

Method of invariant manifold for chemical kinetics

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Abstract

In this paper, we review the construction of low-dimensional manifolds of reduced description for equations of chemical kinetics from the standpoint of the method of invariant manifold (MIM). The MIM is based on a formulation of the condition of invariance as an equation, and its solution by Newton iterations. A review of existing alternative methods is extended by a thermodynamically consistent version of the method of intrinsic low-dimensional manifolds. A grid-based version of the MIM is developed, and model extensions of low-dimensional dynamics are described. Generalizations to open systems are suggested. The set of methods covered makes it possible to effectively reduce description in chemical kinetics.

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1. Introduction

In this paper, we present a general method of constructing the reduced description for dissipative systems of reaction kinetics. Our approach is based on the method of invariant manifold which was developed at the end of the 1980s–early 1990s by Gorban and Karlin (1992a, b). Its realization for a generic dissipative systems was discussed by Gorban and Karlin (1994, 1996, 1996a); Gorban et al., 1996, 1999; Gorban, Karlin, Ilg, and Öttinger (2001a). This method was applied to a set of problems of classical kinetic theory based on the Boltzmann kinetic equation (Gorban & Karlin, 1994; Karlin, Dukek, & Nonnenmacher, 1997; Karlin, Gorban, Dukek, & Nonnenmacher, 1998). The method of invariant manifold was successfully applied to a derivation of the reduced description for kinetic equations of polymeric solutions (Zmievskii, Karlin, & Deville, 2000). It has also been tested on systems of chemical kinetics (Gorban, Karlin, Zmievskii, & Dymova, 2000).

The goal of nonequilibrium statistical physics is the understanding of how a system with many degrees of freedom acquires a description with few degrees of freedom.

This should lead to reliable methods of extracting the macroscopic description from a detailed microscopic description.

While this general problem is still far from the final solution, it is reasonable to study simplified models, where, on the one hand, a detailed description is accessible to numerics, and on the other hand, analytical methods designed to the solution of problems in real systems can be tested.

In this paper, we address the class of finite-dimensional systems, well known from the theory of reaction kinetics. These are equations governing a complex relaxation in perfectly stirred closed chemically active mixtures. The dissipative properties of such systems are characterized by a global convex Lyapunov function G (thermodynamic potential) which implements the second law of thermodynamics: as the time t tends to infinity, the system reaches the unique equilibrium state, while in the course of the transition the Lyapunov function decreases monotonically.

Although the limiting behavior of the dissipative systems just described is certainly very simple, there are still interesting questions to be asked about it. One of these is closely related to the above general problem of nonequilibrium statistical physics. Indeed, evidence of numerical integration of such systems often demonstrates that the relaxation has a certain geometrical structure in the phase space. Namely, typical individual trajectories tend to manifolds of lower dimension, and further proceed to the equilibrium essentially along these manifolds. Thus, such systems demonstrate a

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dimensional reduction, and therefore establish a more macroscopic description after some time since the beginning of the relaxation.

There are two intuitive ideas behind our approach, and we shall now discuss them informally. The objects to be considered below are manifolds (surfaces) Ω in the phase space of the reaction kinetic system (the phase space is usually a convex polytope in a finite-dimensional real space). The ‘ideal’ picture of the reduced description we have in mind is as follows: a typical phase trajectory, $c(t)$, where t is the time and c is an element of the phase space, consists of two pronounced segments. The first segment connects the beginning of the trajectory, $c(0)$, with a certain point, $c(t_1)$, on the manifold Ω (rigorously speaking, we should think of $c(t_1)$ not on Ω but in a small neighborhood of Ω , but this is inessential for the ideal picture). The second segment belongs to Ω and connects the point $c(t_1)$ with the equilibrium $c^{\text{eq}} = c(\infty)$, $c^{\text{eq}} \in \Omega$. Thus, the manifolds appearing in our ideal picture are “patterns” formed by the segments of individual trajectories, and the goal of the reduced description is to “filter out” this manifold.

There are two important features behind this ideal picture. The first feature is the *invariance* of the manifold Ω : once the individual trajectory has started on Ω , it does not leave Ω anymore. The second feature is the *projecting*: the phase points outside Ω will be projected onto Ω . Furthermore, the dissipativity of the system provides an *additional* information about this ideal picture: regardless of what happens on the manifold Ω , the function G was decreasing along each individual trajectory before it reached Ω . This ideal picture is the guide to extract slow invariant manifolds.

One more point needs a clarification before going any further. Low-dimensional invariant manifolds exist also for systems with a more complicated dynamic behavior, so why to study the invariant manifolds of slow motions for a particular class of purely dissipative systems? The answer is in the following: most of the physically significant models include non-dissipative components in the form of either a conservative dynamics, or in the form of external forcing or external fluxes. An example of the first kind is the free flight of particles on top of the dissipation-producing collisions in the Boltzmann equation. For the second type of example one can think of irreversible reactions among the suggested stoichiometric mechanism (inverse processes are so improbable that we discard them completely, thereby effectively “opening” the system to the remaining irreversible flux). For all such systems, the present method is applicable almost without special refinements, and bears the significance that invariant manifolds are constructed as a “deformation” of the relevant manifolds of slow motion of the purely dissipative dynamics. An example of this construction for open systems is presented in Section 10. Till then we focus on the purely dissipative case for the reason just clarified.

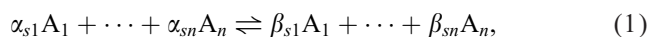
The paper is organized as follows. In Section 2, we review the reaction kinetics (Section 2.1), and discuss the

main methods of model reduction in chemical kinetics (Section 2.2). In particular, we present two general versions of extending partially equilibrium manifolds to a single relaxation time model in the whole phase space, and develop a thermodynamically consistent version of the intrinsic low-dimensional manifold (ILDM) approach. In Section 3, we introduce the method of invariant manifold in the way appropriate to this class of nonequilibrium systems. In Sections 4 and 5, we give some details on the two relatively independent parts of the method, the thermodynamic projector, and the iterations for solving the invariance equation. We also introduce a general symmetric linearization procedure for the invariance equation, and discuss its relevance to the picture of decomposition of motions. In Section 6, these two procedures are combined into a unique algorithm. In Section 7, we demonstrate an illustrative example of computations for a model catalytic reaction. In Section 8, we demonstrate how the thermodynamic projector is constructed without the a priori parameterization of the manifold. This result is essentially used in Section 9, where we introduce a computationally effective grid-based method to construct invariant manifolds. In Section 10, we describe an extension of the method of invariant manifold to open systems. Finally, results are discussed in Section 11.

2. Equations of chemical kinetics and their reduction

2.1. Outline of dissipative reaction kinetics

We begin with an outline of reaction kinetics (for details see, e.g., the book of Yablonskii, Bykov, Gorban, & Elokhin, 1991). Let us consider a closed system with n chemical species A_1, \dots, A_n , participating in a complex reaction. The complex reaction is represented by the following stoichiometric mechanism:



where the index $s = 1, \dots, r$ enumerates the reaction steps, and where the integers α_{si} and β_{si} are stoichiometric coefficients. For each reaction step s , we introduce n -component vectors α_s and β_s with components α_{si} and β_{si} . The notation γ_s stands for the vector with integer components $\gamma_{si} = \beta_{si} - \alpha_{si}$ (the stoichiometric vector). We adopt an abbreviated notation for the standard scalar product of the n -component vectors:

$$\langle \mathbf{x}, \mathbf{y} \rangle = \sum_{i=1}^n x_i y_i.$$

The system is described by the n -component concentration vector \mathbf{c} , where the component $c_i \geq 0$ represents the concentration of the species A_i . Conservation laws impose linear constraints on admissible vectors \mathbf{c} (balances):

$$\langle \mathbf{b}_i, \mathbf{c} \rangle = B_i, \quad i = 1, \dots, l, \quad (2)$$

where \mathbf{b}_i are fixed and linearly independent vectors, and B_i are given scalars. Let us denote as \mathbf{B} the set of vectors which

satisfy the conservation laws (2):

$$\mathbf{B} = \{c \langle \mathbf{b}_1, \mathbf{c} \rangle = B_1, \dots, \langle \mathbf{b}_l, \mathbf{c} \rangle = B_l\}.$$

The phase space \mathcal{V} of the system is the intersection of the cone of n -dimensional vectors with nonnegative components, with the set \mathbf{B} , and $\dim \mathcal{V} = d = n - l$. In the sequel, we term a vector $\mathbf{c} \in \mathcal{V}$ the state of the system. In addition, we assume that each of the conservation laws is supported by each elementary reaction step, that is

$$\langle \boldsymbol{\gamma}_s, \mathbf{b}_i \rangle = 0, \quad (3)$$

for each pair of vectors $\boldsymbol{\gamma}_s$ and \mathbf{b}_i .

Reaction kinetic equations describe variations of the states in time. Given the stoichiometric mechanism (1), the reaction kinetic equations read:

$$\dot{\mathbf{c}} = \mathbf{J}(\mathbf{c}), \quad \mathbf{J}(\mathbf{c}) = \sum_{s=1}^r \boldsymbol{\gamma}_s W_s(\mathbf{c}), \quad (4)$$

where the overdot denotes the time derivative, and W_s is the reaction rate function of the step s . In particular, the mass action law suggests a polynomial form for the reaction rates:

$$W_s = k_s^+ \prod_{i=1}^n c_i^{\alpha_i} - k_s^- \prod_{i=1}^n c_i^{\beta_i}, \quad (5)$$

where k_s^+ and k_s^- are the constants of the direct and of the inverse reactions rates of the s th reaction step. The phase space \mathcal{V} is a positive-invariant of system (4): if $\mathbf{c}(0) \in \mathcal{V}$, then $\mathbf{c}(t) \in \mathcal{V}$ for all the times $t > 0$.

In the sequel, we assume that the kinetic equation (4) describes the evolution towards the unique equilibrium state, \mathbf{c}^{eq} , in the interior of the phase space \mathcal{V} . Furthermore, we assume that there exists a strictly convex function $G(\mathbf{c})$ which decreases monotonically in time due to Eq. (4):

$$\dot{G} = \langle \nabla G(\mathbf{c}), \mathbf{J}(\mathbf{c}) \rangle \leq 0. \quad (6)$$

Here ∇G is the vector of partial derivatives $\partial G / \partial c_i$, and the convexity assumes that the $n \times n$ matrices

$$\mathbf{H}_c = \|\partial^2 G(\mathbf{c}) / \partial c_i \partial c_j\|, \quad (7)$$

are positive definite for all $\mathbf{c} \in \mathcal{V}$. In addition, we assume that the matrices (7) are invertible if \mathbf{c} is taken in the interior of the phase space.

The function G is the Lyapunov function of system (4), and \mathbf{c}^{eq} is the point of global minimum of the function G in the phase space \mathcal{V} . Otherwise stated, the manifold of equilibrium states $\mathbf{c}^{\text{eq}}(B_1, \dots, B_l)$ is the solution to the variational problem,

$$G \rightarrow \min \text{ for } \langle \mathbf{b}_i, \mathbf{c} \rangle = B_i, \quad i = 1, \dots, l. \quad (8)$$

For each fixed value of the conserved quantities B_i , the solution is unique. In many cases, however, it is convenient to consider the whole equilibrium manifold, keeping the conserved quantities as parameters.

For example, for perfect systems in a constant volume under a constant temperature, the Lyapunov function G reads:

$$G = \sum_{i=1}^n c_i [\ln(c_i / c_i^{\text{eq}}) - 1]. \quad (9)$$

It is important to stress that \mathbf{c}^{eq} in Eq. (9) is an *arbitrary* equilibrium of the system, under arbitrary values of the balances. In order to compute $G(\mathbf{c})$, it is unnecessary to calculate the specific equilibrium \mathbf{c}^{eq} which corresponds to the initial state \mathbf{c} . Moreover, for ideal systems, the function G is constructed from the thermodynamic data of individual species, and, as a result of this construction, it turns out that it has the form of Eq. (9). Let us mention here the classical formula for the free energy $F = RTVG$:

$$F = VRT \sum_{i=1}^n c_i [(\ln(c_i V_{Q_i}) - 1) + F_{\text{int } i}(T)], \quad (10)$$

where V is the volume of the system, T is the temperature, $V_{Q_i} = N_0 (2\pi\hbar^2 / m_i kT)^{3/2}$ is the quantum volume of one mole of the species A_i , N_0 is the Avogadro number, m_i is the mass of a molecule of A_i , $R = kN_0$, and $F_{\text{int } i}(T)$ is the free energy of the internal degrees of freedom per mole of A_i .

Finally, we recall an important generalization of the mass action law (5), known as the Marcelin–De Donder kinetic function. This generalization was developed by Feinberg (1972) based on ideas of the thermodynamic theory of affinity (De Donder & Van Rysselberghe, 1936). We use the kinetic function suggested by Bykov, Gorban, and Yablonskii (1982). Within this approach, the functions W_s are constructed as follows: for a given strictly convex function G , and for a given stoichiometric mechanism (1), we define the gain (+) and the loss (–) rates of the s th step,

$$W_s^+ = \varphi_s^+ \exp[\langle \nabla G, \boldsymbol{\alpha}_s \rangle], \quad W_s^- = \varphi_s^- \exp[\langle \nabla G, \boldsymbol{\beta}_s \rangle], \quad (11)$$

where $\varphi_s^\pm > 0$ are kinetic factors. The Marcelin–De Donder kinetic function reads: $W_s = W_s^+ - W_s^-$, and the right-hand side of the kinetic equation (4) becomes

$$\mathbf{J} = \sum_{s=1}^r \boldsymbol{\gamma}_s \{ \varphi_s^+ \exp[\langle \nabla G, \boldsymbol{\alpha}_s \rangle] - \varphi_s^- \exp[\langle \nabla G, \boldsymbol{\beta}_s \rangle] \}. \quad (12)$$

For the Marcelin–De Donder reaction rate (11), the dissipation inequality (6) reads:

$$\begin{aligned} \dot{G} &= \sum_{s=1}^r [\langle \nabla G, \boldsymbol{\beta}_s \rangle - \langle \nabla G, \boldsymbol{\alpha}_s \rangle] \\ &\times \{ \varphi_s^+ e^{\langle \nabla G, \boldsymbol{\alpha}_s \rangle} - \varphi_s^- e^{\langle \nabla G, \boldsymbol{\beta}_s \rangle} \} \leq 0. \end{aligned} \quad (13)$$

The kinetic factors φ_s^\pm should satisfy certain conditions in order to make valid the dissipation inequality (13). A well-known sufficient condition is the detail balance:

$$\varphi_s^+ = \varphi_s^-, \quad (14)$$

other sufficient conditions are discussed in detail elsewhere (Yablonskii et al., 1991; Gorban, 1984; Karlin, 1989, 1993). For the function G of the form (9), the Marcelin–De Donder equation casts into the more familiar mass action law form (5).

2.2. The problem of reduced description in chemical kinetics

What does it mean, “to reduce the description of a chemical system”? This means the following:

- (1) To shorten the list of species. This, in turn, can be achieved in two ways:
 - (i) To eliminate inessential components from the list;
 - (ii) To lump some of the species into integrated components.
- (2) To shorten the list of reactions. This also can be done in several ways:
 - (i) To eliminate inessential reactions, those which do not significantly influence the reaction process;
 - (ii) To assume that some of the reactions “have been already completed”, and that the equilibrium has been reached along their paths (this leads to dimensional reduction because the rate constants of the “completed” reactions are not used thereafter, what one needs are equilibrium constants only).
- (3) To decompose the motions into fast and slow, into independent (almost-independent) and slaved, etc. As the result of such a decomposition, the system admits a study “in parts”. After that, results of this study are combined into a joint picture. There are several approaches which fall into this category: the famous method of the quasi-steady state (QSS), pioneered by Bodenstein and Semenov and explored in considerable detail by many authors, in particular, by Bowen, Acrivos, and Oppenheim (1963); Chen (1988); Segel and Slemrod (1989); Fraser (1988); Roussel and Fraser (1990, 1991), and many others; the quasi-equilibrium approximation (Orlov & Rozonoer, 1984; Gorban, 1984; Volpert & Hudjaev, 1985; Fraser, 1988; Karlin, 1989, 1993); methods of sensitivity analysis (Rabitz, Kramer, & Dacol, 1983; Lam & Goussis, 1994); methods based on the derivation of the so-called intrinsic low-dimensional manifolds (ILDm, as suggested by Maas & Pope, 1992). Our method of invariant manifold (MIM, Gorban & Karlin, 1992, 1992a, b, 1994; Gorban et al., 2000, 2001a) also belongs to this kind of methods.

Why reduce description in the times of supercomputers?

First, in order to gain understanding. In the process of reducing the description one is often able to extract the essential, and the mechanisms of the processes under study become more transparent. Second, if one is given the detailed description of the system, then one should be able also to solve the initial-value problem for this system. But what should one do in the case where the system is representing just a point in a three-dimensional flow? The problem of reduction becomes particularly important for modeling the spatially distributed physical and chemical processes. Third, without reducing the kinetic model, it is impossible to con-

struct this model. This statement seems paradoxical only at the first glance: how come, the model is first simplified, and is constructed only after the simplification is done? However, in practice, the statement of the problem that is typical for a mathematician (“let the system of differential equations be *given*, then...”) is only rarely applicable in chemical engineering science for detailed kinetics. Some reactions are known precisely, some other only hypothetically. Some intermediate species are well studied, some others not, not much is known about them. The situation is even worse with reaction rates. On the contrary, the thermodynamic data (energies, enthalpies, entropies, chemical potentials, etc.) for sufficiently rarefied systems are quite reliable. The final identification of the model is always done on the basis of comparison with experiments and with the help of fitting. For this purpose, it is extremely important to reduce the dimension of the system, and to reduce the number of tunable parameters. The normal logic of modeling for the purpose of chemical engineering science is the following: Exceedingly detailed but coarse with respect to parameters system \rightarrow reduction \rightarrow fitting \rightarrow reduced model with specified parameters (cycles are allowed in this scheme, with returns from fitting to more detailed models, etc.). A more radical viewpoint is also possible: “in chemical engineering science, detailed kinetics is impossible, useless, and does not exist.” For a recently published discussion on this topic see Levenspiel (1999, 2000); Yablonsky (2000).

Alas, with a mathematical statement of the problem related to reduction, we all have to begin with the usual: let the system of differential equations be given Enormous difficulties related to the question of how well the original system is modeling the real kinetics remain out of focus of these studies.

Our present work is devoted to studying reductions in a given system of kinetic equations to invariant manifolds of slow motions. We begin with a brief discussion of existing approaches.

2.3. Partial equilibrium approximations

Quasi-equilibrium with respect to reactions is constructed as follows: from the list of reactions (1), one selects those which are assumed to equilibrate first. Let these be indexed with the numbers s_1, \dots, s_k . The quasi-equilibrium manifold is defined by the system of equations,

$$W_{s_i}^+ = W_{s_i}^-, \quad i = 1, \dots, k. \quad (15)$$

This system of equations looks particularly elegant when written in terms of conjugated (dual) variables, $\mu = \nabla G$:

$$\langle \gamma_{s_i}, \mu \rangle = 0, \quad i = 1, \dots, k. \quad (16)$$

In terms of conjugated variables, the quasi-equilibrium manifold forms a linear subspace. This subspace, L^\perp , is the orthogonal complement to the linear envelope of vectors, $L = \text{lin}\{\gamma_{s_1}, \dots, \gamma_{s_k}\}$.

Quasi-equilibrium with respect to species is constructed practically in the same way but without selecting the subset of reactions. For a given set of species, A_{i_1}, \dots, A_{i_k} , one assumes that they evolve fast to equilibrium and remain there. Formally, this means that in the k -dimensional subspace of the space of concentrations with the coordinates c_{i_1}, \dots, c_{i_k} , one constructs the subspace L which is defined by the balance equations, $\langle \mathbf{b}_i, \mathbf{c} \rangle = 0$. In terms of the conjugated variables, the quasi-equilibrium manifold, L^\perp , is defined by equations,

$$\boldsymbol{\mu} \in L^\perp, \quad (\boldsymbol{\mu} = (\mu_1, \dots, \mu_n)). \quad (17)$$

The same quasi-equilibrium manifold can also be defined with the help of fictitious reactions: let $\mathbf{g}_1, \dots, \mathbf{g}_q$ be a basis in L . Then Eq. (17) may be rewritten as follows:

$$\langle \mathbf{g}_i, \boldsymbol{\mu} \rangle = 0, \quad i = 1, \dots, q. \quad (18)$$

Illustration: Quasi-equilibrium with respect to reactions in hydrogen oxidation: let us assume equilibrium with respect to dissociation reactions, $\text{H}_2 \rightleftharpoons 2\text{H}$, and $\text{O}_2 \rightleftharpoons 2\text{O}$, in some subdomain of reaction conditions. This gives:

$$k_1^+ c_{\text{H}_2} = k_1^- c_{\text{H}}^2, \quad k_2^+ c_{\text{O}_2} = k_2^- c_{\text{O}}^2.$$

Quasi-equilibrium with respect to species: for the same reaction, let us assume equilibrium over H, O, OH, and H_2O_2 , in a subdomain of reaction conditions. The subspace L is defined by balance constraints:

$$c_{\text{H}} + c_{\text{OH}} + 2c_{\text{H}_2\text{O}_2} = 0, \quad c_{\text{O}} + c_{\text{OH}} + 2c_{\text{H}_2\text{O}_2} = 0.$$

The subspace L is two-dimensional. Its basis, $\{\mathbf{g}_1, \mathbf{g}_2\}$ in the coordinates c_{H} , c_{O} , c_{OH} , and $c_{\text{H}_2\text{O}_2}$ reads:

$$\mathbf{g}_1 = (1, 1, -1, 0), \quad \mathbf{g}_2 = (2, 2, 0, -1).$$

The corresponding Eq. (18) is

$$\mu_{\text{H}} + \mu_{\text{O}} = \mu_{\text{OH}}, \quad 2\mu_{\text{H}} + 2\mu_{\text{O}} = \mu_{\text{H}_2\text{O}_2}.$$

General construction of the quasi-equilibrium manifold: In the space of concentration, one defines a subspace L which satisfies the balance constraints:

$$\langle \mathbf{b}_i, L \rangle \equiv 0.$$

The orthogonal complement of L in the space with coordinates $\boldsymbol{\mu} = \nabla G$ defines then the quasi-equilibrium manifold Ω_L . For the actual computations, one requires the inversion from $\boldsymbol{\mu}$ to \mathbf{c} . The duality structure $\boldsymbol{\mu} \leftrightarrow \mathbf{c}$ is well studied by many authors (Orlov & Rozonoer, 1984; Dukek, Karlin, & Nonnenmacher, 1997).

Quasi-equilibrium projector. It is not sufficient to just derive the manifold, it is also required to define a *projector* which will transform the vector field defined on the space of concentrations to a vector field on the manifold. The quasi-equilibrium manifold consists of points which minimize G on the affine spaces of the form $\mathbf{c} + L$. These affine planes are hypothetical planes of fast motions (G is decreasing in the course of the fast motions). Therefore, the

quasi-equilibrium projector maps the whole space of concentrations on Ω_L parallel to L . The vector field is also projected onto the tangent space of Ω_L parallel to L .

Thus, the quasi-equilibrium approximation implies the decomposition of motions into the fast (parallel to L) and the slow (along the quasi-equilibrium manifold). In order to construct the quasi-equilibrium approximation, knowledge of reaction rate constants of “fast” reactions is not required (stoichiometric vectors of all these fast reaction are in L , $\boldsymbol{\gamma}_{\text{fast}} \in L$, thus, knowledge of L suffices), one only needs some confidence in that they all are sufficiently fast (Volpert & Hudjaev, 1985). The quasi-equilibrium manifold itself is constructed based on the knowledge of L and of G . Dynamics on the quasi-equilibrium manifold is defined as the quasi-equilibrium projection of the “slow component” of the kinetic equations (4).

2.4. Model equations

The assumption behind the quasi-equilibrium is the hypothesis of the decomposition of motions into fast and slow. The quasi-equilibrium approximation itself describes slow motions. However, sometimes it becomes necessary to return to the whole system, and to take into account the fast motions as well. With this, it is desirable to keep intact one of the important advantages of the quasi-equilibrium approximation—its independence of the rate constants of fast reactions. For this purpose, the detailed fast kinetics is replaced by a model equation (*single relaxation time approximation*).

Quasi-equilibrium models (QEM) are constructed as follows: for each concentration vector \mathbf{c} , consider the affine manifold, $\mathbf{c} + L$. Its intersection with the quasi-equilibrium manifold Ω_L consists of one point. This point delivers the minimum to G on $\mathbf{c} + L$. Let us denote this point as $\mathbf{c}_L^*(\mathbf{c})$. The equation of the quasi-equilibrium model reads:

$$\dot{\mathbf{c}} = -\frac{1}{\tau} [\mathbf{c} - \mathbf{c}_L^*(\mathbf{c})] + \sum_{\text{slow}} \boldsymbol{\gamma}_s W_s(\mathbf{c}_L^*(\mathbf{c})), \quad (19)$$

where $\tau > 0$ is the relaxation time of the fast subsystem. Rates of slow reactions are computed in the points $\mathbf{c}_L^*(\mathbf{c})$ (the second term in the right-hand side of Eq. (19), whereas the rapid motion is taken into account by a simple relaxational term (the first term in the right-hand side of Eq. (19)). The most famous model kinetic equation is the BGK equation in the theory of the Boltzmann equation (Bhatnagar, Gross, & Krook, 1954). The general theory of the quasi-equilibrium models, including proofs of their thermodynamic consistency, was constructed by Gorban and Karlin (1992c, 1994a).

Single relaxation time gradient models (SRTGM) were considered by Ansumali and Karlin (2000, 2002, 2002a) in the context of the lattice Boltzmann method for hydrodynamics. These models are aimed at improving the obvious

drawback of quasi-equilibrium models (19): in order to construct the QEM, one needs to compute the function,

$$c_L^*(c) = \arg \min_{x \in c+L, x > 0} G(x). \quad (20)$$

This is a convex programming problem. It does not always have a closed-form solution.

Let g_1, \dots, g_k is the orthonormal basis of L . We denote as $D(c)$ the $k \times k$ matrix with the elements $\langle g_i, H_c g_j \rangle$, where H_c is the matrix of second derivatives of G (7). Let $C(c)$ be the inverse of $D(c)$. The single relaxation time gradient model has the form:

$$\dot{c} = -\frac{1}{\tau} \sum_{i,j} g_i C(c)_{ij} \langle g_j, \nabla G \rangle + \sum_{\text{slow}} \gamma_s W_s(c). \quad (21)$$

The first term drives the system to the minimum of G on $c + L$, it does not require solving problem (20), and its spectrum in the quasi-equilibrium is the same as in the quasi-equilibrium model (19). Note that the slow component is evaluated in the “current” state c .

Models (19) and (21) lift the quasi-equilibrium approximation to a kinetic equation by approximating the fast dynamics with a single “reaction rate constant” – relaxation time τ .

2.5. Quasi-steady state approximation

The quasi-steady state approximation (QSS) is a tool used in a huge amount of works. Let us split the list of species in two groups: the basic and the intermediate (radicals, etc.). Concentration vectors are denoted accordingly, c^s (slow, basic species), and c^f (fast, intermediate species). The concentration vector c is the direct sum, $c = c^s \oplus c^f$. The fast subsystem is Eq. (4) for the component c^f at fixed values of c^s . If it happens that the fast subsystem defined this way relaxes to a stationary state, $c^f \rightarrow c_{qss}^f(c^s)$, then the assumption that $c^f = c_{qss}^f(c^s)$ is precisely the QSS assumption. The slow subsystem is the part of the system (4) for c^s , in the right-hand side of which the component c^f is replaced with $c_{qss}^f(c^s)$. Thus, $J = J_s \oplus J_f$, where

$$\dot{c}^f = J_f(c^s \oplus c^f), \quad c^s = \text{const}; \quad c^f \rightarrow c_{qss}^f(c^s); \quad (22)$$

$$\dot{c}^s = J_s(c^s \oplus c_{qss}^f(c^s)). \quad (23)$$

Bifurcations in system (22) under variation of c^s as a parameter are confronted to kinetic critical phenomena. Studies of more complicated dynamic phenomena in the fast subsystem (22) require various techniques of averaging, stability analysis of the averaged quantities, etc.

Various versions of the QSS method are possible, and are actually used widely, for example, the hierarchical QSS method. There, one defines not a single fast subsystem but a hierarchy of them, c^{f_1}, \dots, c^{f_k} . Each subsystem c^{f_i} is regarded as a slow system for all the foregoing subsystems, and it is regarded as a fast subsystem for the following members of the hierarchy. Instead of one system of

equations (22), a hierarchy of systems of lower-dimensional equations is considered, each of these subsystems being easier to study analytically.

The theory of singularly perturbed systems of ordinary differential equations is used to provide a mathematical background and further development of the QSS approximation (Bowen et al., 1963; Segel & Slemrod, 1989). In spite of a broad literature on this subject, it remains, in general, unclear, what is the smallness parameter that separates the intermediate (fast) species from the basic (slow). The reaction rate constant cannot be such a parameter (unlike in the case of the quasi-equilibrium). Indeed, intermediate species participate in the *same* reactions as the basic species (for example, $H_2 \rightleftharpoons 2H$, $H + O_2 \rightleftharpoons OH + O$). It is therefore incorrect to state that c^f evolves faster than c^s . In the sense of reaction rate constants, c^f is not faster.

For catalytic reactions, it is not difficult to figure out what is the smallness parameter that separates the intermediate species from the basic, and which allows to upgrade the QSS assumption to a singular perturbation theory rigorously (Yablonskii et al., 1991). This smallness parameter is the ratio of balances: intermediate species include the catalyst, and their total amount is simply significantly less than the amount of all the c_i 's. After renormalizing to variables of the same order of magnitude, the small parameter appears explicitly.

For the usual radicals, the origin of the smallness parameter is quite similar. There are much less radicals than the basic species (otherwise, the QSS assumption is inapplicable). In the case of radicals, however, the smallness parameter cannot be extracted directly from the balances B_i (2). Instead, one can come up with a thermodynamic estimate: the function G decreases in the course of reactions, whereupon we obtain the limiting estimate of concentrations of any species:

$$c_i \leq \max_{G(c) \leq G(c(0))} c_i, \quad (24)$$

where $c(0)$ is the initial composition. If the concentration c_R of the radical R is small both initially and in the equilibrium, then it should remain small also along the path to the equilibrium. For example, in the case of the ideal G (9) under relevant conditions, for any $t > 0$, the following inequality is valid:

$$c_R [\ln(c_R(t)/c_R^{eq}) - 1] \leq G(c(0)). \quad (25)$$

Inequality (25) provides the simplest (but rather coarse) thermodynamic estimate of $c_R(t)$ in terms of $G(c(0))$ and c_R^{eq} uniformly for $t > 0$. The complete theory of thermodynamic estimates of dynamics has been developed by Gorban (1984). One can also do computations without a priori estimates, if one accepts the QSS assumption until the values c^f stay sufficiently small.

Let us assume that an a priori estimate has been found, $c_i(t) \leq c_{i \max}$, for each c_i . These estimate may depend on the initial conditions, thermodynamic data, etc. With these estimates, we are able to renormalize the variables in the

kinetic equations (4) in such a way that the renormalized variables take their values from the unit segment $[0, 1]$: $\tilde{c}_i = c_i/c_{i \max}$. Then system (4) can be written as follows:

$$\frac{d\tilde{c}_i}{dt} = \frac{1}{c_{i \max}} J_i(\mathbf{c}). \quad (26)$$

The system of dimensionless parameters, $\varepsilon_i = c_{i \max}/\max_i c_{i \max}$ defines a hierarchy of relaxation times, and with its help one can establish various realizations of the QSS approximation. The simplest version is the standard QSS assumption: parameters ε_i are separated in two groups, the smaller ones, and those of the order 1. Accordingly, the concentration vector is split into $\mathbf{c}^s \oplus \mathbf{c}^f$. Various hierarchical QSS are possible: with this, the problem becomes more tractable analytically.

Corrections to the QSS approximation can be addressed in various ways (see, e.g., Vasil'eva, Butuzov, & Kalachev, 1995; Strygin & Sobolev, 1988). There exists a variety of ways to introduce the smallness parameter into kinetic equations, and one can find applications for each of the realizations. However, two particular realizations remain basic for chemical kinetics: (i) fast reactions (under given thermodynamic data); (ii) small concentrations. In the first case, one is led to the quasi-equilibrium approximation, in the second case, to the classical QSS assumption. Both of these approximations allow for hierarchical realizations, which include not just two but many relaxation time scales. Such a multi-scale approach essentially simplifies analytical studies of the problem.

The method of invariant manifold which we present below in Section 6 allows to use both the QE and the QSS as initial approximations in the iterative process of seeking slow invariant manifolds. It is also possible to use a different initial ansatz chosen by a physical intuition, like, for example, the Tamm–Mott–Smith approximation in the theory of strong shock waves (Gorban & Karlin, 1992).

2.6. Methods based on spectral decomposition of Jacobian fields

The idea to use the spectral decomposition of Jacobian fields in the problem of separating the motions into fast and slow originates from methods of analysis of stiff systems (Gear, 1971), and from methods of sensitivity analysis in control theory (Rabitz et al., 1983). There are two basic statements of the problem for these methods: (i) the problem of the slow manifold, and (ii) the problem of a complete decomposition (complete integrability) of kinetic equations. The first of these problems consists in constructing the slow manifold Ω , and a decomposition of motions into the fast one (towards Ω), and the slow one (along Ω) (Maas & Pope, 1992). The second of these problems consists in a transformation of the kinetic equations (4) to a diagonal form, $\dot{\zeta}_i = f_i(\zeta_i)$ (the so-called *full nonlinear lumping* or *modes decoupling*, Lam & Goussis, 1994; Li, Rabitz, & Tóth, 1994; Tóth, Li, Rabitz, & Tomlin, 1997).

Clearly, if one finds a sufficiently explicit solution to the second problem, then system (4) is completely integrable, and nothing more is needed, the result has to be simply used. The question is only to what extent such a solution can be possible, and how difficult it would be, as compared to the first problem, to find it.

One of the currently most popular methods is the construction of the so-called *intrinsic low-dimensional manifold* (ILDm, Maas & Pope, 1992). This method is based on the following geometric picture: for each point \mathbf{c} , one defines the Jacobian matrix of Eq. (4), $\mathbf{F}_c \equiv \partial \mathbf{J}(\mathbf{c})/\partial \mathbf{c}$. One assumes that, in the domain of interest, the eigenvalues of \mathbf{F}_c are separated into two groups, λ_i^s and λ_j^f , and that the following inequalities are valid:

$$\operatorname{Re} \lambda_i^s \geq a > b \geq \operatorname{Re} \lambda_j^f, \quad a \gg b, \quad b < 0.$$

Let us denote as L_c^s and L_c^f the invariant subspaces corresponding to λ^s and λ^f , respectively, and let \mathbf{Z}_c^s and \mathbf{Z}_c^f be the corresponding spectral projectors, $\mathbf{Z}_c^s L_c^s = L_c^s$, $\mathbf{Z}_c^f L_c^f = L_c^f$, $\mathbf{Z}_c^s L_c^f = \mathbf{Z}_c^f L_c^s = \{0\}$, $\mathbf{Z}_c^s + \mathbf{Z}_c^f = 1$. The operator \mathbf{Z}_c^s projects onto the subspace of “slow modes” L_c^s , and it annihilates the “fast modes” L_c^f . The operator \mathbf{Z}_c^f does the opposite, it projects onto fast modes, and it annihilates the slow modes. The basic equation of the ILDM reads:

$$\mathbf{Z}_c^f \mathbf{J}(\mathbf{c}) = 0. \quad (27)$$

In this equation, the unknown is the concentration vector \mathbf{c} . The set of solutions to Eq. (27) is the ILDM manifold Ω_{ildm} .

For linear systems, \mathbf{F}_c , \mathbf{Z}_c^s , and \mathbf{Z}_c^f , do not depend on \mathbf{c} , and $\Omega_{\text{ildm}} = \mathbf{c}^{\text{eq}} + L^s$. On the other hand, obviously, $\mathbf{c}^{\text{eq}} \in \Omega_{\text{ildm}}$. Therefore, procedures of solving of Eq. (27) can be initiated by choosing the linear approximation, $\Omega_{\text{ildm}}^{(0)} = \mathbf{c}^{\text{eq}} + L_c^s$, in the neighborhood of the equilibrium \mathbf{c}^{eq} , and then continued parametrically into the nonlinear domain. Computational technologies of the continuation of solutions with respect to parameters are well developed (see, for example, Khibnik, Kuznetsov, Levitin, & Nikolaev, 1993; Roose De Dier & Spence, 1990). The problem of the relevant parameterization is solved locally: In the neighborhood of a given point \mathbf{c}^0 one can choose $\mathbf{Z}_c^s(\mathbf{c} - \mathbf{c}^0)$ for a characterization of the vector \mathbf{c} . In this case, the space of parameters is L_c^s . There exist other, physically motivated ways to parameterize manifolds (Gorban & Karlin, 1992; see also Section 4.1).

There are two drawbacks of the ILDM method which call for its refinement: (i) “*Intrinsic*” does not imply “*invariant*”. Eq. (27) is not an invariant of the dynamics (4). If one differentiates Eq. (27) in time due to Eq. (4), one obtains a new equation which is the implication of Eq. (27) only for linear systems. In a general case, the motion $\mathbf{c}(t)$ takes off the Ω_{ildm} . The invariance of a manifold Ω means that $\mathbf{J}(\mathbf{c})$ touches Ω in every point $\mathbf{c} \in \Omega$. It remains unclear how the ILDM (27) corresponds to this condition. Thus, from the dynamical perspective, the status of the ILDM remains not well defined, or “ILDM is ILDM”, defined self-consistently

by Eq. (27), and that is all what can be said about it. (ii) From the geometrical standpoint, spectral decomposition of Jacobian fields is not the most attractive way to compute manifolds. If we are interested in the behavior of trajectories, how they converge or diverge, then one should consider the symmetrized part of F_c , rather than F_c itself.

The symmetric part, $F_c^{\text{sym}} = (1/2)(F_c^\dagger + F_c)$, defines the dynamics of the distance between two solutions, c and c' , in a given local Euclidean metric. The skew-symmetric part defines rotations. If we want to study manifolds based on the argument about convergence/divergence of trajectories, then we should use in Eq. (27) the spectral projector Z_c^{fsym} for the operator F_c^{sym} . This, by the way, is also a significant simplification from the standpoint of computations. It remains to choose the metric. This choice is unambiguous from the thermodynamic perspective. In fact, there is only one choice which fits into the physical meaning of the problem, this is the metric associated with the thermodynamic (or entropic) scalar product,

$$\langle\langle x, y \rangle\rangle = \langle x, H_c y \rangle, \quad (28)$$

where H_c is the matrix of second-order derivatives of G (7). In the equilibrium, the operator F_c^{eq} is selfadjoint with respect to this scalar product (Onsager's reciprocity relations). Therefore, the behavior of the ILDM in the vicinity of the equilibrium does not alter under the replacement, $F_{c^{\text{eq}}} = F_{c^{\text{eq}}}^{\text{sym}}$. In terms of the usual matrix representation, we have:

$$F_c^{\text{sym}} = \frac{1}{2}(F_c + H_c^{-1} F_c^T H_c), \quad (29)$$

where F_c^T is the ordinary transposition.

The ILDM constructed with the help of the symmetrized Jacobian field will be termed the *symmetric entropic intrinsic low-dimensional manifold* (SEILDM). The selfadjointness of F_c^{sym} (29) with respect to the thermodynamic scalar product (28) simplifies considerably computations of spectral decomposition. Moreover, it becomes necessary to do spectral decomposition in only one point—in the equilibrium. Perturbation theory for selfadjoint operators is a very well developed subject (Kato, 1976), which makes it possible to easily extend the spectral decomposition with respect to parameters. A more detailed discussion of the selfadjoint linearization will be given in section 5.2.

Thus, when the geometric picture behind the decomposition of motions is specified, the physical significance of the ILDM becomes more transparent, and it leads to its modification into the SEILDM. This also gains simplicity in the implementation by switching from non-selfadjoint spectral problems to selfadjoint. The quantitative estimate of this simplification is readily available: let d be the dimension of the phase space, and k the dimension of the ILDM ($k = \dim L_c^s$). The space of all the projectors Z with k -dimensional image has the dimension $D = 2k(d - k)$. The space of all the selfadjoint projectors with the k -dimensional image has the dimension $D^{\text{sym}} = k(d - k)$. For $d = 20$ and

$k = 3$, we have $D = 102$ and $D^{\text{sym}} = 51$. When the spectral decomposition by means of parametric extension is addressed, one considers equations of the form:

$$\frac{dZ_{c(\tau)}^s}{d\tau} = \Psi^s \left(\frac{dc}{d\tau}, Z_{c(\tau)}^s, F_{c(\tau)}, \nabla F_{c(\tau)} \right), \quad (30)$$

where τ is the parameter, and $\nabla F_c = \nabla \nabla J(c)$ is the differential of the Jacobian field. For the selfadjoint case, where we use $-F_c^{\text{sym}}$ instead of F_c , this system of equations has twice fewer independent variables, and also the right hand is of a simpler structure.

It is more difficult to improve on the first of the remarks (ILDM is not invariant). The following naive approach may seem possible:

(i) Take $\Omega_{\text{ildm}} = c^{\text{eq}} + L_{c^{\text{eq}}}^s$ in a neighborhood U of the equilibrium c^{eq} . [This is also a useful initial approximation for solving Eq. (27).]

(ii) Instead of computing the solution to Eq. (27), integrate the kinetic equations (4) *backwards in time*. It is sufficient to take initial conditions $c(0)$ from a dense set on the boundary, $\partial U \cap (c^{\text{eq}} + L_{c^{\text{eq}}}^s)$, and to compute the solutions $c(t)$, $t < 0$.

(iii) Consider the obtained set of trajectories as an approximation of the slow invariant manifold.

This approach will guarantee invariance, by construction, but it is prone to pitfalls in what concerns the slowness. Indeed, the integration backwards in time will see exponentially divergent trajectories, if they were exponentially converging in the normal time progress. This way one finds *some* invariant manifold which touches $c^{\text{eq}} + L_{c^{\text{eq}}}^s$ in the equilibrium. Unfortunately, there are infinitely many such manifolds, and they fill out almost all the space of concentrations. However, we must select the slow component of motions. Such a regularization is possible. Indeed, let us replace in Eq. (4) the vector field $J(c)$ by the vector field $Z_c^{\text{ssym}} J(c)$, and obtain a regularized kinetic equation,

$$\dot{c} = Z_c^{\text{ssym}} J(c). \quad (31)$$

Let us replace integration backwards in time of the kinetic equation (4) in the naive approach described above by integration backwards in time of the regularized kinetic equation (31). With this, we obtain a rather convincing version of the ILDM (SEILDM). Using Eq. (30), one also can write down an equation for the projector Z_c^{ssym} , putting $\tau = t$. Replacement of Eq. (4) by Eq. (31) also makes the integration backwards in time in the naive approach more stable. However, *regularization will again conflict with invariance*. The “naive refinement” after the regularization (31) produces just a slightly different version of the ILDM (or SEILDM) but it does not construct the slow invariant manifold. So, where is the way out? We believe that the ILDM and its version SEILDM are, in general, good initial approximations of the slow manifold. However, if one is indeed interested in finding the invariant manifold, one has to write out the true condition of invariance and solve it. As for the initial

approximation for the method of invariant manifold one can use any ansatz, in particular, the SEILDm.

The problem of a complete decomposition of the kinetic equations can be solved indeed in some cases. The first such solution was the spectral decomposition for linear systems (Wei & Prater, 1962). Decomposition is sometimes possible also for nonlinear systems (Li et al., 1994; Tóth et al., 1997). The most famous example of a complete decomposition of infinite-dimensional kinetic equations is the complete integrability of the space-independent Boltzmann equation for Maxwell's molecules found by Bobylev (1988). However, in the general case, there exist no analytical, not even a twice differentiable transformation which will decouple modes. The well known Grobman–Hartman theorem (Hartman, 1963, 1982) states only the existence of a continuous transform, which decomposes modes in a neighborhood of the equilibrium. For example, the analytic planar system, $dx/dt = -x$, $dy/dt = -2y + x^2$, is not C^2 linearizable. These problems remain of interest (Chicone & Swanson, 2000). Therefore, in particular, it becomes quite ineffective to construct such a transformation in the form of a series. It is more effective to solve a simpler problem of extraction of a slow invariant manifold (Beyn & Kless, 1998).

Sensitivity analysis (Rabitz et al., 1983; Rabitz, 1987; Lam & Goussis, 1994) makes it possible to select essential variables and reactions, and to decompose motions into fast and slow. In a sense, the ILDM method is a development of sensitivity analysis. In particular, the computational singular perturbation (CSP) method of Lam and Goussis (1994) includes ILDM (or any other reasonable initial choice of the manifold) into a procedure of consequent refinements. Recently, a further step in this direction was done by Zhu and Petzold (1999). In this work, the authors use a nonlocal in time criterion of closeness of solutions of the full and of the reduced systems of chemical kinetics. They require not just a closeness of derivatives but a true closeness of the dynamics.

Let us be interested in the dynamics of the concentrations of just a few species, A_1, \dots, A_p , whereas the rest of the species, A_{p+1}, \dots, A_n are used for building the kinetic equation, and for understanding the process. Let \mathbf{c}_{goal} be the concentration vector with components c_1, \dots, c_p , $\mathbf{c}_{\text{goal}}(t)$ be the corresponding components of the solution to Eq. (4), and $\mathbf{c}_{\text{goal}}^{\text{red}}$ be the solution to the simplified model with corresponding initial conditions. Zhu and Petzold (1999) suggest to minimize the difference between $\mathbf{c}_{\text{goal}}(t)$ and $\mathbf{c}_{\text{goal}}^{\text{red}}$ on the segment $t \in [0, T]$: $\|\mathbf{c}_{\text{goal}}(t) - \mathbf{c}_{\text{goal}}^{\text{red}}\| \rightarrow \min$. In the course of the optimization under certain restrictions one selects the optimal (or appropriate) reduced model. The sequential quadratic programming method and heuristic rules of sorting the reactions, substances, etc., were used. In the result, for some stiff systems studied, one avoids typical pitfalls of the local sensitivity analysis. In simpler situations this method should give similar results as the local methods.

2.7. Thermodynamic criteria for selection of important reactions

One of the problems addressed by sensitivity analysis is selecting the important and discarding the unimportant reactions. Bykov, Yablonskii, and Akramov (1977) suggested a simple principle to compare the importance of different reactions according to their contribution to the entropy production (or, which is the same, according to their contribution to \dot{G}). Based on this principle, Dimitrov (1982) described domains of parameters in which the reaction of hydrogen oxidation, $\text{H}_2 + \text{O}_2 + \text{M}$, proceeds due to different mechanisms. For each elementary reaction, he has derived the domain inside which the contribution of this reaction is essential (nonnegligible). Due to its simplicity, this entropy production principle is especially well suited for analysis of complex problems. In particular, recently, a version of the entropy production principle was used in the problem of selection of boundary conditions for Grad's moment equations (Struchtrup & Weiss, 1998; Grmela, Karlin, & Zmievski, 2002). For ideal systems (9), the contribution of the s th reaction to \dot{G} has a particularly simple form:

$$\dot{G}_s = -W_s \ln \left(\frac{W_s^+}{W_s^-} \right), \quad \dot{G} = \sum_{s=1}^r \dot{G}_s. \quad (32)$$

For nonideal systems, the corresponding expressions (13) are also not too complicated.

3. Outline of the method of invariant manifold

In many cases, dynamics of the d -dimensional system (4) leads to a manifold of a lower dimension. Intuitively, a typical phase trajectory behaves as follows: given the initial state $\mathbf{c}(0)$ at $t = 0$, and after some period of time, the trajectory comes close to some low-dimensional manifold Ω , and after that proceeds towards the equilibrium essentially along this manifold. The goal is to construct this manifold.

The starting point of our approach is based on a formulation of the two main requirements:

- (i) *Dynamic invariance*: The manifold Ω should be (positively) invariant under the dynamics of the originating system (4): if $\mathbf{c}(0) \in \Omega$, then $\mathbf{c}(t) \in \Omega$ for each $t > 0$.
- (ii) *Thermodynamic consistency of the reduced dynamics*: Let some (not obligatorily invariant) manifold Ω is considered as a manifold of reduced description. We should define a set of linear operators, \mathbf{P}_c , labeled by the states $\mathbf{c} \in \Omega$, which project the vectors $\mathbf{J}(\mathbf{c})$, $\mathbf{c} \in \Omega$ onto the tangent bundle of the manifold Ω , thereby generating the induced vector field, $\mathbf{P}_c \mathbf{J}(\mathbf{c})$, $\mathbf{c} \in \Omega$. This induced vector field on the tangent bundle of the manifold Ω is identified with the reduced dynamics along the manifold Ω . The thermodynamicity requirement for this induced vector field reads

$$\langle \nabla G(\mathbf{c}), \mathbf{P}_c \mathbf{J}(\mathbf{c}) \rangle \leq 0 \text{ for each } \mathbf{c} \in \Omega. \quad (33)$$

In order to meet these requirements, the method of invariant manifold suggests two complementary procedures:

- (i) To treat the condition of dynamic invariance as an equation, and to solve it iteratively by a Newton method. This procedure is geometric in its nature, and it does not use the time dependence and small parameters.
- (ii) Given an approximate manifold of reduced description, to construct the projector satisfying condition (33) in a way which does not depend on the vector field \mathbf{J} .

We shall now outline both these procedures starting with the second. The solution consists, in the first place, in formulating the *thermodynamic condition* which should be met by the projectors \mathbf{P}_c : for each $c \in \Omega$, let us consider the linear functional

$$M_c^*(\mathbf{x}) = \langle \nabla G(c), \mathbf{x} \rangle. \quad (34)$$

Then the thermodynamic condition for the projectors reads:

$$\ker \mathbf{P}_c \subseteq \ker M_c^* \text{ for each } c \in \Omega. \quad (35)$$

Here $\ker \mathbf{P}_c$ is the null space of the projector, and $\ker M_c^*$ is the hyperplane orthogonal to the vector M_c^* . It has been shown (Gorban & Karlin, 1992, 1994) that condition (35) is the necessary and sufficient condition to establish the thermodynamic induced vector field on the given manifold Ω for all possible dissipative vector fields \mathbf{J} simultaneously.

Let us now turn to the requirement of invariance. By definition, the manifold Ω is invariant with respect to the vector field \mathbf{J} if and only if the following equality is true:

$$[1 - \mathbf{P}]\mathbf{J}(c) = 0 \text{ for each } c \in \Omega. \quad (36)$$

In this expression \mathbf{P} is an *arbitrary* projector on the tangent bundle of the manifold Ω . It has been suggested to consider condition (36) as an *equation* to be solved iteratively starting with some appropriate initial manifold.

Iterations for the invariance equation (36) are considered in Section 5. The next section presents the construction of the thermodynamic projector using a specific parameterization of manifolds.

4. Thermodynamic projector

4.1. Thermodynamic parameterization

In this section, Ω denotes a generic p -dimensional manifold. First, it should be mentioned that *any* parameterization of Ω generates a certain projector, and thereby a certain reduced dynamics. Indeed, let us consider a set of m independent functionals $M(c) = \{M_1(c), \dots, M_p(c)\}$, and let us assume that they form a coordinate system on Ω in such a way that $\Omega = c(M)$, where $c(M)$ is a vector function of the parameters M_1, \dots, M_p . Then the projector associated with this parameterization reads:

$$\mathbf{P}_{c(M)}\mathbf{x} = \sum_{j=1}^p \frac{\partial c(M)}{\partial M_j} \langle \nabla M_j|_{c(M)}, \mathbf{x} \rangle. \quad (37)$$

This somewhat involved notation is intended to stress that projector (37) is dictated by the choice of the parameterization. Subsequently, the induced vector field of the reduced dynamics is found by applying projectors (37) on the vectors $\mathbf{J}(c(M))$, thereby inducing the reduced dynamics in terms of the parameters M as follows:

$$\dot{M}_j = \langle \nabla M_j|_{c(M)}, \mathbf{J}(c(M)) \rangle. \quad (39)$$

Depending on the choice of the parameterization, the dynamic equations (39) are (or are not) consistent with the thermodynamic requirement (33). The *thermodynamic parameterization* makes use of condition (35) in order to establish the thermodynamic projector. Specializing to case (37), let us consider the linear functionals,

$$DM_i|_{c(M)}(\mathbf{x}) = \langle \nabla M_i|_{c(M)}, \mathbf{x} \rangle. \quad (40)$$

Then condition (35) takes the form:

$$\bigcap_{i=1}^p \ker DM_i|_{c(M)} \subseteq \ker M_{c(M)}^*, \quad (41)$$

that is, the intersection of the null spaces of functionals (40) should belong to the null space of the differential of the Lyapunov function G , in each point of the manifold Ω .

In practice, in order to construct the thermodynamic parameterization, we take the following set of functionals in each point c of the manifold Ω :

$$M_1(\mathbf{x}) = M_c^*(\mathbf{x}), \quad c \in \Omega, \quad (42)$$

$$M_i(\mathbf{x}) = \langle \mathbf{m}_i, \mathbf{x} \rangle, \quad i = 2, \dots, p. \quad (43)$$

It is required that vectors $\nabla G(c), \mathbf{m}_2, \dots, \mathbf{m}_p$ are linearly independent in each state $c \in \Omega$. Inclusion of functionals (34) as a part of system (42) and (43) implies the thermodynamic condition (41). Also, any linear combination of the parameter set (42), (43) will meet the thermodynamicity requirement.

It is important to notice here that the thermodynamic condition is satisfied whatsoever the functionals M_2, \dots, M_p are. This is very convenient, for it gives an opportunity to take into account the conserved quantities correctly. The manifolds we are going to deal with should be consistent with the conservation laws (2). While the explicit characterization of the phase space V is a problem on its own, in practice, it is customary to work in the n -dimensional space while keeping constraints (2) explicitly on each step of the construction. For this technical reason, it is convenient to consider manifolds of dimension $p > l$, where l is the number of conservation laws, in the n -dimensional space rather than in the phase space V . The thermodynamic parameterization is then concordant also with the conservation laws if l of the linear functionals (43) are identified with the conservation laws. In the sequel, only projectors consistent with the conservation laws are considered.

Very frequently, the manifold Ω is represented as a p -parametric family $c(a_1, \dots, a_p)$, where the a_i are coordinates on the manifold. The thermodynamic *reparameterization* suggests a representation of the coordinates a_i in terms of M_c^*, M_2, \dots, M_p (42), (43). While the explicit construction of these functions may be a formidable task, we notice that the construction of the thermodynamic projector of the form (37) and of the dynamic equations (39) is relatively easy because only the derivatives $\partial c / \partial M_i$ enter these expressions. This point was discussed in a detail by Gorban and Karlin (1992, 1994).

4.2. Decomposition of motions: thermodynamics

Finally, let us discuss how the thermodynamic projector is related to the decomposition of motions. Assuming that the decomposition of motions near the manifold Ω is true indeed, let us consider states which were initially close enough to the manifold Ω . Even without knowing the details about the evolution of the states towards Ω , we know that the Lyapunov function G was decreasing in the course of this evolution. Let us consider a set of states U_c which contains all those vectors c' that have arrived (in other words, have been projected) into the point $c \in \Omega$. Then we observe that the state c furnishes the minimum of the function G on the set U_c . If a state $c' \in U_c$, and if it deviates small enough from the state c so that the linear approximation is valid, then c' belongs to the affine hyperplane

$$\Gamma_c = c + \ker M_c^*, \quad c \in \Omega. \quad (44)$$

This hyperplane actually participates in the condition (35). The consideration was entitled ‘thermodynamic’ (Gorban & Karlin, 1992) because it describes the states $c \in \Omega$ as points of minimum of the function G over the corresponding hyperplanes (44).

5. Corrections

5.1. Preliminary discussion

The thermodynamic projector is needed to induce the dynamics on a given manifold in such a way that the dissipation inequality (33) holds. Coming back to the issue of constructing corrections, we should stress that the projector participating in the invariance condition (36) is arbitrary. It is convenient to make use of this point: when Eq. (36) is solved iteratively, the projector may be kept non-thermodynamic unless the induced dynamics is explicitly needed.

Let us assume that we have chosen the initial manifold, Ω_0 , together with the associated projector P_0 , as the first approximation to the desired manifold of reduced description. Although the choice of the initial approximation Ω_0 depends on the specific problem, it is often reasonable to consider quasi-equilibrium or quasi steady-state approximations. In most cases, the manifold Ω_0 is not an invariant manifold.

This means that Ω_0 does not satisfy the invariance condition (36):

$$\Delta_0 = [1 - P_0]J(c_0) \neq 0 \text{ for some } c_0 \in \Omega_0. \quad (45)$$

Therefore, we seek a correction $c_1 = c_0 + \delta c$. Substituting $P = P_0$ and $c = c_0 + \delta c$ into the invariance equation (36), and after the linearization in δc , we derive the following linear equation:

$$[1 - P_0][J(c_0) + L_{c_0}\delta c] = 0, \quad (46)$$

where L_{c_0} is the matrix of first derivatives of the vector function J , computed in the state $c_0 \in \Omega_0$. The system of linear algebraic equations (46) should be supplied with the additional condition.

$$P_0\delta c = 0. \quad (47)$$

In order to illustrate the nature of Eq. (46), let us consider the case of linear manifolds for linear systems. Let a linear evolution equation is given in the finite-dimensional real space: $\dot{c} = Lc$, where L is negatively definite symmetric matrix with a simple spectrum. Let us further assume the quadratic Lyapunov function, $G(c) = \langle c, c \rangle$. The manifolds we consider are lines, $I(a) = ae$, where e is the unit vector, and a is a scalar. The invariance equation for such manifolds reads: $e\langle e, Le \rangle - Le = 0$, and is simply a form of the eigenvalue problem for the operator L . Solutions to the latter equation are eigenvectors e_i , corresponding to eigenvalues λ_i .

Assume that we have chosen a line, $l_0 = ae_0$, defined by the unit vector e_0 , and that e_0 is not an eigenvector of L . We seek another line, $l_1 = ae_1$, where e_1 is another unit vector, $e_1 = y_1 / \|y_1\|$, $y_1 = e_0 + \delta y$. The additional condition (47) now reads: $\langle \delta y, e_0 \rangle = 0$. Then the Eq. (46) becomes $[1 - e_0\langle e_0, \cdot \rangle]L[e_0 + \delta y] = 0$. Subject to the additional condition, the unique solution is as follows: $e_0 + \delta y = \langle e_0, L^{-1}e_0 \rangle^{-1}L^{-1}e_0$. Rewriting the latter expression in the eigen-basis of L , we have: $e_0 + \delta y \propto \sum_i \lambda_i^{-1}e_i\langle e_i, e_0 \rangle$. The leading term in this sum corresponds to the eigenvalue with the minimal absolute value. The example indicates that the method of linearization (46) seeks the direction of the *slowest relaxation*. For this reason, the method (46) can be recognized as the basis of an iterative method for constructing the manifolds of slow motions.

For the nonlinear systems, the matrix L_{c_0} in Eq. (46) depends nontrivially on c_0 . In this case system (46) requires a further specification which will be done now.

5.2. Symmetric linearization

The invariance condition (36) supports a lot of invariant manifolds, and not all of them are relevant to the reduced description (for example, any individual trajectory is itself an invariant manifold). This should be carefully taken into account when deriving a relevant equation for the correction in the states of the initial manifold Ω_0 which are located far from equilibrium. This point concerns the procedure of the linearization

of the vector field \mathbf{J} , appearing in Eq. (46). We shall return to the explicit form of the Marcelin–De Donder kinetic function (11). Let \mathbf{c} be an arbitrary fixed element of the phase space. The linearization of the vector function \mathbf{J} (12) about \mathbf{c} may be written $\mathbf{J}(\mathbf{c} + \delta\mathbf{c}) \approx \mathbf{J}(\mathbf{c}) + \mathbf{L}_c \delta\mathbf{c}$ where the linear operator \mathbf{L}_c acts as follows:

$$\mathbf{L}_c \mathbf{x} = \sum_{s=1}^r \gamma_s [W_s^+(\mathbf{c}) \langle \boldsymbol{\alpha}_s, \mathbf{H}_c \mathbf{x} \rangle - W_s^-(\mathbf{c}) \langle \boldsymbol{\beta}_s, \mathbf{H}_c \mathbf{x} \rangle]. \quad (48)$$

Here \mathbf{H}_c is the matrix of second derivatives of the function G in the state \mathbf{c} [see Eq. (7)]. The matrix \mathbf{L}_c in the Eq. (48) can be decomposed as follows:

$$\mathbf{L}_c = \mathbf{L}'_c + \mathbf{L}''_c. \quad (49)$$

The matrices \mathbf{L}'_c and \mathbf{L}''_c act as follows:

$$\mathbf{L}'_c \mathbf{x} = -\frac{1}{2} \sum_{s=1}^r [W_s^+(\mathbf{c}) + W_s^-(\mathbf{c})] \gamma_s \langle \gamma_s, \mathbf{H}_c \mathbf{x} \rangle, \quad (50)$$

$$\mathbf{L}''_c \mathbf{x} = \frac{1}{2} \sum_{s=1}^r [W_s^+(\mathbf{c}) - W_s^-(\mathbf{c})] \gamma_s \langle \boldsymbol{\alpha}_s + \boldsymbol{\beta}_s, \mathbf{H}_c \mathbf{x} \rangle. \quad (51)$$

Some features of this decomposition are best seen when we use the thermodynamic scalar product (28); the following properties of the matrix \mathbf{L}'_c are verified immediately:

- (i) The matrix \mathbf{L}'_c is symmetric in the scalar product (28):

$$\langle \langle \mathbf{x}, \mathbf{L}'_c \mathbf{y} \rangle \rangle = \langle \langle \mathbf{y}, \mathbf{L}'_c \mathbf{x} \rangle \rangle. \quad (52)$$

- (ii) The matrix \mathbf{L}'_c is nonpositive definite in the scalar product (28):

$$\langle \langle \mathbf{x}, \mathbf{L}'_c \mathbf{x} \rangle \rangle \leq 0. \quad (53)$$

- (iii) The null space of the matrix \mathbf{L}'_c is the linear envelope of the vectors $\mathbf{H}_c^{-1} \mathbf{b}_i$ representing the complete system of conservation laws:

$$\ker \mathbf{L}'_c = \text{Lin}\{\mathbf{H}_c^{-1} \mathbf{b}_i, i = 1, \dots, l\} \quad (54)$$

- (iv) If $\mathbf{c} = \mathbf{c}^{\text{eq}}$, then $W_s^+(\mathbf{c}^{\text{eq}}) = W_s^-(\mathbf{c}^{\text{eq}})$, and

$$\mathbf{L}'_{\mathbf{c}^{\text{eq}}} = \mathbf{L}_{\mathbf{c}^{\text{eq}}}. \quad (55)$$

Thus, the decomposition Eq. (49) splits the matrix \mathbf{L}_c into two parts: one part, Eq. (50) is symmetric and nonpositive definite, while the other part, Eq. (51), vanishes in the equilibrium. The decomposition Eq. (49) explicitly takes into account the Marcelin–De Donder form of the kinetic function. For other dissipative systems, decomposition (49) is possible as soon as the relevant kinetic operator is written in a gain–loss form (for instance, this is straightforward for the Boltzmann collision operator).

In the sequel, we shall make use of the properties of the operator \mathbf{L}'_c (50) for constructing the dynamic correction by extending the picture of the decomposition of motions.

5.3. Decomposition of motions: kinetics

The assumption about the existence of the decomposition of motions near the manifold of reduced description $\boldsymbol{\Omega}$ has led to the *thermodynamic* specifications of the states $\mathbf{c} \in \boldsymbol{\Omega}$. This was accomplished in Section 4.2, where the thermodynamic projector was backed by an appropriate variational formulation, and this helped us to establish the induced dynamics consistent with the dissipation property. Another important feature of the decomposition of motions is that the states $\mathbf{c} \in \boldsymbol{\Omega}$ can be specified *kinetically*. Indeed, let us do it again as if the decomposition of motions were valid in the neighborhood of the manifold $\boldsymbol{\Omega}$, and let us ‘freeze’ the slow dynamics along the $\boldsymbol{\Omega}$, focusing on the fast process of relaxation towards a state $\mathbf{c} \in \boldsymbol{\Omega}$. From the thermodynamic perspective, fast motions take place on the affine hyperplane $\mathbf{c} + \delta\mathbf{c} \in \Gamma_{\mathbf{c}_0}$, where $\Gamma_{\mathbf{c}_0}$ is given by Eq. (44). From the kinetic perspective, fast motions on this hyperplane should be treated as a *relaxation* equation, equipped with the quadratic Lyapunov function $\delta G = \langle \langle \delta\mathbf{c}, \delta\mathbf{c} \rangle \rangle$. Furthermore, we require that the linear operator of this evolution equation respects Onsager’s symmetry requirements (selfadjointness with respect to the entropic scalar product). This latter crucial requirement describes fast motions under the frozen slow evolution in the similar way, as *all* the motions near the equilibrium.

Let us consider now the manifold $\boldsymbol{\Omega}_0$ which is not the invariant manifold of the reduced description but, by our assumption, is located close to it. Consider a state $\mathbf{c}_0 \in \boldsymbol{\Omega}_0$, and the states $\mathbf{c}_0 + \delta\mathbf{c}$ close to it. Further, let us consider an equation

$$\dot{\delta\mathbf{c}} = \mathbf{L}'_{\mathbf{c}_0} \delta\mathbf{c}. \quad (56)$$

Due to the properties of the operator $\mathbf{L}'_{\mathbf{c}_0}$ (50), this equation can be regarded as a model of the assumed true relaxation equation near the true manifold of the reduced description. For this reason, we shall use the symmetric operator \mathbf{L}'_c (50) *instead* of the linear operator \mathbf{L}_c when constructing the corrections.

5.4. Symmetric iteration

Let the manifold $\boldsymbol{\Omega}_0$ and the corresponding projector \mathbf{P}_0 be the initial approximation to the invariant manifold of the reduced description. The dynamic correction $\mathbf{c}_1 = \mathbf{c}_0 + \delta\mathbf{c}$ is found upon solving the following system of linear algebraic equations:

$$[1 - \mathbf{P}_0][\mathbf{J}(\mathbf{c}_0) + \mathbf{L}'_{\mathbf{c}_0} \delta\mathbf{c}] = 0, \quad \mathbf{P}_0 \delta\mathbf{c} = 0. \quad (57)$$

Here $\mathbf{L}'_{\mathbf{c}_0}$ is matrix (50) taken in the states on the manifold $\boldsymbol{\Omega}_0$. An important technical point here is that the linear system (57) always has a unique solution for any choice of the manifold $\boldsymbol{\Omega}$. This point is crucial since it guarantees the opportunity of carrying out the correction process for an arbitrary number of steps.

6. The method of invariant manifold

We shall now combine together the two procedures discussed above. The resulting method of invariant manifold intends to seek iteratively the reduced description, starting with an initial approximation.

(i) *Initialization*. In order to start the procedure, it is required to choose the initial manifold Ω_0 , and to derive corresponding thermodynamic projector P_0 . In the majority of cases, initial manifolds are available in two different ways. The first case is that of the quasi-equilibrium manifolds described in Section 2.3. The macroscopic parameters are $M_i = c_i = \langle \mathbf{m}_i, \mathbf{c} \rangle$, where \mathbf{m}_i is the unit vector corresponding to the species A_i . The quasi-equilibrium manifold, $\mathbf{c}_0(M_1, \dots, M_k, B_1, \dots, B_l)$, compatible with the conservation laws, is the solution to the variational problem:

$$G \rightarrow \min, \quad \begin{aligned} \langle \mathbf{m}_i, \mathbf{c} \rangle &= c_i, \quad i = 1, \dots, k, \\ \langle \mathbf{b}_j, \mathbf{c} \rangle &= B_j, \quad j = 1, \dots, l. \end{aligned} \quad (58)$$

In the case of quasi-equilibrium approximation, the corresponding thermodynamic projector can be written most straightforwardly in terms of the variables M_i :

$$P_0 \mathbf{x} = \sum_{i=1}^k \frac{\partial c_0}{\partial c_i} \langle \mathbf{m}_i, \mathbf{x} \rangle + \sum_{i=1}^l \frac{\partial c_0}{\partial B_i} \langle \mathbf{b}_i, \mathbf{x} \rangle. \quad (59)$$

For quasi-equilibrium manifolds, a reparameterization with set (42), (43) is *not* necessary (Gorban & Karlin, 1992, 1994).

The second source of initial approximations are quasi-stationary manifolds (Section 2.5). Unlike the quasi-equilibrium case, the quasi-stationary manifolds must be reparameterized in order to construct the thermodynamic projector.

(ii) *Corrections*. Iterations are organized in accord with the rule: if \mathbf{c}_m is the m th approximation to the invariant manifold, then the correction $\mathbf{c}_{m+1} = \mathbf{c}_m + \delta \mathbf{c}$ is found from the linear algebraic equations,

$$[1 - P_m](J(\mathbf{c}_m) + L'_{\mathbf{c}_m} \delta \mathbf{c}) = 0, \quad (60)$$

$$P_m \delta \mathbf{c} = 0. \quad (61)$$

Here $L'_{\mathbf{c}_m}$ is the symmetric matrix (50) evaluated at the m th approximation. The projector P_m is not obligatorily thermodynamic at that step, and it is taken as follows:

$$P_m \mathbf{x} = \sum_{i=1}^k \frac{\partial c_m}{\partial c_i} \langle \mathbf{m}_i, \mathbf{x} \rangle + \sum_{i=1}^l \frac{\partial c_m}{\partial B_i} \langle \mathbf{b}_i, \mathbf{x} \rangle. \quad (62)$$

(iii) *Dynamics*. Dynamics on the m th manifold is obtained with the thermodynamic re-parameterization.

In the next section we shall illustrate how this all works.

7. Illustration: two-step catalytic reaction

Here we consider a two-step four-component reaction with one catalyst A_2 :



We assume that the Lyapunov function is of the form (9), $G = \sum_{i=1}^4 c_i [\ln(c_i/c_i^{\text{eq}}) - 1]$. The kinetic equation for the four-component vector of concentrations, $\mathbf{c} = (c_1, c_2, c_3, c_4)$, has the form

$$\dot{\mathbf{c}} = \gamma_1 W_1 + \gamma_2 W_2. \quad (64)$$

Here $\gamma_{1,2}$ are stoichiometric vectors,

$$\gamma_1 = (-1, -1, 1, 0), \quad \gamma_2 = (0, 1, -1, 1), \quad (65)$$

while the functions $W_{1,2}$ are reaction rates:

$$W_1 = k_1^+ c_1 c_2 - k_1^- c_3, \quad W_2 = k_2^+ c_3 - k_2^- c_2 c_4. \quad (66)$$

Here $k_{1,2}^\pm$ are reaction rate constants. The system under consideration has two conservation laws,

$$c_1 + c_3 + c_4 = B_1, \quad c_2 + c_3 = B_2, \quad (67)$$

or $\langle \mathbf{b}_{1,2}, \mathbf{c} \rangle = B_{1,2}$, where $\mathbf{b}_1 = (1, 0, 1, 1)$ and $\mathbf{b}_2 = (0, 1, 1, 0)$. The nonlinear system (64) is effectively two-dimensional, and we consider a one-dimensional reduced description.

We have chosen the concentration of the species A_1 as the variable of reduced description: $M = c_1$, and $c_1 = \langle \mathbf{m}, \mathbf{c} \rangle$, where $\mathbf{m} = (1, 0, 0, 0)$. The initial manifold $\mathbf{c}_0(M)$ was taken as the quasi-equilibrium approximation, i.e., the vector function \mathbf{c}_0 is the solution to the problem:

$$G \rightarrow \min \text{ for } \langle \mathbf{m}, \mathbf{c} \rangle = c_1, \quad \langle \mathbf{b}_1, \mathbf{c} \rangle = B_1, \quad \langle \mathbf{b}_2, \mathbf{c} \rangle = B_2. \quad (68)$$

The solution to problem (68) reads:

$$c_{01} = c_1,$$

$$c_{02} = B_2 - \phi(c_1),$$

$$c_{03} = \phi(c_1),$$

$$c_{04} = B_1 - c_1 - \phi(c_1),$$

$$\phi(M) = A(c_1) - \sqrt{A^2(c_1) - B_2(B_1 - c_1)},$$

$$A(c_1) = \frac{B_2(B_1 - c_1^{\text{eq}}) + c_3^{\text{eq}}(c_1^{\text{eq}} + c_3^{\text{eq}} - c_1)}{2c_3^{\text{eq}}}. \quad (69)$$

The thermodynamic projector associated with manifold (69) reads:

$$P_0 \mathbf{x} = \frac{\partial c_0}{\partial c_1} \langle \mathbf{m}, \mathbf{x} \rangle + \frac{\partial c_0}{\partial B_1} \langle \mathbf{b}_1, \mathbf{x} \rangle + \frac{\partial c_0}{\partial B_2} \langle \mathbf{b}_2, \mathbf{x} \rangle. \quad (70)$$

Computing $\Delta_0 = [1 - P_0]J(\mathbf{c}_0)$ we find that inequality (45) takes place, and thus the manifold \mathbf{c}_0 is not invariant. The first correction, $\mathbf{c}_1 = \mathbf{c}_0 + \delta \mathbf{c}$, is found from the linear algebraic

system (60)

$$(1 - \mathbf{P}_0)\mathbf{L}'_0\delta\mathbf{c} = -[1 - \mathbf{P}_0]\mathbf{J}(\mathbf{c}_0), \quad (71)$$

$$\delta c_1 = 0,$$

$$\delta c_1 + \delta c_3 + \delta c_4 = 0,$$

$$\delta c_3 + \delta c_2 = 0, \quad (72)$$

where the symmetric 4×4 matrix \mathbf{L}'_0 has the form (we write 0 instead of \mathbf{c}_0 in the subscript in order to simplify notations):

$$L'_{0,kl} = -\gamma_{1k} \frac{W_1^+(\mathbf{c}_0) + W_1^-(\mathbf{c}_0)}{2} \frac{\gamma_{1l}}{c_{0l}} - \gamma_{2k} \frac{W_2^+(\mathbf{c}_0) + W_2^-(\mathbf{c}_0)}{2} \frac{\gamma_{2l}}{c_{0l}}. \quad (73)$$

The explicit solution $\mathbf{c}_1(c_1, B_1, B_2)$ to the linear system (71) is easily found, and we do not reproduce it here. The process was iterated. On the $k + 1$ iteration, the following projector \mathbf{P}_k was used:

$$\mathbf{P}_k \mathbf{x} = \frac{\partial \mathbf{c}_k}{\partial c_1} \langle \mathbf{m}, \mathbf{x} \rangle + \frac{\partial \mathbf{c}_k}{\partial B_1} \langle \mathbf{b}_1, \mathbf{x} \rangle + \frac{\partial \mathbf{c}_k}{\partial B_2} \langle \mathbf{b}_2, \mathbf{x} \rangle. \quad (74)$$

Notice that the projector \mathbf{P}_k (74) is the thermodynamic projector only if $k = 0$. As we have already mentioned above, in the process of finding the corrections to the manifold, non-thermodynamic projectors are allowed. The linear equation at the $k + 1$ iteration is thus obtained by replacing \mathbf{c}_0 , \mathbf{P}_0 , and \mathbf{L}'_0 with \mathbf{c}_k , \mathbf{P}_k , and \mathbf{L}'_k in all the entries of the Eqs. (71) and (73).

Once the manifold \mathbf{c}_k was obtained on the k th iteration, we derived the corresponding dynamics by introducing the thermodynamic parameterization (and the corresponding thermodynamic projector) with the help of the function (42). The resulting dynamic equation for the variable c_1 in the k th approximation has the form:

$$\langle \nabla G|_{\mathbf{c}_k}, \partial \mathbf{c}_k / \partial c_1 \rangle \dot{c}_1 = \langle \nabla G|_{\mathbf{c}_k}, \mathbf{J}(\mathbf{c}_k) \rangle. \quad (75)$$

Here $[\nabla G|_{\mathbf{c}_k}]_i = \ln[c_{ki}/c_i^{\text{eq}}]$.

Analytic results were compared with the results of the numerical integration. The following set of parameters was used:

$$k_1^+ = 1.0, \quad k_1^- = 0.5, \quad k_2^+ = 0.4, \quad k_2^- = 1.0;$$

$$c_1^{\text{eq}} = 0.5, \quad c_2^{\text{eq}} = 0.1, \quad c_3^{\text{eq}} = 0.1, \quad c_4^{\text{eq}} = 0.4,$$

$$B_1 = 1.0, \quad B_2 = 0.2.$$

Direct numerical integration of the system has demonstrated that the manifold $c_3 = c_3^{\text{eq}}$ in the plane (c_1, c_3) attracts all individual trajectories. Thus, the reduced description in this example should extract this manifold.

Fig. 1 demonstrates the quasi-equilibrium manifold (69) and the first two corrections found analytically. It should be stressed that we spend no special effort on the construction of the initial approximation, that is, of the quasi-equilibrium

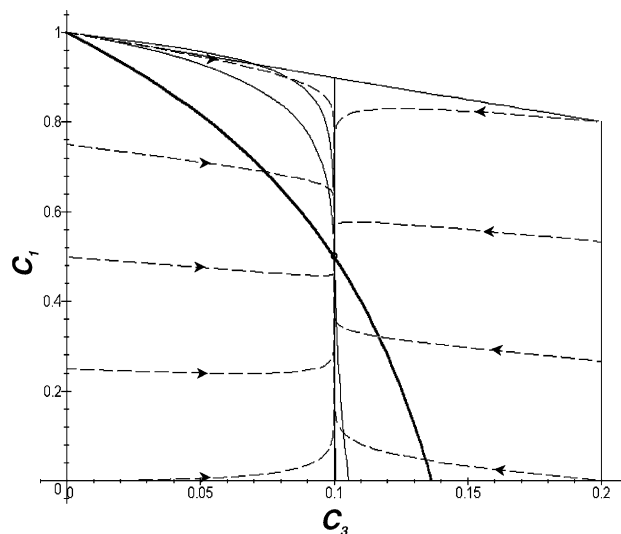


Fig. 1. Images of the initial quasi-equilibrium manifold (bold line) and the first two corrections (solid normal lines) in the phase plane $[c_1, c_3]$ for two-step catalytic reaction (63). Dashed lines are individual trajectories.

manifold, have not used any information about the Jacobian field (unlike, for example, the ILDM or CSP methods discussed above), etc. It is therefore not surprising that the initial quasi-equilibrium approximation chosen in this way is in rather poor agreement with the reduced description. However, it should be appreciated that the further corrections *rapidly* improve the situation while no small parameter considerations were used. This confirms our expectation of the advantage of using the iteration methods in comparison to methods based on a small parameter expansions for model reduction problems.

8. Method of invariant manifold without a priori parameterization

Formally, the method of invariant manifold does not require a global parameterization of the manifolds. However, in most of the cases, one makes use of a priori defined “macroscopic” variables M . This is motivated by the choice of quasi-equilibrium initial approximations.

Let a manifold Ω be defined in the phase space of the system, and let its tangent space in the point \mathbf{c} be $T_{\mathbf{c}}\Omega$. How to define the projector of the whole concentrations space onto $T_{\mathbf{c}}\Omega$ without using any a priori parameterization of Ω ?

The basis of the answer to this question is the condition of thermodynamicity (35). Let us denote E as the concentration space, and consider the problem of the choice of the projector in the quadratic approximation to the thermodynamic potential G :

$$G_q = \langle \mathbf{g}, \mathbf{H}_c \Delta \mathbf{c} \rangle + \frac{1}{2} \langle \Delta \mathbf{c}, \mathbf{H}_c \Delta \mathbf{c} \rangle = \langle \langle \mathbf{g}, \Delta \mathbf{c} \rangle \rangle + \frac{1}{2} \langle \langle \Delta \mathbf{c}, \Delta \mathbf{c} \rangle \rangle, \quad (76)$$

where H_c is the matrix of the second-order derivatives of G (7), $\mathbf{g} = H_c^{-1} \nabla G$, Δc is the deviation of the concentration vector from the expansion point.

Let a linear subspace T be given in the concentrations space E . *Problem:* For every $\Delta c \in T$, and for every $\mathbf{g} \in E$, define a subspace $L_{\Delta c}$ such that: (i) $L_{\Delta c}$ is a complement of T in E :

$$L_{\Delta c} + T = E, \quad L_{\Delta c} \cap T = \{\mathbf{0}\}.$$

(ii) Δc is the point of minimum of G_q on $L_{\Delta c} + \Delta c$:

$$\Delta c = \arg \min_{x - \Delta c \in L_{\Delta c}} G_q(x). \quad (77)$$

Besides (i) and (ii), we also impose the requirement of a *maximal smoothness* (analyticity) on $L_{\Delta c}$ as a function of \mathbf{g} and Δc . Requirement (77) implies that Δc is the quasi-equilibrium point for the given $L_{\Delta c}$, while the problem in a whole is the *inverse* quasi-equilibrium problem: we construct $L_{\Delta c}$ such that T will be the quasi-equilibrium manifold. Then subspaces $L_{\Delta c}$ will actually be the kernels of the quasi-equilibrium projector.

Let $\mathbf{f}_1, \dots, \mathbf{f}_k$ be the orthonormalized basis of T with respect to $\langle\langle \cdot, \cdot \rangle\rangle$ scalar product, and let the vector \mathbf{h} be orthogonal to T , $\langle\langle \mathbf{h}, \mathbf{h} \rangle\rangle = 1$, $\mathbf{g} = \alpha \mathbf{f}_1 + \beta \mathbf{h}$. Condition (77) implies that the vector ∇G is orthogonal to $L_{\Delta c}$ in the point Δc .

Let us first consider the case $\beta = 0$. The requirement of analyticity of $L_{\Delta c}$ as the function of α and Δc implies $L_{\Delta c} = L_0 + o(1)$, where $L_0 = T^\perp$ is the orthogonal complement of T with respect to the scalar product $\langle\langle \cdot, \cdot \rangle\rangle$. The constant solution, $L_{\Delta c} \equiv L_0$ also satisfies (77). Let us fix $\alpha \neq 0$, and extend this latter solution to $\beta \neq 0$. With this, we obtain a basis, $\mathbf{l}_1, \dots, \mathbf{l}_{n-k}$. Here is the simplest construction of this basis:

$$\mathbf{l}_1 = \frac{\beta \mathbf{f}_1 - (\alpha + \Delta c_1) \mathbf{h}}{(\beta^2 + (\alpha + \Delta c_1)^2)^{1/2}}, \quad (78)$$

where $\Delta c_1 = \langle\langle \Delta c, \mathbf{f}_1 \rangle\rangle$ is the first component in the expansion, $\Delta c = \sum_i \Delta c_i \mathbf{f}_i$. The rest of the basis elements, $\mathbf{l}_2, \dots, \mathbf{l}_{n-k}$ form the orthogonal complement of $T \oplus (\mathbf{h})$ with respect to scalar product $\langle\langle \cdot, \cdot \rangle\rangle$, (\mathbf{h}) is the line spanned by \mathbf{h} .

The dependence $L_{\Delta c}$ (78) on Δc , α and β is singular: at $\alpha + \Delta c_1$, vector $\mathbf{l}_1 \in T$, and then $L_{\Delta c}$ is not the complement of T in E anymore. For $\alpha \neq 0$, the dependence $L_{\Delta c}$ gives one of the solutions to the inverse quasi-equilibrium problem in the neighborhood of zero in T . We are interested only in the limit,

$$\lim_{\Delta c \rightarrow \mathbf{0}} L_{\Delta c} = \text{Lin} \left\{ \frac{\beta \mathbf{f}_1 - \alpha \mathbf{h}}{\sqrt{\alpha^2 + \beta^2}}, \mathbf{l}_2, \dots, \mathbf{l}_{n-k} \right\}. \quad (79)$$

Finally, let us define now the projector P_c of the space E onto $T_c \Omega$. If $H_c^{-1} \nabla G \in T_c \Omega$, then P_c is the orthogonal projector with respect to the scalar product $\langle\langle \cdot, \cdot \rangle\rangle$:

$$P_c \mathbf{z} = \sum_{i=1}^k \mathbf{f}_i \langle\langle \mathbf{f}_i, \mathbf{z} \rangle\rangle. \quad (80)$$

If $H_c^{-1} \nabla G \notin T_c \Omega$, then, according to Eq. (79),

$$P_c \mathbf{z} = \frac{\langle\langle \mathbf{f}_1, \mathbf{z} \rangle\rangle - \langle\langle \mathbf{l}_1, \mathbf{z} \rangle\rangle \langle\langle \mathbf{f}_1, \mathbf{l}_1 \rangle\rangle}{1 - \langle\langle \mathbf{f}_1, \mathbf{l}_1 \rangle\rangle^2} \mathbf{f}_1 + \sum_{i=2}^k \mathbf{f}_i \langle\langle \mathbf{f}_i, \mathbf{z} \rangle\rangle, \quad (81)$$

where $\{\mathbf{f}_1, \dots, \mathbf{f}_k\}$ is the orthonormal basis of $T_c \Omega$ with respect to $\langle\langle \cdot, \cdot \rangle\rangle$, \mathbf{h} is orthogonal to T , $\langle\langle \mathbf{h}, \mathbf{h} \rangle\rangle = 1$, $H_c^{-1} \nabla G = \alpha \mathbf{f}_1 + \beta \mathbf{h}$, $\mathbf{l}_1 = (\beta \mathbf{f}_1 - \alpha \mathbf{h}) / \sqrt{\alpha^2 + \beta^2}$, $\langle\langle \mathbf{f}_1, \mathbf{l}_1 \rangle\rangle = \beta / \sqrt{\alpha^2 + \beta^2}$.

Thus, for solving the invariance equation iteratively, one needs only the projector P_c (81), and one does not need an a priori parameterization of Ω anymore.

9. Method of invariant grids

Grid-based approximations of manifolds are attractive from the computational perspective. Since no a priori parameterization is required in the method of invariant manifold, in this section we develop its grid-based realization. Let us consider a regular grid Q in R^k , and its mapping F into the concentrations space E . It makes sense to consider only F which map a finite part of the grid into the phase space V . This part of the map is termed *essential*. Extension of the map F onto the rest of the nodes is done by a simple (for example, linear) extrapolation of the essential part (in practice, one needs to extrapolate only onto the next neighbors of the essential nodes).

Let operators of grid differentiation D_i be defined for functions on the grid, where $i = 1, \dots, k$ label the grid coordinates x_i . With this, the tangent space to the image of the grid in the point $\mathbf{c}(x) = F(x)$ is defined for each node of the grid x :

$$T_x = \text{Lin} \{ \varphi_1, \dots, \varphi_k \},$$

$$\varphi_i = D_i \mathbf{c}(x) = (D_i c_1(x), \dots, D_i c_n(x)). \quad (82)$$

The grid is termed invariant if, for each essential node,

$$\mathbf{J}(\mathbf{c}(x)) \in T_x.$$

For the essential nodes, we write down the invariance equation with the projector, $P_{\mathbf{c}(x)} : E \rightarrow T_x$: this equation is solved using the Newton method as was described above in Section 6. A good initial approximation is a linear map of the grid on the affine manifold corresponding to slow relaxation in the vicinity of the equilibrium. It is convenient to take this map isometric with respect to the metric generated by the entropic scalar product in the equilibrium.

If the vector field of the reduced model, $\dot{\mathbf{c}} = P_{\mathbf{c}(x)} \mathbf{J}(\mathbf{c}(x))$, is defined on the nodes $F(x)$, then one can define the dynamics \dot{x}_i on the nodes. In order to do this, we expand $\dot{\mathbf{c}}$ over φ_i : $\dot{\mathbf{c}} = \sum_{i=1}^k a_i \varphi_i$. The dynamics on the nodes is then defined by equations, $\dot{x}_i = a_i$. Using interpolation, we can define the vector field \dot{x} within the essential cells of the grid (those cells for which all the nodes are essential). The system of equations thus obtained models the dynamics on the invariant manifold.

The essence of this construction is that, by solving a set of uncomplicated linear equations arising from the linearization of the invariance equations on the nodes one gets a reliable numerical scheme for constructing invariant manifolds. The use of grid differentiation rather than a differentiable approximation to the manifold makes the scheme suited for parallel realizations. We stress once again that such realizations are only possible if no a priori global parameterization of manifolds is required. Further refinements of the scheme, taking into account the process of moving the inessential nodes into the phase space, and the opposite process of essential nodes leaving the phase space can be done in the same way as for grid-based data analysis (Gorban & Rossiev, 1999; Gorban, Pitenko, Zinovyev, & Wunsch, 2001b; Gorban & Zinovyev, 2001).

10. Method of invariant manifold for open systems

One of the problems to be focused on when studying closed systems is to prepare extensions of the result for systems that are open or driven by flows. External flows are usually taken into account by additional terms in the kinetic equations (4):

$$\dot{\mathbf{c}} = \mathbf{J}(\mathbf{c}) + \mathbf{\Pi}. \quad (83)$$

Zero-order approximation assumes that the flow does not change the invariant manifold. The equations of the reduced dynamics, however, do change: instead of $\mathbf{J}(\mathbf{c}(M))$ we substitute $\mathbf{J}(\mathbf{c}(M)) + \mathbf{\Pi}$ into Eq. (39):

$$\dot{M}_i = \sum_{j=1}^p N_{ij}^{-1} \langle \nabla M_j |_{\mathbf{c}(M)}, \mathbf{J}(\mathbf{c}(M)) + \mathbf{\Pi} \rangle. \quad (84)$$

Zero-order approximation assumes that the fast dynamics in the closed system strongly couples the variables \mathbf{c} , so that flows cannot influence this coupling.

First-order approximation takes into account the shift of the invariant manifold by $\delta\mathbf{c}$. The equations for Newton's iterations have the same form (57), but instead of the vector field \mathbf{J} they take into account the presence of the flow:

$$[1 - \mathbf{P}_c](\mathbf{\Pi} + \mathbf{L}'_c \delta\mathbf{c}) = 0, \quad \mathbf{P}_c \delta\mathbf{c} = 0, \quad (85)$$

where projector \mathbf{P}_c corresponds to the unperturbed manifold.

The first-order approximation means that fluxes change the coupling between the variables (concentrations). It is assumed that this new coupling is also set instantaneously (neglect of inertia).

Remark. Various realizations of the first-order approximation in physical and chemical dynamics implement the viewpoint of an infinitely small chemical reactor driven by the flow. In other words, this approximation is applicable in the Lagrangian system of coordinates (Karlin et al., 1998; Zmievskii et al., 2000). Transition to Eulerian coordinates is possible but the relations between concentrations and the flow will change their form. In contrast to this, the simpler

zero-order approximation is equally applicable in both coordinate systems, if it is valid.

11. Conclusion

In this paper, we have presented the method for constructing invariant manifolds for reducing systems of chemical kinetics. Our approach to the computation of invariant manifolds of dissipative systems is close in spirit to the Kolmogorov–Arnold–Moser theory of invariant tori of Hamiltonian systems (Arnold, 1963, 1983): we also base our consideration on the Newton method instead of Taylor series expansions (Beyn & Kless, 1998), and systematically use duality structures. Recently, a version of an approach based on the invariance equations was used by Kazantzis (2000). He was solving the invariance equation by a Taylor series expansion. A counterpart of Taylor series expansions for constructing the slow invariant manifolds in the classical kinetic theory is the famous Chapman–Enskog method. The question of how this compares to iteration methods was studied extensively for certain classes of Grad moment equations (Gorban & Karlin, 1996a; Karlin, Dukek, & Nonnenmacher, 1997a; Karlin, 2000).

Thermodynamic parameterization and the selfadjoint linearization arise in a natural way in the problem of finding the slowest invariant manifolds for closed systems. This also leads to various applications in different approaches to reducing the description, in particular, to a thermodynamically consistent version of the intrinsic low-dimensional manifold, and to model kinetic equations for lifting the reduced dynamics. Use of the thermodynamic projector makes it unnecessary to assume a global parameterization of manifolds, and thus leads to computationally promising grid-based realizations.

Invariant manifolds are constructed for closed space-independent chemical systems. We also describe how to use these manifolds for modeling open and distributed systems.

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