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Stability of perturbed thermodynamic systems

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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)