Droplets with information processing ability

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December 22, 2010

Abstract

Nonlinear chemical medium can be used to perform information processing functions. In typical applications information is coded in excitation pulses and required operations are performed by interaction of pulses forced by intentionally introduced geometrical structure of the medium. Here we describe a structured system that seems promising for information processing. It is composed of droplets, covered with a lipid layer, that contain reagents of Belousov-Zhabotinsky reaction. The presence of lipids stabilizes the droplets so they do not merge in time scale much longer than that characteristic for chemical phenomena. On the basis of experimental results for period of oscillations within droplets we fit parameters of Rovinsky-Zhabotinsky model that qualitatively describes system evolution. This model for oscillations is used to predict the experimental conditions at which the medium becomes excitable and estimate the size of droplets for which a chemical signal diode can be constructed.

1 Introduction

A bridge linking the ideas coming from computer science with phenomena observed in nature is being built nowadays. For example, time evolution of complex systems can be interpreted as a sequence of information processing operations on the initial conditions of evolution. Studies on relationships between processes occurring in nature and their applications for information processing benefit computer science, because some of observed phenomena suggest new algorithms for classical problems that can be adopted on standard silicon-based computers [1, 2]. The field of research called natural computing covers interdisciplinary studies on this subject. It focuses special attention on unconventional strategies of information processing. The conventional information processing is associated with von Neumann computer architecture in which a processing unit is controlled by a clock that governs the sequence of performed operations and regulates the data flow between processor and memory [3]. In unconventional processing the operations are sequenced and controlled by the time evolution of computing system governed by the laws of physics.

Nonequilibrium chemical systems have been studied as potential information processing media for more than 20 years [4, 5, 6]. Among these systems spatially distributed excitable media look especially interesting, because excitable chemical reactions are responsible for information processing in nerve systems of living organisms [7]. In an excitable medium pulses of concentration can propagate in space because reagents diffuse. The pulses keep stationary shapes at the cost of medium energy. Following the nature we can code information in excitation pulses or trains of them. In the simplest approach the presence of excitation pulse at a selected point of space represents the logical TRUE state and the absence of excitation corresponds to the logical FALSE. Within such representation we can construct the basic binary logical gates [6, 8, 9, 10]. It is also easy to build more complex devices like memory cells [11, 12] or frequency filters [14]. In all these systems information is processed as the result of interactions between excitation pulses forced by a suitably selected geometrical distribution of excitable and non-excitable regions, where the system has one strongly attractive stationary state, so excitations rapidly vanish. Chemical reactions occurring in excitable and nonexcitable regions are linked via diffusion of reagents. Therefore, for the proper functioning of chemical information processing devices, the geometry of excitable and non-excitable regions is equally important as the kinetics of reactions involved. A medium with Ru-catalyzed Belousov-Zhabotinsky (BZ) reaction is used in typical experiments on chemical information processing [4, 10]. This variant of BZ reaction is inhibited by light, so it is relatively

easy to prepare a medium with the required excitability levels by a proper selection of local illumination. However, such approach involves a human factor, because the experimentalist controls the structure. It would be much more interesting to find a system, where a structure capable of performing interesting information processing tasks appears spontaneously, without (or with a little of) human influence. As suggested in [13] a multicomponent unmiscible fluids are potential candidates for information processing systems, because the relevant structures can appear spontaneously at carefully selected thermodynamic conditions.

In this paper we are concerned with a simple example of such system. It is formed of droplets containing aqueous solution of reagents of BZ reaction surrounded by the solution of lipids in decane. We show that the layer of lipids stabilizes the droplets if compared with the droplets immersed in pure decane and does not significantly affect the reaction kinetics. In our experiment droplets are a few orders on magnitude larger than nanodoplets in BZ-AOT system [15], so it is quite easy to observe their time evolution. The structure can be introduced, for example, by individual dropping or forced stirring and it remains stable for times that are sufficiently long to perform observations of information processing operations resulting from interactions of excitation pulses. Experiments demonstrate that excitation can pass the boundary between droplets, so one droplet can excite another. In the paper we describe oscillations in droplets for different initial concentrations of reagents. Measuring the oscillation period as a function of solution acidity we estimate the values of parameters in Rovinsky-Zhabotynski model of BZ-reaction. On this basis we predict conditions at which the system becomes excitable. We show that the difference in droplet diameters can introduce an asymmetry that is strong enough to force unidirectional propagation of excitations. For example, the radii of two droplets can be selected such that excitations in a large droplet pass into the smaller one, but excitations of the small droplet are not sufficient to excite the other. Thus, a chemical signal diode can be constructed in a system composed of excitable droplets with different diameters. Qualitative predictions of the model have been confirmed by experiments in which we observed size controlled asymmetry in droplet cross excitation.

2 Belousov-Zhabotinsky reaction in lipid covered droplets

The medium used in our experiments is composed of two unmiscible phases. One is the solution of a phospholipid L-α-phosphatidylcholine (Soy-20% - Avanti Polar Lipids, Inc.) in decane, prepared by dissolving 1 g of lipids in 50 ml of decane, which gives a yellowish solution. The second phase is the aqueous solution of reagents of ferroin-catalyzed BZ reaction corresponding to an oscillating regime. It is prepared as follows: water, 3.0 M sulfuric acid (for detailed proportions see Table I), 0.75 ml of 1.5 M $NaBrO_3$, 0.875 ml of 1.0 M malonic acid (MA) and 0.15 ml of 1.0 M KBr were mixed in a beaker. After the disappearance of brown color of bromine 0.17 ml of 0.025 M ferroin solution was added, so that the final concentrations were: 0.45 M $NaBrO_3$, 0.35 M MA, 0.06 M KBr and $1.7 \cdot 10^{-3}$ M ferroin. All the reagents were used without further purification. In ferroin catalyzed BZ reaction changes in concentration of reagents are indicated by changes in color: the solution is blue for a high concentration of oxidixed catalyst and red when the catalyst is reduced. Therefore, information on the time evolution can obtained from visual observation of the system. When a small amount of solution of BZ reagents was dropped into a Petri dish containing the solution of lipids and mechanically stirred, a number of droplets of different radii surrounded by decane was obtained. Lipids have hydrophilic heads and hydrophobic tails so droplets were covered by a lipid monolayer (see Fig. 1). Since the solution of BZ reagents is denser than decane, so the droplets settle on the bottom of the dish. Their typical diameters are between 1 and 3 milimeters and the time evolution of such droplets can be easily recorded with a popular digital video camera (SONY DCR-HC88) with attached magnifying lens Raynox -505. Droplets of that size touch the bottom of the dish but, due to the presence of covering lipids, do not stick to it. Moreover, due to the elasticity of the covering layer they retain spherical shape.

The layer of lipids stabilizes droplets, as is evident from the comparison with similar system containing no lipids. Fig. 2 illustrates merging of BZ droplets in pure decane and compares it with the time evolution of droplets in the solution of lipids in decane. Snapshots in the left column (Fig. 2A) show the behavior of droplets containing BZ solution in pure decane. The stability of individual droplets is measured in seconds. Within 100 seconds the most of them merge into a big one. The right column illustrates the behavior of droplets in the solution of lipids. In this case droplets retain their stability for much longer. Of course some of them merge , but as shown in Fig. 2B, where the time between the first and the last snapshot is 17 min-

utes, the system keeps the original droplet structure for times which seem to be long enough for studying complex interactions of excitations necessary for information processing. In both cases BZ solution inside the droplets oscillates with period of the order of 1 minute. Therefore, in the studied system the characteristic time of chemical phenomena important for information processing is clearly shorter than the time scale describing the structural stability of the system.

If droplets are separated than each of them can be regarded as an unstirred batch reactor. The period of homogeneous oscillations observed in droplets with diameter above 1 mm and the period of oscillations in the same solution stirred in a glass beaker are almost the same. It indicates that the presence of lipid layer has no significant influence on the kinetics of reactions which proceed inside a droplet. We observed that if droplet diameter is larger than 2 mm then there is a high probability that oscillations within the droplet are inhomogeneous. The scroll waves are the most frequently observed inhomogeneous structure. A transition between homogeneous oscillations and an inhomogeneous structure is indicated as a significant decrease in oscillation period.

Fig. 3 presents the period of oscillation in droplets as a function of droplet diameter. In the experiment a number of small glass test tubes (circa 1 cm long with the internal diameter of 6 mm) were placed together in a plastic holder. At the beginning all test tubes were filled with the solution of lipids. Next, different amount of BZ reagents were pipetted into each test tube. As the result we obtained droplets with different diameters containing the same solution of BZ reagents (cf. Fig. 3A). In such system the observed differences in oscillation period can be attributed to droplet size, provided that oscillations are homogeneous. To analyze the evolution recorded by a digital camera we selected one of droplet diameters and digitalized information on color of the solution along this line at times corresponding to the successive frames of the film. The section was one pixed wide. Combined information extracted from all frames was represented in a form of a space-time plot (Fig. 3B). Horizontal position of blue stripes on the red background indicates that oscillations inside a droplet are homogeneous. Another test for oscillation homogeneity comes from comparison of space-time plots obtained for two perpendicular diameters. Intensities of different color components on a space-time plot can be digitalized. The most precise information on the period of oscillations comes form the intensity of a blue color component, because the interval of time when catalyst stays in the oxidized form is much shorter that that when it is reduced. A typical result showing the time evolution of the blue color component at the droplet center is shown in Fig. 3C. These data were used to extract oscillation period as a function of droplet

diameter. For typical sizes of droplets (1-2.5 mm) the period of homogeneous oscillations is almost constant. For smaller droplets the period increases, but we have not observed the critical diameter below which the BZ medium fails to oscillate. The increase in oscillation period with the decreasing system size is well known and has been observed for example for oscillations in BZ-droplets covered by the silicone oil [16]. Using our experimental setup we are able to observe oscillations in droplets with diameter above 0.5 mm, thus the critical increase of oscillation period, if exists, occurs for droplets below this size. The fact that the period of oscillations in typical droplets (1-2.5 mm) does not strongly depend on droplet size is important for future studies on information processing in multiple droplet system with reduced models (for example cellular automata), because the evolution within all droplets can be described by the same rules without considering droplet size as yet another variable of the model.

3 Rovinsky-Zhabotynski model of Belousov-Zhabotinsky reaction

In order to set parameters of a numerical model describing BZ-reaction in lipid droplets we can use experimental data for periods of oscillations at different acidity of solution. Rovinsky-Zhabotynski(RZ) model seems to be a good candidate for a simple description of oscillations. RZ model can be derived from the widely accepted Field-Koros-Noyes reaction mechanism [17, 18]. The values of parameters are related to the rate constants of non-elementary reactions introduced within the model and concentrations of reagents that are assumed to be constant during the process.

The RZ model uses two variables: x and z, corresponding to the dimensionless concentrations of the activator $HBrO_2$ and of the oxidized form of catalyst $Fe(phen)_3^{3+}$. The time evolution of the concentrations of x and z is described by Eqs. (1-2):

$$\frac{\partial x}{\partial \tau} = \frac{1}{\epsilon}[x(1-x) - (2q\alpha\frac{z}{1-z} + \beta)\frac{x-\mu}{x+\mu}] \tag{1}$$

$$\frac{\partial z}{\partial \tau} = x - \alpha\frac{z}{1-z} \tag{2}$$

All variables and coefficients in Eqs.(1-2) are dimensionless and the real concentrations of $HBrO_2$ and $Fe(phen)^{3+}{}_3$ (X, Z) are related to (x, z) in the following way:

$$X = \frac{k_1 A}{2k_4}x \tag{3}$$

$$Z = Cz \tag{4}$$

where k_1 and k_4 denote the rate constants of the corresponding reactions in the Field - Koros - Noyes model [19, 18], $A = [HBrO_3]$ and $C = [Fe(phen)_3^{2+}] + [Fe(phen)_3^{3+}]$. The value of q is fixed at 0.5 and the parameters α, β, μ and ϵ are defined in [19, 20]. It can be shown that they are related to system acidity in the following way:

$$\alpha = \alpha_1 \cdot h_0^{-2}$$

$$\beta = \beta_1 \cdot h_0^{-1}$$

where h_0 is the Hammet acidity function of the solution. The values of α_1, β_1, ϵ, and μ do not depend on h_0. The relationships between the dimensionless units of time τ used in Eqs. (1-2) and the real time t is the following:

$$t = \gamma_1 \cdot h_0^{-1} \cdot \tau \tag{5}$$

Oscillation frequency increases with growing acidity of solution. The model parameters α_1, β_1, μ, γ_1 and ϵ have been obtained from experimental results for period as a function of h_0. In the experiments the initial solutions of reagents were prepared such that concentrations of $NaBrO_3$, malonic acid, KBr and ferroin were identical We assumed that the acidity of BZ solution is the same as the solution of sulfuric acid and calculated it interpolating the data given in [23]. We used optimization procedure that minimized differences between observed and calculated periods as a function of α_1, β_1, μ and ϵ . The best fit has been obtained for $\alpha_1 = 1.13 * 10^{-3}$, $\beta_1 = 5.9 * 10^{-4}$, $\mu = 0.002$, $\gamma_1 = 1.0 * sec$ and $\epsilon = 0.3$. Periods of oscillations calculated from the fitted values agrees very well with experimental data as illustrated in Fig.4.

We can transform fitted parameters such that the model based on Eqs.(1,2) shows excitable behavior. For example the system becomes excitable if: $h_0 = 0.05$, $\alpha_1 = 1.5 * 1.13 * 10^{-3}$ and$\beta_1 = 1.5 * 5.9 * 10^{-4}$. The reduction of FKN scheme to the Rovinsky-Zhabotynski model indicates that the values of both α_1 and β_1 are proportional to the concentration of bromomalonic acid. Therefore, the selected parameter values correspond to the case where concentration of sulfuric acid is significantly reduced and concentration of mallonic acid increased by 50% if compared to oscillatory system. These modified parameters will be used in our calculations for droplet interactions.

4 Unidirectional signal propagation between droplets of different size

For information processing applications it is important that droplets can interact via diffusion of reagents through the separating membranes. Fig. 5 illustrates master-slave type behavior of two droplets. The excitations in the bottom droplet force excitations in the other. Therefore, an excitation of one droplet can spread on the whole medium. This brings a loose analogy with a nerve system and collective phenomena within it.

The formation of a chemical signal diode that forces propagation of excitation pulses in one direction only is one of the basic properties expected from any information processing medium. The first realization of a chemical signal diode [21] was based on non-uniform distribution of catalyst on the junction between two pieces of excitable medium. In a droplet system unidirectional propagation of excitations between droplets of different sizes can be expected. The mechanism is the same as observed in experiments on propagation of chemical excitations through a capillary [22]. Let us assume that a certain amount of activator passes from one droplet to another. If the droplet is small then this amount of activator can be sufficient to initiate the excitation inside. However, if a similar amount of activator appears in a large droplet it has more room to diffuse around and its concentration may fail below the threshold value necessary to initiate excitation.

To verify if such effect take place we performed simulations for two contacting disks of different sizes. We represented them as overlapping circles on a square grid ($\Delta_x = \Delta_y = 0.1$) and studied the time evolution with the time step $\Delta_t = 0.0005$. In order to describe diffusion of reagents the Laplacian term was added to Eq. (1) so now it reads:

$$\frac{\partial x}{\partial \tau} = \frac{1}{\epsilon}[x(1-x) - (2q\alpha\frac{z}{1-z} + \beta)\frac{x-\mu}{x+\mu}] + \Delta x \qquad (6)$$

In such approach the unit of distance is such that the diffusion of activator equals $h0 * sec^{-1}$. We do not consider the diffusion of ferriine because the molecule is much larger than $HBrO_2$ and its migration is much slower. Even if the Rovinsky-Zhabotynski model gives quite accurate estimation of periods in a homogeneous system we should not expect that it is equally accurate with respect to the spatio-temporal phenomena because transport of many reagents is neglected.

In calculations we assumed no flow conditions at the disk boundary. It means that activator do not diffuse into decane. Numerically such condition is executed by considering the grid points surrounding the disks at which

the concentration of activator is calculated as the mean concentration of x in the nearest grid points representing the BZ medium inside the disks. Those surrounding points can be interpreted as representing the lipid layer. We assume that $HBrO_2$ molecules can enter the lipid layer, but do not migrate into decane. The interactions between two droplets occur via penetration of $HBrO_2$ molecules through the separating lipid layers. In numerical simulations we considered two different disks: a large one with radius $r_b = 10$ distance units (100 grid points) and a small one with radius $r_s = 1.5$ distance units (15 grid points). The centers of disks are separated by $d = 11.3$ distance units (113 grid points). For such conditions the length of boundary at which the interaction between disks occurs ($l = 1.3$ distance units - 13 grid points) is almost as large as the radius of the smaller disk. Initially we set concentrations inside the disks that correspond to the stable state ($x_s = 0.00258$, $z_s = 0.00379$) and, after relaxation, the excitation is introduced by increasing activator concentration at the leftmost part of the left disk. The snapshots illustrating propagation of excitation pulses are presented on Fig. 6. In the both cases excitations pass from one sphere into the other. However, in the first case the appearing excitation is sufficiently strong to excite the small disk, whereas in the second case the excitation disappears before reaching the center of the big disk.

We have observed unidirectional transmission of excitation between droplets of different sizes predicted by the model in experiments with droplets filled with the oscillatory medium. Fig. 7 illustrate one of such cases. Let us observe two droplets: the upper prolonged one and a small that attaches it from the bottom. The system exhibits spatio-temporal oscillations and droplets interact via diffusion of reactants. The upper row of snapshots shows the case when an excitation appearing inside the big droplet crosses the boundary and excites the small one circa $15sec$ later. The lower row of photos illustrates the situation where an excitation of the small droplet does not influence the big droplet for almost 30 sec. Finally, the big droplet gets excited after the oscillation originating from its center expands.

5 Conclusions:

The recent years has brought many results that try to mimic brain by other physical processes in which a number of individual objects show a neuron-like behavior and mutual excitations [24, 25, 26]. It is known that a non-homogeneous structure combined with a complex nonlinear dynamics can produce a medium able to process information. In the paper we make a step towards such medium. Its structure capable of performing interest-

ing information processing appears as the result of nonequilibrium condition with quite limited influence of the experimentalist. The medium is formed of droplets containing reagents of Belousov-Zhabotinsky reaction surrounded by the solution of lipids in decane. Although many sophisticated methods can be used to make a droplet structure, a representative geometry can be produced when an amount of aqueous solution of BZ-reagents is rapidly stirred. In such system information can be coded in the presence of excitations at a given droplet and at a selected time. The presence of lipids in the surrounding solution stabilizes the droplets. The structure composed of individual droplets remains stable for hours. Such time is long enough to observe information processing activity of this medium.

Each individual droplet has a complex chemical dynamics, however it seems that the presence of lipid layer has no influence on the chemical kinetics, so the time evolution can be described by standard models of BZ-reaction. Here we considered the Rovinski-Zhabotinsky model and fitted its parameters on the basis of experimental data. The equation with fitted parameters correctly describes the period of oscillations as a function of solution acidity. We have used it to estimate the chemical conditions at which the system becomes excitable. Excitable medium is more interesting for information processing operations than the oscillatory one, because in such medium pulses of excitation can be introduced in a controllable manner.

We have observed that excitations can be transmitted for one droplets to its neighbors. For the future studies on neuron-like systems it will be important to introduce long range interactions between droplets. In two dimensional system of uniform droplets interactions are restricted to the nearest neighbors. In order to create more complex interactions we can use droplets with different properties. We have shown that droplet radius can be used to control communication between them. Simulations for a model of excitable medium have demonstrated that by using droplets with the same concentrations of reagents, but different radii we can make a chemical signal diode that transmits excitation in one direction only. This prediction has been confirmed by experiments in which we observed unidirectional propagation of excitations on the boundary of droplets with different diameters. Therefore, we can direct chemical signals composed of excitation pulses by setting the proper sequence of droplets with different diameters. It seems to be an important step towards information processing medium composed of droplets with BZ-reaction.

6 Acknowlgement

The research was supported by the NEUNEU project sponsored by the European Community within FP7-ICT-2009-4 ICT-4-8.3 - FET Proactive 3: Bio-chemistry-based Information Technology (CHEM-IT) program.

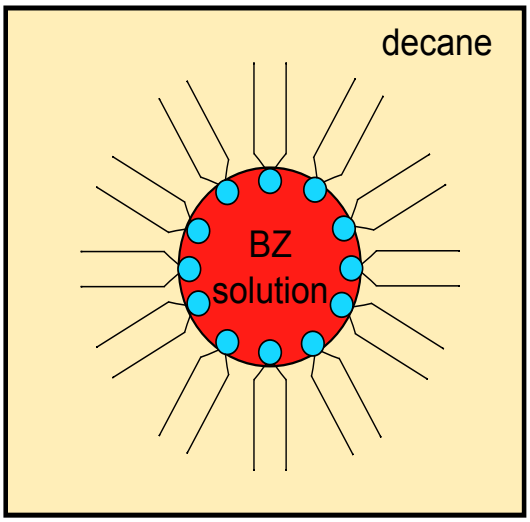

Figure 1: A schematic representation of BZ-droplet in solution of lipids in decane.

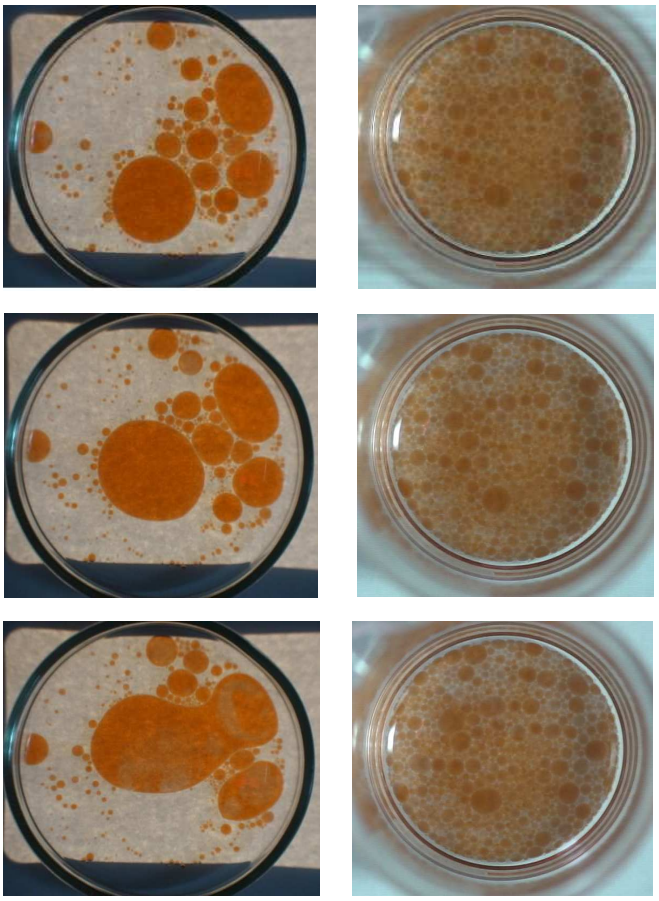

Figure 2: Comparison of stability of droplets in pure decane (left) and in solutions of lipids in decane (right). Droplets are red or light blue and decane (solutions of lipids in decane) is transparent. For droplets in pure decane successive figures correspond to $t = 0$ (the upper illustration), $t = 82.5sec$ (the mid illustration), $t = 157.5sec$ (the lower illustration). For droplets in the solution of lipids in decane (the right column) the successive figures correspond to $t = 0$ (the upper illustration), $t = 500sec$ (the mid illustration), $t = 1000sec$ (the lower illustration). The light blue areas correspond to high concentration of oxidized catalyst. The diameter of Petri dish is 50 mm.

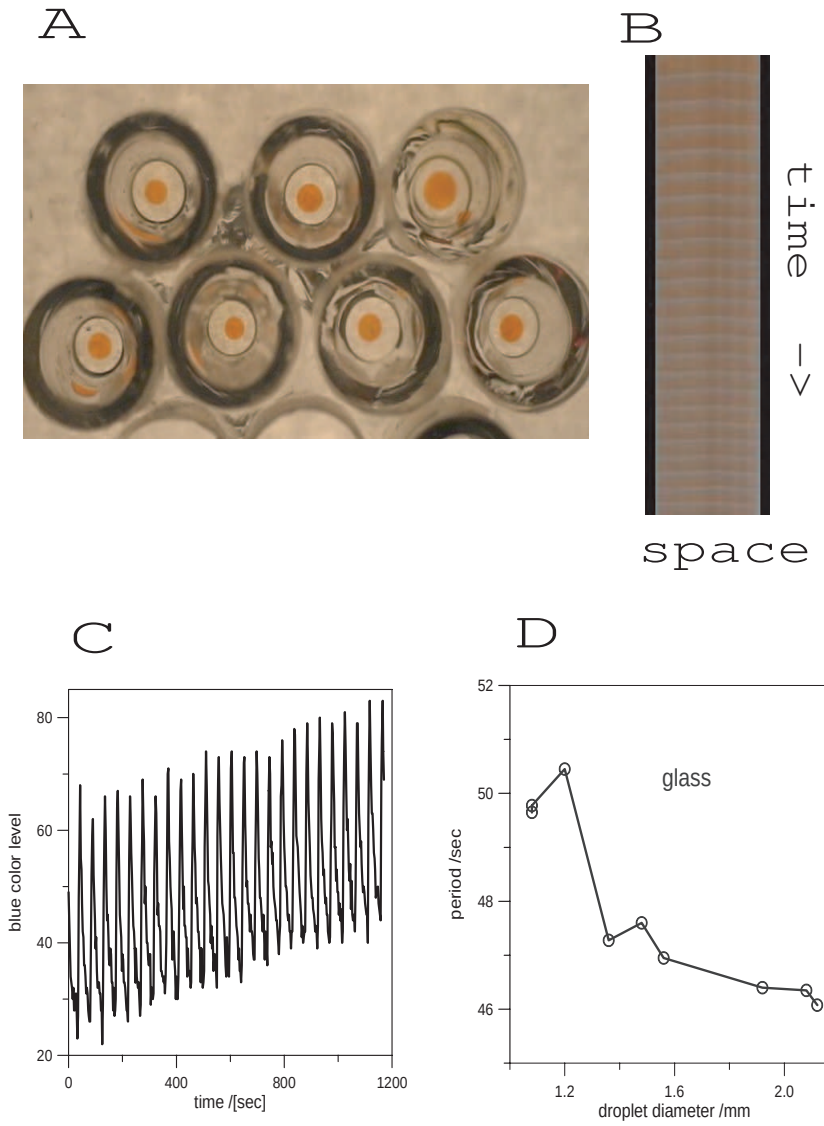

Figure 3: A procedure used to measure the period of oscillations in droplets.(A) droplets of different radius are pipetted to small glass test tubes (6 mm diameter). The color changes in droplets is recorded on a digital video camera. (B) Time evolution of color along a selected diameter of a droplet is combined into a single space-time plot. Lines extracted from successive one pixel wide sections are placed one below the other and form a space-time plot. The space scale corresponds to the selected diameter. (C) The time evolution of the blue component intensity in the droplet center is extracted from the space-time plot. On the basis of these data the oscillation period is calculated as the average time between the successive maxima. Figure(D) shows the oscillation period as a function of droplet diameter.

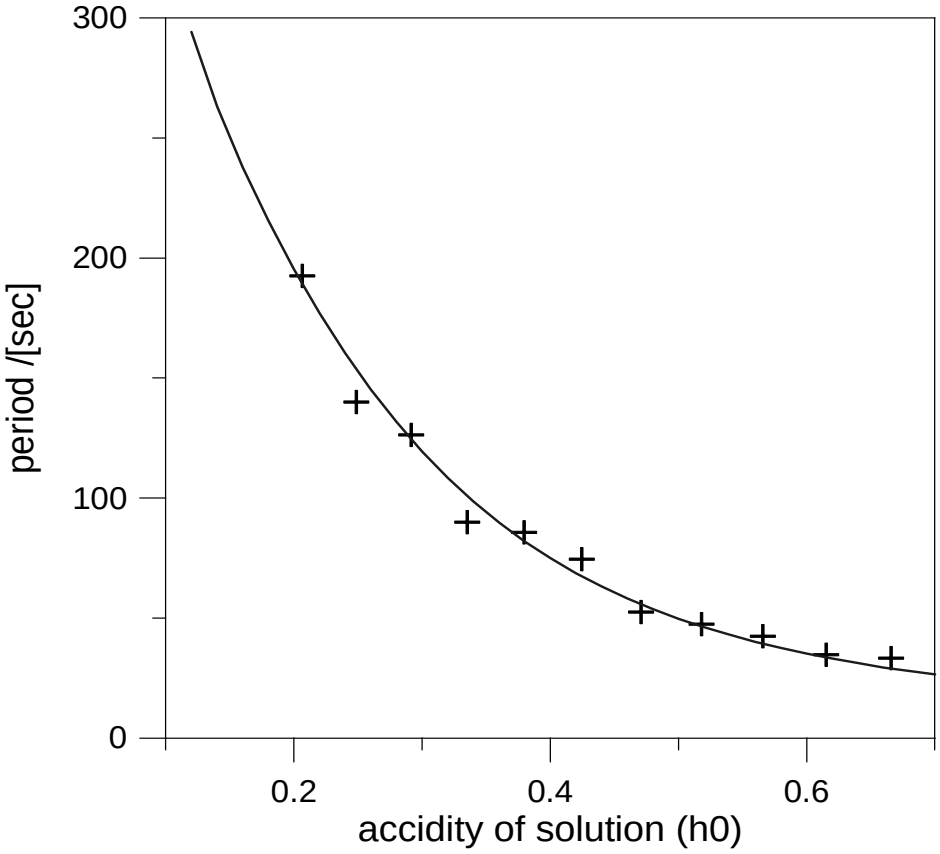

Figure 4: Period of homogeneous oscillations inside a droplet as a function of the accidity of solution of reagents. Crosses correspond to experimental results obtained for the solution where; $[NaBrO_3] = 0.45M$, $[MA] = 0.35M$, $[KBr] = 0.06M$ and the concentration of ferroin $=1.7 \cdot 10^{-3}$ M. The solid line has been calculated from the Rovinsky-Zhabotinsky model with parameters given in the text.

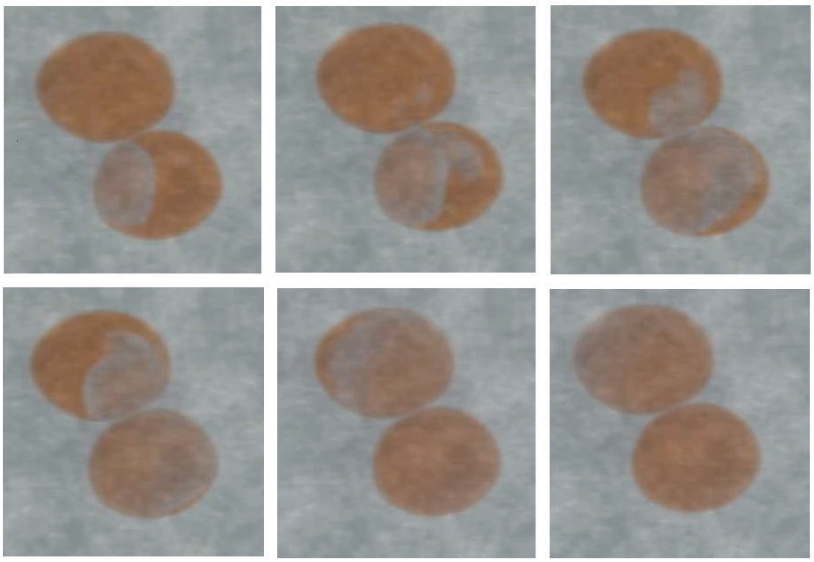

Figure 5: The transmission of excitation between droplets. The droplet diameters are 2 mm. Consecutive figures show the time evolution for times $t = 0s$, $t = 7.5s$, $t = 15s$, $t = 25s$, $t = 42.5s$ and $t = 52.5s$.
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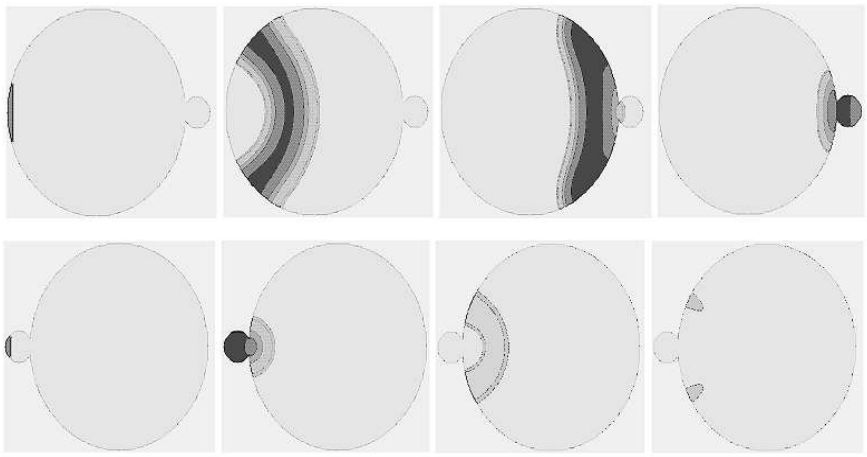

Figure 6: Snapshots illustrating propagation of excitation pulses between disks of different sizes ($r_b = 10$ and $r_s = 1.5$). The time evolution was calculated of the basis of Rovinsky-Zhabotynski model. Consecutive figures show correspond to times $t = 0$, $t = 5.5$, $t = 11$ and $t = 12.75$ time units for propagation from big to small disk and to times $t = 0$, $t = 2.0$, $t = 5.5$ and $t = 6.0$ time units for initial excitation of a small disk.
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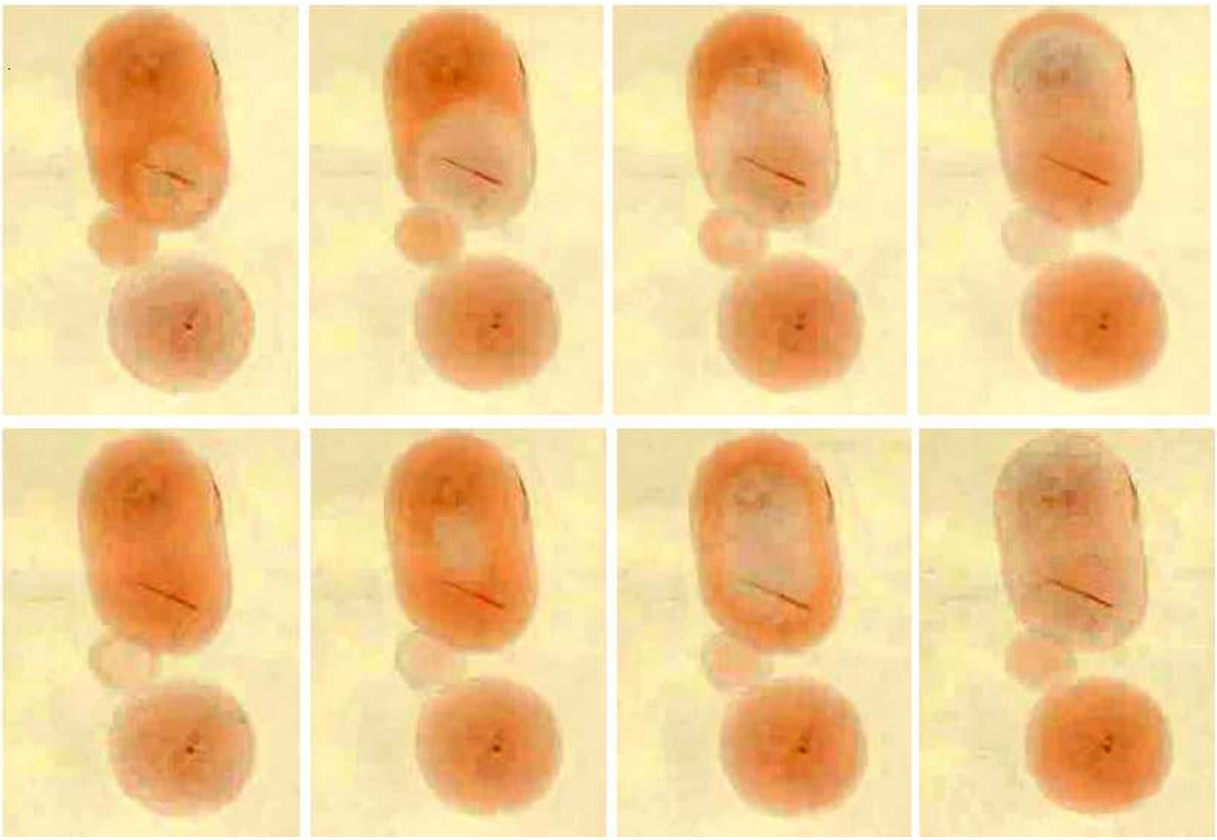

Figure 7: Unidirectional transmission of excitation between droplets of different sizes observed in an experiment with oscillatory medium. The diameter of the bottom droplet is $2mm$. The upper row of snapshots, corresponding to times $t = 0s$, $t = 16s$, $t = 31s$ and $t = 43s$, illustrates the case where excitation of the upper, prolonged droplet propagates into the small one. The lower row of snapshots, corresponding to times $t = 0s$, $t = 11s$, $t = 25s$ and $t = 34s$, illustrates the case where excitation of the small droplet does not perturb the upper, prolonged one for almost $30s$.

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