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Invariant grids for reaction kinetics

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Abstract

In this paper, we construct low-dimensional manifolds of reduced description for equations of chemical kinetics from the standpoint of the method of invariant manifold (MIM). MIM is based on a formulation of the condition of invariance as an equation, and its solution by Newton iterations. A grid-based version of MIM is developed (the method of invariant grids). We describe the Newton method and the relaxation method for the invariant grids construction. The problem of the grid correction is fully decomposed into the problems of the grid's nodes correction. The edges between the nodes appear only in the calculation of the tangent spaces. This fact determines high computational efficiency of the method of invariant grids. The method is illustrated by two examples: the simplest catalytic reaction (Michaelis–Menten mechanism), and the hydrogen oxidation. The algorithm of analytical continuation of the approximate invariant manifold from the discrete grid is proposed. Generalizations to open systems are suggested. The set of methods covered makes it possible to effectively reduce description in chemical kinetics. © 2003 Elsevier B.V. All rights reserved.

Keywords: Kinetics; Model reduction; Grids; Invariant manifold; Entropy; Nonlinear dynamics; Mathematical modeling; Numerical method

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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 and a new method of invariant grids. Our approach is based on the method of invariant manifold which was introduced in Refs. [1–3]. Its realization for a generic dissipative systems was discussed in Refs. [4,5]. This method was applied to a set of problems of classical kinetic theory based on the Boltzmann kinetic equation [4,6,7]. The method of invariant manifold was successfully applied to a derivation of reduced description for kinetic equations of polymeric solutions [8]. It was also been tested on systems of chemical kinetics [9,10]. In order to construct manifolds of a relatively low dimension, grid-based representations of manifolds become a relevant option. The idea of invariant grids was suggested recently in Ref. [10].

The goal of nonequilibrium statistical physics is the understanding of how a system with many degrees of freedom acquires a description with a few degrees of freedom. This should lead to reliable methods of extracting the macroscopic description from a detailed microscopic description.

Meanwhile 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, on the other hand, analytical methods designed to the solution of problems in real systems can be tested.

In this paper we address the well known class of finite-dimensional systems known from the theory of reaction kinetics. These are equations governing a complex relaxation in perfectly stirred closed chemically active mixtures. Dissipative properties of such systems are characterized with 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.

While the limiting behavior of the dissipative systems just described is certainly very simple, there are still interesting questions to be asked about. One of these questions 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 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. 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 (strictly 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 nondissipative components in a form of either a conservative dynamics, or in the form of external forcing or external fluxes. 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 process 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. Example of this construction for open systems is presented below in Section 10. Till then we focus on the purely dissipative case for the reason just clarified.

The most essential new element of this paper is the systematic consideration of a discrete analogue of the slow (stable) positively invariant manifolds for dissipative systems, *invariant grids*. The invariant grid in phase space of a dynamical system is a discrete (locally finite) set. The tangent space for each point of the grid is defined on the base of finite-difference approximation of differential operators. The grid is invariant, if the vector field of velocities belongs to this tangent space in each point of the grid. The grid is approximate invariant, if the *defect of invariance* in each point of grid is small. We are looking for the approximate invariant grids.

These invariant grids were introduced in Ref. [10]. Here we will describe the Newton method subject to incomplete linearization and the relaxation methods for the invariant grids. It is worth to mention, that the problem of the grid correction is fully decomposed into the problems of the grid’s nodes correction. The edges between the nodes appears only in the calculation of the tangent spaces. This fact determines high computational efficiency of the invariant grids method.

The algorithm of analytical continuation of the approximate invariant manifold from the discrete grid is proposed.

Due to the famous Lyapunov auxiliary theorem [11,12], we can construct analytical invariant manifolds for kinetic equations with analytical right hand side. Moreover, the

analyticity can serve as a “selection rule” for selection of the unique analytic positively invariant manifold from the infinite set of smooth positively invariant manifolds. The analyticity gives a possibility to use the powerful technique of analytical continuation and Carleman’s formulae [13–16]. It leads us to *superresolution effects*: A small grid may be sufficient to present a “large” analytical manifold immersed into the whole space.

The paper is organized as follows. In Section 2, for the sake of completeness, we review the reaction kinetics (Section 2.1), and discuss the main methods of model reduction in chemical kinetics (Section 2.2). In Section 3, we discuss 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 describe 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 the unique algorithm. In Section 7, we introduce the relaxation method for solution the invariance equation. This relaxation method is an alternative to the Newton iteration method. In Section 8, we demonstrate how the *thermodynamic projector* is constructed without the a priori parameterization of the manifold.¹ This result is essentially used in Section 9 where we introduce a computationally effective grid-based method to construct invariant manifolds. It is the central section of the paper. We present the Newton method and the relaxation method for the grid construction. The Carleman formulas for analytical continuation of a manifold from a grid are proposed.

Two examples of kinetic equations are analyzed: a two-dimensional catalytic reaction (four species, two balances), and a four-dimensional oxidation reaction (six species, two balances). There are three most celebrated examples in chemical kinetics:

- The simplest homogeneous catalytic reaction (Michaelis–Menten kinetics);
- The simplest homogeneous oxidation reaction (hydrogen burning);
- The simplest heterogeneous catalytic reaction (oxidation of CO on Pt).

Thousands of papers are written about each of these reactions. The Michaelis–Menten kinetics is studied exhaustively, and it is the usual simple illustrative example. For two other reactions many open questions remain. We choose the Michaelis–Menten kinetics for the first illustration, and the simplest reaction scheme of hydrogen burning (with provisional rate constants) for the second example.

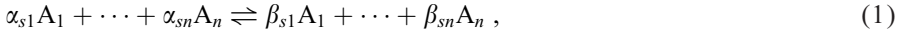
In Section 10, we describe an extension of the method of invariant manifold to open systems. Finally, results are discussed in Section 11.

¹ This thermodynamic projector is the unique operator which transforms the arbitrary vector field equipped with the given Lyapunov function into a vector field with the same Lyapunov function (and also this happens on any manifold which is not tangent to the level of the Lyapunov function).

2. Equations of chemical kinetics and their reduction

2.1. Outline of the dissipative reaction kinetics

We begin with an outline of the reaction kinetics (for details see e.g. the book [17]). 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 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} . Notation γ_s stands for the vector with integer components $\gamma_{si} = \beta_{si} - \alpha_{si}$ (the stoichiometric vector).

For every A_i an *extensive variable* N_i , “the number of particles of that species”, is defined. The concentration of A_i is $c_i = N_i/V$, where V is the volume.

Given the stoichiometric mechanism (1), the reaction kinetic equations read:

$$\dot{\mathbf{N}} = V\mathbf{J}(\mathbf{c}), \mathbf{J}(\mathbf{c}) = \sum_{s=1}^r \gamma_s W_s(\mathbf{c}), \quad (2)$$

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

$$W_s(\mathbf{c}) = W_s^+(\mathbf{c}) - W_s^-(\mathbf{c}) = k_s^+(T) \prod_{i=1}^n c_i^{\alpha_{si}} - k_s^-(T) \prod_{i=1}^n c_i^{\beta_{si}}, \quad (3)$$

where $k_s^+(T)$ and $k_s^-(T)$ are the constants of the direct and of the inverse reactions rates of the s th reaction step, T is the temperature. The (generalized) Arrhenius equation gives the most popular form of dependence $k_s^+(T)$:

$$k_s^\pm(T) = a_s^\pm T^{b_s^\pm} \exp(S_s^\pm/k_B) \exp(-H_s^\pm/k_B T), \quad (4)$$

where a_s^\pm , b_s^\pm are constants, H_s^\pm are activation enthalpies, S_s^\pm are activation entropies.

The rate constants are not independent. The *principle of detail balance* gives the following connection between these constants: there exists such a positive vector $\mathbf{c}^{\text{eq}}(T)$ that

$$W_s^+(\mathbf{c}^{\text{eq}}) = W_s^-(\mathbf{c}^{\text{eq}}) \text{ for all } s = 1, \dots, r. \quad (5)$$

The necessary and sufficient conditions for existence of such \mathbf{c}^{eq} can be formulated as the system of polynomial equalities for $\{k_s^\pm\}$, if the stoichiometric vectors $\{\gamma_s\}$ are linearly dependent (see, for example, Ref. [17]).

The reaction kinetic equations (2) do not give us a closed system of equations, because dynamics of the volume V is not yet defined still. Four classical conditions for the closure of this system are well studied: $U, V = \text{const}$ (isolated system, U is the internal energy); $H, P = \text{const}$ (thermal isolated isobaric system, P is the pressure, $H = U + PV$ is the enthalpy), $V, T = \text{const}$ (isochoric isothermal conditions);

$P, T = const$ (isobaric isothermal conditions). For $V, T = const$ we do not need additional equations and data. It is possible just to divide equation (2) by the constant volume and to write

$$\dot{c} = \sum_{s=1}^r \gamma_s W_s(\mathbf{c}). \tag{6}$$

For nonisothermal and nonisochoric conditions we do need addition formulae to derive T and V . For all four classical conditions the thermodynamic Lyapunov functions G for kinetic equations are known:

$$\begin{aligned} U, V = const, G_{U,V} = -S/k_B; \quad V, T = const, G_{V,T} = F/k_B T = U/k_B T - S/k_B; \\ H, P = const, G_{H,P} = -S/k_B; \quad P, T = const, G_{P,T} = G/k_B T = H/k_B T - S/k_B, \end{aligned} \tag{7}$$

where $F = U - TS$ is the free energy (Helmholtz free energy), $G = H - TS$ is the free enthalpy (Gibbs free energy). All the thermodynamic Lyapunov functions are normalized to dimensionless scale (if one measures the number of particles in moles, then it is necessary to change k_B to R). All these function decrease in time. For classical conditions the correspondent thermodynamic Lyapunov functions can be written in the form: $G_{\bullet}(const, N)$. The derivatives $\partial G_{\bullet}(const, N)/\partial N_i$ are the same functions of \mathbf{c} and T for all classical conditions:

$$\mu_i(\mathbf{c}, T) = \frac{\partial G_{\bullet}(const, N)}{\partial N_i} = \frac{\mu_{chemi}(\mathbf{c}, T)}{k_B T}, \tag{8}$$

where $\mu_{chemi}(\mathbf{c}, T)$ is the chemical potential of A_i .

Usual $G_{\bullet}(const, N)$ are strictly convex functions of N , and the matrix $\partial \mu_i / \partial c_j$ is positively definite. The dissipation inequality (9) holds

$$\frac{dG_{\bullet}}{dt} = V(\boldsymbol{\mu}, \mathbf{J}) \leq 0, \tag{9}$$

where $(a, b) = \sum_i a_i b_i$ is the usual scalar product. This inequality is the restriction on possible kinetic laws and on possible values of kinetic constants.

The most important generalization of the mass action law (3) is the Marcelin–De Donder kinetic function. This generalization [18,19] is based on ideas of the thermodynamic theory of affinity [20] (discussion of the kinetics based on the theory of affinity for driven systems can be found in the paper [21]). We use the kinetic function suggested in its final form in Ref. [19]. Within this approach, the functions W_s are constructed as follows: For a given $\boldsymbol{\mu}(\mathbf{c}, T)$ (8), and for a given stoichiometric mechanism (1), we define the gain (+) and the loss (–) rates of the s th step,

$$W_s^+ = \varphi_s^+ \exp(\boldsymbol{\mu}, \boldsymbol{\alpha}_s), \quad W_s^- = \varphi_s^- \exp(\boldsymbol{\mu}, \boldsymbol{\beta}_s), \tag{10}$$

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 (2) becomes,

$$\mathbf{J} = \sum_{s=1}^r \gamma_s \{ \varphi_s^+ \exp(\boldsymbol{\mu}, \boldsymbol{\alpha}_s) - \varphi_s^- \exp(\boldsymbol{\mu}, \boldsymbol{\beta}_s) \}. \tag{11}$$

For the Marcelin–De Donder reaction rate (10), the dissipation inequality (9) reads

$$\dot{G} = \sum_{s=1}^r [(\boldsymbol{\mu}, \boldsymbol{\beta}_s) - (\boldsymbol{\mu}, \boldsymbol{\alpha}_s)] \{ \varphi_s^+ e^{(\boldsymbol{\mu}, \boldsymbol{\alpha}_s)} - \varphi_s^- e^{(\boldsymbol{\mu}, \boldsymbol{\beta}_s)} \} \leq 0. \quad (12)$$

The kinetic factors φ_s^\pm should satisfy certain conditions in order to make valid the dissipation inequality (12). A well known sufficient condition is the detail balance:

$$\varphi_s^+ = \varphi_s^-, \quad (13)$$

other sufficient conditions are discussed in detail elsewhere [17,22,23].

For ideal systems, function G_\bullet is constructed from the thermodynamic data of individual species. It is convenient to start from the isochoric isothermal conditions. The Helmholtz free energy for ideal system is

$$F = k_B T \sum_i N_i [\ln c_i - 1 + \mu_{0i}] + \text{const}_{T,V}, \quad (14)$$

where the internal energy is assumed to be a linear function:

$$U = \sum_i N_i u_i(T) = \sum_i N_i (u_{0i} + C_{Vi} T)$$

in given interval of c , T , $u_i(T)$ is the internal energy of A_i per particle. It is well known that $S = -(\partial F / \partial T)_{V,N=const}$, $U = F + TS = F - T(\partial F / \partial T)_{V,T=const}$, hence, $u_i(T) = -k_B T^2 d\mu_{0i}/dT$ and

$$\mu_{0i} = \delta_i + u_{0i}/k_B T - (C_{Vi}/k_B) \ln T, \quad (15)$$

where $\delta_i = \text{const}$, C_{Vi} is the A_i heat capacity at constant volume (per particle).

In concordance with the form of ideal gas free energy (14) the expression for $\boldsymbol{\mu}$ is

$$\mu_i = \ln c_i + \delta_i + u_{0i}/k_B T - (C_{Vi}/k_B) \ln T. \quad (16)$$

For the function $\boldsymbol{\mu}$ of form (16), the Marcelin–De Donder equation casts into the more familiar mass action law form (3). Taking into account the principle of detail balance (13) we get the ideal rate functions:

$$W_s(\mathbf{c}) = W_s^+(\mathbf{c}) - W_s^-(\mathbf{c}),$$

$$W_s^+(\mathbf{c}) = \varphi(\mathbf{c}, T) T^{-\sum_i \alpha_{si} C_{Vi}/k_B} e^{\sum_i \alpha_{si} (\delta_i + u_{0i}/k_B T)} \prod_{i=1}^n c_i^{\alpha_i},$$

$$W_s^-(\mathbf{c}) = \varphi(\mathbf{c}, T) T^{-\sum_i \beta_{si} C_{Vi}/k_B} e^{\sum_i \beta_{si} (\delta_i + u_{0i}/k_B T)} \prod_{i=1}^n c_i^{\beta_i}, \quad (17)$$

where $\varphi(\mathbf{c}, T)$ is an arbitrary (from the thermodynamic point of view) positive function.

Let us discuss further the vector field $\mathbf{J}(\mathbf{c})$ in the concentration space (6). Conservation laws (balances) impose linear constrains on admissible vectors $d\mathbf{c}/dt$:

$$(\mathbf{b}_i, \mathbf{c}) = B_i = \text{const}, \quad i = 1, \dots, l, \quad (18)$$

where \mathbf{b}_i are fixed and linearly independent vectors. Let us denote as \mathbf{B} the set of vectors which satisfy the conservation laws (18) with given B_i :

$$\mathbf{B} = \{ \mathbf{c} \mid (\mathbf{b}_1, \mathbf{c}) = B_1, \dots, (\mathbf{b}_l, \mathbf{c}) = B_l \}.$$

The natural phase space X of system (6) is the intersection of the cone of n -dimensional vectors with nonnegative components, with the set B , and $\dim X = d = n - l$. In the sequel, we term a vector $c \in X$ the state of the system. In addition, we assume that each of the conservation laws is supported by each elementary reaction step, that is

$$(\gamma_s, b_i) = 0, \tag{19}$$

for each pair of vectors γ_s and b_i .

Reaction kinetic equations describe variations of the states in time. The phase space X is positive-invariant of system (6): If $c(0) \in X$, then $c(t) \in X$ for all the times $t > 0$.

In the sequel, we assume that the kinetic equation (6) describes evolution towards the unique equilibrium state, c^{eq} , in the interior of the phase space X . Furthermore, we assume that there exists a strictly convex function $G(c)$ which decreases monotonically in time due to Eq. (6):

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

$$H_c = \|\partial^2 G(c) / \partial c_i \partial c_j\|, \tag{20}$$

are positive definite for all $c \in X$. In addition, we assume that matrices (20) are invertible if c is taken in the interior of the phase space.

The matrix H defines an important Riemann structure on the concentration space, the thermodynamic (or entropic) scalar product:

$$\langle x, y \rangle_c = (x, H_c y). \tag{21}$$

This choice of the Riemann structure is unambiguous from the thermodynamic perspective.

The function G is the Lyapunov function of system (2), and c^{eq} is the point of global minimum of the function G in the phase space X . Otherwise stated, the manifold of equilibrium states $c^{eq}(B_1, \dots, B_l)$ is the solution to the variational problem,

$$G \rightarrow \min \text{ for } (b_i, c) = B_i, \quad i = 1, \dots, l. \tag{22}$$

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:

$$G = \sum_{i=1}^n c_i [\ln(c_i / c_i^{eq}) - 1]. \tag{23}$$

It is important to stress that c^{eq} in Eq. (23) is an *arbitrary* equilibrium of the system, under arbitrary values of the balances. In order to compute $G(c)$, it is unnecessary to calculate the specific equilibrium c^{eq} which corresponds to the initial state c . Let us

compare the Lyapunov function G (23) with the classical formula for the free energy (14). This comparison gives a possible choice for c^{eq} :

$$\ln c_i^{eq} = -\delta_i - u_{0i}/k_B T + (C_{Vi}/k_B) \ln T. \quad (24)$$

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, in Refs. [24–29], and many others. It follows the Chapman–Enskog method of the Boltzmann equation theory [30]. The *partial equilibrium approximations* [22,27,31–34] are predecessors of the Grad method and quasiequilibrium approximations in physical kinetics. These two family of methods have different physical backgrounds and mathematical forms.

There exist a set of methods to construct an ansatz for the invariant manifold based on the spectral decomposition of the Jacobian. 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 [35], and from methods of sensitivity analysis in control theory [36–38]. One of the currently most popular methods based on the spectral decomposition of Jacobian fields is the construction of the so-called *intrinsic low-dimensional manifold* (ILDM) [39].

These methods were thoroughly analyzed in two recent papers [40,41]. It was shown that the successive applications of the Computational Singular Perturbation algorithm (developed in Ref. [38]) generate, order by order, the asymptotic expansion of a slow manifold, and the manifold identified by the ILDM technique (developed in Ref. [39]) agrees with the invariant manifold to some order.

Recently, a further step in this direction was done in Ref. [42]. 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.

The problem of a complete decomposition (linearization, [43]) of kinetic equations can be solved in some cases. The first such solution was the spectral decomposition for linear systems [44]. Decomposition is sometimes possible also for nonlinear systems [45,46]. The most famous example of a complete decomposition of infinite-dimensional kinetic equation is the complete integrability of the space-independent Boltzmann equation for Maxwell’s molecules found in Ref. [47].

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 them be indexed with the numbers s_1, \dots, s_k . The quasi-equilibrium manifold is defined by the system of equations,

$$W_{s_i}^+ = W_{s_i}^-, \quad i = 1, \dots, k. \tag{25}$$

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

$$(\boldsymbol{\gamma}_{s_i}, \boldsymbol{\mu}) = 0, \quad i = 1, \dots, k. \tag{26}$$

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, $L = \text{lin}\{\boldsymbol{\gamma}_{s_1}, \dots, \boldsymbol{\gamma}_{s_k}\}$.

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, $(\mathbf{b}_i, \mathbf{c}) = 0$. In terms of the conjugated variables, the quasi-equilibrium manifold, L^\perp , is defined by equations,

$$\boldsymbol{\mu} \in L^\perp, \quad (\boldsymbol{\mu} = (\mu_1, \dots, \mu_n)). \tag{27}$$

The same quasi-equilibrium manifold can be also defined with the help of fictitious reactions: Let $\mathbf{g}_1, \dots, \mathbf{g}_q$ be a basis in L . Then Eq. (27) may be rewritten as follows:

$$(\mathbf{g}_i, \boldsymbol{\mu}) = 0, \quad i = 1, \dots, q. \tag{28}$$

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. Subspace L is defined by balance constraints:

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

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

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

Corresponding Eq. (28) is

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

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

$$(\mathbf{b}_i, L) \equiv 0.$$

The orthogonal complement of L in the space with coordinates $\boldsymbol{\mu} = \nabla G$ defines then the quasi-equilibrium manifold $\boldsymbol{\Omega}_L$. For the actual computations, one requires the inversion from $\boldsymbol{\mu}$ to \mathbf{c} . Duality structure $\boldsymbol{\mu} \leftrightarrow \mathbf{c}$ is well studied by many authors [23,31].

Quasi-equilibrium projector. It is not sufficient to just derive the manifold, it is also required to define a *projector* which would transform the vector field defined on the space of concentrations to a vector field on the manifold. Quasi-equilibrium manifold consists of points which minimize G on the affine spaces of 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 $\boldsymbol{\Omega}_L$ parallel to L . The vector field is also projected onto the tangent space of $\boldsymbol{\Omega}_L$ 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 [32]. 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 kinetic equations (2).

For the quasi-equilibrium approximation the fast and the slow directions in concentration space are orthogonal with respect to entropic scalar product (21).

2.4. Model equations

The rationale 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 restore 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:

$$\dot{\mathbf{c}} = -\frac{1}{\tau}[\mathbf{c} - \mathbf{c}_L^*(\mathbf{c})] + \sum_{\text{slow}} \gamma_s W_s(\mathbf{c}_L^*(\mathbf{c})), \tag{29}$$

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. (29), whereas the rapid motion is taken into account by a simple relaxational term (the first term in the right hand side of Eq. (29)). The most famous model kinetic equation is the BGK equation in the theory of the Boltzmann equation [48]. The general theory of the quasi-equilibrium models, including proofs of their thermodynamic consistency, was constructed in the papers [49,50].

Single relaxation time gradient models (SRTGM) were considered in the context of the lattice Boltzmann method for hydrodynamics [51,52]. These models are aimed at improving the obvious drawback of quasi-equilibrium models (29): In order to construct the QEM, one needs to compute the function,

$$\mathbf{c}_L^*(\mathbf{c}) = \arg \min_{\mathbf{x} \in \mathbf{c} + L, \mathbf{x} > 0} G(\mathbf{x}). \tag{30}$$

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

Let $\mathbf{g}_1, \dots, \mathbf{g}_k$ is the orthonormal basis of L . We denote as $\mathbf{D}(\mathbf{c})$ the $k \times k$ matrix with the elements $(\mathbf{g}_i, \mathbf{H}_c \mathbf{g}_j)$, where \mathbf{H}_c is the matrix of second derivatives of G (20). Let $\mathbf{C}(\mathbf{c})$ be the inverse of $\mathbf{D}(\mathbf{c})$. The single relaxation time gradient model has the form:

$$\dot{\mathbf{c}} = -\frac{1}{\tau} \sum_{i,j} \mathbf{g}_i \mathbf{C}(\mathbf{c})_{ij} (\mathbf{g}_j, \nabla G) + \sum_{\text{slow}} \gamma_s W_s(\mathbf{c}). \tag{31}$$

The first term drives the system to the minimum of G on $\mathbf{c} + L$, it does not require solving problem (30), and its spectrum in the quasi-equilibrium is the same as in the quasi-equilibrium model (29). Note that the slow component is evaluated in the “current” state \mathbf{c} .

Eq. (31) has a simple form

$$\dot{\mathbf{c}} = -\frac{1}{\tau} \text{grad} G, \tag{32}$$

if one calculates $\text{grad}G$ with the entropic scalar product² (20,21) $\langle \mathbf{x}, \mathbf{y} \rangle = (\mathbf{x}, \mathbf{H}_c \mathbf{y})$.

Models (29) and (31) lift the quasi-equilibrium approximation to a kinetic equation by approximating the fast dynamics with a single “reaction rate constant”—relaxation time τ .

²Let us remind that $\text{grad}G$ is the Riesz representation of the differential of G in the phase space X : $G(\mathbf{c} + \Delta\mathbf{c}) = G(\mathbf{c}) + \langle \text{grad}G(\mathbf{c}), \Delta\mathbf{c} \rangle + o(\Delta\mathbf{c})$. It depends on the scalar product, and from thermodynamic point of view there is only one distinguished scalar product in concentration space, the entropic one. The usual definition of $\text{grad}G$ as the vector of partial derivatives corresponds to the standard scalar product (\bullet, \bullet) .

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. (2) for the component c^f at fixed values of c^s . If it happens that in this way defined fast subsystem relaxes to a stationary state, $c^f \rightarrow c_{\text{qss}}^f(c^s)$, then the assumption that $c^f = c_{\text{qss}}^f(c)$ is precisely the QSS assumption. The slow subsystem is the part of the system (2) for c^s , in the right hand side of which the component c^f is replaced with $c_{\text{qss}}^f(c)$. Thus, $J = J_s \oplus J_f$, where

$$\dot{c}^f = J_f(c^s \oplus c^f), \quad c^s = \text{const}; \quad c^f \rightarrow c_{\text{qss}}^f(c^s); \quad (33)$$

$$\dot{c}^s = J_s(c^s \oplus c_{\text{qss}}^f(c^s)). \quad (34)$$

Bifurcations in system (33) under variation of c^s as a parameter are confronted with the kinetic critical phenomena. Studies of more complicated dynamic phenomena in the fast subsystem (33) require various techniques of averaging, stability analysis of the averaged quantities, etc.

Various versions of the QSS method are well 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 Eqs. (33), a hierarchy of systems of lower-dimensional equations is considered, each of these subsystem is easier to study analytically.

Theory of singularly perturbed systems of ordinary differential equations is used to provide a mathematical background and further development of the QSS approximation. 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). Reaction rate constants 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, $\text{H}_2 \rightleftharpoons 2\text{H}$, $\text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O}$). It is therefore incorrect to state that c^f evolve 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 [17]. This smallness parameter is the ratio of balances: Intermediate species include the catalyst, and their total amount is simply much smaller than the amount of all the c_i 's. After renormalizing to the variables of one order of magnitude, the small parameter appears explicitly. The simplest example gives the catalytic reaction $A + Z \rightleftharpoons AZ \rightleftharpoons P + Z$ (here Z is a catalyst, A and P are an initial substrate and a product). The kinetic equations are

(in self-explaining notation):

$$\begin{aligned}
 \dot{c}_A &= -k_1^+ c_A c_Z + k_1^- c_{AZ} , \\
 \dot{c}_Z &= -k_1^+ c_A c_Z + k_1^- c_{AZ} + k_2^+ c_{AZ} - k_2^- c_Z c_P , \\
 \dot{c}_{AZ} &= k_1^+ c_A c_Z - k_1^- c_{AZ} - k_2^+ c_{AZ} + k_2^- c_Z c_P , \\
 \dot{c}_P &= k_2^+ c_{AZ} - k_2^- c_Z c_P .
 \end{aligned} \tag{35}$$

The constants and the reactions rates are the same for concentrations c_A, c_P , and for c_Z, c_{AZ} , and cannot be a reason for a relative slowness of c_A, c_P in comparison with c_Z, c_{AZ} , but there may be another source of slowness. There are two balances for this kinetics: $c_A + c_P + c_{AZ} = B_A$, $c_Z + c_{AZ} = B_Z$. Let us switch to dimensionless variables:

$$\begin{aligned}
 \varsigma_A &= c_A/B_A, \quad \varsigma_P = c_P/B_A, \quad \varsigma_Z = c_Z/B_Z, \quad \varsigma_{AZ} = c_{AZ}/B_Z; \\
 \dot{\varsigma}_A &= B_Z \left[-k_1^+ \varsigma_A \varsigma_Z + \frac{k_1^-}{B_A} \varsigma_{AZ} \right] , \\
 \dot{\varsigma}_Z &= B_A \left[-k_1^+ \varsigma_A \varsigma_Z + \frac{k_1^-}{B_A} \varsigma_{AZ} + \frac{k_2^+}{B_A} \varsigma_{AZ} - k_2^- \varsigma_Z \varsigma_P \right] , \\
 c \varsigma_A + \varsigma_P + \frac{B_Z}{B_A} \varsigma_{AZ} &= 1, \quad \varsigma_Z + \varsigma_{AZ} = 1; \varsigma_{\bullet} \geq 0 .
 \end{aligned} \tag{36}$$

For $B_Z \ll B_A$ the slowness of ς_A, ς_P is evident from these Eqs. (36).

For 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 balances B_i (18). Instead, one can come up with a thermodynamic estimate: function G decreases in the course of reactions, whereupon we obtain the limiting estimate of concentrations of any specie:

$$c_i \leq \max_{G(c) \leq G(c(0))} c_i , \tag{37}$$

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 ideal G (23) under relevant conditions, for any $t > 0$, the following inequality is valid:

$$c_R [\ln (c_R(t)/c_R^{eq}) - 1] \leq G(c(0)) . \tag{38}$$

Inequality (38) provides the simplest (but rather coarse) thermodynamic estimate of $c_R(t)$ in terms of $G(c(0))$ and c_R^{eq} uniformly for $t > 0$. Complete theory of thermodynamic estimates of dynamics has been developed in the book [22].

One can also do computations without a priori estimations, if one accepts the QSS assumption until the values c^f stay sufficiently small. It is the simplest way to operate with QSS: Just use it *until* c^f remain 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 (2) in such a way that renormalized variables take their values from the unit segment $[0, 1]$: $\tilde{c}_i = c_i/c_{i \max}$. Then system (2) can be written as follows:

$$\frac{d\tilde{c}_i}{dt} = \frac{1}{c_{i \max}} J_i(\mathbf{c}). \quad (39)$$

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 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., Refs. [53,54]). There exist a variety of ways to introduce the smallness parameter into kinetic equations, and one can find applications to each of the realizations (the good example with the thorough analysis can be find in the paper [55]). However, the two particular realizations remain basic for chemical kinetics: (i) fast reactions (under a 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, those 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 iterational 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 [1].

2.6. Thermodynamic criteria for selection of important reactions

One of the problems addressed by the sensitivity analysis is the selection of the important and discarding the unimportant reactions. In the paper [56], a simple principle was suggested to compare 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 [57] 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 [58]. For ideal systems (23), as well, as for the Marcelin–De Donder kinetics (12) the contribution of the s th

reaction to \dot{G} has a particularly simple form:

$$\dot{G}_s = -W_s \ln \left(\frac{W_s^+}{W_s^-} \right), \dot{G} = \sum_{s=1}^r \dot{G}_s. \quad (40)$$

2.7. Opening

One of the problems to be focused on when studying closed systems is to prepare extensions of the result for open or driven by flows systems. External flows are usually taken into account by additional terms in the kinetic equations (2):

$$\dot{\mathbf{N}} = V\mathbf{J}(\mathbf{c}) + \mathbf{\Pi}(\mathbf{c}, t). \quad (41)$$

It is important to stress here that the vector field $\mathbf{J}(\mathbf{c})$ in Eq. (41) is the same, as for the closed system, with thermodynamic restrictions, Lyapunov functions, etc. The thermodynamic structures are important for analysis of open systems (41), if the external flow $\mathbf{\Pi}$ is small in some sense, is linear function of \mathbf{c} , has small time derivatives, etc. There are some general results for such “weakly open” systems, for example the Prigogine minimum entropy production theorem [59] and the estimations of possible steady states and limit sets for open systems, based on thermodynamic functions and stoichiometric equations [22].

There are general results for another limiting case: for very intensive flows the dynamics becomes very simple again [17]. Let the flow have a natural structure: $\mathbf{\Pi}(\mathbf{c}, t) = v_{in}(t)\mathbf{c}_{in}(t) - v_{out}(t)\mathbf{c}(t)$, where v_{in} and v_{out} are the rates of inflow and outflow, $\mathbf{c}_{in}(t)$ is the concentration vector for the inflow. If $\mathbf{c}(t)$ is bounded, and v_{out} is sufficiently large, $v_{out}(t) > v_0$, for some critical value v_0 , and all $t > 0$, then for the open system (41) the Lyapunov norm exists: for any two solutions $\mathbf{c}^1(t)$ and $\mathbf{c}^2(t)$ the function $\|\mathbf{c}^1(t) - \mathbf{c}^2(t)\|$ monotonically decreases in time. Such a critical value v_0 exists for any norm, for example, for usual Euclidian norm $\|\bullet\|^2 = (\bullet, \bullet)$.

For arbitrary form of $\mathbf{\Pi}$, system (41) can loose all signs of being a thermodynamic one. Nevertheless, thermodynamic structures often can be helpful in the study of open systems.

The seminal questions are: what happens with slow/fast motion separation after the opening? Which slow invariant manifold for the closed system can be deformed to the slow invariant manifold for the open system? Which slow invariant manifold for the closed system can be used as the approximate slow invariant manifold for the open system? There exist more or less useful techniques to seek the answers for specific systems under consideration.

The way to study an open system as the result of opening a closed system may be fruitful. In any case, out of this way we have just a general dynamical system (41) and no hints what to do with it, in general.

3. Outline of the method of invariant manifold

In many cases, dynamics of the d -dimensional system (2) 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 (2): 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 obligatory invariant) manifold Ω is considered as a manifold of reduced description. We should define a field 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

$$(\nabla G(\mathbf{c}), \mathbf{P}_c \mathbf{J}(\mathbf{c})) \leq 0 \quad \text{for each } \mathbf{c} \in \Omega. \quad (42)$$

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 (42) 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 $\mathbf{c} \in \Omega$, let us consider the linear functional

$$M_c^*(\mathbf{x}) = (\nabla G(\mathbf{c}), \mathbf{x}). \quad (43)$$

Then the thermodynamic condition for the projectors reads:

$$\ker \mathbf{P}_c \subseteq \ker M_c^*, \quad \text{for each } \mathbf{c} \in \Omega. \quad (44)$$

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 [1,4] that condition (44) 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 a definition, the manifold Ω is invariant with respect to the vector field \mathbf{J} if and only if the following equality is true:

$$[1 - \mathbf{P}]\mathbf{J}(\mathbf{c}) = 0 \quad \text{for each } \mathbf{c} \in \Omega. \quad (45)$$

In this expression \mathbf{P} is an *arbitrary* projector on the tangent bundle of the manifold Ω . It has been suggested to consider condition (45) as an *equation* to be solved iteratively starting with some appropriate initial manifold.

There are two possible senses of the notion “approximate solution of invariance equations” (45):

1. The approximation of the solution;
2. The map F with small defect of invariance (the right-hand side approximation).

If one looks for the approximation of the first kind, then he needs theorems of existence of solutions, he should find the estimations of deviations from the exact solution, because the right hand side does not always give a good estimation, etc. The second kind of approximations does not require hypothesis of existence of exact solution. It is important, for example, for applications to systems with flows and 3D Navier–Stokes equation.

Moreover, the manifold with sufficiently small defect of invariance can serve as a slow manifold by itself. This is important for any system, finite-dimensional as well as infinite-dimensional. Thus, we shall adopt the concept of the approximate invariant manifold (the manifold with a small defect of invariance) instead of the approximation of the invariant manifold (see also Refs. [60,61] and other works about approximate inertial manifolds). Sometimes these approximate invariant manifolds will give approximations of the invariant manifolds, sometimes not, but it is an additional and often difficult problem to distinguish between these situations.

Iterations for the invariance equation (45) are considered in Section 5. The next section presents 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 $M(\mathbf{c}) = \{M_1(\mathbf{c}), \dots, M_p(\mathbf{c})\}$, and let us assume that they form a coordinate system on Ω in such a way that $\Omega = \mathbf{c}(M)$, where $\mathbf{c}(M)$ is a vector function of the parameters M_1, \dots, M_p . Then the projector associated with this parameterization reads:

$$\mathbf{P}_{\mathbf{c}(M)}\mathbf{x} = \sum_{i=1}^p \frac{\partial \mathbf{c}(M)}{\partial M_i} (\nabla M_i |_{\mathbf{c}(M)}, \mathbf{x}), \quad (46)$$

Subsequently, the induced vector field of the reduced dynamics is found by applying projectors (46) on the vectors $\mathbf{J}(\mathbf{c}(M))$, thereby inducing the reduced dynamics in terms of the parameters M as follows:

$$\dot{M}_i = (\nabla M_i |_{\mathbf{c}(M)}, \mathbf{J}(\mathbf{c}(M))), \quad (47)$$

Depending on the choice of the parameterization, dynamic equations (47) are (or are not) consistent with the thermodynamic requirement (42). The *thermodynamic*

parameterization makes use of condition (44) in order to establish the thermodynamic projector. Specializing to case (46), let us consider linear functionals,

$$DM_i|_{c(M)}(\mathbf{x}) = (\nabla M_i|_{c(M)}, \mathbf{x}). \quad (48)$$

Then condition (44) takes the form:

$$\bigcap_{i=1}^p \ker DM_i|_{c(M)} \subseteq \ker M_{c(M)}^*, \quad (49)$$

that is, the intersection of null spaces of functionals (48) 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, one can take the following set of functionals in each point c of the manifold Ω :

$$M_1(\mathbf{x}) = M_c^*(\mathbf{x}), c \in \Omega, \quad (50)$$

$$M_i(\mathbf{x}) = (\mathbf{m}_i, \mathbf{x}), i = 2, \dots, p. \quad (51)$$

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 the functionals (43) as a part of system (50) and (51) implies the thermodynamic condition (49). Also, any linear combination of the parameter set (50), (51) 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 (18). 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 (18) explicitly on each step of the construction. For this technical reason, it is convenient to consider manifolds of the 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 consistent also with the conservation laws if l of the linear functionals (51) are identified with the conservation laws. In the sequel, only projectors consistent with conservation laws are considered.

Very frequently, the manifold Ω is represented as a p -parametric family $c(a_1, \dots, a_p)$, where a_i are coordinates on the manifold. The thermodynamic *re-parameterization* suggests a representation of the coordinates a_i in terms of M_c^*, M_2, \dots, M_p (50), (51). While the explicit construction of these functions may be a formidable task, we notice that the construction of the thermodynamic projector of form (46) and of the dynamic equations (47) is relatively easy because only the derivatives $\partial c / \partial M_i$ enter these expressions. This point was discussed in a detail in Refs. [1,4].

The choice of the rest of functionals (50) may sound somewhat arbitrary. In Section 8 we demonstrate, that the requirement that the projector field $\mathbf{P}_{c(M)}$ is smooth and transforms *any* smooth vector field \mathbf{J} with Lyapunov function G into the vector field $\mathbf{P}_{c(M)}\mathbf{J}$ with the same Lyapunov function G , defines the thermodynamic projector uniquely.

4.2. Decomposition of motions: thermodynamics

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 little from the state c , so that the linear approximation is valid, then c' belongs to the affine hyperplane

$$\Gamma_c = c + \ker M_c^*, \quad c \in \Omega. \quad (52)$$

This hyperplane actually participates in condition (44). The consideration was entitled ‘thermodynamic’ [1] because it describes the states $c \in \Omega$ as points of minimum of the function G over the corresponding hyperplanes (52).

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 (42) holds. Coming back to the issue of constructing corrections, we should stress that the projector participating in the invariance condition (45) is arbitrary. It is convenient to make use of this point: when Eq. (45) is solved iteratively, the projector may be kept nonthermodynamic 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. Though 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 (45):

$$\Delta_0 = [1 - P_0]J(c_0) \neq 0 \quad \text{for some } c_0 \in \Omega_0. \quad (53)$$

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 (45), and after the linearization in δc , we derive the following linear equation:

$$[1 - P_0][J(c_0) + L_{c_0} \delta c] = 0, \quad (54)$$

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 (54) should be supplied with

the additional condition.

$$P_0 \delta c = 0 . \tag{55}$$

In order to illustrate the nature of Eq. (54), 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, $G(c) = (c, c)$. The manifolds we consider are lines, $l(a) = ae$, where e is the unit vector, and a is a scalar. The invariance equation for such manifolds reads: $e(e, Le) - Le = 0$, 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 (55) now reads: $(\delta y, e_0) = 0$. Then the Eq. (54) becomes $[1 - e_0(e_0, \cdot)]L[e_0 + \delta y] = 0$. Subject to the additional condition, the unique solution is as follows: $e_0 + \delta y = (e_0, L^{-1}e_0)^{-1}L^{-1}e_0$. Rewriting the latter expression in the eigen-basis of L , we have: $e_0 + \delta y \propto \sum_i \lambda_i^{-1} e_i(e_i, e_0)$. The leading term in this sum corresponds to the eigenvalue with the minimal absolute value. The example indicates that the method of linearization (54) seeks the direction of the *slowest relaxation*. For this reason, method (54) 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. (54) depends nontrivially on c_0 . In this case, system (54) requires a further specification which will be done now.

5.2. Symmetric linearization

The invariance condition (45) 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 J , appearing in Eq. (54). We shall return to the explicit form of the Marcelin–De Donder kinetic function (10). Let c is an arbitrary fixed element of the phase space. The linearization of the vector function J (11) about c may be written $J(c + \delta c) \approx J(c) + L_c \delta c$ where the linear operator L_c acts as follows:

$$L_c x = \sum_{s=1}^r \gamma_s [W_s^+(c)(\alpha_s, H_c x) - W_s^-(c)(\beta_s, H_c x)] . \tag{56}$$

Here H_c is the matrix of second derivatives of the function G in the state c [see Eq. (20)]. The matrix L_c in the Eq. (56) can be decomposed as follows:

$$L_c = L'_c + L''_c . \tag{57}$$

Matrices L'_c and L''_c act as follows:

$$L'_c \mathbf{x} = -\frac{1}{2} \sum_{s=1}^r [W_s^+(\mathbf{c}) + W_s^-(\mathbf{c})] \gamma_s(\gamma_s, \mathbf{H}_c \mathbf{x}), \quad (58)$$

$$L''_c \mathbf{x} = \frac{1}{2} \sum_{s=1}^r [W_s^+(\mathbf{c}) - W_s^-(\mathbf{c})] \gamma_s(\boldsymbol{\alpha}_s + \boldsymbol{\beta}_s, \mathbf{H}_c \mathbf{x}). \quad (59)$$

Some features of this decomposition are best seen when we use the thermodynamic scalar product (21): The following properties of the matrix L'_c are verified immediately:

(i) The matrix L'_c is symmetric in the scalar product (21):

$$\langle \mathbf{x}, L'_c \mathbf{y} \rangle = \langle \mathbf{y}, L'_c \mathbf{x} \rangle. \quad (60)$$

(ii) The matrix L'_c is nonpositive definite in the scalar product (21):

$$\langle \mathbf{x}, L'_c \mathbf{x} \rangle \leq 0. \quad (61)$$

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

$$\ker L'_c = \text{Lin}\{\mathbf{H}_c^{-1} \mathbf{b}_i, i = 1, \dots, l\}. \quad (62)$$

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

$$L'_{\mathbf{c}^{\text{eq}}} = L_{\mathbf{c}^{\text{eq}}}. \quad (63)$$

Thus, the decomposition Eq. (57) splits the matrix L_c in two parts: one part, Eq. (58) is symmetric and nonpositive definite, while the other part, Eq. (59), vanishes in the equilibrium. The decomposition Eq. (57) explicitly takes into account the Marcelin–De Donder form of the kinetic function. For other dissipative systems, the decomposition (57) 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 L'_c (58) 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 Ω has led to the *thermodynamic* specifications of the states $\mathbf{c} \in \Omega$. 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 $\mathbf{c} \in \Omega$ can be specified *kinetically*. Indeed, let us do it again as if the decomposition of motions were valid in the neighborhood of the manifold Ω , and let us ‘freeze’ the slow dynamics along the Ω , focusing on the fast process of relaxation towards a state $\mathbf{c} \in \Omega$. 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. (52). From the kinetic perspective, fast motions on this hyperplane should be treated as a *relaxation* equation, equipped with the quadratic Lyapunov function $\delta G = \langle \delta \mathbf{c}, \delta \mathbf{c} \rangle$. Furthermore, we require that the linear operator of this evolution equation should respect 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 Ω_0 which is not the invariant manifold of the reduced description but, by our assumption, is located close to it. Consider a state $\mathbf{c}_0 \in \Omega_0$, and the states $\mathbf{c}_0 + \delta \mathbf{c}$ close to it. Further, let us consider an equation

$$\delta \dot{\mathbf{c}} = \mathbf{L}'_{\mathbf{c}_0} \delta \mathbf{c} . \quad (64)$$

Due to the properties of the operator $\mathbf{L}'_{\mathbf{c}_0}$ (58), 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 $\mathbf{L}'_{\mathbf{c}}$ (58) *instead* of the linear operator $\mathbf{L}_{\mathbf{c}}$ when constructing the corrections.

5.4. Symmetric iteration

Let the manifold Ω_0 and the corresponding projector \mathbf{P}_0 are 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:

$$[1 - \mathbf{P}_0][\mathbf{J}(\mathbf{c}_0) + \mathbf{L}'_{\mathbf{c}_0} \delta \mathbf{c}] = 0, \mathbf{P}_0 \delta \mathbf{c} = 0 . \quad (65)$$

Here $\mathbf{L}'_{\mathbf{c}_0}$ is matrix (58) taken in the states on the manifold Ω_0 . An important technical point here is that the linear system (65) always has the unique solution for any choice of the manifold Ω . This point is crucial since it guarantees the opportunity of carrying out the correction process for 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 \mathbf{P}_0 . In the majority of cases, initial manifolds are available in two different ways. The first case are the quasi-equilibrium manifolds described in Section 2.3. The macroscopic parameters are $M_i = c_i = (\mathbf{m}_i, \mathbf{c})$, where \mathbf{m}_i is the unit vector corresponding to the specie 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:

$$\begin{aligned} G \rightarrow \min \quad & (\mathbf{m}_i, \mathbf{c}) = c_i, i = 1, \dots, k , \\ & (\mathbf{b}_j, \mathbf{c}) = B_j, j = 1, \dots, l . \end{aligned} \quad (66)$$

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

$$\mathbf{P}_0 \mathbf{x} = \sum_{i=1}^k \frac{\partial \mathbf{c}_0}{\partial c_i}(\mathbf{m}_i, \mathbf{x}) + \sum_{i=1}^l \frac{\partial \mathbf{c}_0}{\partial B_i}(\mathbf{b}_i, \mathbf{x}) . \tag{67}$$

For quasi-equilibrium manifolds, a reparameterization with set (50), (51) is *not* necessary [1,4].

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,

$$[1 - \mathbf{P}_m](\mathbf{J}(\mathbf{c}_m) + \mathbf{L}'_{\mathbf{c}_m} \delta \mathbf{c}) = 0 , \tag{68}$$

$$\mathbf{P}_m \delta \mathbf{c} = 0 . \tag{69}$$

Here $\mathbf{L}'_{\mathbf{c}_m}$ is the symmetric matrix (58) evaluated at the m th approximation. The projector \mathbf{P}_m is not obligatory thermodynamic at that step, and it is taken as follows:

$$\mathbf{P}_m \mathbf{x} = \sum_{i=1}^k \frac{\partial \mathbf{c}_m}{\partial c_i}(\mathbf{m}_i, \mathbf{x}) + \sum_{i=1}^l \frac{\partial \mathbf{c}_m}{\partial B_i}(\mathbf{b}_i, \mathbf{x}) . \tag{70}$$

(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. Relaxation methods

Relaxation method is an alternative to the Newton iteration method described in Section 5. It is a one-dimensional Galerkin approximation for the linearized invariance equation (54,55). We shall solve the invariance equation (54,55) (or symmetric invariance equation (68,69)) in projection on the defect of invariance (53) $\Delta = [1 - \mathbf{P}_c] \mathbf{J}(\mathbf{c})$.

Let Ω_0 be the initial approximation to the invariant manifold, and we seek the first correction, $\mathbf{c}_1 = \mathbf{c}_0 + \tau_1(\mathbf{c}_0) \Delta(\mathbf{c}_0)$, where function $\tau(\mathbf{c}_0)$ has a dimension of the time, and is found from the condition that the linearized vector field attached to the points of the new manifold is orthogonal to the initial defect,

$$\langle \Delta(\mathbf{c}_0), (1 - \mathbf{P}_{\mathbf{c}_0})[\mathbf{J}(\mathbf{c}_0) + \tau_1(\mathbf{c}_0)(D_c \mathbf{J})_{\mathbf{c}_0} \Delta(\mathbf{c}_0)] \rangle_{\mathbf{c}_0} = 0 . \tag{71}$$

Explicitly,

$$\tau_1(\mathbf{c}_0) = - \frac{\langle \Delta(\mathbf{c}_0), \Delta(\mathbf{c}_0) \rangle_{\mathbf{c}_0}}{\langle \Delta(\mathbf{c}_0), (D_c \mathbf{J})_{\mathbf{c}_0} \Delta(\mathbf{c}_0) \rangle_{\mathbf{c}_0}} . \tag{72}$$

Further steps $\tau_k(\mathbf{c})$ are found in the same way. It is clear from the latter equations that the step of the relaxation method is equivalent to the Galerkin approximation

for solving the step of the Newton method. Actually, the relaxation method was first introduced in these terms in [62]. An advantage of Eq. (72) is the explicit form of the size of the steps $\tau_k(\mathbf{c})$. This method was successfully applied in the context of the Fokker–Plank equation [62].

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, its tangent space in the point \mathbf{c} be $T_c\Omega$. How to define the projector of the whole concentrations space onto $T_c\Omega$ without using any a priori parameterization of Ω ?

The basis of the answer to this question is the condition of thermodynamicity (44). 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 :

$$G_q = (\mathbf{g}, \mathbf{H}_c \Delta \mathbf{c}) + \frac{1}{2} (\Delta \mathbf{c}, \mathbf{H}_c \Delta \mathbf{c}) = \langle \mathbf{g}, \Delta \mathbf{c} \rangle + \frac{1}{2} \langle \Delta \mathbf{c}, \Delta \mathbf{c} \rangle, \quad (73)$$

where \mathbf{H}_c is the matrix of the second-order derivatives of G (20), $\mathbf{g} = \mathbf{H}_c^{-1} \nabla G$, $\Delta \mathbf{c}$ 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 $\Delta \mathbf{c} \in T$, and for every $\mathbf{g} \in E$, define a subspace $L_{\Delta \mathbf{c}}$ such that: (i) $L_{\Delta \mathbf{c}}$ is a complement of T in E :

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

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

$$\Delta \mathbf{c} = \arg \min_{\mathbf{x} \in L_{\Delta \mathbf{c}} + \Delta \mathbf{c}} G_q(\mathbf{x}). \quad (74)$$

Besides (i) and (ii), we also impose the requirement of a *maximal smoothness* (analyticity) on $L_{\Delta \mathbf{c}}$ as a function of \mathbf{g} and $\Delta \mathbf{c}$. Requirement (74) implies that $\Delta \mathbf{c}$ is the quasi-equilibrium point for the given $L_{\Delta \mathbf{c}}$, while the problem in a whole is the *inverse* quasi-equilibrium problem: We construct $L_{\Delta \mathbf{c}}$ such that T will be the quasi-equilibrium manifold. Then subspaces $L_{\Delta \mathbf{c}}$ will actually be the kernels of the quasi-equilibrium projector.

Let $\mathbf{f}_1, \dots, \mathbf{f}_k$ be the orthonormalized with respect to $\langle \cdot, \cdot \rangle$ scalar product basis of T , vector \mathbf{h} be orthogonal to T , $\langle \mathbf{h}, \mathbf{h} \rangle = 1$, $\mathbf{g} = \alpha \mathbf{f}_1 + \beta \mathbf{h}$. Condition (74) implies that the vector ∇G is orthogonal to $L_{\Delta \mathbf{c}}$ in the point $\Delta \mathbf{c}$.

Let us first consider the case $\beta = 0$. The requirement of analyticity of $L_{\Delta \mathbf{c}}$ as the function of α and $\Delta \mathbf{c}$ implies $L_{\Delta \mathbf{c}} = L_0 + o(1)$, where $L_0 = T^\perp$ is the orthogonal complement of T with respect to scalar product $\langle \cdot, \cdot \rangle$. The constant solution, $L_{\Delta \mathbf{c}} \equiv L_0$

also satisfies (74). 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:

$$\mathbf{l}_1 = \frac{\beta \mathbf{f}_1 - (\alpha + \Delta c_1) \mathbf{h}}{(\beta^2 + (\alpha + \Delta c_1)^2)^{1/2}}, \tag{75}$$

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

Dependence $L_{\Delta c}$ (75) on $\Delta \mathbf{c}$, 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 $\alpha \neq 0$, 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,

$$\lim_{\Delta c \rightarrow 0} L_{\Delta c} = \text{Lin} \left\{ \frac{\beta \mathbf{f}_1 - \alpha \mathbf{h}}{\sqrt{\alpha^2 + \beta^2}}, \mathbf{l}_2, \dots, \mathbf{l}_{n-k} \right\}. \tag{76}$$

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

$$\mathbf{P}_c \mathbf{z} = \sum_{i=1}^k \mathbf{f}_i \langle \mathbf{f}_i, \mathbf{z} \rangle. \tag{77}$$

If $\mathbf{H}_c^{-1} \nabla G \notin T_c \Omega$, then, according to Eq. (76),

$$\mathbf{P}_c \mathbf{z} = \frac{\langle \mathbf{f}_1, \mathbf{z} \rangle - \langle \mathbf{l}_1, \mathbf{z} \rangle \langle \mathbf{f}_1, \mathbf{l}_1 \rangle}{1 - \langle \mathbf{f}_1, \mathbf{l}_1 \rangle^2} \mathbf{f}_1 + \sum_{i=2}^k \mathbf{f}_i \langle \mathbf{f}_i, \mathbf{z} \rangle, \tag{78}$$

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

Thus, for solving the invariance equation iteratively, one needs only projector \mathbf{P}_c (78), and one does not need a priori parameterization of Ω anymore.

9. Method of invariant grids

Elsewhere above in this paper, we considered the invariant manifold, and methods for their construction, without addressing the question of how to implement it in a *constructive way*. In most of the works (of us and of other people on similar problems), analytic forms were needed to represent the manifolds. However, in order to construct manifolds of a relatively low dimension, grid-based representations of manifolds become a relevant option. The *Method of invariant grids* (MIG) was suggested recently in Ref. [10].

The principal idea of MIG is to find a mapping of a finite-dimensional grids into the phase space of a dynamic system. That is, we construct not just a point approximation of the invariant manifold, but an *invariant grid*. When refined, in the limit it is expected to converge, of course, to the invariant manifold, but it is a separate, independently defined object.

Let us denote $L = \mathbf{R}^n$, \mathbf{G} is a discrete subset of \mathbf{R}^n . A natural choice would be a regular grid, but, this is not crucial for the general formalism. For every point $y \in \mathbf{G}$, a neighborhood of y is defined: $V_y \subset \mathbf{G}$, where V_y is a finite set, and, in particular, $y \in V_y$. On regular grids, V_y includes, as a rule, the nearest neighbors of y . It may also include next to the nearest points.

For our purposes, one should define a grid differential operator. For every function, defined on the grid, also all derivatives are defined:

$$\left. \frac{\partial f}{\partial y_i} \right|_{y \in \mathbf{G}} = \sum_{z \in V_y} q_i(z, y) f(z), i = 1, \dots, n. \quad (79)$$

where $q_i(z, y)$ are some coefficients.

Here we do not specify the choice of the functions $q_i(z, y)$. We just mention in passing that, as a rule, Eq. (79) is established using some interpolation of f in the neighborhood of y in \mathbf{R}^n by some differentiable functions (for example, polynomial). This interpolation is based on the values of f in the points of V_y . For regular grids, $q_i(z, y)$ are functions of the difference $z - y$. For some of y 's which are close to the edges of the grid, the functions are defined only on the part of V_y . In this case, the coefficients in (79) should be modified appropriately in order to provide an approximation using available values of f . Below we will assume this modification is always done. We also assume that the number of points in the neighborhood V_y is always sufficient to make the approximation possible. This assumption restricts the choice of the grids \mathbf{G} . Let us call *admissible* all such subsets \mathbf{G} , on which one can define differentiation operator in every point.

Let F be a given mapping of some admissible subset $\mathbf{G} \subset \mathbf{R}^n$ into U . For every $y \in V$ we define tangent space:

$$T_y = \text{Lin}\{\mathbf{g}_i\}_1^n, \quad (80)$$

where vectors $\mathbf{g}_i (i = 1, \dots, n)$ are partial derivatives (79) of the vector-function F :

$$\mathbf{g}_i = \frac{\partial F}{\partial y_i} = \sum_{z \in V_y} q_i(z, y) F(z), \quad (81)$$

or in the coordinate form:

$$(\mathbf{g}_i)_j = \frac{\partial F_j}{\partial y_i} = \sum_{z \in V_y} q_i(z, y) F_j(z). \quad (82)$$

Here $(\mathbf{g}_i)_j$ is the j th coordinate of the vector \mathbf{g}_i , and $F_j(z)$ is the j th coordinate of the point $F(z)$.

The grid \mathbf{G} is *invariant*, if for every node $y \in \mathbf{G}$ the vector field $J(F(y))$ belongs to the tangent space T_y (here J is the right-hand side of the kinetic equations (2)).

So, the definition of the invariant grid includes:

- (1) Finite admissible subset $\mathbf{G} \subset \mathbf{R}^n$;
- (2) A mapping F of this admissible subset \mathbf{G} into U (where U is the phase space for kinetic equations (2));
- (3) The differentiation formulas (79) with given coefficients $q_i(z, y)$;

The grid invariance equation has a form of inclusion:

$$\mathbf{J}(F(y)) \in T_y \text{ for every } y \in \mathbf{G},$$

or a form of equation:

$$(1 - \mathbf{P}_{F(y)})\mathbf{J}(F(y)) = 0 \text{ for every } y \in \mathbf{G},$$

where $\mathbf{P}_{F(y)}$ is the thermodynamic projector (78).

The grid differentiation formulas (79) are needed, in the first place, to establish the tangent space T_y , and the null space of the thermodynamic projector $\mathbf{P}_{F(y)}$ in each node. It is important to realise that locality of construction of thermodynamic projector enables this without a need for a global parametrization.

Basically, in our approach, the grid specifics is in: (a) differentiation formulas, (b) grid construction strategy (the grid can be extended, contracted, refined, etc.) The invariance equations (53), the iteration Newton method (54,55), and the formulas of the relaxation approximation (72) do not change at all. For convenience, let us repeat all these formulas in the grid context.

Let $\mathbf{c} = F(y)$ be position of a grid's node y immersed into phase space U . We have set of tangent vectors $\mathbf{g}_i(x)$, defined in \mathbf{c} (81,82). Thus, the tangent space T_y is defined by (80). Also, one has the thermodynamic Lyapunov function $G(\mathbf{c})$, the linear functional $D_c G|_c$, and the subspace $T_{0y} = T_y \cap \ker D_c G|_c$ in T_y . Let $T_{0y} \neq T_y$. In this case we have a vector $\mathbf{e}_y \in T_y$, orthogonal to T_{0y} , $D_c G|_c(\mathbf{e}_y) = 1$. Then, the thermodynamic projector is defined as

$$\mathbf{P}_c \bullet = \mathbf{P}_{0c} \bullet + \mathbf{e}_y D_c G|_c \bullet, \tag{83}$$

where \mathbf{P}_{0c} is the orthogonal projector on T_{0y} with respect to the entropic scalar product \langle, \rangle_x .

If $T_{0y} = T_y$, then the thermodynamic projector is the orthogonal projector on T_y with respect to the entropic scalar product \langle, \rangle_c .

For the Newton method with incomplete linearization, the equations for calculating new node position $\mathbf{c}' = \mathbf{c} + \delta\mathbf{c}$ are:

$$\begin{aligned} \mathbf{P}_c \delta\mathbf{c} &= 0, \\ (1 - \mathbf{P}_c)(\mathbf{J}(\mathbf{c}) + D\mathbf{J}(\mathbf{c})\delta\mathbf{c}) &= 0. \end{aligned} \tag{84}$$

Here $D\mathbf{J}(\mathbf{c})$ is a matrix of derivatives of \mathbf{J} , calculated in \mathbf{c} . The self-adjoint linearization may be useful too (see Section 5.2).

Eq. (84) is a system of linear algebraic equations. In practice, it is convenient to choose some orthonormal (with respect to the entropic scalar product) basis \mathbf{b}_i in $\ker \mathbf{P}_c$. Let $r = \dim(\ker \mathbf{P}_c)$. Then $\delta\mathbf{c} = \sum_{i=1}^r \delta_i \mathbf{b}_i$, and the system becomes

$$\sum_{k=1}^r \delta_k \langle \mathbf{b}_i, D\mathbf{J}(\mathbf{c})\mathbf{b}_k \rangle_c = -\langle \mathbf{J}(\mathbf{c}), \mathbf{b}_i \rangle_c, i = 1 \dots r. \tag{85}$$

Here $\langle \cdot, \cdot \rangle_c$ is the entropic scalar product (21). This is the system of linear equations for adjusting the node position accordingly to the Newton method with incomplete linearization.

For the relaxation method, one needs to calculate the defect $\Delta_c = (1 - P_c)\mathbf{J}(c)$, and the relaxation step

$$\tau(x) = -\frac{\langle \Delta_c, \Delta_c \rangle_c}{\langle \Delta_c, D\mathbf{J}(c)\Delta_c \rangle_c}. \quad (86)$$

Then, new node position x' is calculated as

$$c' = c + \tau(c)\Delta_c. \quad (87)$$

This is the equation for adjusting the node position according to the relaxation method.

9.1. Grid construction strategy

From all reasonable strategies of the invariant grid construction we will consider here the following two: *growing lump* and *invariant flag*.

9.1.1. Growing lump

In this strategy one chooses as initial the equilibrium point y^* . The first approximation is constructed as $F(y^*) = c^*$, and for some initial $V_0 (V_{y^*} \subset V_0)$ one has $F(y) = c^* + A(y - y^*)$, where A is an isometric embedding (in the standard Euclidean metrics) of \mathbf{R}^n in E .

For this initial grid one makes a fixed number of iterations of one of the methods chosen (Newton's method with incomplete linearization or the relaxation method), and, after that, puts $V_1 = \bigcup_{y \in V_0} V_y$ and extends F from V_0 onto V_1 using linear extrapolation and the process continues. One of the possible variants of this procedure is to extend the grid from V_i to V_{i+1} not after a fixed number of iterations, but when the invariance defect Δ_y becomes smaller than a given ε (in a given norm, which is entropic, as a rule), for all nodes $y \in V_i$. The lump stops growing when it reaches the boundary and is within a given accuracy $\|\Delta\| < \varepsilon$.

9.1.2. Invariant flag

For the invariant flag one uses sufficiently regular grids \mathbf{G} , in which many points are situated on the coordinate lines, planes, etc. One considers the standard flag $\mathbf{R}^0 \subset \mathbf{R}^1 \subset \mathbf{R}^2 \subset \dots \subset \mathbf{R}^n$ (every next space is constructed by adding one more coordinate). It corresponds to a succession of grids $\{y\} \subset \mathbf{G}^1 \subset \mathbf{G}^2 \dots \subset \mathbf{G}^n$, where $\{y^*\} = \mathbf{R}^0$, and \mathbf{G}^i is a grid in \mathbf{R}^i .

First, y^* is mapped in c^* and further $F(y^*) = c^*$. Then an invariant grid is constructed on $V^1 \subset \mathbf{G}^1$ (up to the boundaries U and within a given accuracy $\|\Delta\| < \varepsilon$). After the neighborhoods in \mathbf{G}^2 are added to the points V^1 , and, using such extensions, the grid $V^2 \subset \mathbf{G}^2$ is constructed (up to the boundaries and within a given accuracy) and so on, until $V^n \subset \mathbf{G}^n$ will be constructed.

We must underline here that, constructing the k th grid $V^k \subset \mathbf{G}^k$, the important role of the grids of smaller dimension $V^0 \subset \dots \subset V^{k-1} \subset V^k$ embedded in it, is

preserved. The point $F(y^*) = x^*$ is preserved. For every $y \in V^q$ ($q < k$) the tangent vectors g_1, \dots, g_q are constructed, using the differentiation operators (79) on the whole V^k . Using the tangent space $T_y = \text{Lin}\{g_1, \dots, g_q\}$, the projector $\mathbf{P}_{F(y)}$ is constructed, the iterations are applied and so on. All this is done to obtain a succession of embedded invariant grids, given by the same map F .

9.1.3. Boundaries check and the entropy

We construct grid mapping of F onto the finite set $V \in \mathbf{G}$. The technique of checking if the grid still belongs to the phase space U of kinetic system ($F(V) \subset U$) is quite straightforward: all the points $y \in V$ are checked to belong to U . If at the next iteration a point $F(y)$ leaves U , then it is returned inside by a homothety transform with the center in x^* . Since the thermodynamic Lyapunov function is a convex function, the homothety contraction with the center in x^* decreases it monotonously. Another variant is cutting off the points leaving U .

By construction (78) the kernel of the thermodynamic projector is annulled by the entropy differential. Thus, in the first order, steps in the Newton method with incomplete linearization (54), (55) as well as in the relaxation methods (71), (72) do not change the entropy. But, if the steps are quite large, then the increasing of the thermodynamic Lyapunov function can become essential and the points are returned on their level by the homothety contraction with the center in the equilibrium point.

9.2. Instability of fine grids

When one reduces the grid step (spacing between the nodes) in order to get a finer grid, then, beginning with some stepsize, it is possible to face the problem of the Courant instability [63]. Instead of converging, at the every iteration the grid becomes entangled (see Fig. 1).

The way to get rid off this instability is well-known. This is decreasing the time step. Instead of the real time step, we have a shift in the Newtonian direction. Formally, we can assign for one complete step in the Newtonian direction a value $h = 1$. Let us consider now the Newton method with an arbitrary h . For this, let us find $\delta c = \delta F(y)$ from (84), but we will change δc proportionally to h : the new value of $c_{n+1} = F_{n+1}(y)$ will be equal to

$$F_{n+1}(y) = F_n(y) + h_n \delta F_n(y), \quad (88)$$

where the lower index n denotes the step number.

One way to choose the h step value is to make it adaptive, controlling the average value of the invariance defect $\|\Delta_y\|$ at every step. Another way is the convergence control: then $\sum h_n$ plays a role of time.

Elimination of Courant instability for the relaxation method can be made quite analogously. Everywhere the step h is maintained as big as it is possible without convergence problems.

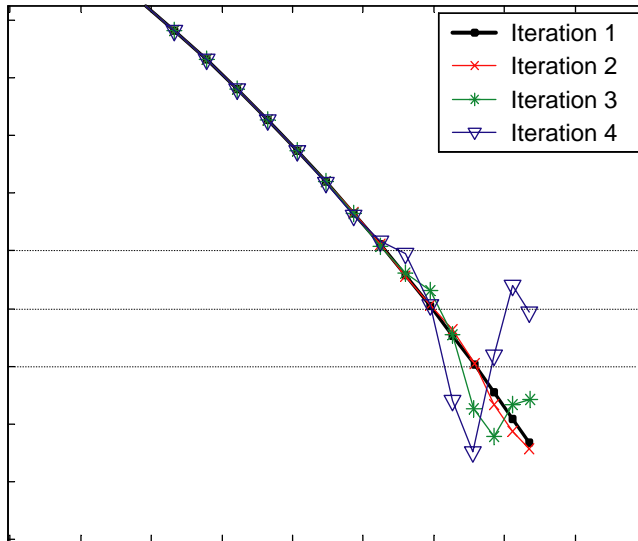


Fig. 1. Example of grid instability in concentrations space. For small grid steps approximations in the calculation of grid derivatives lead to the grid instability effect. On the figure several successive iterations of the algorithm without adaptation of the time step are shown that lead to undesirable “oscillations”, which eventually destruct the grid starting from one of its ends.

9.3. Which space is the most appropriate for the grid construction?

For the kinetics systems there are two distinguished representations of the phase space:

- The densities space (concentrations, energy or probability densities, etc.)
- The spaces of conjugate intensive quantities (temperature, chemical potentials, etc.)

The density space is convenient for the construction of quasi-chemical representations. Here the balance relations are linear and the restrictions are in the form of linear inequalities (the densities themselves or some linear combinations of them must be positive).

The conjugate variables space is convenient in the sense that the equilibrium conditions, given the linear restrictions on the densities, are in the linear form (with respect to the conjugate variables). In these spaces the quasi-equilibrium manifolds exist in the form of linear subspaces and, vice versa, linear balance equations turns out to be equations of the conditional entropy maximum.

The duality we have just described is very well-known and studied in details in many works on thermodynamics and Legendre transformations [64,65]. In the previous section, the grids were considered in the density space. But the procedure of constructing them in the space of the conjugate variables seems to be more consistent. The principal argument for this is the specific role of the quasi-equilibrium, which exists as

a linear manifold. Therefore, linear extrapolation gives a thermodynamically justified quasi-equilibrium approximation. Linear approximation of the slow invariant manifold in the neighborhood of the equilibrium in the conjugate variables space already gives the global quasi-equilibrium manifold, which corresponds to the motion separation (for slow and fast motions) in the neighborhood of the equilibrium point.

A deep analysis of Legendre duality in equilibrium and nonequilibrium thermodynamics is presented in the paper [66].

For the mass action law, transition to the conjugate variables is simply the logarithmic transformation of the coordinates.

9.4. Carleman's formulas in the analytical invariant manifolds approximations. First profit from analyticity: superresolution

When constructing invariant grids, one must define the differential operators (79) for every grid node. For calculating the differential operators in some point y , an interpolation procedure in the neighborhood of y is used. As a rule, it is an interpolation by a low-order polynomial, which is constructed using the function values in the nodes belonging to the neighbourhood of y in \mathbf{G} . This approximation (using values in the closest nodes) is natural for smooth functions. But, for systems (2) with analytical right hand side we are looking for the *analytical* invariant manifold (due to Lyapunov auxiliary theorem [11,12]). Analytical functions have much more “rigid” structure than the smooth ones. One can change a smooth function in the neighborhood of any point in such a way, that outside this neighborhood the function will not change. In general, this is not possible for analytical functions: a kind of “long-range” effect takes place (as is well known).

The idea is to use this effect and to reconstruct some analytical function $f_{\mathbf{G}}$ using function given on \mathbf{G} . There is one important requirement: if these values on \mathbf{G} are values (given in the points of \mathbf{G}) of some function f which is analytical in the given neighborhood U , then if the \mathbf{G} is refined “correctly”, one must have $f_{\mathbf{G}} \rightarrow f$. The sequence of reconstructed function $f_{\mathbf{G}}$ should converge to the “proper” function f .

What is the “correct refinement”? For smooth functions for the convergence $f_{\mathbf{G}} \rightarrow f$ it is necessary and sufficient that, in the course of refinement, \mathbf{G} would approximate the whole U with arbitrary accuracy. For analytical functions it is only necessary that, under the refinement, \mathbf{G} would approximate some uniqueness set³ $A \subset U$. Suppose we have a sequence of grids \mathbf{G} , each next is finer than previous, which approximates a set A . For smooth functions, using function values defined on the grids, one can reconstruct the function in A . For analytical functions, if the analyticity domain U is known, and A is a uniqueness set in U , then one can reconstruct the function in U . The set U can be essentially bigger than A ; because of this such extension was named a *superresolution effect* [13,14]. There exist constructive formulas for construction of analytical functions $f_{\mathbf{G}}$ for different domains U , uniqueness sets $A \subset U$ and for different ways of discrete

³ Let us remind that $A \subset U$ is called *uniqueness set* in U if for analytical in U functions ψ and ϕ from $\psi|_A \equiv \phi|_A$ it follows $\psi = \phi$.

approximation of A by a sequence of refined grids \mathbf{G} [13]. Here we provide only one Carleman’s formula which is the most appropriate for our purposes.

Let domain $U = Q_\sigma^n \subset \mathbf{C}^n$ be a product of strips $Q_\sigma \subset \mathbf{C}$, $Q_\sigma = \{z \mid \text{Im}z < \sigma\}$. We will construct functions holomorphic in Q_σ^n . This is effectively equivalent to the construction of real analytical functions f in whole \mathbf{R}^n with a condition on the convergence radius $r(x)$ of the Taylor series for f as a function of each coordinate: $r(x) \geq \sigma$ in every point $x \in \mathbf{R}^n$.

The sequence of refined grids is constructed as follows: let for every $l = 1, \dots, n$ a finite sequence of distinct points $N_l \subset Q_\sigma$ be defined:

$$N_l = \{x_{lj} \mid j = 1, 2, 3, \dots\}, x_{lj} \neq x_{li} \quad \text{for } i \neq j \tag{89}$$

The uniqueness set A , which is approximated by a sequence of refined finite grids, has the form:

$$A = N_1 \times N_2 \times \dots \times N_n = \{(x_{1i_1}, x_{2i_2}, \dots, x_{ni_n}) \mid i_1, \dots, i_n = 1, 2, 3, \dots\}. \tag{90}$$

The grid \mathbf{G}_m is defined as the product of initial fragments N_l of length m :

$$\mathbf{G}_m = \{(x_{1i_1}, x_{2i_2} \dots x_{ni_n}) \mid 1 \leq i_1, \dots, i_n \leq m\} \tag{91}$$

Let us denote $\lambda = 2\sigma/\pi$ (σ is a half-width of the strip Q_σ). The key role in the construction of the Carleman’s formula is played by the functional $\omega_m^\lambda(u, p, l)$ of 3 variables: $u \in U = Q_\sigma^n$, p is an integer, $1 \leq p \leq m$, l is an integer, $1 \leq l \leq n$. Further u will be the coordinate value in the point where the extrapolation is calculated, l will be the coordinate number, and p will be an element of multi-index $\{i_1, \dots, i_n\}$ for the point $(x_{1i_1}, x_{2i_2}, \dots, x_{ni_n}) \in \mathbf{G}$:

$$\omega_m^\lambda(u, p, l) = \frac{(e^{\lambda x_{lp}} + e^{\lambda \bar{x}_{lp}})(e^{\lambda u} - e^{\lambda x_{lp}})}{\lambda(e^{\lambda u} + e^{\lambda \bar{x}_{lp}})(u - x_{lp})e^{\lambda x_{lp}}} \times \prod_{j=1, j \neq p}^m \frac{(e^{\lambda x_{lp}} + e^{\lambda \bar{x}_{lj}})(e^{\lambda u} - e^{\lambda x_{lj}})}{(e^{\lambda x_{lp}} - e^{\lambda x_{lj}})(e^{\lambda u} + e^{\lambda \bar{x}_{lj}})}. \tag{92}$$

For real-valued x_{pk} formula (92) becomes simpler:

$$\omega_m^\lambda(u, p, l) = 2 \frac{e^{\lambda u} - e^{\lambda x_{lp}}}{\lambda(e^{\lambda u} + e^{\lambda \bar{x}_{lp}})(u - x_{lp})} \times \prod_{j=1, j \neq p}^m \frac{(e^{\lambda x_{lp}} + e^{\lambda x_{lj}})(e^{\lambda u} - e^{\lambda x_{lj}})}{(e^{\lambda x_{lp}} - e^{\lambda x_{lj}})(e^{\lambda u} + e^{\lambda \bar{x}_{lj}})}. \tag{93}$$

The Carleman’s formula for extrapolation from \mathbf{G}_M on $U = Q_\sigma^n$ ($\sigma = \pi\lambda/2$) has the form ($z = (z_1, \dots, z_n)$):

$$f_m(z) = \sum_{k_1, \dots, k_n=1}^m f(x_k) \prod_{j=1}^n \omega_m^\lambda(z_j, k_j, j), \tag{94}$$

where $k = k_1, \dots, k_n$, $x_k = (x_{1k_1}, x_{2k_2}, \dots, x_{nk_n})$.

There exists a theorem [13]:

If $f \in H^2(Q_\sigma^n)$, then $f(z) = \lim_{m \rightarrow \infty} f_m(z)$, where $H^2(Q_\sigma^n)$ is the Hardy class of holomorphic in Q_σ^n functions.

It is useful to present the asymptotics of (94) for big $|\operatorname{Re} z_j|$. For this we will consider the asymptotics of (94) for big $|\operatorname{Re} u|$:

$$|\omega_m^\lambda(u, p, l)| = \left| \frac{2}{\lambda u} \prod_{j=1, j \neq p}^m \frac{e^{\lambda x_{lp}} + e^{\lambda x_{lj}}}{e^{\lambda x_{lp}} - e^{\lambda x_{lj}}} \right| + o(|\operatorname{Re} u|^{-1}). \tag{95}$$

From formula (94) one can see that for the finite m and $|\operatorname{Re} z_j| \rightarrow \infty$ function $|f_m(z)|$ behaves like $\text{const} \cdot \prod_j |z_j|^{-1}$.

This property (zero asymptotics) must be taken into account when using formula (94). When constructing invariant manifolds $F(W)$, it is natural to use (94) not for the immersion $F(y)$, but for the deviation of $F(y)$ from some analytical ansatz $F_0(y)$.

The analytical ansatz $F_0(y)$ can be obtained using Taylor series, just as in the Lyapunov auxiliary theorem [11]. Another variant is using Taylor series for the construction of Pade-approximations.

It is natural to use approximations (94) in dual variables as well, since there exists for them (as the examples demonstrate) a simple and very effective linear ansatz for the invariant manifold. This is the slow invariant subspace E_{slow} of the operator of linearized system (2) in dual variables in the equilibrium point. This invariant subspace corresponds to the set of “slow” eigenvalues (with small $|\operatorname{Re} \lambda|$, $\operatorname{Re} \lambda < 0$). In the initial space (of concentrations or densities) this invariant subspace is the quasi-equilibrium manifold. It consist of the maximal entropy points on the affine manifolds of the $x + E_{\text{fast}}$ form, where E_{fast} is the “fast” invariant subspace of the operator of linearized system (2) in the initial variables in the equilibrium point. It corresponds to the “fast” eigenvalues (big $|\operatorname{Re} \lambda|$, $\operatorname{Re} \lambda < 0$).

9.5. Example: two-step catalytic reaction

Let us consider a two-step four-component reaction with one catalyst A_2 :



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

$$\dot{\mathbf{c}} = \gamma_1 W_1 + \gamma_2 W_2. \tag{97}$$

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

$$\gamma_1 = (-1, -1, 1, 0), \quad \gamma_2 = (0, 1, -1, 1), \tag{98}$$

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

$$W_1 = k_1^+ c_1 c_2 - k_1^- c_3, \quad W_2 = k_2^+ c_3 - k_2^- c_2 c_4. \tag{99}$$

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

$$c_1 + c_3 + c_4 = B_1, \quad c_2 + c_3 = B_2, \tag{100}$$

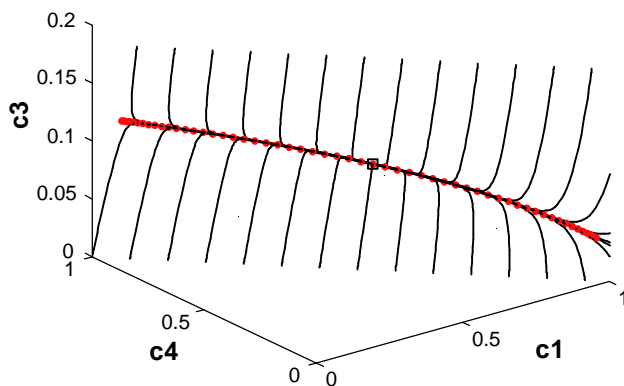


Fig. 2. One-dimensional invariant grid (circles) for two-dimensional chemical system. Projection into the 3d-space of c_1 , c_4 , c_3 concentrations. The trajectories of the system in the phase space are shown by lines. The equilibrium point is marked by square. The system quickly reaches the grid and further moves along it.

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 (96) is effectively two-dimensional, and we consider a one-dimensional reduced description. For our example, we chose the following set of parameters:

$$\begin{aligned} k_1^+ &= 0.3, k_1^- = 0.15, k_2^+ = 0.8, k_2^- = 2.0 ; \\ c_1^* &= 0.5, c_2^* = 0.1, c_3^* = 0.1, c_4^* = 0.4 ; \\ B_1 &= 1.0, B_2 = 0.2 \end{aligned} \quad (101)$$

In Fig. 2 one-dimensional invariant grid is shown in the (c_1, c_4, c_3) coordinates. The grid was constructed by the growing lump strategy, as described above. We used Newton iterations to adjust the nodes. The grid was grown up to the boundaries of the phase space.

The grid derivatives for calculating tangent vectors \mathbf{g} were taken as $\mathbf{g}(c_i) = (\mathbf{c}_{i+1} - \mathbf{c}_{i-1}) / \|\mathbf{c}_{i+1} - \mathbf{c}_{i-1}\|$ for the internal nodes and $\mathbf{g}(c_1) = (\mathbf{c}_1 - \mathbf{c}_2) / \|\mathbf{c}_1 - \mathbf{c}_2\|$, $\mathbf{g}(c_n) = (\mathbf{c}_n - \mathbf{c}_{n-1}) / \|\mathbf{c}_n - \mathbf{c}_{n-1}\|$ for the grid's boundaries. Here x_i denotes the vector of the i th node position, n is the number of nodes in the grid.

Close to the phase space boundaries we had to apply an adaptive algorithm for choosing the time step h : if, after the next growing step and applying $N=20$ complete Newtonian steps, the grid did not converged, then we choose a new $h_{n+1} = h_n/2$ and recalculate the grid. The final value for h was $h \approx 0.001$.

The nodes positions are parametrized with entropic distance to the equilibrium point measured in the quadratic metrics given by $\mathbf{H}_c = \|\partial^2 G(\mathbf{c}) / \partial c_i \partial c_j\|$ in the equilibrium \mathbf{c}^* . It means that every node is on a sphere in this quadratic metrics with a given radius, which increases linearly. In this figure the step is chosen to be 0.05. Thus, the first node is at the distance 0.05 from the equilibrium, the second is at the distance 0.10, and so on. Fig. 3 shows several basic values which facilitate understanding the object (invariant grid) extracted. The sign on the x -axis of the graphs at Fig. 3 is

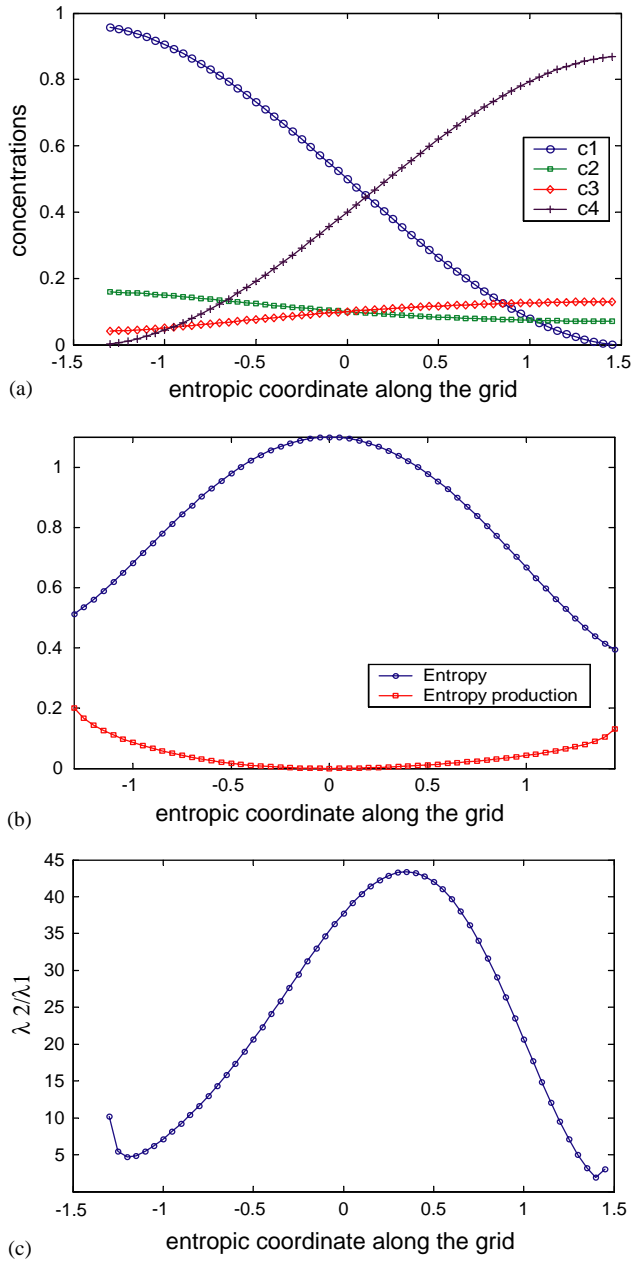


Fig. 3. One-dimensional invariant grid for two-dimensional chemical system. (a) Values of the concentrations along the grid. (b) Values of the entropy ($-G$) and the entropy production ($-dG/dt$) along the grid. (c) Relation of the relaxation times “toward” and “along” the manifold. The nodes positions are parametrized with entropic distance measured in the quadratic metrics given by $\mathbf{H}_c = \|\partial^2 G(\mathbf{c})/\partial c_i \partial c_j\|$ in the equilibrium c^* . Zero corresponds to the equilibrium.

meaningless, since the distance is always positive, but in this situation it denotes two possible directions from the equilibrium point.

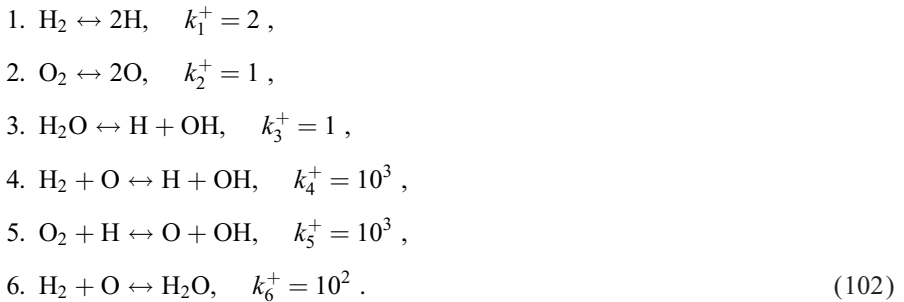
Fig. 3a and b effectively represents the slow one-dimensional component of the dynamics of the system. Given any initial condition, the system quickly finds the corresponding point on the manifold and starting from this point the dynamics is given by a part of the graph on Fig. 3a and b.

One of the useful values is shown on the Fig. 3c. It is the relation between the relaxation times “toward” and “along” the grid (λ_2/λ_1 , where λ_1, λ_2 are the smallest and the second smallest by absolute value nonzero eigenvalue of the system, symmetrically linearized in the point of the grid node). It shows that the system is very stiff close to the equilibrium point, and less stiff (by one order of magnitude) on the borders. This leads to the conclusion that the reduced model is more adequate in the neighborhood of the equilibrium where fast and slow motions are separated by two orders of magnitude. On the very end of the grid which corresponds to the positive abscissa values, our one-dimensional consideration faces problems (slow manifold becomes not well-defined).

9.6. Model hydrogen burning reaction

In this section we consider a more difficult example, where the phase space is 6-dimensional, and the system is 4-dimensional. We construct an invariant flag which consists of 1- and 2-dimensional invariant manifolds.

We consider chemical system with six species called (provisionally) H_2 (hydrogen), O_2 (oxygen), H_2O (water), H , O , OH (radicals). We assume the Lyapunov function of the form $G = \sum_{i=1}^6 c_i [\ln(c_i/c_i^*) - 1]$. The subset of the hydrogen burning reaction and corresponding (direct) rate constants have been taken as



The conservation laws are:

$$2c_{H_2} + 2c_{H_2O} + c_H + c_{OH} = b_H,$$

$$2c_{O_2} + c_{H_2O} + c_O + c_{OH} = b_O.$$
(103)

For parameter values we took $b_H = 2, b_O = 1$, and the equilibrium point:

$$c_{H_2}^* = 0.27 \quad c_{O_2}^* = 0.135 \quad c_{H_2O}^* = 0.7 \quad c_H^* = 0.05 \quad c_O^* = 0.02 \quad c_{OH}^* = 0.01.$$
(104)

Other rate constants k_i^- , $i = 1 \dots 6$ were calculated from c^* value and k_i^+ . For this system the stoichiometric vectors are:

$$\begin{aligned} \gamma_1 &= (-1, 0, 0, 2, 0, 0), & \gamma_2 &= (0, -1, 0, 0, 2, 0), \\ \gamma_3 &= (0, 0, -1, 1, 0, 1), & \gamma_4 &= (-1, 0, 0, 1, -1, 1), \\ \gamma_5 &= (0, -1, 0, -1, 1, 1), & \gamma_6 &= (-1, 0, 1, 0, -1, 0). \end{aligned} \quad (105)$$

We stress here once again that the system under consideration is fictitious in that sense that the subset of equations corresponds to a simplified picture of this physical–chemical process, and the constants do not correspond to any measured ones, but reflect only basic orders of magnitudes of the real-world system. In this sense we consider here a qualitative model system which allows us to illustrate the invariant grids method without excessive complications. Nevertheless, modeling of realistic systems differs only in the number of species and equations. This leads, of course, to computationally harder problems, but not the crucial ones, and the efforts on the modeling of real-world systems are on the way.

Fig. 4a presents a one-dimensional invariant grid constructed for the system. Fig. 4b demonstrates the reduced dynamics along the manifold (for the explanation of the meaning of the x -coordinate, see the previous subsection). In Fig. 4c the three smallest by the absolute value nonzero eigenvalues of the symmetrically linearized Jacobian matrix of system (58) L'_c are shown. One can see that the two smallest values almost interchange at one of the grid end. This means that the one-dimensional “slow” manifold faces definite problems in this region, it is just not well defined there. In practice, it means that one has to use at least a two-dimensional grids there.

Fig. 5a presents the two-dimensional invariant grid constructed for the system using the “invariant flag” strategy. The grid was grown starting from the 1D-grid constructed at the previous step. At the first iteration for every node of the initial grid, two nodes (and two edges) were added. The direction of the step was chosen as the direction of the eigenvector of the matrix L'_c (in the point c of the node), corresponding to the second “slowest” direction. The value of the step was chosen to be $\varepsilon = 0.05$ in terms of entropic distance. After several Newton iterations done until convergence, new nodes were added in the direction “orthogonal” to the 1D-grid. This time it is done by linear extrapolation of the grid on the same step $\varepsilon = 0.05$. When some new nodes have one or several negative coordinates (the grid reaches the boundaries) they were cut off. If a new node has only one edge, connecting it to the grid, it was excluded (since it does not allow calculating 2D-tangent space for this node). The process continues until the expansion is possible (after this, every new node has to be cut off).

A strategy of calculating tangent vectors for this regular rectangular 2D-grid was chosen to be quite simple. The grid consists of *rows*, which are co-oriented by construction to the initial 1D-grid, and *columns* that consist of the adjacent nodes in the neighboring rows. The direction of columns corresponds to the second slowest direction along the grid. Then, every row and column is considered as 1D-grid, and the corresponding tangent vectors are calculated as it was described before:

$$\mathbf{g}_{row}(c_{k,i}) = (c_{k,i+1} - c_{k,i-1}) / \|c_{k,i+1} - c_{k,i-1}\|$$

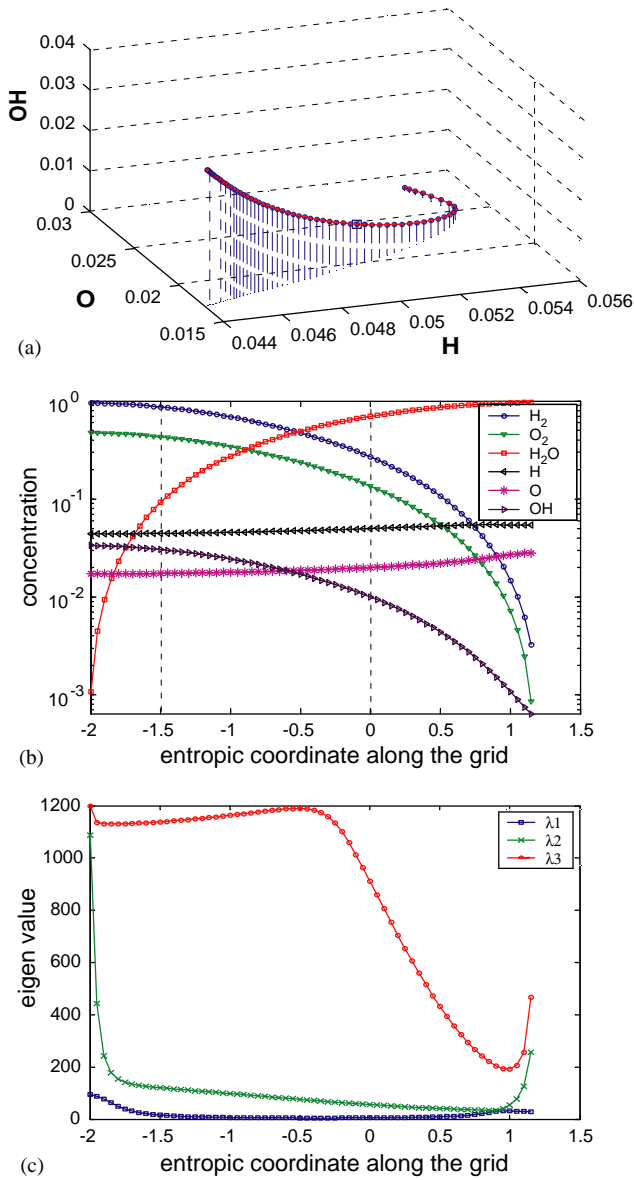


Fig. 4. One-dimensional invariant grid for model hydrogen burning system. (a) Projection into the 3d-space of c_H , c_O , c_{OH} concentrations. (b) Concentration values along the grid. (c) three smallest by absolute value nonzero eigenvalues of the symmetrically linearized system.

for the internal nodes and

$$\begin{aligned}
 \mathbf{g}_{row}(\mathbf{c}_{k,1}) &= (\mathbf{c}_{k,1} - \mathbf{c}_{k,2}) / \|\mathbf{c}_{k,1} - \mathbf{c}_{k,2}\|, \mathbf{g}_{row}(\mathbf{c}_{k,n_k}) \\
 &= (\mathbf{c}_{k,n_k} - \mathbf{c}_{k,n_k-1}) / \|\mathbf{c}_{k,n_k} - \mathbf{c}_{k,n_k-1}\|
 \end{aligned}$$

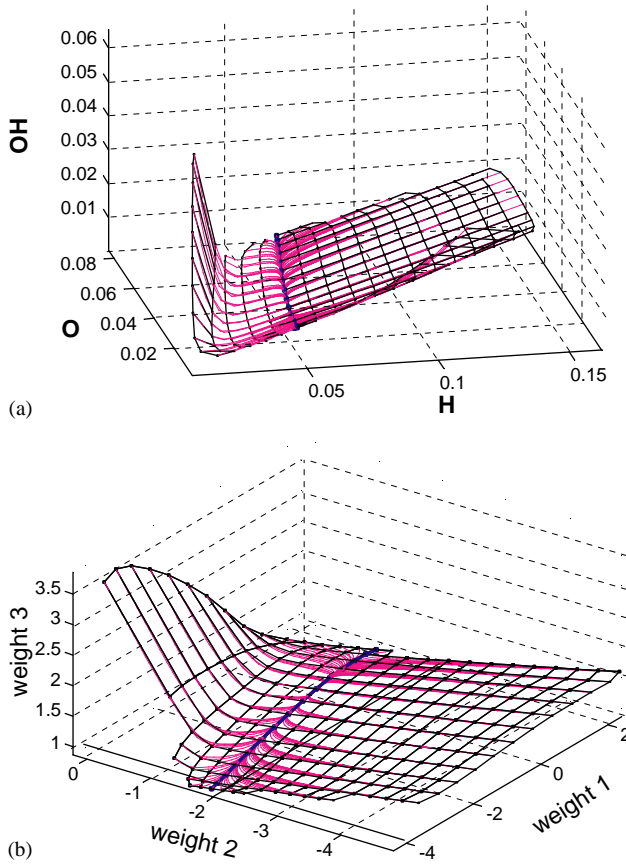


Fig. 5. Two-dimensional invariant grid for the model hydrogen burning system. (a) Projection into the 3D-space of c_H , c_O , c_{OH} concentrations. (b) Projection into the principal 3D-subspace. Trajectories of the system are shown coming out from the every grid node. Bold line denotes the one-dimensional invariant grid, starting from which the 2D-grid was constructed.

for the nodes which are close to the grid’s edges. Here $x_{k,i}$ denotes the vector of the node in the k th row, i th column; n_k is the number of nodes in the k th row. Second tangent vector $\mathbf{g}_{col}(c_{k,i})$ is calculated analogously. In practice, it is convenient to orthogonalize $\mathbf{g}_{row}(c_{k,i})$ and $\mathbf{g}_{col}(c_{k,i})$.

Since the phase space is four-dimensional, it is impossible to visualize the grid in one of the coordinate 3D-views, as it was done in the previous subsection. To facilitate visualization one can utilize traditional methods of multi-dimensional data visualization. Here we make use of the principal components analysis (see, for example, Ref. [67]), which constructs a three-dimensional linear subspace with maximal dispersion of the orthogonally projected data (grid nodes in our case). In other words, method of principal components constructs in multi-dimensional space such a three-dimensional box

inside which the grid can be placed maximally tightly (in the mean square displacement sense). After projection of the grid nodes into this space, we get more or less adequate representation of the two-dimensional grid embedded into the six-dimensional concentrations space (Fig. 5b). The disadvantage of the approach is that the new axes do not have explicit meaning, being some linear combinations of the concentrations.

One attractive feature of two-dimensional grids is the possibility to use them as a screen, on which one can display different functions $f(\mathbf{c})$ defined in the concentrations space. This technology was exploited widely in the nonlinear data analysis by the elastic maps method [68,69]. The idea is to “unfold” the grid on a plane (to present it in the two-dimensional space, where the nodes form a regular lattice). In other words, we are going to work in the internal coordinates of the grid. In our case, the first internal coordinate (let us call it s_1) corresponds to the direction, co-oriented with the one-dimensional invariant grid, the second one (let us call it s_2) corresponds to the second slow direction. By construction, $s_2 = 0$ line corresponds to the one-dimensional invariant grid. Units of s_1 and s_2 are entropic distances in our case.

Every grid node has two internal coordinates (s_1, s_2) and, simultaneously, corresponds to a vector in the concentration space. This allows us to map any function $f(\mathbf{c})$ from the multi-dimensional concentration space to the two-dimensional space of the grid. This mapping is defined in a finite number of points (grid nodes), and can be interpolated (linearly, in the simplest case) between them. Using coloring and isolines one can visualize the values of the function in the neighborhood of the invariant manifold. This is meaningful, since, by the definition, the system spends most of the time in the vicinity of the invariant manifold, thus, one can visualize the behaviour of the system. As a result of applying the coloring technology, one obtains a set of color illustrations (a stack of information layers), put onto the grid as a map. This allows applying all the methods, working with stack of information layers, like geographical information systems (GIS) methods, which are very well developed.

In short, the technique is a useful tool for exploration of dynamical systems. It allows to see simultaneously many different scenarios of the system behaviour, together with different system’s characteristics.

The simplest functions to visualize are the coordinates: $c_i(\mathbf{c}) = c_i$. On Fig. 6 we displayed four colorings, corresponding to the four arbitrarily chosen concentrations functions (of H_2 , O, H and OH; Fig. 6a–d). The qualitative conclusions that can be made from the graphs are that, for example, the concentration of H_2 practically does not change during the first fast motion (towards the 1D-grid) and then, gradually changes to the equilibrium value (the H_2 coordinate is “slow”). The O coordinate is the opposite case, it is “fast” coordinate which changes quickly (on the first stage of motion) to the almost equilibrium value, and then it almost does not change. Basically, the slope angles of the coordinate isolines give some presentation of how “slow” a given concentration is. Fig. 6c shows interesting behaviour of the OH concentration. Close to the 1D grid it behaves like “slow coordinate”, but there is a region on the map where it has clear “fast” behaviour (middle bottom of the graph).

The next two functions which one could wish to visualize are the entropy $S = -G$ and the entropy production $\sigma(\mathbf{c}) = -dG/dt(\mathbf{c}) = -\sum_i \ln(c_i/c_i^*)c_i$. They are shown in Fig. 7a and b.

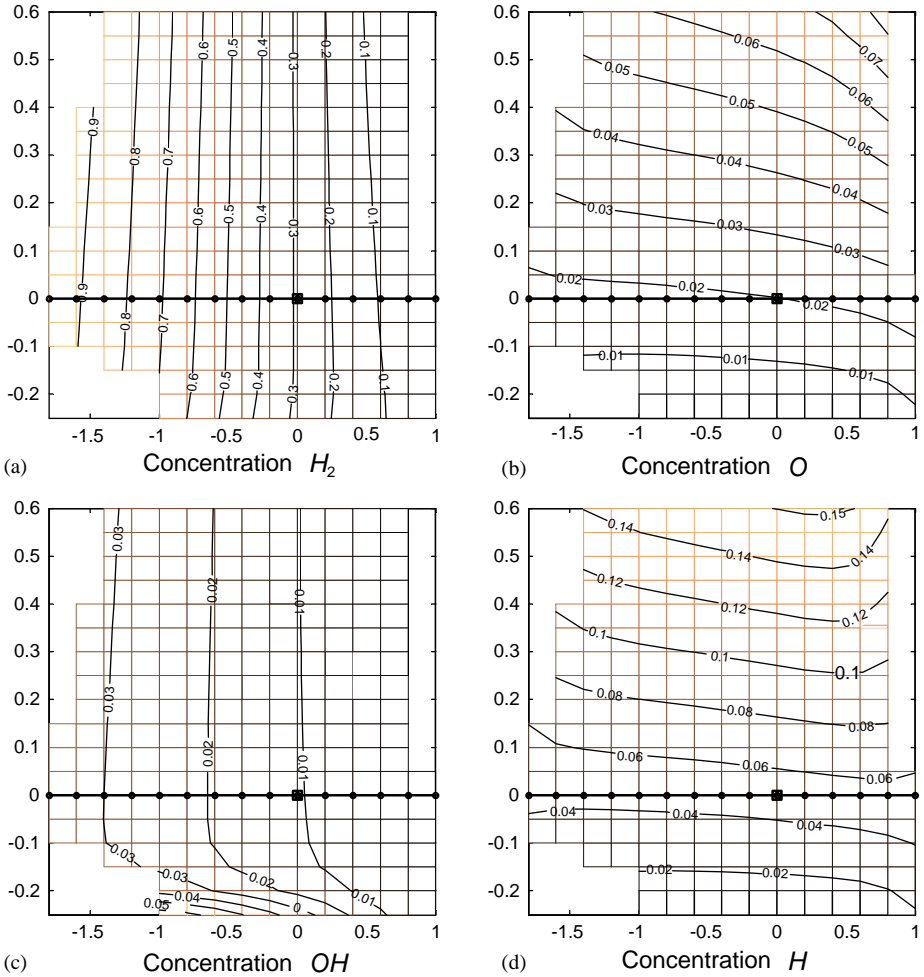


Fig. 6. Two-dimensional invariant grid as a screen for visualizing different functions defined in the concentrations space. The coordinate axes are entropic distances (see the text for the explanations) along the first and the second slowest directions on the grid. The corresponding 1D invariant grid is denoted by bold line, the equilibrium is denoted by square. (a) Concentration H_2 , (b) concentration O (c) concentration OH , and (d) concentration H .

Finally, we visualize the relation between the relaxation times of the fast motion towards the 2D-grid and along it. This is given on the Fig. 7c. This picture allows to make a conclusion that two-dimensional consideration can be appropriate for the system (especially in the “high H_2 , high O ” region), since the relaxation times “towards” and “along” the grid are clearly separated. One can compare this to the Fig. 7d, where the relation between relaxation times towards and along the 1D-grid is shown.

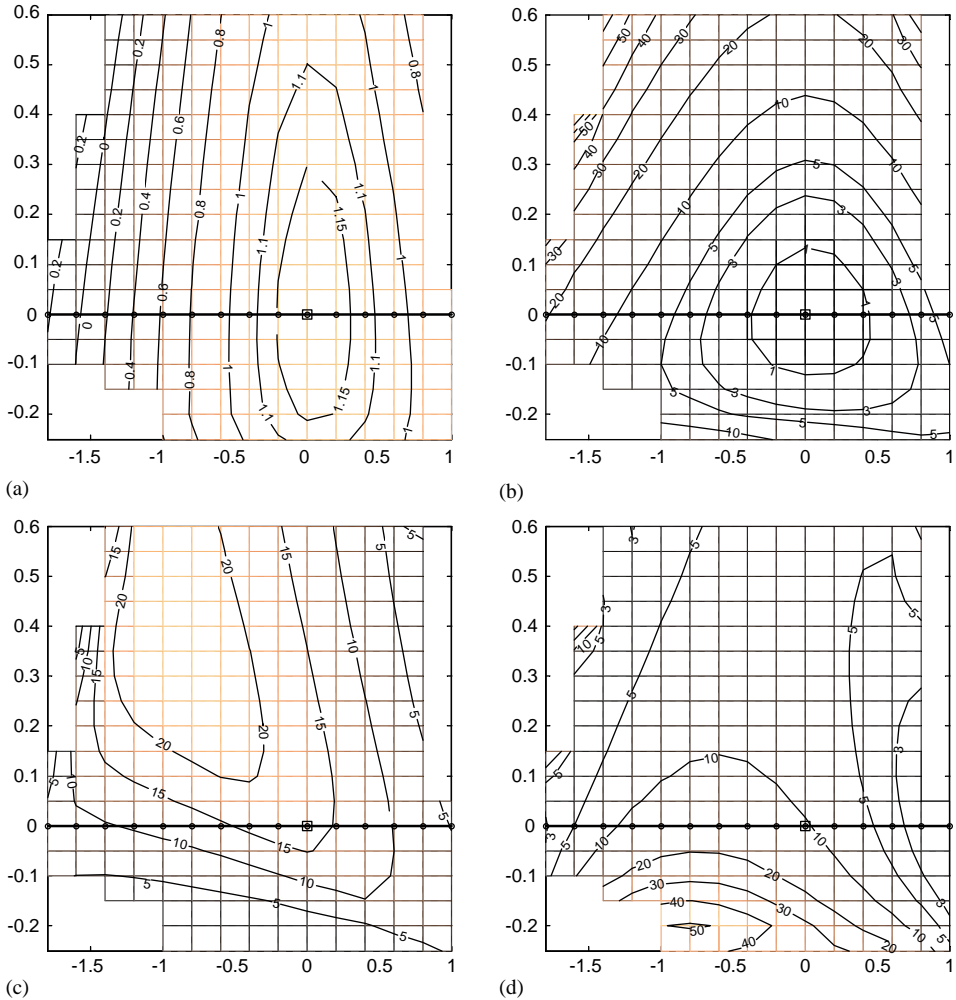


Fig. 7. Two-dimensional invariant grid as a screen for visualizing different functions defined in the concentrations space. The coordinate axes are entropic distances (see the text for the explanations) along the first and the second slowest directions on the grid. The corresponding 1D invariant grid is denoted by bold line, the equilibrium is denoted by square. (a) Entropy, (b) entropy production, (c) λ_3/λ_2 relation, and (d) λ_2/λ_1 relation.

9.7. Spectral degeneracy and numerical instability of grids

Our computational experiments demonstrate instability of computation near some of the points of spectral degeneracy of symmetrized Jacobian: Let the grid be k -dimensional, and the eigenvalues of symmetrized Jacobian (58) be $\lambda_1 \geq \lambda_2 \geq \dots \geq \lambda_n$. For numerical stability the spectral gap between λ_k and λ_{k+1} , $\delta = \lambda_k - \lambda_{k+1}$, should not vanish. The process of grids computation becomes unstable in neighborhood of points where

$\delta = 0$. In generic case the set of parameters where the symmetric operator degenerates has codimension 2. Hence, for one-dimensional grids the spectral gap is nongeneric, for two-dimensional grids this kind of instabilities can be expected only near finite number of points, for three-dimensional grids it is possible only near curves, etc.

In Fig. 3(c) we can see two minima of λ_2/λ_1 on the one-dimensional grid. One minimal value is near 5, another is near 2. In Fig. 4(c) we can find one such point: the minimum of spectral gap between λ_2 and λ_1 for one-dimensional grid is finite again (but small), and the grid computation remains stable, but the slowness of the manifold this point and on the left is questionable. In Fig. 7(c) it is possible to observe how the spectral gap between λ_3 and λ_2 vanishes near two of the corners, and near these points the calculation became unstable.

If the necessary spectral gap is sufficiently big uniformly, then it is possible to use algorithms of invariant grids construction without thermodynamic projector (with orthogonal projector, for example). The theory of systems with sufficiently big spectral gaps was developed in context the theory of “inertial manifolds” for finite-dimensional as well as for infinite-dimensional systems [70–72]. The further discussion of these problems is beyond the scope of this paper.

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 open or driven by flows systems. External flows are usually taken into account by additional terms in the kinetic equations (2):

$$\dot{\mathbf{c}} = \mathbf{J}(\mathbf{c}) + \mathbf{\Pi} . \quad (106)$$

Zero-order approximation assumes that the flow does not change the invariant manifold. 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. (47):

$$\dot{M}_i = (\nabla M_i|_{\mathbf{c}(M)}, \mathbf{J}(\mathbf{c}(M)) + \mathbf{\Pi}) . \quad (107)$$

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

First-order approximation takes into account the shift of the invariant manifold by $\delta\mathbf{c}$. Equations for Newton’s iterations have the same form (65) but instead of the vector field \mathbf{J} they take into account the presence of the flow:

$$[1 - \mathbf{P}_c](\mathbf{\Pi} + \mathbf{L}'_c \delta\mathbf{c}) = 0, \mathbf{P}_c \delta\mathbf{c} = 0 , \quad (108)$$

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 these 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 [7,8]. Transition to Eulerian coordinates is possible but the relations between concentrations and the flow will change its form. In a contrast, the more simplistic zero-order approximation is equally applicable in both the coordinate system, if it is valid.

11. Conclusion

In this paper, we have presented the method for constructing the invariant manifolds for reducing systems of chemical kinetics. Our approach to computations of invariant manifolds of dissipative systems is close in spirit to the Kolmogorov–Arnold–Moser theory of invariant tori of Hamiltonian systems [73,74]: We also base our consideration on the Newton method instead of Taylor series expansions [75], and systematically use duality structures.

Recently, the geometrical approach became more and more popular in applied model reduction: one constructs a slow approximate invariant manifold, and dynamical equations on this manifold instead of an approximation of solutions to the initial equations. After that, the equations on the slow manifold can be studied separately, as well as the fast motion to this manifold (the initial layer problem [76]).

This approach follows the classical ideas of Lapunov [11], Poincare [77], Kolmogorov [78]. The benefits from this geometrical splitting of motions is now recognized not only in physical problems (mechanics, kinetics, etc.), but also, for example, in the control theory [12,79,80].

The thermodynamic parameterization and the selfadjoint linearization arise in a natural way in the problem of finding slowest invariant manifolds for closed systems. Use of the thermodynamic projector makes it unnecessary a global parameterizations of manifolds, and thus leads to computationally promising grid-based realizations.

The notion of invariant grid may be useful beyond the chemical kinetics. This discrete invariant object can serve as a representation of approximate slow invariant manifold, and as a screen (a map) for visualization of different functions and properties. The problem of the grid correction is fully decomposed into the problems of the grid's nodes correction. The next step should be the implementation of the method of invariant grids for investigation of high-dimensional systems “kinetics+transport”. The asymptotic analysis of the methods of analytic continuation the manifold from the grid should lead to further development of these methods and modifications of the Carleman formula.

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