Vol. 39 (2008) *ACTA PHYSICA POLONICA B* No 5

ONE DIMENSIONAL SIGNAL DIODES CONSTRUCTED WITH EXCITABLE CHEMICAL SYSTEM*

Yasuhiro Igarashi[a†], Jerzy Górecki[a,b], Joanna N. Górecka[c]

[a]Institute of Physical Chemistry, Polish Academy of Sciences
Kasprzaka 44/52, 01-224 Warsaw, Poland

[b]Faculty of Mathematics and Natural Sciences, College of Sciences
Kardynał Stefan Wyszyński University
Dewajtis 5, 01-815 Warsaw, Poland

[c]Institute of Physics, Polish Academy of Sciences
Al. Lotników 36/42, 02-668 Warsaw, Poland

(Received January 31, 2008)

Excitable chemical system can process information coded in excitation pulses. Here we discuss the simplest realization of a chemical signal diode that transmits pulses in one direction only. The construction of such diode just requires a geometrical combination of three areas characterized by different excitability. The proposed construction of chemical signal diode has been tested in numerical simulations and verified in experiments with ruthenium (Ru) catalyzed Belousov–Zhabotinsky (BZ) reaction.

PACS numbers: 05.45.–a, 05.70.Ln, 89.75.Kd, 82.40.Ck

1. Introduction

Information processing with excitable media is one of hot topics in unconventional (non von-Neumann type) computing. It is widely known that excitable chemical media play important roles in information processing in real living organisms [1]. From this point of view, it seems interesting to answer the following questions:

1. *What are the minimum requirements to build a device that executes a given information processing function?*

* Presented at the XX Marian Smoluchowski Symposium on Statistical Physics, Zakopane, Poland, September 22–27, 2007.

† igar@ichf.edu.pl

2. *What are the relationships between functions typically performed in living organisms and the geometrical structures of the excitable medium?*

Information processing with excitable media can be classified as "reaction-diffusion computing" [2]. The time evolution of the medium is described by a complex nonlinear dynamics involving reaction (local kinetic term) and transport of reagents (described with the diffusion operator). An "excitation" can be defined as a rapid change of medium state (*e.g.* concentration of a selected reagent) stimulated by a small perturbation, and the spatial propagation of this excitation is called a "pulse" or a "propagating wave". Medium's excitability can be controlled by adjusting parameters in kinetic term. According to their values, the medium is classified as excitable, sub-excitable, or non-excitable.

A chemical signal, associated with the existence of a pulse or a series of pulses carries information. Therefore, information processing is based on the dynamics of medium and on interaction of pulses. By geometric combination of excitable and sub (or non)-excitable media, a required type of interactions between pulses can be forced and thus the information coded in pulses can be processed in the required way. It means that each geometrical structure of an inhomogeneous excitable medium defines its own information processing function. Recent years have brought a number of interesting results in the field of chemical pulse based computing. The signal processing devices such like logical gates [3, 4], pulse coincidence detectors [5], signal filters [6, 7], direction and distance detectors [8], and many others has been described and tested experimentally. In this paper, we are concerned with the realization of the signal diode with a chemical excitable media: one of the most fundamental devices for information processing. We focus our attention on showing the minimum conditions required for unidirectional signal transmission.

Of course, in order to obtain unidirectional signal transmission, the symmetry of the system should be broken. The conventional structure of a chemical signal diode is shown in Fig. 1(a) [9, 10] where the black areas are excitable and the white ones are non-excitable.

In the two dimensional system, two discrete levels of excitability are embedded on the medium. An asymmetrical junction is introduced with a rectangular active channel on one side (A) and a triangular active channel on the other (B). A non-excitable gap lies between them. It can be shown [9, 10] that the gap width between the tip of the triangle and the side of the rectangle can be selected such that:

1. An excitation pulse from channel A gives sufficient perturbation to the triangle tip to generate an excitation, and this excitation pulse propagates on channel B.

2. The strength of excitation pulse propagating from channel B towards A significantly decreases while propagating through this gap and the consequent perturbation introduced at the side of channel A is too small to generate an excitation. Therefore, no pulse propagates on channel A.

As the result, the asymmetrical junction illustrated in Fig. 1(a) transmits pulses in one direction only (from A to B). This construction of the chemical signal diode is generic (it can be applied for any excitable chemical system). Although the medium is composed of regions with only two types of excitability, two dimensional structures are required for diode realization.

In 2001, Tóth and her collaborators showed that the chemical signal diode can be constructed in one-dimensional systems (Fig. 1(b)) [11]. They demonstrated that parameters of a triangular excitability profile can be adjusted such that pulses of excitation are transmitted in one direction only. In Fig. 1(b) pulses from channel B are not transmitted to left, but those which arrive from channel A can propagate through to the channel B. In this case, the number of spatial dimensions is reduced to one but this realization requires a medium with continuously varying excitability.

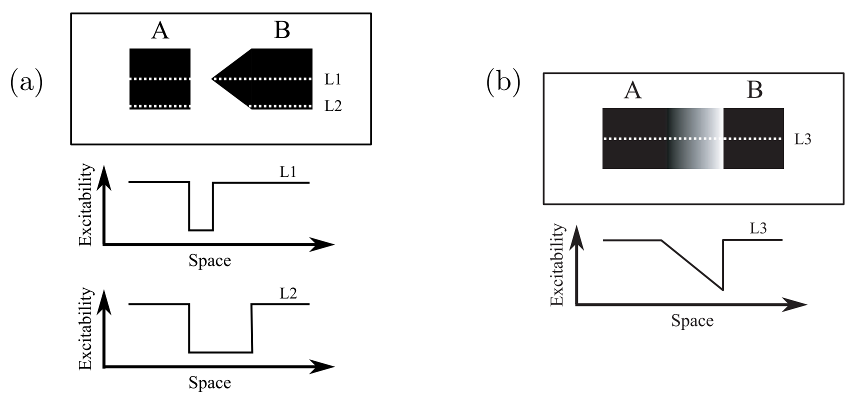


Fig. 1. Structures for diode realizations concerned in previous studies. Black, gray, and white regions represent excitable, sub-excitable, and non-excitable field. Spatial profiles of excitability along dashed lines(L1, L2, L3) are shown below.

Recently we have found yet simpler construction of the diode [12]. Unlike previous studies, our structures just require three different levels of excitability. The excitability in each of these three areas is constant and the system is one dimensional. As first case, we consider symmetrical inputs and the asymmetry in the order of appearance of non-excitable gaps that form the diode. However, the diode can be yet simpler if the excitability levels of input channels are asymmetrical. As the second example we discuss a new construction of the diode that has just a single excitable gap. We have confirmed that both suggested realizations of a chemical signal diode actually work using numerical simulations based on Oregonator model [13] and experiments with Ru-catalyzed BZ reaction.

2. Simulation method

In simulations, we used three variable Oregonator model, adopted for the photosensitive Ru-catalyzed BZ reaction [13],

$$\varepsilon_1 \frac{\partial u}{\partial t} = u(1-u) - w(u-q) + D_u \nabla^2 u \,, \tag{1}$$

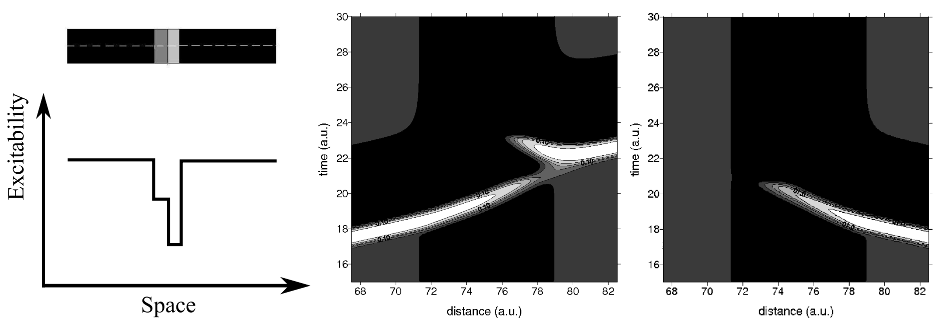
$$\frac{\partial v}{\partial t} = u - v \,, \tag{2}$$

$$\varepsilon_2 \frac{\partial w}{\partial t} = \Phi + fv - w(u+q) + D_w \nabla^2 w \,, \tag{3}$$

where u, v and w are dimensionless concentrations of $HBrO_2$, Ru(4,4′-dm-bpy)$_3^{3+}$, and Br^-, respectively. The units of space and time are dimensionless and they have been chosen to scale the reaction rates and the diffusion coefficient $D_u = 1$. We have neglected the diffusion of the Ru-catalytic complex because it is much smaller than that of the other reagents. For simplicity we set $D_w = 1$. The parameter Φ represents the rate of bromide production caused by illumination and it is proportional to the applied light intensity. Br^- is an inhibitor of Ru-catalyzed BZ reaction so the regions with low illumination level are excitable and those where illumination is high are not. Therefore, by adjusting a local value of Φ, we can create regions with required level of excitability. The values of the other parameters, q, ε_1 and ε_2 have been selected as 0.002, 0.08 and 0.00097, respectively. In numerical simulations, we considered two types of Oregonator models with $f = 1.12$ and $f = 2.12$.

First, chemical signal diode composed of double barrier stripes was studied. Its structure is illustrated in Fig. 2(a). Two excitable channels are separated by a sub-excitable barrier stripe (in the left) and a non-excitable one (in the right). The equations (1)–(3) have been numerically solved in one spatial dimension that corresponds to the position of the white dashed line in Fig. 2(a). We have used the 4-th order Runge–Kutta method for the chemical kinetics and the explicit Euler algorithm for diffusion. One-dimensional grids of 4 000 points and the spatial and temporal steps of integration equal to 0.075 and 0.00005, respectively, were used. No-flow boundary conditions have been applied at the ends of the system. The pulses are initiated by setting the value u to 0.4 on two grid points at one of the ends of the grid.

Figs. 2(b), 2(c) illustrate the space-time plots of central domain. It can be seen that an excitation coming into the sub-excitable barrier first and next into non-excitable one is transmitted (Fig. 2(b)), whereas the one propagating in the opposite direction is stopped (Fig. 2(c)). One can also see that the excitation splits after crossing the barriers (around $t = 23$ in Fig. 2(b)). In the considered kinetic term, the pulse propagating backwards dies in the non-excitable barrier and it does not influence the work of diode. This pulse splitting phenomenon may be used in other functions (*e.g.* generator of periodic train of pulses [14]).



(a) (b) (c)

Fig. 2. (a): The diode structure (1), the description is the same as Fig. 1. The barriers are formed by the 41 grid points interval with $\Phi = 0.03$ (sub-excitable, dark-gray part) and 41 grid points interval with $\Phi = 0.045$ (non-excitable, gray part). The excitable channels (black regions) are characterized by $\Phi = 0.008$. The calculations has been performed for $f = 1.12$. (b) and (c): space-time plot of wave propagation over the central barrier region. White domain corresponds to a high concentration of u and so it represents a propagating excitation.

We checked the working range of barrier stripe widths. The results are summarized in Fig. 3. The reaction parameters were $f = 2.12$, $\Phi = 0.0007$ for the excitable channel, $\Phi = 0.02$ for sub-excitable barrier, and $\Phi = 0.01$ for non-excitable one. The calculations indicate that the width of non-excitable barrier is important and that it has to be selected with high precision. For the selected parameters above, the diode behavior is observed only when the width of non-excitable barrier is within 3.075 and 3.3 distance units. On the other hand, if the width of non-excitable barrier is properly selected, the construction of diode is quite tolerant of the width of the sub-excitable barrier (in our case the diode function is observed within 2.0 and 15 distance units).

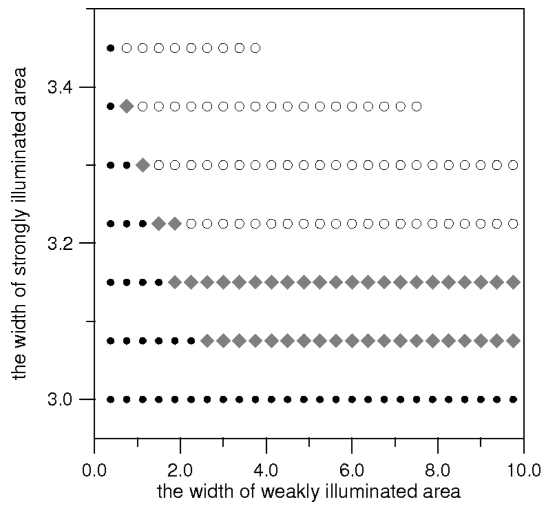


Fig. 3. The function performed by two barrier system as the function of widths of sub-excitable barrier ($\Phi = 0.01$), and non-excitable one ($\Phi = 0.02$). Empty circles correspond to combinations of widths for which the system annihilates all pulses, dots denote transmission in both directions, diamond represent the signal diode.

Next, the chemical signal diode composed of a single barrier stripe was examined. Here non-excitable barrier stripe lies between two excitable channels characterized by different excitability levels, as illustrated in Fig. 4(a). Equations (1)–(3) have been numerically solved in one spatial dimension that corresponds to the white dashed line in Fig. 4(a). Similarly to Figs. 2(b), 2(c), Figs. 4(b), 4(c) illustrate the time evolution of the central domain in the form of space-time plots. In this case, the excitation coming from the sub-excitable channel is transmitted (Fig. 4(b)), whereas the one in opposite direction just disappear (Fig. 4(c)).

More detailed investigation on the range of parameters for which the diode action appears is illustrated in Fig. 4(d). It summarizes results of simulations for the propagation in the diode where the value of Φ in the left input channel is given on the horizontal axis, the value of Φ in the gap is on the vertical axis and the right input channel of the diode is characterized by $\Phi = 0.0065$. Gray dots show the cases where the gap is not penetrable, the empty circles denote bi-directional propagation. The triangles mark sets of parameters where diode function is observed. The tip of the triangle marks propagation direction. It can be seen that the transmitting direction (*i.e.* from highly excitable input channel to excitable one ore *vice versa*) depends on the parameters of the system and it can be reversed by the change in their values in a narrow range.

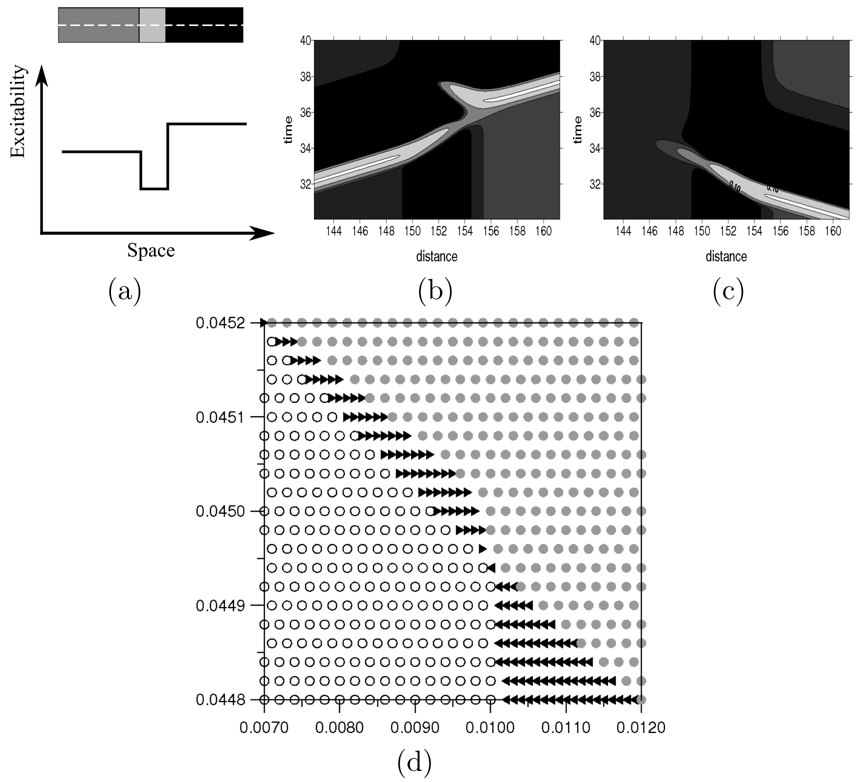
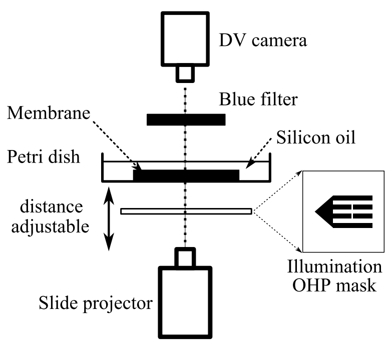


Fig. 4. Diode structure(2), the description is the same as Fig. 2. (a): the right excitable signal channel (black region) is characterized by $\Phi = 0.0065$ and the left excitable one (dark-gray region) by $\Phi = 0.008$. 51 grid points (3.825 distance units) of non-excitable stripe (gray part) ($\Phi = 0.04485$) form the diode. The calculations have been performed for $f = 1.12$. (d): the propagation of signals in the structure where the value of Φ in the left input channel is given on the horizontal axis, the value of Φ in the gap is on the vertical axis and $\Phi = 0.0065$ in the right input channel. Gray dots show the cases where the gap is not penetrable, the empty circles denote bi-directional propagation triangles mark sets of parameters where diode function is observed (the tip of the triangle marks propagation direction).

3. Experiments

We employed Ru-catalyzed BZ reaction because of its photosensitivity; the illumination suppresses reaction so that the light intensity could be the key parameter of medium's excitability. The experimental setup is shown in Fig. 5. The propagation of excitation pulses have been studied on a celulose-nitrate membrane filters (pore size 0.1 μm, diameter 2.5 cm, Advantec, A100A025A). The membrane was filled with the following solution listed in table in Fig. 5. Then it was placed on a Petri dish and immediately covered with silicon oil to prevent it from drying and to protect from the influence of oxygen. The membrane was illuminated from the bottom with a slide projector as a light source. The global light intensity has been controlled by the distance between the projector and the membrane. Under the membrane, we put a piece of a transparent film with the shape of diode printed on. Black printed areas reduce the illumination, so excitable channels are created on a membrane according to the density of darkness. In order to ensure reliability, we studied a set of two diodes with different orientations in a single experiment. The diodes were placed close together in order to be under identical light intensity. For the image enhancement, a blue optical filter is attached. The pulse propagation has been recorded with a digital video camera and analyzed using standard image processing.



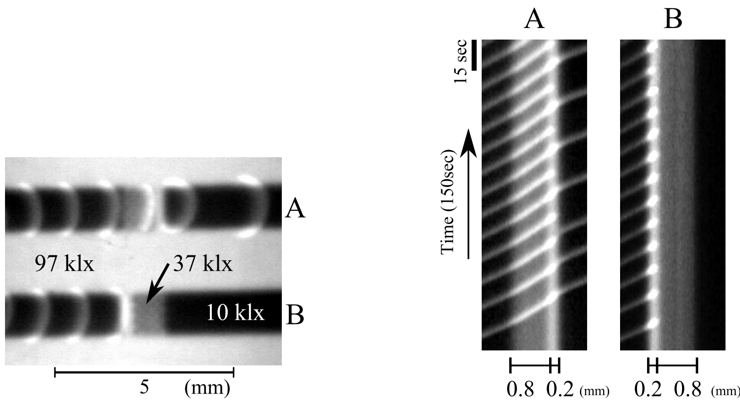
The recipe used in this study.

Reagent	Molar	µl
H_2O		50
$NaBrO_3$	1.5 M	400
H_2SO_4	3.0 M	100
Malonic acid	1.0 M	200
KBr	1.0 M	50
$Ru(bpy)_3Cl_2$	8.5 mM	200

Fig. 5. Experimental setup and the recipe of experiment.

First, we tried experiments with the structure shown in Fig. 6(a), which corresponds to the numerical simulation shown in Fig. 2. Results of the experiment are shown in Figs. 6(b). A barrier gap composed of sub- and non-excitable areas actually worked as a chemical signal diode. Pulses arriving firstly to the sub-excitable area pass through the gap barrier. Those propagating in opposite direction died out.

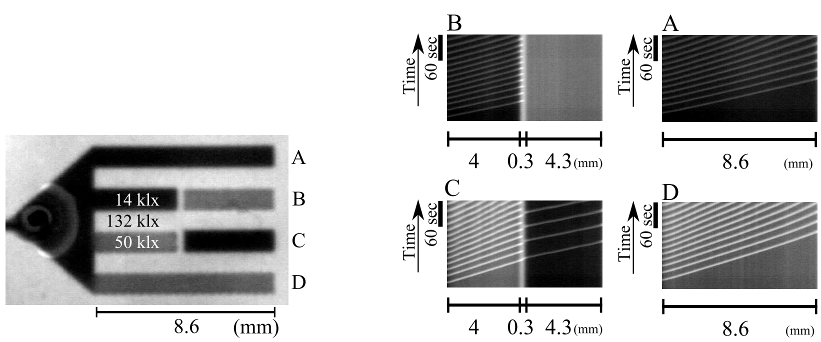
Second, we extended this structure: just one barrier between channels of different excitability as shown in Fig. 7(a), which corresponds to the numerical simulation shown in Fig. 4. We examined a set of four channels with different structure in a single experiment, **A**: long highly excitable channel, **B**: half-long highly excitable channel followed by a narrow non-excitable gap and excitable channel, **C**: half-long excitable followed by a narrow non-excitable gap and highly excitable channel, **D**: long excitable channel. The presented results fit into this scenario illustrated in Fig. 4(b), 4(c). Pulses



(a) (b)

Fig. 6. Experimental result which corresponds to simulation shown in Fig. 2. Estimated light intensity in the black (excitable) areas, the gray (sub-excitable) and the white (non-excitable) regions were 10, 37 and 97 (klx), respectively. (b): space-time plots of wave propagation over central barrier region on channel A and B.

first propagating on the excitable area pass through the barrier separating the input from the highly excitable channel. The pulses propagating in the reverse direction has been stopped. It is worth noticing that the reference pulses propagated through the all length both in channel **A** and in **D**. It means that the survival of pulses only depends on the appearance order of channel's excitability. In other set of experiments, differing by applied illuminations, we observed reverse situation: the diode transmitted only pulses moving from highly excitable channel towards excitable one and stopped those propagating in the opposite direction.



(a) (b)

Fig. 7. Experimental result which corresponds to simulation shown in Fig. 4. Estimated light intensity in three differently illuminated areas were 7, 24 and 68 (klx), respectively. (b) space-time plots of wave propagation over channels A, B, C and D.

The experiments have shown another interesting property of the diode. It can be noticed that the frequency of outgoing pulses in experiments is half of the incoming one. A frequency transformation through a barrier gap is a well known effect, and for a fixed barrier, it depends on the frequency of incoming pulses [8, 15, 16]. In experiment, the frequency of arriving pulses suddenly increased (they were generated by a metal wire touching the medium outside the observed area) and as the result, the frequency of outgoing signal became half of the incoming one. The same effect can be easily seen in simulations. Figs. 8(a), 8(b) show the results obtained for the system composed of two barriers. In the first case, the period of arriving train of pulses is 15 time unit. And the second case, it is 12.5. As seen in Figs. 8, the output signal is unchanged in the first case, whereas in the second case the output frequency become half of that of input one.

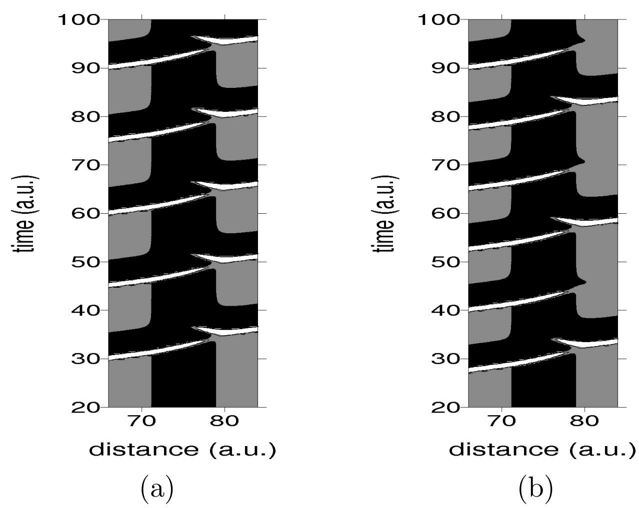


Fig. 8. The space-time plot showing the evolution of u for two different frequencies of incoming excitations. The diode is formed by two barriers: 41 grid points with $\Phi = 0.045$ and 43 grid points with $\Phi = 0.03$ and $f = 1.12$.

4. Discussion

We have demonstrated that a simple system composed of two areas with different excitability levels can work as a chemical signal diode and the results of simulations nicely agree with the experimental results. Based on our result, difference of excitability between both sides of the non-excitable gap seems to be crucial for diode realization: pulses prefer to propagate on more-excitable channel. This direction of transmission is the same as in a diode with a triangular shaped excitability in previous study [11]. We have also shown that if the input channels are non-symmetric a single non-excitable gap can work as the diode. The second case seems to be interesting because the direction of propagation can be reversed by a small change in excitabilities of the gap and of one of the input channels. One can imagine that such situation can occur in biological systems and the direction of information flow can be controlled by the characteristic of cell body and membrane channels. It would be important to verify such scenario.

The research was supported by the Polish State Committee for Scientific Research (KBN) project 1 P03B 035 27.

REFERENCES

[1] J.M. Berg, J.L. Tymoczko, L. Stryer, *Biochemistry*, W.H. Freeman & Co Ltd., New York 2002.

[2] A. Adamatzky, B. De Lacy Costello, T. Asai, *Reaction-Diffusion Computers*, Elsevier Science, UK 2005.

[3] O. Steinbock, P. Kettunen, K. Showalter, *J. Phys. Chem.* **100**, 18970 (1996).

[4] I.N. Motoike, K. Yoshikawa, *Phys. Rev.* **E59**, 5354 (1999).

[5] J. Górecki, K. Yoshikawa, Y. Igarashi, *J. Phys. Chem.* **A107**, 1664 (2003).

[6] J. Górecka, J. Górecki, *Phys. Rev.* **E67**, 067203 (2003).

[7] I.N. Motoike, K. Yoshikawa, *Chaos, Solitons and Fractals* **17**, 455 (2003).

[8] J. Górecki, J.N. Górecka, K. Yoshikawa, Y. Igarashi, H. Nagahara, *Phys. Rev.* **E72**, 046201 (2005).

[9] K. Agladze, R.R. Aliev, T. Yamaguchi, K. Yoshikawa, *J. Phys. Chem.* **100**, 13895 (1996).

[10] T. Kusumi, T. Yamaguchi, R.R. Aliev, T. Amemiya, T. Ohmori, H. Hashimoto, K. Yoshikawa, *Chem. Phys. Lett.* **271**, 355 (1997).

[11] Á. Tóth, D. Horváth, K. Yoshikawa, *Chem. Phys. Lett.* **345**, 471 (2001).

[12] J.N. Górecka, J. Górecki, Y. Igarashi, *J. Phys. Chem.* **A111**, 885 (2007).

[13] H.J. Krug, L. Pohlmann, L. Kuhnert, *J. Phys. Chem.* **94**, 4862 (1990).

[14] J. Górecka, J. Górecki, *Phys. Chem. Chem. Phys.* **7**, 2915 (2005).

[15] J. Sielewiesiuk, J. Górecki, *Phys. Chem. Chem. Phys.* **4**, 1326 (2002).

[16] J. Sielewiesiuk, J. Górecki, *Phys. Rev.* **E66**, 016212 (2002).