On the Relation Between Reaction Dynamics and Thermodynamics in Closed Systems

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Abstract— **A reactive system's slow dynamic behavior is approximated well by its evolution on manifolds of dimension lower than the dimensionality of the full composition space. This work addresses the relation between the isothermal reactive systems' slow dynamics, described by the actual slow invariant manifolds, and notions from thermodynamics. In addition to mathematical proof, a realistic reactive system is utilized to show that other than identifying the actual equilibrium point, traditional thermodynamic potentials provide no guidance in determining a system's actual slow invariant manifold. A comparison between several published thermodynamics-based manifolds and the actual slow invariant manifolds is presented.**

I. INTRODUCTION

Dimension reduction can significantly reduce the computational cost of modeling detailed kinetics reactive systems. The technique is based on representing the chemistry of a reactive system's variables in terms of the chemistry of a reduced number of variables. Thus, several methods to describe the multi-scale kinetics that employ a geometrical approach have been developed to reduce the dimensionality of reactive systems.

A number of these methods employ classical thermodynamics to construct the attractive manifolds. Examples include the method of rate-controlled constrained equilibrium (RCCE) [1], the method of invariant manifold (MIM) [2], the minimal entropy production trajectory (MEPT) method [3], the invariant constrained equilibrium edge preimage curve method (ICE-PIC) [4], and other methods which are based on them [5]-[7]. The MEPT approach relies on the principle of entropy production. Utilizing such a principle allows classical thermodynamics quantities to be used away from equilibrium, although the validity of doing this is debatable [8]. The RCCE, MIM and ICE-PIC approaches rely on employing equilibrium thermodynamics potentials away from the equilibrium state. By minimizing the appropriate classical thermodynamics quantities, at some point in the procedure, their low-dimensional manifolds are constructed.

Ref. [9] provides a procedure to construct reactive systems' actual slow invariant manifolds (SIMs). Such manifolds describe the asymptotic structures of the invariant attracting reactive systems' trajectories during their relaxation toward equilibrium. Utilizing this procedure to construct reactive systems' actual one-dimensional (1-D) SIMs makes it possible to examine the relation between thermodynamics and reactive systems' slow dynamics.

II. ANALYSIS

We consider a closed, spatially homogenous, premixed reactive mixture of calorically imperfect ideal gases described by detailed mass-action kinetics. The mixture is confined to a volume V at temperature T and pressure p. This mixture consists of N species composed of L atomic elements which undergo J reversible reactions.

Here, we confine our attention to isothermal reactive systems. For such a reactive system, the evolution of the species specific moles $\mathbf{z}$ with time t is described by [9]

$$\frac{d\mathbf{z}}{dt} = \dot{\mathbf{w}}(\mathbf{z}), \quad \{\mathbf{z}, \dot{\mathbf{w}}\} \in \mathbb{R}^R, \tag{1}$$

where $\mathbb{R}^R \subset \mathbb{R}^N$ is the reduced composition space, and $\dot{\mathbf{w}}$ is the molar production rate of species in the reduced composition space. The dimensionality of the composition space is reduced to R as a consequence of the conservation of elements, and any additional constraints that can possibly arise. The system's actual 1-D SIM can be constructed by using the procedure described in [9].

A. Thermodynamic conditions

For a mixture of ideal gases, the Gibbs free energy G is given by the following relation [10],

$$G = \sum_{i=1}^{N} n_i \bar{\mu}_i, \tag{2}$$

where n_i is the number of moles of species i, and $\bar{\mu}_i$ is the chemical potential of species i. This thermodynamic property is of special interest; the global minimum of G corresponds to the reactive system's equilibrium state $\mathbf{z}^e$ which satisfies $\dot{\mathbf{w}}(\mathbf{z}^e) = \mathbf{0}$ [10]. This state is unique [11] within the physical region of composition space and is identified by the following relation,

$$\sum_{i=1}^{N} \nu_{ij} \bar{\mu}_i = 0, \quad j = 1, \ldots, J, \tag{3}$$

where ν_{ij} is net stoichiometric matrix.

Similarly, the entropy S of such mixture is given by [10],

$$S = \sum_{i=1}^{N} n_i \left(\bar{s}_i^o - \bar{\Re} \ln \left(\frac{p \; n_i}{p^o \; n} \right) \right), \tag{4}$$

where $\bar{\Re}$ is the universal gas constant, p^o is the reference pressure, $\bar{s}_i^o$ is the partial molar entropy evaluated at p^o, and $n = \sum_{i=1}^{N} n_i$ is the total number of moles. The differential change of this scalar quantity is postulated by the second law of thermodynamics [10], though it is stated differently in non-equilibrium thermodynamics and classical thermodynamics [12]. In non-equilibrium thermodynamics, the differential change of S for such system is given by

$$dS = d_e S + d_i S, \tag{5}$$

where $d_e S$ is the change in S due to the system's exchange of matter and energy with its surroundings, and

$$d_i S = -\frac{1}{T} \sum_{i=1}^{N} \bar{\mu}_i dn_i, \tag{6}$$

is the change in entropy due to irreversible processes within the system boundary [13]. Thus, an expression for the irreversibility production rate σ, (*i.e.* entropy production rate), can be introduced as [14]

$$\sigma \equiv \frac{d_i S}{dt} = -\frac{1}{T} \sum_{i=1}^{N} \bar{\mu}_i \frac{dn_i}{dt}. \tag{7}$$

Similar to G, σ is a convex function in the composition space with a global minimum at $\mathbf{z}^e$.

B. Thermodynamics and SIM

In a 2-D composition space, the scalar fields G and σ can be represented by iso-contours. Near equilibrium these contours approach ellipses. For each of these functions, the major axes of these ellipses are aligned with the eigenvector associated with the largest eigenvalue of that function's local Hessian matrix $\mathbf{H}^e$. Similarly, the minor axes are aligned with the eigenvector associated with the smallest eigenvalue of $\mathbf{H}^e$. The deviations from these two functions' equilibrium values are described by,

$$\begin{aligned} G - G|_{\mathbf{z}=\mathbf{z}^e} &= \frac{1}{2}\mathbf{z}^T \cdot \mathbf{H}^e_G \cdot \mathbf{z} + \ldots, & (8) \\ \sigma - \sigma|_{\mathbf{z}=\mathbf{z}^e} &= \frac{1}{2}\mathbf{z}^T \cdot \mathbf{H}^e_\sigma \cdot \mathbf{z} + \ldots. & (9) \end{aligned}$$

In general, all the system's trajectories within the physically accessible domain $\mathbb{S}$ approach $\mathbf{z}^e$ in infinite time. Near equilibrium, the system's dynamics relax onto the eigenvector associated with the slowest time scale. At $\mathbf{z}^e$, the eigenvector associated with the least negative eigenvalue of the local Jacobian $\mathbf{J}^e$ defines the direction of the system's slowest mode. At $\mathbf{z}^e$ there is a relation between $\mathbf{H}^e_G$ and $\mathbf{H}^e_\sigma$; one can show that

$$\mathbf{H}^e_\sigma = -\frac{1}{T}\left(\mathbf{H}^e_G \cdot \mathbf{J}^e + (\mathbf{H}^e_G \cdot \mathbf{J}^e)^T\right), \tag{10}$$

where the two terms on the right hand side of (10) are transposes of one another, and their summation is a symmetric matrix.

In the highly unusual case in which $\mathbf{H}^e_G$ is diagonal with identical eigenvalues, the SIM can be identified by consideration of the eigenvectors of $\mathbf{H}^e_\sigma$. In general, this is not the case for reactive systems. Thus, $\mathbf{H}^e_G$ operates on $\mathbf{J}^e$ in a non-uniform way, such that the eigenvalues and the eigenvectors of $\mathbf{H}^e_\sigma$ are not the same as those of $\mathbf{J}^e$. Thus, the system's dynamics cannot be deduced by σ or G. We can state that employing equilibrium thermodynamic potentials to obtain a reactive system's dynamic behavior is incorrect. Full details are given by Al-Khateeb, *et al.* [9].

III. MODEL PROBLEM

Here, the Zeldovich mechanism will be employed as a model problem to examine the relation between slow dynamics and thermodynamics. The system's actual 1-D SIM constructed using the procedure described in [9] is shown in Fig. 1.

After calculating G and σ for this system, their iso-contours, along with the system's actual 1-D SIM, are shown in Fig. 2. The top panel of Fig. 2 shows the contours of G and σ far away from the system's physical equilibrium point, R_3. The bottom panel of Fig. 2 is an expansion in its vicinity, where stretching has been employed to expose the difference between the contours' major/minor axes and the 1-D SIM. Even within the close neighborhood of R_3, the contours' axes are not aligned with the 1-D SIM! Here equilibrium thermodynamics quantities cannot elucidate the 1-D SIM, which describes the system's preferred path towards equilibrium. Subsequently, the gradients of these thermodynamic scalar functions do not drive the system's dynamics.

Explicitly, the eigenvalues and the associated eigenvectors of $\mathbf{H}^e_\sigma$ and $\mathbf{H}^e_G$ for the Zel'dovich model are

$$\begin{aligned} \mathbf{H}^e_\sigma &: (\boldsymbol{\lambda}, \boldsymbol{\upsilon}) = (8.17 \times 10^{23}, 1.01 \times 10^{20}), \\ &\quad ([1.78 \times 10^{-3}, -1.00]^T, [-1.00, -1.78 \times 10^{-3}]^T), \\ \mathbf{H}^e_G &: (\boldsymbol{\lambda}, \boldsymbol{\upsilon}) = (9.44 \times 10^{19}, 1.06 \times 10^{18}), \\ &\quad ([5.97 \times 10^{-4}, -1.00]^T, [-1.00, -5.97 \times 10^{-4}]^T). \end{aligned}$$

However, the direction of the slow mode is assigned by the eigenvector associated with the least negative

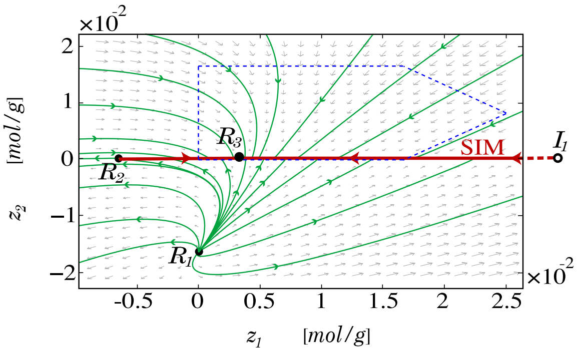

Fig. 1. A region of the finite phase space for the Zel'dovich mechanism. The solid dots represent finite critical points, the open circle represents an infinite critical point, the arrows indicate the flow direction, and the dashed simplex represents $\mathbb{S}$. The SIM is illustrated as a thick line, the thin lines represent trajectories, and R_3 represents the system's physical equilibrium state.

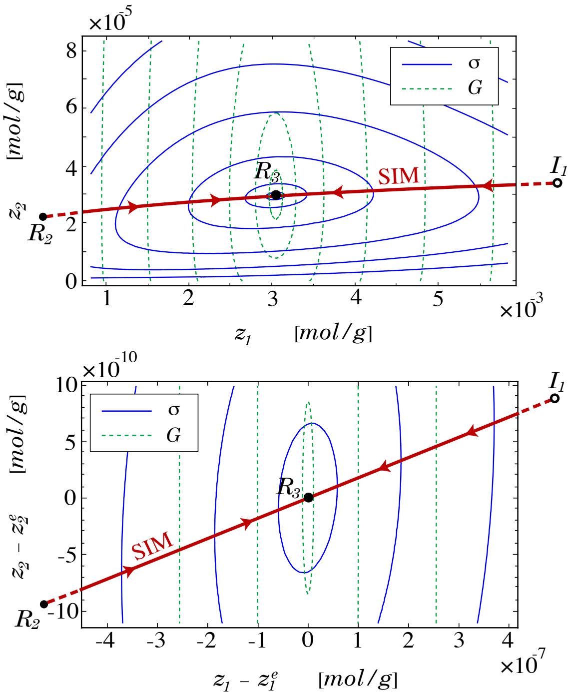

Fig. 2. The 1- D SIM for the Zel'dovich mechanism near the physical equilibrium state, R_3. The dashed lines and the solid lines represent different levels of the system's irreversibility production rate and Gibbs free energy, respectively. R_2 is a finite critical point, and I_1 is an infinite critical point.

eigenvalue of $\mathbf{J}^e$, where

$$\mathbf{J}^e : (\boldsymbol{\lambda}, \boldsymbol{\upsilon}) = (-1.73 \times 10^7, -1.91 \times 10^5),$$
$$([-1.07 \times 10^{-1}, 9.94 \times 10^{-1}]^T, [1.00, 1.79 \times 10^{-3}]^T).$$

Here, the eigenvalues' and eigenvectors' units are $1/s$ and g/mol, respectively. It is clear that the second eigenvector of $\mathbf{J}^e$ is not aligned with any eigenvector of $\mathbf{H}^e_G$ or $\mathbf{H}^e_\sigma$. Indeed, at R_3 the difference with σ is small. But, as shown in the first panel of Fig. 2, this error grows as we move away from R_3.

IV. THERMODYNAMICS-BASED MANIFOLDS

Here, a comparison between previously published reactive systems' low dimensional manifolds and the actual SIMs for these reactive systems is performed.

A. SIM and MEPT

A simple closed reactive system containing three species given by the following kinetics model, $A + A \rightleftharpoons B \rightleftharpoons C$, is considered. This system is identical to the example employed in [3] to present the MEPT method. To construct the system's actual 1-D SIM, the methodology presented in [9] is employed. In Fig. 3, the system's actual 1-D SIM is shown. We note that the system's 1-D SIM contains only one branch.

The MEPT method is based on minimizing a classical thermodynamic potential, S. Given by the dashed line in the first panel of Fig. 4, the MEPT path shown is identical to the one presented in Fig. 4 of [3]. A closer look at the system's dynamical behavior near the physical equilibrium shows that the MEPT is not an attractive manifold; see the second panel of Fig. 4. Consequently, it does not correspond to the actual SIM of the system.

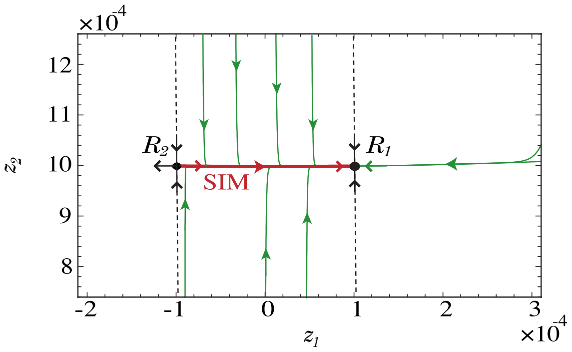

Fig. 3. A small region of the actual finite phase space. The thick line is the SIM, the thin lines represent trajectories, the dashed lines represent the fast invariant manifolds, R_2 is a non-physical finite critical point, and R_1 represents the system's physical equilibrium state.

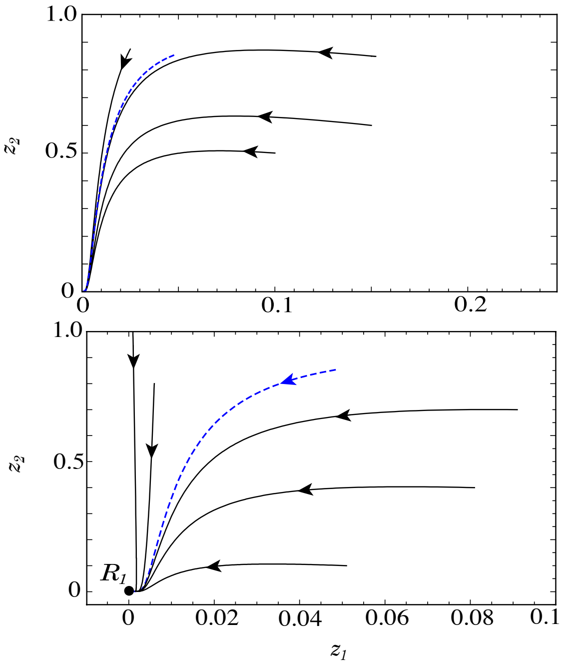

Fig. 4. The dashed line represents the calculated MEPT and the thin lines represent trajectories. The top panel is identical to Fig. (4) in [3], while the bottom panel is a closer look with a different set of trajectories is illustrated. R_1 represent the physical equilibrium state of the system.

From Figs. 3-4, we note that none of the trajectories other than the SIM are attractive. Furthermore, due to the fact that all trajectories will approach R_1, this possibly led to the incorrect conclusion in [3] that the MEPT corresponds to the SIM.

B. SIM and ICE-PIC

Here, the simple hydrogen-oxygen reactive system employed in [4] to illustrate the idea of constructing the ICE-PIC manifold is adopted. To construct the system's actual 1-D SIM, the methodology presented in [9] is used, and the system's 1-D SIM is shown in Fig. 5. The right branch of the SIM is not presented completely due to scaling effects. Some of the trajectories in Fig. 5 have been generated from inside the physical domain, while others have been initiated from the boundaries of the physical domain. The attractiveness of the SIM is revealed by visually examining the relaxation of several trajectories rapidly onto it.

Generating the ICE manifold is based on minimizing a classical thermodynamics potential. First, the constrained equilibrium manifold (CEM) is developed by minimizing G. The intersection between the CEM and $\mathbb{S}$ defines a closed curve. Then, starting from several points located on this closed curve, trajectories are generated. The collection of all these trajectories defines the ICE manifold. Fig. 6 shows the constructed 1-D SIM and the 2-D ICE manifold. The ICE manifold shown is identical to the manifold illustrated in Fig. 4 of [4].

From Fig. 6, it is clear that there are trajectories within $\mathbb{S}$ which are not attracted to the 2-D ICE manifold. However, all of the system's trajectories are attracted to the actual 1-D SIM. Moreover, the 1-D SIM is not a subset of the 2-D ICE manifold. Consequently, the 2-D ICE manifold cannot fully identify the system's SIM. Although it is difficult to visualize in Fig. 6, the 2-D ICE manifold is not aligned with the system's 1-D SIM. The error in the ICE manifold grows as we move away from R_7.

V. CONCLUSION

The relationship between thermodynamics and a reactive system's SIM is investigated. It has been illustrated that the 1-D SIM for a realistic reactive system does not coincide with the path identified by minimizing a classical thermodynamic function, such as σ, S, or G, even at the equilibrium state! This point has been confirmed by mathematical proof which shows that classical equilibrium thermodynamic potentials do not provide information about reactive systems' dynamics during their approach towards the physical equilibrium.

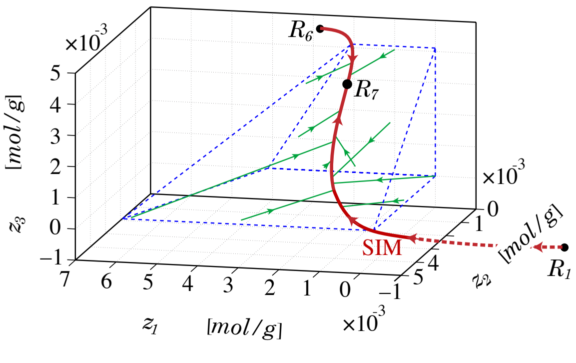

Fig. 5. The SIM for the simple hydrogen-oxygen reactive system as a thick line. R_7 represents the physical equilibrium state, R_1 and R_6 are non-physical finite critical points, the dashed simplex represents $\mathbb{S}$, and the thin lines illustrate several trajectories.

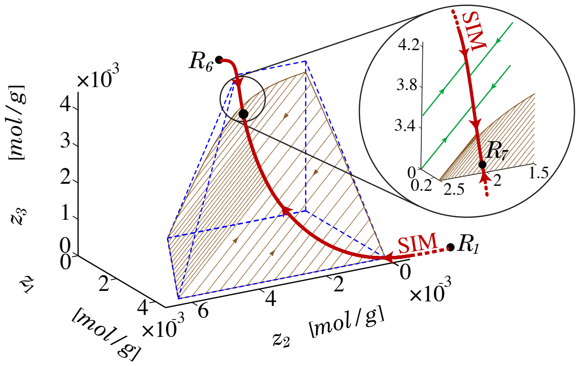

Fig. 6. A comparison between the actual 1-D SIM, illustrated as thick line, and the 2-D ICE manifold, illustrated in brown, for the simple hydrogen-oxygen reactive system. Thin lines illustrate trajectories inside $\mathbb{S}$.

ACKNOWLEDGMENTS

The authors recognize the support of the National Science Foundation (NSF) under $CBET$-0650843, and the Center for Applied Mathematics (CAM) at the University of Notre Dame. A. J. Sommese is supported by NSF grants DMS-0410047 and DMS-0712910, and J. A. Diller is supported by NSF grant DMS-0653678.

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