Effect of mesoscopic conservative phenomena in the dynamics of chemical reactions at the macroscopic scale[☆]

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HIGHLIGHTS

- Mesoscopic conservative phenomena can be implicit in macroscopic reaction rates.
- An isolated reacting system may have increments in the entropy production.
- A formulation of the dynamics that enhances the stability analysis is proposed.
- Coupling in reaction networks as a source of instability is pointed out.

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ABSTRACT

This paper studies the influence of conservative phenomena at the mesoscopic scale that affect the behavior of macroscopic variables in chemical reactions, generally understood as purely dissipative processes and whose mathematical formulation is usually derived using macroscopic variables. It is shown that conservative phenomena at the mesoscopic scale can affect the entropy production by transiently "pulling away" the system from the thermodynamic equilibrium. Two case studies are presented to illustrate this fact: the first one is an isolated system with a single reaction including two different scenarios, a purely dissipative reaction; and a second one that considers the influence of conservative elements at the mesoscopic scale. The second case generalizes the results to multiple reactions.

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1. Introduction

The non-linear nature of chemical reactions along with their activated behavior have been common difficulties to model dynamics with enough physical consistency for several applications where stability properties are of special concern. For instance, in process control several approaches where the dissipative properties of chemical reactions have been exploited using thermodynamic properties as state variables [2–5], but only recently the importance of using thermodynamically consistent reaction rates has been recognized, motivating the use of potential driven expressions to formulate mass action kinetics [6–8]. A thermodynamically consistent formulation of the kinetics can generate new insights in the study of stability properties of chemical reaction networks if transient properties such as energy dissipation or entropy production are

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computed [9,10]. Also, many hypothetical reaction models that qualitatively reproduce experimentally observed complex dynamics such as chaos or oscillations have been proposed (*e.g.*, the Brusselator in [11]), and although these models have been helpful to understand the importance of the reaction mechanisms in the stability properties, their physical interpretation still might not be complete.

For a more thoughtful stability analysis, then detail of the transition from reactants into products should be considered at some degree. A direct macroscopic formulation, specially using empiric expressions, may lack information of the energetic transitions that could lead to less accurate entropy production rates. A summary of the mesoscopic phenomena should be considered for the macroscopic formulation [12].

There are several approaches to obtain a mesoscopic description of physical phenomena depending on the desired level of detail, *i.e.*, some are "more microscopic" than others. The use of extended state spaces in order to introduce fluctuations or detail of the fluxes [13], specifically the reaction rates as independent state variables has been studied, allowing a description for both fast and slow variables, and fluctuations due to random forces [14] or coupling it with mechanics, for instance [15]. Other approaches that result in a stochastic description of the dynamics have been made [12,16,14,17].

On the other hand, with the use of internal variables, de Groot and Mazur (see [18]) showed that the nonlinear relation between the driving forces and the kinetics expressions for chemical reactions at macroscopic scale can be derived by considering a linear relation of the driving forces at the mesoscopic scale. This approach was further developed in [19,20,17] to derive thermodynamically consistent expressions, in a formalism known as mesoscopic non-equilibrium thermodynamics (MNET), an extension to classical linear non-equilibrium thermodynamics that considers nonlinear force–flux relations. Some of the applications using internal variables can range from the description of intermediate states in a chemical reaction, dipole orientation in an electric field, conformational stages in a macromolecule, among others.

The conservative phenomena affect the stability properties specially far from the thermodynamic equilibrium and in this regard, in [21] a methodology to analyze the stability and passivity properties of thermodynamic systems has been proposed by considering the entropy production as a Lyapunov or a storage candidate function [1,22,23]. Following this idea, this contribution analyzes the effect of the conservative dynamics at the mesoscopic scale on the stability and convergence properties at the macroscopic scale using a particular reformulation of the reaction dynamics that enhances the stability analysis. Thus, the purpose of this paper is to show how conservative phenomena at the mesoscopic scale can influence the macroscopic variables, in particular it is shown that the entropy production for isolated reacting systems can transiently increase, due to the reversible energy conversions that occur when an energy barrier is present, producing also diverse qualitative behaviors in macroscopic variables such as conversion and temperature.

This paper is organized as follows. In Section 2, the class and the properties of the thermodynamic systems considered are defined and analyzed. In Section 3 following the MNET approach proposed by [19,20,17] we derive a reaction rate considering a reversible phenomenon when an energy barrier is present using an alternative definition for the mesoscopic affinity along the reaction path. Then, in Section 4, an entropic formulation for macroscopic phenomena is proposed, showing how the mesoscopic conservative phenomena can manifest in macroscopic systems far from equilibrium. Finally, in Section 5, two case studies are developed. First, two scenarios for a single reaction are considered: A purely dissipative reaction at the mesoscopic scale; and a case that considers the influence of a conservative element. Those scenarios are fully developed using the ideal gas state equation to easily compute all the thermodynamic properties. The second example generalizes the results to multiple reactions, leading to a quasi-quadratic structure whose stability properties can be analyzed through the elements of a computed matrix.

2. Spatially homogeneous reacting systems

Let us consider an isochoric isolated system Π assumed to be completely mixed. It is assumed that no spatial gradients are present, and the system Π can be fully characterized by two extensive properties: The moles, $\mathbf{N}$; and the total internal energy, $U = \mathbf{N}^{\mathrm{T}}\mathbf{u}$.[1] The internal energy vector is denoted by $\mathbf{u}$, thus the state vector is $\boldsymbol{\eta} = \mathrm{col}\{\mathbf{N}, U\} \in (\mathbb{R}_{\geq 0}^{n} \times \mathbb{R})$. The associated intensive properties vector is given by $\boldsymbol{\zeta} = \mathrm{col}\{-\boldsymbol{\mu}/T, 1/T\} \in (\mathbb{R}^{n} \times \mathbb{R}_{+})$.

Since the system is isolated, the mass and internal energy of the system are constant, *i.e.*, given the initials mole vector, $\mathbf{N}_0$, and internal energy, U_0, it holds that $\mathbf{M}_w^{\mathrm{T}}\mathbf{N}_0 = \mathbf{M}_w^{\mathrm{T}}\mathbf{N}$ and $U_0 = U$, where $\mathbf{M}_w = \mathrm{col}\{m_{w,1}, \ldots, m_{w,n}\}$ is the vector of molar masses. We consider that ω reversible chemical reactions involving n chemical species can take place in the system. Thus the dynamical behavior of the state vector is given by

$$\Pi : \dot{\boldsymbol{\eta}} = MV\mathbf{r}(\boldsymbol{\zeta}), \tag{1}$$

where $V \in \mathbb{R}_+$ is the volume, $\mathbf{r} : (\mathbb{R}^n \times \mathbb{R}_+) \to \mathbb{R}^\omega$ is the vector field of the specific chemical reactions kinetics, which are considered to be function of the intensive properties, and $M = \left(\Gamma^{\mathrm{T}} \quad \mathbf{0}_{1\times\omega}^{\mathrm{T}}\right)^{\mathrm{T}}$ is an interconnection matrix, where Γ is the stoichiometric matrix and $\mathbf{0}$ is a vector of zeros. The general chemical reaction used here is of the form

$$\mathbf{A}^{\mathrm{T}}\mathbf{E} \rightleftharpoons \mathbf{B}^{\mathrm{T}}\mathbf{E}, \tag{2}$$

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[1] In order to simplify operations a vector notation is used, *e.g.*, $\mathbf{N}^{\mathrm{T}}\mathbf{u}$ instead of $\sum_{i=1}^{n} N_i u_i$. All vectors, including gradients, are column vectors.