

# FEATURES IN CHEMICAL KINETICS. III. ATTRACTING SUBSPACES IN A HYPER-SPHERICAL REPRESENTATION OF THE REACTIVE SYSTEM

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## Abstract

In this work we deal with general reactive systems involving  $N$  species and  $M$  elementary reactions under applicability of the mass-action law. Starting from the dynamic variables introduced in two previous works [P. Nicolini and D. Frezzato, *J. Chem. Phys.*, **138**, 234101 (2013); *ibid.*, *J. Chem. Phys.*, **138**, 234102 (2013)], we turn to a new representation in which the system state is specified in a  $(N \times M)^2$ -dimensional space by a point whose coordinates have physical dimension of inverse-of-time. By adopting hyper-spherical coordinates (a set of dimensionless "angular" variables and a single "radial" one with physical dimension of inverse-of-time), and by examining the properties of their evolution law both formally and numerically on model kinetic schemes, we show that the system evolves towards the equilibrium as being attracted by a sequence of fixed subspaces (one at a time) each associated with a compact domain of the concentration space. Thus, we point out that also for general non-linear kinetics there exist fixed "objects" on the global scale, although they are conceived in such an abstract and extended space. Moreover we propose a link between the persistence of the belonging of a trajectory to such subspaces and the closeness to the slow manifold which would be perceived by looking at the bundling of the trajectories in the concentration space.

## I. INTRODUCTION

Since one and a half century, the mass-action law is the theoretical paradigm to describe the time evolution of macroscopic and well-stirred reactive systems under isothermal conditions. Mathematically, it leads to a system of polynomial ordinary differential equations (ODEs) for the species volumetric concentrations taken as dynamic variables[1]. If the concentrations of  $N$  involved species are collected in the vector  $\mathbf{x}$ , the ODE system is  $\dot{\mathbf{x}} = \mathbf{F}(\mathbf{x})$ , with  $F_j(\mathbf{x})$  multivariate polynomials.

In a couple of recent works, “Part I”[2] and “Part II”[3], we have shown that the conversion of the original ODE system into “canonical formats” can be an efficient strategy to unveil some ubiquitous features which would remain otherwise hidden due to the non-linear nature of the evolution. With the expression “canonical format” we mean an evolution law whose mathematical structure is “universal”, namely related to the given class of dynamics but devoid of any specific parameter of the system under consideration. All the system-dependent parameters (stoichiometric coefficients, values of the kinetic constants, initial state of the reactive system in the concentration space) should affect *only* the initial conditions. In our perspective, a canonical format may be achieved by means of a suitable change/extension of the set of dynamic variables. Such an extension clearly implies mutual constraints among the new variables, which keep the number of degrees of freedom equal to  $N$ . If some “characteristic feature” emerges from the examination of a canonical format, then one returns back to the original physical space to see what such a feature implies in terms of traits that can be observed (or expected *a priori*). This kind of approach has been adopted in Ref. [2], where a “quadratization” procedure was applied to work out a universal ODE system with quadratic equations in the new variables. By means of a combined formal/heuristic examination of such a format, we could provide a definition of the slow(est) manifold (SM). Qualitatively, the SM is the perceived hyper-surface in whose neighborhood the trajectories of the reactive system bundle before approaching the equilibrium states[3]. Formal definition and operative identification of the SM play a crucial role in strategies aimed to achieve a simplification of the kinetics description via a dimensionality reduction of the problem (*i.e.*, a reduction of the number of relevant degrees of freedom) in the final and slowest tail of evolution. For a review on this topic we address the interested reader to the excellent introductions of Refs. [4–6] (see also our outline in Ref. [3] and references therein).

In this “Part III” of our investigation into deterministic chemical kinetics, we consider the following question:

*In spite of the non-linearity of the original ODEs, is there a canonical representation*

of the reactive system capable to “let emerge” the existence of fixed subspaces (in the extended space of the new dynamic variables) which attract the system during its evolution?

Such a question arises by the consideration that, in linear kinetics (*i.e.*, with only first-order elementary reactions/steps so that the system evolution can be written as  $\dot{\mathbf{x}} = -\mathbf{K}\mathbf{x}$ , with  $\mathbf{K}$  fixed), the eigenvectors of the kinetic matrix  $\mathbf{K}$  define a hierarchy of fixed subspaces in the physical concentration space. The projections of the system state  $\mathbf{x}(t)$  on these subspaces give the picture of trajectories going through a sequence of attracting subspaces[7]. The same picture is kept when passing to non-linear kinetics, that is, the trajectories pass through a “cascade” of manifolds [8] of lower and lower dimension. However, the analysis sketched above becomes *local* in the sense of point-dependent (see for example the construction of intrinsic low dimensional manifolds, ILDMs, based on a local linearization of the velocity field [9, 10]) and the formal definition of such “global” objects is challenging. Here we focus on such an issue and demonstrate that one can still specify fixed subspaces which attract the trajectories when the system evolution is represented in a suitable abstract and extended space. Turning back to the physical variables  $\mathbf{x}$ , one can then make a partition of the concentration space into domains, each of them corresponding to one of these attracting subspaces. Thus the evolution in the physical space becomes a transition between these distinct domains.

To achieve the goal we shall restart from the universal format of ODEs presented in Ref. [2], and perform a further transformation to achieve what we term a “hyper-spherical representation” of the reactive system in an extended space. In fact, in such a new representation, the dynamic variables are a “radial” coordinate  $S$ , which has physical units of inverse-of-time, and a normalized “state-vector”  $\boldsymbol{\psi}$ , whose components can be assimilated to dimensionless “angular” coordinates. The evolution equations of the  $(S, \boldsymbol{\psi})$  variables constitute a new canonical format of ODEs. The examination of such a format will let emerge the existence of subspaces which, one by one, attract  $\boldsymbol{\psi}$  during the system evolution.

To develop the methodological path, in Section II we outline the essential features of our past works and integrate them with some remarks which are due for this continuation. In Section III we introduce the hyper-spherical representation of the reactive system, and derive the canonical format of ODEs for the new variables  $(S, \boldsymbol{\psi})$ . In Section IV we analyze such a format, define the attracting subspaces, and illustrate the concepts by adopting a simple kinetic scheme, namely the Lindemann-Hinshelwood mechanism also studied by Fraser in Ref. [11] and already adopted by us in our previous works[2, 3]. Then we formulate a tentative relation between the persistence of a trajectory within the attracting subspaces and the closeness to the perceived SM. Such ideas will be elaborated in a subsequent work targeted to devise a low-computational-cost route (and related code) to produce candidate points in

the SM proximity. In the Supporting Information[12] we present some preliminary outcomes obtained with a tentative algorithmic implementation of the concepts here formulated. In Section V we draw the main conclusions.

## II. BACKGROUND AND PRELIMINARIES

By applying the mass-action law to the elementary reactions, the original ODE system reads

$$\dot{x}_j = \sum_{m=1}^M \left( \nu_{P_j}^{(m)} - \nu_{R_j}^{(m)} \right) r_m(\mathbf{x}) \quad , \quad r_m(\mathbf{x}) = k_m \prod_i x_i^{\nu_{R_i}^{(m)}} \quad (1)$$

being  $k_m$  the kinetic constant of the  $m$ -th elementary step/reaction,  $\nu_{R_j}^{(m)}$  and  $\nu_{P_j}^{(m)}$  the stoichiometric coefficients of species  $j$  as reactant and product respectively (coefficients are null if the species does not appear in the elementary reaction) and  $r_m(\mathbf{x})$  the reaction rate of step  $m$ . The starting point in Ref. [2] is to pursue the following change of dynamic variables:

$$\mathbf{x} \rightarrow \mathbf{h}(\mathbf{x}) \quad , \quad h_{jm}(\mathbf{x}) := x_j^{-1} r_m(\mathbf{x}) \quad (2)$$

These new variables are positive-valued and have physical dimension of inverse-of-time. One deals with  $N \times M$  of such variables which are, however, mutually related by a number of non-linear constraints so that only  $N$  of them are independent. From the knowledge of the set  $h_{jm}(\mathbf{x})$ , the state of the system in the concentration space can be retrieved by means of an inversion transformation[13].

Although derived by us in Ref. [2], the kind of transformation in Eq. (2) turned out to be already known for decades and was even re-discovered independently by several authors with minor variations, at least (to the best of our knowledge) by Brenig and Goriely in the context of general transformations amongst equivalence classes of representation for continuous-time systems[14], by Fairén and Hernández-Bermejo[15, 16], and by Gouzé[17]. Notably, in Ref. [15], the authors argue that the resulting quadratic structure can facilitate the achievement of power-series approximations of the solution of the ODE system[18, 19].

The subsequent step is to introduce the square matrix  $\mathbf{V}$  with elements

$$V_{jm,j'm'}(\mathbf{x}) = M_{jm,j'm'} h_{j'm'}(\mathbf{x}) \quad (3)$$

where  $\mathbf{M}$  is the fixed “connectivity” matrix whose elements are

$$M_{jm,j'm'} = \left( \nu_{P_{j'}}^{(m')} - \nu_{R_{j'}}^{(m')} \right) \left( \delta_{j,j'} - \nu_{R_{j'}}^{(m)} \right) \quad (4)$$

where  $\delta$  denotes the Kronecker delta function. The elements of  $\mathbf{V}$  form a further enlarged set of dynamic variables. By knowing  $\mathbf{M}$ , the physical state of the reactive system can be

retrieved by a two-step backward transformation  $\mathbf{V}(t) \rightarrow \mathbf{h}(t) \rightarrow \mathbf{x}(t)$ [20]. By introducing the cumulative index  $Q = (j, m)$  for the species-step pair, with  $Q = 1, 2, \dots, Q_s$  where  $Q_s = N \times M$ , the evolution of any mass-action based system is finally put into the following extended system of ODEs:

$$\dot{V}_{Q,Q'} = -V_{Q,Q'} \sum_{Q''} V_{Q',Q''} \quad (5)$$

The quadratic format of Eq. (5) is universal (*i.e.*, it can represent any kinetic scheme regardless of the number of species and elementary reactions) and parameter-free. In the Appendix we demonstrate the crucial property that while the factors  $h_{j'm'}(\mathbf{x})$  in Eq. (3) may diverge to  $+\infty$  tending to the stationary state, the elements of matrix  $\mathbf{V}$  take always a finite value for any possible kinetic scheme. Thus, according to Eq. (5), each of the  $V_{Q,Q'}(t)$  can be either constantly null or never null. In the latter case, the element cannot change sign along a trajectory, and tends to a limit value (possibly zero) at the stationary state.

Notably, at this level the reactive system can be represented as a weighted/oriented graph with  $Q_s$  nodes, and Eq. (5) specifies the evolution of its links if  $V_{Q,Q'}(t)$  is interpreted as the connection from node  $Q$  to node  $Q'$ . The equation states that the rate of evolution of  $V_{Q,Q'}(t)$  is proportional to the magnitude of the connection itself, and to the sum of the connections between the arrival node and all the nodes of the graph. A pictorial representation is given in Figure 1. In ref. [2] we have shown that some properties of these sums play a crucial role in relation with the SM, as summarized here below.

Let us define

$$z_Q(\mathbf{x}) := \sum_{Q'} V_{Q,Q'}(\mathbf{x}) \quad (6)$$

where  $z_Q(\mathbf{x})$  are point-dependent “rates” which control the evolution of the  $h_Q$  variables via  $\dot{h}_Q = -h_Q z_Q$ , and hence of the connections  $V_{Q^*Q}$  for all starting nodes  $Q^*$  in the graph representation. These rates are mutually related by linear constraints so that at most  $N$  of them are independent, as detailed in the Supporting Information of Ref. [2]. Note that some rates may be identically null (in these cases the corresponding  $h_Q$  coincide with kinetic constants of first-order steps). Moreover, it may happen that some rate  $z_Q$  is identically equal to some other, say  $z_{Q_1}(\mathbf{x}) = z_{Q_2}(\mathbf{x}) = \dots$ . This means that the corresponding  $h_{Q_1}(\mathbf{x})$ ,  $h_{Q_2}(\mathbf{x})$ ,  $\dots$  are multiples one of the others. By means of phenomenological observations, we could formulate the conjecture that a trajectory enters a region of the concentration space, termed by us “Attractiveness Region” (AR). Within the AR, the high-order time-derivatives  $z_Q^{(n)}(\mathbf{x}(t)) \equiv d^n z_Q(\mathbf{x}(t))/dt^n$  tend to become multiples one of the others and monotonically decay to zero towards the equilibrium. In terms of point-dependent functions, these derivatives are expressed as  $z_Q^{(n)}(\mathbf{x}) = (\mathbf{F}(\mathbf{x}) \cdot \partial/\partial \mathbf{x})^n z_Q(\mathbf{x})$  and are easily computed by exploiting recursive formulas derived by the quadratic form of Eq. (5) (see the Supporting

Information of Ref. [2]). The SM is then defined as the hyper-surface formed by points  $\mathbf{x}$ , within the AR, where  $z_Q^{(n)}(\mathbf{x}) = 0$  for *all*  $Q$  as  $n \rightarrow \infty$  (while on the equilibrium manifold one has the stronger and exact condition  $z_Q^{(n \geq 1)}(\mathbf{x}) = 0$ ). This provides a geometric *definition* of SM as a global object in the concentration space.

### III. HYPER-SPHERICAL REPRESENTATION OF THE REACTIVE SYSTEM

Let us introduce the index  $J$  through the association

$$J \equiv (Q, Q') \quad , \quad J = 1, 2, \dots, Q_s^2 \quad (7)$$

and use it to “unroll” the matrix  $\mathbf{V}$  into a column-array  $\mathbf{v}$

$$v_J \equiv V_{QQ'} \quad (8)$$

Let  $\mathbf{C}$  be the  $Q_s^2 \times Q_s^2$  matrix

$$C_{J_1 \equiv (Q_1, Q'_1), J_2 \equiv (Q_2, Q'_2)} = \begin{cases} 0 & \text{if } Q'_1 \neq Q_2 \\ 1 & \text{if } Q'_1 = Q_2 \end{cases} \quad (9)$$

The ODE system in Eq. (5) turns into

$$\dot{v}_J = -v_J \sum_{J'} C_{JJ'} v_{J'} \quad (10)$$

In this vectorial representation, the actual state of the system is described by a point  $\mathbf{v}(\mathbf{x})$  in a  $Q_s^2$ -dimensional space spanned by the orthogonal unit vectors

$$\mathbf{e}_J = \begin{pmatrix} 0 \\ \dots \\ 1 \\ \dots \\ 0 \end{pmatrix} \leftarrow \text{at } J\text{-th pos.} \quad , \quad \mathbf{e}_J \cdot \mathbf{e}_{J'} = \delta_{JJ'} \quad (11)$$

The final step consists in turning to an equivalent hyper-spherical representation of  $\mathbf{v}$  by writing it as a product of a normalized and dimensionless *state vector*  $\boldsymbol{\psi}$  (with  $Q_s^2 - 1$  independent components) and a single positive-valued variable  $S$  with physical units of inverse-of-time. There are several possibilities to define  $S$  (each one based on a specific kind of norm in the space of the  $v_J$  elements) and thus to build  $\boldsymbol{\psi}$ ; here we pursue the use of the Euclidean norm  $\|\cdot\|$ . Namely, as state vector we consider

$$\boldsymbol{\psi} := \mathbf{v}/S \quad , \quad \boldsymbol{\psi} \cdot \boldsymbol{\psi} = 1 \quad (12)$$

with

$$S := \|\mathbf{v}\| = \sqrt{\text{Tr}(\mathbf{V}^T \mathbf{V})} \quad (13)$$

where the last identity shows that  $S$  is also the Frobenius norm of the matrix  $\mathbf{V}$ . Then we introduce the auxiliary (dimensionless) array  $\boldsymbol{\rho} := \mathbf{C}\mathbf{v}/Z$ , with  $Z$  the root-mean-square average rate computed on the ensemble of rates in Eq. (6),

$$Z(\mathbf{x}) = \sqrt{Q_s^{-1} \sum_Q z_Q(\mathbf{x})^2} \quad (14)$$

The  $Q_s^2$  components of  $\boldsymbol{\rho}$  are explicitly given by

$$\rho_{J \equiv (Q, Q')} = z_{Q'}/Z \quad (15)$$

and their mean-square average is constantly equal to 1 by construction. Such an array is related to  $\boldsymbol{\psi}$  via

$$\mathbf{P}\mathbf{1} = \frac{Z}{S}\boldsymbol{\rho} \quad , \quad P_{JJ'} := C_{JJ'}\psi_{J'} \quad (16)$$

where  $\mathbf{1}$  stands for the  $Q_s^2$ -dimensional column-array with all entries equal to 1.

The equations for the time evolution of  $S$  and of the vector  $\boldsymbol{\psi}$  are readily obtained with few steps of algebra by using Eqs. (12) and (13) with Eq. (10) written as  $\dot{v}_J = -ZS\psi_J\rho_J$ . One gets[21]

$$\dot{\psi}_J = -Z(\rho_J - \Phi_1)\psi_J \quad , \quad \Phi_1 = \boldsymbol{\psi} \cdot \text{diag}(\boldsymbol{\rho})\boldsymbol{\psi} \quad (17)$$

and

$$\dot{S} = -ZS\Phi_1 \quad (18)$$

Equations (17) and (18) form an autonomous set of ODEs for the variables  $\boldsymbol{\psi}(t)$  and  $S(t)$ [22] which can be solved by providing the initial conditions  $\boldsymbol{\psi}(0)$  and  $S(0)$ , corresponding to the starting point  $\mathbf{x}(0)$  in the concentration space. At any time, the actual state  $\mathbf{x}(t)$  can be retrieved by applying the inversion route:  $S(t)\boldsymbol{\psi}(t) = \mathbf{v}(t) \rightarrow \mathbf{V}(t) \rightarrow \mathbf{h}(t) \rightarrow \mathbf{x}(t)$ . Moreover, the evolution equation for  $\boldsymbol{\rho}$  turns out to be

$$\dot{\boldsymbol{\rho}} = -S(\mathbf{P} - \Phi_2\mathbf{I})\boldsymbol{\rho} \quad , \quad \Phi_2 := Q_s^{-2} \boldsymbol{\rho} \cdot \mathbf{P}\boldsymbol{\rho} \quad (19)$$

As demonstrated in the Supporting Information,[12] the following bounds (to be possibly sharpened) apply to the factors  $\Phi_1$  and  $\Phi_2$ :  $|\Phi_1| \leq Q_s$  and  $|\Phi_2| \leq Q_s$ . Finally, it also follows

$$\dot{Z} = -ZS\Phi_2 \quad (20)$$

## IV. DYNAMICAL FEATURES

### A. Attracting subspaces in the $Q_s^2$ -dimensional space

Let us first provide some preliminary definitions. Given a point  $\mathbf{x}$ , let

$$z_{\min}(\mathbf{x}) := \min_Q \{z_Q(\mathbf{x})\} \quad (21)$$

There may be a number  $d$  of identically degenerate  $z_Q(\mathbf{x})$  rates whose value is the lowest one. Then, let  $\mathbf{J}_{\mathcal{A}} = (J_1, J_2, \dots, J_{D_{\mathcal{A}}})$  be the set of indexes  $J = (Q, Q')$  with no restrictions on  $Q$ , while  $Q'$  is such that  $z_{Q'}(\mathbf{x}) = z_{\min}(\mathbf{x})$ . The number of entries of such a set is

$$D_{\mathcal{A}} = Q_s \times d \quad (22)$$

Then, let us associate to each of the indexes  $J \in \mathbf{J}_{\mathcal{A}}$  a (fixed) versor  $\mathbf{e}_J$  defined in Eq. (11). let  $\mathcal{A}$  be the  $D_{\mathcal{A}}$ -dimensional subspace

$$\mathcal{A} = \text{span}(\mathbf{e}_{J_1}, \mathbf{e}_{J_2}, \dots, \mathbf{e}_{J_{D_{\mathcal{A}}}}) \quad (23)$$

Finally, let  $c(\mathcal{A})$  be a compact domain in the concentration space such that  $\mathbf{x} \in c(\mathcal{A})$  if the functions  $z_Q(\mathbf{x})$  individuate the set  $\mathbf{J}_{\mathcal{A}}$  and hence the subspace  $\mathcal{A}$ .

With these positions, in what follows we show that

$$\text{While } \mathbf{x}(t) \in c(\mathcal{A}) \text{ then } \boldsymbol{\psi}(\mathbf{x}(t)) \rightarrow \mathcal{A} \quad (24)$$

The attractiveness of  $\boldsymbol{\psi}(\mathbf{x}(t))$  towards the actual  $\mathcal{A}$ , indicated by the arrow in Eq. (24), can be revealed by looking at the Euclidean distance  $d_{\mathcal{A}}$  of the point  $\boldsymbol{\psi}$  on the unit  $Q_s^2$ -dimensional hyper-sphere from the subspace itself:

$$d_{\mathcal{A}}(\mathbf{x}(t)) = \sqrt{\sum_{J \notin \mathbf{J}_{\mathcal{A}}} \psi_J(\mathbf{x}(t))^2} \quad (25)$$

In essence, *as long as* the set of degenerate smallest  $z_Q$  functions remains unaltered (regardless of their magnitude that may change), the vector  $\boldsymbol{\psi}$  tends to the subspace  $\mathcal{A}$  which, therefore, we call an ‘‘attracting subspace’’. [23] Figure 2 gives a schematic of the concept.

The proof of such a behavior starts by combining Eqs. (17) and (18) to get the formal integrated forms of  $\boldsymbol{\psi}(t)$  and  $S(t)$  (that can be checked by back substitution):

$$\begin{aligned} \boldsymbol{\psi}(t) &= \frac{\exp\{-\int_{t_0}^t dt' Z(t') \text{diag}(\boldsymbol{\rho}(t'))\} \boldsymbol{\psi}(t_0)}{\|\exp\{-\int_{t_0}^t dt' Z(t') \text{diag}(\boldsymbol{\rho}(t'))\} \boldsymbol{\psi}(t_0)\|} \\ S(t) &= S(t_0) \left\| \exp\left\{-\int_{t_0}^t dt' Z(t') \text{diag}(\boldsymbol{\rho}(t'))\right\} \boldsymbol{\psi}(t_0) \right\| \end{aligned} \quad (26)$$

For each component  $J$ , let us introduce the time-averaged rates

$$\bar{\omega}_J(t, t_0) := \frac{1}{t - t_0} \int_{t_0}^t dt' Z(t') \rho_J(t') \quad (27)$$

Note that  $\bar{\omega}_{J \equiv (Q, Q')}(t, t_0) = (t - t_0)^{-1} \int_{t_0}^t dt' z_{Q'}(t')$ . This implies that if the trajectory  $\mathbf{x}(t)$  is contained in a certain domain  $c(\mathcal{A})$  during some interval  $[t_0, t]$ , then

$$\bar{\omega}_{J \notin \mathbf{J}_{\mathcal{A}}}(t, t_0) > \omega_{\min}(t, t_0) \quad , \quad \omega_{\min}(t, t_0) := \bar{\omega}_{J \in \mathbf{J}_{\mathcal{A}}}(t, t_0) \quad (28)$$

For each component  $J$ , the first of Eqs. (26) becomes

$$\psi_J(t) = \frac{\psi_J(t_0) e^{-(t-t_0)(\bar{\omega}_J(t, t_0) - \omega_{\min}(t, t_0))}}{\sqrt{\sum_{J'} \psi_{J'}(t_0)^2 e^{-2(t-t_0)(\bar{\omega}_{J'}(t, t_0) - \omega_{\min}(t, t_0))}}} \quad (29)$$

Now consider a situation in which  $\boldsymbol{\psi}(t_0)$  has a non-null projection on the subspace  $\mathcal{A}$ . In this case, by taking the absolute value at both members in Eq. (29), one sees that all  $|\psi_J(t)|$  with  $J \in \mathbf{J}_{\mathcal{A}}$  monotonically increase as time passes (since the numerator of the ratio is constantly equal to  $|\psi_J(t_0)|$  but the denominator monotonically decreases), while all  $|\psi_J(t)|$  with  $J \notin \mathbf{J}_{\mathcal{A}}$  monotonically decrease (since the numerator decreases faster than the denominator). In practice, this means that the state vector  $\boldsymbol{\psi}$  tends to the attracting subspace  $\mathcal{A}$ , as  $t$  increases, in the sense that the Euclidean distance in Eq. (25) decreases[24]. Since the instants  $t_0$  and  $t > t_0$  are arbitrarily chosen under the sole condition[25] that the corresponding physical points  $\mathbf{x}(t')$  for  $t_0 \leq t' \leq t$  belong to the same domain  $c(\mathcal{A})$ , the global message is that  $\boldsymbol{\psi}$  tends to  $\mathcal{A}$  while the trajectories are contained in  $c(\mathcal{A})$ . Hence we have proved Eq. (24).

Although not explicitly indicated in Eq. (24) for sake of notation,  $\mathcal{A}$  clearly depends on the actual point in the concentration space. However,  $\mathcal{A}$  is the same for all the points within a compact domain  $c(\mathcal{A})$ . This means that even if the kinetic scheme is non-linear, there still exist such *fixed* subspaces which *persistently* attract  $\boldsymbol{\psi}$  within delimited domains of the physical space. A trajectory may cross several of these domains, each characterized by a *specific* attracting subspace. Note that the subspaces are mutually orthogonal (in the sense that they have null mutual projections), and that their dimension may differ. Given the kinetic scheme, the number of attracting subspaces is finite, at most  $Q_s$  in case of no degeneracies between the  $z_Q$  functions. However, the number of corresponding domains in the concentration space can be larger since  $\boldsymbol{\psi}(\mathbf{x}(t))$ , along a trajectory, can be in principle attracted by the same subspace  $\mathcal{A}$  within different disjointed domains. In all generality, by labeling with letters  $n, n', n'', \dots$  the domains in the concentration space, one expects that  $\boldsymbol{\psi}(\mathbf{x}(t))$  will move as attracted, one by one, by the terms of a sequence

$$\dots \rightarrow \mathcal{A}_n \rightarrow \mathcal{A}_{n'} \rightarrow \mathcal{A}_{n''} \rightarrow \dots \quad (30)$$

while the trajectory goes across the domains ...,  $c(\mathcal{A}_n)$ ,  $c(\mathcal{A}_{n'})$ ,  $c(\mathcal{A}_{n''})$ , ... As stated above, each term in the sequence Eq. (30) is "picked" by an ensemble of at most  $Q_s$  elements.

The switch of attracting subspace is a consequence of the existing mutual constraints on the  $v_J$  components, hence on the  $\psi_J$  components. Because of these constraints, the vector  $\psi$  cannot lie on the actual  $\mathcal{A}$ , hence such a subspace *cannot* be reached otherwise the dynamics would stop there. The exception is indeed represented by the last term in the sequence in Eq. (30), which will be reached in the infinitely long timescale.

In relation with the slowest manifold features, and regardless of the specific situation, we stress that if a SM is observed in the concentration space, there must be an ensemble of attracting subspaces which are visited by trajectories once they lie in the SM proximity. In particular, in case of a uni-dimensional SM it is for sure that all trajectories will share a common sub-sequence of terms. In a pictorial fashion, the reactive system quickly goes through the first terms of the sequence in Eq. (30) and then "falls" into a "funnel" of terms associated to the SM neighborhood. This might be a new way of looking at the bundles of trajectories in a coarse-grained fashion.

## B. Illustration for a simple kinetic scheme

To illustrate the main features of our approach we adopt the Lindemann-Hinshelwood kinetic scheme [1] reported here below:



The corresponding system of ODEs, here omitted, is readily generated by applying the mass-action law to the elementary steps. All quantities are dimensionless, meaning that the time variable and the volumetric concentrations (hereafter indicated with  $[\cdot]$ ) are implicitly expressed in some units  $t_s$  and  $c_s$ , respectively. Values of the kinetic constants are  $k_1 = 2$ ,  $k_2 = 1$ ,  $k_3 = 0.6$  (the same values adopted by Fraser in Ref. [11] and by us in Refs. [2, 3]). Trajectories have been generated by using the DVODE solver[26] as implemented in the routine from Ref. [27]. FORTRAN codes have been written for the specific computations.

Concerning the numbering  $Q \leftrightarrow (j, m)$ , an outer loop is made on the species  $j$  and an inner loop on the elementary steps  $m$ . The species are labeled by  $j = 1, 2, 3$  following the sequence X, Y, P. For such a scheme,  $Q_s = 9$ . However, since the species P is irreversibly formed, the concentrations of the species X and Y evolve autonomously and [P] can be obtained by exploiting the mass-conservation constraint  $[X] + [Y] + [P] = \text{const.}$  for a given

initial composition. Thus it suffices to consider the reduced system of ODEs for  $[X]$  and  $[Y]$  only, that is, in practice, to focus on the projection on the sub-dimensional space of the reactant concentrations. Correspondingly, only the “reduced” set of the first 6 elements  $Q = 1, \dots, 6$  is required in the analysis. All considerations will refer to such a reduced set[28]. For the explicit expressions of the  $h_Q$  functions and related rates  $z_Q$  we address the reader to Refs. [2, 3]. In particular it can be seen that  $z_6(\mathbf{x}) = 0$  and  $z_1(\mathbf{x}) = z_5(\mathbf{x})$  identically.

Several trajectories have been generated from initial points drawn at random in the reactant concentration region displayed in Fig. 3. Red and blue lines are a pair of “pilot trajectories” (laying above and below the perceived SM), which will be used to illustrate the relevant features. Each colored area corresponds to a domain within which the state vector  $\boldsymbol{\psi}(\mathbf{x}(t))$  tends to a specific attracting subspace  $\mathcal{A}$ . The domains have been identified by constructing a dense grid with homogeneous partition on the logarithms of  $[X]$  and  $[Y]$ , and by increasing the sampling in the proximity of the perceived SM where a narrow domain appears. Since only the first six components of the  $\mathbf{z}$  vector are used in the analysis, the full space of the  $\boldsymbol{\psi}$  vector is 36-dimensional. For each meshing point,  $\mathcal{A}$  was assigned by looking at the smallest  $z_Q$  rates and accounting for possible degeneracies as discussed above. In the specific case no degeneracies are found (*i.e.*,  $d = 1$  in all situations), hence all attracting subspaces, which are listed in the lower panel of the figure, are 6-dimensional. Figure 4 shows, for the two pilot trajectories, the belonging of the trajectory to the domains (the integer number on the ordinate axis is the  $n$  given in the lower panel of Fig. 3). From Figures 3 and 4 it is possible to see that the initial (fast) part of the pilot trajectories take place within the wide domains 1 and 2, while the slow tail of evolution occurs for both trajectories within the domain 1 (namely at the border of such a domain) and domain 3 (the narrow one in Fig. 3). The vertical lines are placed at times which correspond to points close to the perceived SM.

For the two pilot trajectories, in the panels of Fig. 5 we show both the time evolution of the distances  $d_{\mathcal{A}}$  defined in Eq. (25) (solid lines) and of the functions  $Z$  (dashed lines). The vertical lines indicate a “switch” of attracting subspace. One can see that, in the global time scale here inspected,  $Z$  rapidly decreases, as it will be rationalized in the following. For the trajectory “from above”, the drop is of about 3 orders of magnitude, while for the trajectory “from below” a huge drop of about 9 orders is observed. Note that the decrease is non-monotonic when approaching the SM from above, as revealed by the slight increase of  $Z$  at  $t \simeq 10^{-1}$ .

At the same time,  $\boldsymbol{\psi}$  tends to the specific local  $\mathcal{A}$  but the quick change of attracting subspace makes that the time of stay within a domain is so short that the approach to  $\mathcal{A}$  could be little. Notably, at the entrance into a domain it appears that the distance from  $\mathcal{A}$

is very close to 1. This means that the state vector  $\boldsymbol{\psi}$  is almost orthogonal to  $\mathcal{A}$  and the attractiveness to  $\mathcal{A}$  is weak. Thus, at least for this kinetic scheme, it happens that where  $Z$  is “large” (far from the SM), the state vector reorients but remains almost orthogonal to the attracting subspace. Conversely, once the magnitude of  $Z$  is decreased, the time of persistence within a domain increases,  $\boldsymbol{\psi}$  approaches more effectively the actual  $\mathcal{A}$ , and a relevant drop of the distance parameter  $d_{\mathcal{A}}$  is detected.

### C. Proximity to the SM

Up to here the rationale of the dynamics in the  $(\boldsymbol{\psi}, S)$ -space is rigorous. From here, the non-linearity of the problem forces us to proceed on qualitative and speculative grounds which will need to be supported by direct checks on model systems.

Let us start from the phenomenological evidence that a trajectory  $\mathbf{x}(t)$  slows down as the neighborhood of the SM is approached. This could be reflected in the fact that also the evolution of the coordinates  $(S, \boldsymbol{\psi})$  in the hyper-spherical representation of the same trajectory becomes smoother. Firstly, note that the average rate  $Z$  appears in *both* differential equations (17) and (18) as multiplier at the right-hand members. Let us focus on Eq. (17) alone. While the other factors are dimensionless and bounded numbers,  $Z$  can change even by orders of magnitude along a trajectory, as shown for the model scheme adopted above. Thus, it is “natural” to expect that the magnitude of  $Z$  drops in the course of the reaction so that going toward the SM the “angular” coordinates  $\boldsymbol{\psi}$  may evolve more and more slowly. Moreover, as  $Z$  becomes smaller, from Eq. (18) also the evolution of the “radial” coordinate  $S$  is expected to become smoother (although the correlation between  $S$  and  $Z$  prevents a sound statement). As a whole, where the average rate  $Z$  takes small values, one likely expects that the SM proximity has been approached. Also note that the variation of  $Z$  is governed by Eq. (20) in which  $Z$  itself enters the right-hand member as multiplicative factor. Thus, starting from points  $\mathbf{x}(0)$  far from the equilibrium, the magnitude of  $Z$  should likely display a rapid depletion (as indeed it has been observed for Scheme A)[29]. By following a trajectory  $\mathbf{x}(t)$ , as long as  $Z(\mathbf{x}(t))$  is large,  $\boldsymbol{\psi}(\mathbf{x}(t))$  should tend rapidly to the actual attracting subspace but, at the same time, such a large  $Z$  also promotes a rapid change of the components of  $\boldsymbol{\rho}(\mathbf{x}(t))$ , hence a possible change of ordering of the  $z_Q$  rates. Ultimately, the attracting subspace also “switches” rapidly.

Thus, the likely (typical) picture should be the following. In the initial (transient) phase of a trajectory, if it starts far enough from the equilibrium manifold, one observes a quick drop of  $Z(\mathbf{x}(t))$  along with rapid transitions between attracting subspaces. Such a transient phase is followed by a slower and smoother evolution for both  $Z(\mathbf{x}(t))$  and  $\boldsymbol{\psi}(\mathbf{x}(t))$  once the trajectory  $\mathbf{x}(t)$  has approached the SM neighborhood and the magnitude of  $Z$  has largely

decreased.

The primary condition of smallness of  $Z$  is here termed as *slowness* of the trajectory progress. The additional condition of smooth evolution of  $Z$  itself, and hence of  $\psi(\mathbf{x}(t))$ , is more related to the *persistence of the slowness*, since such a property is observed and kept once the primary condition holds. For the simple scheme here adopted, from Figures 4 and 5 it appears that the latter property arises in terms of persistence of the attracting subspaces. We may *guess* that, in general cases, a trajectory “slides” over a series of domains whose attracting subspaces  $\mathcal{A}$  (a sub-sequence of Eq. (30)) last for long times.

On the basis of such a guess, for the actual attracting subspace to be persistent, the set of indexes  $\mathbf{J}_{\mathcal{A}}$  must remain unaltered as long as possible. A strong condition to meet this requisite is that the whole array  $\boldsymbol{\rho}$  varies smoothly in time. As a global measure of such a smoothness we take the root-mean-square average of the derivatives  $\dot{\rho}_J$ . With few algebraic steps one gets

$$\sqrt{Q_s^{-2} \sum_J \dot{\rho}_J^2} = Z^{-1} \sqrt{Z_1^2 - \dot{Z}^2} \quad (31)$$

where  $Z_1(\mathbf{x})$  is the analogous of Eq. (14) for the first-order derivatives:

$$Z_1(\mathbf{x}) = \sqrt{Q_s^{-1} \sum_Q z_Q^{(1)}(\mathbf{x})^2} \quad (32)$$

Equation (31) shows that where  $Z$  is *almost* constant (slowness), it is required that  $Z_1$  be small for  $\boldsymbol{\rho}$  to vary smoothly. Thus, in the neighborhood of the SM one *likely* expects that *both*  $Z$  and  $Z_1$  take small values. To translate the expression “small values” into quantitative and operative terms, one may exploit the landscapes of functions  $Z(\mathbf{x})$  and  $Z_1(\mathbf{x})$ . Such landscapes are expected to feature “grooves” which fall close to the perceived SM. As example, in Fig. 6 we show the landscapes of  $Z(\mathbf{x})$  and  $Z_1(\mathbf{x})$  as functions of the reactant concentrations for Scheme A. The expected grooves are indeed observed.

These ideas will be elaborated in a following article where we shall devise a computational route, with related implementation, to produce “candidate points” to the proximity of the SM. At this preliminary stage, in the Supporting Information[12] the interested reader may find an early algorithmic implementation of the procedure together with the outcomes for Scheme A and for a higher non-linear scheme with elementary steps up to the fourth order.

It is interesting to note that the reasoning above can be extended by accounting for the higher-order time-derivatives of the rates  $z_Q$ . By recursively differentiating the components of  $\boldsymbol{\rho}$  and then considering their root-mean-square average where  $Z \simeq \text{const.}$ , it follows that in the region of slowness also the averages  $Z_n(\mathbf{x}) = \sqrt{Q_s^{-1} \sum_Q z_Q^{(n)}(\mathbf{x})^2}$  of *any* order should feature a “groove” close to the SM. Notably, a (constrained) minimization of  $Z_n$  to locate such a groove implies that all components  $z_Q^{(n)}$  are globally minimized. Such an outcome can

be taken as an approximate version of the definition of SM[3] recalled in the Introduction, stating that on the SM all components  $z_Q^{(n)}$  vanish as  $n$  tends to infinity. We recall that such a condition strictly holds within the Attractiveness Region in the concentration space, thus only the “right groove” of  $Z_n(\mathbf{x})$  within such a region has to be considered.

## V. CONCLUSIONS

In this work we have shown that the mathematical description of any reactive system involving  $N$  chemical species, under applicability of mass-action law to its  $M$  elementary reactions, can be put into a hyper-spherical format in a  $Q_s^2$ -dimensional space where  $Q_s = N \times M$ . Such a format has been obtained by further elaborating the quadratic ODE system derived in Ref. [2]; hence also in the present case the achieved formulation is “universal” and parameter-free. Thus, any consideration which emerges from the examination of such a mathematical structure holds in all generality for the mass-action class of evolving chemical systems.

In particular we have shown that also for general non-linear kinetic schemes there exist *fixed* subspaces, each one with dimension at most equal to  $Q_s$ , which monotonically attract the state vector  $\psi$ . For general non-linear kinetics, these subspaces replace the ones which, only for linear schemes, are spanned (in the concentration space) by the eigenvectors of the kinetic matrix. This result may open new lines to inspect the paths of a reactive system under a coarse-grained-like view, where the focus is not on the trajectory, rather on the sequence of “visited” domains, each one associated to an attracting subspace.

The next step is to attribute to these domains some characteristic properties which are recognizable in the physical space. Along this line we have formulated a tentative link between persistence of the attracting subspaces (in the extended space) and closeness of trajectories to the perceived slow manifold (in the concentration space). This opens perspectives to devise low cost computational strategies to locate candidate points in the proximity of the slow manifold. These strategies could employ just the lowest order time-derivatives of the rates  $z_Q$  to build “potential functions” whose landscape can guide the individuation of candidate points. Work on this line is currently underway but the preliminary results presented in the Supporting Information[12] are already encouraging. Efforts in this direction are worthwhile since once a set of candidate points is evaluated and spurious solutions are rejected *a posteriori*, interpolation routes could yield an approximation of the slow manifold. Such an interpolating surface is clearly non-invariant with respect to the system’s dynamics, but it could be taken as starting guess for various iterative refinement methods [30, 31]. The resulting surface can be then employed in a procedure to reduce the dimensionality of the

kinetics description in the slow part of the evolution.

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#### APPENDIX. Finite value of the elements of the matrix $\mathbf{V}$

As stated in the main text, the functions  $h_{jm}$  may diverge to  $+\infty$  as the system evolves toward equilibrium along a trajectory  $\mathbf{x}(t)$ . This could happen if there are species which are completely consumed in the global reactive process. Let  $j^*$  be the label of such a kind of species, *i.e.*,  $\lim_{t \rightarrow \infty} x_{j^*}(t) = 0$ , and let  $m'$  be a generic step. Then,  $h_{j^*m'}(\mathbf{x}(t)) = x_{j^*}(t)^{-1} r_{m'}(\mathbf{x}(t))$  may diverge. Regardless of these possible divergences, in the following we show that *none* of the matrix elements  $V_{jm,j^*m'}(\mathbf{x}(t)) = M_{jm,j^*m'} h_{j^*m'}(\mathbf{x}(t))$  diverges in the course of the evolution of a chemical system for any pair  $j, m$ .

Let us consider the three possible cases that may be encountered: 1) the species  $j^*$  enters as reactant in the step  $m'$  (regardless of its appearance also as product in the same step); 2) the species  $j^*$  is not involved in the step  $m'$ ; 3) the species  $j^*$  enters only as product in the step  $m'$ .

In case 1) one has that  $h_{j^*m'}(\mathbf{x}(t)) = x_{j^*}^{-1} r_{m'}(\mathbf{x}(t)) = x_{j^*}^{\nu_{R_{j^*}}^{(m')} - 1} k_{m'} \prod_{i \neq j^*}^N x_i^{\nu_{R_i}^{(m'')}}$ . Since  $\nu_{R_{j^*}}^{(m')} \geq 1$ , it follows that  $\lim_{t \rightarrow \infty} h_{j^*m'}(\mathbf{x}(t)) = 0$  in this case. Thus any matrix element  $V_{jm,j^*m'}$  for such a kind of elementary steps vanishes at equilibrium.

In case 2) there may be actually situations in which the terms  $h_{j^*m'}$  diverge at equilibrium. However one has  $\nu_{R_{j^*}}^{(m')} = \nu_{P_{j^*}}^{(m')} = 0$ , hence  $M_{jm,j^*m'} = \left( \nu_{P_{j^*}}^{(m')} - \nu_{R_{j^*}}^{(m')} \right) \left( \delta_{j,j^*} - \nu_{R_{j^*}}^{(m')} \right) = 0$  for any pair  $j, m$ . This implies that the elements  $V_{jm,j^*m'} = M_{jm,j^*m'} h_{j^*m'}$  are identically null.

In case 3), firstly consider that the rates of all the elementary steps in which  $j^*$  is produced or consumed must vanish as tending to the stationary state. To see this, let us divide the steps into a set of production processes, labelled by  $m_+$ , and consumption processes,

labelled by  $m_-$ . All the rates  $r_{m_-}(\mathbf{x}(t))$  go to zero, hence also all the rates  $r_{m_+}(\mathbf{x}(t))$  must vanish to have  $\dot{x}_{j^*}(t) \rightarrow 0$ . In this situation,  $h_{j^*m'}(\mathbf{x}(t)) = r_{m'}(\mathbf{x}(t))/x_{j^*}(t)$  takes an indefinite form “0/0”, whose limit is however finite. In fact, approaching the stationary state the magnitude of the maximum rate amongst the steps of production of  $j^*$ ,  $r_{m_+}^{\max}(\mathbf{x}(t)) = \max_{m_+} \{r_{m_+}(\mathbf{x}(t))\}$ , will become an infinitesimal of the same (or greater) order of the maximum rate amongst the steps of consumption of  $j^*$ ,  $r_{m_-}^{\max}(\mathbf{x}(t)) = \max_{m_-} \{r_{m_-}(\mathbf{x}(t))\}$ . By considering that the step  $m'$  belongs to the set  $m_+$ , it follows

$$t \rightarrow \infty : h_{j^*m'}(\mathbf{x}(t)) = \frac{r_{m'}(\mathbf{x}(t))}{x_{j^*}(t)} \leq \frac{r_{m_+}^{\max}(\mathbf{x}(t))}{x_{j^*}(t)} \lesssim \frac{r_{m_-}^{\max}(\mathbf{x}(t))}{x_{j^*}(t)}$$

where the symbol  $\lesssim$  indicates that  $r_{m_+}^{\max}(\mathbf{x}(t))$  goes to zero, towards the stationary state, with a velocity comparable or faster than that of  $r_{m_-}^{\max}(\mathbf{x}(t))$ . Since  $x_{j^*}(t)$  enters each of the rates  $r_{m_-}(\mathbf{x}(t))$  (and thus also the dominant term  $r_{m_-}^{\max}(\mathbf{x}(t))$ ) with a power of order at least 1, the latter ratio tends always to a finite limit, and thus also  $h_{j^*m'}$  and  $V_{j^*m'}$  take a finite value approaching the stationary state.

Since the analysis above holds for any trajectory  $\mathbf{x}(t)$ , we have shown that *all* elements of the matrix  $\mathbf{V}(\mathbf{x})$  take a finite value in all points of the concentration space.

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- [12] See supplemental material at [URL to be inserted ...] for some bounds about the factors  $\Phi_1$  and  $\Phi_2$ , and for a basic algorithm to produce candidate points in the proximity of the Slow Manifold.
- [13] As shown in the Supporting Information of Ref. [2],  $x_j = \prod_{j'm} (h_{j'm}/k_m) (\mathbf{U}^{-1})_{jj'}^{1/M}$  with the matrix  $U_{jj'} = -\delta_{j,j'} + M^{-1} \sum_m \nu_{R_{j'}}^{(m)}$ . Such an inversion route is inapplicable for linear kinetic schemes, since the matrix  $\mathbf{U}$  is singular (however, constraints from the mass-conservation can be exploited to retrieve  $\mathbf{x}$ ). On the other hand, linear kinetics can be easily solved analytically via an eigenvector/eigenvalues analysis, hence we do not consider such a category of problems.
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general function of the concentrations evaluated along a specific trajectory starting (implicitly) at some point  $\mathbf{x}(0)$ . Both notations are used through the text and should be properly interpreted.

- [21] It may be interesting to consider that Eq. 17 can be reformulated as follows. Let  $\mathbf{f}$  be a general array with entries  $f_J$ , possibly time-dependent. Let us introduce the *average* over the distribution of weight generated by the state-vector:  $\langle f_J \rangle := \sum_J f_J \psi_J^2$ . On this basis, Eq. 17 turns into  $\dot{\psi}_J = -Z(\rho_J - \langle \rho_J \rangle) \psi_J$ . A straight connection with a time-commutator can be achieved in terms of a Fisher-like equation [M. O. Vlad, S. E. Szedlacsek, N. Pourmand, L. L. Cavalli-Sforza, P. Oefner, J. Ross, “Fisher’s theorem for multivariable, time- and space-dependent systems, with applications in population genetics and chemical kinetics”, *Proc. Natl. Acad. Sci. USA* **102**(28), 9848 (2005)]. By multiplying both members by  $\psi_J f_J$  and summing on  $J$ , in a few steps one gets  $\frac{d}{dt} \langle f_J \rangle - \langle \frac{df_J}{dt} \rangle = -2Z(\langle f_J \rho_J \rangle - \langle f_J \rangle \langle \rho_J \rangle)$  where the left-hand term can be interpreted as the time-commutator  $C_t(\mathbf{f})$  between the time-derivative and the operation of averaging over the distribution associated to  $\psi$ . Notably, in the special case  $\mathbf{f} \equiv \boldsymbol{\rho}$  one has  $C_t(\boldsymbol{\rho}) = -2Z[\langle \rho_J^2 \rangle - \langle \rho_J \rangle^2] < 0$ .
- [22] Clearly, the time variable can be eliminated in favor of a pure geometrical representation of the trajectories, if  $S$  is employed as progress variable. The “contracted” ODE system is immediately obtained by dividing member-by-member Eq. 17 by Eq. 18 under the condition that  $\dot{S}$  is not null. The integration of such an ODE system would then require to split each trajectory into “portions” where  $S(t)$  is strictly monotonically decreasing or increasing to ensure  $\dot{S} \neq 0$ .
- [23] By adopting the graph representation of the reactive system (see Fig.1) such a set of relevant  $z_Q$  functions turns out to be associated to the nodes for which the logarithms of the non-null inward connections (taken in absolute value) evolve with the *highest* and equal rate (with sign). As long as such an ensemble of  $d$  nodes remains the same, the subspace  $\mathcal{A}$  attracts the state vector  $\psi$ . To see this, let us turn to a new graph whose connections are  $\epsilon_{Q,Q'} = \ln |V_{Q,Q'}|$  if  $V_{Q,Q'} \neq 0$ . By considering that  $V_{Q,Q'}$  does not change sign during the evolution, one has that  $\dot{\epsilon}_{Q,Q'} = -z_{Q'}$ . Now consider the set of  $d$  nodes  $Q_1^*, Q_2^*, \dots, Q_d^*$  such that  $z_{Q_i^*}(\mathbf{x}(t)) = z_{\min}(\mathbf{x}(t))$ . Then,  $\dot{\epsilon}_{Q,Q_i^*} = -z_{\min}$ . By taking into account the negative sign, the statement made above follows.
- [24] The first of Eqs. 26 is nothing but a specific implementation of the continuous realization of the iterative “power method” to find the dominant eigenvector of a matrix [M. T. Chu, “On the continuous realization of iterative processes”, *SIAM Review* **30**(3), 375 (1988)]. In all generality, consider a matrix  $\mathbf{B}(t)$  with *constant* eigenvectors (such that  $\mathbf{B}(t)$  and  $\int_{t_0}^t \mathbf{B}(t') dt'$  do commute). Then call  $\mathbf{d}$  the “dominant” eigenvector associated to the eigenvalue with *lowest*

real part. Given a unit vector  $\mathbf{n}(t)$  which evolves according to  $\dot{\mathbf{n}} = -\mathbf{B}\mathbf{n} + (\mathbf{n} \cdot \mathbf{B}\mathbf{n})\mathbf{n}$ , and such that  $\mathbf{n}(t_0)$  has a non-null projection on  $\mathbf{d}$ , then  $\lim_{t \rightarrow \infty} \mathbf{n}(t) = \mathbf{d}$ . In the present case,  $\mathbf{B}(t) \equiv Z(t)\text{diag}(\boldsymbol{\rho}(t))$  and the eigenvectors of  $\text{diag}(\boldsymbol{\rho}(t))$  are indeed fixed. However, the degeneracy on the lowest eigenvalue (which is at least  $Q_s$ -fold) implies that  $\boldsymbol{\psi}$  is attracted by a subspace rather than by a single dominant eigenvector.

- [25] There may be cases in which  $\mathcal{A}$  is defined but the attractiveness is missing, namely when  $v_J(\mathbf{x}) = 0$  for all  $J \in \mathbf{J}_{\mathcal{A}}$ . This happens for schemes with rates  $z_{Q^*}$  which tend to finite negative values at the stationary state. The corresponding  $h_{Q^*}$  functions diverge but  $V_{Q,Q^*}$  are identically null for all  $Q$  as demonstrated in the Appendix. Thus, the components  $\psi_{J=(Q,Q')}(\mathbf{x}(t))$  are identically null for all  $J \in \mathbf{J}_{\mathcal{A}}$ , hence the vector  $\boldsymbol{\psi}(\mathbf{x}(t))$  cannot be attracted by  $\mathcal{A}$  when  $\mathbf{x}(t)$  is inside the related domain in the concentration space. But this simply means that the dynamics of the  $\psi_J$  elements is confined outside the subspace  $\mathcal{A}$ . Also in this case, it is possible to find *other* attracting subspaces by following the procedure described in the main text taking into account only the subspace complementary to  $\mathcal{A}$  for the search.
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- [27] The FORTRAN code has been downloaded from: <http://www.radford.edu/~thompson/vodef90web/vodef90source/misc.html>. Last view: 30<sup>th</sup> September 2015.
- [28] It is important to stress that the choice of working with the “reduced” set of  $z_Q$  components is determined only by practical reasons. Of course, the conclusions drawn in the following hold also if the complete set is taken into account.
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## CAPTIONS TO FIGURES

### Figure 1

Schematic of the quadratic ODE system in Eq. (5) in terms of evolution of the connections of a weighted/oriented graph with  $Q_s$  nodes, each labelling a pair species/reaction.

### Figure 2

Schematic of the connection between a trajectory  $\mathbf{x}(t)$  in the concentration space, and the set of lowest  $z_Q$  faunctions that specify the actual attracting subspace for the corresponding dynamics of the state vector  $\boldsymbol{\psi}(\mathbf{x}(t))$  in the hyper-spherical representation. As long as the trajectory lies within a domain  $c(\mathcal{A})$  such that the set of the smallest  $z_Q$  functions remains unaltered, the state vector is monotonically attracted towards the subspace  $\mathcal{A}$  (unequivocally specified) in the  $Q_s^2$ -dimensional extended space.

### Figure 3

Projection of the concentration space portrait on the reactants plane for Scheme A. Black lines are trajectories generated from initial points drawn at random. Red and blue lines are “pilot trajectories” (which are tracked in the following figures) starting from above and from below the perceived projection of SM. Each colored domain corresponds to the related attracting subspace  $\mathcal{A}$  associated to the smallest  $z_Q$  function (in this case  $d = 1$  with reference to the schematic of Fig. 2). The legend for the color code is provided in the lower panel.

### Figure 4

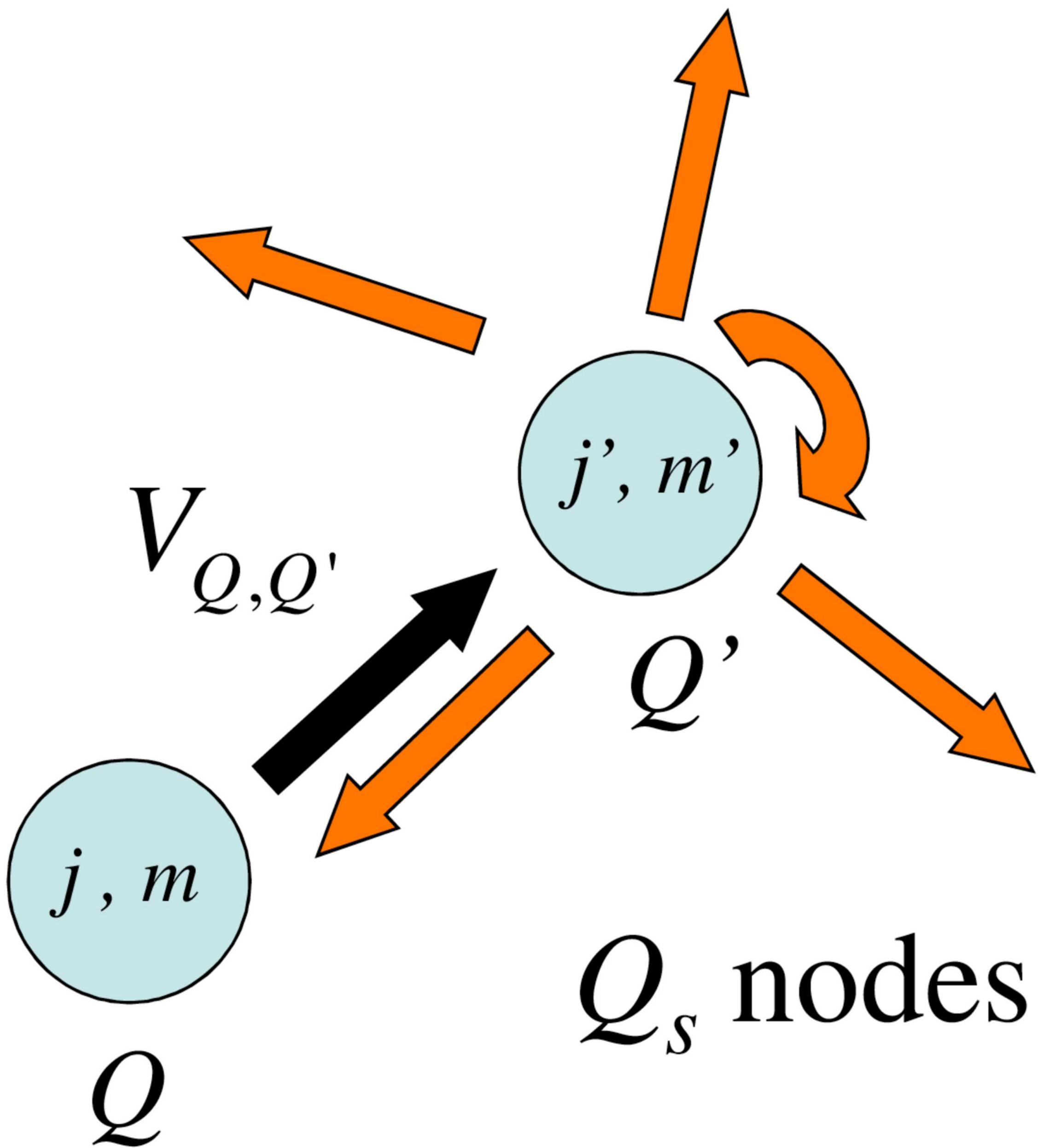
Associations of the pilot trajectories of Scheme A to the attracting subspaces (same colors as in Fig. 3). The number on the ordinate axis identifies each attracting subspace  $\mathcal{A}$  according to the associations given in the lower panel of Fig. 3. The inset magnifies the initial fast evolution by means of logarithmic scale on the time axis. The vertical dashed lines are placed at times which correspond, for the two trajectories, to points close to the perceived SM.

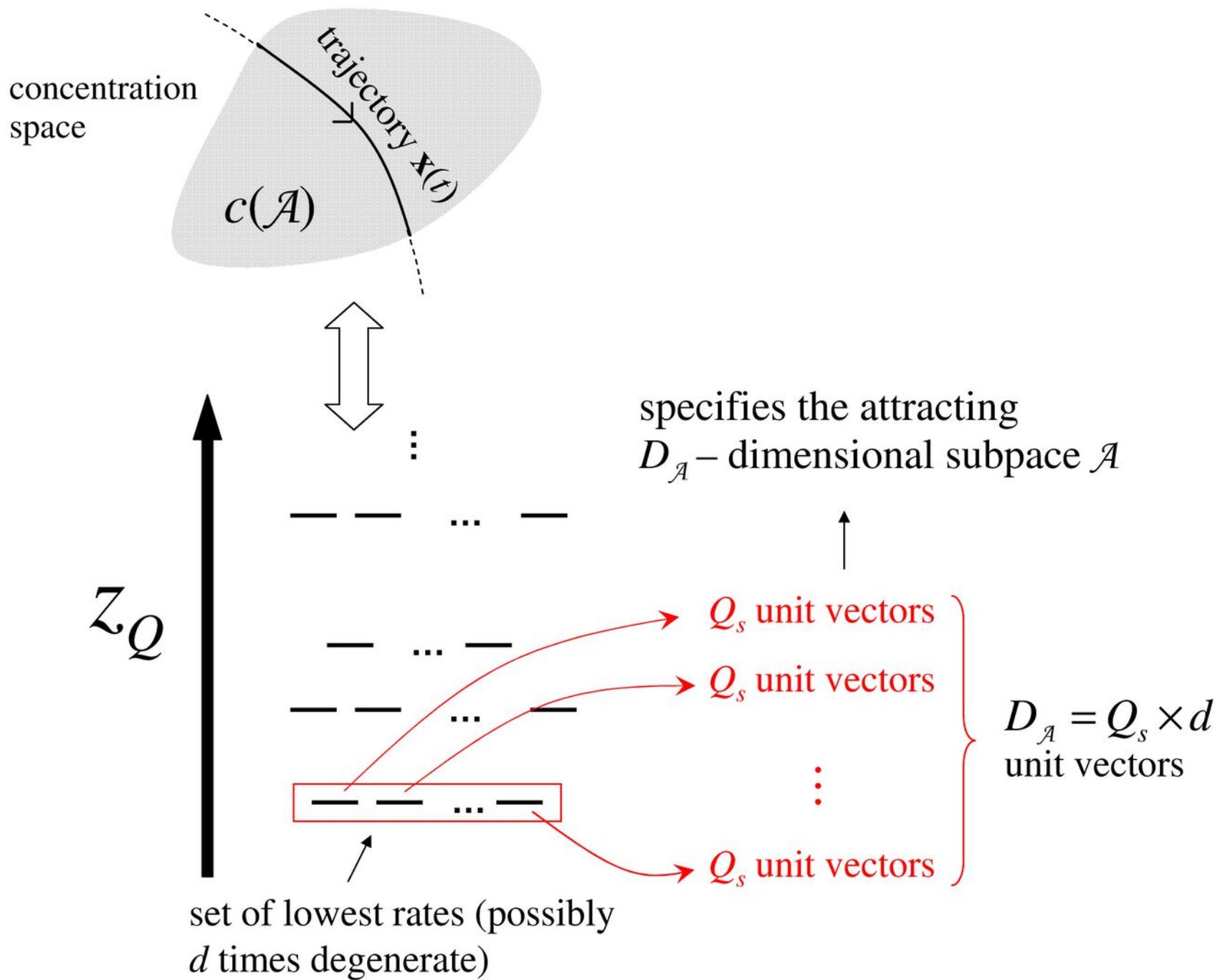
### Figure 5

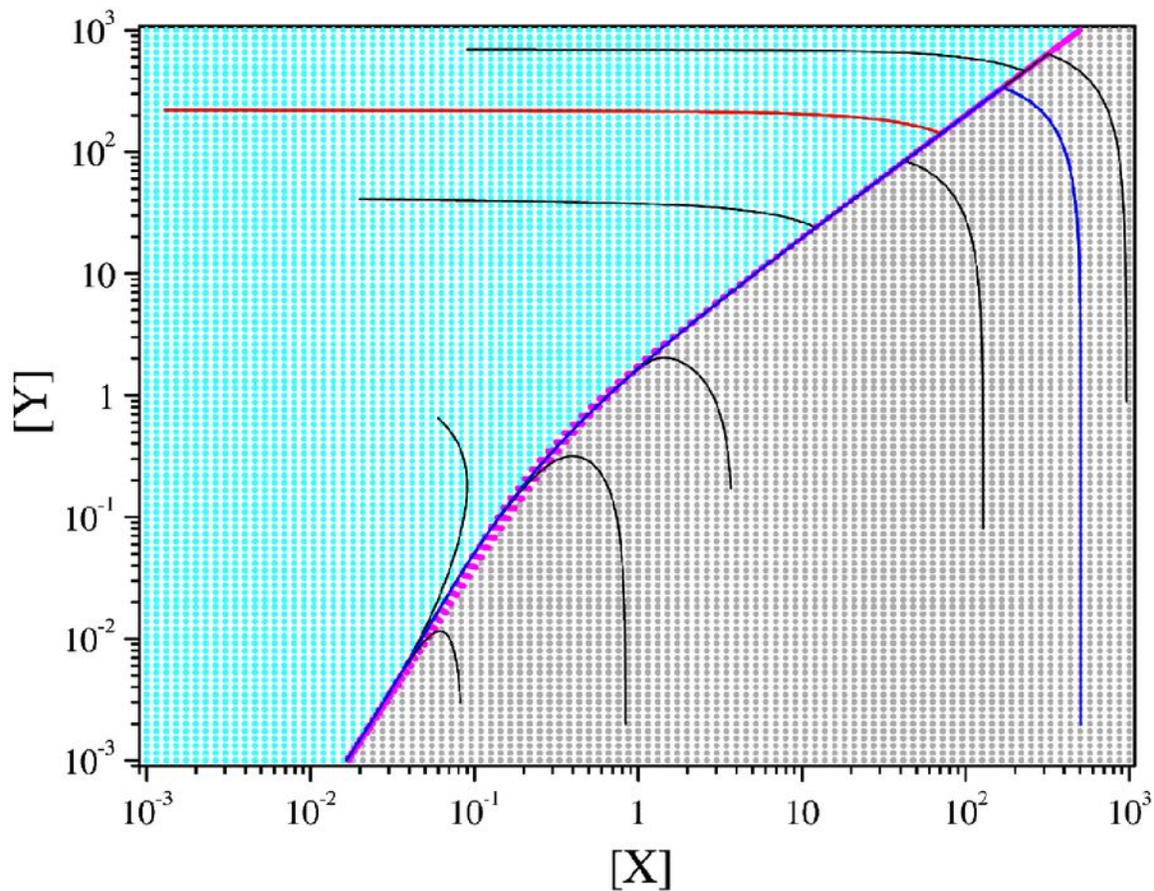
Approach of  $\boldsymbol{\psi}(t)$  to the actual attracting subspace  $\mathcal{A}$  in terms of Euclidean distance  $d_{\mathcal{A}}$  (solid lines), and evolution of  $Z$  (dashed lines), for the two pilot trajectories of Scheme A displayed in Fig. 3 (red and blue colors refer to the corresponding trajectories). Vertical lines indicate the change of attracting subspace (*i.e.*, the change of domain in Fig. 3).

**Figure 6**

Landscapes of  $Z(\mathbf{x})$  and  $Z_1(\mathbf{x})$  as functions of the reactants concentrations for Scheme A (only the first six  $z_Q$  components are considered). The insets show the contour plots with colors from red to blue corresponding to the decrease of magnitude.







$n \leftrightarrow \mathcal{A}$	lowest $z_Q$
1	$z_4$
2	$z_3$
3	$z_6 = 0$

