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Stability of perturbed thermodynamic systems

Nicolas Hudon * **Juan Paulo García-Sandoval** **
N. Ha Hoang *** **Denis Dochain** ****

* *Department of Chemical Engineering, Queen's University, Kingston, ON, Canada (*nicolas.hudon@queensu.ca*)*
** *Departamento de Ingeniería Química, Universidad de Guadalajara, Calzz. Gral. Marcelino García Barragán 1451, Guadalajara, Jalisco 44430, Mexico (*paulo.garcia@cucei.udg.mx*)*
*** *Faculty of Chemical Engineering, University of Technology, VNU-HCM, 268 Ly Thuong Kiet Str., Dist. 10, HCM City, Vietnam (*ha.hoang@uclouvain.be*)*
**** *ICTEAM, Université catholique de Louvain, Louvain-la-Neuve, Belgium (*denis.dochain@uclouvain.be*)*

Abstract: In this note, we consider the problem of studying systems with a thermodynamic structure, *i.e.*, generated by a potential (or a function of a given potential), where the potential contains perturbation components. The objective here is to study how robust thermodynamic-based approaches to study stability of an isolated equilibrium are when the generating potential are not well-known. Generally, through the proposed analysis, it is shown, for a particular class of problems, that general structural properties are preserved under perturbations, in particular the dissipative structure of a particular system identified through homotopy is preserved.

Keywords: Thermodynamic, Dynamical systems, Pertubation, Stability

1. INTRODUCTION

The problem of assessing stability for dynamical systems under thermodynamic constraints has received a lot of attention, for example in the contributions by (Ydstie and Alonso, 1997), Favache and Dochain (2009), Hoang and Dochain (2013), and García-Sandoval et al. (2015b). A key idea used in this context is to relate a potential function generating the dynamics (or elements of the dynamics in the case of open systems) to Lyapunov stability theory. Generating functions from classical thermodynamic, for example the energy, the entropy, or functions generated by a Legendre transformation of a fundamental generating function (Callen, 1985), were investigated. Extending this simple, yet powerful, point of view, it has been shown in (Hoang et al., 2014), provided that a potential is known, that it is possible to construct feedback controls using potential shaping techniques. Another outcome from (Hoang et al., 2014) was the description of invariants (or equilibria) for reacting systems using potentials, in that particular case the affinity function. A different approach was presented in (Garcia-Sandoval et al., 2016), where stability results were developed for closed and open chemical thermodynamic systems by exploiting the internal entropy generation function. An interesting outcome of the contribution (Garcia-Sandoval et al., 2016) was to observe, in the Lyapunov argument derivation, a separation between local effects and far from equilibrium effects, a key question when multiple isolated equilibria coexist, an issue already outlined in the original contribution (Favache and Dochain, 2009). Moreover, following a derivation from (Kjelstrup et al., 2010), the contribution (Garcia-Sandoval et al., 2016) demonstrated an approach to express reaction kinetics in terms of reacting forces, which outlined, it turns out, how particular structural properties of reaction kinetics could be used in the formulation of stability and stabilization problems.

From a certain point of view, a limitation of those results lies in the assumption that the generating potential function is known *a priori*. This is not necessarily a bad standpoint, as this approach was considered in Classical Irreversible Thermodynamics (de Groot and Mazur, 1962), and is, plausibly, valid for chemical process control applications. However, one might want to go beyond that classical approach, and ask the following question: What happens if the generating function is not perfectly known *a priori*, and if so, is it still possible to derive a formalism for stability that takes into account the structural thermodynamic constraints? And, following the work initiated in (Hoang et al., 2014), is it still possible to achieve some control design, in particular through potential shaping, which obviously leads to the problem of describing the structure of a system equilibria, but for partially unknown dynamics.

In this note, we propose one possible approach to consider those general questions, by considering the analysis of closed reaction dynamics generated by perturbed potentials. Following some ideas explored in (Hudon et al., 2015) (see also the contribtion by Yong (2012)), we take a route that seeks to separate dissipative and conservative structures in thermodynamic systems, but adding

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a perturbation to the generating potential, an idea exposed in classical mechanics, and classically related to Kolmogoroc–Arnold–Moser (KAM) theory, as exposed in (Arnold, 1989) and (Verhulst, 1990, 2005). As mentioned in (Nicolis, 1986), the perturbation of a deterministic thermodynamic problem is one possible route to extend the analysis to stochastic thermodynamic systems, a field yet to be considered by the process control community, as opposed to the nonequilibrium thermodynamic community, see for example the contributions (Grmela, 2012) and (Grmela, 2015) for a formal approach to stochastic thermodynamic systems based on fluctuations theory.

The approach proposed here is exploratory. We first consider expression of mass-action kinetics for closed reacting systems based on generating potential functions from (Grmela, 2012), and as in the previous contribution (Hudon et al., 2015), use homotopy decomposition to extract the dissipative component, which can be used for stability analysis, see for example the contribution (Guay and Hudon, 2016). Then, we study how small perturbations of the generating potentials affect the dissipative structure. In general cases, such as those considered in (Nicolis, 1986), small perturbations affect stability, however in the present case, it is shown that as the structure of the dissipative terms are preserved, small perturbations have an effect on the analysis, but conclusions remain the same.

The paper is organized as follows. We first present the problem in its generality. Then we consider the case of reacting systems based on unperturbed potentials, following (Grmela, 2012). Analysis of the perturbed case is exposed in Section 4, as an extension of the construction proposed in (Hudon et al., 2015). An example and a discussion for future investigations are given in Sections 5 and 6, respectively.

2. FORMULATION OF A GENERAL PROBLEM

The general problem that we consider is the following. Denoting the extensive variables vector by $\boldsymbol{\eta} \in \mathbb{R}^n$, we would like to study the stability of isolated equilibrium of the dynamical system

$$\dot{\boldsymbol{\eta}} = \boldsymbol{f}(\eta), \quad \boldsymbol{\eta}(0) = \boldsymbol{\eta}_0, \tag{1}$$

in a thermodynamical setting [1] . More precisely, assuming the knowledge of a generating potential function of the extended variables $\Theta(\boldsymbol{\eta})$, and defining the intensive variables vector by the relation $\boldsymbol{m} = \nabla^T \Theta(\boldsymbol{\eta})$.

By assuming certain properties of the generating potential function, and in particular its concavity, *i.e.*, the Hessian of the potential

$$\text{Hess } \Theta(\eta) = \frac{\partial^2 \Theta}{\partial \boldsymbol{\eta}^2}$$

being negative semi-definite, we wish to re-write the dynamical system in terms of the intensive variables, *i.e.*, we consider the system

$$\dot{\boldsymbol{\eta}} = \tilde{\boldsymbol{f}}(\boldsymbol{m}), \tag{2}$$

where the intensive variables are defined as above.

One advantage of this analytic approach is that one can use the entropy generation function, parameterized by the Hessian of the generating potential, as a candidate Lyapunov function, see for example the contributions (García-Sandoval et al., 2015b) and (Garcia-Sandoval et al., 2016), where the concepts of thermodynamical forces, fluxes, and potentials are exploited to identify invariants (equilibrium of the dynamics) and stability analysis. Furthermore, in (García-Sandoval et al., 2015a), it was shown, within that framework, how to identify conservative and dissipative structures of the dynamics through a careful analysis of the different phenomena in the deterministic model.

In the present note, we want to initiate a different line of investigation, that is: What happens if the generating potential is given as

$$\Theta(\cdot) = \Theta_0(\boldsymbol{\eta}) + \sum_{i=1}^{N} \epsilon_i(\boldsymbol{\eta}) \Theta_i(\boldsymbol{\eta}),$$

and where, possibly, N tends to infinity. This could also include cases where non-vanishing and periodic potentials show as perturbations of the nominal potential. The challenge, therefore, lies in the following questions within the above framework: (1) Under which conditions the structure, *i.e.*, the invariants and the stability properties of the nominal system are conserved?; and (2) How are the dissipative and conservative structures preserved through this small perturbation analysis?

There are, it seems, strong links between this line of inquiries and classical results in classical mechanics, and in particular Kolmogorov–Arnold–Moser (KAM) theory, as exposed in (Arnold, 1989) and (Verhulst, 1990). Following the approach proposed by (Nicolis, 1986), it seems, that, at the limit, there is a link between those questions and stochastic dissipation.

The scope of the present note is not as grandiose as the above questions. We focus on a simple example and revisiting a particular approach to study dynamical systems presented in (Hudon et al., 2015) — where dissipative and conservative structures are identified through homotopy integration — as a starting point for further inquiries.

3. UNPERTURBED MASS-ACTION KINETICS

We consider a closed thermodynamical system, consisting of a homogeneous chemical mixture with 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

$$\alpha_1^j \mathbb{A}_1 + \ldots + \alpha_p^j \mathbb{A}_p \underset{k_r^j}{\overset{k_f^j}{\rightleftharpoons}} \beta_1^j \mathbb{A}_1 + \ldots + \beta_p^j \mathbb{A}_p,$$

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

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

[1] The general open controlled dynamical setting is developed, for the unperturbed case, in (Garcia-Sandoval et al., 2016). One can related this general setting to the particular case of reacting systems, covered in the following, to previous results presented in (Hoang et al., 2014)

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 $j = 1, 2, \ldots, q$. We denote the reaction fluxes vector as

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

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

$$\frac{d\boldsymbol{n}}{dt} = \boldsymbol{\gamma}\boldsymbol{Y}. \tag{3}$$

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 (Hudon et al., 2015), 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, the proposed approach consisted 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.

As a result, the analysis presented in (Hudon et al., 2015) consisted in studying of the following dynamical system:

$$\frac{d\boldsymbol{n}}{dt} = \boldsymbol{\gamma}\boldsymbol{Y}(\boldsymbol{n}, \boldsymbol{m}), \tag{4}$$

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 $j = 1, 2, \ldots, q$, and $\boldsymbol{m} = \frac{\partial S}{\partial \boldsymbol{n}}$, where S was a simple quadratic function of the concentrations n_i.

In the present note, we consider the same problem, but we set the generating potential S to be of the form

$$S(\boldsymbol{n}) = S_0(\boldsymbol{n}) + \epsilon S_1(\boldsymbol{n}), \tag{5}$$

where ϵ is a small parameter [2].

4. DERIVATION OF PERTURBED GRADIENT APPROXIMATIONS

We first derive the approach to study stability of systems of the form (4) with perturbed potentials, following the approach proposed in (Hudon et al., 2015) to extract the gradient dynamical structure and a potential from the structured mass-action kinetics representation proposed above.

4.1 Homotopy Decomposition

We follow the approach from (Hudon et al., 2008) to derive a suitable dissipative potential for the dynamics, which can be used for local stability analysis, see (Guay and Hudon, 2016). The derivation of a differential one-form associated to the system (4), 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 $\mathbb{R}^p$, 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.*,

$$\begin{aligned} j &= \left(\sum_{i=1}^{p} \bar{X}_{0,i}(\boldsymbol{n}, \boldsymbol{m}) \frac{\partial}{\partial n_i} \right) \lrcorner \mu \\ &= \sum_{i=1}^{p} (-1)^{i-1} \bar{X}_{0,i}(\boldsymbol{n}, \boldsymbol{m}) dn_1 \wedge \ldots \wedge \widehat{dn_i} \wedge \ldots \wedge dn_p, \end{aligned} \tag{6}$$

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,

$$dj = \sum_{i=1}^{p} \frac{\partial \bar{X}_{0,i}}{\partial n_i}(\boldsymbol{n}, \boldsymbol{m}) dn_1 \wedge \ldots \wedge dn_p = \mathrm{div}\bar{X}_0(\boldsymbol{n}, \boldsymbol{m})\mu. \tag{7}$$

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.*,

[2] Obviously, the perturbation considered here in (5) is rather simple, and does not cover the general case, covered for example in (Verhulst, 1990).

$$\omega = \star j = \star(\bar{X}_0(\boldsymbol{n},\boldsymbol{m}) \lrcorner \mu) = (-1)^{p-1} \sum_{i=1}^{p} \bar{X}_{0,i}(\boldsymbol{n},\boldsymbol{m}) dn_i. \quad (8)$$

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

$$\omega = d(\mathbb{H}\omega) + \mathbb{H}d\omega. \quad (9)$$

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

$$(\mathbb{H}\omega) = \int_0^1 \mathfrak{X}(\boldsymbol{n}^* + \lambda(\boldsymbol{n}-\boldsymbol{n}^*)) \lrcorner \omega(\boldsymbol{n}^* + \lambda(\boldsymbol{n}-\boldsymbol{n}^*)\boldsymbol{m}) d\lambda, \quad (10)$$

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

$$\omega_e(\boldsymbol{n},\boldsymbol{m}) = \sum_{i=1}^{p} \frac{\partial \psi(\boldsymbol{n},\boldsymbol{m})}{\partial n_i} dn_i, \quad (11)$$

$$\omega_a(\boldsymbol{n},\boldsymbol{m}) = \omega(\boldsymbol{n},\boldsymbol{m}) - \omega_e(\boldsymbol{n},\boldsymbol{m}) = \sum_{i=1}^{p} \left((-1)^{p-1} \bar{X}_{0,i}(\boldsymbol{n},\boldsymbol{m}) - \frac{\partial \psi(\boldsymbol{n},\boldsymbol{m})}{\partial n_i} \right) dn_i. \quad (12)$$

4.2 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, the desired one-form ω is simply

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

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 $k^j_{r,f}$, in particular on the dependence 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 $k^j_{f,b} = \exp\left(\gamma^j_i m_i\right)$, 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 $k^j_{f,b}$, we obtain an explicit formulation for $\psi(\boldsymbol{n})$.

The key element to be considered in the present note is to perturb the generating potential, and in particular, to study how stability can be studied for perturbed potentials, for example

$$S(\boldsymbol{n}) = \underbrace{\sum_{i=1}^{p} n_i^2}_{S_0(\boldsymbol{n})} + \epsilon \underbrace{\sum_{i=1}^{p} n_i^* \ln n_i}_{S_1(\boldsymbol{n})},$$

which would lead to dual variables of the form

$$m_i = n_i + \epsilon \frac{n_i^*}{n_i}.$$

The key advantage of the homotopy decomposition, a linear integral operator, 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), 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, 2016). 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 proposed approach to study stability and the invariant structure of reacting systems proposed in (Hudon et al., 2015), based on the computation of a potential for the perturbed system, can be summarized as follows:

(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 4, 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 $\omega_e(\boldsymbol{n})$.

5. EXAMPLE

To illustrate the above approach, we consider the following reaction network (Demirel, 2007, Chapter 8):

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

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

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

$$\begin{bmatrix} \dot{n}_1 \\ \dot{n}_2 \\ \dot{n}_3 \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} k_f^1(\boldsymbol{m})n_1 - k_r^1(\boldsymbol{m})n_2 \\ k_f^2(\boldsymbol{m})n_2 - k_r^2(\boldsymbol{m})n_3 \end{bmatrix}. \tag{13}$$

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

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

5.1 Nominal case

In (Hudon et al., 2015), the entropy, as a generating function, was assumed to be of the form

$$S(\boldsymbol{n}) = \frac{1}{2}\sum_{i=1}^{3} n_i^2,$$

, and the kinetic coefficients were of the form $k_{f,b}^j = \exp \gamma_i^j m_i$. By computing

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

and by homotopy integration centered at an equilibrium $\boldsymbol{x}^*$, the computed potential for the unperturbed problem was of the form:

$$\begin{aligned} \psi(\boldsymbol{n}) = &\exp\{-n_1\}(1 - n_1 - n_1 n_2 - n_1 n_3) \\ &- n_1^* \exp\{-n_1^*\}(1 - n_1) \\ &+ \exp\{-n_3\}(1 - n_3 - n_1 n_3 - n_2 n_3) \\ &- n_3^* \exp\{-n_3^*\}(1 - n_3). \end{aligned} \tag{14}$$

This potential generated the dissipative structure of the dynamics. Following previous contributions, stability of the unperturbed dynamics can be studied through the properties of the Hessian of the computed potential, see for example the exposition (Guay and Hudon, 2016). Furthermore, potential shaping can be achieved using this potential as a basis.

5.2 Perturbed case

We now consider a perturbed potential $S(\boldsymbol{n}, \epsilon)$ of the form

$$S(\boldsymbol{n}) = \underbrace{\frac{1}{2}\sum_{i=1}^{3} n_i^2}_{S_0(\boldsymbol{m})} + \epsilon \underbrace{\sum_{i=1}^{3} n_i^* n_i}_{S_1(\boldsymbol{m})},$$

keeping the kinetic coefficients of the form $k_{f,b}^j = \exp \gamma_i^j m_i$. By computing

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

and by homotopy integration centered at an equilibrium $\boldsymbol{x}^*$, the computed potential for the unperturbed problem is now of the form:

$$\begin{aligned} \psi(\boldsymbol{n}) = &\exp\{-\phi_1(n_1, n_1^*, \epsilon)\}(1 - n_1 - n_1 n_2 - n_1 n_3) \\ &- n_1^* \exp\{-\phi_1(n_1, n_1^*, \epsilon)\}(1 - n_1) \\ &+ \exp\{-\phi_3(n_3, n_3^* \epsilon)\}(1 - n_3 - n_1 n_3 - n_2 n_3) \\ &- n_3^* \exp\{-\phi_3^*(n_3, n_3^*, \epsilon)\}(1 - n_3), \end{aligned} \tag{15}$$

where $\phi_i(\cdot)$ are smooth functions.

In other words, for the motivating class of dynamical system — and as expected from, for example the representation of reacting dynamics in (Kjelstrup et al., 2010), (García-Sandoval et al., 2015b), and (Hoang et al., 2014) — only the force terms are modified by a perturbation of the generating potential, and in particular, the general structure of the system, and in particular, the stoichiometry of the system remains intact, which is the key element outlined by homotopy computation of dissipative potentials. It remains to consider if that property is a generic one.

5.3 Discussion

To borrow the nomenclature used in (García-Sandoval et al., 2015b), small perturbations of generating potentials thus affect the amplitude of the thermodynamic forces, and hence, do not affect the structure of the dynamics. The dissipative structure, and as a result, the stability analysis based on that dissipative structure remains intact. In other words, looking back at the setup outlined in Section 2, by perturbing the potential $\Theta(\boldsymbol{m}) = \Theta_0(\boldsymbol{m}) + \epsilon\Theta_1(\boldsymbol{m}) + \ldots$, the structure of the vector field

$$\dot{\boldsymbol{\eta}} = \tilde{\boldsymbol{f}}(\boldsymbol{m})$$

is not modified.

However, the stability analysis would differ, through the Hessian matrix of the potential, *i.e.*, one has to consider the properties of Hess $\Theta(\boldsymbol{m})$, and in particular, if this matrix remains negative-semidefinite, at least in a neighborhood of an equilibrium of the system. The computation of a dissipative potential and the associated dissipative structure, as proposed above, remains a plausible approach for analysis.

6. CONCLUSIONS

In this note, we considered the problem of studying dynamical systems with a thermodynamic structure, *i.e.*, generated by a potential, in the case where the potential is perturbed, specializing our discussion to closed homogeneous reacting systems. Following an approach considered previously where the gradient structure of the dynamical system is extracted by homotopy integration, we obtain a perturbed potential to assess stability. The key question here is to decide if dynamical properties, in particular stability and invariant structure, are altered by those perturbations. Following the discussion from the classical contribution (Nicolis, 1986), this constitutes an approach from deterministic to stochastic systems, the latter class of systems to be considered in future research.

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