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Numerical Methods for Ordinary Differential Equations Systems with Small Parameter with Applications in Kinetics Chemistry

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Abstract

Mathematical modelling is a more and more frequently used working tool, located, in this particular case, at the intersection between two basic sciences: mathematics and chemistry. We can wonder: can mathematical models offer predictions on the evolution of a chemical reaction? .Chemical reactions of a wide variety can be modelled with coupled differential equations. These describe the time evolution of the concentrations of the various chemical species: reactants, intermediaries, catalysts, and products. Such problems are quite simple to set up and solve with Matlab. The Matlab functions can numerically integrate the differential equations that arise. The resulting concentrations can be plotted as a function of time and also be used to accurately compute the expected concentration of the molecular species. The use of MATLAB in this article illustrates the important role of informatics in research in chemical reactions modelling. An important advantage of using a numerical method is that the mathematical representation of the chemical processes allows transparency and correctness in relation to chemical assumptions, thus allowing us to test our understanding on the chemical reactions by comparing the graphs obtained with other chemical models observed.

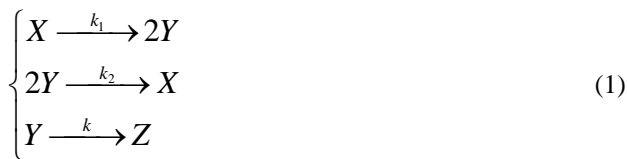
Keywords: Chemical kinetics Reaction, Numerical Methods, Matlab, Small Parameter

Introduction

Chemical kinetics, a topic in several chemistry courses, illustrates the connection between mathematics and chemistry .Differential equations systems with small parameter are of basic importance in kinetics chemistry because many biological laws and relations appear mathematically in the form of a ordinary differential equation systems. The kinetic equations which describe the performance of a chemical kinetics are governed by linear differential equations and a general analytical solution was successfully derived using differential equations theory. When modelling the kinetics of a composite chemical reaction, it is necessary to take into account all available information on the reaction mechanism. When we draw a more complex reaction mechanism, each and every arrow corresponds to a term in the differential equation, and the sign of the term depends on the direction of the arrow (O'Malley : 1991) . Differential equations systems derived from chemical kinetics must often be solved numerically. The following article is a detailed numerical method on how to use Matlab to numerically integrate sets of differential equations with small parameter forms of rate laws, and plot the solution as time-dependent concentrations. A critical evaluation of methods for the numerical solution of differential systems with small parameter suggests that the availability of more than one method is an important element in the numerical analyst's arsenal. Instead of allowing the program to integrate over the largest time increment consistent with the error parameters, we force it to compute and store the values of the variables each ϵ , where ϵ is a small number (Linß & Stynes: 2009).

Materials and methods

Consider three chemical reactions involving three substances:



Given the reactions represented in (1), how can we use numerical integration to solve for the concentrations of X, Y and Z for all combinations of rate constants k_1, k_2 , and k ?

A macroscopic model of this reaction assumes that the concentrations and reaction constants are well-defined. Furthermore, the concentrations vary deterministically and continuously (Vasil'eva & Butuzov : 1995). Assume that:

1. $k_1 = k_2 = \frac{1}{\varepsilon}$, the forward and reverse reactions involving substance X and Y are fast

$$\frac{1}{\varepsilon}$$

2. $k \ll \varepsilon$, the last reaction is slow.

The system of equations for concentration x and y has the form:

$$\begin{cases} \varepsilon \frac{dx}{dt} = -x + y^2 \\ \varepsilon \frac{dy}{dt} = 2x - 2y^2 - ky \end{cases} \quad (2)$$

If we denote the concentrations of substances X and Y by x and y . Instantaneous rate is the slope of a concentration versus time plot and is shown by the

differential equations: $\frac{dx}{dt}$ and $\frac{dy}{dt}$. The speed of a

reaction (1) is expressed as the change in concentration of a reactant or product over a certain amount of time.

To determine the numerical algorithm (Roos & Tobiska: 2008), we will use the Euler method on a well-specified range $[0, \tau_1]$.

$$\begin{cases} D^{s+1}v(t) = D^s v(t+T) - D^s v(t) \\ D^0 v(t) = v(t) \end{cases} \quad (3)$$

From the algorithm of Euler's method we obtain:

$$D^{s+1}v(t) = T^{s+1} \frac{d^{s+1}v}{dt^{s+1}} + O(T^{s+2}) \quad (4)$$

Suppose there are functions $\bar{u}(t), \bar{v}(t)$ that approximate the functions $u(t+T)$ and $v(t+T)$:

$$\begin{cases} u(t+T) \approx \bar{u}(u(t), v(t)) \\ v(t+T) \approx \bar{v}(u(t), v(t)) \end{cases} \quad (5)$$

We build the algorithm of the form:

$$\begin{cases} t_n = t_o + nT \\ u_{i+1} = \bar{u}(u_i, v_i) \approx u(t_{i+1}), \quad i = \overline{0, s} \\ v_{i+1} = \bar{v}(u_i, v_i) \approx v(t_{i+1}) \end{cases} \quad (6)$$

The algorithm consists in determining v_0 it under the conditions it u_0 is given so that the relationship (3) is true has the form (Miller & Shishkin : 1996) :

- The value u_0 is specified , v_0 is to be determined
- Consider the number of iterations: $l = 1$
- We consider initialization $v_0^{(1)} = v_0$
- For $u_0, v_0^{(l)}$, we get the values: $v_1^{(l)}, v_2^{(l)}, \dots, v_{s+1}^{(l)}$ (7)
- We introduce the notation: $\theta = (-1)^s D^{s+1}v_0^{(l)}$
- If θ it is small, the iteration is convergent
- if θ not small : $v_0^{(s+1)} = v_0^{(s)} + \theta$
- Increasing the value of l and returning to step four.

For $s = 0$ we get: $\theta = v_1 - v_0 \approx T \frac{dv}{dt}(t_0)$ (8)

For $s = 1$ obtain: $\theta = -v_2 + 2v_1 - v_0$ (9)

Results & Discussion

Using Euler's method for n steps and fixed pitch p (

$T = np$), we have implemented the values of functions \bar{u} and \bar{v} from relations (7).

Table.1: For $\varepsilon = 0,1$, $p = \frac{\varepsilon}{100}$, $n = 1$, we got the estimates

s	Soluția iterată y	Soluția asimptotică y
0	0.500000000	0.500000000
1	0.502038375	0.50211400
2	0.502021875	0.502016233
3	0.502021813	-
4	0.502021813	-

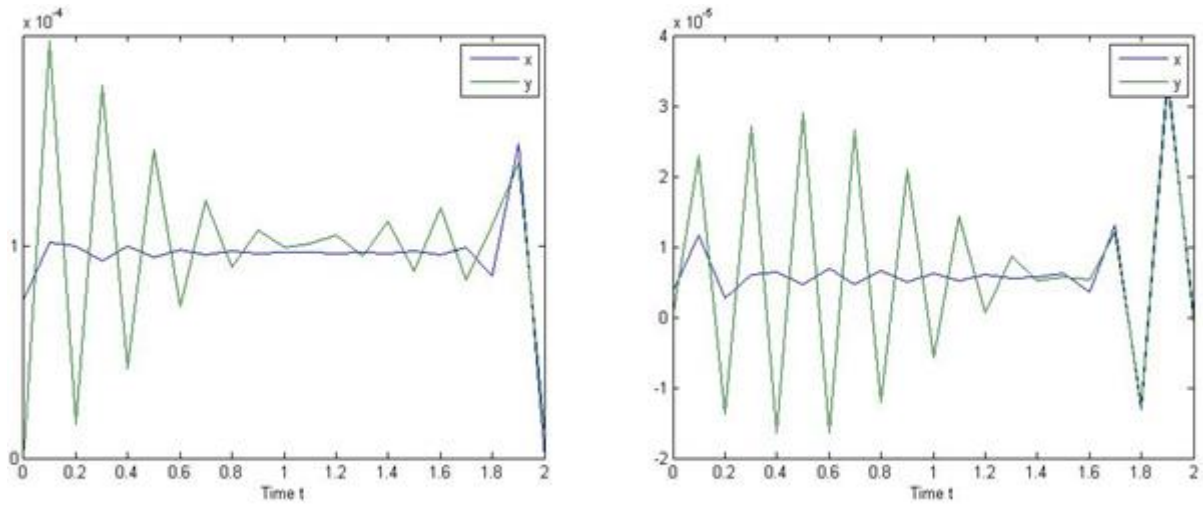


Fig.1: Simulations of system solutions (1) for $\epsilon = 0,1$.

Table.2: For $\epsilon = 0,1$, $p = \frac{\epsilon}{10}$, $n = 4$, we got the estimates

s	Soluția iterată y	Soluția asimptotică y
0	0.497775080	0.500000000
1	0.502056821	0.502014000
2	0.502024335	0.502016233
3	0.502024087	-
4	0.502024017	-

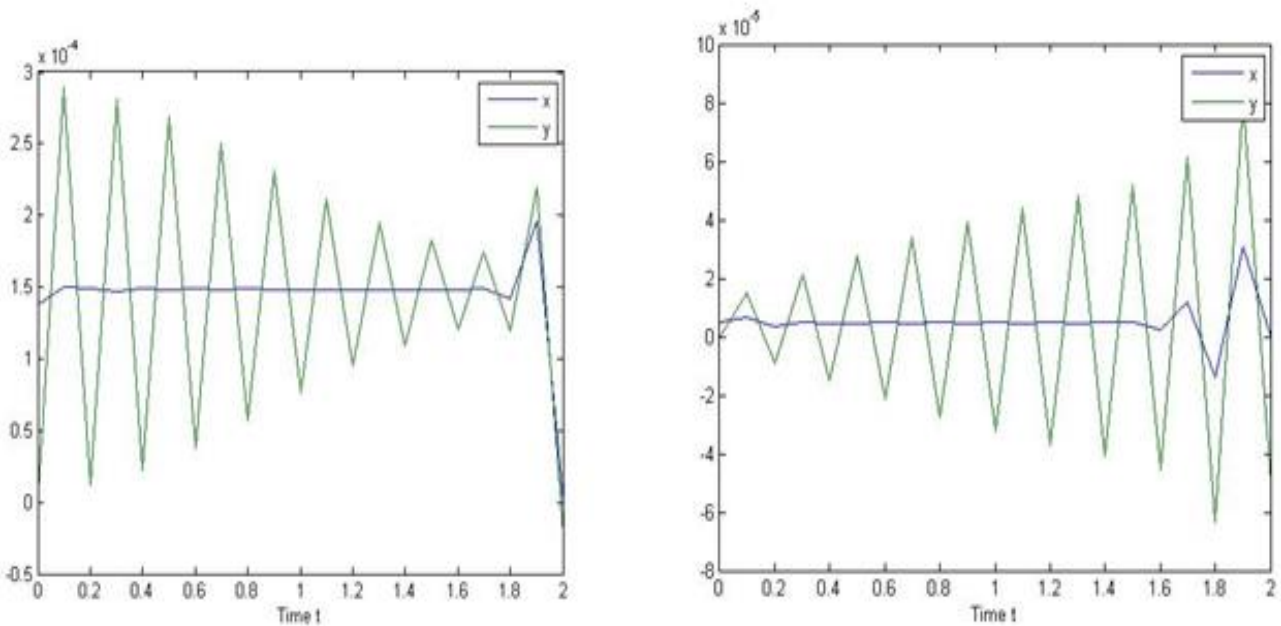


Fig. 2: Comparison of system solutions (1) for $\epsilon = 0,01$, in connection with changing the domain. Whatever small ϵ we take, from a transparent and exact solution of the simple model at $\epsilon = 0$, we abruptly face a far more complicated solution of a model that is just a little bit better.

Table .3: For $\epsilon = 0,01$, $p = \frac{\epsilon}{100}$, $n = 1$, we got the estimates

s	Soluția iterată y	Soluția asimptotică y
0	0.500000000	0.500000000
1	0.500200614	0.500201400
2	0.500200422	0.50200412

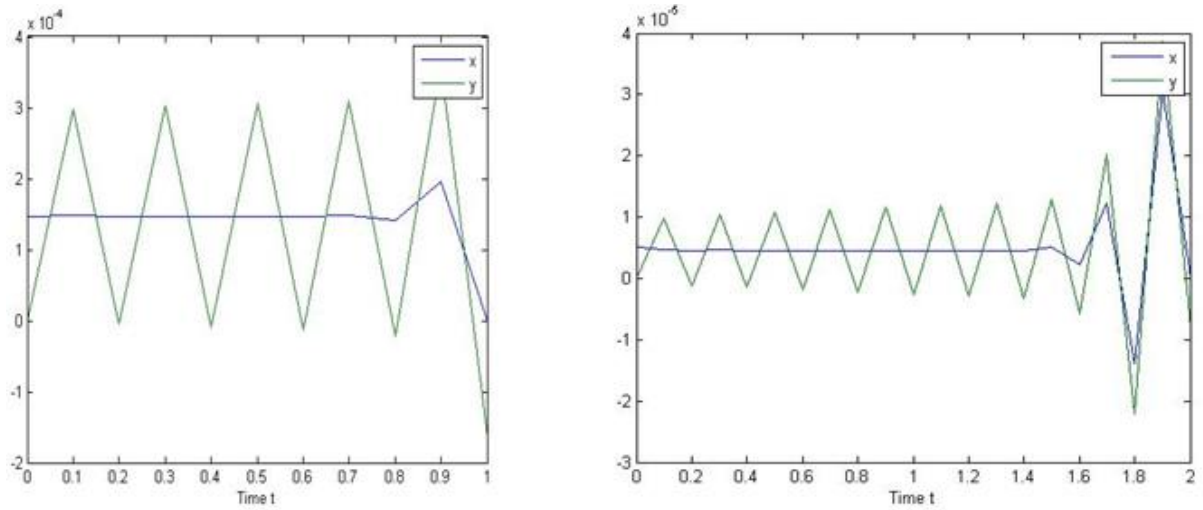


Fig.3: Simulation of system solutions (1) for $\epsilon = 0,001$. It is noticeable that for T quite large, we will have a rapid convergence. The smallness of ϵ is relative to the size of the solution domain.

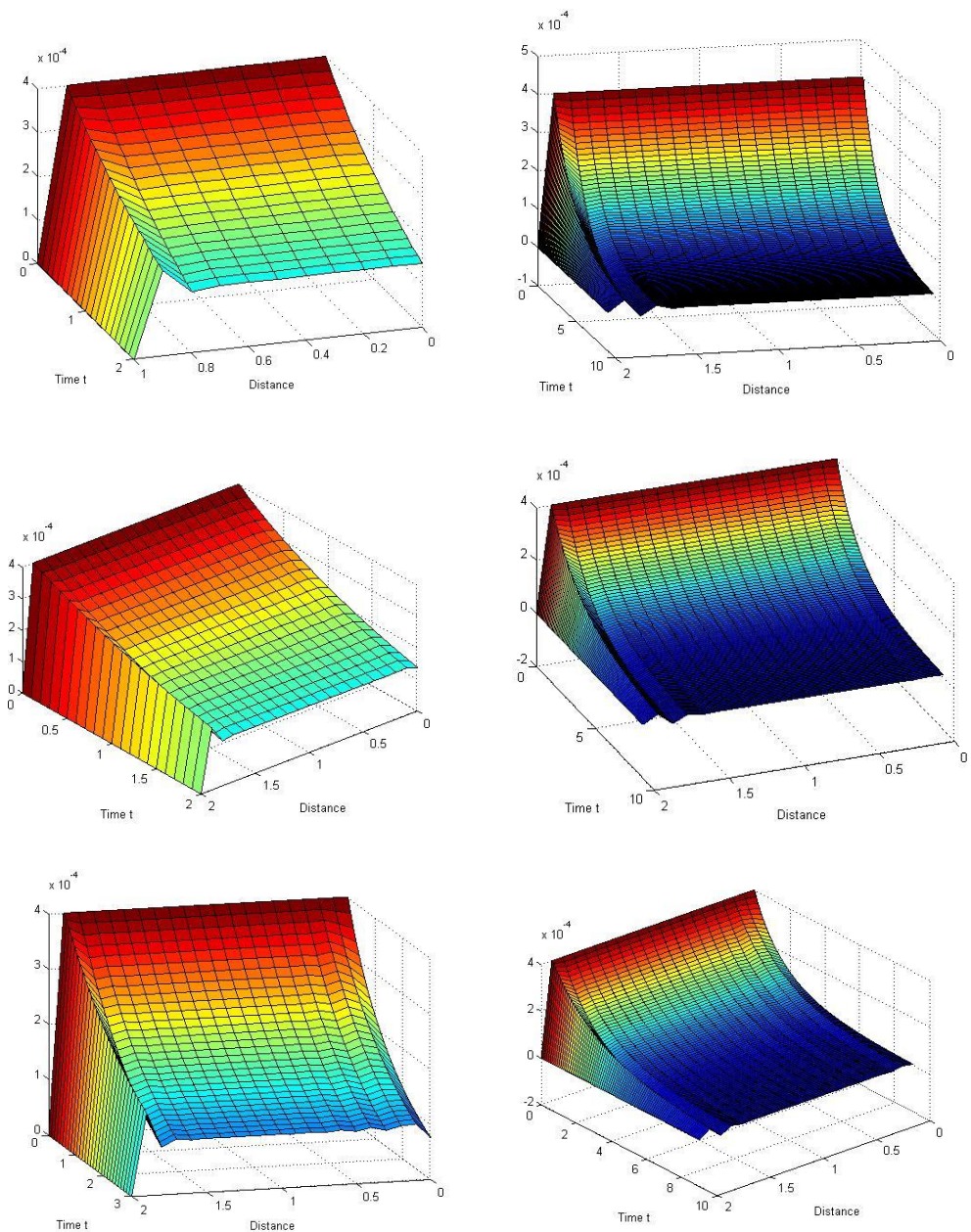


Fig. 4: 3D simulation of the "quick" solutions of the system (1) for different parameter ϵ . Of the 6 graphs, there is no significant difference in the behavior of the solution graphs.

Conclusions

Chemical kinetics deals with chemistry experiments and interprets them in terms of differential equations systems with small parameters. Chemistry has difficulty with developing their own conceptual framework of what a differential equation with small parameters really represents. We studied a system of differential equations with small parameter for chemical reactions. Solutions to ordinary differential equations cannot be determined uniquely without some outside condition typically an initial value or a boundary value. We used numerical methods to find approximate solutions to the system. All the equations system includes small parameter ε . We compared types of solutions graphically and observed that the solutions get closer to each other as $\varepsilon \rightarrow 0$. This property of the solutions suggests that the numerical method gives a very accurate approximation to the solution of our model. Simulation of the system of differential equations containing a small parameter depending on various values of $\varepsilon (0 < \varepsilon \ll 1)$ parameter can generate new work hypotheses work. We note that this work highlights how a simple mathematical model with small parameter can be used to predict the biologically relevant behaviors of a chemical reaction. We hope that the numerical simulations from our model can help to build a more efficient path to chemical discovery. Hopefully our article is a useful pedagogic tool for understanding the equations of chemical kinetics.

References

1. O'Malley Jr., R. E. Singular perturbation methods for ordinary differential equations, 1991, Springer-Verlag, New York.
2. Linß T., Stynes M., Numerical solution of systems of singularly perturbed differential equations ,2009 , Comput. Methods Appl. Math., 9: 165–191.
3. Vasil'eva A.B , Butuzov V.F. , Kalachev L.V., The Boundary Function Method for Singular Perturbation Problems, 1995 ,SIAM, Philadelphia, PA .
4. Roos H.G., Stynes M. ,Tobiska L., Robust Numerical Methods for Singularly Perturbed Differential Equations, 2008 ,Springer Series in Computational Mathematics, vol. 24. Springer, Berlin, 2nd edition .
5. Miller J. J. H, O'Riordan E. , Shishkin G. I., Fitted Numerical Methods for Singular Perturbation Problems, 1996, World-Scientific, Singapore.