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Potential-based analysis of closed reacting systems [1]

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Abstract: This paper studies the properties of closed reacting systems described by mass-action kinetics. Following recent developments in potential-driven kinetic representations and stability analysis of (open) reacting systems, this paper seeks to develop a framework where both thermodynamically-consistent reaction fluxes and stoichiometry play a role in the identification of invariants and on stability analysis. Following some observations from the literature, the proposed approach seek to re-express mass-action kinetics in terms a potential-driven dynamical system. The proposed approach consists in the homotopy decomposition of the mass-action kinetic to compute such a potential-driven representation. An example is considered to illustrate the proposed approach.

Keywords: Reacting systems, mass-action kinetics, homotopy decomposition, stability analysis.

1. INTRODUCTION

In recent years, the idea of using thermodynamics as a modelling and analytic theory to be exploited for the design of feedback controllers in the context of chemical process control was revived by many researchers, see for example the contribution (Ydstie and Alonso, 1997) and references therein. Beyond the questions of stability analysis and stabilizing feedback control design under a thermodynamical evolution constraint (Hoang and Dochain, 2013; Ramirez et al., 2013), stability analysis using entropy production as a Lyapunov function candidate (Favache and Dochain, 2009; García-Sandoval et al., 2014), (classical) thermodynamics theory was also exploited for the design of state observers in (Dochain et al., 2009). From an application point of view, many studies have been conducted on the Continuously Stirred Tank Reactor (CSTR), and the proposed techniques showed great potential in applications and uncovered interesting aspects from a theoretical point of view. The general approach adopted so far consists in complementing the mass and energy balance equations with an entropy balance. In most applications considered however, it seemed that the key difficulty is the inclusion of chemical reactions, both from a modelling point of view and from the derivation of the entropy generation term associated to the chemical reactions. As illustrated in the contributions (Hoang et al., 2014) and (García-Sandoval et al., 2014), one way to alleviate this problem is to rewrite the mass-action kinetics in a thermodynamically-consistent manner, *i.e.*, to re-express mass-action kinetics a potential-driven flux.

The question of re-writing mass-action kinetics by using (irreversible) thermodynamics has been considered elsewhere in the literature, for example in (Demirel, 2007; Kjelstrup et al., 2010) (see also the contribution by Ederer and Gilles (2007) and references therein). Based on these representations, a geometric description of chemical reactions has been proposed by (Quevedo and Tapias, 2014) within the framework of geometrothermodynamics, making used of a metric structure on the thermodynamical phase space. A recent contribution by Grmela (2012) also suggests a lift of the reacting system dynamics to contact geometry in order to identify the conservative and dissipative structures associated to mass-action kinetics, once re-written in a thermodynamically-consistent manner. In (Ramírez et al., 2014), a reaction network was transformed as a dissipative Hamiltonian system, a practical formulation for stability and feedback stabilization design problems (Ortega et al., 2002). The stoichiometric aspect of the problem was also considered in recent research, see for example (Alonso, 2013) and reference therein. It should be mentioned that the contributions (van der Schaft et al.,

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2013b,a) considered both the stoichiometric network structure and the thermodynamic aspect of the problem.

In (Hoang et al., 2014), conditions for the existence of an asymptotically stable equilibrium (in that particular case, for open chemically reacting systems consisting of one reversible reaction) required two elements: (1) The equilibrium was an isolated minimum of a potential derived from the reaction affinity (Callen, 1985); and (2) The equilibrium was required to lie on a homogeneity set defined from the stoichiometry. In the present paper, we seek to extend the analysis proposed in (Hoang et al., 2014) to systems with multiple reactions, with the objective of allowing for complex dynamical behaviors, for example periodic orbits. Limiting ourselves to homogeneous closed systems, the key problem here is to understand the respective contributions of the stoichiometry and the thermodynamically-consistent mass-action kinetic expressions to the existence of such dynamical behavior.

Following observations from (Demirel, 2007, Chapter 8) and (Grmela, 2012), our first approach to this problem consists in using a homotopy decomposition approach to identify the dissipative structure of mass-action kinetics for closed homogeneous systems. In some sense, the idea here is, from the mass balance equations, to compute a potential by homotopy integration. Such integration, although not completely equivalent, could be related to the notion of integration along the "reaction path" exploited in the same context in (Kjelstrup et al., 2010) and reported in a recent study (García-Sandoval et al., 2014). The homotopy decomposition approach proposed here follows the approach developed originally in (Hudon et al., 2008), following the exposition in (Edelen, 2005), briefly reviewed in Section 3.

The paper is organized as follows. Section 2 introduce the problem following the contribution by Grmela (2012). The characterization of the invariant structure as well as stability analysis based on the homotopy decomposition are presented in Section 3. An example illustrating the approach is developed in Section 4. Conclusions and further areas for research are discussed in Section 5.

2. PROBLEM FORMULATION

We first develop the problem considered in the present paper. As stated above, the system under study is a closed homogeneous single-phase reacting system. Following the mass-action kinetics developments from (Grmela, 2012, Section 2), consider p chemical species $\mathbb{A}_1$, ..., $\mathbb{A}_p$, and denote their respective number of moles per unit volume as the vector $\boldsymbol{n} = (n_1, \ldots, n_p)^T$. Those p species are subjected to a set of q chemical reactions

$$\alpha_1^j \mathbb{A}_1 + \ldots + \alpha_p^j \mathbb{A}_p \xrightleftharpoons[k_r^j]{k_f^j} \beta_1^j \mathbb{A}_1 + \ldots + \beta_p^j \mathbb{A}_p,$$

for $j = 1, \ldots, q$. Define the (i, j)-th stoichiometric coefficients as

$$\gamma_i^j = \beta_i^j - \alpha_i^j,$$

and define the stoichiometric matrix as

$$\boldsymbol{\gamma} = \left[\gamma_i^j\right].$$

The reaction fluxes for the mass-action kinetic laws are defined as

$$Y^j = k_f^j \prod_{i=1}^{p} n_i^{\alpha_i^j} - k_r^j \prod_{i=1}^{p} n_i^{\beta_i^j},$$

for $j = 1, 2, \ldots, q$. Define the reaction fluxes vector as

$$\boldsymbol{Y} = \left[Y^j\right].$$

The time evolution of each species follows the mass-action kinetics

$$\frac{d\boldsymbol{n}}{dt} = \boldsymbol{\gamma}\boldsymbol{Y}. \tag{1}$$

In his development of the problem, Grmela (2012) studied the system (1) by developing the constitutive relation $\boldsymbol{Y}$ as the gradient of a potential Θ, which depends on the concentrations $\boldsymbol{n}$ and reactions forces, which are derived from a different potential, the entropy. To contrast this approach, the contribution (Hoang et al., 2014) re-expressed the reaction fluxes $\boldsymbol{Y}$ as functions of the affinity, *i.e.*, the dual of the extended variables are fixed by using classical irreversible thermodynamics theory (de Groot and Mazur, 1962).

Remark 1. One aspect of the approach proposed by Grmela (2012) is that the function used to generate the dual field is modulated in order to ensure certain desired properties of the potential function Θ, namely:

(P1) Θ is a real valued and sufficiently regular function of $(\boldsymbol{n}, \boldsymbol{X})$;
(P2) $\Theta(\boldsymbol{n}, 0) = 0$;
(P3) $\Theta(\boldsymbol{n}, \boldsymbol{X})$ reaches its minimum at $\boldsymbol{X} = 0$; and
(P4) $\Theta(\boldsymbol{n}, \boldsymbol{X})$ is a convex function of $\boldsymbol{X}$ in a neighborhood $\boldsymbol{X} = 0$.

In the present paper, the objective is to develop a framework such that it is possible to investigate the structure of the dynamics by using both the stoichiometry and the contributions of the reaction fluxes. To achieve this objective, our approach consists in computing a dissipative potential by homotopy decomposition. In order to keep the discussion as general as possible, we elect not to fix, at this point, the exact structure of the reaction fluxes $\boldsymbol{Y}$, beyond the dependency of the terms k_f^j and k_f^j on dual variables denoted $\boldsymbol{m}$, with respect to an unknown potential. In practice, this unknown potential is evidently the entropy, *i.e.*, $\boldsymbol{m} = \frac{\partial S}{\partial \boldsymbol{n}}$.

As a result, in the sequel, we are interested in the analysis of the following dynamical system:

$$\frac{d\boldsymbol{n}}{dt} = \boldsymbol{\gamma}\boldsymbol{Y}(\boldsymbol{n}, \boldsymbol{m}), \tag{2}$$

with, following the above notation,

$$Y^j = k_f^j(\boldsymbol{m}) \prod_{i=1}^{p} n_i^{\alpha_i^j} - k_r^j(\boldsymbol{m}) \prod_{i=1}^{p} n_i^{\beta_i^j},$$

for $j = 1, 2, \ldots, q$.

3. DECOMPOSITION, INVARIANT STRUCTURE, AND STABILITY

3.1 Homotopy Decomposition

Here, we follow the approach from (Hudon et al., 2013) to derive a suitable dissipative potential for the dynamics. The derivation of a differential one-form associated to the system (2), in the present context given in coordinates by

$$\bar{X}_0(\boldsymbol{n},\boldsymbol{m}) = \boldsymbol{\gamma}\boldsymbol{Y}(\boldsymbol{n},\boldsymbol{m})\frac{\partial}{\partial \boldsymbol{n}}$$

relies on the canonical Riemannian metric in $\mathbb{R}^n$, given as $g = dn_1 \otimes dn_1 + \ldots + dn_p \otimes dn_p$ with its associated volume form in $\Lambda^p(\mathbb{R}^p)$, expressed as $\mu = dn_1 \wedge dn_2 \wedge \ldots \wedge dn_p$. For the given drift vector field $\bar{X}_0(\boldsymbol{n},\boldsymbol{m}) = \sum_{i=1}^p \bar{X}_{0,i}(\boldsymbol{n},\boldsymbol{m})\frac{\partial}{\partial n_i}$. We first compute the divergence of the vector field $\bar{X}_0(\boldsymbol{n},\boldsymbol{m})$, computed as follows Lee (2006). A $(p-1)$ differential form j is first obtained by taking the interior product of the volume form $\mu \in \Lambda^p$ with respect to the drift vector field $\bar{X}_0(\boldsymbol{n})$, *i.e.*,

$$\begin{aligned} j &= \left(\sum_{i=1}^p \bar{X}_{0,i}(\boldsymbol{n},\boldsymbol{m})\frac{\partial}{\partial n_i}\right) \lrcorner \mu \\ &= \sum_{i=1}^p (-1)^{i-1}\bar{X}_{0,i}(\boldsymbol{n},\boldsymbol{m}) dn_1 \wedge \ldots \wedge \widehat{dn_i} \wedge \ldots \wedge dn_p, \end{aligned} \tag{3}$$

where $\widehat{dn_i}$ denotes a removed element such that j is a $(p-1)$ form. Taking the exterior derivative of j, and by the property of the wedge product that $dn_i \wedge dn_i = 0$, we obtain,

$$dj = \sum_{i=1}^p \frac{\partial \bar{X}_{0,i}}{\partial n_i}(\boldsymbol{n},\boldsymbol{m}) dn_1 \wedge \ldots \wedge dn_p = \text{div}\bar{X}_0(\boldsymbol{n},\boldsymbol{m})\mu. \tag{4}$$

The proposed construction consists in computing a differential one-form $\omega \in \Lambda^1(\mathbb{R}^p)$ that encodes the divergence of the extended drift vector field $\bar{X}_0(\boldsymbol{n},\boldsymbol{m})$. Such a one-form is obtained by using the Hodge star operator $\star$ of the $(p-1)$ form j, *i.e.*,

$$\begin{aligned} \omega = \star j &= \star(\bar{X}_0(\boldsymbol{n},\boldsymbol{m}) \lrcorner \mu) \\ &= (-1)^{p-1}\sum_{i=1}^p \bar{X}_{0,i}(\boldsymbol{n},\boldsymbol{m}) dn_i. \end{aligned} \tag{5}$$

If the one-form ω is closed, *i.e.*, if $d\omega = 0$, it can be shown that it is also locally exact, by virtue of the Poincaré Lemma, and the system is conservative (in particular, the dynamics is generated by the gradient of a potential function). However, if the one-form is not closed, ω can be decomposed as the sum of an exact component and an anti-exact component. Such decomposition can be carried locally using a homotopy operator $\mathbb{H}$ Edelen (2005), such that

$$\omega = d(\mathbb{H}\omega) + \mathbb{H}d\omega. \tag{6}$$

As a result, the one-form ω is decomposed in terms of an exact component and an anti-exact components, denoted by $\omega_e = d(\mathbb{H}\omega)$ and $\omega_a = \mathbb{H}d\omega$, respectively. In coordinates, for a differential one-form ω on a star-shaped region S centered at an equilibrium n^*, the homotopy operator is given as

$$(\mathbb{H}\omega) = \int_0^1 \mathfrak{X}(\boldsymbol{n}^* + \lambda(\boldsymbol{n}-\boldsymbol{n}^*)) \lrcorner \omega(\boldsymbol{n}^* + \lambda(\boldsymbol{n}-\boldsymbol{n}^*)\boldsymbol{m}) d\lambda, \tag{7}$$

where $\omega(\boldsymbol{n}^*+\lambda(\boldsymbol{n}-\boldsymbol{n}^*))$ denotes the differential form evaluated on the star-shaped domain in the local coordinates centered at $\boldsymbol{n}^*$. By the properties of exterior derivative, we have $d \circ d = 0$, hence the exact part ω_e is closed and exact (*i.e.*, ω_e is the exterior derivative of a 0-form, the function $\psi(\boldsymbol{n},\boldsymbol{m}) = \mathbb{H}\omega$). In terms of the obtained potential $\psi(\boldsymbol{n},\boldsymbol{m})$ and the given drift vector fields, the exact and non-exact components of the differential system are given as

$$\omega_e(\boldsymbol{n},\boldsymbol{m}) = \sum_{i=1}^p \frac{\partial \psi(\boldsymbol{n},\boldsymbol{m})}{\partial n_i} dn_i, \tag{8}$$

$$\begin{aligned} \omega_a(\boldsymbol{n},\boldsymbol{m}) &= \omega(\boldsymbol{n},\boldsymbol{m}) - \omega_e(\boldsymbol{n},\boldsymbol{m}) \\ &= \sum_{i=1}^p \left((-1)^{p-1}\bar{X}_{0,i}(\boldsymbol{n},\boldsymbol{m}) - \frac{\partial \psi(\boldsymbol{n},\boldsymbol{m})}{\partial n_i}\right) dn_i. \end{aligned} \tag{9}$$

3.2 Invariant Structure and Stability

By using the canonical metric g and the associated volume μ as defined above, it should be clear that up to a sign depending, the desired one-form ω is simply

$$\boldsymbol{\omega} = (-1)^p \boldsymbol{\gamma}\boldsymbol{Y} d\boldsymbol{n}.$$

As a result, the stoichiometry matrix does not play a prominent role in the computation of the potential $\psi(\boldsymbol{n},\boldsymbol{m})$. The key part in the integration to compute the desired potential depends on the two following factors:

- The formulation of the coefficients $k_{r,f}^j$, in particular on the dependence of their dependance on the dual variables $\boldsymbol{m}$; and
- The formulation of the auxiliary potential from which the dual variables are derived.

For example, if one considers the auxiliary potential

$$S(\boldsymbol{n}) = \sum_{i=1}^p n_i^* \ln n_i,$$

leading to dual variables of the form

$$m_i = \frac{n_i^*}{n_i},$$

and consider kinetic parameters of the form $k_{f,b}^j = \exp\left(\gamma_i^j m_i\right)$, the potential $\psi(\boldsymbol{n})$ boils down to the integration around the equilibrium point $\boldsymbol{n}^*$ (which is the minimum of the potential function by construction), of a sum of exponentials weighted by their stoichiometric weights. Alternatively, for a quadratic function $S(\boldsymbol{n})$, with the same structure for $k_{f,b}^j$, we obtain a explicit formulation for $\psi(\boldsymbol{n})$. This will be illustrated in the next section.

The key advantage of the homotopy decomposition is that it enables to distinguish two parts of the dynamics: A part that is dissipative and a part that is conserved. More precisely, once a potential $\psi(\boldsymbol{n})$ is obtained from the homotopy integration, as demonstrated in the contributions

(Hudon et al., 2008) and (Guay et al., 2012), we can compute the dissipative part of the dynamics, given by

$$\omega_e(\boldsymbol{n}) = \sum_{i=1}^{p} \frac{\partial \psi(\boldsymbol{n})}{\partial n_i} dn_i.$$

Since this one-form is exact, it is generated by a dissipative potential (hence, it defines a gradient system). Since that component is divergence-free by construction, trajectories along that part of the dynamics can be related to the stationary states following the nomenclature given in (Demirel, 2007, Chapter 8). Stability analysis based on that exact one-form can then be achieved, see for example the contribution (Guay and Hudon, 2013). As hinted by the contribution (Grmela, 2012), the potential should be convex, which is not guaranteed by construction, but it was shown in (Guay and Hudon, 2013) that under a non-degeneracy condition of the Hessian, a non-convex potential $\psi(\cdot)$ could be transformed into the desired form.

The identification of invariants of the dynamics, using that potential, can be achieved by analyzing the anti-exact part of the dynamics, *i.e.*, the one-form

$$\omega_a = \omega - \omega_e.$$

In (Guay et al., 2012), it was shown that by defining a dual to the homotopy operator, one can recover the expression for the conserved part of the dynamics.

The proposed approach to study stability and the invariant structure of reacting systems proposed here, based on the computation of a potential for the system, can be summarized as follows for a closed system of p components with their concentrations denoted by $\boldsymbol{n}$ undergoing q reactions:

1. Identify the $(p \times q)$ stoichiometric matrix $\boldsymbol{\gamma}$ and the q reaction fluxes vector $\boldsymbol{Y}$;
2. Define a potential for which the dual variables $\boldsymbol{m}$ can be computed and the structure of the kinetic parameters $k^j_{f,r}$ (from thermodynamical arguments);
3. From the vector field 2, derive a one-form ω associated to the system;
4. Compute, by homotopy integration, the dissipative potential $\psi(\boldsymbol{n})$;
5. Study the structure of the invariants by inspection of the anti-exact part $\omega_a(\boldsymbol{n})$ and the stability along the divergence-free dynamics encoded in the exact part $\omega_e(\boldsymbol{n})$.

4. EXAMPLE

To illustrate the above procedure, we consider the following reaction network:

$$S \underset{k_r^1}{\overset{k_f^1}{\rightleftharpoons}} X$$

$$X \underset{k_r^2}{\overset{k_f^2}{\rightleftharpoons}} P$$

We denote the species respective concentrations by $n_1 = S$, $n_2 = X$, and $n_3 = P$. The stoichiometric matrix is given as

$$\boldsymbol{\gamma} = \begin{bmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \end{bmatrix},$$

ad the vector of reaction fluxes is written as

$$\boldsymbol{Y}(\boldsymbol{n}, \boldsymbol{m}) = \begin{bmatrix} k_f^1(\boldsymbol{m})n_1 - k_r^1(\boldsymbol{m})n_2 \\ k_f^2(\boldsymbol{m})n_2 - k_r^2(\boldsymbol{m})n_3 \end{bmatrix},$$

leading to the dynamics

$$\begin{bmatrix} \dot{n}_1 \\ \dot{n}_2 \\ \dot{n}_3 \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} k_f^1(\boldsymbol{m})n_1 - k_r^1(\boldsymbol{m})n_2 \\ k_f^2(\boldsymbol{m})n_2 - k_r^2(\boldsymbol{m})n_3 \end{bmatrix}. \tag{10}$$

Letting the dual variable $\boldsymbol{m}$ be generated by

$$\frac{\partial S(\boldsymbol{n})}{\partial \boldsymbol{n}},$$

with $S(\boldsymbol{n})$ given by $S(\boldsymbol{n}) = \frac{1}{2}\sum_{i=1}^{3} n_i^2$, and let the kinetic coefficients be of the form $k^j_{f,b} = \exp \gamma^j_i m_i$.

$$\begin{aligned} \omega &= \star(\bar{X}_0 \lrcorner dn_1 \wedge dn_2 \wedge dn_3) \\ &= -Y^1 dn_1 + (Y^1 - Y^2) dn_2 + Y^3 dn_3. \end{aligned}$$

By homotopy integration centered at an equilibrium $\boldsymbol{x}^*$, we obtain a potential which is of the form :

$$\begin{aligned} \psi(\boldsymbol{n}) = {} & \exp\{-n_1\}(1 - n_1 - n_1 n_2 - n_1 n_3) \\ & - n_1^* \exp\{-n_1^*\}(1 - n_1) \\ & + \exp\{-n_3\}(1 - n_3 - n_1 n_3 - n_2 n_3) \\ & - n_3^* \exp\{-n_3^*\}(1 - n_3). \end{aligned} \tag{11}$$

We should remark that the terms in $\exp x_2$ cancel out, due to the particular stoichiometry of this reacting system.

Following the previous discussion at the contributions (Hudon et al., 2008) and (Guay et al., 2012), one could study the stability by using the exact part ω, *i.e.*, $\omega_e = d\psi$ and study the invariant structure of the dynamics by inspecting the anti-exact part of the dynamics, encoded by $\omega_a = \omega - \omega_e$. This will be addressed in future work.

5. CONCLUSION

We proposed an approach to study (closed) reacting systems described by thermodynamically-consistent mass-action kinetics. The objective was to identify the invariants structure of the dynamics (equilibria, periodic orbits) as parameterized by both the stochiometry and the potential-driven thermodynamical fluxes governing the kinetics. Using a homotopy decomposition, it was possible to derive a procedure to compute a general potential driving the reaction fluxes, depending on an auxiliary potential, left free at this stage of the research. Following the contribution (Grmela, 2012), the long-term objective is to develop a variational formulation for mass action kinetics, complementing the original contributions given in (Sieniutycz, 1987), using a contact geometry formalism, as studied for example in (Ramirez et al., 2013) and (Quevedo and Tapias, 2014).

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