On the Positivity of Entropy Production in Multiphase Thermodynamic Systems

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Abstract: Multiphase processes are frequently assumed to evolve restricted by thermodynamic equilibrium relations. In this article, we study the possibility of multiphase systems to evolve far from thermodynamic equilibrium while contained in what we call a domain of physical feasibility. We show that processes evolving in the domain of feasibility have a positive definite internal entropy production rate. Being positive definite, the internal entropy production stands as a Lyapunov function candidate to characterize the stability of equilibrium for irreversible multiphase systems contained in the feasibility domain. In addition, the thermodynamic-based approach considered in our study provides phenomenological insight into the dynamic properties of multiphase systems. Counter-flow interface molar transport processes, for instance, are found to be thermodynamically stable provided that the transport is bounded by a function that depends on the deviation from thermodynamic equilibrium.

Keywords: Non-equilibrium thermodynamics, Irreversible thermodynamics, Multiphase systems, Flash-drum, Lyapunov stability, Internal entropy production

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1. INTRODUCTION

Design, analysis, and operation of thermodynamic systems stand as fundamental aspects of process systems engineering. In this paper, we investigate the possibility of characterizing irreversible multiphase processes using physics-based criteria. Multiphase systems are frequently assumed as reversible quasistationary processes–an idealization that presupposes that the state-space of the system is contained inside a manifold defined by thermodynamic equilibrium relations (Ydstie, 2016). In our research, we suggest the possibility of multiphase systems to operate far from the equilibrium manifold. Using the second law of thermodynamics, we provide conditions for thermodynamic stability in multiphase systems far from equilibrium.

Multiphase systems are widespread in process engineering. Bio-engineering liquid-gas-solid operations (Cabral et al., 2001), crystal growth processes in organic powder manufacturing (Paul et al., 2005), and complex membrane distillation separations (Alkhudhiri et al., 2012) are some examples worth mentioning. Nonlinear complex behavior has been reported to occur in multiphase systems: chaos, steady state multiplicity, and limit cycles are well documented in the literature (Decroly and Goldbeter, 1982; Field and Noyes, 1974; Skogestad, 1997). We strongly believe that the establishment of physics-based analysis techniques should help to attain a phenomenological explanation of the sources of complex phenomena. In turn, a better understanding of the dynamical properties of thermodynamic systems would lead to improved methods for design and operation of chemical processes.

Physics-based formulations have been proved useful to characterize the dynamic properties of process systems. Energy, for instance, has served to establish the stability properties of physical systems in dissipative analysis (Willems, 1972). With clear applications to electromechanical systems, the early applications of dissipative analysis to chemical processes were unfortunately limited. It is in not until the late 1990s, after being introduced by Alonso and Ydstie (1996), that chemical systems dissipative theory received an increasing level of attention.

Thermodynamic potentials have well-defined convexity properties. Entropy, for instance, is a concave function of the extensive variables in simple thermodynamic systems [1] (Callen, 1985) (Figure 1, left). The convexity of entropy has allowed to assess the stability and the control properties of chemical systems (Antelo et al., 2007; Favache and Dochain, 2009; García-Sandoval et al., 2015; Hoang and Dochain, 2013). In irreversible multiphase systems however, thermodynamic potentials are no longer globally convex (Callen, 1985) (Figure 1, right). To characterize a multiphase system regardless of its convexity properties, in this paper we propose to study the dynamic properties of the system using an entropy production-based approach.

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[1] A closed single-phase system with no electromagnetic charge is known as a simple thermodynamic system (Callen, 1985).

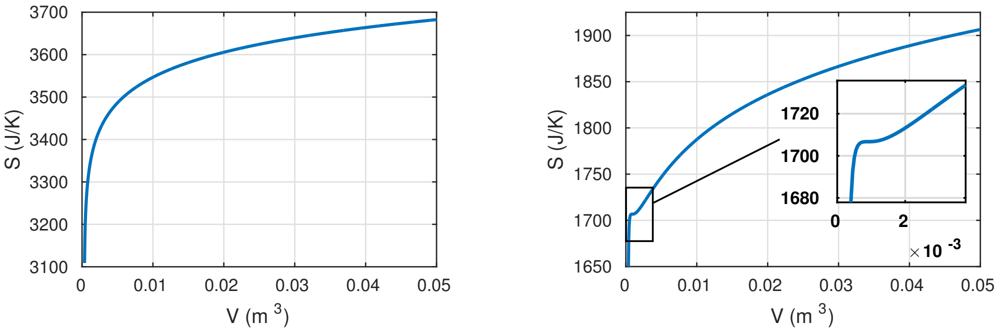

Fig. 1. Van der Waals entropy-volume graph for vapor (left) and liquid-gas (right) water in a closed system.

The linear stability properties of multiphase irreversible systems were previously characterized by Romo-Hernandez et al. (2019). As an attempt to extend the stability results using nonlinear stability theory, in this article we provide conditions for the positivity of internal entropy production in multiphase systems. Being positive definite, the internal entropy production is a Lyapunov function candidate for equilibrium in multiphase systems.

The article is structured as follows. In Section 2, we write the internal entropy production equation for multiphase systems. In Section 3, we define a Lyapunov function in the context of multiphase process systems. In Sections 4 and 5 we show that that internal entropy production is semipositive definite when restricted to what we call a domain of physical feasibility. Conclusions are presented in Section 6.

2. INTERNAL ENTROPY PRODUCTION

Internal flows of mass and energy occur in thermodynamic systems that operate far from thermodynamic equilibrium (Prigogine, 1968). Let the pairs (J_{nj}, J_e) and (X_{nj}, X_e) represent molar and energy interface flows and their respective driving forces. The rate of internal entropy production inside a multiphase corresponds to

$$\Sigma_\imath = \sum_{\jmath=1}^{c} J_{nj}\, X_{nj} + J_e\, X_e, \tag{1}$$

where c represents the number of volatile chemical components in the system.

The driving forces behind interface flows in Equation (1) are written as

$$X_e = \frac{1}{T_g} - \frac{1}{T_l}, \quad X_{nj} = \frac{-\mu_{gj}}{T_g} - \frac{-\mu_{lj}}{T_l}, \; j = 1, \dots, c. \tag{2}$$

Assuming that neither mass nor energy accumulate between phases, we write interface flow rates as [2]

$$J_{nj} := \beta_{\alpha j}\, \delta x_{\alpha j} + x_{\alpha j} J_n, \;\; j = 1, \dots, c, \quad \alpha \in \{g, l\} \tag{3a}$$

$$J_e := \sum_{j=1}^{c} J_{nj}\, \bar{h}_{\alpha j} + \lambda_{\alpha i} \delta T_\alpha, \qquad \alpha \in \{g, l\}, \tag{3b}$$

where $J_n = \sum_{j=1}^{c} J_{nj}$ corresponds to the total interface molar transport, $\beta_{\alpha j} = \beta(C_\alpha) \geq 0$ depends on the concentration of phase α, $\bar{h}_{\alpha j}$ stands for the partial molar enthalpy for component j, and $\lambda_{\alpha i}$ corresponds to a heat exchange parameter.

The molar fraction of component j in Equation (3) is

$$x_{\alpha j} := \begin{cases} y_j, & j = 1, \dots, c, \quad \text{when } \alpha = g \\ x_j, & j = 1, \dots, c, \quad \text{when } \alpha = l. \end{cases}$$

The term $\delta x_{\alpha j}$ in Equation (3) stands for composition discontinuities between the bulk-phase and the interface

$$\delta x_{\alpha j} = \begin{cases} \delta y_j := y_{ij} - y_j, & j = 1, \dots, c, \quad \alpha = g \\ \delta x_j := x_j - x_{ij}, & j = 1, \dots, c, \quad \alpha = l. \end{cases} \tag{4a}$$

Similarly, temperature discontinuities are represented as

$$\delta T_\alpha = \begin{cases} T_i - T_g, & \text{when } \alpha = g \\ T_l - T_i, & \text{when } \alpha = l. \end{cases} \tag{4b}$$

Starting from transport equations (3), we can write stationary-mass/energy balances for the interface as:

$$\beta_{lj}\, \delta x_j + x_j J_n = \beta_{gj}\, \delta y_j + y_j J_n, \;\; j = 1, \dots, c \tag{5a}$$

$$\sum_{\jmath=1}^{c} J_{n,j} \bar{h}_{lj} + \lambda_{li}\, \delta T_l = \sum_{\jmath=1}^{c} J_{n,j} \bar{h}_{gj} + \lambda_{gi}\, \delta T_g. \tag{5b}$$

Solving the mass balance (5a) for J_n, we can describe the total molar transport as a function of the $\delta-$terms

$$J_n = \frac{\beta_{lj} \delta x_j - \beta_{gj} \delta y_j}{\Delta x_j}, \tag{6}$$

where the denominator corresponds to $\Delta x_j := y_j - x_j$.

As illustrated in the following example, the direction of interface transport processes is defined by the signs and magnitudes of the jump discontinuities (4a)-(4b).

Example 1: Interface transport in multiphase systems.

Assume that that there is at least one component in a multiphase system which composition satisfies

$$\Delta x_j \geq 0 \tag{7a}$$

$$y_{ij} - y_j = \delta y_j \geq 0 \tag{7b}$$

$$x_j > x_j - \delta y_j \beta_{gj} / \beta_{lj} \geq x_{ji}. \tag{7c}$$

It follows that

$$J_n = \big(\beta_{lj} \delta x_j - \beta_{gj} \delta y_j\big) / \Delta x_j \geq 0, \tag{7d}$$

and thus $J_{nj} = \beta_{\alpha j}\, \delta x_{\alpha j} + x_{\alpha j} J_n \geq 0$. Therefore, if the molar profile of a component j in an lg-system is described as (7), we can conclude that component j moves from the $l-$phase to the $g-$phase. A graphic representation of the non-equilibrium profile is depicted in Figure 2. △

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[2] In the reminder of this paper, we use a subscript $\alpha \in \{g, l\}$ or subscript i to refer a variable to a bulk-phase or to the interface inside a multiphase system, respectively.

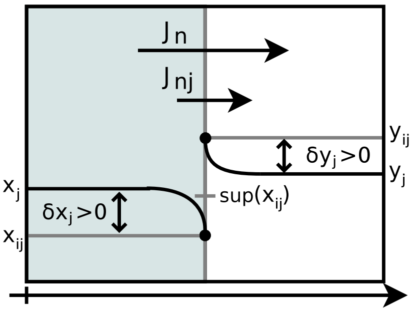

Fig. 2. Liquid-gas j-composition profile in Example 1.

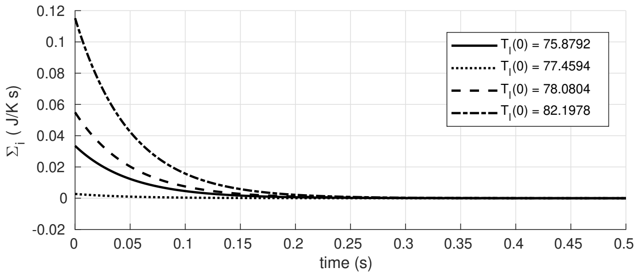

Fig. 3. $\Sigma_\imath$−trajectories for a multiphase system starting far from thermodynamic equilibrium, $T_{\text{eq}} = 78.09°C$. Image from (Romo-Hernandez et al., 2019).

Numerical evidence shows that internal entropy production is semipositive definite and decreases in time in multiphase systems (Romo-Hernandez et al., 2019), see Figure 3. This exhibits evidence that $\Sigma_\imath$ can be considered as a Lyapunov function candidate to characterize the stability of multiphase systems.

3. ENTROPY PRODUCTION AS A LYAPUNOV FUNCTION CANDIDATE

In this section, we establish the properties required for Equation (1) to be a Lyapunov function to characterize the stability of multiphase thermodynamic systems. First, we recall the definition of a Lyapunov function as presented in (Hirsch et al., 2004).

Definition 1. (Lyapunov function). Let f be a continuously differentiable function $f : U \to \mathbb{R}^n$, for some neighborhood U around the initial condition $\zeta_o \in \mathbb{R}^n$. Consider the ODE

$$\frac{d\zeta}{dt} = f(\zeta), \quad \zeta(0) = \zeta_o. \tag{8}$$

Let ζ_{ss} stand for a steady state of (8). Assume that there exists a real valued continuously differentiable function Σ defined in a neighborhood $V \subset U$ around ζ_{ss}. We call Σ a Lyapunov function for the state ζ_{ss} if:

1. The function Σ is equal to zero at ζ_{ss}.
2. The derivative of Σ is semi-negative definite in V, *i.e.*,
$$\frac{d\Sigma}{dt} \leq 0 \quad \forall \zeta \in V.$$

The following is a well-established result whose proof can be consulted in (Hirsch et al., 2004, §9.2):

Theorem 1. If Σ is a Lyapunov function for the steady state ζ_{ss} of (8), then ζ_{ss} is stable.

The thermodynamic equilibrium state $\zeta^\star$ is a stationary state for irreversible multiphase processes (Romo-Hernandez et al., 2019). To demonstrate that the internal entropy production $\Sigma_\imath$ is a Lyapunov function for equilibrium in multiphase systems, we have to show $\Sigma_\imath$ satisfies the properties established in Definition 1.

We dedicate the remaining sections to show conditions such that $\Sigma_\imath \geq 0$. Being positive definite, the internal entropy production is a Lyapunov function candidate for equilibrium. The seminegativity of the time derivative of $\Sigma_\imath$ is not explored in this note; we outline this as an area for future research in our concluding remarks.

4. ENTROPY PRODUCTION AT EQUILIBRIUM

In this section, we show that $\Sigma_\imath$ is zero for multiphase systems that operate at thermodynamic equilibrium.

Definition 2. A superscript $\star$ is used to define the thermodynamic equilibrium value of a variable[3]. We denote thermodynamic equilibrium as a state $\zeta^\star$ where pressure P, temperature T, and chemical potentials μ_j are homogeneous in space (Callen, 1985).

Definition 2 implies that (P, T, μ_j) at equilibrium satisfy: $P^\star = P_l = P_g$, $T^\star = T_l = T_g$, $\mu_j^\star = \mu_{gj} = \mu_{lj}$, $j = 1, \ldots, c$. Chemical potentials $\mu_{\alpha j}$, $\alpha \in \{g, l\}$, can be written as a function of $(T_\alpha, P_\alpha, x_{\alpha,j})$ (Smith et al., 2005). Therefore the intensive variables for a two phase system at thermodynamic equilibrium are given as the solution of

$$0 = \mu_j^\star - \mu_{gj}(P, T, y_1, \ldots, y_c), \qquad j = 1, \ldots, c \tag{9a}$$

$$0 = \mu_j^\star - \mu_{lj}(P, T, x_1, \ldots, x_c), \qquad j = 1, \ldots, c \tag{9b}$$

where the molar compositions are restricted by

$$1 = \sum_{j=1}^{c} x_j = \sum_{j=1}^{c} y_j. \tag{9c}$$

System (9) represents a nonlinear algebraic system with $2c + 2$ variables and $2c + 2$ equations. Assuming that solutions of (9) are unique, it follows that the interface conditions in a two phase system at thermodynamic equilibrium satisfy

$$P_i = P^\star, \; T_i = T^\star, \; x_j^\star = x_{ij}, \; y_j^\star = y_{ij}, \; j = 1, \ldots, c. \tag{10}$$

We refer to (10) as a spatial homogeneity condition. It can be easily shown through spatial homogeneity that interface flows and forces are zero in multiphase systems at equilibrium.

Lemma 2. Let $\zeta^\star$ stand for the thermodynamic equilibrium state for a multiphase non-azeotropic system[4]. Then

$$J_e(\zeta^\star) = 0, \; X_e(\zeta^\star) = 0, \; \text{ and } J_{nj}(\zeta^\star) = 0 \; X_{nj}(\zeta^\star) = 0,$$

for every component j.

Proof. It follows from the spatial homogeneity (10) that

$$X_e(\zeta^\star) = X_e\big|_{(T_g = T_l)} = 0,$$

$$X_{nj}(\zeta^\star) = X_{nj}\big|_{(T_g = T_l,\, \mu_{gj} = \mu_{lj})} = 0.$$

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[3] The thermodynamic equilibrium state must not be confused with the steady state of a dynamical system. A dynamical system can be at a steady state while being far from thermodynamic equilibrium, *e.g.* (Prigogine, 1968, §6).

[4] For a non-azeotropic system $\Delta x_j := y_j - x_j \neq 0 \; \forall j$.

and thus

$$\delta x_{\alpha j}(\zeta^\star) = \delta x_{\alpha j}\big|_{(x_j=x_{ij},\; y_j=y_{ij})} = 0, \quad \alpha \in \{g,l\} \tag{11a}$$

$$\delta T_{\alpha}(\zeta^\star) = \delta T_{\alpha}\big|_{(T_g=T_i=T_l)} = 0, \qquad \alpha \in \{g,l\}. \tag{11b}$$

As the system is non-azeotropic J_n is well defined. Then it follows from (11) that

$$J_n(\zeta^\star) = \left.\frac{\beta_{lj}\delta x_j - \beta_{gj}\delta y_j}{\Delta x_j}\right|_{\zeta^\star} \overset{(11a)}{=} 0,$$

and therefore

$$J_{nj}(\zeta^\star) = (\beta_{\alpha j}\,\delta x_{\alpha j} + J_n x_{\alpha j})|_{\zeta^\star} \overset{(11a)}{=} 0, \ \forall j. \tag{12}$$

Thus, from (11b) and (12), we get

$$J_e(\zeta^\star) = \left.\left(\sum_{j=1}^{c} J_{nj}\bar{h}_{\alpha j} + \lambda_{\alpha i}\,\delta T_{\alpha}\right)\right|_{\zeta^\star} = 0.$$

□

Corollary 3. For a non-azeotropic system, internal entropy production is zero at thermodynamic equilibrium.

5. POSITIVITY OF ENTROPY PRODUCTION

The aim now is to show the existence of a set Θ such that

$$\Sigma_\imath(\zeta) > 0, \ \forall \zeta \in \Theta. \tag{13}$$

The domain Θ represents a subset of the state-space of irreversible multiphase systems where internal transport processes occur without breaking the second law.

5.1 Alternative flows and forces

The first step towards establishing the existence of Θ is to rewrite the entropy production using alternative flows and forces. Setting $\alpha = l$ in (3b) allows to rewrite (1) as:

$$\Sigma_\imath = \sum_{j=1}^{c} J_{nj}\left(X_{nj} + \bar{h}_{lj}\,X_e\right) + \lambda_{li}\,\delta T_l\,X_e, \tag{14}$$

where $\lambda_{li} > 0$ represents a heat transport parameter. For the next step, we need to write[5]

$$\begin{aligned} X_{nj} + \bar{h}_{lj}\,X_e &= -\frac{1}{T_l}(\mu_{gj} - \mu_{lj})\big|_{T_l}. \qquad (15)\\ &= \left(\frac{-\mu^p_{gj}}{T_l} - R\ln y_j\right) - \left(\frac{-\mu^p_{lj}}{T_l} - R\ln(x_j\gamma_j)\right)\\ &= -R\ln\left(\frac{y_j}{x_j\gamma_j}\right) + \frac{1}{T_l}(\mu^p_{lj} - \mu^p_{gj}), \end{aligned}$$

where $\gamma_j = \gamma_j(P_l, T_l, x_1, \ldots, x_c)$ stands for an activity coefficient and superscript p is used to represent the pure component chemical potential of j. Setting $\mu^p_{gj} := \mu^{ig}_{gj}$, we can take advantage of the definition of chemical fugacity (Smith et al., 2005) to write

$$\frac{f_{lj}}{P_l} := \exp\left(\frac{\mu^p_{lj} - \mu^{ig}_{gj}}{RT_l}\right) = \exp\left(\frac{\mu^p_{lj} - \mu^p_{gj}}{RT_l}\right),$$

and thus

$$X_{nj} + \bar{h}_{lj}\,X_e = -R\ln\left(\frac{y_j}{x_j\gamma_j}\right) + R\ln\left(\frac{f_{lj}}{P_l}\right).$$

At low pressures, liquid fugacity can be approximated as the saturation pressure $f_{lj} = P^{\mathrm{sat}}_j(T_l)$, which leads to

$$X_{nj} + \bar{h}_{lj}\,X_e = -R\ln\left(\frac{y_j}{K_{lj}x_j}\right), \tag{16}$$

where

$$K_{lj}(T_l, P_l, x_1, \ldots, x_c) = \gamma_j P^{\mathrm{sat}}_j / P|_{(T_l, P_l, x_1, \ldots, x_c)}$$

is the liquid vapor equilibrium ratio evaluated at the $l-$bulk phase conditions.

Substitution of (16) into (14) allows to rewrite the internal entropy production using alternative flows and forces as

$$\Sigma_\imath = J_Q\,X_Q + \sum_{j=1}^{c} J'_{nj}\,X'_{nj}. \tag{17}$$

where

$$X_Q = T_l - T_g, \quad J_Q = \lambda_{li}\,\frac{\delta T_l}{T_g T_l}.$$

and

$$J'_{nj} = RJ_{nj}, \quad X'_{nj} = \ln\left(\frac{y^\star_j}{y_j}\right).$$

In the previous equation, $y^\star_j$ stands for the gas equilibrium composition:

$$y^\star_j = K_{lj}\,x_j,$$

Assuming that interface transport processes are independent from each other, Θ can be defined as:

$$\Theta := \left\{\zeta \middle| J_Q X_Q > 0,\ J'_{nj}X'_{nj} > 0,\ j = 1, \ldots, c.\right\}. \tag{18}$$

To show that Θ exists, we need to derive conditions such that Equation (17), is positive definite term by term. We dedicate Sections 5.2 to 5.3 to find such conditions.

5.2 Positivity of heat flow entropy production

Proposition 4. Assume that $f_1 = \delta T_l \cdot \delta T_g \geq 0$, then entropy production due to heat flow is semipositive definite.

Proof. Note that, as $\delta T_l \cdot \delta T_g \geq 0$, temperature profiles change monotonically in the direction of the phase change. Considering the case when temperature increases from the $l-$phase to the $g-$phase we have $0 < T_l < T_i < T_g$ and thus

$$J_Q\,X_Q = \lambda_{li}\,\delta T_l\left(\frac{1}{T_g} - \frac{1}{T_l}\right) = \frac{\lambda_{li}}{T_g T_l}\,(T_l - T_i)(T_l - T_g) > 0.$$

The inequality still holds when $0 < T_g < T_i < T_l$. □

5.3 Positivity of molar exchange entropy production

Showing positivity of the molar entropy production in Equation (17) is equivalent to show that

$$\ln\left(\frac{y^\star_j}{y_j}\right) J_{nj} > 0, \qquad \forall\, j. \tag{19}$$

Hereunder we establish conditions such that (19) is true for every deviation from thermodynamic equilibrium.

Let w_j represent a vector function

$$w_j = [\delta x_j,\ \delta y_j,\ \Delta x_j,\ \beta_{lj}\delta x_j - \beta_{gj}\delta y_j]. \tag{20}$$

We call (20) a spatial composition profile for component j. The signs of the elements in (20) determine the direction of transport J_{nj}, as shown in Example 1. Each sign combination in (20) has a one to one correspondence with an irreversible concentration profile. The profile in Example 1 corresponds to the sign combination depicted in the first row in Table 1. There are therefore $2^4 = 16$ possible concentration profiles that determine the sign of

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[5] Equation (15) is a well established result which can be found in (Prigogine, 1968, Eq. 4.19), and (de Groot and Mazur, 1984, Eq. 65).

J_{nj}. It is worth noting that not every sign combination has a physical significance[6]. The twelve physically significant sign combinations for (20) are depicted in Table 1.

Our task now is to establish conditions for Equation (19) to be valid for every possible concentration profile (Table 1).

Proposition 5. Assume that the interface transport of component j occurs in a system described by a profile among lines p1-p4 in Table 1. Assume in addition that

$$K_{lj} - y_{ij}/x_{ij} = 0. \tag{21}$$

Then the internal entropy production term $J_{nj}X'_{nj}$ in Equation (14) is positive definite.

Proof. Consider a system described by row p1 in Table 1. In Example 1, we have shown that for such profile:

$$J_{nj} > 0. \tag{22}$$

Next note that

$$\left.\begin{aligned} \delta y_j = y_{ij} - y_j > 0 \;\Rightarrow\; y_{ij} > y_j \\ \delta x_j = x_j - x_{ij} > 0 \;\Rightarrow\; x_{ij} < x_j \end{aligned}\right\} \Rightarrow \frac{y_{ij}}{x_{ij}} > \frac{y_j}{x_j},$$

and thus from (21)

$$\ln\left(\frac{y_j^\star}{y_j}\right) = \ln\left(\frac{K_j x_j}{y_j}\right) = \ln\left(\frac{y_{ij}/x_{ij}}{y_j/x_j}\right) > \ln(1). \tag{23}$$

The positivity of $J'_{nj}X'_{nj}$ follows from (22) and (23). Proposition 5 is still valid for profiles p2-p4. ☐

Proposition 6. Assume that the interface molar transport of component j in a multiphase process occurs in a system described by a profile among lines p5-p8 in Table 1. Assume in addition that

$$\big(y_j^\star - y_j\big)J_n > 0. \tag{24}$$

Then the internal entropy production term $J_{nj}X'_{nj}$ in Equation (17) is positive definite.

Proof. To demonstrate the stability of molar transport processes for this case, we consider a system described by row p5 in Table.

Following the same lines as in Example 1, it can be shown that $J_n > 0$ in a system described by row p5. It follows then from (24) that y_j is below equilibrium, that is $y_j^\star \geq y_j$. Note in addition that, as $\delta x_j > 0$ and $J_n > 0$ we have

$$J_{nj}\big|_{\alpha=l} = \beta_{lj}\delta x_j + J_n x_j > 0. \tag{25}$$

And thus

$$\ln\left(\frac{y_j^\star}{y_j}\right) \geq \ln(1) = 0. \tag{26}$$

Positivity of molar entropy production follows from equations (25) and (26). The result still holds true for profiles p6-p8. ☐

Proposition 7. Consider the internal transport of component j in a multiphase system described by a profile among lines p9-p12 in Table 1. Assume in addition that (21) is valid and that

$$(y_j^\star - y_j)\psi_j > 0 \tag{27}$$

where

$$\psi_j := \begin{cases} J_n - \max\limits_{\alpha\in\{g,l\}} \big(-\beta_{\alpha j}\delta x_{\alpha j}/x_{\alpha j}\big) & \text{for p9-p10,} \\ J_n - \min\limits_{\alpha\in\{g,l\}} \big(-\beta_{\alpha j}\delta x_{\alpha j}/x_{\alpha j}\big) & \text{for p11-p12.} \end{cases}$$

Then the internal entropy production term $J_{nj}X'_{nj}$ in (17) is positive definite for profiles p9-p12.

	δy_j	δx_j	Δx_j	$\beta_{lj}\delta x_j - \beta_{gj}\delta y_j$
p1	+	+	+	+
p2	-	-	-	+
p3	+	+	-	-
p4	-	-	+	-
p5	-	+	+	+
p6	+	-	+	-
p7	-	+	-	+
p8	+	-	-	-
p9	+	+	+	-
p10	+	+	-	+
p11	-	-	+	+
p12	-	-	-	-

Table 1. Composition profiles for component j.

Proof. To demonstrate the stability of molar transport processes, we consider a system described by row p9 in Table 1.

Following the same lines as in Example 1 we can show that $J_n < 0$. Then it follows from the same arguments used in the proof for Proposition 5 that

$$y_j^\star - y_j > 0. \tag{28}$$

Equations (27) and (28) bound the j-transport to satisfy

$$\max_{\alpha\in\{g,l\}} \big(-\beta_{\alpha j}\delta x_{\alpha j}/x_{\alpha j}\big) < J_n < 0. \tag{29}$$

It follows from bound (29) that

$$J_{nj} = \beta_{\alpha j}\delta x_{\alpha j} + J_n x_{\alpha j} > 0. \tag{30}$$

Thermodynamic consistency of molar transport in a system described by line p9 in Table 1 follows from equations (28) and (30). The result of Proposition 7 still holds for profiles p10-p12. ☐

Below, we collect the results from Propositions 4-7 in a theorem that states conditions for the positivity of internal entropy production in multiphase systems.

5.4 The domain of feasibility

Definition 3. Let $f = [f_1,\, f_2]^{\mathrm{t}}$ and g represent functions that measure the deviation of a thermodynamic system from thermodynamic equilibrium defined as

$$f_1(\zeta) = \delta T_l \cdot \delta T_g \tag{31a}$$

$$f_2(\zeta) = \big(y_j^\star - y_j\big)\cdot \phi(\zeta) \tag{31b}$$

$$g(\zeta) = K_{lj} - y_{ij}/x_{ij}, \tag{31c}$$

where $\phi(\cdot)$ is a piecewise function

$$\phi(\zeta) := \begin{cases} 1/(y^\star - y_j) & \text{for p1-p4} \\ J_n & \text{for p5-p8} \\ \psi_j & \text{for p9-p12,} \end{cases}$$

and pj stands for a molar composition profiles (Table 1).

Theorem 8. Let ζ represent the state for a multiphase system far from thermodynamic equilibrium. Let the thermodynamic variables be defined as a mapping

$$\zeta \mapsto (T_\alpha, P_\alpha, x_1, y_1, \ldots, x_c, y_c, x_{i1}, y_{i1}, \ldots, x_{ic}, y_{ic}, J_n),$$

where the output represents temperature, pressure, molar composition, and total interface transport, respectively.

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[6] Setting $\beta_{lj}\delta x_j - \beta_{gj}\delta y_j > 0$, $\delta y_j > 0$, and $\delta x_j < 0$, in w_j, for instance, gives one of the four physically inconsistent profiles.

Then the domain of thermodynamic consistency for a multiphase system corresponds to the set

$$\Theta := \left\{\zeta \,\middle|\, f(\zeta) \geq 0, \text{ and } g(\zeta) = 0\right\}, \tag{32}$$

where f and g are given by Equation (31).

The proof for Theorem 8 consists on using Lemma 2 and Propositions 4-7 to show that the internal entropy production for a multiphase process is semipositive definite.

Theorem 8 represents the main result of this paper. The theorem establishes the existence of a set of states that produces deviations from thermodynamic equilibrium in multiphase systems where internal entropy production is positive semidefinite. Being positive semidefinite, the internal entropy production is a Lyapunov function candidate to characterize irreversible systems contained in Θ.

6. CONCLUSIONS AND FUTURE WORK

In this article, we have shown that there exists a feasibility domain Θ where irreversible multiphase processes are consistent with thermodynamic principles. This is evidence that irreversible systems do not occur arbitrarily. A deviation from equilibrium that produces a system that falls outside from Θ violates the second law of thermodynamics. As the positivity of internal production has been established, future research includes a study on the conditions such that entropy production decreases in time along the dynamics of multiphase systems, as modeled by Romo-Hernandez et al. (2019) (Figure 3). Once the time decreasing property of entropy production is established, we can show that entropy production is a Lyapunov function to characterize multiphase process systems.

Physics-based characterization of irreversible processes brings phenomenological insight on behavior of multiphase systems. We have shown that interface transport processes where internal flows go against gradients in intensive variables are thermodynamically stable, see Propositions 4-6. We came upon the conclusion that counter flow processes can be thermodynamically stable provided that total molar flows are bounded, see Proposition 7.

We strongly believe that the feasibility domain Θ can be expanded by formulating a less restrictive version of Theorem 8. This issue represents another line of future work. It is worth mentioning that the work developed here is oriented to demonstrate the stability of non-azeotropic systems with unique equilibrium solutions. The extension of the methodology proposed here to azeotropic systems and processes with multiple equilibria also represents a potentially fruitful line of future research.

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