Information coding with frequency of oscillations in Belousov-Zhabotinsky encapsulated disks

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Information processing with an excitable chemical medium, like the Belousov-Zhabotinsky (BZ) reaction, is typically based on information coding in the presence or absence of excitation pulses. Here we present a new concept of Boolean coding that can be applied to an oscillatory medium. A medium represents the logical TRUE state if a selected region oscillates with a high frequency. If the frequency fails below a specified value, it represents the logical FALSE state. We consider a medium composed of disks encapsulating an oscillatory mixture of reagents, as related to our recent experiments with lipid-coated BZ droplets. We demonstrate that by using specific geometrical arrangements of disks containing the oscillatory medium one can perform logical operations on variables coded in oscillation frequency. Realizations of a chemical signal diode and of a single-bit memory with oscillatory disks are also discussed.

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I. INTRODUCTION

Unconventional computing [1–4] is a field of research dedicated to chemistry-, physics-, or biology-inspired computational strategies, structures, and substrates. In contrast to the conventional computer technology based on semiconductors and the von Neumann concept of computer architecture [5], unconventional computing interprets the natural time evolution of a medium as a series of information processing operations. The time clock sequencing performed operations is hidden in speeds of considered phenomena and in interactions among different parts of the medium. Various types of media can be used for unconventional computation. Information processing operations executed by a chemical medium seem especially interesting, because the activity of nervous systems, including that of our brain, is based on chemical reactions. Excitable media are considered in the majority of studies on chemical information processing [6,7] because there are obvious qualitative analogies between the behavior of such media and of nerve cells. If a perturbation of an excitable medium does not exceed the threshold value than the system remains at its stationary state and shows no activity that can be interpreted as information processing. Perturbations that are sufficiently strong can generate excitations of the medium observed as high concentrations of selected reagents. If a perturbation is local and diffusion of reagents is allowed, than pulses of excitation formed by peaks of concentrations can propagate through the medium. In chemical information processing media, as well as in biological systems, information can be coded in the presence of excitations or in trains of excitation pulses.

The binary representation is the simplest information coding that can be implemented in a chemical excitable medium. A high concentration of the reagent responsible for excitation observed at a given point of space and at a given time represents the logical TRUE state. A concentration below the assumed threshold is interpreted as the logical FALSE. Such binary coding has been considered in the majority of publications on information processing with the excitable Belousov-Zhabotinsky (BZ) reaction [6–8]. Within such an interpretation a propagating excitation pulse represents a bit of information traveling in space. Information is processed in regions of space, where pulses interact. As a consequence, in information processing applications, the geometrical structure of medium is equally important as the kinetics of reactions involved [6,7]. Complex information processing operations can be performed even for relatively simple reaction kinetics if the geometrical distribution of regions with high or low excitability levels is carefully prepared. A clever geometrical distribution of such regions can force interactions that lead to unidirectional propagation of signals (a chemical signal diode) [9] or to a band-pass signal filter [10]. An important benchmark for the usefulness of unconventional computing medium is its ability to produce the logic gates [6,8]. Logic gates are the physical embodiment of Boolean logic operations that form the foundation for digital information processing. Circuits of logic gates can be connected to create machines capable of performing universal computation [11]. If we show that a functionally complete set of logic gates can be constructed in a medium, then the medium can be seen as a universal computer.

Studies on logic operations executed by excitation pulses have a long history. Toth and Showalter described logic gates with BZ waves traveling along thin capillary tubes [12]. Steinbock and collaborators implemented logic gates by "printing" a catalyst of the BZ reaction onto a facilitating medium [13]. In simulation studies [8,14] the construction of logic gates relies upon geometric patterns of nonexcitable regions imposed on an excitable field. Adamatzky presented yet alternative designs by combining the principles of collision-based computing on a precipitating chemical substrate [15,16].

In the series of recent papers Adamatzky and collaborators [17–21] considered the logic gates as well as some selected arithmetic operations executed by a system of subexcitable disks. Their numerical simulations were based on the Oregonator model for a light inhibited BZ reaction [22]. The simulation results were supported by experiments with Ru-catalyzed

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BZ reaction in which the catalyst was immobilized on a membrane and the membrane was placed in the solution of the other reagents of BZ reaction [21]. Areas of low-intensity illumination formed a subexcitable interiors of disks. The disks were separated by regions of high-intensity illumination where excitation pulses decayed rapidly. The authors speculated that the medium composed of disks is qualitatively similar to a set of droplets containing the solution of BZ reaction separated by a nonoscillatory organic phase. Experiments on micelles and droplets encapsulating BZ medium [23–26] started a new trend in chemical information processing. It has been observed that droplets stabilized by lipids or surfactants can communicate [24–28] and their time evolution reminds operations performed by an artificial neural network. In millimeter-size droplets excitation pulses can propagate through a separating lipid bilayer and transmit information [28,29]. Arrays of BZ droplets can be assembled in microfluidic devices [26] so one can think of using these methods to generate functional information processing devices.

However, our recent experiments performed within the NEUNEU project [30] have shown that it is relatively easy to make a structure composed of interacting droplets containing oscillatory BZ. It is also easy to fix required period of oscillations by selecting proper concentrations of reagents. On the other hand, it is seems difficult to prepare a stable network with excitable BZ droplets. These experimental facts encouraged us to present here a new concept of information coding based on frequency of local oscillations. The aim of this paper is to demonstrate that the idea of frequency-based Boolean information coding is universal and can be applied to any oscillatory medium. As an example, we show that the ideas and realizations of information processing devices described in Ref. [20] for 2D disks containing subexcitable medium and information coded in the presence of excitation pulses can be directly translated into the oscillatory medium with frequency-based information coding. We discuss the construction of two basic logic gates, OR and NOT, that allow us to build all other gates. Moreover, we show that both a single-bit memory cell and a signal diode can be constructed using a few disks. Our results are based on simulations performed for exactly the same Oregonator model of a photosensitive BZ medium that has been used in Refs. [17–19]. A good qualitative agreement between simulations and experiments was demonstrated in those papers. Therefore, we expect that the presented disk-based constructions of gates, a signal diode and a memory cell can be also easily verified in experiments with a photosensitive BZ reaction and the Ru-catalyst immobilized on a membrane. On the other hand, simple, realistic models of kinetics of BZ droplets [31] are formally similar to the Oregonator model, so we think that a structure of oscillating lipid covered droplets that performs a given information processing function should be similar to the structure of disks presented in this paper.

II. THE INFORMATION PROCESSING STRUCTURES OF OSCILLATING DISKS

A. The basic properties of the model

The idea of frequency-based information coding comes from the observation that in a typical oscillatory medium the region with the highest oscillation frequency becomes a pacemaker that forces the neighboring areas to oscillate with the same frequency [29]. The frequency of BZ oscillations can be controlled by many factors. In experiments with lipid-covered BZ droplets the frequency of oscillations depends on the initial concentrations of reagents and experimental conditions, including temperature and illumination intensity. Here in numerical simulations based on a model of a photosensitive BZ reaction we fix the oscillation frequency by selecting the value of illumination level in a term that describes the influence of light on reaction kinetics. In our simulations we intentionally use exactly the same two-variable version of the Oregonator model adapted for photosensitive Ru-catalyzed medium as in Ref. [19] to show that the frequency-based coding is generic and it can be applied to any oscillatory medium. The model equations read as follows:

$$\frac{\partial u}{\partial t} = \frac{1}{\epsilon}\left[u - u^2 - (fv + \phi)\frac{u-q}{u+q}\right] + D_u \nabla^2 u, \quad (1)$$

$$\frac{\partial v}{\partial t} = u - v + D_v \nabla^2 u. \quad (2)$$

Here u and v denote the dimensionless concentrations of the bromous acid $HBrO_2$, that is, the reaction activator, and of the oxidized form of the catalyst $Ru(bpy)_3^{3+}$ that acts as its inhibitor.

In Eq. (1) ϕ is the rate of bromide production and it is proportional to the applied light intensity. Bromide Br^- is an inhibitor of the BZ reaction and the Ru-catalyzed BZ reaction can be controlled by light intensity. Experimental conditions can be set up such that at low illuminations the medium oscillates. For larger light intensity it becomes excitable. It means that the medium has a stable steady state directly attracting all small perturbations. However, if medium perturbation exceeds a threshold value, then the relaxation towards the steady state proceeds through a significant increase of u and v. If a perturbation is local, then the relaxation is related with propagation of an excitation pulse that converges to a stationary shape. For yet larger illumination the medium becomes subexcitable. Now its local excitations can generate traveling pulses that are no longer stable and shrink as they travel. A very careful tunning of medium parameters produces wave fragments that do not expand while propagating inside a droplet [17]. If the medium is exposed to high intensity of light, then it exhibits no nonlinear behavior, because the system of Eqs. (1) and (2) has a strongly attractive stable state.

In simulations reported below we used the same values of model parameters as in Ref. [19]. The ratio of time scales for the evolution of u and v variables $\epsilon = 0.022$. The stoichiometric coefficient $f = 1.4$ and $q = 0.0002$. Like in Ref. [19] we assume that the mobility of the catalyst can be neglected if it is compared to the activator. Thus the diffusion coefficients D_u and D_v of u and v were set to unity and zero, respectively. To get numerical results presented below we solved Eqs. (1) and (2) using a fourth-order Runge-Kutta algorithm with $dt = 2 \times 10^{-5}$. One- and two-dimensional evolution was studied on a square grid with spatial steps $\Delta_x = \Delta_y \in [0.038,0.06]$. The exact value of the space grid was separately selected for each particular problem.

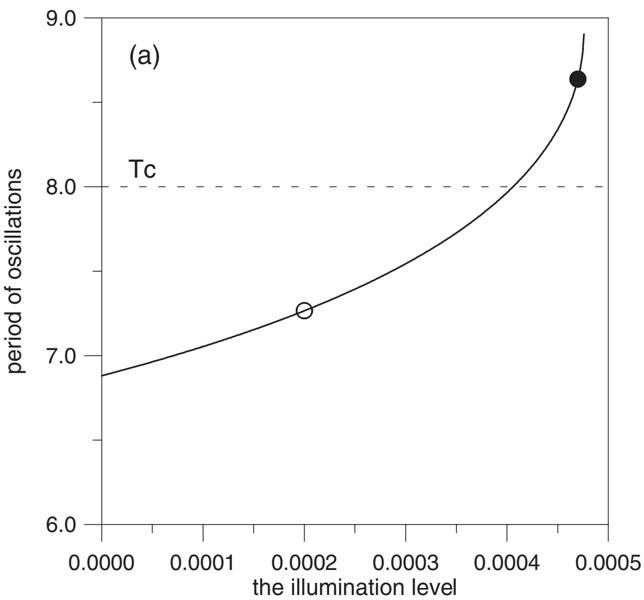

FIG. 1. The period of homogeneous oscillations as a function of illumination level ϕ calculated for the model parameters used in the paper. White and black circles mark periods of oscillations corresponding to the TRUE and the FALSE states.

Figure 1 illustrates the period of oscillations as a function of ϕ calculated using Eqs. (1) and (2) with the considered parameter values. The range of ϕ where oscillations appear is very limited and oscillations are dumped for $\phi \geqslant 0.000477$. For the following analysis of frequency-coded information processing by structures of BZ disks we considered two arbitrary selected illumination levels, $\phi_1 = 0.0002$ and $\phi_2 = 0.00047$. The periods of homogeneous oscillations at these illuminations are $T_1 = 7.26554$ and $T_2 = 8.63774$, respectively, and we use them as the inputs of binary, frequency-coded information. These periods visibly differ, so we can introduce the following information coding. We assume that a medium oscillating with period close to T_1 or shorter represents the logical TRUE state. If the oscillation period is T_2 or longer than such oscillations represents the logical FALSE state. Of course, our choice of T_1 and T_2 is arbitrary. Within the considered model one can select other, visibly different, periods provided that they can be related to illumination levels. We believe that for another set of periods representing the logic states the structures of disks performing a given function will be similar to those described below.

Experiments with lipid-covered BZ droplets have shown that a droplet oscillating with a high frequency emits a train of excitation pulses that perturb the neighboring droplets. As a result, high-frequency oscillations expand onto droplets oscillating with a lower frequency [29]. Keeping in mind that propagating spikes are responsible for droplet communication, we can expect that structures of disks for processing information coded in frequency of local oscillations are similar to those that process information coded in the presence of excitation pulses [17–21].

In order to illustrate that locally forced high-frequency oscillations in a medium oscillating with a low frequency behave qualitatively similarly to pulses in an excitable medium, let us consider a one-dimensional system with nonhomogeneous illumination. The system is composed of five dark segments [labeled A, B, C, D, and E in Fig. 2(a)] that are 100 grid points wide ($\Delta_x = 0.05$). The dark segments are separated by illuminated gaps (illumination $\phi_0 = 0.25$). For illumination level ϕ_0 the considered reaction kinetics has a single, strongly attracting stationary state characterized by a low concentration of the activator ($u_s = 0.0002$). The illumination of dark segments B, C, D, and E is constant and is equal to ϕ_2. For such illumination the period of oscillations inside a segment is T_2. The illumination of the segment A depends on time. For $t \leqslant 100$ it is equal to ϕ_2. For times $100 \leqslant t \leqslant 300$ the illumination of the A segment decreases to ϕ_1 and the period of oscillations in this segment becomes T_1. For $t \geqslant 300$ the illumination of the first dark segment increases again to ϕ_2 and the period of oscillations increases to T_2.

We assume that the activator u can freely diffuse between regions characterized by different illumination levels. If the illuminated gaps are wide (six grid points, $\Delta_x = 0.05$), then pulses of activator outgoing from the dark segments are dumped in the gaps. As a result, the interactions among dark segments are weak and their oscillations are uncorrelated. The increase of oscillation frequency in segment A has no influence on the time evolution in other segments. If the illuminated gaps separating dark segments are narrow (five grid points), then oscillations in segments correlate via diffusion of the activator. In the case illustrated in Fig. 2(b), high-frequency oscillations in A segment force fast oscillations in the segment B for $t \geqslant 100$. However, if the concentration of the activator is just plotted as a function of time, then it is quite difficult to spot the change in oscillation frequency from T_2 to T_1, especially when a long-time evolution of $u(t)$ is shown [cf. Fig. 2(b)]. In order to analyze the simulation data and visualize slow and fast oscillations at a given point of medium, we introduce a function $D(t)$ that maps time t on the difference between the moment of the next maximum of activator concentration at the selected point and the current time,

$$D(t) = \gamma(t) - t, \tag{3}$$

where $\gamma(t)$ is the time when the next maximum of activator concentration after time t appears. Of course, $D(t) \to 0$ if t approaches from below the moments when excitation reaches its peak. For an oscillating medium $D(t)$ plotted in linear x and y axes is a triangular function and the maxima of $D(t)$ are equal to the oscillation period. The function $D(t)$ at the centers of disks A, B, and C is plotted in Fig. 2(c). Now the change in oscillation frequency can be spotted much more easily, but the relative difference between T_1 and T_2 is still rather small. In order to distinguish the changes more precisely, we introduce a transformation $\tau(t)$ that enhances differences between numbers around T_c. Here we use a nonlinear transformation,

$$t \to \tau(t) = \frac{1}{1 + \exp\left[-\alpha(t - T_c)\right]}, \tag{4}$$

with $\alpha = 3$ and $T_c = 8$. It has to be stressed that the selected expression for $\tau(t)$ has no physical meaning and any function with derivative larger than 1 in $[T_1, T_2]$ can be used. Formula (4) gives $\tau_1 = \tau(T_1) = 0.11$ and $\tau_2 = \tau(T_2) = 0.89$ and thus the differences between τ_1 and τ_2 are significantly better

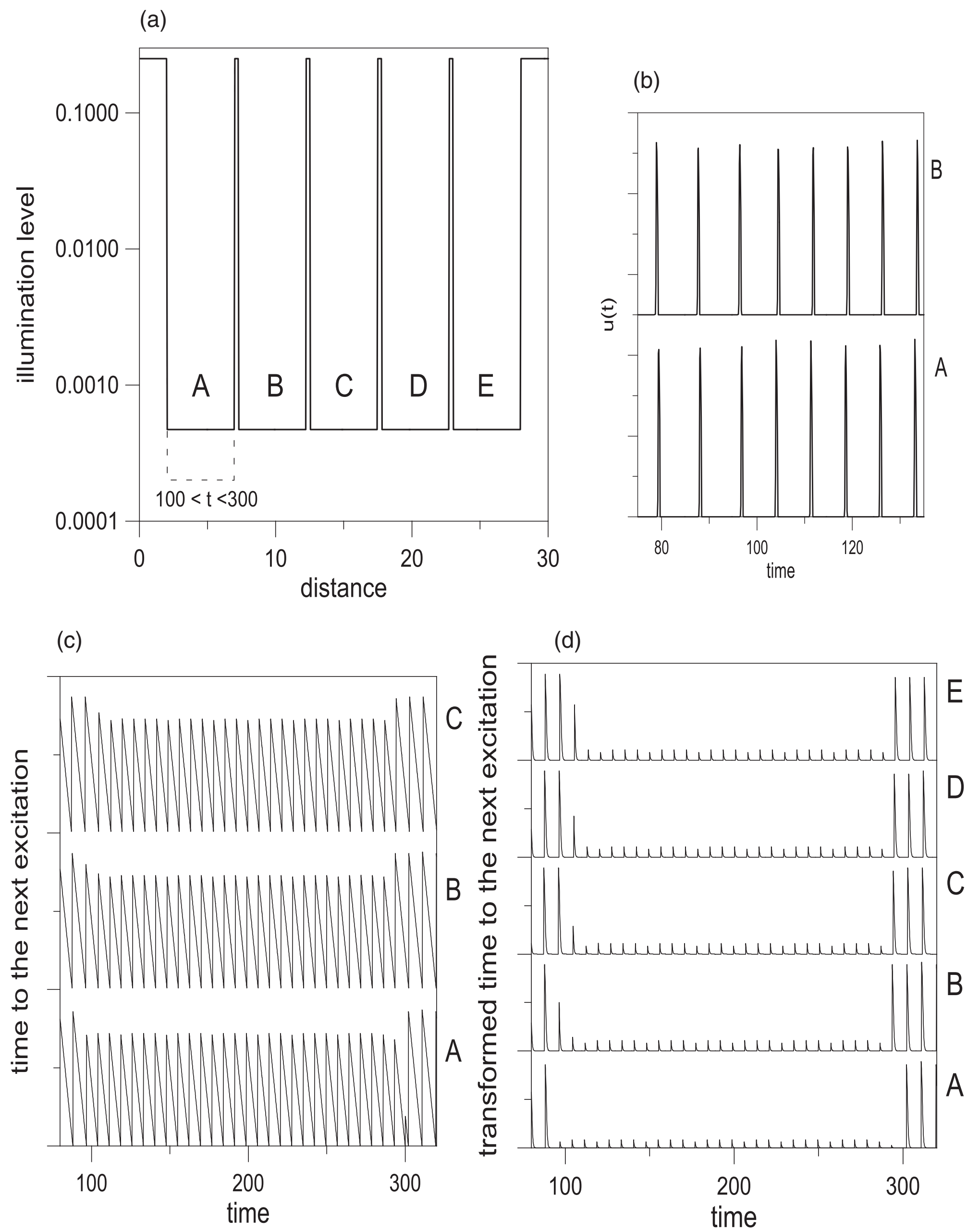

FIG. 2. Coupled oscillations in one-dimensional medium with time-dependent, inhomogeneous illumination. (a) The time-dependent illumination of the medium. (b) The time evolution of activator concentrations in the centers of segments A and B for $t \in [85,135]$. (c) $D(t)$ calculated at centers of A, B, and C segments as a function of time ($t \in [80,320]$). (d) $\tau(D(t))$ at the centers of all disks.

pronounced than those between T_1 and T_2. If in an interval of time the maxima of $\tau(D(t)) < 0.11$, then the period of oscillations is shorter than T_1 and the medium represents the TRUE state. In the following we plot $\tau(D(t))$ to present the time evolution of the activator at selected points in the information processing device discussed above.

Figure 2(d) presents $\tau(D(t))$ at the centers of all segments. It can be noticed that shortly after the segment A starts to oscillate with a high frequency (at $t = 100$), high-frequency oscillations are subsequently forced in the segments B, C, D, and E. Simulations show that locally forced high-frequency oscillations in a compartmented oscillatory medium behave similarly to spikes in a spatially distributed excitable medium introduced by a local, external stimulus. Their expansion proceeds with a constant velocity like propagation of a pulse in an excitable medium. On the other hand, if the illumination in segment A increases and the system is no longer perturbed with high-frequency pulses, then the periods of oscillations increase almost instantaneously in all segments.

In the following we show that the basic concepts of information processing with excitation pulses propagating in a compartmented medium can be translated onto an oscillatory medium and information coded with the frequency of oscillations. Let us consider a medium composed of dark disks on illuminated background. The medium is very similar to that studied in Refs. [17–21], but in those papers dark

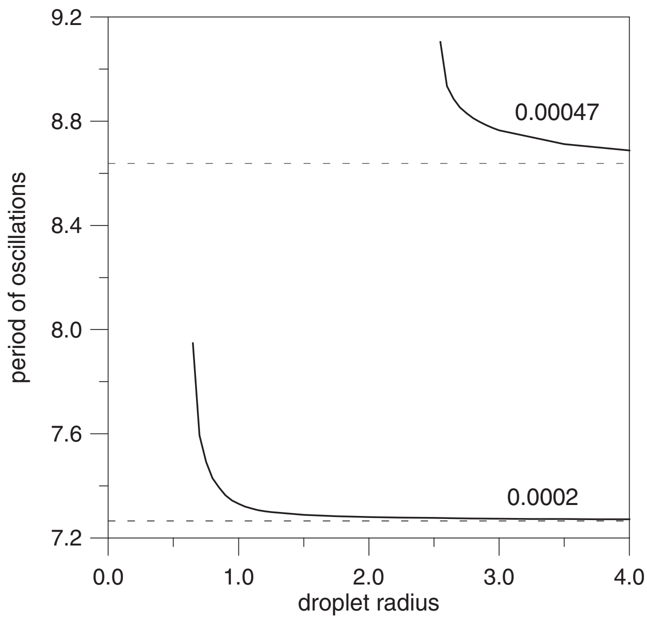

FIG. 3. The period of oscillations in a dark disk as a function of its radius. A dark disk is surrounded by an illuminated medium ($\phi_0 = 0.25$). The results for two illuminations of a dark disk, $\phi_1 = 0.0002$ and $\phi_2 = 0.00047$, are shown.

disks were subexcitable, whereas here the medium inside dark disks is oscillatory. As an experimental realization of such a medium one can use a membrane with an immobilized catalyst of photosensitive BZ that is placed inside a solution of the other reagents [32]. In such a system the reaction proceeds on the membrane surface. An external illumination can be applied to define the structure of dark disks on an illuminated background. The regions with high-intensity illumination define the structure of barriers.

In a two-dimensional system the number of neighbors is larger than in the one-dimensional case and so the connectivity of disks can be more complex. This feature obviously extends the information processing functionality. It is also well known that the oscillation period increases when a disk gets smaller [33]. Within the considered reaction model the effect can be explained by diffusion of activator to the surrounding nonexcitable region where it quickly degenerates. The activator outflow depends on surface-to-volume ratio, so size-dependent changes in period are more pronounced for small droplets. For selected parameters of the model the period of oscillations as a function of disk radius is illustrated in Fig. 3. The period was calculated from the rotationally symmetric numerical solution of Eqs. (1) and (2). One-fourth of the grid points described a dark disk and the illumination at these points was ϕ_1 or ϕ_2. The other grid points represented the surrounding strongly illuminated medium (ϕ_0) outside the disk. We allow for activator diffusion between the disk and the medium. The no-flow boundary conditions were imposed at the grid ends corresponding to the disk center and a point in the medium far from the disk. The critical radius below which a disk does not oscillate strongly depends on illumination level and for ϕ_2 is about 3 times larger than for ϕ_1. The dependence of self-oscillation period on disk radius gives us another parameter that can be used to control propagation of high-frequency oscillations in a droplet array.

B. A signal channel constructed with disks

In the following subsections we present BZ-disk-based realizations of a few basic units that can be used to construct more complex information processing devices. Let us start with a signal channel within which chemical signals can be transmitted. Figure 4 illustrates the propagation of high-frequency oscillations through an array of five disks arranged as shown in Fig. 4(a). The radius of each disk is 80 grid points. The illumination of medium between disks is ϕ_0. The leftmost disk, characterized by a low illumination (ϕ_1) oscillates with higher frequency than the others, illuminated with the light intensity ϕ_2. The gap between disks measured at the line of centers is 5 grid points. The time evolution of oscillations in coupled disks is illustrated in Figs. 4(b) and 4(c) that show $\tau(D(t))$ calculated at disk centers. As seen in Fig. 4(b) for a narrow nonexcitable gap separating disks ($\Delta_x = \Delta_y = 0.04$, the gap is 0.20 distance units wide), the disk A oscillating with the highest frequency immediately dominates the time evolution of the whole array. The oscillations that start with random initial phases are synchronized within a single period. If the grid distances are larger $\Delta_x = \Delta_y = 0.05$ (now the gap is 0.025 distance unit wide), then the coupling between disks is weaker and synchronization of oscillations takes around 40 time units [Fig. 4(c)]. For yet wider gaps (0.03 distance units wide) the oscillations in disks do not synchronize. Figure 4 shows that the array of disks placed close one to another can play the role of a signal channel for information coded in the frequency of oscillations transmitting high-frequency oscillations from one disk to another.

C. The signal diode

A signal diode that transmits signals in one direction only is an important component of many information processing devices because it can be used to separate input channels from the region of medium where information is processed. For example, a diode can eliminate potential interferences between inputs. If frequency of excitations is used for information coding, then the signal diode is a device that transmits a high-frequency stimulus in one direction and does not transmit it in the reverse direction. Having in mind a successful realization of a chemical signal diode with a junction between triangular and rectangular channels [9] we considered a chain of five disks with the radii equal to 80, 80, 160, 20, and 80 grid points, respectively. The geometry of such disk array is illustrated in Figs. 5(a) and 5(c). The disks were separated by five grid points of the strongly illuminated medium (illumination ϕ_0). The illumination level in all disks except the input one was ϕ_2. Numerical simulations were performed on a square grid with $\Delta_x = \Delta_y = 0.03975$. The signal was introduced from the input disk (I) that oscillates with a high frequency because its illumination is lower (ϕ_1) than the other. The disk at the other end of the chain represents diode output (O). The time evolution of oscillation in the array have been studied for both orientations of the big and the small disk with respect to the input disk. Figures 5(b) and 5(d) show the transformed time between successive maxima of activator

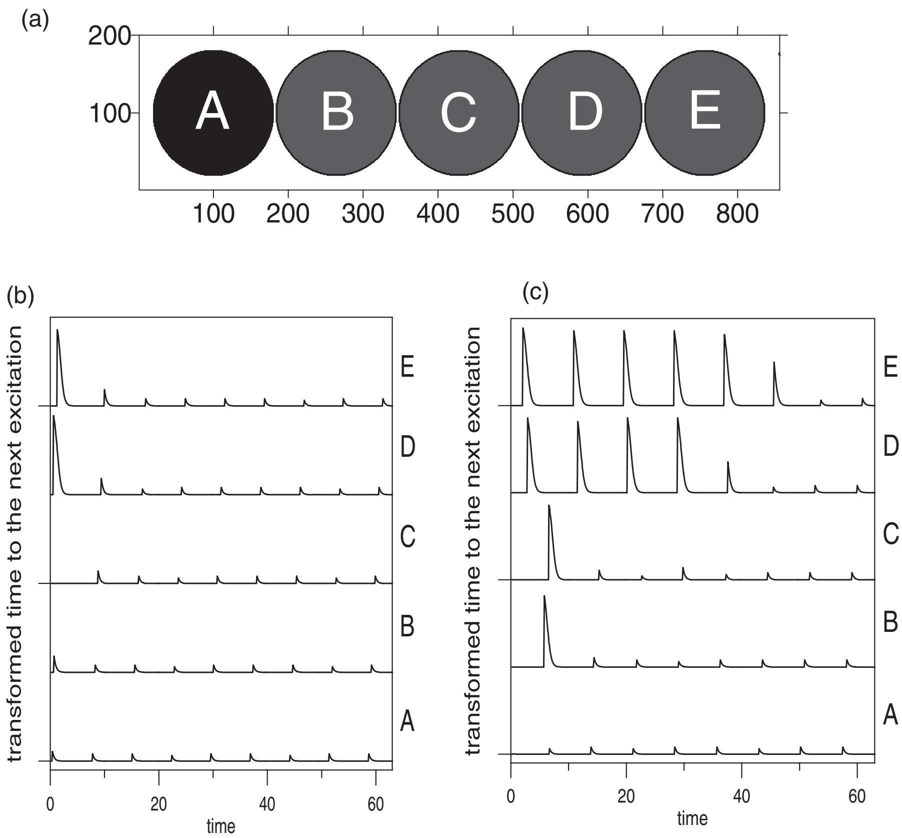

FIG. 4. A signal channel formed by an array of disks. (a) A system's geometry; illumination level is shown in gray scale: the dark disk $\phi_1 = 0.0002$, gray disks $\phi_2 = 0.00047$, the white area around $\phi = 0.25$. [(b) and (c)] The function $\tau(D(t))$ calculated at disk centers for the following gaps separating disks: 0.20 distance units (b) and 0.25 distance units (c).

concentration at the disk centers for a high-frequency stimulus arriving from both directions. The output signals differ and depend on orientation of big and small disks. If a train of high-frequency pulses propagates from the big disk towards the small one, we observe high-frequency oscillations with the period T_1 at the output disk 30 time units after the medium is initiated. For the reversed orientation of big and small disks with respect to the input [cf. Figs. 5(c) and 5(d)], high-frequency oscillations of a small disk B are too weak to force oscillations at disk C. Now the medium relaxation takes a bit longer, but after 50 time units the output disk O oscillates with the frequency T_2 corresponding to the FALSE state. Therefore, the array of disks presented at Fig. 5 functions as a chemical signal diode for a signal coded in oscillation frequency.

D. The OR gate

High-frequency oscillations propagate through an array of coupled disks so two joined arrays should work as the OR gate for information coded in oscillation frequency. Let us consider a structure of disks illustrated on Fig. 6(a). The bottom disk (I1) and the top disk (I2) are considered as the gate inputs and the rightmost disk is the gate output (O). The illumination of all disks except I1 and I2 is fixed and equal to ϕ_2, so the periods of unforced oscillations at these disks are T_2. The illumination of I1 and I2 can be ϕ_1 or ϕ_2 depending on whether the input represents the TRUE or FALSE state. In numerical simulations of the time evolution we used a square grid with $\Delta_x = \Delta_y = 0.045$. The radii of all disks are the same and equal to 60 grid points (2.7 distance units). The disks are separated by a highly illuminated region (ϕ_0) and the widths of separating gaps at the line of centers are five grid points.

Figure 6(b) shows the transformed time to the next excitation when both inputs are in the FALSE state. In such case all disks synchronize in phase at the low-frequency oscillations. Synchronization of oscillations means that even if initially the central disk C is perturbed by different phase oscillations of its neighbors, then after one or two cycles its oscillations synchronize with one of the neighbors and the period of oscillation drops becomes T_2. Therefore, when both inputs are in the FALSE state the output state is also FALSE. Figure 6(c) shows the transformed time to the next excitation when the input disk I1 oscillates with a high frequency (its logic state is TRUE) and the input I2 oscillates with a low frequency, so its state is FALSE. Now fast oscillations of I1 expand over the whole system and the output represents the TRUE state. In this case the vertical chain of disks behaves like the signal channel shown in Fig. 4. Quickly after initiation the fast oscillations are forced on disk I2. In order to avoid such interference one can locate signal diodes between the central droplet C and inputs I1 and I2. Figure 6(d) illustrates the case when both input disks I1 and I2 oscillate with a high frequency, so both inputs are in the TRUE state. Similarly to the case shown in Fig. 6(c), the output disk oscillates with period T_1 so its state is TRUE. Therefore the disk structure illustrated on Fig. 6(a) operates as the OR gate.

E. The negation gate

The structure of disks that functions as the negation gate is illustrated in Fig. 7(a). The time evolution of the system

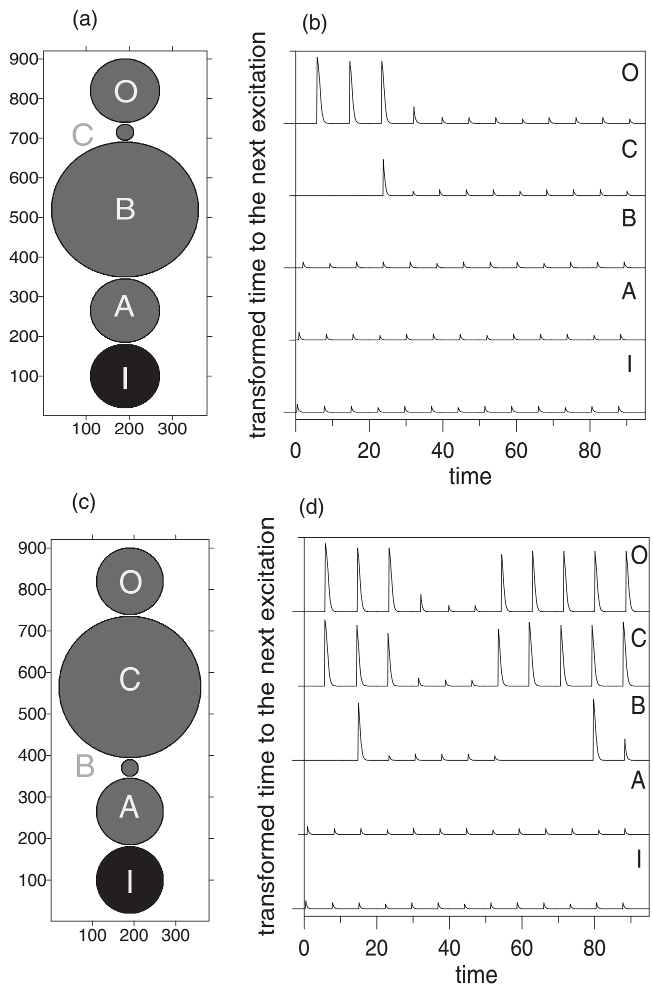

FIG. 5. The geometry of an array of disks that forms a signal diode and the time evolution of the activator at disk centers. The illumination level is shown in gray scale: dark input disk ϕ_1, gray disk ϕ_2, and the white area around ϕ_0. Figures on the right show the transformed time to the next maximum of activator concentration at disk centers for a high-frequency stimulus arriving from the input disk (I). The orientation of big and small disks is indicated in the left figure.

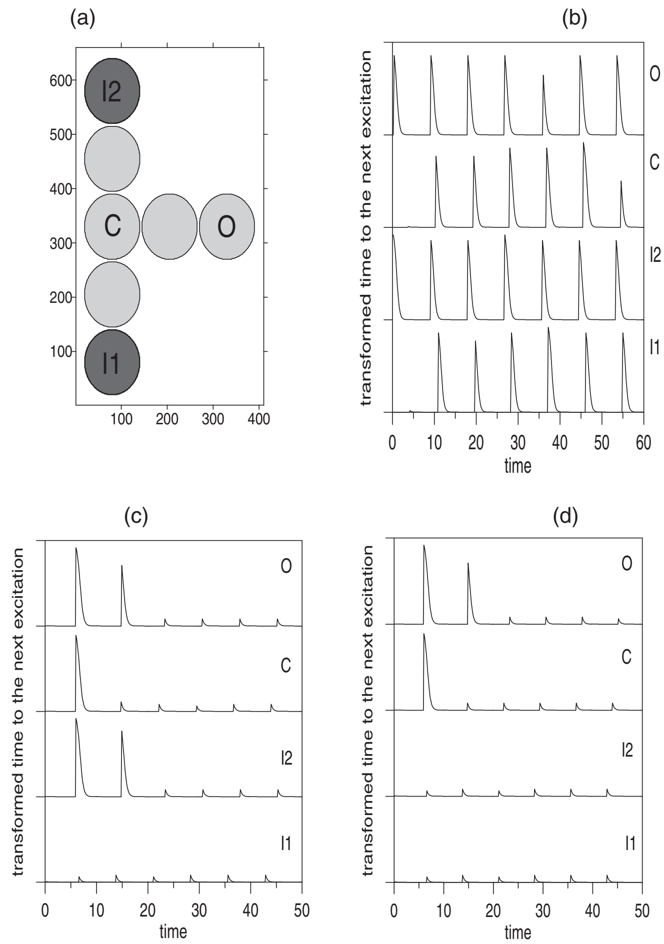

FIG. 6. The OR gate build with disks. (a) A system geometry; illumination level is shown in gray scale: dark input disk I1 and I2 can have illuminations $\phi_1 = 0.0002$ or $\phi_2 = 0.00047$ depending on the input, illuminations of gray disks is ϕ_2, of the white background ϕ_0. [(b), (c), and (d)] The function $\tau(D(t))$ calculated at centers of selected disks. (b) The state of both inputs is FALSE (illumination ϕ_2 at I1 and I2). (c) The state of input I1 is TRUE (illumination ϕ_1 at I1) and the state of input I2 is FALSE (illumination ϕ_2 at I2). (d) The state of both inputs is TRUE (illumination ϕ_1 both at I1 and I2).

of disks has been studied on a square grid with $\Delta_x = \Delta_y = 0.0505$. The gate is composed of six disks with different diameters separated by a highly illuminated medium (ϕ_0). The oscillating part of the central disk has a ring shape with the outer radius 100 grid points and the inner radius 70 grid points. The central disk contacts with a small (radius 30 grid points) output disk O via a gap that is 5 grid points wide. The radii of input disks I1 and I2 are 60 grid points. They contact the central disk via separating gaps that are 4 grid points wide and disks with radii equal 50 grid points. The idea of the NOT gate is inspired by geometries of the coincidence detector [34] and direction detector [35]. The gap between the ring and the output droplet O has been selected such that the output gets excited by two pulses colliding at the point C on the ring, but no excitation occurs when a single pulse propagates along the output disk. Illumination of all disks except the input ones is ϕ_2. Illumination of the disk I1 is always ϕ_1, so it oscillates with a short period. Illumination of the input disk I2 is ϕ_1 if it represents the TRUE state or ϕ_2 if it represents FALSE. At the beginning let us assume that I2 is in the FALSE state. Now fast excitations coming from I1 spread out through the disk network. As seen in Fig. 7(b) within less than 10 time units they enter the disk I2 and force fast oscillations there. The excitation pulses propagating in the lower and upper parts of the central ring meet at point C in front of the output ring and force high-frequency oscillations there [Fig. 7(b)]. It means that if the state of I2 is FALSE, then the output is TRUE. If both disks I1 and I2 oscillate with a high frequency, then excitations generated by I1 are interfering on the ring with those coming from I2. Depending on the initial phase difference they meet somewhere outside C and do not activate the output. The transformed times to the next excitation are shown in Fig. 7(c) and output oscillations are very slow. This is because the disk O ($r \sim 1.5$) is too small to self-oscillate and only a fraction of its excitations generate oscillations [36,37].

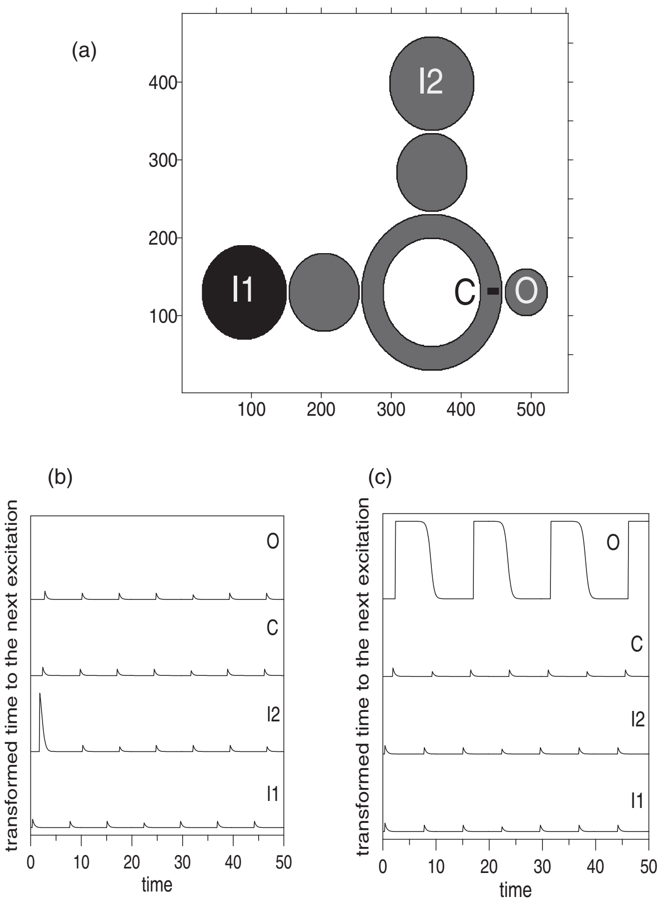

FIG. 7. (a) The geometry of an array of disks that forms a NOT gate. [(b) and (c)] The function $\tau(D(t))$ calculated at centers of selected disks illustrated in (a). (b) The input I2 is in the FALSE state. (c) The input I2 is in the TRUE state.

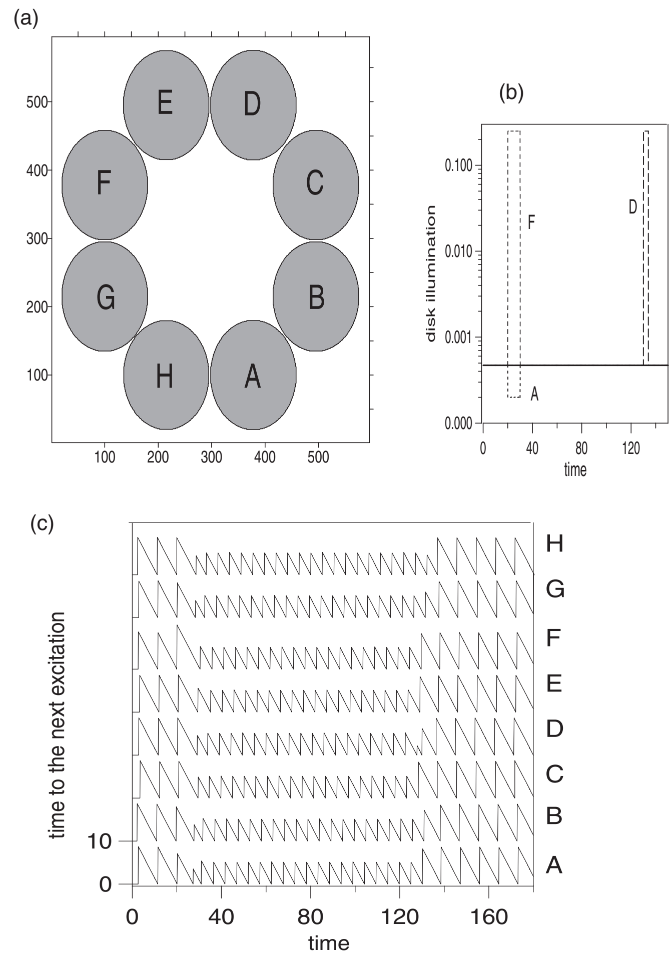

FIG. 8. (a) The geometry of a ring of disks that works as a memory cell. The diameters of all disks are the same and equal to 80 grid points. Disks are separated by an illuminated gaps (ϕ_0) that are 5 grid points wide. (b) The illumination of selected disks as a function of time: the solid line is an illumination of disks B, C, E, G, and H; the short dashed line is illumination of disk A; the medium dashed line is illumination of disk F; and the long dashed line is illumination of disk D. (c) The function $D(t)$ calculated at centers of disks.

If I2 is in the TRUE state the period of output oscillations is longer than T_2, which means that the output state is FALSE. Therefore, the structure of disks shown in Fig. 7 functions as the NOT gate. If we add another output disk below the central one and link the outputs together, then such a set of disks represents the XOR gate activated when one of the inputs is in the TRUE state and the state of another is FALSE.

F. One-bit memory

If a medium is excitable, then a ringlike structure can support stable rotation of an excitation pulse provided that the ring diameter is large enough [38]. If information is coded in excitation pulses, then a ring supporting a stable rotation can be used as a single-bit memory cell. The presence of rotating excitation represents memory in the TRUE state and a ring in its stationary state corresponds to the logical FALSE [39,40]. The idea of ring-shaped memory can be also used for information coded in oscillation frequency. Let us consider a ringlike structure of eight interacting disks, separated by a highly illuminated medium (illumination ϕ_0) as illustrated in Fig. 8(a). The time evolution of disk oscillations has been studied on a square grid with $\Delta_x = \Delta_y = 0.040$. The diameters of all disks are the same and equal to 80 grid points (3.2 distance units). Keeping in mind that forced high-frequency oscillations spread out on an array of oscillating disks (cf. Fig. 4) we can initiate stable high-frequency oscillations on the ring of oscillating disks in a similar way to initiation of rotating excitation on ring-shaped excitable medium. If illumination of a selected disk is reduced, then the frequency of chemical oscillations increases. A disk oscillating with a high frequency forces such oscillations on the neighboring disks. As a result, high-frequency oscillations originating from a single disk spread out clockwise and counterclockwise round the ring. In order to get unidirectional rotation of high-frequency oscillations one of these directions should be blocked. This can be done by a short, nonsymmetrical (with respect to the source) illumination of one disk with a high-intensity light. Alternatively, unidirectional rotation on a ring can be achieved if a signal diode is incorporated somewhere on the ring [40], but it makes the system more complex and in the following we discuss the first scenario. As a result of this illumination, the limit cycle vanishes and the system is characterized by a strongly attracting stationary state. If illumination is synchronized with the moment when a stimulus arrives, then the disk does not get excited and it does not transmit the stimulus to its neighbor on the other side. The idea is illustrated on Fig. 8. Figure 8(a) illustrates the geometry of a memory ring composed of eight oscillatory disks separated by a highly illuminated medium (ϕ_0). Figure 8(b) shows illuminations off all disks as a function of time. The illumination of disks B, C, E, G, and H is constant and equal to $\phi_2 = 0.00047$ so periods of oscillations at these disks is T_2. High-frequency oscillations are introduced by disk A. At the beginning its illumination is ϕ_2, but during the time interval $t \in [20,30]$ it drops to ϕ_1 and returns to ϕ_2 for $t > 30$. Within the time interval [20,30] disk A perturbs its neighbors B and H with high-frequency excitations. High-frequency oscillations are transmitted through disks B and H to disks C and G. In order to force unidirectional rotation of high-frequency oscillations the symmetry of expansion was broken at disk F, where a high illumination level ϕ_0 was applied for $t \in [20,30]$. If such an illumination level is applied disk F does not respond to an excitation coming from disk G. However, the illumination at disk F is ϕ_2 again when the stimulus arrives from disk E. As a result, disk F gets excited and a rotating excitation appears on the ring. In the considered case the period of forced oscillations is short and equals 5.2 time units. It depends on two factors. Its lower boundary is determined by the refractory phase of chemical oscillations within which the medium does not answer to external perturbations. If the time of subsequent excitation is longer than the refractory time, then the period of forced oscillations is given by the time within which an excitation makes a full rotation on the ring. It depends on the number of disks and on disk diameters. Using a few more disks one can make it equal to T_1. Of course, if there are too many disks and the time of rotation is longer than T_2, then the rotating pulse becomes unstable. The memory can be erased by breaking the rotation of excitation. In the presented case an arbitrary disk (here disk D) was illuminated with light intensity ϕ_0 for a time similar to the oscillation period [here 5 time units; see the long dashed line in Fig. 8(b)]. As a result, high-frequency oscillations disappear and all disks oscillate with period T_2.

III. DISCUSSION

The majority of recent studies on chemical reaction-diffusion computing have been concerned with a spatially distributed medium and the Boolean information coding related to the presence of excitation pulses at selected points in the medium. The construction of information processing devices is based on a specific geometrical distribution of excitable and nonexcitable regions [7,41,42]. In order to design a device that performs a complex operation a bottom-up approach is used. It would be more challenging to find a chemical medium in which information processing devices can be self-generated at carefully selected nonequilibrium conditions. A promising candidate for such a flexible computing medium is a system of droplets containing reagents of the BZ reaction. However, the experiments [30] have shown that it is relatively easy to prepare a structure composed of interacting oscillatory droplets but it seems to be very hard to make the droplets excitable, so in such a medium the concept of information coded in excitation pulses does not work. In this paper we have demonstrated that a compartmentalized oscillatory medium can be equally useful in information processing applications as the excitable one. We introduced frequency-based information coding and presented constructions of the basic logic gates as well as of a signal diode and one-bit memory. The idea of frequency coding is general and it can be applied to any oscillating medium if oscillation frequency can be controlled by external factors. We also believe that the designs of information processing devices presented in the paper are generic and can be applied to other oscillatory media. Such an opinion is supported by the fact that in simulations we intentionally considered exactly the same Oregonator model that was used in simulations of the logic gates constructed with an excitable photosensitive medium [17–21]. The selected model was not especially suitable for the frequency coding because for the values of model parameters copied from papers concerned with an excitable medium the period of oscillations does not significantly change with illumination except in the region where oscillations vanish (cf. Fig. 1). In the considered example of frequency coding the periods associated with the FALSE and TRUE states does not by more than 20%, whereas in typical experiments with a photosensitive BZ reaction it is easy to get stable oscillations with the period reduced by more than 50% if compared to the dark state. Despite the fact that we have not optimized model properties for frequency coding we were able to demonstrate its computational universality.

Numerical simulations indicate that functionality of an ensemble of disks should be more stable if information is coded in oscillation frequency than if it is coded in excitation pulses. For example, the gates described in Ref. [17] require a subexcitable medium with illumination in the range [0.07873,0.07878]. This means that system parameters should be fixed to within five-digit precision. The devices described in this paper operate in a wider range of medium parameters. In most cases they will still perform their function if the values of radii are changed within a few percentages. Therefore, it should be easier to do experiments on devices operating with information coded in the frequency of chemical oscillations than with those based on the presence of excitation pulses.

In this paper we considered a deterministic model and we neglected the influence of noise of the system. Previous experience with a membrane containing an immobilized catalyst [32] tells that if a dark part of the medium is not too small (2 mm or larger), then oscillations are quite stable and repeatable if the same reagents and illumination are used. We think that if the disk structures described in this paper are repeated in experiments with centimeter-size disks, then the internal noise will not disturb the predicted behavior.

Simulation results show that the considered Oregonator model quickly converges to another cycle after the illumination level changes. This feature agrees quite well with experiments with lipid-covered droplets containing a mixture of ferroine and Ru-catalyst that makes the reaction photosensitive. It has been observed that if a strong illumination is switched off then a droplet instantaneously starts to oscillate with the frequency characteristic for dark conditions. Moreover, the changes in oscillation frequency are recorded within a cycle after illumination is modified.

Obviously, processing information coded in frequency is much slower than in the case of information coding with the presence of excitation pulses. In the second case the output state is known immediately after an excitation pulse arrives. On the other hand, if information is coded in frequency of oscillations, then the output should be observed for a number of periods to decode its state. As seen in the presented results there are cases in which the transient evolution before the stable output state is reached can last for few periods (cf. Figs. 5 and 6). Despite its slowness, frequency coding allows one to process information with an oscillatory medium, where the coding based on the presence or absence of excitation pulses does not work.

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