

Mini-Projet: Traveling waves and spiral waves in excitable media : Belousov-Zhabotinsky

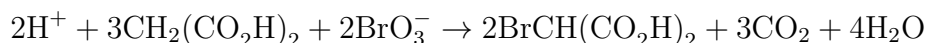
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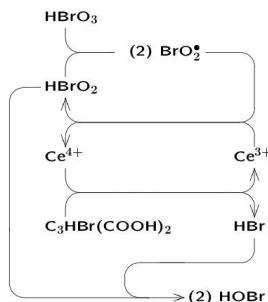
December 2018

1 Introduction

A Belousov-Zhabotinsky reaction, or BZ reaction, is a well-known chemical oscillation reaction and a classic example of non-equilibrium thermodynamics. It has many versions, the most common of which is the reaction of malonic acid by bromate in a dilute aqueous solution of sulfuric acid when the cerium is used as a catalyst.



In one version of the explanations for the mechanism of B-Z reaction, the total reaction consists of two processes A and B, the A process is an ion reaction of two electron transfer, and the B process involves free radical and single electron transfer. Bromide ion is a controlled species here : in the process A, the bromide ion is consumed to form a bromine element, which reduced the concentration of bromide ion. When the concentration is lower than the critical concentration, the process B mainly occurs, during which bromate ions oxidize metal ions and also form bromine. Then bromine elemental and high-valent metal ions oxidize the organic substrate to obtain reduced metal ions and bromide ions, so that the concentration of bromide ions increases, and the process A occurs again. Therefore, the system oscillates repeatedly between the A and B processes. Such oscillations in a closed system can last for thousands of times, and no reactants need to be replenished during the reaction, so such reactions provide great convenience for the study of chemical waves.



2 Traveling waves for the BZ reaction in 1D

2.1 Nature of the dynamical system

In this first time, we would like to concentrate on the 3 equations model, which is presented as below to show the travelling waves through time.

By default, we consider a 1D configuration of problem with homogeneous Neumann boundary conditions for a free-boundary condition and we set parameters :

$$\varepsilon = 10^{-2}, \quad \mu = 10^{-5}, \quad f = 3, \quad q = 2 \times 10^{-4},$$

and with diffusion coefficients :

$$D_a = 1/400, \quad D_b = 1/400, \quad D_c = 0.6/400$$

$$\begin{cases} \partial_t a - D_a \partial_x^2 a = \frac{1}{\mu}(-qa - ab + fc), \\ \partial_t b - D_b \partial_x^2 b = \frac{1}{\epsilon}(qa - ab + b(1 - b)), \\ \partial_t c - D_c \partial_x^2 c = b - c \end{cases}$$

At the code level, we use a typical discretization for second order derivative as :

$$\partial_x^2 y = \frac{2y^{(i)} - y^{(i-1)} - y^{(i+1)}}{dx^2}$$

To demonstrate this phenomena, we used **Radau5** methods to guarantee its numerical accuracy and with tolerance $tol = 10^{-6}$. The 11 time sample points are chose from $t = 0$ to $t = 5.5$. The result can be seen as Figure 1.

By same means, we show below three configuration of $a(x) - c(x)$ (resp. $b(x) - c(x)$ and $a(x) - b(x)$) for different instant. However, the remark should be made that this is not a phase plan, since the phase plan usually represents the link between two non-spatial 1 dimension variables : $a(t) - c(t)$. Yet, the Figure 2 shown here has the aim to demonstrate a stable travelling waves configuration for those three reactants.

From the third image from Figure 2, we can also conclude non-coexistence between substance a and b .

We can see from Figure 3 the travel velocity is not uniform during time : for the three equations model, the velocity of the waves increases in general and tends to stabilize at the end of the reaction. That phenomena responses quiet well to our intuition : at the beginning of the reaction, the initial configuration is trying to converge to the stable one, however, those chemical reactants were just too concentrated at $x = 0$, the spatial concentration diffusion dominates the system. Afterwards, the reaction being on, a so called "limit cycle" appears spatially. (Figure 2)

We can meanwhile observe, the travelling speed is not necessarily the same. The substance b travels faster than the others, and a travels most slowly. We may imagine the chemical mechanism : to obtain a we should have a relatively high concentration of c . And to product c we might need b as the raw material.

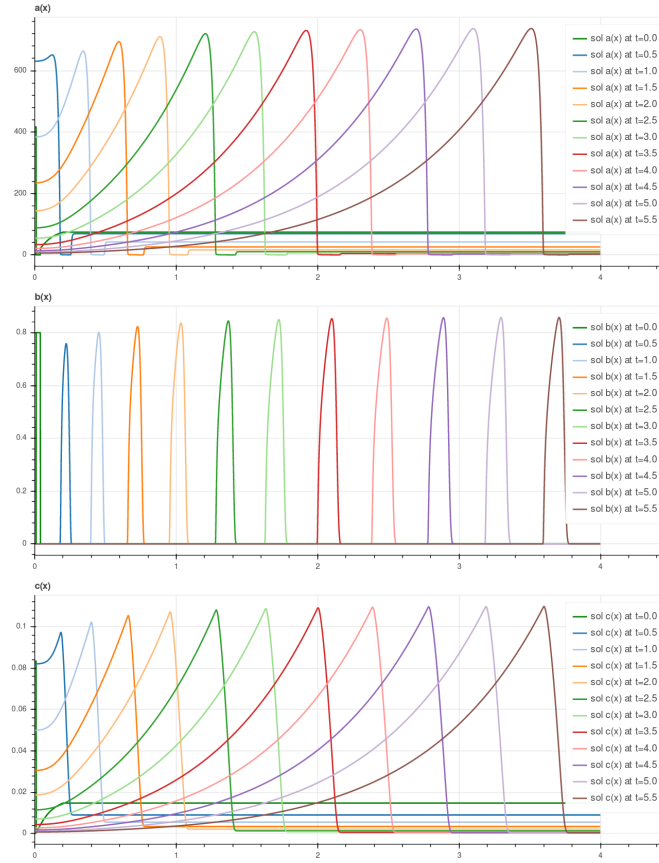


Figure 1 – Travelling waves representation for, respectively a, b and c

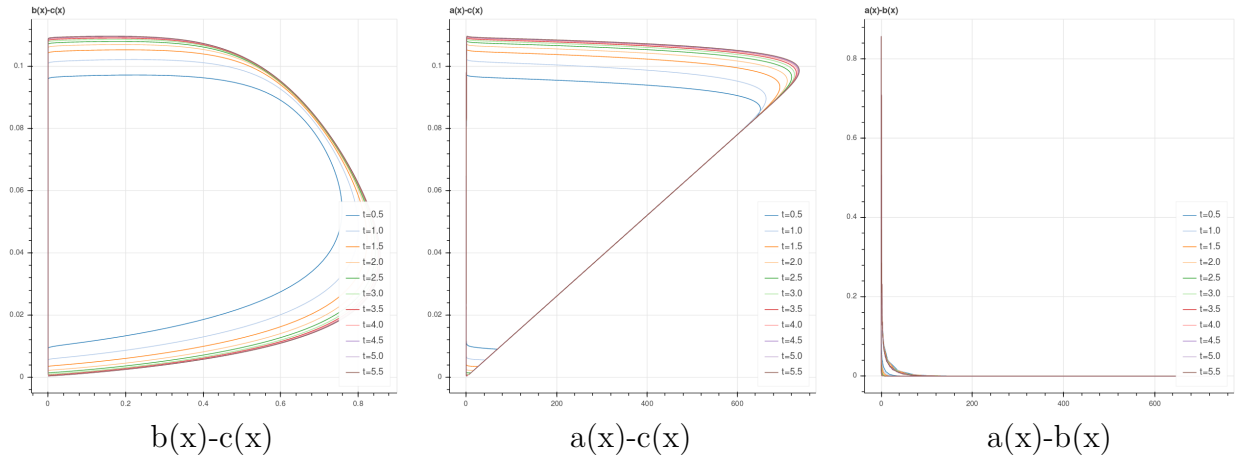


Figure 2 – Link between spatial concentration for different reactants, respectively a, b and c

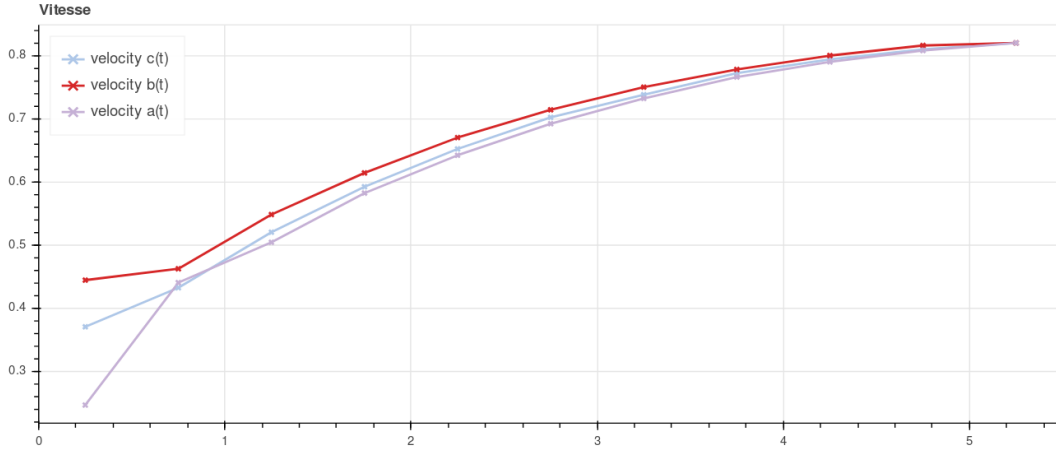


Figure 3 – Waves' speed for a, b and c

2.2 Competition between different Numerical resolution methods

We show the dynamical system which can be also represented as :

$$\begin{cases} \partial_t a - D_a \partial_x^2 a = \frac{1}{\mu}(-qa - ab + fc), \\ \partial_t b - D_b \partial_x^2 b = \frac{1}{\epsilon}(qa - ab + b(1 - b)), \\ \partial_t c - D_c \partial_x^2 c = b - c \end{cases}$$

$$\underbrace{d_\tau \begin{bmatrix} a \\ b \\ c \end{bmatrix}}_{\text{reaction}} - \underbrace{D \cdot \partial_x^2 \begin{bmatrix} a \\ b \\ c \end{bmatrix}}_{\text{diffusion}} = \underbrace{\begin{bmatrix} \frac{1}{\mu}(-qa^{eq} - a^{eq}b + fc) \\ \frac{1}{\epsilon}(qa^{eq} - a^{eq}b + b(1 - b)) \\ b - c \end{bmatrix}}_{\Omega}$$

$$\Omega = \underbrace{\begin{bmatrix} 0 \\ \frac{1}{\epsilon}(qa^{eq} - a^{eq}b + b(1 - b)) \\ b - c \end{bmatrix}}_{\mathcal{A}} + \underbrace{\frac{1}{\mu} \begin{bmatrix} -qa^{eq} - a^{eq}b + fc \\ 0 \\ 0 \end{bmatrix}}_{\mathcal{B}}$$

where D is $[D_a, D_b, D_c]^T$. Therefore, we distinguish two parts of the system. In the first place, we can execute a splitting to separate the diffusion process and reaction process. For a second thought, we could simplify the problem by a singular perturbation (by preserving only the part \mathcal{A} and supposing that a is always equal to a certain a^{eq}), which leads us to a 2-equations system.

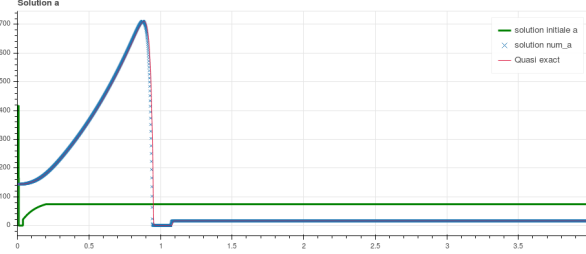
Yet, it could be useful to mention that the splitting strategy is no more the same one of PC5 where we had no diffusion term and the splitting was about the rigid term \mathcal{B} and mild term \mathcal{A} . Again, during PC5, we used Radau5, implicit method to guarantee the precision for \mathcal{B} and explicit DOPRI for \mathcal{A} to take advantage of its mild characteristic.

However, the splitting we have applied here is to separate reaction and diffusion. And the splitting is "interwoven". In Lie- Reaction-Diffusion method, we integrate at first the reaction process during $[t_i, t_{i+1}]$, then the diffusion process during $[t_i, t_{i+1}]$ by considering $[a(t_i), b(t_i), c(t_i)]$ as the initial datum. Therefore, contrarily to what we have applied during PC5 by integrating \mathcal{A} (or \mathcal{B}) and then \mathcal{B} (or \mathcal{A}), our strategy here is to integrate separately the diffusion and reaction process within a δt , then the interaction between integrator lies on the choice of initial datum for t_i .

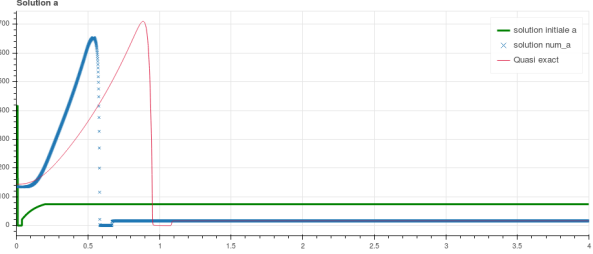
2.2.1 Splitting

What is the limit time step length to apply a splitting strategy ?

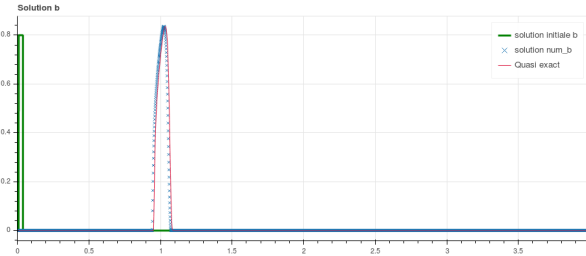
We set manually $t_{end} = 2.0$, for that we would like to compare two results with different time steps at the end of 2 seconds. We apply in the first time the Strang splitting to see the influence of the time step on the accuracy of splitting.



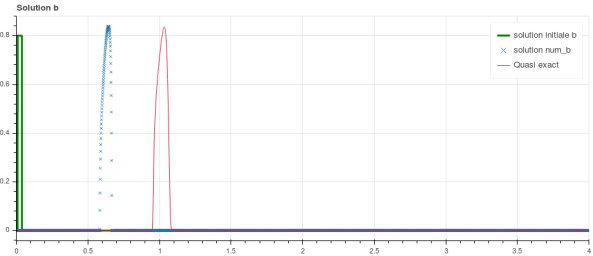
Solution for $a(x)$



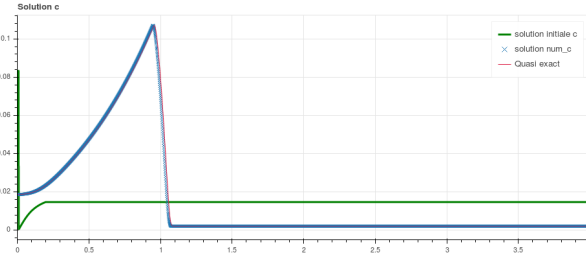
Solution for $a(x)$



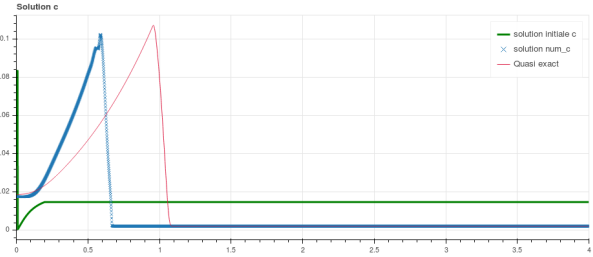
Solution for $b(x)$



Solution for $b(x)$



Solution for $c(x)$



Solution for $c(x)$

$$||Error_a|| = 34.72$$

$$||Error_b|| = 0.05821$$

$$||Error_c|| = 0.003355$$

$$\Delta t = 0.01$$

$$||Error_a|| = 359.8$$

$$||Error_b|| = 0.2977$$

$$||Error_c|| = 0.05389$$

$$\Delta t = 0.1$$

For this three equations model, we can see if we set time step length $\Delta t < 0.1$, the numerical splitting method deviates three variables completely, solution being unacceptable.

What errors for which method ?

To perform an comprehensive error analyze we fix the ending time of the reaction at 2s. We use the three equations model and 4000 points for spatial discretization. Since the magnitude of different reactants is not the same, we use relative error in the aim of a better image representation. This relative notation comes from the ratio of the norm $(\int_{\Omega} |\cdot|^2 dx)$ between the error and the variable itself.

Here, we list four error analyzes for different splitting strategies : Strang diffusion-reaction-diffusion, Strang reaction-diffusion-reaction, Lie reaction-diffusion and Lie diffusion-reaction.

Figure 4 shows us that even though the Strang splitting is of second order. But when time steps become large, Strang splitting suffers from order reduction and yield to a first order method.

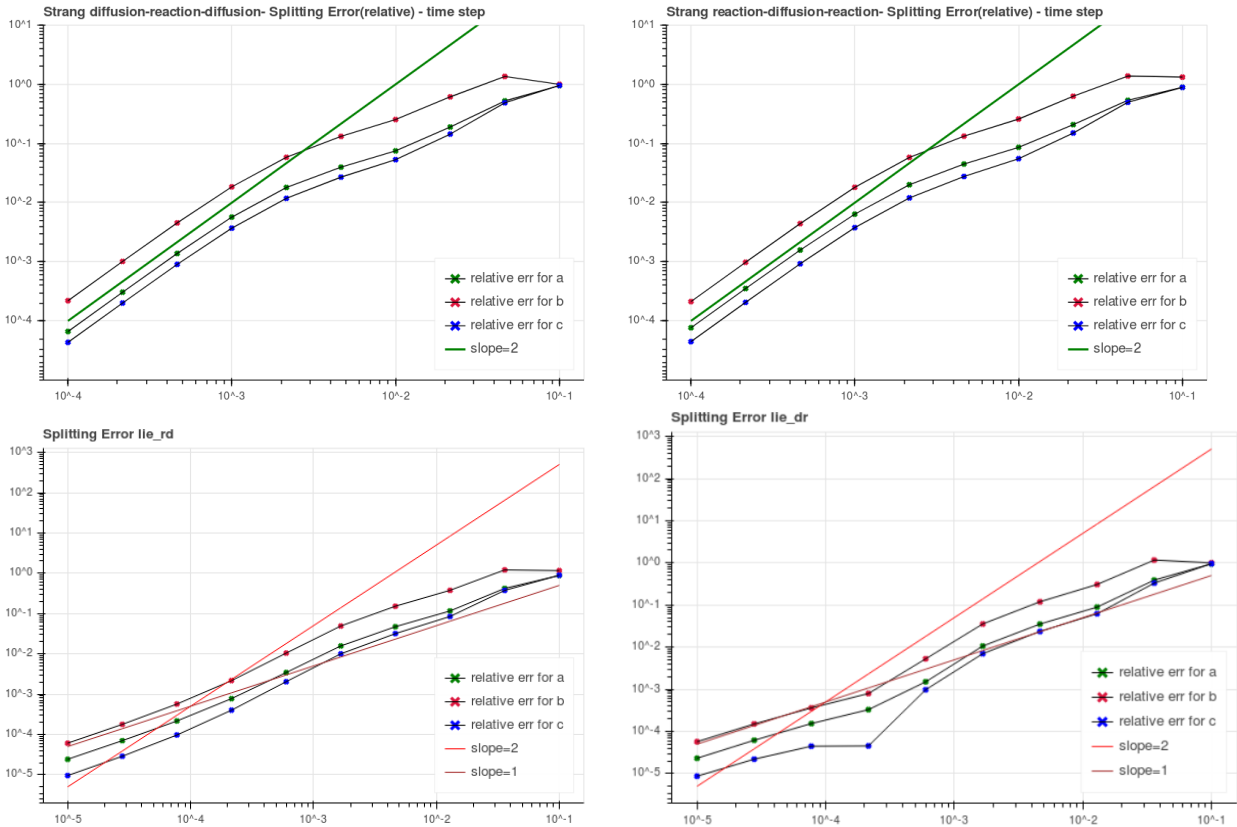


Figure 4 – Error Analyze : top left : Strang_drd; top right : Strang_rdr; bottom left : Lie_rd; bottom right : Lie_dr. Green line : slope 2, Red line : slope 1. Axis X : length of time steps. Axis Y : relative error

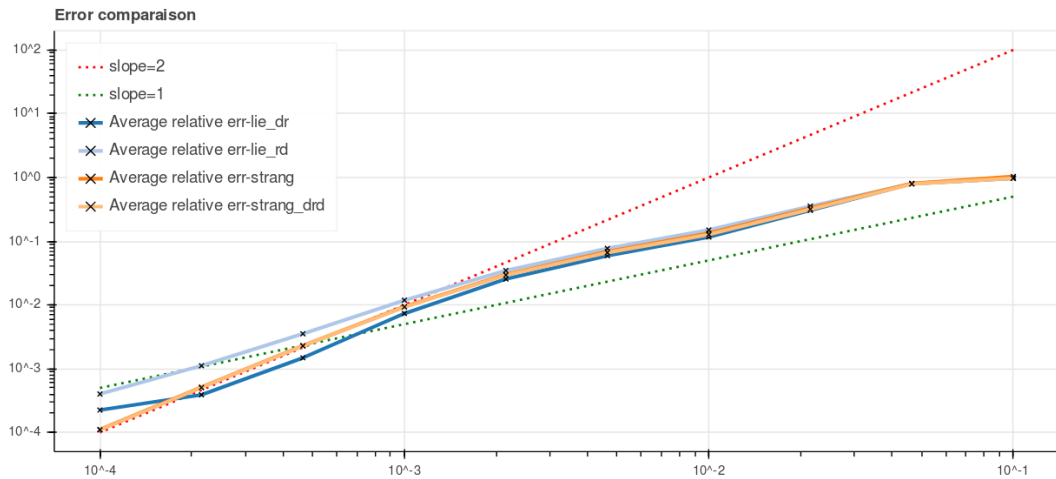


Figure 5 – Comparison of average error from different splitting strategies

2.2.2 Singular perturbation - 3 equations system VS. 2 equations simplified system

By singular perturbation, we suppose the concentration of a depends explicitly on those of b and c . That is because μ is so small ($\frac{1}{\mu} = 10^5$) that the quantity of $(-qa - ab + fc)$ should not be large (in the following, we suppose $(-qa - ab + fc) = 0$ by singular perturbation), or else the variance of a would be violent and it will be contradictory to reality.

Two equations system can be shown as :

$$\begin{cases} \partial_t b - D_b \partial_x^2 b = \frac{1}{\epsilon} \left(\frac{fc(q-b)}{q+b} + b(1-b) \right), \\ \partial_t c - D_c \partial_x^2 c = b - c \end{cases}$$

To compare the effect of singular perturbation, we use Radau5, tolerance being 10^{-6} for both systems to guarantee that the only difference is due to the choice of models.

We takes two time as example $t = 1.0$ and $t = 2.0$ to observe the difference between 2 and 3 equations systems.

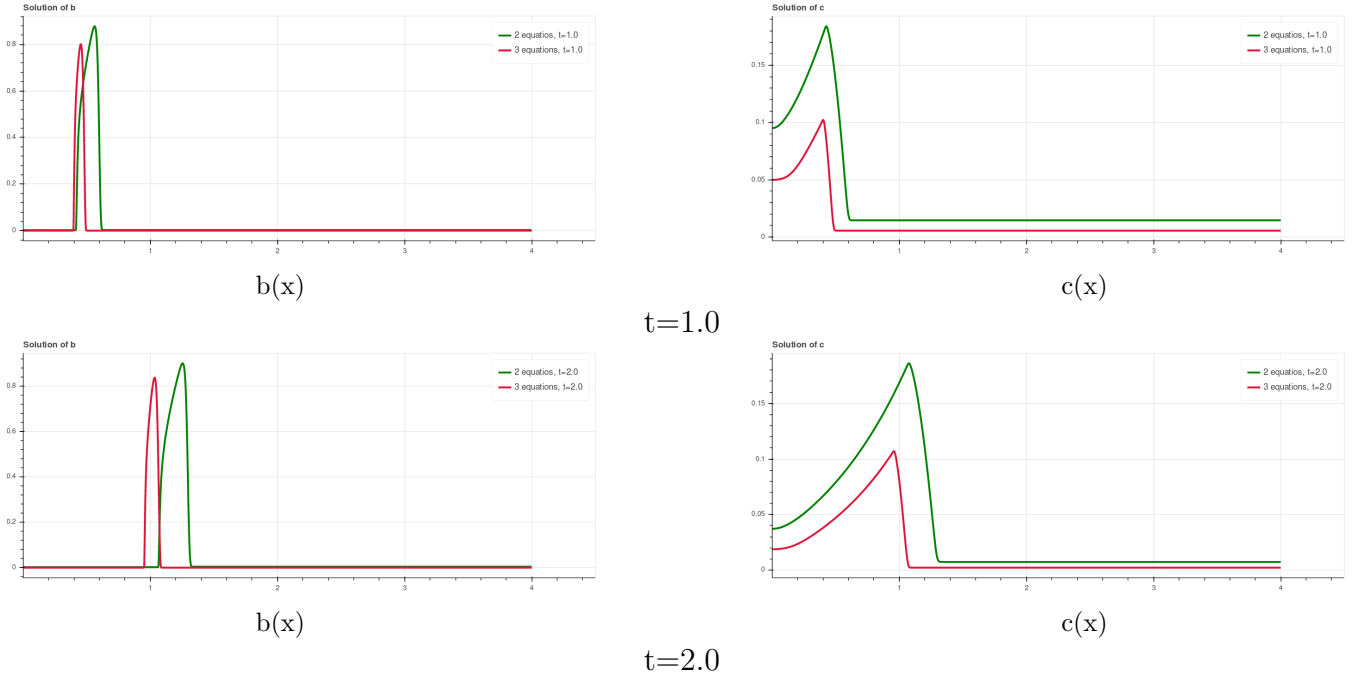


Figure 6 – Image representation of two system when $\mu = 10^{-5}$

In the case above parameter μ is set $\mu = 10^{-5}$. As discussed in the PC5, if μ becomes smaller, we may expect that 2-equation dynamics approaches more to the 3-equations system. We have changed μ to 10^{-9} to demonstrate this phenomena and visually we have :

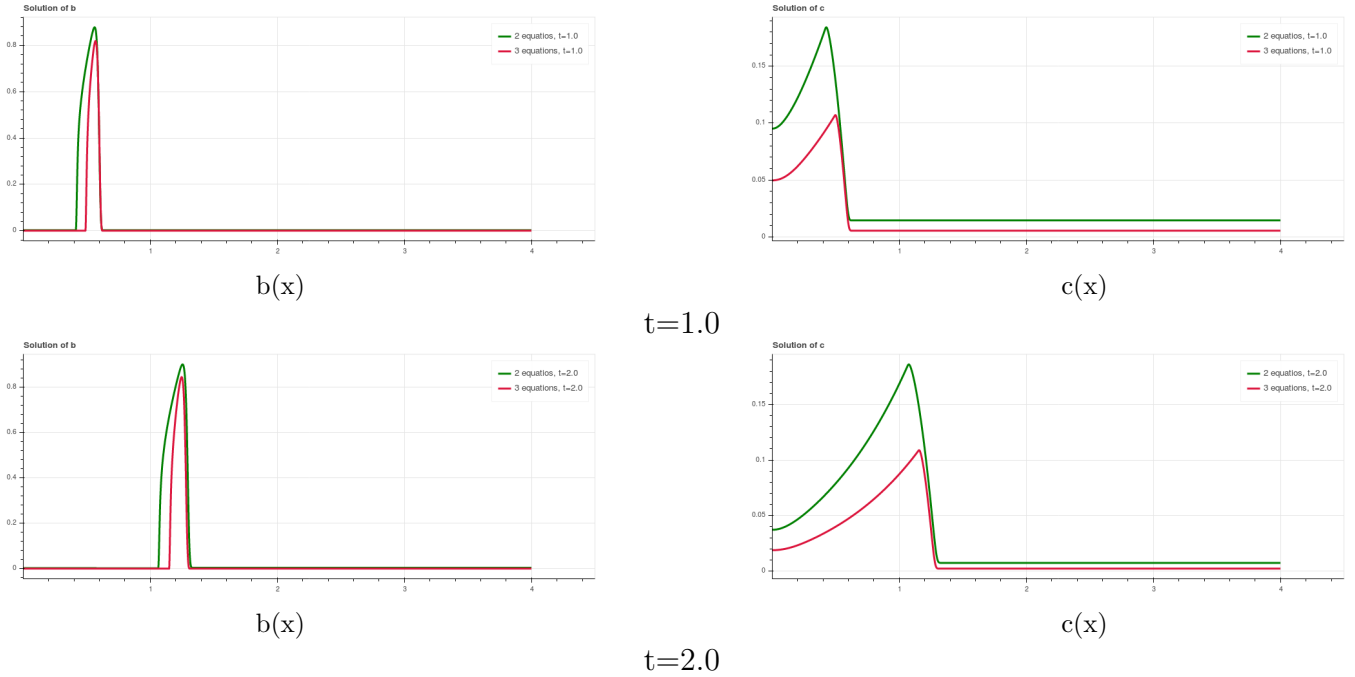


Figure 7 – Image representation of two system when $\mu = 10^{-9}$

Effectively, the performance of 2-equations modelization is more convincing when μ becomes smaller.

However, when we want to show the travelling waves with time, there is another difference between the model of 3 equations and 2 equations.

To show this difference clearly, we used also Radau5 method with tolerance $tol = 10^{-6}$. We changed the time duration from $t = 0$ to $t = 20$. The result can be seen as Figure 8 (we show only the wave of c).

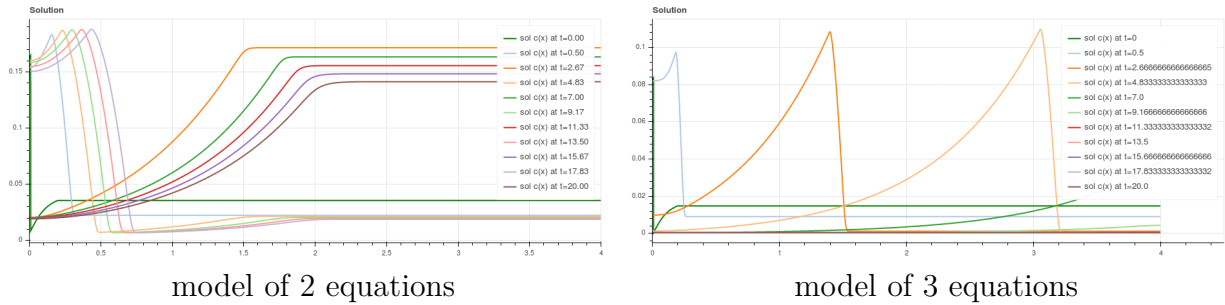


Figure 8 – The different phenomena of these two models

It's quite interesting to observe that for the 3 equation model, we will see clearly **A** travelling wave. That's to say the wave won't show up again; but for the 2 equation model, the wave oscillates. With the time, we could observe that the chemical waves appear again and again.

We studied the phase portraits of $b(t)$ and $c(t)$, choosing the point at $x=1$, and we could see clearly the limit cycle, so comes the oscillation.

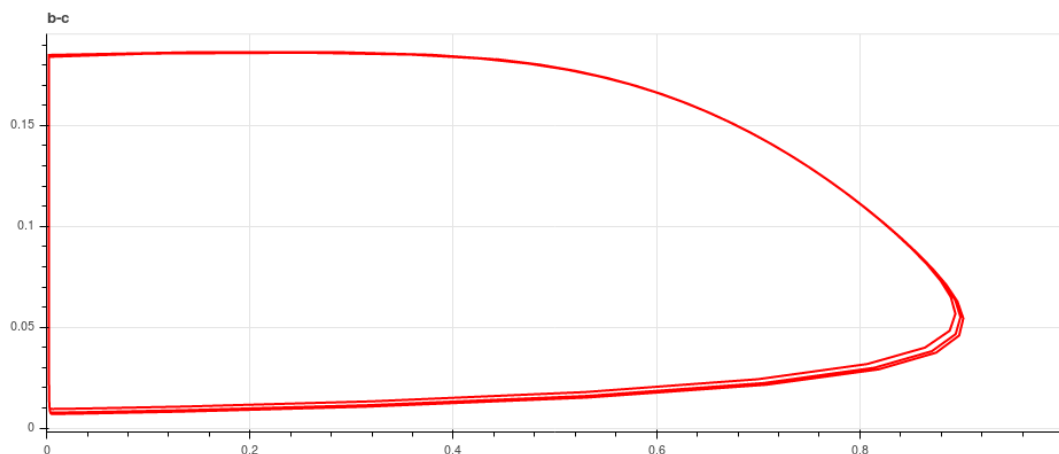


Figure 9 – Phase portraits of $b(t)$ - $c(t)$ at the point $x = 1$

2.3 Parallelization

The splitting method divides the computation into reaction and diffusion so that when we calculate the reaction part the influence of time doesn't need to be considered although we use the result of the diffusion part. Therefore, for each time of computation, the space can be divided into several independent parts and parallel computing is possible. It gives us the inspiration to increase the speed of computation.

3 Conclusion

In this Mini-Projet, we have mainly studied the traveling waves in the system Belousov-Zhabotinsky with the model of 3 equations and 2 equations in one dimension. We could observe the oscillating wave which accords with the mechanism of this system.

In the case that we have studied, the implicit Radau5 has its own advantages in terms of computation cost. However, even for a 2D problem, we will increase immensely the difficulty for a numerical resolution, for that we need to discretize the space with N^2 points. To inverse an matrix, the cost is at least $O(n^{2.373})$ (Optimized CW-like algorithms). Discretization being squared, cost will increase to $O(N^{4.7})$. Not to mention a high demand for memory to store a sparse matrix.

The splitting offers us with a possibility to solve the problem partially with explicit method (for non-rigid dynamics). And the matrix multiplication can be easily paralyzed because of the separation of diffusion and reaction, which will increase the speed of computation substantially.

4 Reference

- [1] S. Descombes, T. Dumont, and M. Massot. Operator splitting for stiff nonlinear reaction-diffusion systems : Order reduction and application to spiral waves. In *Patterns and waves(Saint Petersburg,2002)*, pages 386-482. AkademPrint, St. Petersburg, 2003.
- [2] I.R Epstein and J.A. Pojman. *An Introduction to Nonlinear Chemical Dynamics*. Oxford University Press, 1998. Oscillations, Waves, Patterns and Chaos.

- [3] R.J. Field, E. Koros, and R.M. Noyes. Oscillations in chemical systems. II. Thorough analysis of temporal oscillation in the bromate-cerium-malonic acid system. *J. Amer. Chem. Soc.*, 94(25) :8649-8664, 1972.
- [4] P. Gray and S.K. Scott. *Chemical Oscillations and Instabilities*. Oxford Univ. Press, 1994.
- [5] W. Jahnke, W.E. Skaggs, and A.T. Winfree. Chemical vortex dynamics in the Belousov-Zhabotinsky reaction and in the two-variable Oregonator model. *J. Phys. Chem.*, 93 :740-749.

