Pressure Control for Liquid-Vapor Systems far from Thermodynamic Equilibrium

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Abstract

In this paper, we investigate the stability analysis and the feedback stabilization design problem for multiphase chemical systems using the formalism of non-equilibrium thermodynamics. We first present a compartmental model for multiphase systems far from thermodynamic equilibrium. The modelling framework allows to describe irreversible multiphase systems as a differential-algebraic (DAE) system of equations. The differential part of the model corresponds to macroscopic balance equations. The algebraic system of equations physically represents the interface as a thermodynamic subsystem that occurs between bulk phases. Integrating the DAE model is equivalent to fix the degrees of freedom prescribed by Gibbs phase rule. A linear stability analysis and numerical simulations for the resulting differential-algebraic model are presented. As a side result, we stabilize the system by introducing a pressure controller using the proposed modelling framework.

Keywords: Non-equilibrium thermodynamics, Liquid-vapor systems, Stability analysis, Pressure control.

1. INTRODUCTION

Design, analysis, and operation of thermodynamic systems stand as fundamental aspects of process systems engineering. In this article, we investigate the possibility of characterizing multiphase chemical operations using physics-based criteria. In reversible systems, the state-space of a process is assumed to be contained inside a manifold defined by thermodynamic equilibrium relations [1]. In our research, we suggest the possibility of thermodynamic systems to operate far from the equilibrium manifold. Following the ideas first presented by Georgakis [2], we propose a methodology to study the time evolution of extensive variables in a multiphase system. Using a compartmental approach, it can be shown that the state variables for each phase in a multiphase system is described as the solution to macroscopic balance equations on mass and energy.

Physics-based methodologies have proven to be useful for the characterization of dynamical systems in process engineering. Dissipative analysis, as proposed by Willems [3] for instance, has clear applications to the study of electro-mechanical systems. From a dissipative theory perspective, the stability properties of chemical systems are understood as a function of certain thermodynamic potentials. Entropy is a Lyapunov function for the equilibrium state in closed adiabatic systems [4]. Gibbs potential is minimized at equilibrium for chemical processes at constant temperature and pressure [5]. Within the same lines of research, Georgakis [2] proposed to use macroscopic thermodynamic variables for the analysis and control of process systems.

The macroscopic analysis proposed by Georgakis [2] served as a starting point for several contributions to modelling, analysis and control of chemical process systems literature. Price et al. [6] proposed inventory control guidelines for the effective design and operation of chemical process plants. Farschman et al. [7] studied chemical systems using thermodynamic inventories. The concept of thermodynamic inventories allows to define low-dimensional passivity structures that permit to establish stability of chemical processes. Favache and Dochain [8] characterized the continuous stirred tank reactor (CSTR) dynamic properties using thermodynamic-based Lyapunov theory. In related publications, Hoang et al. [9, 10] represented the CSTR utilizing a thermodynamic structured model where Gibbs free energy and an entropy-related formulations are considered as Hamiltonian functions. Moreover, the thermodynamic analysis performed in [9, 10] leads to intuitive (availability-based) control laws with clear phenomenological interpretations.

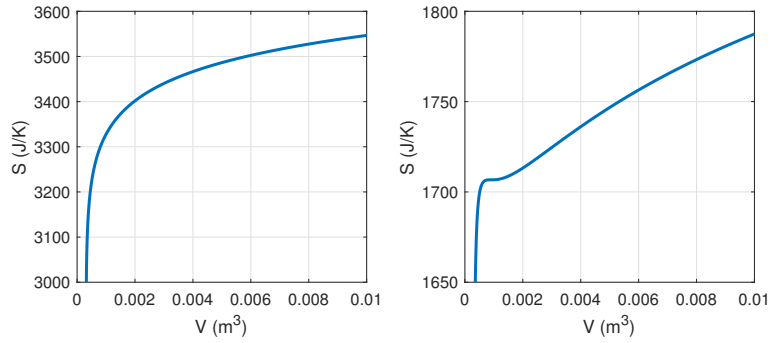

Figure 1: Van der Waals entropy-volume graph for vapor (right) and liquid-gas (left) water in a closed system.

As for chemical reaction networks, Hoang and Dochain [11] presented an evolution stability criterion based on chemical availability to characterize the stability of reaction networks in non-isothermal CSTRs. A recent contribution to the literature worth to be mentioned is the work presented by García-Sandoval et al. [12, 13] where the authors utilize an entropy dissipation-based approach to discuss on the stability of different physical and chemical systems.

The line of research in contributions [6, 7, 8, 9, 10, 11, 12, 13], which is strongly related with the idea of studying chemical process systems using macroscopic variables as proposed originally by Georgakis [2], represents a sound physics-based framework. The authors would like to remark that the references previously discussed are focused on the study of chemical systems where only one (usually liquid or gaseous) phase appears.

Regarding multiphase process systems, Rouchon and Creff [14] studied the multi-component flash drum using a differential algebraic system that describes the evolution of macroscopic variables in the process. Rouchon and Creff concluded that a single stage isobaric flash-drum with constant volume holdup is stable. The analysis by Rouchon and Creff [14] shows that the rate at which entropy is produced in a flash drum is a Lyapunov function. Unfortunately, such conclusion does not extend to distillation columns as entropy production is no longer a minimized at equilibrium for multi-stage processes. Rouchon and Creff [14] suggest that studying the hydraulic effects on multiphase systems could lead to different conclusions. Using a compartmental-based modeling approach, Hangos et al. [15] conclude that

the flash drum with constant molar flows is a passive asymptotically stable system. Using a passivity-based Lyapunov analysis based on the formalism proposed by Hangos et al. [15], the stability properties of chemical proces plants are established by Antelo et al. in [16]. Following the same lines of research, Ydstie [1] considers the problem of characterizing the flash drum using thermodynamic availability and concludes on the existence of a unique stable steady-state for adiabatic systems operating inside an equilibrium manifold. Our objective is to extend the multiphase systems theory by analyzing processes that evolve far from the equilibrium manifold.

Thermodynamic potentials have well-defined convexity properties. For closed simple thermodynamic systems[1], entropy (resp. internal energy) is a strictly concave (resp. convex) function of the extensive variables [5], see Figure 1 (right). Such geometric properties have permitted to assess stability and to build control structures through dissipative analysis [8, 12, 9, 10]. One of the main problems when trying to apply this class of methodologies to multiphase systems is that the convexity properties are not strict in multiphase systems [5, 17], see Figure 1 (left). To characterize the dynamical properties of a system regardless of its convexity properties, we propose to use the internal entropy production. Being semipositive definite, internal entropy production is a Lyapunov function candidate to characterize the stability properties of equilibria in multiphase systems. Internal entropy production can be described as a function of the extensive variables in a thermodynamic system [18]. Therefore, it is our objective to establish a macroscopic model to describe the dynamic evolution of irreversible multiphase systems.

The article is structured as follows. In Section 2, we define what we consider as a macroscopic thermodynamic system. In Section 3, we model a multiphase system far from equilibrium as the interconnection between two macroscopic thermodynamic systems connected through an interface subsystem. Mass and energy balances define the state of the bulk phases. In addition, the interface subsystem is modelled using a local equilibrium assumption. A linear analysis of the model is presented in Section 4. The multiphase system is shown to be unstable due to the presence of positive eigenvalues. To stabilize the system, a pressure controller is introduced to the model in Section **??**. Conclusions and future lines for research are presented in Section 6.

[1] An homogeneous system with no electric charge is a simple system. See Definition 1.

2. Thermodynamic open systems

It is within the interest of the research presented in this paper to establish the dynamical properties of macroscopic systems, in particular of simple macroscopic systems.

Definition 1 (Simple Macroscopic System)**.** *A system that is large enough to be macroscopically homogeneous, isotropic, and to have no electric charge is called a simple thermodynamic system. Surface effects, gravity, and electromagnetic fields are considered to not have an effect on simple thermodynamic systems [5].*

All the physical properties of a macroscopic system are determined once its state is known. For instance, an ideal gas at thermodynamic equilibrium where pressure P, temperature T, and volume V are known is completely determined[2]. Callen's first postulate of thermodynamics states that, in a simple system with c components, only $c+2$ thermodynamic coordinates are required to determine the equilibrium state for simple systems [5].

Definition 2 (First Postulate)**.** *The equilibrium states for a simple thermodynamic system can be determined as a function of a coordinate $z \in \mathbb{R}^{c+2}_{\geq 0}$. The choice for the coordinate points of z, although not uniquely defined, may be represented as the set of macroscopic extensive variables*

$$z := [U,\ V,\ N_1,\ \ldots\ N_c]^t, \tag{1}$$

where U (J) represents the internal energy, V (m^3) the volume, and $N_1, \ldots, N_c$ (mol) the mole numbers for each component[3].

Under a local equilibrium assumption, see Appendix B, Definition 1 is considered to be valid for open macroscopic systems [19].

2.1. Open thermodynamic systems

Consider an open simple thermodynamic system as the one depicted in Figure 2, where a fluid mixture with c chemical components is contained. Through its open boundaries, the system exchanges mass and energy with the surroundings. Moles flow through the system at an average speed υ

[2] See Appendix A.

[3] The state (1) is sometimes referred as the micro-canonical ensemble [7, 1]

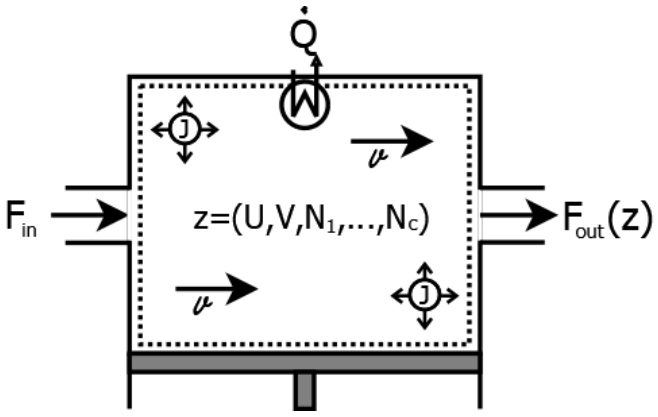

Figure 2: Open thermodynamic system with internal sources. The system has a state z and it is contained within the dotted box.

(m/s). Molar and enthalpy flow from the environment into the system at fixed rates $F_{N_j,\text{in}}$ (mol/s) and $F_{H,\text{in}}$ (J/s), respetively. Convective flows are discharged from the system at a volumetric flow rate $F_{V,\text{out}}(z)$ (m^3/s). Non-convective sources/sinks of moles and internal energy (chemical reactions, ionic-exchange resines, or catalyzer beds for instance) are represented as J in Figure 2. As the system is not necessarily considered adiabatic, a thermal source of energy is represented as $\dot{Q}$ (J/s).

Assumption 1. For modeling purposes, for any open simple thermodynamic system in this paper, we assume that:

- A1 The system is locally at thermodynamic equilibrium[4].
- A2 Gibbs phase rule is valid for the system.
- A3 Potential energy is constant over the system.
- A4 The discharge flow is at the same pressure and flows at the the same average speed as the bulk-phase flow.
- A5 Kinetic energy variations are insignificant when compared to variations in enthalpy or in internal energy.
- A6 Velocity profiles are perpendicular to the inflow (outflow) cross-sections.
- A7 Density and pressure are uniform over the inflow (outflow) cross-sections.

[4]As a consequence of thermodynamic equilibrium, The fluid flow is perfectly mixed.

A8 Compressibility and viscous losses in the fluid flows are negligible.

In the next section we consider these assumptions to describe a liquid-vapor system as the interconnection between two open simple thermodynamic systems using mass and energy balances.

3. Multiphase systems far from thermodynamic equilibrium

We consider a liquid-gas process with c chemical components inside a rigid vessel as depicted in Figure 3 (left). Liquid enters the vessel at a rate $F_{l,\text{in}}$ (mol/sec) and it is discharged to the environment at a rate $F_{l,\text{in}}$ (mol/sec). Bubbles flow in and out the liquid bulk phase at rates $F_{g,\text{in}}$ (mol/sec) and $F_{g,\text{out}}$ (mol/sec), respectively. The system is represented as the union of three simple macroscopic structures, Figure 3 (right). The blue block stands for the liquid bulk phase. The white block represents the aggregate of all dispersed bubbles, which we refer to as the gas bulk phase. The gray block in between stands for the interface that corresponds to the combined surface of the gas bubbles within the liquid. Under assumptions A1-A8, the state of the system can be recovered as the solution to the differential equations described below.

Molar balances over gas and liquid phases, denoted with subscripts g and l, respectively, are given as

$$\frac{dN_{jg}}{dt} = F_{N_j,g,\text{in}} - \frac{N_{jg}}{V_g} F_{V,g,\text{out}} + J_{N_j,g} \tag{2a}$$

$$\frac{dN_{jl}}{dt} = F_{N_j,l,\text{in}} - \frac{N_{jl}}{V_l}\, F_{V,l,\text{out}} - J_{N_j,l}, \tag{2b}$$

where subscript $j = 1, ..., c$, is used to refer a variable to a chemical component in the system. Energy balances over each phase give

$$\frac{dU_g}{dt} = F_{H,g,\text{in}} - \left(\frac{U_g}{V_g} + P_g\right) F_{V,g,\text{out}} - P_g \frac{dV_g}{dt} + \dot{Q}_g + J_{E,g} \tag{3a}$$

$$\frac{dU_l}{dt} = F_{H,l,\text{in}} - \left(\frac{U_l}{V_l} + P_l\right) F_{V,l,\text{out}} - P_l \frac{dV_l}{dt} + \dot{Q}_l - J_{E,l}. \tag{3b}$$

Assuming that the interface dynamics is much faster than the bulk phases, we can set the interconnection system in Figure 3 to be at stationary state.

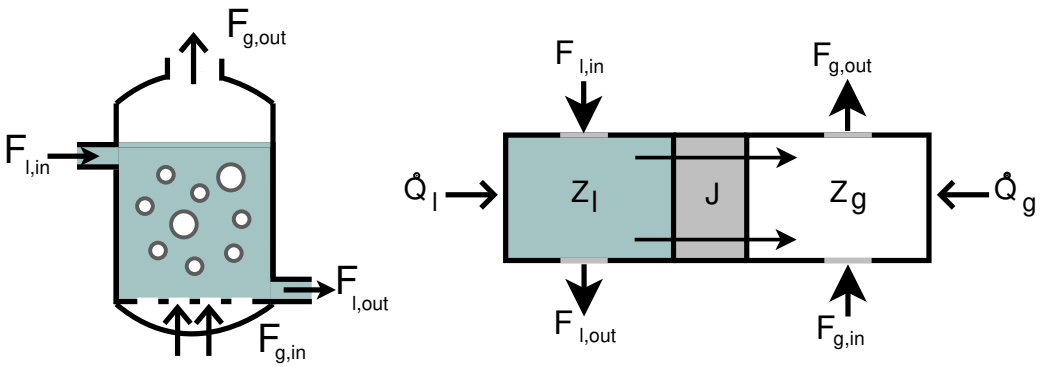

Figure 3: A liquid-gas separation system (left) and its representation as the interconnection of macroscopic thermodynamic subsystems (right).

Mass and energy balances around the interface thus lead to algebraic conditions

$$0 = J_{g,N_j} - J_{l,N_j} \qquad j = 1, \ldots, c-1 \tag{4a}$$

$$0 = J_{g,E} - J_{l,E}. \tag{4b}$$

Neglecting the effects of crossed component transport, temperature and pressure gradients, interface molar transport processes correspond to [20, 21]

$$\begin{aligned} J_{g,N_j} &= C_g k_{j,g} \left(y_{ji} - y_j\right) + J_N \, y_j \\ J_{l,N_j} &= C_l \, k_{j,l} \left(x_j - x_{ji}\right) + J_N \, x_j, \end{aligned}$$

where C_α (mol/m^3) represents the molar concentration of phase $\alpha \in \{l, g\}$, $k_{\alpha,g}$ (m^3/s) is a transport parameter, the pair (x_j, y_j) (mol/mol) represents the molar composition in the liquid and gas bulk phases, the pair (x_{ji}, y_{ji}) (mol/mol) stands for the liquid and gas molar composition in the interface[5], and $J_N = \sum_{j=1}^{c} J_{g,N_j} = \sum_{j=1}^{c} J_{l,N_j}$ (mol/s) is the total molar transport moving between phases. Neglecting the Dufour effect[6], the rate $J_{\alpha,E}$ (J/sec) at which energy flows from phase α towards/from the interface can be written

[5]Subscript i is used to refer a variable to the interface.

[6]The Dufour energy flux is caused by mass, pressure, and force field gradients [21].

as the sum of convective and thermal energy contributions [20, 21]

$$J_{g,E} = \sum_{j=1}^{c} J_{N_j,g}\,\bar{h}_{jg} + \ \lambda_{gi}(T_i - T_g)$$
$$J_{l,E} = \sum_{j=1}^{c} J_{N_j,l}\,\bar{h}_{jl} \ + \ \lambda_{li}(T_l - T_i),$$

where $\bar{h}_{j\alpha}$ (J/mol) stands as the partial molar enthalpy of component j in phase α, $\lambda_{\alpha i}$ (J/K·s) is a known thermal exchange parameter, T_α (K) represents the bulk-phase temperature, and T_i (K) stands for the interface temperature.

To complete the description of the model, we follow the ideas from Taylor and Krishna [20] and assume that the interface is locally at thermodynamic equilibrium to write

$$0 = y_{ji} - K_j(T_i, x_{i1}, \ldots, x_{ic})x_{ji}, \quad j = 1, \ldots, c \tag{5a}$$
$$0 = 1 - \textstyle\sum_{j=1}^{c} y_{ji} \tag{5b}$$
$$0 = 1 - \textstyle\sum_{j=1}^{c} x_{ji}. \tag{5c}$$

The functions $K_j(\cdot)$ in the previous equation represent the liquid-vapor composition ratio for component j. Even though the composition ratio is frequently assumed as a constant parameter, in many liquid-vapor models this term is, in general, a nonlinear function of the intensive interface variables, as it can be seen in the following example.

Example 1. Consider a liquid-vapor system at low pressure. Assume that Antoine's equation and Margules' two-parameter activity coefficient model describe the liquid vapor-ratio k_j. Then, the interface pressure, temperature and composition satisfy the following equilibrium relation

$$\begin{bmatrix} 0 \\ 0 \\ 1 \\ 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & k_1 & 0 \\ 0 & -1 & 0 & k_2 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \end{bmatrix} \begin{bmatrix} y_1 \\ y_2 \\ x_1 \\ x_2 \end{bmatrix},$$

where the liquid-vapor ratio functions correspond to

$$k_1 = \frac{1}{P}\left(A_1 - \frac{B_1}{T - C_1}\right) \exp\left[2A_{12}x_1x_2(1-x_1) + A_{21}(1-2x_1)x_2^2\right]$$
$$k_2 = \frac{1}{P}\left(A_2 - \frac{B_2}{T - C_2}\right) \exp\left[2A_{21}x_1x_2(1-x_2) + A_{12}x_1^2(1-2x_2)\right].$$

Here A_j, B_j, C_j, $j = 1, 2$, $l = 1, 2$, A_{12}, and A_{21} are known thermodynamic parameters.

3.1. DAE system

Balance equations (2)-(3) restricted by the interface equations (4)-(5) sum to $4c+4$ coupled equations that can be represented a semi-explicit DAE system of index one [22]

$$\frac{dz}{dt} = f(z, w) \tag{6a}$$
$$0 = g(z, w), \tag{6b}$$

where we call the vector z, of dimension $2c + 2$, the vector of dynamic variables:

$$z = [N_{1g} \dots N_{cg} \;\; N_{cl} \dots N_{cl} \;\; U_g \;\; U_l]^{\mathrm{t}}, \tag{7a}$$

and we call the vector of dimension $2c + 2$

$$w = [y_{1i} \dots y_{ci} \;\; x_{1i} \dots x_{ci} \;\; T_i \;\; J_N]^{\mathrm{t}}, \tag{7b}$$

the vector of algebraic variables. To complete the description of the model, in the next section we present the constitutive equations to describe the volume, pressure, temperature, conductive heat flows, and volumetric outflows for the DAE system (6).

3.2. Constitutive equations

We write the liquid volume as a function of the molar holdup [23]

$$V_l(z) = \bar{v}_1 N_{1l} + \cdots + \bar{v}_c N_{cl}, \tag{8a}$$

where $\bar{v}_j$ (m^3/mol) corresponds to the partial molar volume of component j in the liquid phase. As the vessel containing both phases is rigid, the gas volume corresponds to the volume that is not occupied by the liquid phase

$$V_g(z) = V_\Omega - V_l, \tag{8b}$$

where V_Ω (m^3) is the (constant) volume of the rigid vessel.

Temperature is a function of internal energy. The internal energy for each phase $\alpha \in \{l, g\}$ can be written as

$$U_\alpha = U_{o,\alpha} + \mathcal{C}_\alpha(T_\alpha - T_o), \tag{9}$$

where $U_{o,\alpha} = \sum \bar{u}_{o,j} N_{j\,\alpha}$ (J) represents the internal energy of the system at a reference temperature T_o, and $\mathcal{C}_\alpha = \sum N_{j\,\alpha}\, \bar{c}_{\alpha,j}$ (J/K) stands for the total heat capacity for phase α. Solving (9) for T we can write

$$T_\alpha(z) = T_o + \frac{U_\alpha - U_{o,\alpha}}{\mathcal{C}_v(z)}. \tag{10}$$

Heat flows $\dot{Q}_\alpha$ (J/s), $\alpha \in \{l, g\}$, in the energy balance equation (3) are written as being proportional to differences between the temperature $T_{\alpha,Q}$ (K) of a heat exchanger, considered a known input, and the bulk-phase temperature T_α (K)

$$\dot{Q}_\alpha(z) = \lambda_\alpha(T_{\alpha,Q} - T_\alpha), \tag{11}$$

where λ_α (J/K) is a known heat exchange parameter.

Without loss of generality, the ideal gas equation is used to write the pressure in the gas phase as a function of the extensive parameters

$$P_g(z) \;=\; R\frac{N_g}{V_g}\left(T_o + \frac{U_g - U_{o,g}}{\mathcal{C}_g}\right). \tag{12a}$$

An accurate description for the liquid pressure would require a detailed study on the hydrodynamic properties of the liquid subsystem, which is beyond the scope of this article[7]. In our study, we assume that the liquid and the interface pressures are equal to the gas pressure

$$P_l(z) = P_i = R\frac{N_g}{V_g}\left(T_o + \frac{U_g - U_{o,g}}{\mathcal{C}_g}\right). \tag{12b}$$

[7]The reader interested on a local study on how to couple hydrodynamic effects in multiphase systems is referred to [24].

To complete the constitutive equations, following the suggestion by Rouchon and Creff [14], we account for the hydraulic effects in the system by adding a stationary mechanical energy balance to the description of the system.

In a number of important cases, the mechanical equilibrium state is reached very quickly in comparison with the thermodynamic process [25]. In the context of this paper, a mechanical equilibrium assumption permits to define an additional constitutive equation that allows to recover the volumetric outflow as a function of the state and the input variables for the system. At equilibrium, the mechanical energy conservation equations for each phase in the system correspond to [21]

$$0 = F_{K,g,\text{in}} - \left(\frac{K_g}{V_g} + P_g\right) F_{V,g,\text{out}} - P_g \frac{dV_g}{dt} + J_{K,g}, \tag{13a}$$

$$0 = F_{K,l,\text{in}} - \left(\frac{K_l}{V_l} + P_l\right) F_{V,g,\text{out}} - P_l \frac{dV_l}{dt} + J_{K,g}, \tag{13b}$$

where $F_{K,\alpha,\text{in}}$ (J/sec) corresponds to the mechanical energy carried in the inflow streamlines, $K_\alpha = Mv^2/2$ (J) stands for the kinetic energy of the mass that flows through phase $\alpha \in \{l, g\}$ and

$$J_{K,\alpha} = \frac{1}{2} v_{\alpha i}^2 J_{M,\alpha} + \frac{P_\alpha}{\rho_\alpha} J_{M,\alpha}, \tag{14}$$

represents the mechanical energy that flows between the interface and the bulk phases. In Equation (14), ρ_α (kg/m^3) represents the mass density of the bulk-phase α. Setting $\bar{m}_j$ (kg/mol) to be the molar mass of component j, we write

$$J_{M,\alpha} = \sum \bar{m}_j \, J_{N,\alpha j}$$

for the mass interface transport rate. The term $v_{\alpha i}$ (m/s) in (14) represents the average velocity of the mass flowing through the boundary layers surrounding the interface. Setting A_i (m^2) as the interface area we define the interface flow velocity in the boundary layer α as

$$v_{\alpha i} = \frac{J_{M,\alpha}}{\rho_\alpha A_i}.$$

Equation (13) determines uniquely the volumetric outflow from each phase as a function the state of the system. In the following Proposition we show that the volumetric outflow is determined as the unique as a state function which corresponds to the solution to the mechanical equilibrium equation.

Proposition 1. Consider an open macroscopic system with a positive amount of mass $M > 0$ at mechanical equilibrium. As the system is at mechanical equilibrium it fulfills

$$0 = F_{K,\text{in}} - \left(\frac{K}{V} + P\right)F_{V,\text{out}} - P\frac{dV}{dt} + J_K. \tag{15}$$

In addition, assume that we can write the volumetric outflow as

$$F_{V,\text{out}} = A_{\text{out}}v,$$

where A_{out} (m^2) is the outflow streamline cross section and v is the velocity of the flow in the system. Then the volumetric outflow can be determined uniquely as a function

$$F_{V,\text{out}} = F_{V,\text{out}}(F_{K,\text{in}}, V, P, J_K).$$

Proof: To demonstrate the result, we start by writting the kinetic energy as

$$K = \frac{1}{2}Mv^2 = \frac{1}{2A_{\text{out}}^2}MF_{V,\text{out}}^2.$$

Substitution of the previous into (15) gives

$$0 = F_{K,\text{in}} - \frac{M}{2VA_{\text{out}}^2}F_{V,\text{out}}^3 - PF_{V,\text{out}} - P\frac{dV}{dt} + J_K$$

which may be rewritten as a cubic equation

$$0 = F_{V,\text{out}}^3 + pF_{V,\text{out}} + q \tag{16}$$

where

$$p = \frac{2PVA_{\text{out}}^2}{M} > 0, \quad q = \frac{2VA_{\text{out}}^2}{M}\left(P\frac{dV}{dt} - F_{K,\text{in}} - J_K\right).$$

The discriminant for the cubic equation corresponds to

$$\Delta = -4p^3 - 27q^2 < 0.$$

As the discriminant is negative, (16) has only one real root [26]. Having only one real root, the volumetric outflow is uniquely determined as a solution to (16). Therefore, at mechanical equilibrium, the outflow $F_{v,\text{out}}$ is uniquely determined as a function of parameters p and q defined in (16).

□

Remark 1. A close look to the constitutive equations that describe the triad (P, V, J_K) suffices to realize that pressure, volume, and interface kinetic transport are functions of the state of the system (6). Proposition 1 implies therefore that, at mechanical equilibrium, the volumetric outflows are uniquely defined as a function of the state in a thermodynamic multiphase system.

Being modeled as independent subsystems, liquid and vapor phases in the DAE model (2)-(5) do not necessarily have the same pressure and temperature. In addition, the molar composition of each bulk phase is not subject to satisfy a liquid-vapor equilibrium relation[8]. The liquid-vapor system depicted in Figure 2 is therefore not necessarily at thermodynamic equilibrium. Being far from equilibrium, we cannot apply Gibbs' phase rule to determine the degrees of freedom of the system as a whole. We can however, through assumption A1, apply the Gibbs' phase rule locally to each subsystem in the liquid-vapor system depicted in Figure 2.

3.3. Local Gibbs phase rule

Gibbs phase rule states that, in a thermodynamic system with c chemical components and p coexistent phases at equilibrium, it is possible to arbitrarily presassign $c - p + 2$ intensive variables from the set [5]

$$(T, P, x_{1,1}, ..., x_{c-1,1}, x_{1,p}, ..., x_{c-1,p}).$$

We call degrees of freedom the number of intensive variables that can be arbitrarily preassigned in a thermodynamic system. Note that in the previous set, $x_{j,k}$ represents the composition of component j in phase k. The intensive variables that are not arbitrarily set are defined by equilibrium relations.

If a multiphase system is far from thermodynamic equilibrium, Gibbs rule does not apply. However, considering the bulk phase (and the interface) subsystems to be locally at equilibrium, see Assumption A2, Gibbs phase rule might be applied locally to each subsystem.

The phase rule states that each bulk phase in Figure 2 has has $c + 1$ degrees of freedom. Let the degrees of freedom for the gas and liquid bulk phases be defined as vectors

$$[T_g(z)\ P_g(z)\ y_1(z)\ \ \dots\ \ y_{c-1}(z)]^{\mathrm{t}}$$

[8]Note that only the local interface compositions are bounded to satisfy (5).

and

$$[T_l(z)\ P_l(z)\ x_1(z)\ \ldots\ x_{c-1}(z)]^{\mathrm{t}}$$

respectively. Note that the intensive variables are written as functions of the state of the system. The functional relations that define the intensive variables as functions of z correspond to Equations (10) and (12). The molar fractions are defined as state functions by $x_j = N_{jl}/\sum_1^c N_{jl}$ and $y_j = N_{jg}/\sum_1^c N_{jg}$.

The phase rule applied to the interconnection subsystem in Figure 2 states that the interface has c degrees of freedom. The degrees of freedom correspond to c variables of the vector (7b) which might be arbitrarily chosen. The remaining $c+2$ variables in (7b) are given by the solution to the equilibrium equation (5).

We conclude from locally using Gibbs phase rule that, if

1. We assume that the solution to (6) is unique and

2. We set the inputs (as fixed values or using control laws),

integrating (6) to establish state trajectories $z(t)$ is equivalent to fix the degrees of freedom for the system.

4. Linear analysis

In this section we show that the model (6) has an unstable steady state. Let $(z^\star, w^\star)$ represent a steady state of (6). The linearization $f_L(\cdot)$ of the right hand side of (6a) around the steady state corresponds to

$$f_L(z,w) = \left.\frac{\partial f}{\partial z}\right|_{(z^\star,w^\star)} (z - z^\star) + \left.\frac{\partial f}{\partial w}\right|_{(z^\star,w^\star)} (w - w^\star), \tag{17}$$

where the partial derivatives represent the Jacobian matrices of f with respect to z and w respectively. Similarly, linearizing (6b) at the steady state gives

$$0 = \left.\frac{\partial g}{\partial z}\right|_{(z^\star,w^\star)} (z - z^\star) + \left.\frac{\partial g}{\partial w}\right|_{(z^\star,w^\star)} (w - w^\star), \tag{18}$$

where the Jacobian matrices of g with respect to z and w are represented using the partial derivatives. As the DAE system (6) is of index one, the

Jacobian $\partial g/\partial w|_{(z^\star,w^\star)}$ is non-singular [22]. Therefore we can solve (18) for $(w - w^\star)$ to obtain

$$(w - w^\star) = -\left(\left.\frac{\partial g}{\partial w}\right|_{(z^\star,w^\star)}\right)^{-1}\left.\frac{\partial g}{\partial z}\right|_{(z^\star,w^\star)}(z - z^\star). \tag{19}$$

Substitution of (19) into (17) allows to write a linearized version of the DAE system (6) as

$$\frac{dz}{dt} = \Theta(z - z^\star) \tag{20}$$

where

$$\Theta = \left(\left.\frac{\partial f}{\partial z}\right|_{(z^\star,w^\star)} - \left.\frac{\partial f}{\partial w}\right|_{(z^\star,w^\star)}\left(\left.\frac{\partial g}{\partial w}\right|_{(z^\star,w^\star)}\right)^{-1}\left.\frac{\partial g}{\partial z}\right|_{(z^\star,w^\star)}\right),$$

stands for the matrix of the linearized dynamics.

4.1. Numerical open loop analysis

To study the stability properties of the model, we consider a liquid-vapor two component mixture. Methanol and water are considered as components 1 and 2 in the mixture, respectively. The inputs for the model are assumed to be fixed at thermodynamic equilibrium conditions described in Table 1. The parameters used for the simulation are reported in Appendix C. For the sake of simplicity we fix the inflow streamline velocities at 1 m/s for each phase. To linearize the system, the inflow conditions fixed at the values established in Table 1. Fixing the inflow conditions to the values reported in Table 1 and the initial volumes for each phase as $V_g(0) = 0.9\text{m}^3$ and $V_g(0) = 0.1\text{m}^3$, the system reaches the steady state reported in Table 2.

Remark 2. At steady state, see Table 2, the system reaches thermodynamic equilibrium. The equilibrium steady state follows as a consequence from the inflows being at thermodynamic equilibrium. When the inflows are far from equilibrium it can be easily shown that there exists a stationary state that is far from thermodynamic equilibrium. We restrict our study to equilibrium steady states. The possibility of studying the dynamic properties of systems where the steady state is far from thermodynamic equilibrium is outlined as a line for future work in the conclusions for the article.

Property	Value	Inflow	Value
$y_{1,\text{in}}$	0.6615 mol/mol	$F_{N_1,g,\text{in}}$	22.9473 mol/s
$x_{1,\text{in}}$	0.2764 mol/mol	$F_{N_2,g,\text{in}}$	11.7401 mol/s
$T_{l,\text{in}}$	351.24 K	$F_{N_1,l,\text{in}}$	1.1419×10^4 mol/s
$T_{g,\text{in}}$	351.24 K	$F_{N_2,l,\text{in}}$	2.9891×10^4 mol/s
$T_{l,Q}$	351.24 K	$F_{H,g,\text{in}}$	1.4005×10^6 J/s
$T_{g,Q}$	351.24 K	$F_{H,l,\text{in}}$	1.8461×10^8 J/s
$P_{l,\text{in}}$	1.013 kPa	$F_{K,g,\text{in}}$	1.0130×10^5 J/s
$P_{g,\text{in}}$	1.013 kPa	$F_{K,l,\text{in}}$	1.0175×10^5 J/s

Table 1: Inflow conditions.

Bulk phase variable	Value	Interface variable	Value
$N^\star_{1,g}$	20.6525 mol	$y^\star_{1i}$	0.6615
$N^\star_{2,g}$	10.5661 mol	$y^\star_{2i}$	0.3385
$N^\star_{1,l}$	1.1419×10^3 mol	$x^\star_{1i}$	0.2764
$N^\star_{2,l}$	2.9891×10^3 mol	$x^\star_{2i}$	0.7236
$U^\star_g$	1.1693×10^6 J	$T^\star_i$	351.24 K
$U^\star_l$	1.8451×10^7 J	$J^\star_N$	0 mol/s

Table 2: Steady State.

λ_1	0.0306
λ_2	-10.0036
λ_3	-10.0003
λ_4	-1.2697
λ_5	-1.1774
λ_6	-2.5×10^{-10}

Table 3: Eigenvalues for the linearized model.

At the steady state reported in Table 2, the matrix Θ for the linearized model (20) has rank 5 and one unstable eigenvalue[9], see Table 3. The unstable properties for the steady state can be better appreciated in state trajectories obtained from numerical simulations. In Figure 4 we present the state

[9]The eigenvalues are computed using Matlab 9.4-R2018a.

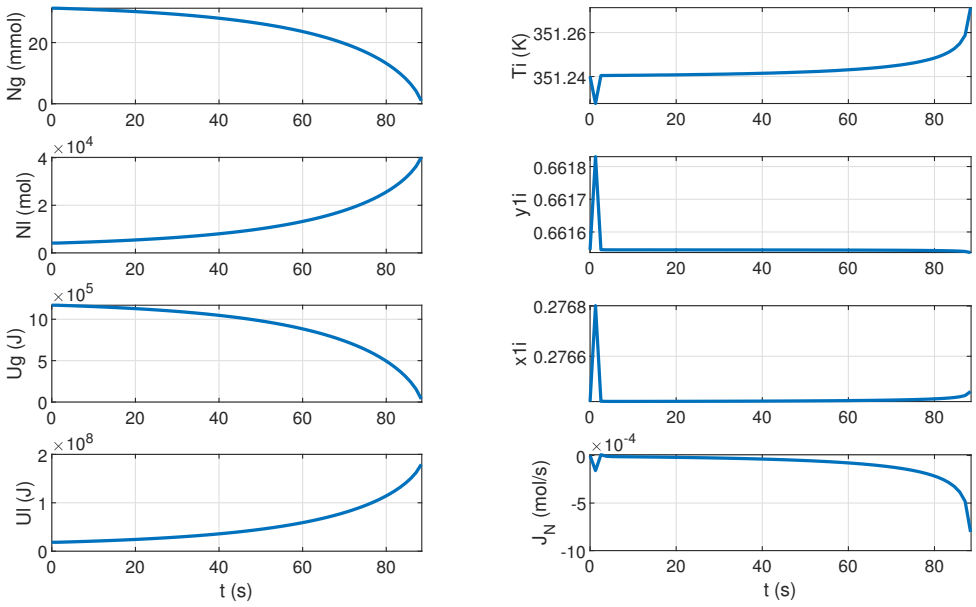

Figure 4: Unstable molar and energy holdup trajectories (left). Unstable interface temperature, composition, and molar transport (right). Simulation started at the stationary state presented in Table 2 and disturbed by the ramp function in Equation (21)

trajectories for a simulation where the inflow streamline is briefly pushed far from equilibrium. To simulate such scenario the liquid composition of methanol in the inflow is disturbed by a ramp

$$x_{1,\text{in}} = \begin{cases} 0.2764 + 2.764 \times 10^{-3}(t-1) & \text{for } t \in [1, 1.5] \\ 0.2764 & \text{for } t \notin [1, 1.5] \end{cases} \tag{21}$$

The instability of the steady state causes the system trajectories to drift, even after the disturbance has been removed, as it is depicted in Figure 4. In Figure 4 it is clear that the gas phase collapses at $t \approx 88.7$s.

5. Pressure controller

Using thermodynamic dissipativity theory, multiphase open thermodynamic systems at constant pressure have been shown to be stable when the pressure of the process is fixed [14]. Numerical evidence shows that open

irreversible multiphase systems are stabilized when pressure is kept constant [18]. Following these ideas, we propose a control structure that fixes the pressure of the system.

Theorem 1. Assume that the inputs and the state of the liquid-vapor system represented by (6) can be measured. Assume that the concentration C_g of the gas phase is constant. Let $\gamma(\cdot)$ stand for a function

$$\begin{aligned}\gamma = &\left(\frac{P^\star}{RC_g} - T_o\right)\sum_{j=1}^{c}\bar{c}_{g,j}\left(F_{N_j,g,\text{in}} - \frac{N_{jg}}{V_g}F_{V,g,\text{out}} + J_{N_j,g}\right)\\ &- F_{H,g,\text{in}} + F_{H,g,\text{out}} + \sum_{j=1}^{c}P_g\bar{v}_j\left(F_{N_j,l,\text{in}} - \frac{N_{jl}}{V_l}F_{V,l,\text{out}} - J_{N_j,l}\right)\\ &- J_{g,E}\end{aligned} \tag{22}$$

where $P^\star$ (K) represents a constant pressure set-point and $F_{\beta,\alpha,\text{out}}$ stands for the convective outflow of property β in phase α[10]. Consider that there is a heat exchanger in the gas phase and let the temperature of the heat exchanger be defined as

$$T_{g,Q} := \frac{\gamma}{\lambda_g} + \left(T_o + \frac{U_g - U_{o,g}}{\mathcal{C}_g}\right). \tag{23}$$

Then the pressure of the liquid-vapor (6) is fixed at $P = P^\star$.

Proof: First note that, using the temperature constitutive relation (10), Equation (23) can be rewritten as

$$\lambda_g(T_{g,Q} - T_g) = \gamma.$$

Thus

$$\begin{aligned}\dot{Q}_g = &\left(\frac{P^\star}{RC_g} - T_o\right)\sum_{j=1}^{c}\bar{c}_{g,j}(F_{N_j,g,\text{in}} - \frac{N_{jg}}{V_g}F_{V,g,\text{out}} + J_{N_j,g})\\ &- F_{H,g,\text{in}} + F_{H,g,\text{out}} + \sum_{j=1}^{c}P_g\bar{v}_j(F_{N_j,l,\text{in}} - \frac{N_{jl}}{V_l}F_{V,l,\text{out}} - J_{N_j,l})\\ &- J_{g,E}.\end{aligned}$$

[10]The remaining variables are defined in Section 3.

After algebraic simplification, substitution of the previous in the energy balance (3) for the gas phase

$$\begin{aligned}\frac{dU_g}{dt} &= \left(\frac{P^\star}{RC_g} - T_o\right)\sum_{j=1}^{c}\bar{c}_{g,j}(F_{N_j,g,\text{in}} - \frac{N_{jg}}{V_g}F_{V,g,\text{out}} + J_{N_j,g}) \\ &= \left(\frac{P^\star}{RC_g} - T_o\right)\sum_{j=1}^{c}\bar{c}_{g,j}\frac{dN_{jg}}{dt}. \end{aligned} \tag{24}$$

Integration of (24) allows us to write

$$U_g = \left(\frac{P^\star}{RC_g} - T_o\right)\sum_{j=1}^{c}\bar{c}_{g,j}N_{jg} + U_{o,g},$$

where the integration constant $U_{o,g}$ corresponds to the internal energy of the gas phase at temperature T_o. To demonstrate the theorem, note that we can rearrange the previous equation to show that the pressure of the gas phase is fixed at the desired set-point

$$P^\star = RC_g\left(T_o + \frac{U_g - U_{o,g}}{\sum_{j=1}^{c}\bar{c}_{g,j}N_{jg}}\right) = RC_gT_g = P_g. \tag{25}$$

□

Linearizing the closed loop system, following the procedure established in Section 4, we conclude that the pressure controller stabilizes the system. The eigenvalues for the closed loop system are presented in Table 4.

λ_1	-10.0036
λ_2	-10.0003
λ_3	-1.1954
λ_4	-1.1111
λ_5	-1.1415×10^{-3}
λ_6	-2.5×10^{-10}

Table 4: Eigenvalues for the closed loop linearized model.

6. Concluding remarks

In this paper, we have shown that macroscopic-based descriptions allow to address the modelling and control aspects of irreversible multiphase systems.

Using a local stability analysis, we concluded that the obtained model, see Equations (2)-(5), predicts the existence of unstable modes for a thermodynamic equilibrium steady state. Finally, we demonstrated that it is possible to stabilize the model through a pressure feedback control structure. The introduction of mechanical effects in the description of the system, Equation (13), allows to describe the volumetric outflow as a function that depends on the state variables. We have shown that the volumetric outflow is uniquely described as a function of the state. In addition, it has been discussed on how establishing an initial condition and fixing the inputs of the dynamic model is equivalent to fix the degrees of freedom of the system. The modeling methodology here presented is focused on describing on a liquid-gas system. Note however, that it can easily be extended other class of fluid multiphase systems by changing interface description presented in Equations (4)-(5).

In this paper we have explored the stability properties of a steady state, see Table 2, in irreversible multiphase system. Nevertheless the authors believe that, as a consequence of the nonlinearities introduced in the local equilibrium relation (5), there exists the possibility for multiple stationary states to occur. Exploring the relations between the thermodynamic equilibrium model and the steady state multiplicity represents a fruitful line for future research. The steady state presented in Table 2 corresponds to a thermodynamic equilibrium state. When the inflows are not at thermodynamic equilibrium there exists a stationary state which is far from equilibrium. It should be remarked that the dynamic properties of such steady state are not known at the present time and should be explored in the immediate future.

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Appendix A. Ideal gas at equilibrium

All the physical properties of an ideal gas at equilibrium can be written as functions of the thermodynamic coordinate (P, T, V), temperature T (K), pressure P (Pa), and chemical potential μ (J/mol). For an ideal gas with one chemical component at thermodynamic equilibrium, concentration and chemical potential are given by

$$C = P/TR \tag{A.1a}$$

$$\mu = -Ts_o + RT(c_p^\star) - RT \ln\left(\left(\frac{P_o}{P}\right)\left(\frac{T}{T_o}\right)^{c_p^\star}\right) \tag{A.1b}$$

where C (mol/m^3) is the concentration of the gas, s_o (J/mol·K) is the entropy computed at a reference state (P_o, T_o), and $c_p^\star = c_p/R$ is the dimensionless isobaric heat capacity of the gas. The extensive variables (N, H) for an ideal gas can be determined as

$$N = V/C \tag{A.2a}$$

$$H = Nh_o + c_p(T - T_o) \tag{A.2b}$$

where N (mol) stands for the molar holdup of the system, H (J) represents the enthalpy, and h_o is the molar enthalpy at the reference temperature T_o.

Appendix B. Local Equilibrium

A macroscopic system can be understood as the interconnection between individual cell-subsystems. Each cell being big enough to be considered as a macroscopic system by itself, but small enough to be at thermodynamic equilibrium. A system where such partition exists is said to be locally at thermodynamic equilibrium. The local equilibrium assumption restricts systems to operate through processes whose evolution can be completely described without any explicit introduction of molecular effects [27].

Let $\tilde{\phi}$ represent the density per unit of volume of a property ϕ in a macroscopic system. Let $\Delta\phi = \lambda|\nabla\phi|$ represent a spatial variation of the property over a distance λ caused by a gradient $\nabla\phi$. The system is locally at thermodynamic equilibrium if there extist a characteristic length λ such that $\Delta\phi/\phi \ll 1$, where $\phi := \tilde{\phi}\lambda^3$ represents the property measured in a cell of length λ [19]. In addition, a time varying process is said to be locally at thermodynamic equilibrium if exists an intrinsic relaxation time scale τ for the system such that macroscopic fluctuations vanish within cells much faster than the overall time evolution of the system τ_{ev}, that is $\tau \ll \tau_{ev}$ [19].

Appendix C. Parameters

$k_{1,g}$	8×10^{-2} m/s
$k_{1,l}$	2×10^{-4} m/s

Table C.5: Mass transport parameters taken from [20]

λ_{gi}	100 J/s·K
λ_{li}	500 J/s·K
$\lambda_g^{\star}$	0 J/s·K
$\lambda_g^{\star\star}$	0 J/s·K
λ_l	600 J/s·K

Table C.6: Energy transport parameters adjusted from [8]

* Parameter for open loop simulation.

** Parameter for closed loop simulation.

A_1	23.402 Pa
A_2	23.196 Pa
B_1	3593 K·Pa
B_2	3816 K·Pa
C_1	-34.29 K
C_2	-46.13 K
A_{12}	0.4648
A_{21}	0.8517

Table C.7: Thermodynamic equilibrium parameters taken from [20]

Total volume	V_Ω	1 m^3
Interface area	A_i	1 m^2
Outflow cross section area	A_{out}	1 m^2

Table C.8: Geometric parameters