



# Model reduction in chemical dynamics: slow invariant manifolds, singular perturbations, thermodynamic estimates, and analysis of reaction graph

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The paper has two goals:

- (1) It presents basic ideas, notions, and methods for reduction of reaction kinetics models: quasi-steady-state, quasi-equilibrium, slow invariant manifolds, and limiting steps.
- (2) It describes briefly the current state of the art and some latest achievements in the broad area of model reduction in chemical and biochemical kinetics, including new results in methods of invariant manifolds, computation singular perturbation, bottleneck methods, asymptotology, tropical equilibration, and reaction mechanism skeletonization.

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methods were developed together with the first theories of complex chemical reactions. Three simple basic ideas have been invented:

- The *Quasi-Equilibrium* approximation or QE (a fraction of reactions approach their equilibrium fast enough and, after that, remain almost equilibrated).
- The *Quasi Steady State* approximation or QSS (some of species, very often these are some of intermediates or radicals, exist in relatively small amounts; they reach quickly their QSS concentrations, and then follow, as a slave, the dynamics of these other species remaining close to the QSS). The QSS is defined as the steady state under condition that the concentrations of other species do not change.
- The *limiting steps* or bottleneck is a relatively small part of the reaction network, in the simplest cases it is a single reaction, which rate is a good approximation to the reaction rate of the whole network.

## Introduction

Three eras (or waves) of chemical dynamics can be associated with their leaders [1]: the van't Hoff wave (the first Nobel Prize in Chemistry, 1901), the Semenov–Hinshelwood wave, and the Aris wave. The problem of modelling of *complex reaction networks* was in the focus of chemical dynamics research since the invention of the concept of ‘chain reactions’ by Semenov and Hinshelwood (the shared Nobel Prize in Chemistry, 1956). Aris’ activity was concentrated on the detailed systematization of mathematical ideas and approaches for the needs of chemical engineering. In the engineering context, the problem of modelling of complex reactions became even more important.

A mathematical model is an intellectual device that works [2]. Creation of such working models is impossible without the well developed technology of model reduction. Therefore, it is not surprising that the model reduction

More precise formal discussion is presented in the following sections.

In 1980s–1990s the model reduction technology was enriched by several ideas. Most important of them are: the Method of Invariant Manifolds (MIM) theory and algorithms [3<sup>•</sup>,4<sup>•</sup>], the special Intrinsic Low Dimensional Manifold (ILDM) method for approximation of slow motion [5<sup>•</sup>], the Computational Singular Perturbation (CSP) method for the iterative approximation of both slow and fast motions [6<sup>•</sup>], and the sensitivity analysis of complex kinetic systems [7<sup>•</sup>].

Development of lumping analysis was important for general understanding of model reduction in chemical kinetics [8<sup>•</sup>]. The lumped species is considered as a linear combination of the original ones. These combinations are often guessed on the basis of known kinetic properties and can be improved by iterative methods and observer

theory. The standard examples are: the lumped species are identified as the sums of species in selected groups (a very popular approach with many practical applications, e. g., [9]); the lumped species are the numbers of links and structural fragments of various types and in different states (this approach has many applications, from petrochemistry [10] and modelling of intracellular networks [11] to the Internet dynamics [12<sup>•</sup>]).

The main achievements of this period (1980s–1990s) in model reduction were summarized in several books and surveys [13,14,15<sup>•</sup>,16].

The technological elaboration of these ideas and assimilation of those by the modelling practice took almost thirty years. Much efforts have been invested into computational improvements and testing with the systems of various complexity. Some new ideas were proposed and developed.

The QE, QSS, MIM, and CSP methods can be applied to any differential equation with explicit or implicit (hidden) separation of time. They use the structure of reaction network as a tool for creation of kinetic equations. In the classical methods, only the limiting step approach (the bottleneck method) works directly with the reaction graph. Recently, the model reduction methods which use the structure of the reaction network, were developed far enough and attract many different techniques, from sensitivity analysis to algebraic geometry and tropical mathematics.

The first step in the next section is a ‘step backwards’, a brief introduction of the classical methods. Then we move to modern development.

### QE, QSS, MIM and CSP in ODE framework

Formally, the standard models of chemical kinetics are systems of Ordinary Differential Equations (ODE). The general framework looks as follows. Let  $U$  be a bounded domain in  $R^n$ . Assume that vector fields  $F_{\text{fast}}(x)$  and  $F_{\text{slow}}(x)$  are defined and differentiable in a vicinity of  $\bar{U}$  (in real applications these vector fields are usually analytical, or even polynomial or rational). Let  $U$  be positively invariant with respect to  $F_{\text{fast}}(x)$  and  $F_{\text{slow}}(x)$ . Consider dynamical system with the explicit *fast–slow time separation*:

$$\frac{dx}{dt} = F_{\text{slow}}(x) + \frac{1}{\varepsilon} F_{\text{fast}}(x), \quad (1)$$

where  $\varepsilon > 0$  is a small parameter. The *fast subsystem* is

$$\frac{dx}{d\tau} = F_{\text{fast}}(x). \quad (2)$$

Here, time  $\tau$  is used to stress that this is the ‘fast time’,  $\tau = t/\varepsilon$ . If the fast system (1) converges to an

asymptotically stable fixed point in  $U$  and has no fixed points on the border of  $U$  then for sufficiently small  $\varepsilon$  the slow vector field becomes practically invisible in the dynamics of (1), that is there is no slow dynamics.

Let the fast system (2) be neither globally stable nor ergodic in  $U$ . Assume that it has the conservation laws  $b_i(x)$  ( $i = 1, \dots, k$ ) and for each  $x_0 \in U$  the fast system on the set  $b_i(x) = b_i(x_0)$  converges to a unique stable fixed point  $x^*(b)$ , where  $b$  is the vector of values  $b_i(x)$ . Then the slow system describes dynamics of conservation laws  $b$ :

$$\frac{db}{dt} = Db_{x=x^*(b)}[F_{\text{slow}}(x^*(b))], \quad (3)$$

where  $Db_{x=x^*(b)}$  is differential of  $b(x)$  at the point  $x^*(b)$ . For linear conservation laws  $Db = b$  and the slow equations have the simple form

$$\frac{db}{dt} = b[F_{\text{slow}}(x^*(b))]. \quad (4)$$

The QE manifold is parametrized by the conservation laws with functions  $x^*(b)$ . It should be stressed that the slow equations in their natural form (3) and (4) describe the dynamics of the conservation laws  $b$  and not the dynamics of the selected ‘slow coordinates’. The problem of projection onto slow manifold is widely discussed [17<sup>•</sup>,18,19<sup>•</sup>]. According to the Tikhonov theorem, dynamics of the general system (1) from an initial state  $x_0$  under the given assumptions can be split in two stages: fast convergence to the QE manifold  $x^*(b)$  (the *initial layer*, convergence to a small vicinity of  $x^*(x_0)$ ), and then slow motion in a small vicinity of the QE manifolds.

The QE assumption is the separation of reactions onto slow and fast:  $F_{\text{slow}}$  includes all the terms from the slow reactions,  $F_{\text{fast}}$  includes all the terms from the fast reactions and the slow manifold  $x^*(b)$  consists of *equilibria* of the fast reactions parametrized by the conservation laws. The ‘thermodynamic’ behaviour of fast reactions (convergence to equilibrium, which is unique for any given values of the conservation laws) is essential to application of the Tikhonov theorem. Slow reactions can be extended by including external fluxes, they do not change the asymptotic form (3) and (4).

Combining of fast subsystems from the fast reactions is so popular [20] that a special warning is needed: there exists another widely used approximation without separation of reactions into fast and slow (see QSS below).

It should be stressed that the physical and chemical nature of the convergence to equilibrium of fast reactions may vary. It may follow from thermodynamic conditions like principle of detailed balance or semi-detailed balance. It may have also completely algebraic nature. For

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