

## VAPOUR-LIQUID PHASE TRANSITION AND METASTABILITY

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**Abstract.** The paper deals with the modelling of the relaxation processes towards thermodynamic equilibrium in a liquid-vapour isothermal mixture. Focusing on the van der Waals equation of state, we construct a constrained optimization problem using Gibbs' formalism and characterize all possible equilibria: coexistence states, pure phases and metastable states. Coupling with time evolution, we develop a dynamical system whose equilibria coincide with the minimizers of the optimization problem. Eventually we consider the coupling with hydrodynamics and use the dynamical system as a relaxation source terms in an Euler-type system. Numerical results illustrate the ability of the whole model to depict coexistence and metastable states as well.

### INTRODUCTION

This paper deals with the modelling of vapour-liquid phase transition and the relaxation towards the thermodynamic equilibrium in liquid-vapour mixture. Focusing on isothermal problems, vapour bubbles may appear in a liquid through a decompression process, which leads to a pressure decrease below the saturation pressure and cavitation. If the process of depressurization is slow or weak enough, then the system may remain entirely liquid, although the pressure is below the saturation pressure. There is a delay in the phase transition, which may be shortened by a (strong enough) dynamic perturbation. This liquid state is commonly called metastable. A similar behaviour holds in a vapour system submitted to a compression. All these phenomena result from the coupling between hydrodynamics and thermodynamics, the former inducing dynamical perturbations of thermodynamic equilibrium states.

Our purpose is therefore to provide a characterization of thermodynamic equilibria which on the one hand copes with coexistence (that is saturation of liquid and vapour), pure phases and metastable states, on the other hand can be coupled in a consistent way to the equations of hydrodynamics, in the present case the isothermal Euler system.

In a first step, we investigate the thermodynamic stability of a system described by a single nonconvex energy, namely the van der Waals equation of state (EoS). It turns out that the nonconvexity of the van der Waals equation of state makes it a standard (even though not physical) tool to describe pure phases, metastable states as well as coexistence states. As suggested for instance in [2, chap. 8], we introduce heterogeneity in the system by decomposing it in an arbitrary number of subsystems described by the same van der Waals EoS. Then stable states are solutions to a constrained minimization problem involving the total energy of the system. In doing

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so, we recover mathematical formulations of classic results in thermodynamics, such as the Gibbs phase rule and an analogue of the Maxwell equal area rule construction. This is the aim of Section 1.

This latter construction allows to recover coexistence states but precludes metastable states. Hence a more accurate study of stable and unstable states is mandatory. In Section 2, we propose an alternative characterization where all the quantities involved in the subsystems depend on time. Thus the characterization is no longer static since we introduce dynamical perturbations. Pure phases, metastable states and coexistence states are now described as attractive points of a carefully chosen dynamical system. The detailed study of the basins of attraction of the dynamical system allows to interpret metastability in terms of some competition between two such basins.

This model allows to define proper relaxation source terms towards thermodynamic equilibrium for Euler-type equations. In Section 3 we provide numerical illustrations of this coupling between thermodynamics and the barotropic one dimensional Euler equations. Using the previous detailed study of the basins of attraction, we are able to perform instantaneous relaxation towards thermodynamic equilibrium.

Actually the idea of the dynamical characterization presented in Section 2 has been introduced in [13]. We propose here a modified system, which allows a more precise study of its equilibrium states, and a careful analysis of the basin of attraction of metastable states. In particular we prove in the present paper that, for an initial state in a metastable zone, there are two possible basins of attraction that are separated by an implicitly defined curve. The accurate characterization of the attraction basins allows us to perform instantaneous relaxation, and then to get rid of spurious numerical artefacts due to the explicit relaxation approximation initially performed in [13], to which we refer for complementary results, notably concerning the coupling, and a more complete reference list.

## 1. THERMODYNAMIC SETTING

This section is devoted to the description of the Gibbs formalism to describe thermodynamic equilibria. We show how to go from simple, homogeneous systems, to more complex, heterogeneous systems. To do so, and following [2, chap. 8], the system is divided in  $I$  subsystems described by the same van der Waals EOS. We investigate the notion of stable equilibria and give their characterization through the minimization of a nonconvex function, namely the Helmholtz free energy of the system.

### 1.1. Simple system modelling

Consider a single fluid with mass  $M > 0$  and volume  $V > 0$ , assumed to be homogeneous and at rest, at a fixed temperature  $T$ . According to Gibbs' formalism, we say that the fluid is at equilibrium if its Helmholtz free energy is a function, denoted by  $F$ , of its mass  $M$  and volume  $V$ :

$$F : (M, V) \mapsto F(M, V). \quad (1)$$

All the variables involved here are extensive, which means that they have the same scaling as the volume  $V$  [5]: this corresponds to the notion of homogeneity of the sample. As a consequence, the function  $F$  has to be positively homogeneous of degree 1:

$$\forall \lambda > 0, \quad F(\lambda M, \lambda V) = \lambda F(M, V). \quad (2)$$

Without loss of generality, we assume here that  $F$  is of class  $C^2$  with respect to  $V$  and  $M$ .

Two fundamental quantities can then be considered, namely the pressure  $p$  and the chemical potential  $\mu$ , defined by

$$p = -\frac{\partial F}{\partial V}(M, V), \quad \mu = \frac{\partial F}{\partial M}(M, V). \quad (3)$$

Then one can write the total differential of  $F$

$$dF = -pdV + \mu dM. \quad (4)$$

These definitions are consistent with the fundamental extensive thermodynamic relation  $TdS = dE + pdV - \mu dM$ , since the function  $F$  is recovered from the internal energy  $E$  and the entropy  $S$  at constant temperature by  $F = E - TS$ . Indeed, taking the exact differential, we obtain  $dF = dE - TdS = -pdV + \mu dM$ , see [5]. From homogeneity, we obtain the so-called Euler relation, which is known in this context as Gibbs' relation:

$$F(M, V) = \nabla F(M, V) \cdot \begin{pmatrix} M \\ V \end{pmatrix} = \mu M - pV. \quad (5)$$

An immediate computation shows that the pressure and the chemical potential are positively homogeneous of degree 0. In other words, they do not scale with the volume. Such quantities are called intensive quantities, typical other ones are the specific volume  $\tau = V/M$ , and the density  $\rho = M/V$ .

In the sequel, we shall work with intensive variables, so we rewrite all the preceding relations in terms of the density  $\rho$ . We first introduce the Helmholtz free energy per unit volume  $f$ :

$$f(\rho) = f\left(\frac{M}{V}\right) = \frac{1}{V}F(M, V) = F\left(\frac{M}{V}, 1\right). \quad (6)$$

Keeping the same notations  $p$  and  $\mu$ , the pressure and the chemical potential as functions of the density  $\rho$  are given by

$$p(\rho) = p\left(\frac{M}{V}\right) = -\frac{\partial F}{\partial V}\left(\frac{M}{V}, 1\right), \quad \mu(\rho) = \mu\left(\frac{M}{V}\right) = \frac{\partial F}{\partial M}\left(\frac{M}{V}, 1\right). \quad (7)$$

We obtain directly from (7)

$$\mu(\rho) = f'(\rho). \quad (8)$$

Next, dividing the extensive Gibbs relation (5) by the volume  $V$  leads to  $f(\rho) = \rho\mu(\rho) - p(\rho)$ , which readily gives the following expression for the pressure

$$p(\rho) = \rho\mu(\rho) - f(\rho). \quad (9)$$

A formula relating a thermodynamic quantity (e.g. the free Helmholtz energy or the pressure) to the mass and volume, or to the density, is called an equation of state (EoS). Usually equations of state are given in an incomplete way, for instance we only know the pressure law  $p(\rho)$ , as in the usual perfect gas law:  $p(\rho) = RT\rho$ ,  $T$  being the given temperature and  $R$  the perfect gases constant. The formalism we use here requires the complete equation of state, that is the energetic representation (1). Recovering such a representation from a partial equation of state can be a challenge, see e.g. [5, 6]. In the simple case of the perfect gas law, the function  $f$  is convex, which besides turns out not to be appropriate to represent phase transitions [2, chap. 9].

We shall use in the following the so-called van der Waals equation of state, which is not a physically relevant EoS, but enjoys the basic properties that allow a toy-model for phase transitions. It is the first example of so-called third order equations of state. It is usually given as a family of pressure laws  $p(\rho)$ , depending on the temperature  $T$  as a parameter. There exists a critical temperature  $T_C$  above which the pressure  $p(\rho)$  is nondecreasing, and below which it is not monotone: there are two local extrema at densities  $\rho^- < \rho^+$ , between which the pressure is a decreasing function, see Figure 1-left. For  $T = T_C$ , there are no local extrema, but merely a unique inflexion point, which defines in turn a critical density  $\rho_C$  and a critical pressure  $p_C$ . We actually make use in this work of a reduced van der Waals law, where the critical temperature  $T_C = 1$  (and  $\rho_C = 1$ ,  $p_C = 1$  as well). We successively give the pressure law  $p$ , then the Helmholtz free energy  $f$  and the

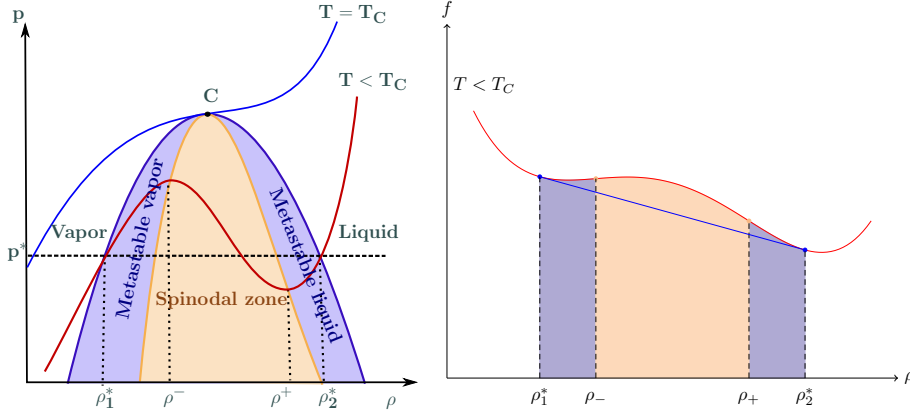


FIGURE 1. Sketch of phase diagram for the van der Waals EoS. Left:  $(p, \rho)$ -plane. Below the critical temperature  $T_C$ , the isotherm curve decreases in the spinodal zone which lays between the two extrema of the pressure at densities  $\rho^- < \rho^+$ . In that area the isotherm is commonly replaced by a horizontal segment (dashed line) which coincides with the isobaric line  $p = p^*$ , obtained by a Maxwell equal area rule-type construction. This construction also defines the two densities  $\rho_1^*$  and  $\rho_2^*$ . Right:  $(f, \rho)$ -plane. The red curve corresponds to the function  $f$  for a given  $T < T_C$ , which is not convex: we recover the two inflexion points  $\rho^-$  and  $\rho^+$ . The blue line is related to the Maxwell-type construction and is bitangent to the graph of  $f$  at densities  $\rho_1^*$  and  $\rho_2^*$  with slope  $\mu^* = \mu(\rho_1^*) = \mu(\rho_2^*)$ . See Section 1.2 for details on these constructions.

resulting chemical potential obtained by (8):

$$\begin{aligned}
 p(\rho) &= -3\rho^2 + \frac{8\rho T}{3 - \rho}, \\
 f(\rho) &= -3\rho^2 + \frac{8}{3}\rho T (\log(3\rho/(3 - \rho)) - 1), \\
 \mu(\rho) &= -6\rho + \frac{8}{3}T \log(3\rho/(3 - \rho)) + \frac{8}{3}T\rho/(3 - \rho),
 \end{aligned} \tag{10}$$

for  $0 < \rho < 3$ . For more details on this classic nonconvex complete EoS and its derivation, we can refer among many references to [2, 14].

For a given subcritical temperature (that is  $T < 1$  in our setting), the pressure is decreasing for  $\rho \in [\rho^-, \rho^+]$ . The locus of these points for all  $T < 1$  is called the spinodal zone and appears as an orange dome in Figure 1-left. A decreasing pressure is not physically relevant: the corresponding states are not observable. On both sides of the spinodal zone lie increasing branches of the pressure curve, which correspond on the contrary to observable states. Classically, the pressure is corrected by the so-called Maxwell equal area rule construction: at a given subcritical temperature ( $T < 1$ ), it determines in a unique way the triplet  $(p^*, \rho_1^*, \rho_2^*)$  and the pressure is replaced by the isobaric line  $p = p^*$  for  $\rho \in [\rho_1^*, \rho_2^*]$ , see Section 1.2 for more details on this construction. This line physically corresponds to coexistence states. Now focusing on  $\rho < \rho^-$ , the increasing branch classically splits in two parts: stable vapour for  $\rho < \rho_1^*$  and metastable vapour for  $\rho \in [\rho_1^*, \rho^-]$ . There is an analogous description for the liquid part, see Figure 1-left. To summarise, the Maxwell construction produces a globally nondecreasing pressure law, which is satisfactory from a physical viewpoint. But the drawback of this construction is that metastable states are not accounted for.

Notice also that these specific quantities can be represented in the  $(f, \rho)$ -plane, as sketched in Figure 1-right. The counterpart of the increasing parts of the pressure are the two convex branches of the van der Waals

Helmholtz free energy  $f$  for  $\rho < \rho^-$  and for  $\rho > \rho^+$ . The blue line is related to the Maxwell-type construction and is bitangent to the graph of  $f$  at densities  $\rho_1^*$  and  $\rho_2^*$  with slope  $\mu^* = \mu(\rho_1^*) = \mu(\rho_2^*)$ .

The aim of the following Section 1.2 is precisely to give a more rigorous insight on the Maxwell-type construction mentioned above (as well as accurate definitions of the quantities  $p^*$ ,  $\mu^*$ ) and to relate it to the notion of thermodynamic stability and the formulation in terms of convexity.

## 1.2. Inhomogeneity and equilibria

As mentioned in [2, chap. 8, p. 203], phase transition is a consequence of instabilities and introducing heterogeneity in a system is the hallmark of phase transition. A way to achieve heterogeneity according to Callen consists in splitting the system into an arbitrary number of subsystems and to investigate the thermodynamic stability of the system. We follow this guideline hereafter. Note that similar studies exist, focusing on decomposition into two subsystems, see for instance [3], [4] and [1].

For given mass  $M$  and volume  $V$ , we split the system into an arbitrary number  $I \geq 1$  of simple subsystems, each one being described by the same EoS. Each subsystem has a mass  $M_i$ , a volume  $V_i$  and its free energy is given by  $F(M_i, V_i)$ , with the same  $F$  function, describing the fluid under consideration. Assuming immiscibility of the subsystems, we recover total mass and volume by

$$M = \sum_{i=1}^I M_i, \quad V = \sum_{i=1}^I V_i, \quad (11)$$

and the total free energy is given by  $\sum_{i=1}^I F(M_i, V_i)$ .

Among these decompositions, we have to select the physically admissible ones: this is the notion of thermodynamic stability. According to Gibbs' formalism, the stable states are those which minimize  $\sum_{i=1}^I F(M_i, V_i)$  under the constraints (11). Thus we have to solve

$$\operatorname{argmin} \left\{ \sum_{i=1}^I F(M_i, V_i), \quad I \geq 1, \quad V = \sum_{i=1}^I V_i, \quad M = \sum_{i=1}^I M_i \right\}. \quad (12)$$

It is more convenient to reformulate the problem in terms of intensive variables, introducing the partial densities  $\rho_i = M_i/M$  and volume fractions  $\alpha_i = V_i/V$ ,  $0 \leq \alpha_i \leq 1$ . A straightforward computation leads to the equivalent formulation of problem (12):

$$\operatorname{argmin} \left\{ \sum_{i=1}^I \alpha_i f(\rho_i), \quad I \geq 1, \quad \sum_{i=1}^I \alpha_i = 1, \quad \sum_{i=1}^I \alpha_i \rho_i = \rho \right\}. \quad (13)$$

Two remarks are in order here. First we do not take into account the positivity constraints on the densities and volume fractions here. We will consider an additional constraint to ensure positivity, see assumption (17) below. Next, and more important, the number of subsystems  $I$  itself is an unknown parameter in the optimization problem.

This last problem is actually related to the so-called Gibbs' phase rule, which gives an upper bound to the number of possibly coexisting phases [2, 15]. A mathematical analogue of this rule results from the analysis of the minimization problem, more precisely from Carathéodory's theorem which states that the set of minima for the problem (13) for a general function  $f$  in  $\mathbb{R}^n$  is a (possibly degenerate) simplex. For more details, see for instance [16] in the general context and [9, 13] for the application to thermodynamics. In other words, for  $n = 1$  as in our case, we have  $I \leq 2$ , that is at most two subsystems may coexist. These two subsystems are now called phases, namely the vapour phase and the liquid phase. Coexistence states are obtained by  $I = 2$ , and  $0 < \alpha_i < 1$ ; a single pure phase can be characterized by  $I = 1$ , or by  $I = 2$  and  $\alpha_1 = 0$  or 1.

To cope with both cases, we choose to consider now  $I = 2$ , and allow the volume fractions  $\alpha_i$  to be 0 or 1. The Helmholtz free energy of the system is therefore defined by

$$\mathcal{F}(\alpha_1, \alpha_2, \rho_1, \rho_2) = \alpha_1 f(\rho_1) + \alpha_2 f(\rho_2). \quad (14)$$

Then the minimization problem rewrites

$$\operatorname{argmin} \{ \mathcal{F}(\alpha_1, \alpha_2, \rho_1, \rho_2), \quad \alpha_1 + \alpha_2 = 1, \quad \alpha_1 \rho_1 + \alpha_2 \rho_2 = \rho \}. \quad (15)$$

In this context, the case of a single subsystem is recovered, either by  $\alpha_i = 0$ , or by  $\rho_1 = \rho_2$ . Notice that if  $\rho_1 \neq \rho_2$ , we can solve for  $\alpha_i$  in the constraints above:

$$\alpha_1 = \frac{\rho_2 - \rho}{\rho_2 - \rho_1}, \quad \alpha_2 = \frac{\rho - \rho_1}{\rho_2 - \rho_1}. \quad (16)$$

Without loss of generality, we can assume  $\rho_2 > \rho_1$ , so that the positivity of  $\alpha_i$  amounts to

$$\rho_1 \leq \rho \leq \rho_2. \quad (17)$$

Introducing the Lagrange multipliers  $\lambda_\alpha$  and  $\lambda_\rho$  corresponding to the constraints in (15), we obtain straightforwardly the optimality conditions for the minima in (15):

$$\begin{aligned} (i) \quad f(\rho_1) + \lambda_\alpha + \rho_1 \lambda_\rho &= 0, & (iii) \quad \alpha_1(\mu(\rho_1) + \lambda_\rho) &= 0, \\ (ii) \quad f(\rho_2) + \lambda_\alpha + \rho_2 \lambda_\rho &= 0, & (iv) \quad \alpha_2(\mu(\rho_2) + \lambda_\rho) &= 0. \end{aligned} \quad (18)$$

For two states  $a$  and  $b$  we introduce the relative Helmholtz free energy of  $a$  with respect to  $b$

$$f(a|b) = f(a) - f(b) - \mu(b)(a - b). \quad (19)$$

This quantity gives a more accurate measurement of the distance between two states in terms of Helmholtz energy, and will be useful in the following.

**Lemma 1.1.** *The equilibrium states are*

(1) **Pure states:**

- $\rho_1 = \rho_2 = \rho$ ,  $\alpha_i$  undetermined,
- $\alpha_1 = 0$ ,  $\alpha_2 = 1$ ,  $\rho_2 = \rho > \rho_1$  and  $\rho_1 = \rho_1^\alpha$  solution to  $f(\rho_1^\alpha|\rho) = 0$ ,
- $\alpha_1 = 1$ ,  $\alpha_2 = 0$ ,  $\rho_1 = \rho < \rho_2$  and  $\rho_2 = \rho_2^\alpha$  solution to  $f(\rho_2^\alpha|\rho) = 0$ .

(2) **Coexistence states:**  $\rho_1 = \rho_1^*$ ,  $\rho_2 = \rho_2^*$ , with  $\alpha_i$  given by (16), where  $\rho_1^* < \rho^- < \rho^+ < \rho_2^*$  are uniquely defined by one of the two following equivalent properties

- equality of the pressure and chemical potential

$$\mu(\rho_1^*) = \mu(\rho_2^*) = \mu^* \quad \text{and} \quad p(\rho_1) = p(\rho_2) = p^*; \quad (20)$$

- Maxwell's area rule on the chemical potential

$$\int_0^1 \mu(\rho_1^* + t(\rho_2^* - \rho_1^*)) dt = \mu(\rho_1^*) = \mu(\rho_2^*). \quad (21)$$

*Proof.* In the pure state case, if  $\rho_1 = \rho_2 = \rho$ , the solution to the optimality conditions is trivial. Assume  $\rho_2 \neq \rho_1$ , then we can use (16) to compute  $\alpha_i$ . If  $\alpha_1 = 0$ , then  $\rho_2 = \rho$  and  $\alpha_2 = 1$ , so that  $\mu(\rho_2) = -\lambda_\rho$  from (18)-(iii) and (iv). From this we get  $f(\rho_1) - f(\rho_2) - \mu(\rho_2)(\rho_1 - \rho_2) = 0$ , that is  $f(\rho_1|\rho_2) = 0$ . The last case in item (1) is treated in the same way. For the coexistence case, we use first (18)-(iii) and (iv) which gives  $\mu(\rho_2) = -\lambda_\rho = \mu(\rho_1)$

since  $\alpha_i \neq 0$ . Next we report this in (18)-(i) and (ii) to obtain  $f(\rho_1) - \rho_1\mu(\rho_1) = -\lambda_\alpha = f(\rho_2) - \rho_2\mu(\rho_2)$ , which readily yields (21) by the fundamental theorem of calculus. The equality of pressures follows then from (9). Finally, the area rule provides a geometric argument which yields uniqueness of  $\mu^*$ , and therefore  $\rho_1^*$  and  $\rho_2^*$ , see Figure 2-right.  $\square$

The densities  $\rho_1^*$  and  $\rho_2^*$  defined by (20) or (21) are called the saturation densities,  $\mu^*$  is the saturation chemical potential, and  $p^*$  the saturation pressure. The Maxwell area rule (21) can easily be rewritten as the equality of the relative free energies:

$$f(\rho_2^*|\rho_1^*) = f(\rho_1^*|\rho_2^*) = 0. \quad (22)$$

This characterization will be useful in the study of the dynamical systems, see Section 2 below.

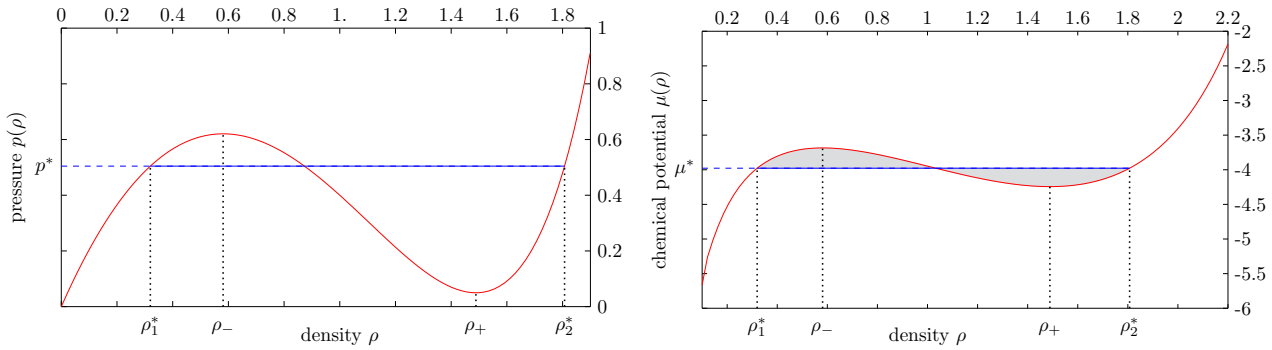


FIGURE 2. Characteristic parameters for the van der Waals EoS (10) at  $T = 0.85$ .

Saturation densities:  $\rho_1^* = 0.31972996451885$ ,  $\rho_2^* = 1.8071403273364$

Inflexion densities:  $\rho^- = 0.5810799446067$ ,  $\rho^+ = 1.4888047089018$

Maxwell-like lines:  $p(\rho_1^*) = p(\rho_2^*) = p^* = 0.504491649787487$ ,  $\mu(\rho_1^*) = \mu(\rho_2^*) = \mu^* = -3.97717851100986$

Left: pressure vs density – Right: chemical potential vs density. The equal area rule is satisfied on the chemical potential: the two grey areas are equal, which uniquely defines the values  $\mu^*$ ,  $\rho_1^*$  and  $\rho_2^*$ .

The equality of chemical potentials and pressures (20) is a classic characterization of coexistence states. Condition (21) is referred to as the Maxwell area rule, as we mentioned in Section 1.1. It appears here as an optimality condition for coexistence states. We refer to Figure 2-right for an illustration: the two grey areas are equal, this geometric construction defines in a unique way the quantities  $\mu^*$ ,  $\rho_1^*$  and  $\rho_2^*$ . An equivalent version, in the  $(p, \tau)$ -plane, where  $\tau = 1/\rho$  is the specific volume, is quite often presented. The Maxwell construction in our context consists in obtaining a globally nondecreasing chemical potential law by replacing the non-monotone part between  $\rho_1^*$  and  $\rho_2^*$  by the horizontal line  $\mu = \mu^*$  (see Figure 2-right). This modification using the pressure formulation is widely used in classic thermodynamic literature, see for instance [2, 14].

As mentioned above, the non monotonicity of the chemical potential for a subcritical temperature  $T < 1$  is related to the non-convexity of the van der Waals Helmholtz free energy, see Figure 1-right. The counterpart of the Maxwell construction here consists in replacing the function  $f$  by its convex hull, which amounts from a geometric viewpoint to replace the function  $f$  between  $\rho_1^*$  and  $\rho_2^*$  by the line with slope  $\mu^*$ , which turns out to be bitangent to the graph of  $f$ . It can be proved that this convex regularization of  $f$  coincides with its Fenchel biconjugate  $f^{**}$ , which in turn is characterized precisely by the minimization problem (15)

$$f^{**}(\rho) = \inf \{ \alpha_1 f(\rho_1) + \alpha_2 f(\rho_2), \quad \alpha_1 + \alpha_2 = 1, \quad \alpha_1 \rho_1 + \alpha_2 \rho_2 = \rho \}. \quad (23)$$

For more details on the proof of this equivalence, we refer to [16] for the general mathematical results and to [7, 11] for applications in thermodynamics.

In doing so, we indeed recover stable states, namely pure phases (vapour for  $\rho < \rho_1^*$ , liquid for  $\rho > \rho_2^*$ ), and coexistence states (for  $\rho_1^* < \rho < \rho_2^*$ ). On the other hand, this construction removes the convex parts of the graph of  $f$  (or equivalently the nondecreasing parts of the graph of  $\mu$ ), for  $\rho_1^* < \rho < \rho^-$  and  $\rho^+ < \rho < \rho_2^*$ , which correspond to metastable states. The aim now is to give a more flexible characterization of the equilibrium states that allow to recover both metastable states and coexistence states. We take advantage that the necessary conditions in Lemma 1.1 include all equilibrium states, regardless of their stability. In particular, we recover in item (1) the complete van der Waals curve, including physically unstable states (spinodal zone), metastable states and pure stable states. A classic way to sort these states would consist in studying the local convexity of  $\mathcal{F}$  in (14). We prefer here, following [13], to introduce a relaxation towards the equilibrium states, by means of a dynamical system.

## 2. A REVISITED DYNAMICAL SYSTEM AND ITS ATTRACTION BASINS

To build the appropriate dynamical systems, we impose two basic criteria, namely:

- long-time equilibria coincide with the physically relevant equilibria in Lemma 1.1,
- the free Helmholtz energy is dissipated along trajectories.

Such dynamical systems in some sense simulate the fluctuations in the thermodynamic system. Since the number of degrees of freedom in the constraints is 2, we need only to provide a dynamical system of dimension 2. Several choices are possible to define the set of extended variables. We propose here to use the partial densities  $(\rho_1, \rho_2)$ , which are naturally involved in the minimization problem. Even within this set, the choice of the dynamical system is not unique. A first example was considered in [13], we propose here another system, which allows a more precise analysis.

### 2.1. Defining the dynamical system

We set  $\mathbf{r} = (\rho_1, \rho_2)$ , and want to use relation (16) to define  $\alpha_i(\mathbf{r})$  and thus reduce the number of variables to 2. As mentioned before, to ensure in addition the positivity of the volume fractions, we must assume in this section that

$$0 < \rho_1 \leq \rho \leq \rho_2 < 3 \quad \text{and} \quad \rho_1 < \rho_2. \quad (24)$$

In this context, the Helmholtz free energy of the system becomes a function of  $\mathbf{r}$ , still denoted by  $\mathcal{F}$ :

$$\mathcal{F}(\mathbf{r}) = \alpha_1(\mathbf{r})f(\rho_1) + \alpha_2(\mathbf{r})f(\rho_2). \quad (25)$$

Using

$$\nabla \alpha_1(\mathbf{r}) = -\nabla \alpha_2(\mathbf{r}) = \frac{1}{\rho_2 - \rho_1} \begin{pmatrix} \alpha_1(\mathbf{r}) \\ \alpha_2(\mathbf{r}) \end{pmatrix},$$

we obtain

$$\nabla \mathcal{F}(\mathbf{r}) = \frac{1}{\rho_2 - \rho_1} \begin{pmatrix} \alpha_1(\mathbf{r})(p(\rho_2) - p(\rho_1) - \rho_2(\mu(\rho_2) - \mu(\rho_1))) \\ \alpha_2(\mathbf{r})(p(\rho_2) - p(\rho_1) - \rho_1(\mu(\rho_2) - \mu(\rho_1))) \end{pmatrix} = \frac{1}{\rho_2 - \rho_1} \begin{pmatrix} -\alpha_1(\mathbf{r})f(\rho_2|\rho_1) \\ \alpha_2(\mathbf{r})f(\rho_1|\rho_2) \end{pmatrix}, \quad (26)$$

where  $f(\rho_2|\rho_1)$  is the relative energy of  $\rho_2$  with respect to  $\rho_1$ , as defined in (19). Both  $\mathcal{F}$  and  $\nabla \mathcal{F}$  are defined only for  $\rho_1 < \rho_2$ , however we have the following result.

**Lemma 2.1.** *The function  $\mathcal{F}$  has a  $C^1$  extension in  $\bar{\mathbf{r}} = (\rho, \rho)^T$ . Still denoted by  $\mathcal{F}$ , it is defined by*

$$\mathcal{F}(\bar{\mathbf{r}}) = f(\rho), \quad \nabla \mathcal{F}(\bar{\mathbf{r}}) = \begin{pmatrix} 0 \\ 0 \end{pmatrix}.$$



*Proof.* For  $0 < \alpha_i < 1$ , we note that  $\rho_i - \rho = O(\rho_2 - \rho_1)$  and then  $f(\rho_i) = f(\rho) + \mu(\rho)(\rho_i - \rho) + o(\rho_2 - \rho_1)$ , so that  $\mathcal{F}(\mathbf{r}) = f(\rho) + o(\rho_2 - \rho_1)$ .

Now concerning the gradient of  $\mathcal{F}$ , we have  $f(\rho_2|\rho_1) = f(\rho_2) - f(\rho_1) - \mu(\rho_1)(\rho_2 - \rho_1) = O((\rho_2 - \rho_1)^2)$  provided  $f$  is  $C^2$ . Therefore

$$\alpha_1(\mathbf{r})f(\rho_2|\rho_1) = \frac{\rho_2 - \rho}{\rho_2 - \rho_1}f(\rho_2|\rho_1) = (\rho_2 - \rho)O(\rho_2 - \rho_1),$$

which tends to 0 as  $(\rho_1, \rho_2) \rightarrow (\rho, \rho)$ . The same holds true for the second component.  $\square$

Now we address the dissipation of the free energy along its trajectories:  $\frac{d}{dt}\mathcal{F}(\mathbf{r}(t)) = \nabla\mathcal{F}(\mathbf{r}) \cdot \dot{\mathbf{r}}(t) \leq 0$ . Then the most obvious choice would be  $\dot{\mathbf{r}} = -\nabla\mathcal{F}(\mathbf{r})$ , which gives  $\frac{d}{dt}\mathcal{F}(\mathbf{r}(t)) = -|\nabla\mathcal{F}(\mathbf{r})|^2 \leq 0$ . However this right-hand side is defined only for  $\rho_1 < \rho_2$  and this may lead to numerical issues close to the pure phase equilibrium point  $(\rho, \rho)$ . A slight modification is obtained by multiplying the right-hand side by  $\rho_2 - \rho_1$ , leading to

$$\begin{cases} \dot{\rho}_1 &= +(\rho_2 - \rho)f(\rho_2|\rho_1), \\ \dot{\rho}_2 &= -(\rho - \rho_1)f(\rho_1|\rho_2), \end{cases} \quad (27)$$

which yields  $\frac{d}{dt}\mathcal{F}(\mathbf{r}(t)) = -\alpha_1^2 f(\rho_2|\rho_1)^2 - \alpha_2^2 f(\rho_1|\rho_2)^2 \leq 0$ . This dynamical system has exactly the same equilibrium states as the minimization problem, but its drawback is that it does not preserve the positivity of  $\alpha_i$ . So in the end, we turn to

$$\begin{cases} \dot{\rho}_1 &= +(\rho - \rho_1)f(\rho_2|\rho_1), \\ \dot{\rho}_2 &= -(\rho_2 - \rho)f(\rho_1|\rho_2), \end{cases} \quad (28)$$

which leads to

$$\frac{d}{dt}\mathcal{F}(\mathbf{r}(t)) = \nabla\mathcal{F}(\mathbf{r}) \cdot \dot{\mathbf{r}}(t) = -\alpha_1(\mathbf{r})\alpha_2(\mathbf{r})(f(\rho_2|\rho_1)^2 + f(\rho_1|\rho_2)^2) \leq 0, \quad (29)$$

provided  $\alpha_i$  remain nonnegative for all times. But this is immediate from the structure of the right-hand side. Notice also that the diagonal  $\{\rho_1 = \rho_2\}$  is preserved in time since then, obviously,  $f(\rho_1|\rho_2) = f(\rho_2|\rho_1) = 0$ . Hence the inequality  $\rho_2 > \rho_1$  is also preserved for all times.

**Proposition 2.2** (Equilibrium states). *The equilibrium states for system (28) are given by  $\mathbb{F}(\mathbf{r}) = 0$ , where*

$$\mathbb{F}(\mathbf{r}) = \begin{pmatrix} +(\rho - \rho_1)f(\rho_2|\rho_1) \\ -(\rho_2 - \rho)f(\rho_1|\rho_2) \end{pmatrix}, \quad (30)$$

is the right-hand side of (28). They can be classified as follows.

- (1) *Coeexistence states:*  $\mathbf{r}^* = (\rho_1^*, \rho_2^*)^T$ ,  $\alpha_1^* = \frac{\rho_2^* - \rho}{\rho_2^* - \rho_1^*}$ ,  $\alpha_2^* = \frac{\rho - \rho_1^*}{\rho_2^* - \rho_1^*}$ , for  $\rho_1^* \leq \rho \leq \rho_2^*$ .
- (2) *Pure phases:*
  - (a)  $\bar{\mathbf{r}} = (\rho, \rho)^T$ ,  $\alpha_i$  undefined,  $\forall \rho \in ]0, 3[$ ,
  - (b)  $\bar{\mathbf{r}}^1 = (\rho, \bar{\rho}_2)^T$  where  $\bar{\rho}_2 > \rho$  satisfies  $f(\rho|\bar{\rho}_2) = 0$ ,  $\bar{\alpha}_1^2 = 1$ ,  $\bar{\alpha}_2^2 = 0$ , for  $\rho^- \leq \rho \leq \rho_2^*$  or  $\rho > \rho^+$ ,
  - (c)  $\bar{\mathbf{r}}^2 = (\bar{\rho}_1, \rho)^T$  where  $\bar{\rho}_1 < \rho$  satisfies  $f(\rho|\bar{\rho}_1) = 0$ ,  $\bar{\alpha}_1^1 = 0$ ,  $\bar{\alpha}_2^1 = 1$ , for  $\rho_1^* \leq \rho \leq \rho^+$  or  $\rho < \rho^-$ .

*Proof.* From  $\mathbb{F}(\mathbf{r}) = 0$ , we obtain three cases:

- $\rho_1 = \rho$  with
  - $\rho_2 = \rho$ , which leads to case (2a);

–  $\rho_2 > \rho$  and  $f(\rho|\rho_2) = 0$ , this is case (2b). Since  $f(b|a) = 0$  means that the tangent to the graph of  $f$  in  $a$  intersects the graph of  $f$  in  $b$ , a solution to  $f(\rho|\rho_2) = 0$  may exist only in two situations, namely

$$\rho^+ < \rho_2 < \rho_2^*, \quad \text{for } \rho_1^* < \rho < \rho^+, \quad (31)$$

$$\rho^- < \rho_2 < \rho^+, \quad \text{for } \rho < \rho^-; \quad (32)$$

- $\rho_2 = \rho$ , by similar arguments to the previous case, we recover on the first hand the case (2a), on the second hand the case (2c);
- $\rho_2 > \rho > \rho_1$  and  $f(\rho_2|\rho_1) = f(\rho_1|\rho_2) = 0$ . This leads to  $\rho_i = \rho_i^*$ , that is the coexistence case (1).

□

We emphasize here that the equilibrium states  $\bar{\mathbf{r}} = (\rho, \rho)$  are valid for all values of  $\rho$  and go over the whole van der Waals curve. This is in accordance with the definition of thermodynamic equilibrium. To go further and identify the physically admissible equilibrium states, we must investigate their stability and attractivity.

## 2.2. Stability and attractivity of the equilibria

Using a Lyapunov technique, we prove in this section that the attractors of the system are either pure liquid/vapour states, including metastable states, or the coexistence states defined in Proposition 2.2-(1). The major result of this paper is the characterization of metastable states in terms of attraction bassins. Actually we improve the definition of the attraction basins for metastable states, originally given in [13].

First we address the attractivity of the equilibria.

**Proposition 2.3** (Attractivity). *The equilibrium states are classified as follows:*

- $\bar{\mathbf{r}} = (\rho, \rho)$  is a strongly degenerate critical point,
- $\mathbf{r}^* = (\rho_1^*, \rho_2^*)$  is an attractive point,
- $\bar{\mathbf{r}}^i$ ,  $i = 1, 2$ , are unstable hyperbolic points.

*Proof.* We compute the Jacobian matrix of  $\mathbb{F}$ :

$$D_{\mathbf{r}}\mathbb{F}(\mathbf{r}) = \begin{pmatrix} -f(\rho_2|\rho_1) & 0 \\ 0 & f(\rho_1|\rho_2) \end{pmatrix} + \begin{pmatrix} -(\rho - \rho_1)(\rho_2 - \rho_1)\mu'(\rho_1) & (\rho - \rho_1)(\mu(\rho_2) - \mu(\rho_1)) \\ (\rho_2 - \rho)(\mu(\rho_2) - \mu(\rho_1)) & -(\rho_2 - \rho)(\rho_2 - \rho_1)\mu'(\rho_2) \end{pmatrix}. \quad (33)$$

In the coexistence case (1) in Proposition 2.2, we have  $f(\rho_2^*|\rho_1^*) = f(\rho_1^*|\rho_2^*) = 0$  and  $\mu(\rho_1^*) = \mu(\rho_2^*)$ , so that the eigenvalues  $\lambda_i(\mathbf{r}^*)$ ,  $i = 1, 2$  read

$$\lambda_1(\mathbf{r}^*) = -(\rho - \rho_1^*)(\rho_2^* - \rho_1^*)\mu'(\rho_1^*) < 0, \quad \lambda_2(\mathbf{r}^*) = -(\rho_2^* - \rho)(\rho_2^* - \rho_1^*)\mu'(\rho_2^*) < 0.$$

So this is an attractive equilibrium point.

In case (2a) of pure phases, one has  $\rho_1 = \rho_2 = \rho$ , then  $D_{\mathbf{r}}\mathbb{F}(\bar{\mathbf{r}}) = 0$  and we have a strongly degenerate equilibrium point.

Finally, the case (2b) leads to

$$D_{\mathbf{r}}\mathbb{F}(\bar{\mathbf{r}}^1) = \begin{pmatrix} -f(\rho_2|\rho) & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ (\rho_2 - \rho)(\mu(\rho_2) - \mu(\rho)) & -(\rho_2 - \rho)^2\mu'(\rho_2) \end{pmatrix}.$$

The eigenvalues are therefore  $\lambda_1(\bar{\mathbf{r}}^1) = -f(\rho_2|\rho)$  and  $\lambda_2(\bar{\mathbf{r}}^1) = -(\rho_2 - \rho)^2\mu'(\rho_2)$ .

Thus in the case (31), we have  $\lambda_1(\bar{\mathbf{r}}^1) > 0$  and  $\lambda_2(\bar{\mathbf{r}}^1) < 0$  (again by convexity arguments), while in the case (32), we have  $\lambda_2(\bar{\mathbf{r}}^1) > 0$  and  $\lambda_1(\bar{\mathbf{r}}^1) < 0$ . In both cases we have an hyperbolic equilibrium. Case (2c) is treated in a similar way. □

To complete the study of equilibrium states, in particular to cope with the degenerate state  $\bar{\mathbf{r}}$ , we investigate the attraction basins for  $\bar{\mathbf{r}}$  and  $\bar{\mathbf{r}}^*$ , which turn out to represent the physically interesting states, namely the pure phases including the metastable states and the coexistence states. We do not consider here the hyperbolic equilibrium states, since they are unstable.

We introduce the following functions, where the index  $P$  stands for Pure phase and  $C$  for Coexistence:

$$G_P(\mathbf{r}) = \mathcal{F}(\mathbf{r}) - \rho\mu(\rho) + p(\rho) = \mathcal{F}(\mathbf{r}) - f(\rho), \quad (34)$$

$$G_C(\mathbf{r}) = \mathcal{F}(\mathbf{r}) - \rho\mu^* + p^* = \mathcal{F}(\mathbf{r}) - f^{**}(\rho), \quad (35)$$

where  $f^{**}$  is the convex hull of  $f$ , as given by (23). Notice that for all  $\mathbf{r}$ , we have  $G_P(\mathbf{r}) = G_C(\mathbf{r})$  for  $\rho \notin ]\rho_1^*, \rho_2^*[$ , and  $G_P(\mathbf{r}) \leq G_C(\mathbf{r})$  for  $\rho \in ]\rho_1^*, \rho_2^*[$ . These two functions are candidates to be Lyapunov functions, and we have indeed the following proposition.

**Proposition 2.4** (Basins of attraction). *The basins of attraction of the equilibrium states are given by the Lyapunov functions (34) and (35) and their domains of definition.*

- In the **spinodal zone**, that is  $\rho \in ]\rho^-, \rho^+[$ ,  $G_C$  is a Lyapunov function on the whole domain  $]0, \rho[\times]\rho, 3[$ .
  - In the **pure stable zones**, that is  $\rho \leq \rho_1^*$  or  $\rho \geq \rho_2^*$ ,  $G_P$  is a Lyapunov function on the whole domain  $]0, \rho[\times]\rho, 3[$ .
  - In the **metastable zones**, that is  $\rho \in ]\rho_1^*, \rho^-]$  or  $\rho \in ]\rho^+, \rho_2^*]$ , there are two basins of attraction:
    - a pure phase basin  $\Omega_P$  where  $G_P$  is a Lyapunov function,
    - a coexistence basin  $\Omega_C = (]0, \rho[\times]\rho, 3[) \setminus \Omega_P$  where  $G_C$  is a Lyapunov function.
- More precisely, in the case of metastable vapour,  $\rho \in ]\rho_1^*, \rho^-]$ , we have

$$\Omega_P = ]0, \rho_1[\times]\rho, 3[\cup]\rho_1, \rho[\times]\rho, \rho_2(\rho_1)[,$$

where  $\rho_1$  is defined by  $\rho_2(\rho_1) = \bar{\rho}_2$  defined in in Proposition 2.2-(2b), and  $\rho_2(\rho_1)$  is an implicit function associated to

$$\varphi(\rho_1, \rho_2) = (\rho_2 - \rho)(f(\rho_1) - f(\rho)) - (\rho_1 - \rho)(f(\rho_2) - f(\rho)), \quad (36)$$

A similar characterization holds in the liquid metastable zone.

*Proof.* Three properties of Lyapunov functions are satisfied by construction:

- $G_P(\bar{\mathbf{r}}) = 0$  and  $G_C(\bar{\mathbf{r}}^*) = 0$ ,
- since  $\nabla G_P(\mathbf{r}) = \nabla G_C(\mathbf{r}) = \nabla \mathcal{F}(\mathbf{r})$ , we obtain as well  $\nabla G_P(\bar{\mathbf{r}}) = \nabla G_C(\bar{\mathbf{r}}^*) = 0$ ,
- for the same reason, and using (29), we have  $\frac{d}{dt}G_P(\mathbf{r}(t)) = \frac{d}{dt}G_C(\mathbf{r}(t)) \leq 0$ .

Thus we are left with positivity, which we study for the three above zones.

**Spinodal zone:**  $\rho \in ]\rho^-, \rho^+[$ . By definition of  $f^{**}$  we have  $G_C(\mathbf{r}) > 0$  if  $\mathbf{r} \neq \bar{\mathbf{r}}^*$ . Then the attraction basin corresponds to the set of states  $\mathbf{r}$  satisfying (24), that is  $\rho \in ]\rho_1^*, \rho_2^*[$ . Notice that for any  $\rho$  in this region  $G_P(\mathbf{r}) < 0$  in a neighborhood of  $\bar{\mathbf{r}}$ .

**Pure stable zones:**  $\rho \leq \rho_1^*$  or  $\rho \geq \rho_2^*$ . First we rewrite  $G_P(\mathbf{r}) = \alpha_1(\mathbf{r})f(\rho_1|\rho) + \alpha_2(\mathbf{r})f(\rho_2|\rho)$ . Direct investigations show that  $f(\rho_1|\rho) > 0$  and  $f(\rho_2|\rho) > 0$  for such values of  $\rho$ . Hence  $G_P(\mathbf{r}) > 0$  for  $\rho_1 < \rho < \rho_2$ . Therefore  $G_P$  is Lyapunov function on the domain  $0 < \rho_1 < \rho < \rho_2 < 3$ .

**Metastables zones.** We study the domain where  $G_P$  is positive. Notice that  $G_P(\rho, \rho_2) = G_P(\rho_1, \rho) = 0$  for any  $\rho_1$  and  $\rho_2$ . Then one can rewrite  $G_P(\mathbf{r}) = \alpha_1(\mathbf{r})(f(\rho_1) - f(\rho)) + \alpha_2(\mathbf{r})(f(\rho_2) - f(\rho))$ . Thus we have  $G_P(\mathbf{r}) > 0$  if and only if

$$\frac{f(\rho_1) - f(\rho)}{\rho_1 - \rho} < \frac{f(\rho_2) - f(\rho)}{\rho_2 - \rho}. \quad (37)$$

The inequality (37) holds true in a neighborhood of  $\rho$ , provided that  $\rho$  belongs to a zone of strict convexity of  $\mathcal{F}$ , that is  $\rho \in ]0, \rho^-[\cup]\rho^+, 3[$ . It is in particular the case in the two metastable zones. We study in more

details the attraction basins of the metastable vapour zone  $\rho \in ]\rho_1^*, \rho^-]$ , the proof being similar for the liquid metastable zone. The question is now to specify the domain of  $\mathbf{r}$  such that  $\rho_1 < \rho < \rho_2$  and  $G_P(\mathbf{r}) > 0$ . To do so, we consider the equation

$$\frac{f(\rho_1) - f(\rho)}{\rho_1 - \rho} = \frac{f(\rho_2) - f(\rho)}{\rho_2 - \rho}. \quad (38)$$

First we notice that when  $\rho_1 \rightarrow \rho$ , the left-hand side goes to  $\mu(\rho)$ . Then the solution tends to  $\rho_2^a$ , defined by  $f(\rho_2^a|\rho) = 0$ , see Lemma 1.1 item (1). Now when  $\rho_1$  decreases to 0, we observe that  $\rho_2(\rho_1)$  increases up to a value  $\rho_2$  such that the line with slope  $(f(\rho_1) - f(\rho))/(\rho_1 - \rho)$  is tangent to the graph of  $f$ , that is  $\mu(\rho_2) = (f(\rho_1) - f(\rho))/(\rho_1 - \rho)$ . From (38), we obtain  $\mu(\rho_2) = (f(\rho_2) - f(\rho))/(\rho_2 - \rho)$ , that is  $f(\rho|\rho_2) = 0$ , which determines  $\bar{\rho}_2$  as in Proposition 2.2-(2b). Therefore

- for  $\rho_1 \in ]\underline{\rho}_1, \rho[$ , (37) holds (that is  $G_P(\mathbf{r}) > 0$ ) if and only if  $\rho_2 < \rho_2(\rho_1)$ ;
- for  $\rho_1 \in ]0, \underline{\rho}_1[$ , (37) is satisfied for any  $\rho_2 > \rho$ .

More insight on the function  $\rho_2(\rho_1)$  is obtained by rewriting (38) as

$$\varphi(\rho_1, \rho_2) = (\rho_2 - \rho)(f(\rho_1) - f(\rho)) - (\rho_1 - \rho)(f(\rho_2) - f(\rho)) = 0.$$

The partial derivatives of  $\varphi$  read

$$\partial_{\rho_1}\varphi = (\rho_2 - \rho)\mu(\rho_1) - (f(\rho_2) - f(\rho)), \quad \partial_{\rho_2}\varphi = f(\rho_1) - f(\rho) + (\rho - \rho_1)\mu(\rho_2).$$

Convexity properties of  $f$  ensure that  $\mu(\rho_1) < (f(\rho_1) - f(\rho))/(\rho_1 - \rho) = (f(\rho_2) - f(\rho))/(\rho_2 - \rho)$ . Then  $\partial_{\rho_1}\varphi < 0$ . On the other hand,  $\partial_{\rho_2}\varphi = 0$  for  $\rho_1 = \rho$  and  $\mathbf{r} = (\underline{\rho}_1, \bar{\rho}_2)$  as defined above. It remains to study the sign of  $\partial_{\rho_2}\varphi$  on  $]\underline{\rho}_1, \rho[$ . Let  $\rho_2 \rightarrow \rho$ . Since  $f$  is convex in a neighborhood of  $\rho$ , it holds  $\mu(\rho_2) > (f(\rho_2) - f(\rho))/(\rho_2 - \rho) = (f(\rho_1) - f(\rho))/(\rho_1 - \rho)$ . Then  $\partial_{\rho_2}\varphi < 0$ . Thus the implicit function theorem applies and  $\rho_2'(\rho_1) = -\partial_{\rho_1}\varphi/\partial_{\rho_2}\varphi < 0$  for  $\rho_1 \in ]\underline{\rho}_1, \rho[$ , with infinite derivative in  $\underline{\rho}_1$  and  $\rho$ . In conclusion  $G_P$  is a Lyapunov function for the attraction basin defined by  $]0, \underline{\rho}_1[ \times ]\rho, 3[\cup ]\underline{\rho}_1, \rho[ \times ]\rho, \rho_2(\rho_1)[$ .  $\square$

We provide in Figure 3 an illustration of the attraction basins depending on the domain of  $\rho$ . The blue areas refer to nonattainable states, in the sense that the positivity constraint (24) is not satisfied.

Figure 3-left corresponds to the attraction basin for an initial state belonging to the pure gaseous zone, that is  $\rho \leq \rho_1^*$ . For any initial state  $\mathbf{r}(0)$  belonging to the white area, the long time limit of the dynamical system (28) satisfy  $\mathbf{r} = (\rho, \rho)$ .

Figure 3-right corresponds to the attraction basin for an initial state belonging to the spinodal zone, that is  $\rho \in ]\rho^-, \rho^+[$ . For any initial state  $\mathbf{r}(0)$  belonging to the white area, the asymptotic state satisfies  $\mathbf{r} = (\rho_1^*, \rho_2^*)$ , defined by the Proposition 2.2-(1).

Figure 3-center corresponds to the attraction basins for an initial state belonging to the metastable gaseous zone, that is  $\rho \in ]\rho_1^*, \rho^-]$ . One observes that there are two attraction basins, a green one and a white one, separated by a curve. This curve corresponds to the set of densities  $(\rho_1, \rho_2)$  satisfying  $\varphi(\rho_1, \rho_2) = 0$ , where  $\varphi$  is defined in equation (36). For any initial state belonging to the green area, the long time limit of (28) will remain a metastable gaseous state with  $\mathbf{r} = (\rho, \rho)$ . On the other hand, for any initial state belonging to the white domain, the asymptotic state will correspond to a coexistence state, that is  $\mathbf{r} = (\rho_1^*, \rho_2^*)$ .

The proof of Proposition 2.4 and in particular the characterization of the basins of attraction of metastable states and the determination of the implicit function associated to  $\varphi(\rho_1, \rho_2)$  in (36), are major improvements of the results initially provided in [13]. In the former paper, the attraction basins for metastable states were also splitted in two parts but we have improved here the determination of the separation border. The complete study of the metastable attraction basin may seem intricate, but we emphasize that condition (37) in the above proof provides an easy characterization, which will be used in the next section.

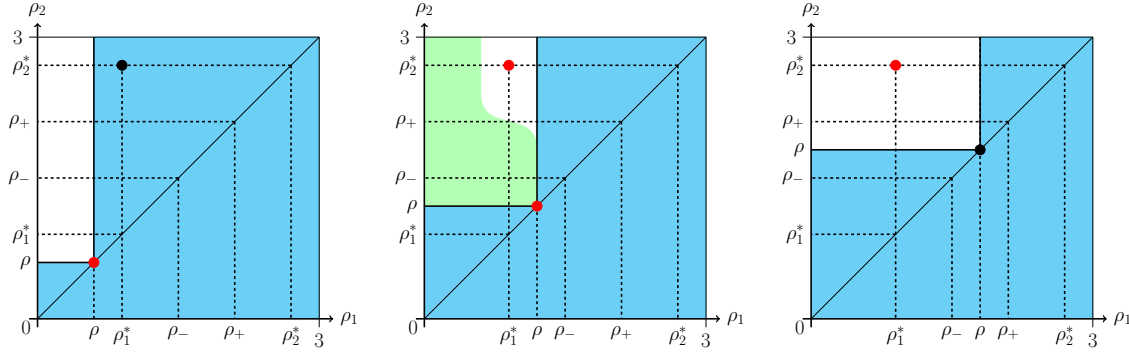


FIGURE 3. Stable equilibrium states and attraction basins for (28): pure gaseous zone (left) – pure gaseous metastable zone (center) – spinodal zone (right). The blue areas refer to nonattainable states according to (24). The stable equilibrium points appear in red. The attraction basins are in white, except for the metastable basin in green.

### 3. ISOTHERMAL EULER SYSTEM

In this section we propose an example of coupling between the above thermodynamic model and hydrodynamics. This toy-model allows us to explore through examples the ability of the system to catch metastable and coexistence states.

#### 3.1. Model and numerical scheme

Following [13], we consider a relaxation model for the isothermal Euler system by adding the two variables  $\rho_1, \rho_2$ , and using the dynamical system (28):

$$\begin{aligned} \partial_t \rho + \partial_x(\rho u) &= 0, \\ \partial_t(\rho u) + \partial_x(\rho u^2 + \pi(\rho, \rho_1, \rho_2)) &= 0, \\ \partial_t \rho_1 + \partial_x(\rho_1 u) &= +\frac{1}{\varepsilon}(\rho - \rho_1)f(\rho_2|\rho_1), \\ \partial_t \rho_2 + \partial_x(\rho_2 u) &= -\frac{1}{\varepsilon}(\rho_2 - \rho)f(\rho_1|\rho_2), \end{aligned}$$

where  $u$  is the fluid velocity and  $\pi(\rho, \rho_1, \rho_2) = \alpha_1(\mathbf{r})p(\rho_1) + \alpha_2(\mathbf{r})p(\rho_2)$  is the pressure. The system can be written in a more compact way as

$$\partial_t W + \partial_x F(W) = \frac{1}{\varepsilon} R(W), \quad (39)$$

where  $W = (\rho, \rho_1, \rho_2, \rho u)^T$ ,  $F(W) = (\rho u, \rho_1 u, \rho_2 u, \rho u^2 + \pi)^T$ , and  $R(W) = (0, 0, \mathbb{F}_1(\mathbf{r}), \mathbb{F}_2(\mathbf{r}))^T$ , where we use again the notations in (30). The system is complemented by initial data  $W(0, x) = W^0(x)$ ,  $W^0$  being a given vector-valued function.

Notice that recombining the equations in  $\rho, \rho_1, \rho_2$  we obtain the following relaxation equation on the volume fraction  $\alpha_1$ :

$$\partial_t \alpha_1 + u \partial_x \alpha_1 = \frac{\alpha_1 \alpha_2}{\varepsilon} (f(\rho_1|\rho_2) - f(\rho_2|\rho_1)). \quad (40)$$

This kind of equation is classic at least for the transport operator, see for instance [8, 12], but the right-hand side is specific to the relaxation model we use.

In system (39),  $\varepsilon$  is a characteristic time, which compares the relaxation time to thermodynamic equilibrium with respect to the hydrodynamical time. Three regimes can be considered here. First the infinite relaxation

regime, where  $\varepsilon = +\infty$ , so that only the convective part of (39) is involved, the thermodynamics is too slow to affect the hydrodynamical motion. At the opposite, the instantaneous relaxation corresponds to  $\varepsilon = 0$ , so that  $(\rho_1, \rho_2)$  and  $(\alpha_1, \alpha_2)$  in (39) are given by the long time limit of the dynamical system (28). In this regime, also known as quasi-static regime, the thermodynamic relaxation is instantaneous, giving rise to a quasilinear system. In between, finite values of  $\varepsilon$  lead to an actual relaxation system. We consider here the quasi-static regime.

The question of hyperbolicity of the homogeneous part has been addressed in [13]. We merely recall here that there are four eigenvalues

$$\lambda_1 = u - c \leq \lambda_2 = \lambda_3 = u \leq \lambda_4 = u + c,$$

where  $c(\rho) = \sqrt{(\alpha_1 \rho_1 p'(\rho_1) + \alpha_2 \rho_2 p'(\rho_2)) / \rho}$  is the sound velocity, defined provided  $\alpha_1 \rho_1 p'(\rho_1) + \alpha_2 \rho_2 p'(\rho_2) \geq 0$ . The non-hyperbolicity zone includes, and is larger than, the spinodal zone (where  $p'(\rho_i) \leq 0$ ). Fields 1 and 4 are genuinely nonlinear, fields 2 and 3 are linearly degenerate. Since we only consider the quasi-static regime, all the equilibrium states belong to hyperbolicity regions of the system (39), so that loss of hyperbolicity is not a concern here.

We now address the numerical discretization. Being given a time step  $\Delta t$  and a space step  $\Delta x$ , we denote as usual by  $W_j^n$  an approximation of  $W(t^n, x_j)$ , where  $t^n = n\Delta t$  and  $x_j = j\Delta x$ ,  $n \geq 0$ ,  $j \in \mathbb{Z}$ . This is complemented by discrete initial data  $W_j^0$ ,  $j \in \mathbb{Z}$ . System (39) is discretized using a time splitting approach. First the convective part of (39) is approximated by a conservative finite volume scheme whose generic form is

$$\widetilde{W}_j^{n+1} = W_j^n - \frac{\Delta t}{\Delta x} (F_{j+1/2}^n - F_{j-1/2}^n),$$

where  $F_{j+1/2}^n$  is determined by a numerical flux  $F(W_j^n, W_{j+1}^n)$ . We choose here the so-called HLLC numerical flux. Recall the classic HLL flux [10] for two states  $W_L$  and  $W_R$  reads

$$F^{HLL}(W_L, W_R) = \begin{cases} F(W_L), & \text{if } 0 \leq s_L, \\ \frac{s_R F(W_L) - s_L F(W_R) + s_L s_R (W_R - W_L)}{s_R - s_L}, & \text{if } s_L \leq 0 \leq s_R, \\ F(W_R), & \text{if } 0 \geq s_R, \end{cases} \quad (41)$$

where

$$s_L = \min(u_L - c_L, u_L + c_L), \quad s_R = \min(u_R - c_R, u_R + c_R).$$

The HLLC variant consists in taking into account the eigenvalue  $u$ , see e.g. [17] for a general presentation. We define the 1st and 4th components of the HLLC flux by  $F_{1,4}^{HLLC}(W_R, W_L) = F_{1,4}^{HLL}(W_R, W_L)$ , and the 2nd and 3rd components by

$$F_{2,3}^{HLLC}(W_R, W_L) = \begin{cases} F_{2,3}^{HLL}(W_R, W_L) \cdot \frac{(W_{2,3})_R}{(W_1)_R} & \text{if } s^* < 0, \\ F_{2,3}^{HLL}(W_R, W_L) \cdot \frac{(W_{2,3})_L}{(W_1)_L} & \text{if } s^* \geq 0, \end{cases}$$

where

$$s^* = \frac{F_4(W_R) - F_4(W_L) - s_R \rho_R u_R - s_L \rho_L u_L}{\rho_R (u_R - s_R) - \rho_L (u_L - s_L)}.$$

In a second step we treat the relaxation source terms of (39). Since we consider instantaneous relaxation with  $\varepsilon = 0$ , this step amounts to determine to which basin of attraction  $\tilde{\mathbf{r}}_j^{n+1}$  belongs to and define  $\mathbf{r}_j^{n+1}$  as the corresponding equilibrium state, according to Proposition 2.4, more precisely using condition (37).

All the following examples are Riemann problems on  $[0, 1]$ , with  $W^0(x) = W_L \mathbf{1}_{x < 1/2}(x) + W_R \mathbf{1}_{x > 1/2}(x)$ ,  $W_L$  and  $W_R$  being two constant vectors. They are computed with 10000 space steps, that is  $\Delta x = 10^{-5}$ , the time

step being computed at each time iteration using the CFL condition

$$\Delta t^n = \sigma_{CFL} \frac{\Delta x}{\max_{j \in \mathbb{Z}, k \in \{1,2,3,4\}} (|\lambda_k(W_j^n)|)},$$

where  $0 < \sigma_{CFL} < 1$  is a constant which was taken equal to 0.95.

### 3.2. Nucleation by compression

We begin with an example of compression of a pure vapour state, for different values of the velocity  $u$ . Initial data for all the cases we consider involve constant densities on  $[0, 1]$  and opposite velocities:

$$\rho_1 = 0.18, \quad \rho = 0.2, \quad \rho_2 = 0.24, \quad u_L = -u_R > 0,$$

so that the initial perturbation remains within the pure vapour phase. We apply successively four values of  $u_L$ :

- very weak compression,  $u_L = 0.55$ ,
- weak compression  $u_L = 0.91$ ,
- strong compression  $u_L = 1.2$ ,
- very strong compression  $u_L = 1.5$ .

For both very weak and weak compression rates, we obtain a solution which remains in the pure vapour phase, with creation of a metastable intermediate state for  $u_L = 0.91$ , see Figure 4. The system actually behaves like a simple Euler system with a monotone pressure law.

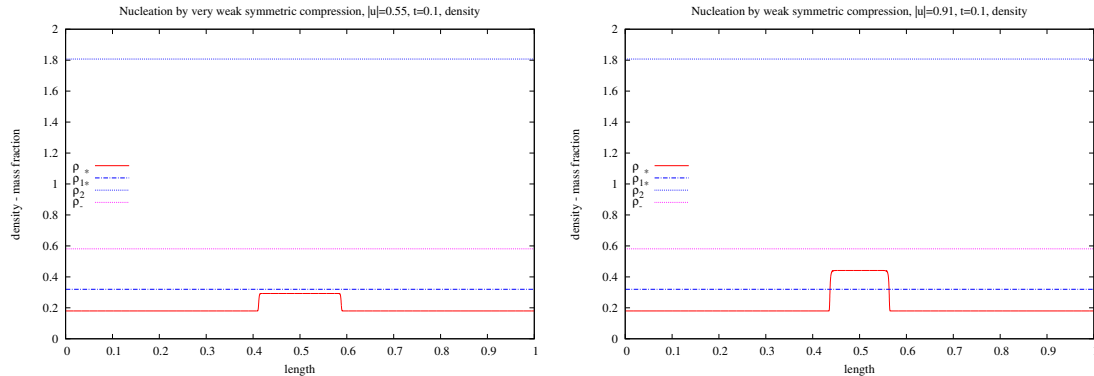


FIGURE 4. Nucleation by symmetric compression at  $t=0.1$ , very weak compression  $u_L = 0.55 = -u_R$  (left) – weak compression  $u_L = 0.91 = -u_R$  (right).

For a stronger compression,  $u_L = 1.2$ , we observe the apparition of a liquid droplet centered at  $x = 0$ , where the density is higher than the value  $\rho_2^*$ . Two remarkable features are first the presence of a metastable zone surrounding the bubble, second a very thin zone of mixture ( $\rho_1 = \rho_1^*$ ,  $\rho_2 = \rho_2^*$ ). It is very clearly evidenced on the volume fraction  $\alpha$  profile, see Figure 5-center left, but appears as “kinks” for instance on the velocity or partial densities pictures.

If we increase the compression, with  $u_L = 1.5$ , we observe that the metastable zone eventually disappears, while the tiny mixture zone is still present, see Figure 6.

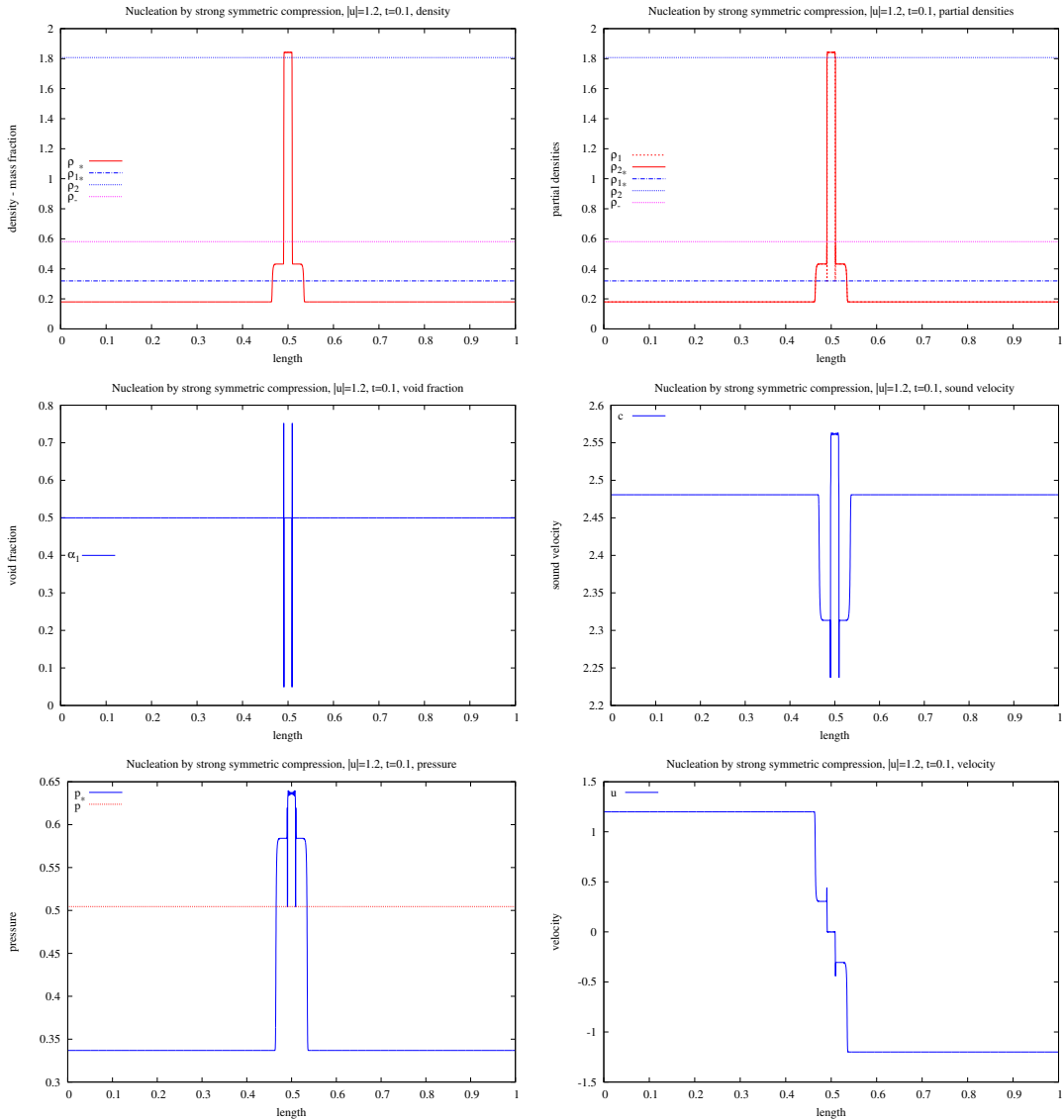


FIGURE 5. Nucleation by symmetric compression at  $t=0.1$ , strong compression  $u_L = 1.2 = -u_R$ .

3.3. Cavitation by decompression

In a somehow symmetric way, we can obtain cavitation, that is creation of a vapour bubble from a liquid initial condition. More precisely, we consider initial densities  $\rho = 1.9 > \rho_2^*$ , with  $\rho_1 = 1.87$  and  $\rho_2 = 1.92$ . To these data we apply a velocity  $u_L = -u_R < 0$ . As in the compressive case, for small values of the velocity we deal with a classic Riemann problem for the Euler system with a monotone pressure law. These results are not shown here. We focus on higher values of the velocity for which a bubble appears, namely  $u_L = -0.4 = u_R$  (strong decompression, Figure 7) and  $u_L = -2 = u_R$  (very strong decompression, Figure 8).

The situation here is more complex than in the compression case. First notice that there is no intermediate metastable state. Next, it seems that the rarefaction induced by the decompression gives rise to composite waves, see Figure 8. The tiny mixture zone exists in both cases, see the void fraction  $\alpha_1$ , Figure 7 and 8-center



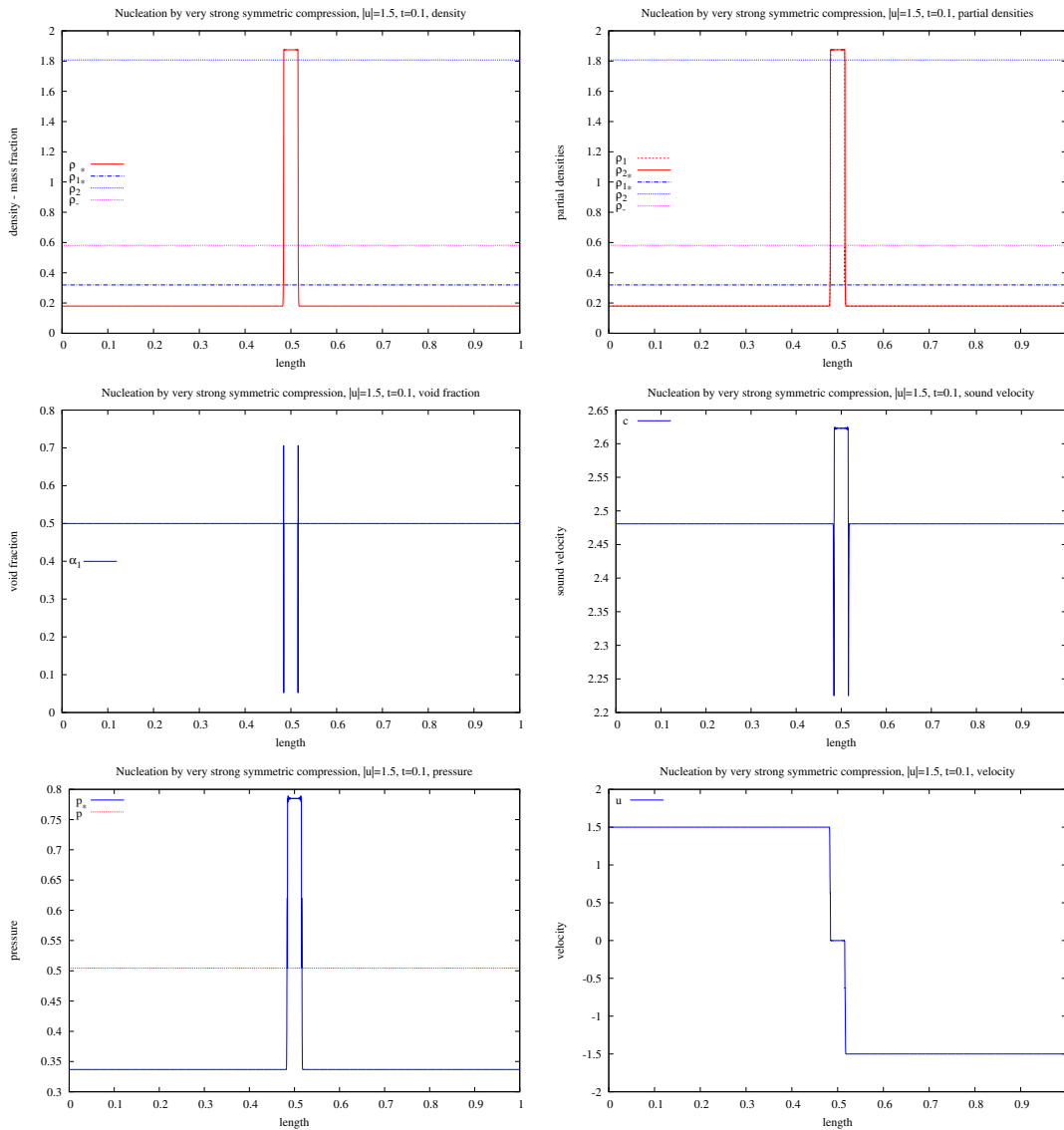


FIGURE 6. Nucleation by symmetric compression at  $t=0.1$ , very strong compression  $u_L = 1.5 = -u_R$ .

left. The situation is more sensitive to the CFL condition: notice the overshoots in the pressure profile in Figure 8-bottom left: they should not go over  $p^*$  in the coexistence zone. If we reduce the CFL condition (e.g.  $\sigma_{CFL} = 0.65$ ), the pressure remains bounded by  $p^*$ .

#### 4. CONCLUSION

We provide in this paper a more detailed analysis of a vapour-liquid phase transition model introduced in [13] to capture metastable states of the reduced van der Waals equation. The improvements are twofold. First the construction of the dynamical system and its analysis have been improved. In particular we have made more precise the determination of the attraction basins in the metastable zone. Second, as the coupling with hydrodynamics is concerned, we propose to exploit at best the characterization of the attraction basins of the

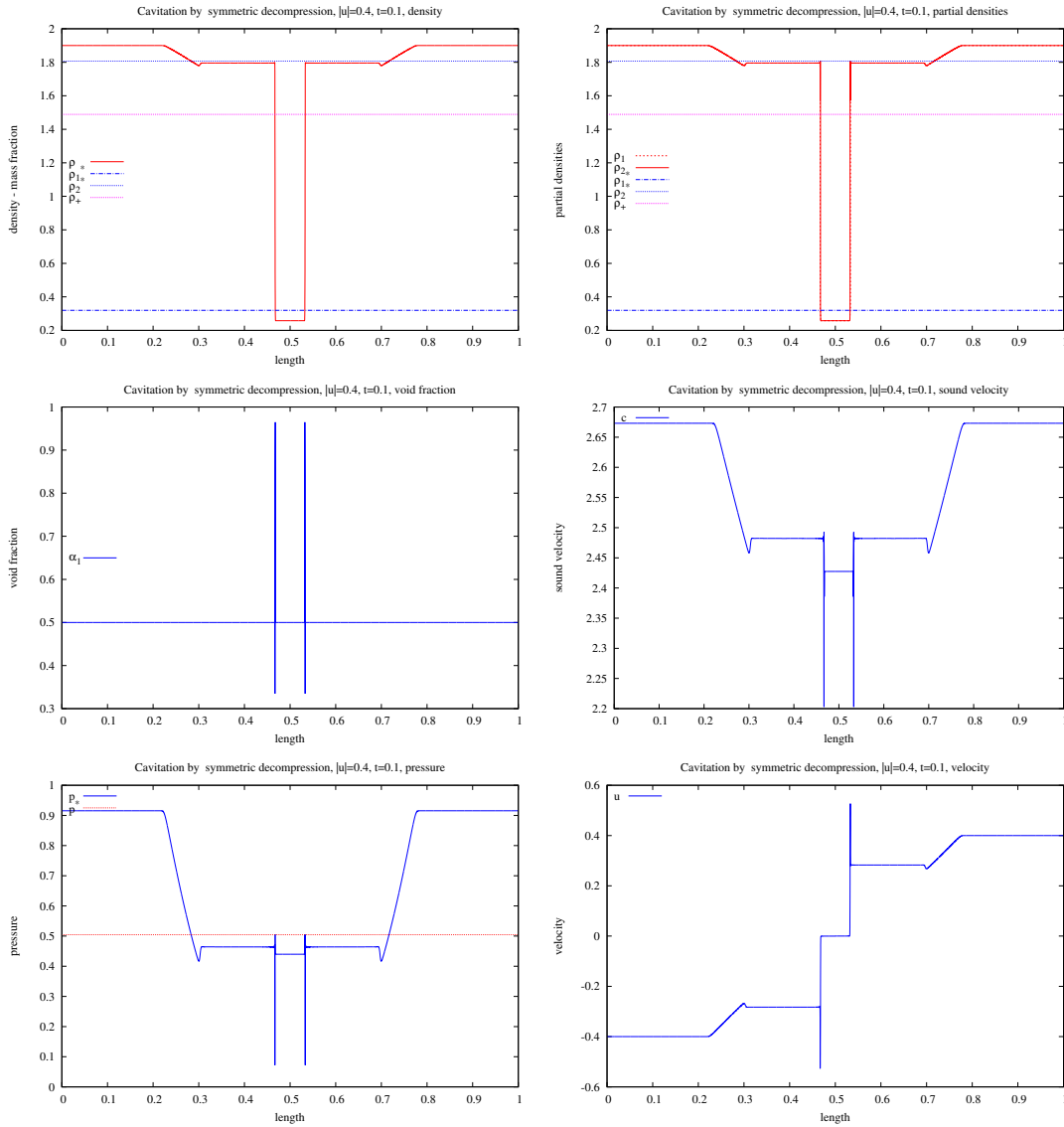


FIGURE 7. Cavitation by symmetric decompression at  $t=0.1$ , strong decompression  $u_L = -0.4 = u_R$ .

dynamical system to perform instantaneous relaxation. Doing so, we get rid of spurious numerical artefacts due to the explicit relaxation approximation, initially performed in [13].

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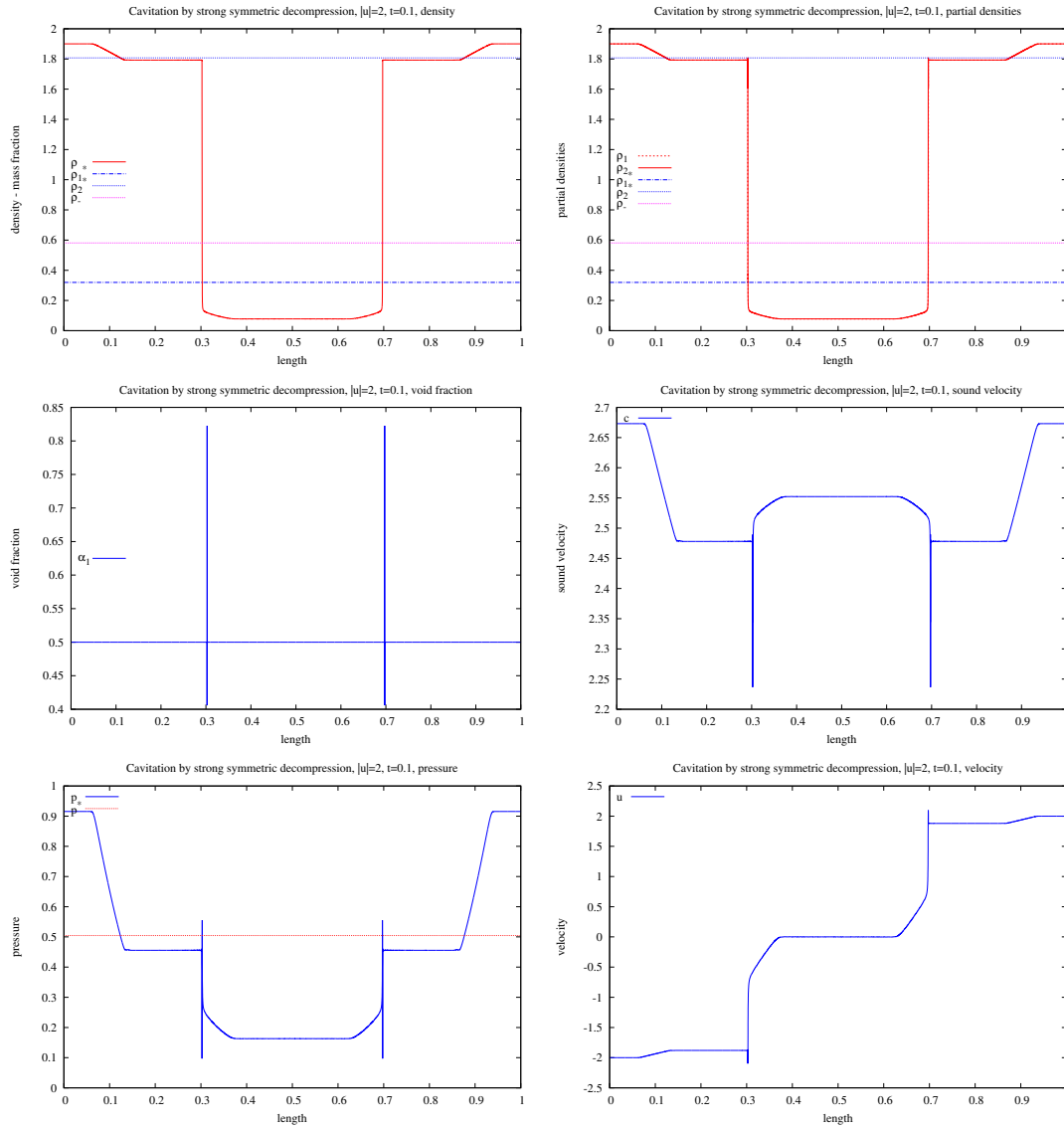


FIGURE 8. Cavitation by symmetric decompression at  $t=0.1$ , very strong decompression  $u_L = -2 = u_R$ .

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