictly concave function of (τ, e) at fixed $\varphi_{\rm g}$. Then the Hessian matrix of $s_{\rm PT}$ is not negative definite such that $c^2 \geq 0$. One has to prove that $c^2 > 0$. Since $s_{\rm PT}$ is not strictly concave, in the non-strict concave region, one has $\partial_{\tau\tau} s_{\rm PT} \partial_{ee} s_{\rm PT} = (\partial_{\tau e} s_{\rm PT})^2$. Hence after factorization, the speed of sound identity (3.7) becomes

$$c^2/\tau^2 = -T \frac{\partial_{\tau e} s_{\rm PT}}{\partial_{\tau\tau} s_{\rm PT}} \left(p - \frac{\partial_{\tau\tau} s_{\rm PT}}{\partial_{\tau e} s_{\rm PT}} \right)^2. \tag{3.8}$$

According to [1] Theorem 2.4, one verifies that $\partial_{\tau\tau} s_{\rm PT} < 0$ (for a detailed proof, see Appendix A in [15]). Moreover for any point $o = (\hat\tau, \hat e, s_{\rm PT}(\hat\tau, \hat e))$ belonging to the non-strict concavity region, there exists a single couple of points $o_1 = (\tau_1, e_1, s_{\rm PT}(\tau_1, e_1))$ and $o_2 = (\tau_2, e_2, s_{\rm PT}(\tau_2, e_2))$ such that o belongs to the segment $(o_1, o_2) = \{y o_1 + (1-y) o_2 |\ y \in [0,1]\}$. For every point belonging to the line segment (o_1, o_2), the authors prove that

$$\partial_{\tau e} s_{\rm PT}(e_1 - e_2) + \partial_{\tau\tau} s_{\rm PT}(\tau_1 - \tau_2) = 0, \tag{3.9}$$

and

$$p > -\frac{e_1 - e_2}{\tau_1 - \tau_2}, \tag{3.10}$$

see Appendix A for details. Coupling (3.9) and (3.10) to (3.8) gives that $c^2 > 0$ as soon as the temperature $T > 0$. This concludes the proof. □

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 are not necessarily explicit. Moreover it is well known, see for instance [4, 31, 37], that such pressure laws may present slope discontinuities or lack of convexity of the isentropes, leading to composite waves in the Riemann problem. These properties actually correspond to physical phenomena and are present for instance in BZT-fluids, see [40, 44]. In order to avoid the resolution of the Riemann problem with a complicated pressure law, one may approximate the equilibrium Euler system by a homogeneous relaxation model, as it is proposed in [4, 21, 24, 28, 29].

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 (3.1), 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 $\alpha_{\rm l}$ and the energy fractions $z_{\rm l}$ and $z_{\rm g}$ defined in (2.17). Hence the pressure depends not only on $\rho, e, \varphi_{\rm l}, \varphi_{\rm g}$ but also on $Y = (\alpha_{\rm l}, z_{\rm l}, z_{\rm g})$. Note that one may choose another set of variables to relax the mixture pressure. The choice of the fractions is actually motivated by several references, see for instance [21, 24, 29]. The key point is to respect the entropy production criterion, see below.

When no mass transfer occurs between the liquid and the gas, the fractions should be perfectly convected *i.e.*

$$\partial_t Y + u\partial_x Y = 0. \tag{4.1}$$

The mass conservation allows to write (4.1) in conservative form

$$\partial_t(\rho Y) + \partial_x(\rho u Y) = 0. \tag{4.2}$$

Thus the resulting HRM model reads

$$\begin{cases} \partial_t(\varphi_k\rho) + \partial_x(\varphi_k\rho u) = 0, \quad k = \mathrm{l}, \mathrm{g}, \\ \partial_t(z_k\rho) + \partial_x(z_k\rho u) = 0, \quad k = \mathrm{l}, \mathrm{g}, \\ \partial_t(\alpha_\mathrm{l}\rho) + \partial_x(\alpha_\mathrm{l}\rho u) = 0, \\ \partial_t\rho + \partial_x(\rho u) = 0, \\ \partial_t(\rho u) + \partial_x(\rho u^2 + p) = 0, \\ \partial_t(\rho\mathcal{E}) + \partial_x((\rho\mathcal{E} + p)u) = 0, \end{cases} \tag{4.3}$$

with the closure pressure law

$$p = p(1/\rho, e, \varphi_\mathrm{l}, \varphi_\mathrm{g}, \alpha_\mathrm{l}, z_\mathrm{l}, z_\mathrm{g}). \tag{4.4}$$

The mixture pressure (4.4) is computed using

$$\begin{aligned} \frac{p(1/\rho, e, \varphi_\mathrm{l}, \varphi_\mathrm{g}, \alpha_\mathrm{l}, z_\mathrm{l}, z_\mathrm{g})}{T(1/\rho, e, \varphi_\mathrm{l}, \varphi_\mathrm{g}, \alpha_\mathrm{l}, z_\mathrm{l}, z_\mathrm{g})} &= \sum_{k=\mathrm{l},\mathrm{g},\mathrm{v}} \alpha_k \frac{p_k\left(\frac{\alpha_k}{\varphi_k}\tau, \frac{z_k}{\varphi_k}e\right)}{T_k\left(\frac{\alpha_k}{\varphi_k}\tau, \frac{z_k}{\varphi_k}e\right)}, \\ \frac{1}{T(1/\rho, e, \varphi_\mathrm{l}, \varphi_\mathrm{g}, \alpha_\mathrm{l}, z_\mathrm{l}, z_\mathrm{g})} &= \sum_{k=\mathrm{l},\mathrm{g},\mathrm{v}} \frac{z_k}{T_k\left(\frac{\alpha_k}{\varphi_k}\tau, \frac{z_k}{\varphi_k}e\right)}, \end{aligned} \tag{4.5}$$

and the constraints on the fractions (2.19), (2.20) and (2.21).

One should add an entropy criterion to the model. With $\rho = 1/\tau$ the concave function $\sigma(\tau, e, \varphi_\mathrm{l}, \varphi_\mathrm{g}, \alpha_\mathrm{l}, z_\mathrm{l}, z_\mathrm{g})$ defined in (2.22) would be an entropy function if it satisfies the first order PDE

$$\partial_\tau\sigma - p(1/\tau, e, \varphi_\mathrm{l}, \varphi_\mathrm{g}, \alpha_\mathrm{l}, z_\mathrm{l}, z_\mathrm{g})\partial_e\sigma = 0. \tag{4.6}$$

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

$$T\mathrm{d}\sigma = \mathrm{d}e + p\mathrm{d}\tau + \sum_{k=\mathrm{l},\mathrm{g}} \partial_{\varphi_k} s\mathrm{d}\varphi_k + \partial_{\alpha_\mathrm{l}} s\mathrm{d}\alpha_\mathrm{l} + \sum_{k=\mathrm{l},\mathrm{g}} \partial_{z_k} s\mathrm{d}z_k.$$

Weak solutions of (4.3)–(4.4) satisfy

$$\partial_t(\rho\sigma) + \partial_x(\rho u\sigma) \geq 0, \tag{4.7}$$

which becomes an equality as regular solutions are concerned. The concavity of σ with respect to $(\tau, e, \varphi_\mathrm{l}, \varphi_\mathrm{g}, \alpha_\mathrm{l}, z_\mathrm{l}, z_\mathrm{g})$ is equivalent to the convexity of $H = -\rho\sigma$ with respect to the conservative variables $(\rho, \rho u, \rho\mathcal{E}, \varphi_\mathrm{l}\rho, \varphi_\mathrm{g}\rho, z_\mathrm{l}\rho, z_\mathrm{g}\rho, \alpha_\mathrm{l}\rho)$, following [9, 19]. Hence $H = -\rho\sigma$ is a Lax entropy for (4.3).

In order to bring the system to thermodynamical equilibrium described in Proposition 2.7-(2.23), a source term has to be added to the fraction equations

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

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

$$\begin{aligned} Y &:= Y_{\text{eq}}^{\text{NPT}}(\tau, e, \varphi_{\text{l}}, \varphi_{\text{g}}) \\ &:= \underset{(\alpha_{\text{l}}, z_{\text{l}}, z_{\text{g}})}{\operatorname{argmax}} \sigma(\tau, e, \varphi_{\text{l}}, \varphi_{\text{g}}, \alpha_{\text{l}}, z_{\text{l}}, z_{\text{g}}). \end{aligned} \tag{4.8}$$

As a result the equilibrium pressure law is

$$p_{\text{eq}}^{\text{NPT}}(\tau, e, \varphi_{\text{l}}, \varphi_{\text{g}}) := p(\tau, e, \varphi_{\text{l}}, \varphi_{\text{g}}, Y_{\text{eq}}^{\text{NPT}}(\tau, e, \varphi_{\text{l}}, \varphi_{\text{g}})), \tag{4.9}$$

defined by Dalton's law (2.16). Following [4, 7, 8, 15, 29], a natural source term is

$$Q = \lambda(Y_{\text{eq}}^{\text{NPT}}(\tau, e, \varphi_{\text{l}}, \varphi_{\text{g}}) - Y) \tag{4.10}$$

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

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

$$\begin{aligned} \partial_t \sigma + u \partial_x \sigma &= \nabla_Y \sigma \cdot (\partial_t Y + u \partial_x Y) \\ &= \lambda \nabla_Y \sigma \cdot (Y_{\text{eq}}^{\text{NPT}}(\tau, e, \varphi_{\text{l}}, \varphi_{\text{g}}) - Y) \\ &\geq \lambda(\sigma(\tau, e, \varphi_{\text{l}}, \varphi_{\text{g}}, Y_{\text{eq}}^{\text{NPT}}) - \sigma(\tau, e, \varphi_{\text{l}}, \varphi_{\text{g}}, \alpha_{\text{l}}, z_{\text{l}}, z_{\text{g}})) \\ &\geq 0, \end{aligned} \tag{4.11}$$

by concavity of the entropy σ.

The drawback of the source term (4.10) 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

$$\begin{aligned} Q &= \nabla_Y \sigma(\tau, e, \varphi_{\text{l}}, \varphi_{\text{g}}, Y), \\ &= \begin{pmatrix} \tau \left(\dfrac{p_{\text{l}}}{T_{\text{l}}} - \left(\dfrac{p_{\text{g}}}{T_{\text{g}}} + \dfrac{p_{\text{v}}}{T_{\text{v}}} \right) \right) \\ e \left(\dfrac{1}{T_{\text{l}}} - \dfrac{1}{T_{\text{v}}} \right) \\ e \left(\dfrac{1}{T_{\text{g}}} - \dfrac{1}{T_{\text{v}}} \right) \end{pmatrix}, \end{aligned} \tag{4.12}$$

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

$$\begin{cases} \partial_t Y + u \partial_x Y = Q, \\ \partial_t(\varphi_{\text{g}} \rho) + \partial_x(\varphi_{\text{g}} \rho u) = 0, \\ \partial_t \rho + \partial_x(\rho u) = 0, \\ \partial_t(\rho u) + \partial_x(\rho u^2 + p) = 0, \\ \partial_t(\rho \mathcal{E}) + \partial_x((\rho \mathcal{E} + p) u) = 0, \end{cases} \tag{4.13}$$

where the fraction vector is $Y = (\varphi_{\text{l}}, \alpha_{\text{l}}, z_{\text{l}}, z_{\text{g}})$ and the closure pressure law

$$p = p(1/\rho, e, \varphi_{\text{g}}, \varphi_{\text{l}}, \alpha_{\text{l}}, z_{\text{l}}, z_{\text{g}}). \tag{4.14}$$

Again the entropy $\sigma(\tau, e, \varphi_g, \varphi_l, \alpha_l, z_l, z_g)$ defined in (2.22) satisfies the entropy inequality (4.7) as soon as it complies with (4.6). The source term Q has to be chosen to recover the thermodynamical equilibrium described by the fractions

$$\begin{aligned} Y &= Y_{\text{eq}}^{\text{PT}}(\tau, e, \varphi_g) \\ &= \underset{(\varphi_l, \alpha_l, z_l, z_g)}{\operatorname{argmax}} \sigma(\tau, e, \varphi_l, \varphi_g, \alpha_l, z_l, z_g), \end{aligned} \tag{4.15}$$

leading to the equilibrium pressure law

$$p_{\text{eq}}^{\text{PT}}(\tau, e, \varphi_g) := p(\tau, e, \varphi_g, Y_{\text{eq}}^{\text{PT}}(\tau, e, \varphi_g)). \tag{4.16}$$

Again the source term Q could be either

$$Q = \lambda(Y_{\text{eq}}^{\text{PT}}(\tau, e, \varphi_g) - Y), \tag{4.17}$$

or

$$\begin{aligned} Q &= \lambda \nabla_Y \sigma(\tau, e, \varphi_g, Y_{\text{eq}}^{\text{PT}}(\tau, e, \varphi_g)) \\ &= \begin{pmatrix} s_l - \tau_l \dfrac{p_l}{T_l} - \dfrac{e_l}{T_l} - s_v + \tau_v \dfrac{p_v}{T_v} + \dfrac{e_v}{T_v} \\ \tau \left(\dfrac{p_l}{T_l} - \left(\dfrac{p_g}{T_g} + \dfrac{p_v}{T_v} \right) \right) \\ e \left(\dfrac{1}{T_l} - \dfrac{1}{T_v} \right) \\ e \left(\dfrac{1}{T_g} - \dfrac{1}{T_v} \right). \end{pmatrix} \end{aligned} \tag{4.18}$$

Using the characterization (2.3) of the chemical potential, the first component of Q boils down to

$$\partial_{\varphi_l} \sigma = -\frac{\mu_l}{T_l} + \frac{\mu_v}{T_v}, \tag{4.19}$$

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

5. Conclusion

We address in this paper the modelling of a three-phase mixture composed of a gas, a liquid and its vapor. We adopt the Gibbs formalism and describe the system in terms of extensive constraints. We assume that the vapor and the gas are perfectly intimate (like ideal gases) and that they share a sharp interface with the liquid phase. No restriction is given on the phasic equations of state as soon as they fulfill classical smoothness assumptions. According to the entropy maximization criterion, we are able to depict the thermodynamical equilibrium that corresponds notably to a partial Dalton's law on the phasic pressures. We study the mixture entropies in terms of optimization problems and focus on their (strict) concavity. The equations of state obtained are then introduced in two HEM models depending on whether phase transition occurs or not between the liquid and its vapor. Hyperbolicity of the systems is investigated, taking advantage of the entropy structure studied in the previous section. To finish the paper we propose a HRM model, which may be easier to approximate than the HEM model. Indeed the numerical approximation of the HEM model with the mixture pressure law is doable but is time-consuming because of the computation of the mixture pressure (see [2]). It would be very interesting to provide a three-pressure three-velocity model in agreement with the intensive volume constraint (2.19), which relaxes toward the thermodynamical equilibrium given by the equality of the temperature (2.13) and the mechanical equilibrium with the Dalton law (2.14). The difficulty would come from the determination of proper closure conditions which define interfacial pressures and velocity as well as relaxation terms while ensuring the entropy growth criterion. This derivation is in progress and one may find some valuable hints in [35, 39].

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