PARAMETERIZATION OF REACTION MECHANISMS USING ORTHONORMAL POLYNOMIALS

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Abstract—Recent methods for mechanism reduction convert large detailed chemical reaction mechanisms into small systems of differential or differential-algebraic equations. A possible further step is the parameterization of reaction mechanisms, i.e. the description of chemical kinetics by explicit functions, obtained by numerical fitting to the numerical solution of differential equations. A new parameterization procedure, based on orthonormal polynomials, is described which is well applicable for fitting high-order polynomials having few effective parameters. A program is provided for the generation of multivariate Horner equations. The method is illustrated by the parameterization of a recent version of the Oregonator, a skeleton model of the oscillating Belousov–Zhabotinsky reaction.

1. INTRODUCTION

Nowadays, the fine details of kinetics are known for numerous important chemical processes. Reaction mechanisms, comprising several hundred elementary reactions, can be constructed and these mechanisms can often reproduce experimental data with sufficient accuracy. The simulation of spatially homogeneous (zero spatial dimensional) systems has caused no problems since the seventies. Recently, software tools and fast-enough hardware has become available for the simulation of spatially one-dimensional systems with detailed reaction mechanisms.

Investigation of several practical and academic problems requires the simulation of spatially two- and three-dimensional systems. The simulation of such systems with detailed reaction mechanisms is impossible or requires several hundred hours of supercomputer CPU time.

The demand for two- and three-dimensional simulations was one of the motivations behind the development of methods for mechanism reduction. In the process of mechanism reduction two main stages can be distinguished. Usually the starting detailed mechanism (typically 80 species and 500 reactions) is reduced to a "short mechanism" (20 species and 50 reactions). This short mechanism reproduces the main features of the process and the concentration profiles of the important species with an accuracy of a few percent. The short mechanism is a subset of the complete mechanism. A systematic procedure for the generation of a short mechanism from a detailed mechanism was published by Turányi (1990).

The next step is the application of a series of kinetic approximations, such as the quasi-steady-state approximation, fast equilibrium approximation, rate limiting step approximation etc. A procedure was recently suggested for the calculation of the error of the QSSA and for the selection of QSSA species (Turányi *et al.*, 1993b). Species lumping has been used for several decades, in the hydrocarbon chemistry and in atmospheric chemistry, without strict mathematical justification. The concentration of lumped species is a sum, a weighted sum, or a non-linear function of the concentration of a group of real species. Recently, a mathematical theory of lumping is being developed (Li & Rabitz, 1991; Li *et al.*, 1993).

The result of the application of all these approximations is a skeleton model with typically 2–8 variables. Unlike the short mechanism, the skeleton model is not a subset of the detailed mechanism. Reactions of the skeleton model are combinations of the original reactions and also the species of the skeleton model are frequently lumped species. Usually the skeleton model is not a mass-action kinetics model, but it is rather a chemical kinetics related small system of differential or differential-algebraic equations.

Alternative methods were also elaborated for the generation of skeleton models, which do not use the quasi-steady-state approximation directly, but which are also based on the existence of very different time scales in kinetic models. These methods are the computational singular perturbation (Lam & Goussis, 1988) and the low-dimensional manifold method (Maas & Pope, 1992).

Although the end of the line of a mechanism simplification procedure is a skeleton model, it is frequently still not applicable for two- or three-dimensional calculations. The solution of a coupled set of differential or differential-algebraic equations in several thousand points of space in each time step requires too much computer time, and the demand on

CPU time is on the edge of, or beyond the capabilities of recent computer hardware.

A promising solution seems to be the description of the information for chemical processes not by differential or differential-algebraic equations, but by explicit algebraic equations. Analytical solution of differential equations provides such explicit functions, but analytical solution of coupled non-linear kinetic differential equations is possible very rarely. However, explicit algebraic equations can always be obtained by *numerical fitting of functions to the numerical solution of differential equations*. This technique is called the *parameterization* of a reaction mechanisms and is a special case of a general procedure called *repro-modelling*.

The paper is structured as follows. In Section 2 the basic ideas of repro-modelling and the possible fields of application in chemical kinetics are described. Very few articles have been published about the parameterization of kinetic mechanisms, but all these papers, enumerated in Section 3, include significant developments. In Section 4, a new method for the parameterization of kinetic models is proposed which is computationally efficient, includes all the achievements of the previous techniques, and is theoretically better established. An algorithm is given in Section 5 for the generation of multivariate Horner equations for the efficient calculation of high-order polynomials. In Section 6, these methods are applied to the parameterization of a recent version of the Oregonator, a skeleton model of the oscillating Belousov–Zhabotinsky reaction.

2. APPLICATION OF REPRO-MODELLING IN CHEMICAL KINETICS

The notion of repro-modelling was introduced by Meisel & Collins (1973). Repro-modelling means the approximation of a sophisticated and time consuming computational model by a simple empirical model, consisting of one or several explicit functions. The repro-model has to reproduce the output of the complex model with high accuracy for any feasible input. The creation of a repro-model requires extra effort, but when it is frequently used, the savings in computer time can be tremendous since the evaluation of these explicit functions is very fast.

There are two main fields of application of repro-modelling in chemical kinetics related simulations.

(i) Chemical kinetic mechanisms are frequently used as submodels in a range of complex models, including air quality models, combustion models, and models of chemical plants. The chemical box is usually well separable from the rest of the model, and the chemical kinetic calculations consume the overwhelming part of computer time. These calculations may result in concentration–time profiles or a time independent solution.

(ii) Simulation of the kinetics of spatially inhomogeneous systems means the calculation of the time history or stationary profiles of concentrations in several points of space, determined by chemical reactions, and transport of mass and energy. Here, the chemical calculations can also be separated from the calculation of transport and therefore the chemical kinetic calculations can be made by a repro-model.

The input of a repro-model has to include the concentrations of all the species, with influence on the concentration of important species or on the important features. These species will be called *basic species*. The problem of selection of basic species deserves a closer investigation, but as a first approach the species of the skeleton model can be applied as basic species. In case of a given model, the result is determined not only by the initial concentration of basic species but also by some variable parameters. Such variable parameters are for example, the photon flux or the initial temperature. The basic species and these variable parameters together will be called *basis variables*. The smaller the number of basic variables, the simpler and/or more accurate the approximating function is. However, the presence of non-effective species or variables among the assumed basic variables does not spoil the repro-model. On the other hand, the input of the repro-model must include all the basic variables.

Assume that the chemical kinetic model is a part of a complex model and the task of the chemical box is to provide the concentrations of the important species at a fixed time later. Inputs of the repro-model are the values of the basic variables at time t_1 and the output is the concentration of important species at a fixed Δt time later. In fact, the *flow* of differential equations of a model (see e.g. Hirsch & Smale, 1974) and not literally the solution of the differential equations is approached by the repro-model. If the requirement is the calculation of a concentration profile, the output has to include the basic variables as well. In this way the repro-model can be called consecutively and provides a series of concentration values belonging to equidistant time steps. Between each call of the repro-model the values of basic variables can be modified. This allows, for example, in an air pollution model the consideration of the effect of variable intensity of sunshine or the effect of emission.

Results of chemical kinetic calculations cannot only be concentration profiles, but also time-independent results like stationary state concentrations, maximum concentrations, time-average concentrations or a feature of a reaction. Such a feature can be the length of an oscillating reaction or the maximum temperature of a combustion reaction. In this case the inputs are the values of basic variables and the output is the value of this time-independent solution.

The repro-model, which relates k results of the kinetic model to the values of m basic variables is an $\mathbb{R}^m \rightarrow \mathbb{R}^k$ funciton. This function is equivalent to k

$\mathbb{R}^m \to \mathbb{R}$ functions. Handling of the latter is technically much simpler and therefore the repro-model will always be considered a set of scalar valued vector functions.

3. LITERATURE OF REPRO-MODELLING

The basic article of repro-modelling by Meisel & Collins (1973) described the general philosophy of repro-modelling and gave three non-chemical examples. These authors applied continuous piecewise linear functions in the repro-model.

Dunker (1986) was the first to apply repro-modelling for chemical kinetic simulations when he parameterized a smog mechanism. Dunker proposed to represent the m-dimensional domain of basic variables as a set of rectangular cells, and to approximate the outputs in each cell with a second-order Taylor expansion about the centre of the cell by the application of initial concentration sensitivities. The Taylor expansions gave an exact value at the centre of the cell and larger errors toward the boundaries.

Marsden et al. (1987), independently from Dunker, also applied repro-modelling for a smog model. They replaced the photochemical model with a single quadratic polynomial obtained as a least squares fit to the model results using standard regression analysis. Marsden et al. selected the input data also according to a lattice applying a complete factorial design at two levels.

Recently Spivakovsky et al. (1990a) developed a sophisticated procedure for the calculation of the coefficients of higher-order polynomials by least squares fit. They warned that when the input data form a lattice, it is impossible to apply high-order polynomials in the repro-model and also some of the input combinations are unrealistic. In this case, the repro-model includes information also for unrealistic situations, but the accuracy of the description of most frequent situations is lower. According to the procedure of Spivakovsky et al., the joint probability density functions (pdf-s) of the inputs of the chemical box have to be determined. Typical input data are selected randomly according to their pdf-s. There

must be about 10 times more data than parameters of the repro-model. These data are fitted by a least-squares approximation for high-order polynomials of m variables. A high-order polynomial of several variables has a high number of coefficients. For example, a general fourth-order polynomial of 10 variables has 1001 coefficients. According to Spivakovsky et al., the polynomial has to include the effective coefficients only. Selection and determination of a small number of effective coefficients among several hundred possible coefficients of an approximating function, fitted to several thousand data, is numerically very difficult. The procedure, applied by Spivakovsky et al., was to fit the parameters in groups of three hundred by applying the method of Housholder triangularization. This method determines the more influential coefficients first. In each turn, the ineffective parameters were discarded and the effective parameters were refitted together with a new group of coefficients. The reason for this uncomfortable procedure was that it was impossible to determine the coefficients of a polynomial independently from the other coefficients, and the determination of all coefficients simultaneously would have required unrealistic computer memory and time. The procedure applied by them selects the effective coefficients first and then makes a final determination of the value of these coefficients. Although this procedure worked well in several cases, there are two possible objections against it. Not only the exact value of coefficients depends on the value of other coefficients, but also the influential nature of them. It is possible, that a coefficient is judged to be uninfluential based on the investigation of one group of coefficients and the same coefficient would be found influential based on the investigation of another group. Also, the procedure requires the recalculation of the influential parameters in each turn and therefore much of the computational effort is wasted.

We completely agree with Spivakovsky et al. (1990a,b) that the approximating function of the repro-model has to be a high-order polynomial having only few effective coefficients, determined

Table 1. Comparison of the applications-to-date of repro-modelling to chemical kinetics

Author	Topics	Function	Number of basic variables	Gain in computer time
Meisel & Collins (1973)	—Freeway on-ramp control —Effect of traffic policies on air pollution —Radar cross-section model	Continuous piecewise linear functions	2, 3, 3, respectively	10^4, 10^2, 150 times, respectively
Dunker (1986)	Urban smog model	20736 second-order polynomials	10	300 times
Marsden et al. (1987)	Urban smog model	One second-order polynomial	15	N/A
Spivakovsky et al. (1990a)	Average [OH] in the atmosphere	30 High-order polynomials	13	600 times
Turányi (this study)	Belousov–Zhabotinsky reaction	Fifth to eighth-order polynomials	3	60 times

by a least-squares approximation from a highly over-determined set of data. Two modifications to the procedure given by Spivakovsky *et al.* are suggested:

(i) The joint probability density function of basic variables is available (sometimes) for problems of atmospheric chemistry, but it is not available in general. An alternative approach is if the original complex model, which includes the "chemical box", is simulated using many representative input values. From these simulations a set of typical input and output of the chemical box is obtained and these constitute the input data of the fitting procedure.

(ii) The above problems of the fitting procedure of Spivakovsky *et al.* can be solved if orthonormal polynomials are used instead of "usual" polynomials. Coefficients of orthonormal polynomials can be determined independently from each other and in this way a simpler and more effective fitting procedure, described in the next section, can be utilized.

4. APPLICATION OF ORTHONORMAL POLYNOMIALS FOR PARAMETERIZATION

Let $x^i = (x_1^i, x_2^i, \ldots, x_m^i)$, $i = 1, \ldots, n$ denote a set of data. Let φ_j, $j = 1, \ldots, l$ be a set of $\mathbb{R}^m \to \mathbb{R}$ functions. A scalar product of functions φ_j and φ_k is given by

$$(\varphi_j, \varphi_k) = \sum_{i=1}^{n} w_i \varphi_j(x^i) \varphi_k(x^i). \tag{1}$$

This scalar product belongs to the set of data x^i and non-negative weights w_i, $i = 1, \ldots, n$. Functions φ_j and φ_k are said to be orthonormal with respect to this scalar product if and only if

$$(\varphi_j, \varphi_k) = \begin{cases} 0 & \text{if } j \neq k \\ 1 & \text{if } j = k. \end{cases} \tag{2}$$

Any function $F: \mathbb{R}^m \to \mathbb{R}$ can be approximated using an orthonormal set of functions (φ_j, $j = 1, \ldots, l$) by an orthonormal (Fourier) expansion:

$$F \approx \sum_{j=1}^{l} (F, \varphi_j)\varphi_j. \tag{3}$$

The deviation between function F and the approximating function can be characterized by the root-mean-square error r:

$$r = \left\| F - \sum_{j=1}^{l} (F, \varphi_j)\varphi_j \right\| \tag{4}$$

where $\| \; \|$ denotes the Euclidean norm. For any $l \leqslant n$ the approximation has a minimum property in such a way that

$$r \leqslant \left\| F - \sum_{j=1}^{l} a_j \varphi_j \right\|$$

where the a_j, $j = 1, \ldots, l$ coefficients are arbitrary numbers.

Equation (3) indicates that if a set of orthonormal functions is available, the construction of the approximating function is easy. The critical step is the construction of an orthonormal set of functions to a given data set.

Let f_j, $j = 1, \ldots, l$ be a set of linearly independent functions. Using the Gram–Schmidt process, a set of orthonormal functions φ_j can be constructed as linear combinations of functions f_j.

$$\varphi_1 = c_{11}f_1$$
$$\varphi_2 = c_{21}\,f_1 + c_{22}f_2$$
$$\varphi_3 = c_{31}f_1 + c_{32}f_2 + c_{33}f_3$$
$$\vdots$$
$$\varphi_l = \sum_{j=1}^{l} c_{lj}f_j. \tag{5}$$

The Gram–Schmidt orthnormalization can be described by the following recursive equations:

$$\varphi_1' = f_1; \qquad\qquad \varphi_1 = \varphi_1'/\|\varphi_1'\|$$
$$\varphi_2' = f_2 - (\varphi_1, f_2)\varphi_1; \qquad \varphi_2 = \varphi_2'/\|\varphi_2'\|$$
$$\vdots$$
$$\dot{\varphi}_l' = f_l - \sum_{j=1}^{l-1} (\varphi_j, f_l)\varphi_j; \qquad \varphi_l = \varphi_l'/\|\varphi_l'\|. \tag{6}$$

Accordingly, the coefficients are

$$c_{11} = 1/\|\varphi_1'\|$$
$$c_{21} = -(\varphi_1, f_2)c_{11}/\|\varphi_2'\|$$
$$c_{22} = 1/\|\varphi_2'\|$$
$$\vdots$$
$$c_{lk} = \left[-\sum_{j=1}^{l-1} (\varphi_j, f_l)c_{jk} \right] \Big/ \|\varphi_l'\|$$
$$c_{ll} = 1/\|\varphi_l'\|. \tag{7}$$

Evaluation of the approximating function has to be as fast as possible and therefore the most practical choice is if the linearly independent set of functions required are monomials of a general m-variable polynomial. For example, in case of three variables and a second-order polynomial, these monomials are:

$$1, x, y, z, x^2, xy, xz, y^2, yz, z^2.$$

Monomials can be represented by following general form:

$$M_j = \prod_{k=1}^{m} x_k^{\mu_j^k}, \quad \mu_j^k \in \{0, 1, 2, \ldots, l\}. \tag{8}$$

The order of monomial M_j is defined as $\sum_{k=1}^{m} \mu_j^k$. The order of a polynomial is equal to the order of its highest order monomial term.

Davies & Rabinowitz (1954) were the first to apply orthonormal polynomials, generated by Gram–Schmidt orthonormalization, for the numerical approximation of single variable functions. Application of a three-term recurrence (Householder,

1953) instead of the Gram–Schmidt orthonormalization is a much faster way for the generation of orthonormal polynomials. The review article of Forsythe (1957) described the approximation of single variable functions using this recurrence equation and made this method very popular.

Weisfeld (1959) generalized the Householder's method for orthonormalizing real polynomials in several variables. The efficiency of this method can be further improved (see Bartels & Jezioranski, 1985) using a more strict ordering of monomials, because in this case some of the coefficients are identical.

Application of the recurrence formulas is superior to the original Gram–Schmidt orthonormalization if the monomials, applied for the construction of orthnormal polynomials, are ordered and if all the monomials are used. The Gram–Schmidt process does not have any requirement for the order of independent functions f_j. Our task was to construct a good approximation to function F, using as few as possible coefficients of the multivariate polynomial, and therefore a new version of the approximation procedure was applied.

Orthonormal polynomials were generated using the Gram–Schmidt process as described by equations (6) and (7). The data have to be approximated with the same percentage accuracy for both high and low concentrations and therefore a relative weighting was applied. Accordingly, weights $w_i = 1/F^2(x^i)$ were used.

As a first step a constant value ($f_1 = 1$) was fitted to the data and an error of approximation (r.m.s.) was calculated. Then an orthonormal polynomial was generated using the next monomial and a new r.m.s. was calculated using equation (4). Using one more monomial, the approximation was always improved but this improvement could be large or small depending on the new monomial applied. If the deviation between the new and old r.m.s. was greater than a given tolerance, the monomial was accepted and the new orthnormal polynomial was preserved. If the decrease of r.m.s. was below the tolerance limit, the monomial and the last orthonormal polynomial was rejected. In both cases, another monomial was tested in a similar way in the next step. Thus all the first-order monomials were investigated, then all the second-order monomials, up to all the lth order monomials. This procedure has two degrees of freedom: the tolerance limit and the maximal order of monomials investigated. The method enabled the selection of the most effective monomials from the several thousand possible monomials of a high-order multivariate polynomial.

Finally, the orthonormal polynomials were converted into "usual" polynomials having the same monomials:

$$F \approx \sum_{j=1}^{l} a_j \varphi_j = \sum_{j=1}^{l} a_j \sum_{h=1}^{j} c_{jh} M_h = \sum_{j=1}^{l} b_j M_j \qquad (9)$$

where

$$a_j = (F, \varphi_j)$$

and

$$b_j = \sum_{s=j}^{l} a_s c_{sj}. \qquad (10)$$

This procedure has several advantageous features over other methods of least-squares fitting. The computational cost is proportional to the square of the number of accepted monomials and depends only linearly on the number of monomials rejected. As an example, the required CPU time was 14 min on an IBM RISC 6000/340 workstation, for the selection and determination of 52 effective coefficients out of the 3003 possible coefficients of a general tenth-order polynomial of five variables, when fitted to 8400 data points. The average deviation between the original and the fitted functions was 0.1%. The program was rather simple and no kind of numerical problems were encountered.

5. HORNER EQUATIONS

The result of the fitting procedure is the vector of coefficients b_j, $j = 1, \ldots, l$ and the indices of monomials μ_j^k, $k = 1, \ldots, m$ and $j = 1, \ldots, l$. Then the polynomial can easily be evaluated via equations (8) and (9). It is well known that this "direct" calculation of polynomials requires a high number of unnecessary multiplications, which can be avoided by appropriate factorization, i.e. using Horner equations. Spivakovsky *et al.* (1990a) also recommended the application of Horner equations but unfortunately they revealed neither the program nor the algorithm for the creation of the Horner equations.

Creation of one-dimensional Horner equations is easy. In case of several variables and high-order polynomials there is an enormous number of possible arrangements of parentheses. The search for a minimal number of multiplications leads to an inconvenient optimization task in a discrete space. The algorithm used here does not ensure an optimal solution, but the result is close to optimal.

First, the variables were ordered according to decreasing $I_k = \Sigma_{j=1}^{l} \mu_j^k$ values. A higher I_k value means that variable k is involved in more multiplications. Index k_1 belongs to the variable having the highest I_k, x_{k_2} has the second highest I_k etc.

Then, the monomials were reordered in the increasing order of μ^{k_1}. In case of identical exponents μ^{k_1}, the order was determined by the value of exponents μ^{k_2}, μ^{k_3}, etc. Now variable x_{k_1} or the powers of variable x_{k_1} were factored out of the monomials. As the cross-application of parentheses for different variables was prohibited, the factoring of x_{k_2} was possible only within the parentheses set by the factoring of x_{k_1}. This procedure was repeated for each variable and possibilities for the factoring of a variable were

```
function clmmp(y)
implicit real*8 (a-h,o-z)
dimension y(*), a(32)
data a/        9.78611E-08, 9.01811E-01,-2.14725E-01, 1.37960E-02,
* 1.03734E+04,-1.30596E+05,-5.98763E+02, 3.54922E+04,-5.93189E+02,
* 7.89811E+00,-6.74104E+08, 3.23016E+09, 3.20665E+08,-1.45277E+07,
*-8.34010E+08,-1.85126E+08, 1.25682E+13, 4.54739E+14,-4.39433E+11,
*-5.69072E+13, 1.58898E+12, 3.04874E+12, 4.05928E+12, 4.37154E+11,
*-2.03126E+16,-1.02632E+19,-9.18160E+18,-1.05173E+18, 2.01871E+15,
* 3.47382E+17,-9.36556E+16,-8.32790E+15/
clmmp =a(1)+y(3)*(a(4)+y(3)*a(10))+y(2)*(a(3)+y(3)*a(9)+y(2)*(a(8)
*+y(3)*(a(16)+y(3)*a(24))+y(2)*(a(15)+y(3)*(a(23)+y(3)*a(32))+y(2)*
*a(22))))+y(1)*(a(2)+y(3)*(a(7)+y(3)*a(14))+y(2)*(a(6)+y(3)*(a(13)+
*y(3)*a(21))+y(2)*(a(12)+y(3)*y(3)*a(31))+y(2)*(a(20)+y(3)*a(30))))+
*y(1)*(a(5)+y(3)*y(3)*(a(19)+y(3)*a(29))+y(1)*(a(11)+y(2)*(a(18)+y(
*3)*a(28)+y(2)*a(27))+y(1)*(a(17)+y(2)*a(26)+y(1)*a(25)))))
return
end
```

Fig. 1. A typical computer written FORTRAN function. This function calculates the concentration of Br^- at $t + 0.1$ s if the input array y contains the concentration of Br^-, $HBrO_2$, and Ce^{IV} at time t at the $d[Br^-]/dt \leqslant 0$, $d[HBrO_2]/dt \leqslant 0$, $d[Ce^{IV}]/dt > 0$ segment of the component space.

investigated only within the parentheses set in the previous steps.

The algorithm above was programmed in FORTRAN. This program finally creates a FORTRAN function for the calculation of the value of the polynomial. A sample result of this program is given in Fig. 1.

6. PARAMETERIZATION OF THE OREGONATOR MODEL

The most intensively studied oscillating reaction is the Belousov–Zhabotinsky reaction (Belousov, 1958; Zhabotinsky, 1964). Although the basic features of its chemistry have been understood for some time (Field et al., 1972) and a skeleton model called the Oregonator was constructed (Field & Noyes, 1974), the fine details of the chemistry are still unknown. In the last decade a series of systematic experimental investigations, carried out by Field, Försterling, Kőrös, Noszticzius, Noyes, Ruoff and their coworkers, gave new insight into the main chemical pathways and provided the value of many rate coefficients. Based on this information, a new detailed reaction mechanism, consisting of 80 reactions and 25 species, was set up by Györgyi et al. (1990). Using a systematic procedure, this mechanism was reduced to a short mechanism (42 reactions and 22 species) and to two skeleton models (Turányi et al., 1993a). The skeleton models have three variables and six reactions and can be considered new versions of the Oregonator. Unlike the original Oregonator, these skeleton models reproduce the period and amplitude of the concentration oscillations of species $HBrO_2$, Br^-, and Ce^{IV} with good

accuracy during the sustained oscillation period of batch experiments.

One of the new skeleton models, denoted as model F in the article of Turányi et al. (1993a), was selected for parameterization. In the present calculations the concentration of malonic acid, sulphuric acid, Ce^{III}, and BrO_3^- was identical to Case 1 in the article of Turányi et al. (1993a).

The input of the repro-model, consisting of polynomials, was the concentration of $HBrO_2$, Br^-, and Ce^{IV} at time t, and the output of the repro-model was the same concentrations at $t + \Delta t$. A time step of $\Delta t = 0.1$ s was used. Consecutive calculation of the concentrations by the polynomials resulted in a series of concentration values and thus gave concentration–time curves.

The data set to be approximated by polynomials was constructed in the following way. The Oregonator model was solved by a stiff ODE solver using the above time step Δt. The simulation was started from near the limit cycle. When the trajectory reached the limit cycle, each of the three concentrations was multiplied by a different random number, having a uniform distribution in the $[-10, +10]$ range. The perturbed solution then approached the limit cycle and when it reached the limit cycle, it was perturbed again. In each step, the actual concentrations and the concentrations belonging to a time Δt later were saved in a disk file. In each fitting about $n = 20000$ data vectors were used.

The data were approximated by a series of polynomials having tenth to fourth orders. The average deviation between the original data and the polynomial fit was in the order of 0.3% for tenth-order polynomials and 2% for the fourth-order
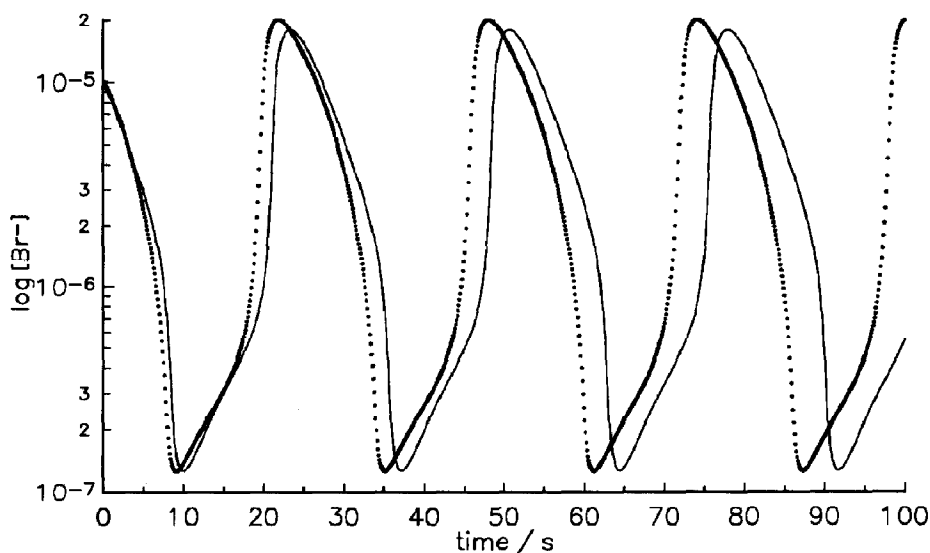
Fig. 2. Bromide ion concentration–time curves calculated from the skeleton model using a stiff ODE solver (solid line) and from a repro-model comprising eighth-order polynomials (dots). Each dot corresponds to a concentration set calculated by the repro-model. Calculation of the dotted line required 60 times less computer time.

polynomials. Trajectories, calculated from the tenth-order polynomials, were in excellent agreement with the solution of the skeleton model. Using lower and lower order polynomials, the agreement became worse and worse. Using low-order polynomials, the period time was shorter and the amplitude of the oscillation was smaller than that of the skeleton model. However, the limit cycle nature and the shape of the oscillations were preserved even in case of using

low-order polynomials in the repro-model. As a trade off between polynomial simplicity and accuracy, the eighth-order polynomials were selected for presentation. The [Br⁻]–time curves, obtained by the simulation the skeleton model and by using the repro-model, are compared in Fig. 2. The agreement between the two solutions is quite good, both for the period of the oscillations and the amplitude of concentration changes. Figure 3 demonstrates that the
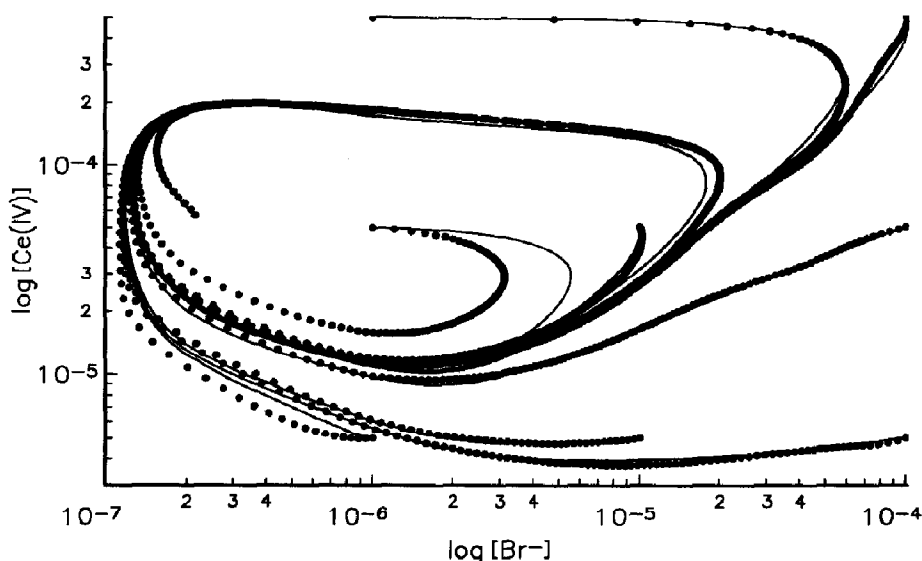

Fig. 3. Comparison of the trajectories in the log[Br⁻]–log[Ce(IV)] phase plane calculated from the skeleton model using a stiff ODE solver (solid line) and from a repro-model comprising eighth-order polynomials (dots).
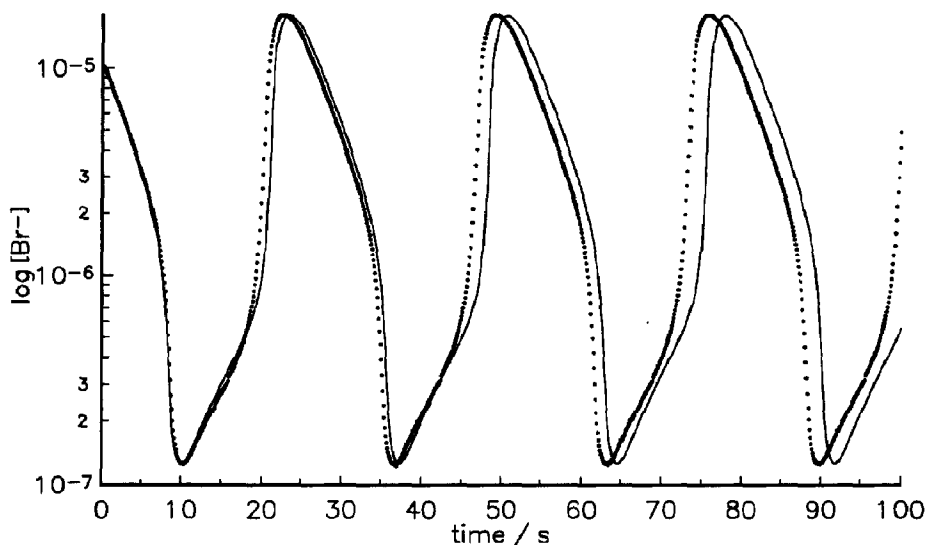
Fig. 4. Bromide ion concentration–time curves calculated from the skeleton model using a stiff ODE solver (solid line) and from a repro-model comprising eight sets of fifth order polynomials (dots).

repro-model mimics the skeleton model well, not only on the limit cycle, but also in a wide concentration range near the limit cycle.

The ratio of CPU time required for simulations applying the polynomials with the Horner arrangement, without the Horner arrangement, and by the ODE solution of the skeleton model was 1:90:60, respectively. This means that the application of the polynomial approach using Horner equations resulted in a 60 times gain in the computer time compared to the simulation of the skeleton model by an ODE solver. It is also clear that the application of the Horner arrangement is very important in practice as the "direct" calculation of the polynomials was 1.5 times slower than the solution of the ODEs.

A possible way for increasing the accuracy and decreasing the CPU time requirement is the application of several smaller polynomials instead of a single large polynomial in the repro-model. The input space of the repro-model has to be divided into segments. The segmentation is effective if, in each segment, the local repro-model is simple and different
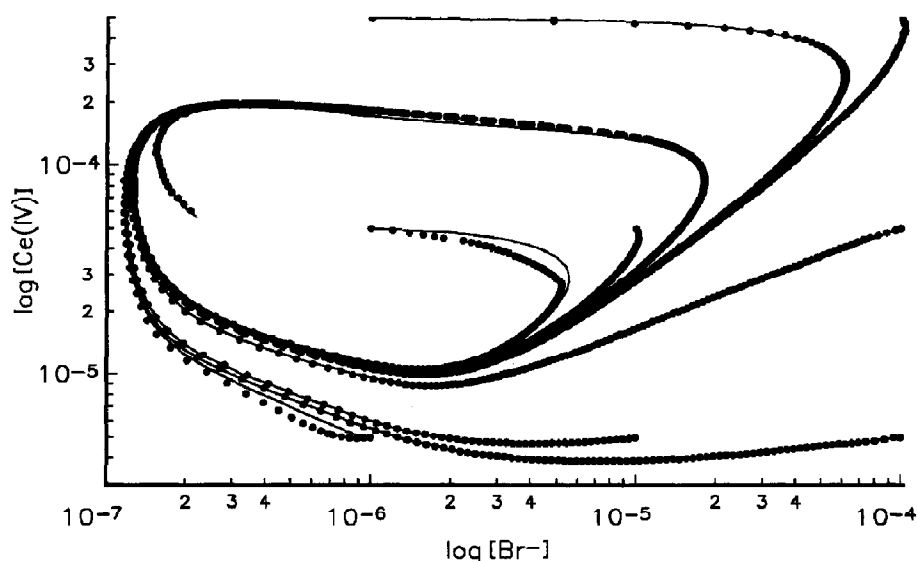

Fig. 5. Comparison of the trajectories in the log[Br⁻]–log[Ce(IV)] phase plane calculated from the skeleton model using a stiff ODE solver (solid line) and from a repro-model comprising eight sets of fifth-order polynomials (dots).

from the repro-models of the other segments. In case of kinetic models, the kinetic processes are usually similar in those segments of the component space where the production rate of each species has the same sign. Therefore, it was expected that the original ODE could be approached by a simple polynomial within each of these segments.

In case of our calculations, the component space was divided into eight segments according to the sign of $d[Br^-]/dt$, $d[HBrO_2]/dt$, and $d[Ce^{IV}]/dt$. In each of the eight segments the data for the three variables were approached by three fifth-order polynomials. In case of the calculation of the concentration of $HBrO_2$ in one of the segments the fifth-order polynomial did not give a good approximation and a sixth-order polynomial was applied.

During the application of the repro-model, the input concentrations were related to one of the segments based on the production rates of species. The output was calculated by the corresponding fifth-order polynomials. Rather unexpectedly, in some cases this method failed when the trajectory approached the border of two segments. A possible reason for this is that the approximation was very good inside the segments and less accurate near the edges. In these cases, the fifth-order polynomials provided unrealistic concentrations near the border for a few steps. This situation was easily recognized by the program, the results were canceled and these steps were calculated by the global eighth-order polynomial.

The $[Br^-]$–time curve, obtained by the ODE solution of the skeleton model and by using this eight-segment repro-model, is shown in Fig. 4. Again, the agreement between the two solutions is very good. Figure 5 shows that the eight-segment repro-model approaches the skeleton model better than the global repro-model.

In case of the segmented repro-model, the ratio of the CPU time required for simulations by applying the polynomials with the Horner arrangement, without the Horner arrangement, and by the ODE solution of the skeleton model was 1:46:50, respectively. Application of the polynomial approach using the Horner equations resulted in a factor of 50 gain in the computer time compared to the simulation of the skeleton model using an ODE solver. In this case the application of the repro-model was slightly more economical even when the polynomials were calculated in a "direct way". Very surprisingly, the application of the segmented repro-model required somewhat more computer time than that of the global repro-model. The reason is that the calculation of the production rates in skeleton model F is very involved as it requires the calculation of the quasi-steady-state concentration of radical BrO_2. In skeleton model G, the explicit calculation of $[BrO_2.]$ was avoided and therefore this model is expected to be better applicable in segmented repro-models. It has to be noted that these results

were not optimized for computer time savings. If less accuracy is tolerated or if a different Δt is used, the computer time economy can be further improved.

The purpose of this example was to demonstrate that the repro-modelling approach may result in considerable savings in computer time even in case of very small systems of algebraic-differential equations. Skeleton models of the Belousov–Zhabotinsky reaction are frequently used in two- and three-dimensional chemical wave simulations. However, the three-variable Oregonator is too stiff for such calculations and therefore simplified, less stiff and less realistic two-variable models are always applied. This example shows that using the parameterized form of the Oregonator model, a very realistic three-variable model can be utilized in numerical simulations of the chemical waves of the Belousov–Zhabotinsky reaction.

7. CONCLUSION

Kinetics of complex chemical processes is described by large reaction mechanisms in several important fields of chemistry, such as atmospheric chemistry, combustion chemistry or chemistry of exotic reactions. These mechanisms are equivalent to large systems of differential equations having several dozen variables. It has been shown that, using systematic methods, these large systems of ODEs can be converted into small systems of differential-algebraic equations. These skeleton models have few variables (usually <10) and give a good approximation to the original model.

Repro-modelling, the approximation of computer time demanding complex models by simple explicit functions, has been used in air pollution modelling. In this article repro-modelling is recommended as a final step of any mechanism reduction process.

Repro-modelling can be done via the following steps:

- A "chemical box" has to be separated within a complex model. The chemical box has to be simplified in such a way that a minimal number of input variables of the box are found. Ideally, these variables are all effective and there is no functional dependence between them.
- The complex model, which includes the chemical box, is simulated using many typical initial data. Several thousand input vectors and the corresponding outputs of the chemical box are collected.
- These data are approximated by high-order polynomials. This approximation can be made comfortably by fitting the data using orthonormal polynomials in several variables. If necessary, the chemical box can be approached by several polynomials, which cover different regions of the input.

● The polynomials are utilized in the form of computer written multivariate Horner equations.

This article includes a detailed description of the fitting procedure via orthonormal polynomials and an algorithm for the generation of Horner equations. It is demonstrated that the parameterization of the Oregonator model results in a 60 times gain in computer time, while the concentration-time curves, calculated from polynomials, are very close to the solution of differential equations.

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