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Conservative and dissipative phenomena in thermodynamical systems stability

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Abstract The entropy production of thermodynamical systems with reversible (conservative) and irreversible (dissipative) phenomena is used as a Lyapunov candidate function to address stability properties. First, based on the conjugated variables of the extensive properties, the dissipative and conservative phenomena are identified, then, the dynamic behavior of entropy production is obtained. Based on the properties of the entropy function Hessian, it is found that dissipative phenomena contribute to stability and attraction of the thermodynamical equilibrium. In particular, when only dissipative phenomena are present, the entropy production is a Lyapunov function that guarantees global or local stability, depending on the nonlinearities. Complex behaviors, for instance transitory increments of the entropy production, are due to both conservative phenomena and, far from equilibrium, non linearities of dissipative phenomena. Finally, a case study consisting in a gas-piston system is presented to illustrate these ideas.

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1. INTRODUCTION

Dissipative systems constitute a very important class of dynamical systems of particular interest in engineering and physics (Nicolis, 1986; Willems, 1972). The notion of dissipativity has been widely used to analyze open systems for which it is assumed that the dissipated energy, which is always non-negative, is the difference between the stored energy variation within the system and the amount of energy supplied by the environment or surroundings. Thus, given this energy-balance feature, it is clear that system stability is intimately related to dissipativity. In this context, it has been shown that many physical processes may be dissipative, including those that are constrained by the laws of thermodynamics (Rojas et al., 2008). In particular, these concepts have been successfully applied to mechanical and electrical systems (García-Canseco et al., 2010; Jeltsema and Scherpen, 2007, 2009; Ortega et al., 2001) to address stability properties in terms of energy or power. However, this approach is not easy to apply, and has not been completely successful, when applied to chemical (or thermodynamical) systems, for instances reacting systems (Favache and Dochain, 2009).

Some results in interpreting stability properties for thermodynamical systems based on the irreversibility have been already achieved (Alonso and Ydstie, 2001; Favache, 2009; Favache and Dochain, 2009; Ydstie, 2002; Ydstie and Alonso, 1997). In particular, when a thermodynamical system is isolated, its total energy and mass remain constant, making impossible to use the energy or power to analyze stability properties, and still, due to irreversibility, the system is able to attain stable equilibrium points. In this context, irreversibility immediately evokes quantities related to the entropy (e.g. the entropy itself, the entropy production, the availability) to be considered as Lyapunov function candidates. For instance, García-Sandoval et al. (2016) presented a procedure to use the entropy production as a Lyapunov (or storage) function for a class of isolated (or open) thermodynamical systems.

In many cases, physical systems are composed of both irreversible and reversible processes, and their interaction may produce more complex behavior. For mechanical systems or fluid dynamics, the reversible processes have been captured in the definition of some differential geometric structures such as Poisson brackets (Arnold, 1989; Olver, 1993), while asymmetric bracket are used to define irreversible processes (Grmela and Öttinger, 1997; Ortega and Planas-Bielsa, 2004). Physical systems, subject simultaneously to reversible and irreversible processes, have been expressed as the sum of gradient and pseudo-Hamiltonian dynamical systems (Dalsmo and van der Schaft, 1998; García-Sandoval et al., 2015; Grmela and Öttinger, 1997; Öttinger and Grmela, 1997).

In this contribution, we combine the results presented in (García-Sandoval et al., 2016) and (García-Sandoval et al., 2015) to include dissipative and conservative processes

in stability analysis. The paper is organized as follows. In section 2 the thermodynamical systems in study and their properties are presented. In section 3, based on the entropy production, the stability analysis is carried out, focusing on the interactions between the dissipative and conservative phenomena. Finally, in section 4, a case study is presented.

2. THERMODYNAMICAL SYSTEMS

Let us consider a system Π composed of *n* subsystems (see scheme in Fig. 1) where thermodynamical phenomena take place, for instance gas expansion, heat or mass transfer, convective flow, chemical reactions, etc. Each subsystem is characterized by a set of extensive properties { $\mathbf{N}_i, U_i, V_i, \mathbf{q}_i, \mathbf{p}_i$ } as well as its associated intensive properties, for instance $\{-\mu_i, T_i, P_i, \phi_{pot}, \mathbf{v}_i\}$, where $\mathbf{N}_i \in \mathbb{R}^{C_i+}, U_i \in \mathbb{R}, V_i \in \mathbb{R}^+, \mathbf{q}_i \in \mathbb{R}^3 \text{ and } \mathbf{p}_i \in \mathbb{R}^3 \text{ are the}$ moles, internal energy, volume, position and momentum, with C_i is the number of chemical species that interact in subsystem *i*, and $\boldsymbol{\mu}_i \in \mathbb{R}^{C_i+}, T_i \in \mathbb{R}^{+}, P_i \in \mathbb{R}^{+}, \boldsymbol{\phi}_{pot} \in \mathbb{R}^{3}$ and $\mathbf{v}_i \in \mathbb{R}^3$ are the chemical potentials vector for each compound, temperature, pressure, potential force vector and velocity vector of subsystem i, with i = 1, 2, ..., n, respectively. Finally, the momentum is equal to $\mathbf{p}_i = m_i \mathbf{v}_i$, where

$$m_i = \mathbf{M}_{w,i}^\mathsf{T} \mathbf{N}_i,\tag{1}$$

with $\mathbf{M}_{w,i} \in \mathbb{R}^{C_i+}$ as the molar mass vector. By considering that the total energy of each subsystem depends on internal energy, U_i , potential energy, $\Phi_{pot} = \int \phi_{pot} \cdot d\mathbf{q}_i$, and kinetic energy, $K_i = \frac{1}{2} \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{m_i} = \frac{1}{2} m_i (\mathbf{v}_i \cdot \mathbf{v}_i)$, and the total energy is

$$E_i = U_i + \int \boldsymbol{\phi}_{pot} \cdot d\mathbf{q}_i + \frac{1}{2} \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{m_i}.$$
 (2)

Depending on the particular configuration and characteristics of each subsystem, the state variables that completely define the behavior of each subsystem, $\eta_i \in \mathbb{R}^{\omega_i}$ for i = 1, 2, ..., n, is the set or a subset of extensive properties $\{\mathbf{N}_i, E_i, V_i, \mathbf{q}_i, \mathbf{p}_i\}$, where internal energy has been substituted by total energy using eq. (2). Then, the total mass and energy for system Π are linear functions of η , i.e.,

$$m = \sum_{i=1}^{n} m_i = \mathbf{M}^\mathsf{T} \boldsymbol{\eta} + m_0 \tag{3}$$

and

$$E = \sum_{i=1}^{n} E_i = \boldsymbol{\Upsilon}^{\mathsf{T}} \boldsymbol{\eta} + E_0, \qquad (4)$$

where **M** and Υ are constant matrices and m_0 and E_0 are the mass and total energy of static compounds. For instance, for $\eta = \operatorname{col} \{\mathbf{N}, E\}$, with $\mathbf{N} \in \mathbb{R}^{C+}$, it holds $\mathbf{M} = \operatorname{col} \{\mathbf{M}_w, 0\}$ and $\Upsilon = \operatorname{col} \{\mathbf{0}_{C\times 0}, 1\}$.

2.1 Entropy and conjugated forces

According to the second principle of thermodynamics, it is possible to introduce for each subsystem Π , as for any macroscopic system, a concave real-valued function



Figure 1. Scheme of system Π .

called entropy $S_i : \mathbb{R}^{\omega_i} \to \mathbb{R}$ at least twice differentiable that depends on the extensive properties, i.e., $S_i = S_i (\mathbf{N}_i, E_i, V_i, \mathbf{q}_i, \mathbf{p}_i)$. Under the assumption of local equilibrium, the derivative of the entropy can be obtained by the Gibbs relation (Kjelstrup et al., 2010): $dG_i =$ $\boldsymbol{\mu}_i^{\mathsf{T}} d\mathbf{N}_i = dU_i + P_i dV_i - T_i dS_i$. By considering eqs. (1) and (2), dS_i is equivalently written as

$$dS_{i} = \frac{1}{T_{i}} dE_{i} + \frac{P_{i}}{T_{i}} dV_{i} - \frac{\left(\boldsymbol{\mu}_{i} - \frac{1}{2} \left(\mathbf{p}_{i} \cdot \mathbf{p}_{i}\right) \mathbf{M}_{w,i}\right)^{\mathsf{T}}}{T_{i}} d\mathbf{N}_{i} - \frac{\boldsymbol{\phi}_{pot} \cdot d\mathbf{q}_{i}}{T_{i}} - \frac{\mathbf{v}_{i} \cdot d\mathbf{p}_{i}}{T_{i}}.$$
(5)

From this expression, it is possible to identify the socalled conjugated variables $\left\{-\frac{\left(\boldsymbol{\mu}_{i}-\frac{1}{2}(\mathbf{p}_{i}\cdot\mathbf{p}_{i})\mathbf{M}_{w,i}\right)}{T_{i}}, \frac{1}{T_{i}}, \frac{P_{i}}{T_{i}}, -\frac{\boldsymbol{\phi}_{pot}}{T_{i}}, -\frac{\mathbf{v}_{i}}{T_{i}}, -\frac{\mathbf{v}_{i}}{T_{i}}\right\}$ of the extensive properties, $\{\mathbf{N}_{i}, E_{i}, V_{i}, p_{i}\}$. Then, depending on the particular configuration and characteristics of each subsystem, the entropy gradient has the form $\boldsymbol{\zeta}_{i} := \left(\frac{\partial S_{i}}{\partial \boldsymbol{\eta}_{i}}\right)^{\mathsf{T}} \in \mathbb{R}^{\omega_{i}}, i = 1, 2, \dots, n.$

In addition, since the entropy is a concave function (Öttinger, 2005), its Hessian matrix, $\Omega_i := \frac{\partial \zeta_i}{\partial \eta_i} \leq 0$, is negative (semi-)definite. Finally, the total entropy of system Π is the sum of the entropy of each subsystem

$$S(\boldsymbol{\eta}) = \sum_{i=1}^{n} S_i(\boldsymbol{\eta}_i), \qquad (6)$$

therefore, its gradient is

$$\boldsymbol{\zeta} := \left(\frac{\partial S}{\partial \boldsymbol{\eta}}\right)^{\mathsf{T}} = \operatorname{col}\left\{ \left(\frac{\partial S_i}{\partial \boldsymbol{\eta}_i}\right)^{\mathsf{T}}, i = 1, 2, \dots, n \right\}, \quad (7)$$

while its Hessian is a block-diagonal matrix, $\Omega := \text{diag} \{\Omega_i, i = 1, 2, ..., n\} \leq 0$, that by construction is negative (semi-)definite.

2.2 Dynamical behavior

In this work, we consider that each subsystem is homogeneous or perfectly mixed, i.e., there is no spatial dependency, while the total system is isolated from the surroundings. Therefore, the dynamical model that describes the behavior of the extensive variables from molar, energy and momentum balances and state equations has the general form

$$\Pi : \dot{\boldsymbol{\eta}} = W(\boldsymbol{\zeta}) f(\boldsymbol{\zeta}), \qquad (8)$$

where $\eta = \operatorname{col} \{\eta_i, i = 1, 2, \ldots, n\} \in \mathbb{R}^{\omega}$, with dimension $\omega = \sum_{i=1}^{n} \omega_i$, represents the vector of the extensive properties, $f : \mathbb{R}^{\omega} \to \mathbb{R}^p$ is a vector field containing the kinetic expression for the reactions, transport and motion phenomena taking place inside the systems, while matrix $W = [W_1, W_2, \ldots, W_p] \in \mathbb{R}^{\omega \times p}$, with $W_j : \mathbb{R}^{\omega} \to \mathbb{R}^{\omega}$ for $j = 1, 2, \ldots, p$, contains the stoichiometric coefficients for each reaction and the interconnection coefficients for each transport or movement phenomena, that is obtained directly from mass, energy and momentum balances. It is important to remark that vector fields $f(\zeta)$ and $W_i(\zeta)$ are functions of the conjugated variables, since they are associated to the driving or conjugated forces that set the behavior of kinetic and transport phenomena taking place in system II. In addition, there exists a direct relation between this conjugated variables, ζ , and its respective extensive variables, η , given by eq. (7).

2.3 Conservative and non conservative variables

The total mass and energy are conservative variables, and since system Π is isolated, by computing the time derivatives of (3) and (4), we obtain

$$\dot{m} = \mathbf{M}^{\mathsf{T}} W(\boldsymbol{\zeta}) f(\boldsymbol{\zeta}) \quad \text{and} \quad E = \boldsymbol{\Upsilon}^{\mathsf{T}} W(\boldsymbol{\zeta}) f(\boldsymbol{\zeta}) .$$
 (9)

Thus, if the system is thermodynamically consistent, it must hold that $\mathbf{M}^{\mathsf{T}}W(\boldsymbol{\zeta}) = 0$ and $\boldsymbol{\Upsilon}^{\mathsf{T}}W(\boldsymbol{\zeta}) = 0$; therefore,

$$\dot{m} = 0, \quad \text{and} \quad \dot{E} = 0.$$
 (10)

On the other hand, the entropy is a non conservative quantity, and the total entropy balance has the form

$$\dot{S} = \frac{\partial S}{\partial \eta} \dot{\eta} := \Sigma, \qquad (11)$$

where $\Sigma \geq 0$ is the entropy production. From the entropy gradient (7), and the extensive variables dynamics (8) the entropy production for system Π is $\dot{S} = \boldsymbol{\zeta}^{\mathsf{T}} W(\boldsymbol{\zeta}) f(\boldsymbol{\zeta}) \geq$ 0,which must be positive (semi-)definite if the system is thermodynamically consistent.

3. STABILITY ANALYSIS

At thermodynamical equilibrium for system (8), that is isolated from the surroundings, we have

$$W(\boldsymbol{\zeta}_e) f(\boldsymbol{\zeta}_e) = 0$$
 and $\Sigma_e = \boldsymbol{\zeta}_e^{\mathsf{T}} W(\boldsymbol{\zeta}_e) f(\boldsymbol{\zeta}_e) = 0$

where ζ_e is the conjugated variables vector at thermodynamical equilibrium. A feasible solution to both equations is $f(\zeta_e) = 0$. In addition, if the driving or conjugated forces that set the thermodynamical equilibrium are considered to be of the form $W^{\mathsf{T}}(\zeta)\zeta$, then at equilibrium, it must also holds $W^{\mathsf{T}}(\zeta_e)\zeta_e = 0$. Therefore, it is reasonable to assume that vector the field f, which contains the kinetic expressions for chemical reactions and transport and motion phenomena taking place inside system Π , depends on these driving forces. Thus, the following Assumption with respect to the structure of f is considered.

Assumption 1. (García-Sandoval et al., 2015) Given the full rank matrix $\Psi(\boldsymbol{\zeta}) : \mathbb{R}^{p \times \omega} \longrightarrow \mathbb{R}^{p \times p}$ whose determinant at thermodynamical equilibrium is bounded and different

from zero and whose symmetric part is positive definite for all ζ , i.e.,

$$0 < |\Psi(\boldsymbol{\zeta}_e)| < \Psi_{\infty}, \qquad \Psi(\boldsymbol{\zeta}) + \Psi^{\mathsf{T}}(\boldsymbol{\zeta}) \ge 0, \qquad (12)$$

it is assumed that f has the following structure

$$f(\boldsymbol{\zeta}) = \Psi(\boldsymbol{\zeta}) W^{\mathsf{T}}(\boldsymbol{\zeta}) \boldsymbol{\zeta}.$$
(13)

Assumption 1 implies that the dynamics of the extensive variables and the entropy are equivalent to

$$\dot{\boldsymbol{\eta}} = W\left(\boldsymbol{\zeta}\right) \Psi\left(\boldsymbol{\zeta}\right) W^{\mathsf{T}}\left(\boldsymbol{\zeta}\right) \boldsymbol{\zeta},\tag{14}$$

$$\dot{S} = \boldsymbol{\zeta}^{\mathsf{T}} W\left(\boldsymbol{\zeta}\right) \Psi\left(\boldsymbol{\zeta}\right) W^{\mathsf{T}}\left(\boldsymbol{\zeta}\right) \boldsymbol{\zeta}, \tag{15}$$

and by construction, according to (12), it holds that $\Sigma = \boldsymbol{\zeta}^{\mathsf{T}} W(\boldsymbol{\zeta}) \Psi(\boldsymbol{\zeta}) W^{\mathsf{T}}(\boldsymbol{\zeta}) \boldsymbol{\zeta} \geq 0$. Thus, although entropy production can be a nonlinear function of the extensive or conjugated variables, it has a "quasi-quadratic" structure of the driving or conjugated forces, $W^{\mathsf{T}}(\boldsymbol{\zeta}) \boldsymbol{\zeta}$. In addition, the fact that $\Psi(\boldsymbol{\zeta})$ satisfies the expressions described in eq. (12) allows to fulfil the second law of thermodynamics and at the same time at equilibrium $W^{\mathsf{T}}(\boldsymbol{\zeta}_e) \boldsymbol{\zeta}_e = 0$.

3.1 Dissipative and conservative phenomena

In general, $\Psi(\boldsymbol{\zeta})$ can be a non symmetric matrix, however it can be always represented as the sum of a symmetric matrix, $\hat{\Psi}(\boldsymbol{\zeta})$, and a skew-symmetric matrix, $\tilde{\Psi}(\boldsymbol{\zeta})$, i.e.,

$$\Psi(\boldsymbol{\zeta}) = \hat{\Psi}(\boldsymbol{\zeta}) + \tilde{\Psi}(\boldsymbol{\zeta}) \tag{16}$$

where

$$\hat{\Psi}(\boldsymbol{\zeta}) = \frac{1}{2} \left[\Psi(\boldsymbol{\zeta}) + \Psi^{\mathsf{T}}(\boldsymbol{\zeta}) \right] \ge 0, \tag{17}$$

$$\tilde{\Psi}(\boldsymbol{\zeta}) = \frac{1}{2} \left[\Psi(\boldsymbol{\zeta}) - \Psi^{\mathsf{T}}(\boldsymbol{\zeta}) \right] = -\tilde{\Psi}^{\mathsf{T}}(\boldsymbol{\zeta}). \quad (18)$$

From here, the following vector fields are defined

$$\psi_d(\boldsymbol{\zeta}) = W(\boldsymbol{\zeta}) \, \Psi(\boldsymbol{\zeta}) \, W^{\mathsf{T}}(\boldsymbol{\zeta}) \, \boldsymbol{\zeta}, \tag{19}$$

$$\psi_{c}\left(\boldsymbol{\zeta}\right) = W\left(\boldsymbol{\zeta}\right)\Psi\left(\boldsymbol{\zeta}\right)W^{\mathsf{T}}\left(\boldsymbol{\zeta}\right)\boldsymbol{\zeta},\tag{20}$$

such that the dynamics of the extensive variables and the entropy given in eqs. (14) and (15) are equivalent to

$$\dot{\boldsymbol{\eta}} = \psi_d\left(\boldsymbol{\zeta}\right) + \psi_c\left(\boldsymbol{\zeta}\right),\tag{21}$$

$$\dot{S} = \boldsymbol{\zeta}^{\mathsf{T}} \psi_d \left(\boldsymbol{\zeta} \right) = \Sigma \ge 0, \tag{22}$$

since by construction $\boldsymbol{\zeta}^{\mathsf{T}}\psi_c(\boldsymbol{\zeta}) = \boldsymbol{\zeta}^{\mathsf{T}}W(\boldsymbol{\zeta}) \tilde{\Psi}(\boldsymbol{\zeta}) W^{\mathsf{T}}(\boldsymbol{\zeta}) \boldsymbol{\zeta} = 0$. It is then easy to infer that $\psi_d(\boldsymbol{\zeta})$ and $\psi_c(\boldsymbol{\zeta})$ represents respectively the dissipative and conservative vector fields that affects system II. In (García-Sandoval et al., 2016) we assume that $W(\boldsymbol{\zeta})$ was constant and $\Psi(\boldsymbol{\zeta})$ was symmetric, therefore the extensive variables dynamics contained only dissipative phenomena, i.e. $\dot{\boldsymbol{\eta}} = \psi_d(\boldsymbol{\zeta})$. Thus, the main contribution of this work in comparison with (García-Sandoval et al., 2016) is the inclusion of conservative phenomena modeled by $\psi_c(\boldsymbol{\zeta})$ and, as shown below, the analysis of their effects on the stability properties.

3.2 Behavior of the entropy production

By looking at eq. (22), it is obvious that the entropy production only depends on ψ_d and not on ψ_c , while its time derivative is $\dot{\Sigma} = \frac{\partial \Sigma}{\partial \zeta} \dot{\zeta}$, and given that

$$\frac{\partial \Sigma}{\partial \boldsymbol{\zeta}} = \psi_d^{\mathsf{T}}(\boldsymbol{\zeta}) + \psi_{dd}^{\mathsf{T}}(\boldsymbol{\zeta}), \text{ with } \psi_{dd}(\boldsymbol{\zeta}) = \left(\frac{\partial \psi_d(\boldsymbol{\zeta})}{\partial \boldsymbol{\zeta}}\right)^{\mathsf{T}} \boldsymbol{\zeta},$$
(23)

the time evolution of the entropy production becomes

$$\dot{\Sigma} = \psi_d^{\mathsf{T}}(\boldsymbol{\zeta}) \,\Omega\psi_d(\boldsymbol{\zeta}) + \psi_{dd}^{\mathsf{T}}(\boldsymbol{\zeta}) \,\Omega\psi_d(\boldsymbol{\zeta}) + \psi_d^{\mathsf{T}}(\boldsymbol{\zeta}) \,\Omega\psi_c(\boldsymbol{\zeta}) + \psi_{dd}^{\mathsf{T}}(\boldsymbol{\zeta}) \,\Omega\psi_c(\boldsymbol{\zeta}) \,, \qquad (24)$$

where $\Omega \leq 0$ is the entropy Hessian. Equation (24) is relevant because stability properties may be inferred for several cases as shown below.

Four terms are distinguished in eq. (24):

- The first term, $\psi_d^{\mathsf{T}}(\boldsymbol{\zeta}) \, \Omega \psi_d(\boldsymbol{\zeta})$ is always (semi-)negative definite, given the properties of the Hessian. It preserves the symmetric properties of the entropy production and can be associated to the first order interactions between the dissipative processes;
- The second term, $\psi_{dd}^{\mathsf{T}}(\boldsymbol{\zeta}) \Omega \psi_d(\boldsymbol{\zeta})$, is (semi-)negative definite at least in a neighborhood of the thermodynamical equilibrium, since, according to the mean value theorem (Isidori, 2000), $\psi_d(\boldsymbol{\zeta})$ can be written

as $\psi_d(\boldsymbol{\zeta}) = A(\boldsymbol{\zeta} - \boldsymbol{\zeta}_e) + \phi_d(\boldsymbol{\zeta})$, where $A = \begin{bmatrix} \frac{\partial \psi_d(\boldsymbol{\zeta})}{\partial \boldsymbol{\zeta}} \end{bmatrix}_{\boldsymbol{\zeta}_e}$ and $\phi_d(\boldsymbol{\zeta}) = \left(\begin{bmatrix} \frac{\partial \psi_d(\boldsymbol{\zeta})}{\partial \boldsymbol{\zeta}} \end{bmatrix}_{z(\boldsymbol{\zeta})} - A \right) (\boldsymbol{\zeta} - \boldsymbol{\zeta}_e)$, with $z(\boldsymbol{\zeta})$ as a mean value between $\boldsymbol{\zeta}$ and $\boldsymbol{\zeta}_e$, and $\lim_{\boldsymbol{\zeta} \to \boldsymbol{\zeta}_e} \frac{\|\phi_d(\boldsymbol{\zeta})\|}{\|\boldsymbol{\zeta} - \boldsymbol{\zeta}_e\|} = 0$; thus, near equilibrium the following limit: $\lim_{\boldsymbol{\zeta} \to \boldsymbol{\zeta}_e} \left\| \begin{bmatrix} \frac{\partial \psi_d(\boldsymbol{\zeta})}{\partial \boldsymbol{\zeta}} \end{bmatrix}_{z(\boldsymbol{\zeta})} \right\| = \|A\|$ holds and therefore $\psi_{dd}^{\mathsf{T}}(\boldsymbol{\zeta}) \Omega \psi_d(\boldsymbol{\zeta}) \leq -\|\Omega\| \|A(\boldsymbol{\zeta} - \boldsymbol{\zeta}_e)\|^2 \leq 0$, while far from equilibrium, depending on the nonlinearities structure for ϕ_d with respect to $\boldsymbol{\zeta}$, it might not have a well-defined sign. This term can be associated to the second order interactions between the dissipative phenomena and, in general, does not preserve the symmetric properties unless ψ_d is linear with respect to $\boldsymbol{\zeta}$, i.e., that in the particular case when $\phi_d(\boldsymbol{\zeta}) = A\boldsymbol{\zeta}$, we have that $\psi_{dd}(\boldsymbol{\zeta}) \approx \psi_d(\boldsymbol{\zeta})$ and, therefore, this term is identical to the first one, that is always (semi-)negative definite;

- The third term, $\psi_d^{\mathsf{T}}(\boldsymbol{\zeta}) \Omega \psi_c(\boldsymbol{\zeta})$, does not have, in general, a well defined sign and can be seen as the first order interaction between the dissipative and conservative processes;
- Finally, the fourth term, $\psi_{dd}^{\mathsf{T}}(\boldsymbol{\zeta}) \, \Omega \psi_c(\boldsymbol{\zeta})$, similarly to the third one, does not have a well defined sign in general and can be seen as the second order interaction between the dissipative and conservative processes.

When only dissipative processes are present, i.e., if $\psi_c(\boldsymbol{\zeta}) = 0$, system Π is similar to systems described in (García-Sandoval et al., 2016), and the entropy production has the following dynamics

$$\dot{\Sigma} = \psi_d^{\mathsf{T}}\left(\boldsymbol{\zeta}\right) \Omega \psi_d\left(\boldsymbol{\zeta}\right) + \psi_{dd}^{\mathsf{T}}\left(\boldsymbol{\zeta}\right) \Omega \psi_d\left(\boldsymbol{\zeta}\right).$$

As it has been shown, due to the property of the entropy function Hessian, near the equilibrium defined as $W^{\mathsf{T}}(\boldsymbol{\zeta}_e) \boldsymbol{\zeta}_e = 0$, it holds that $\dot{\boldsymbol{\Sigma}} \leq 0$. Therefore the entropy production, which has a "quasi-quadratic" structure guaranteeing that $\boldsymbol{\Sigma} > 0$, can be used as a Lyapunov



Figure 2. Adiabatic piston from (Favache et al., 2010)

function whose time derivative is negative definite near the thermodynamical equilibrium, and this guarantees at least locally asymptotic stability near equilibrium ζ_e . On the other hand, far from thermodynamical equilibrium, the term $\psi_d^{\mathsf{T}}(\boldsymbol{\zeta}) \Omega \psi_d(\boldsymbol{\zeta})$ in equation (24), which is (semi-)negative definite, produces a decrease on Σ . However, this cannot be said for the second term, $\psi_{dd}^{\mathsf{T}}(\boldsymbol{\zeta}) \Omega \psi_d(\boldsymbol{\zeta})$, which can be positive or negative. Thus, far from thermodynamical equilibrium, i.e., for large driving forces, $|W^{\mathsf{T}}\boldsymbol{\zeta}| \gg 0$, the sum of both terms might have positive values (the entropy production is still positive definite, but its time derivative increases), and this might restrict the region of attraction for the equilibrium and another state becomes stable (Kurzynski, 2006), which may be a new state of "broken symmetry" (one of few alternatives) either periodically oscillating in time or with chaotic dynamics. Hence, in general, the state referred to by Prigogine as a dissipative structure (Kondepudi and Prigogine, 1998; Prigogine, 1980) and by Haken (1990) as a synergetic structure.

On the other hand, when in addition to dissipative processes, the system has conservative ones ($\psi_c(\zeta) \neq 0$), the last two terms of eq. (24) appear and their signs are not well defined; moreover those terms might take positive values near the thermodynamical equilibrium, reducing the region of attraction of the equilibrium defined as $M^{\mathsf{T}}(\zeta_e) \zeta_e = 0$ (or even making the equilibrium unstable). From this analysis, it is possible to infer that these complex behaviors (and the lost of symmetry) is due to the nonlinearities of $\psi_d(\zeta)$ and the presence of conservative phenomena ($\psi_c(\zeta) \neq 0$).

4. CASE STUDY

Let us consider an adiabatic gas-piston system similar to the described by Favache et al. (2010) (see Figure 2) and previously analyzed under ideal gas assumption to derive a quasi port-controlled Hamiltonian-like representation (García-Sandoval et al., 2015).

Model As described in (García-Sandoval et al., 2015) the adiabatic piston model considering no external forces is

$$\begin{pmatrix} \dot{U}_1 \\ \dot{V}_1 \\ \dot{U}_2 \\ \dot{z}_2 \\ \dot{p}_2 \end{pmatrix} = \begin{pmatrix} \kappa \left(T_2 - T_1 \right) - Av_2 P_1 \\ Av_2 \\ -\kappa \left(T_2 - T_1 \right) + \alpha v_2^2 \\ \nu_2 \\ AP_1 - m_2 g - \alpha v_2 \end{pmatrix}$$

where $U_1 = N_1 \left(u_{1,0} + \int_{T_0}^{T_1} c_{v,1} dT \right)$ and $V_1 = Az_2$ represent the internal energy and volume of the gas (named subsystem 1) whose moles, temperature and pressure are

 N_1 , T_1 and $P_1 = N_1 R T_1 / V_1$, respectively, while $U_2 =$ $m_2\left(u_{2,0} + \int_{T_0}^{T_2} c_{v,2} dT\right), z_2, \text{ and } p_2 = m_2 v_2 \text{ are the internal}$ energy, position and momentum of the piston (named subsystem 1) with mass m_2 , temperature T_2 and velocity v_2 . Here, R is the ideal gas constant, A is the transverse chamber area, α is the friction coefficient, κ is a heat exchange constant and g is the gravity constant. Finally, c_{v1} , c_{v2} , $u_{1,0}$ and $u_{2,0}$ are the molar and mass heat capacities and reference internal energy per unit of mole or mass at temperature T_0 , respectively. By looking at V_1 and z_2 dynamics, it is obvious that the volume of the chamber can be correlated with the piston position, reducing to 4 the system state variables. In particular, in this analysis, we choose $\eta = \operatorname{col}(E_1, E_2, z_2, p_2)$, where $E_1 = U_1$ and $E_2 = U_2 + \frac{1}{2}mv_2^2 + mgz_2$ are the total energies of the gas and the piston defined as the gas internal energy and the sum of the piston's internal, kinetic and potential energy, respectively. Therefore, the dynamical behavior of the piston energy is $\dot{E}_2 = -\kappa (T_2 - T_1) + AP_1v_2$, that depends on the gas-piston heat and work exchange rate. On the other hand, by looking at eqs. (5) and (6), the total entropy differential is $dS = (dE_1 + P_1Adz_2)/T_1 +$ $(dE_2 - v_2 dp_2 - m_2 g dz_2)/T_2$ and therefore the conjugated vector is $\boldsymbol{\zeta} = \operatorname{col}\left\{\frac{1}{T_1}, \frac{1}{T_2}, \left(\frac{P_1A}{T_1} - \frac{m_2g}{T_2}\right), -\frac{v_2}{T_2}\right\}$. Thus, the dynamics can be rewritten as in eq. (8) with

$$W(\boldsymbol{\zeta}) = \begin{pmatrix} 1 & -AP_1 & 0\\ -1 & AP_1 & 0\\ 0 & 1 & 0\\ 0 & -\alpha & 1 \end{pmatrix} \text{ and } f(\boldsymbol{\zeta}) = \begin{pmatrix} \kappa (T_2 - T_1)\\ v_2\\ AP_1 - m_2g \end{pmatrix}.$$

Note that the dynamic of the total gas-piston system energy, $E = (1 \ 1 \ 0 \ 0) \eta$, is $\dot{E} = 0$ in accordance with eqs. (4) and (10), while the total mass, which is constant, is $m = M_{w1}N_1 + m_2$, where M_{w1} is the molecular mass of the gas. The equilibrium is reached when $f(\boldsymbol{\zeta}) = 0$, i.e. $T_1 = T_2$, $v_2 = 0$ and $AP_1 = m_2g$. Three phenomena are identified in $f(\boldsymbol{\zeta})$: heat transfer $\kappa (T_2 - T_1)$, movement v_2 and force balance $AP_1 - m_2g$. To obtain the structure described in eq. (13) first we compute

$$W^{\mathsf{T}}(\boldsymbol{\zeta}) \, \boldsymbol{\zeta} = \begin{pmatrix} \frac{1}{T_1} - \frac{1}{T_2} \\ \frac{AP_1 - m_2g}{T_2} + \frac{\alpha v_2}{T_2} \\ -\frac{v_2}{T_2} \end{pmatrix},$$

from here the driving forces associated to each phenomena are clarified and $\Psi(\boldsymbol{\zeta})$ can be easily derived

$$\Psi(\boldsymbol{\zeta}) = \begin{pmatrix} \kappa T_1 T_2 & 0 & 0\\ 0 & 0 & -T_2\\ 0 & T_2 & \alpha T_2 \end{pmatrix}.$$

Note that $\Psi(\boldsymbol{\zeta})$ is not symmetric, but according to eqs. (17) and (18) can be split in

$$\hat{\Psi}(\boldsymbol{\zeta}) = \begin{pmatrix} \kappa T_1 T_2 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & \alpha T_2 \end{pmatrix} \text{ and } \tilde{\Psi}(\boldsymbol{\zeta}) = \begin{pmatrix} 0 & 0 & 0\\ 0 & 0 & -T_2\\ 0 & T_2 & 0 \end{pmatrix},$$

thus, the dissipative and conservative vector field, as defined in eqs. (19) and (20), are respectively

$$\psi_{d}\left(\boldsymbol{\zeta}\right) = \begin{pmatrix} \kappa \left(T_{2} - T_{1}\right) \\ -\kappa \left(T_{2} - T_{1}\right) \\ 0 \\ -\alpha v_{2} \end{pmatrix} \text{ and } \psi_{c}\left(\boldsymbol{\zeta}\right) = \begin{pmatrix} -AP_{1}v_{2} \\ AP_{1}v_{2} \\ v_{2} \\ AP_{1} - m_{2}g \end{pmatrix}.$$

The dissipative phenomena are associated to heat transfer and heat production due to friction, while the conservative phenomena are the work done by the gas AP_1v_2 , the motion and the force balance. The entropy production is therefore

$$\Sigma = \boldsymbol{\zeta}^{\mathsf{T}} \psi_d \left(\boldsymbol{\zeta} \right) = \frac{\kappa \left(T_2 - T_1 \right)^2}{T_1 T_2} + \frac{\alpha v_2^2}{T_2}$$

which is identified with the irreversibility of the heat exchange and the momentum dissipation due to the pistonchamber friction, and it is easy to verify that $\boldsymbol{\zeta}^{\mathsf{T}}\psi_{c}(\boldsymbol{\zeta})=0$, while the Hessian of the entropy function is

$$\Omega = \begin{pmatrix} -\frac{1}{N_1 c_{v,1} T_1^2} & 0 & 0 & 0\\ 0 & -\frac{\gamma}{m_2 g} & \gamma & \frac{\gamma v_2}{m_2 g}\\ 0 & \gamma & -\beta & -\gamma v_2\\ 0 & \frac{\gamma v_2}{m_2 g} & -\gamma v_2 & -\frac{1 + \frac{v_2^2}{c_{v,2} T_2}}{m_2 T_2} \end{pmatrix} < 0.$$

where $\beta = \frac{AP_1}{z_2T_1} + m_2\gamma g$ and $\gamma = \frac{g}{c_{v,2}T_2^2}$. From here, the four term of the entropy production dynamics (see eq. (24)) are identified:

$$\begin{split} \psi_{d}^{\mathsf{T}}\left(\boldsymbol{\zeta}\right)\Omega\psi_{d}\left(\boldsymbol{\zeta}\right) &= -\frac{\kappa^{2}\left(T_{2}-T_{1}\right)^{2}}{N_{1}c_{v,1}T_{1}^{2}} - \frac{\left(\kappa\left(T_{2}-T_{1}\right)-\alpha v_{2}^{2}\right)^{2}}{m_{2}c_{v,2}T_{2}^{2}} \\ &-\frac{\alpha^{2}v_{2}^{2}}{m_{2}T_{2}} < 0 \\ \psi_{dd}^{\mathsf{T}}\left(\boldsymbol{\zeta}\right)\Omega\psi_{d}\left(\boldsymbol{\zeta}\right) &= -\frac{\kappa^{2}\left(T_{2}-T_{1}\right)^{2}}{N_{1}c_{v,1}T_{1}T_{2}} - \frac{\kappa^{2}\left(T_{2}-T_{1}\right)^{2}}{m_{2}c_{v,2}T_{1}T_{2}} \\ &-\frac{\alpha^{2}v_{2}^{2}}{m_{2}T_{2}} + \frac{\alpha\kappa\left(T_{2}-T_{1}\right)v_{2}^{2}}{m_{2}c_{v,2}T_{1}T_{2}} \\ \psi_{d}^{\mathsf{T}}\left(\boldsymbol{\zeta}\right)\Omega\psi_{c}\left(\boldsymbol{\zeta}\right) &= \frac{\kappa\left(T_{2}-T_{1}\right)Av_{2}P_{1}}{N_{1}c_{v,1}T_{1}^{2}} + \frac{\alpha\left(AP_{1}-m_{2}g\right)v_{2}}{m_{2}T_{2}} \\ \psi_{dd}^{\mathsf{T}}\left(\boldsymbol{\zeta}\right)\Omega\psi_{c}\left(\boldsymbol{\zeta}\right) &= \frac{\kappa AP_{1}\left(T_{2}-T_{1}\right)v_{2}}{N_{1}c_{v,1}T_{1}T_{2}} + \frac{\alpha\left(AP_{1}-m_{2}g\right)v_{2}}{m_{2}T_{2}}. \end{split}$$

As expected, the first term, $\psi_d^{\mathsf{T}}(\boldsymbol{\zeta}) \Omega \psi_d(\boldsymbol{\zeta})$, is negative definite, however the second term, $\psi_{dd}^{\mathsf{T}}(\boldsymbol{\zeta}) \Omega \psi_d(\boldsymbol{\zeta})$, has three negative compounds, the two first negative terms are quadratic functions of the heat transfer, the third negative term is quadratic with respect to heat production due to friction, while the fourth term, which does not have well defined sign, is a third order product of both heat transfer and production due to friction. On the other hand, $\psi_d^{\mathsf{T}}(\boldsymbol{\zeta}) \Omega \psi_c(\boldsymbol{\zeta})$ and $\psi_{dd}^{\mathsf{T}}(\boldsymbol{\zeta}) \Omega \psi_c(\boldsymbol{\zeta})$ do not have a well defined sign. Adding these terms the dynamic behavior of the entropy production is

$$\Sigma = -\sigma_d\left(\boldsymbol{\zeta}\right) + \sigma_c\left(\boldsymbol{\zeta}\right)$$

$$\sigma_d\left(\boldsymbol{\zeta}\right) = \frac{\kappa^2 \left(1 + \frac{T_2}{T_1}\right) \left(T_2 - T_1\right)^2}{N_1 c_{v,1} T_1 T_2} + 2 \frac{\alpha^2 v_2^2}{m_2 T_2}$$

$$+\frac{\left(\kappa\left(1+\frac{T_{2}}{T_{1}}\right)(T_{2}-T_{1})-\alpha v_{2}^{2}\right)^{2}}{m_{2}c_{v,2}T_{2}^{2}}\geq0,$$

and

$$\sigma_{c}(\boldsymbol{\zeta}) = \frac{\kappa \left(T_{2} - T_{1}\right) v_{2}}{T_{1}T_{2}} \left(\frac{AP_{1}\left(1 + \frac{T_{2}}{T_{1}}\right)}{N_{1}c_{v,1}} - \frac{\alpha v_{2}}{m_{2}c_{v,2}}\right) + 2\frac{\alpha \left(AP_{1} - m_{2}g\right) v_{2}}{m_{2}T_{2}}.$$

Therefore, the entropy production dynamics can be seen as the sum of two functions, one with well defined sign, $\sigma_d(\zeta)$, associated to the dissipative processes, that contributes to the stability and attraction to the thermodynamical equilibrium and the other one, $\sigma_c(\zeta)$, mostly associate to conservative processes and to nonlinearities of dissipative processes far from equilibrium, without a well defined sign that might pull the system out of the thermodynamical equilibrium, inducing (transitory) instabilities.

5. CONCLUSIONS

In this contribution, it has been shown that dissipative phenomena contribute to stability and attraction to thermodynamical equilibrium for isolated systems. In particular, when only dissipative phenomena are present, the entropy production is at least a local Lyapunov function. On the other hand, complex behaviors, for instance transitory increments on the entropy production, are due to both conservative phenomena and, far from equilibrium, non linearities of dissipative phenomena, that break symmetry in the entropy production dynamics. Thus, the proposed methodology allows to identify the source of complexity of isolated thermodynamic systems in a systematic manner. Currently, the authors are making efforts to generalize this methodology to opened systems.

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