

Oscillations and turbulence induced by an activating agent in an active medium

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An excitable Belousov-Zhabotinsky reagent becomes oscillatory above a threshold of methanol concentration [Me]. The oscillation period decreases with increasing [Me]. A model describes these observations quantitatively. In a spatiotemporal setup, a [Me] gradient causes waves with spatially varying properties; this leads to wave breaks that end up in turbulence, both in experiments and in simulations with partial differential equations.

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Active media are ubiquitous in nature. They appear in heart tissue [1], living cells [2], the retina [3], social amoeba [4], catalytic surface reactions [5], and the Belousov-Zhabotinsky (BZ) reaction [6–8]. These media can be excitable [9,10] or oscillatory [11]. In spatially extended, nonhomogeneous systems, they can lead to periodic waves [6,9–12] or to spatiotemporal chaos; the latter has been observed on the surface of catalysts [5], in heart muscle [13] (where it has been associated with the fatal ventricular fibrillation [14]), and in the ruthenium-catalyzed BZ reaction when exposed to sufficiently large light intensities [8].

It has been reported that methanol decreases the period of the oscillations of a BZ reagent [15]. In the present work we aim to explain the transition to these oscillations and to model quantitatively the dependence of their period on the concentration of methanol [Me]. We use the following set C_I of initial concentrations: $[\text{NaBrO}_3]=0.174M$, $[\text{NaBr}]=0.089M$, $[\text{H}_2\text{SO}_4]=0.345M$, $[\text{malonic acid}]=0.167M$, and $[\text{ferroin}]=1\text{ mM}$. [Me] was varied throughout this work. It has been shown before [16] that methanol acts as an activating agent, since it reacts with bromate, thus producing bromous acid, the system's activator. We found that, while the system is excitable at $[\text{Me}]=0\text{ mM}$, a transition to oscillations occurs at $[\text{Me}]=[\text{Me}]^*=2.1\text{ mM}$.

Figure 1 shows the signal at a photodiode after absorbance of green light ($\lambda=520\text{ nm}$, light intensity= 0.3 W/m^2) through a cuvette (absorbing distance: 10 mm) containing the magnetically stirred BZ reagent. Figure 1(a) exemplifies the situation at $[\text{Me}]<[\text{Me}]^*$, while Figs. 1(b)–1(d) show oscillations at $[\text{Me}]>[\text{Me}]^*$. In Fig. 2 we show the measured oscillation period as a function of [Me].

In order to simulate the oscillations (such as those in Figs. 1 and 2), we used “Model G” by Turányi *et al.* [17]. We chose this particular model because it was shown that it yields about half the period than the simpler “Oregonator” model and is thus closer to experimental observations [17]. The drawback of Model G, however, is that it renders only oscillations and not excitability. In order to include the effect of methanol and to obtain excitability, we made two extensions of Model G: (i) a term accounting for the reaction of methanol with bromate (which is in excess), producing bro-

mous acid [16], which is the activator of the system; (ii) an additional term αV for bromide production. Extension (ii) yields the observed excitability at low values of Me; α can be considered as an approximate lumping of several bromide-producing reactions among the 80 BZ reaction steps (see [17]) that were neglected to obtain the three-variable Model G. The equations of the extended Model G read

$$\frac{dU}{dt} = -k_3 H U W + k_5 A H^2 W - 2k_7 U^2 + k_9 A H U - 0.5k_{14} U V + 2k_m A H [\text{Me}], \quad (1)$$

$$\frac{dW}{dt} = -k_3 H U W - k_5 A H^2 W + k_{26} B V + \alpha V, \quad (2)$$

$$\frac{dV}{dt} = 2k_9 A H U - k_{14} U V - 2k_{26} B V. \quad (3)$$

A is $[\text{NaBrO}_3]$, B is $[\text{malonic acid}]$, H is $[\text{H}^+]$, U is $[\text{HBrO}_2]$, V is $[\text{oxidized catalyst}]$, and W is $[\text{Br}^-]$. After bromination, the concentrations C_I become $A=0.13M$, $B=0.167M$, and $H=0.212M$. ($k_3=2.0 \times 10^6 M^{-2} s^{-1}$, $k_5=2.0 M^{-3} s^{-2}$, $k_7=3.0 \times 10^3 M^{-1} s^{-1}$, $k_9=33.0 M^{-2} s^{-1}$, $k_{14}=7.0 \times 10^3 M^{-1} s^{-1}$, $k_{26}=0.23 M^{-1} s^{-1}$). The last terms in Eqs. (1) and (2) correspond to the model extensions (i) and (ii) given above ($k_m=3.8$

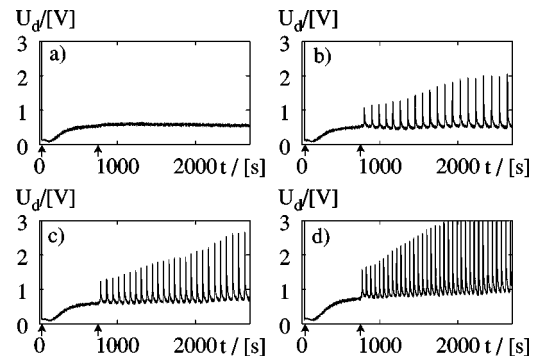


FIG. 1. Measured time series of the potential U_d at a photodiode after absorbance of light ($\lambda=520\text{ nm}$) by the BZ reagent. The first arrow in each picture indicate the addition of ferroin, the second arrow the addition of methanol. (a) $[\text{Me}]=1.9\text{ mM}$. (b) $[\text{Me}]=3.9\text{ mM}$. (c) $[\text{Me}]=7.8\text{ mM}$. (d) $[\text{Me}]=13.7\text{ mM}$.

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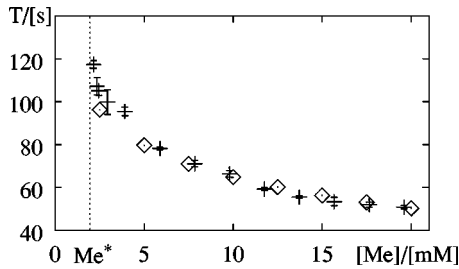


FIG. 2. Oscillation period (ordinate) vs methanol concentration (abscissa). Crosses with bars: measurements. Diamonds: simulations using Eqs. (1), (2), and (3). The dotted line indicates the transition from excitable to oscillatory behavior at $[\text{Me}]^* = 2.1 \text{ mM}$.

$\times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$ [16], $\alpha = 9.1 \times 10^{-2} \text{ s}^{-1}$). Equations (1)-(3) were integrated using a fourth-order Rosenbrock method with adaptive stepsize [18]. Simulation results, shown by diamonds in Fig. 2, are in surprisingly good agreement with the observations shown in the same figure.

The nullclines shown in Fig. 3 give an insight into the effect of methanol on the extended Model G. In order to obtain this display on the U - V plane, we made the quasistationarity assumption $dW/dt \approx 0$, permitting to eliminate W . This assumption preserves the transition to oscillations, decreasing however $[\text{Me}]^*$ from 2.1 mM to 1.6 mM.

In addition to the above investigations of the homogeneous (stirred) system at varying $[\text{Me}]$, we also investigated a nonstirred system with a $[\text{Me}]$ gradient. In experiments, ferroin was incorporated in a silica-gel matrix (using a solution of 10.3% sodium silicate, 1 mM ferroin and 0.18M H_2SO_4 ; preparation as in Ref. [19]) in a Petri dish (diameter: 6 cm; thickness: 1 mm). The solution (twice the concentrations given above; without Me) was poured onto the gel. As the volumes of the solution and the gel were

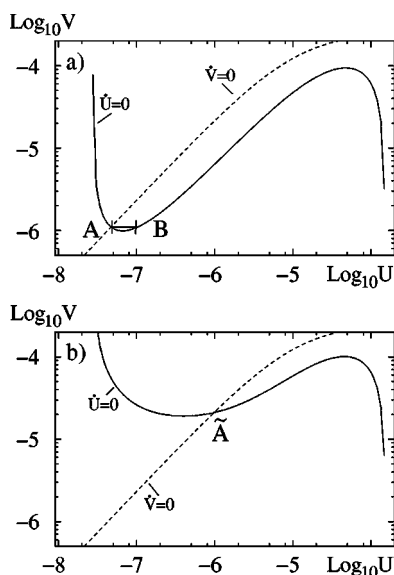


FIG. 3. Nullclines obtained from Eqs. (1) and (3). (a) Excitable system at $[\text{Me}] = 0 \text{ mM}$; A: stable stationary state; AB: excitation gap. (b) Oscillatory system at $[\text{Me}] = 5 \text{ mM}$; \bar{A} : unstable focus.

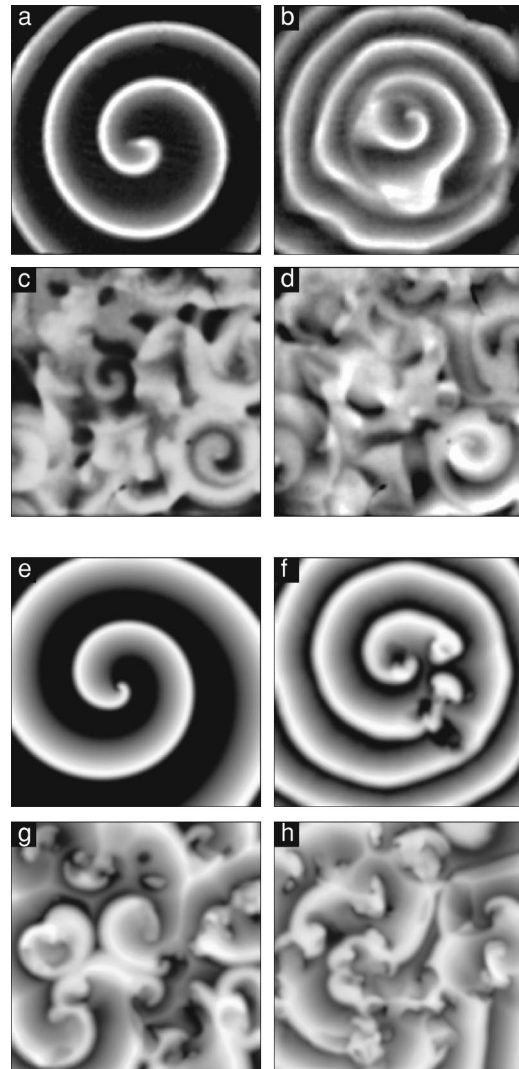


FIG. 4. (a)–(d) Observation of turbulence due to a vertical methanol gradient in the BZ reagent. (e)–(h) Three-dimensional simulations with Eqs. (4) and (5). Times since pouring the solution containing methanol above the gel: (a), (e) 0 min; (b), (f) 8 min; (c), (g) 28 min; (d), (h) 32 min. Image-size: $10 \times 10 \text{ mm}$.

equal, the concentrations decreased to one half of their initial value, namely to C_I . The temperature was held at $25 \pm 1 \text{ }^\circ\text{C}$. White light (250-W halogen lamp; light intensity: 6 W/m^2) first passed a diffusion screen, then the Petri dish, an interference filter (450.6 nm; transmission, 56%), and finally, video equipment for image recording. A spiral was allowed to develop for 20 min. We then poured away the solution above the gel and exchanged it by a new one including 0.15M Me and the concentrations C_I . After a few minutes, we observed the first breakup of the spiral at its tip. The number of breakups increased until we obtained turbulent modes, such as those exemplified in Figs. 4(c) and 4(d). (Note: when we omitted methanol in the solution we exchanged above the gel, the spiral did not change.)

In order to understand the disordered dynamics illustrated in Figs. 4(a)–4(d), we performed simulations with partial differential equations. Since such simulations are time-

consuming, and since understanding is easier if the model is simpler, we decided at this point to sacrifice quantitative accuracy and use the more modest Oregonator (see [17]), modified to contain the production of activator by methanol [last term of Eq. (1)]:

$$\begin{aligned} dU/dt = & k_3AHU - 2k_4U^2 + 2k_mAH[\text{Me}] \\ & - hk_5BV \frac{U - k_1AH/k_2}{U + k_1AH/k_2} + D_u \nabla^2 U, \end{aligned} \quad (4)$$

$$dV/dt = 2k_3AHU - k_5BV + D_v \nabla^2 V. \quad (5)$$

($k_1 = 2M^{-3} \text{ s}^{-1}$, $k_2 = 1 \times 10^6 M^{-2} \text{ s}^{-1}$, $k_3 = 40M^{-2} \text{ s}^{-1}$, $k_4 = 2 \times 10^3 M^{-1} \text{ s}^{-1}$, $k_5 = 0.4M^{-1} \text{ s}^{-1}$, $h = 1.5$, $D_u = 2 \times 10^{-3} \text{ mm}^2/\text{s}$, $D_v = 0$). (Note that W was eliminated here by setting $dW/dt = 0$.) Although the Oregonator is not so accurate in the quantitative reproduction of oscillation periods as Model G, it has the advantage over the latter model that it yields both excitable and oscillatory behavior; thus, no extension, as the one in the last term of Eq. (2) was necessary. Equations (4) and (5) were integrated using the explicit Euler method in a rectangular grid imposing noflux boundary conditions. In order to simplify calculations, we assumed a constant gradient of $[\text{Me}]$, between $0.15M$ at the top of the gel and $0.0M$ at its bottom. We assumed that the experimental step of pouring away the solution above the gel does not alter the concentrations within the gel. Typical results are shown in Figs. 4(e)–4(h) and compare qualitatively well with observations [Figs. 4(a)–4(d)].

A detailed inspection of the simulations revealed the mechanism leading to turbulence, as follows. A methanol gradient appears, as it diffuses down the gel. Thus, the upper zone of the gel becomes oscillatory, and the lower zone excitable. In the cases considered here, the height of the excitable zone would be of the order 10^{-2} mm , which can be neglected, considering the total height (0.8 mm). Spirals are sustained in the oscillatory medium (see [11]). The spiral period \tilde{T} decreases with increasing $[\text{Me}]$, although the effect is much less pronounced than the $T([\text{Me}])$ -dependence shown in Fig. 2. Typically, $d\tilde{T}/d[\text{Me}] \approx -120 \text{ s}/M$, $d\tilde{v}/d[\text{Me}] \approx 67 \mu\text{m}/(\text{s}M)$, and $d\tilde{\lambda}/d[\text{Me}] \approx -5 \text{ mm}/M$. At $[\text{Me}] = 0$, $\tilde{T} \approx 50 \text{ s}$, spiral velocity $\tilde{v} \approx 60 \mu\text{m}/\text{s}$, spiral wavelength $\tilde{\lambda} \approx 3 \text{ mm}$. Since methanol increases the wave velocity, the vertical Me gradient causes an inclination of the wave fronts that increases in time. However, $d\tilde{v}/d[\text{Me}]$ is not strictly constant in the vertical direction. This causes wave inclinations to develop a nonlinear ‘‘S’’-like shape. Thus, at about half the height of the gel, wave backs from the inclined fronts collide with wave fronts of waves previously

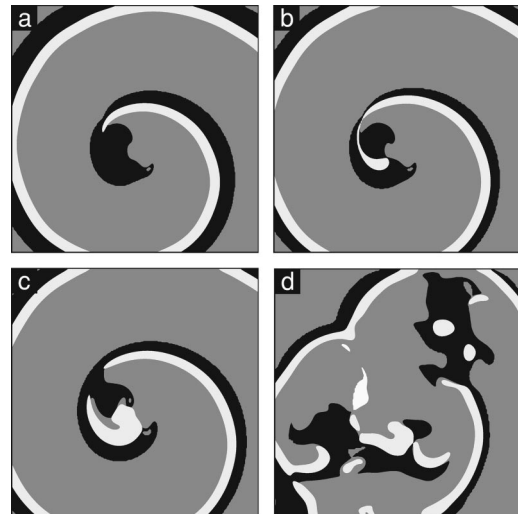


FIG. 5. Simulation of a first wave break close to the spiral tip (a)–(c) leading later to spatially extended disorder (d). Times since addition of the solution containing methanol: (a) 3 min, (b) 3.2 min, (c) 3.4 min, and (d) 12.2 min. Zones around the maxima of the activator U (white) and the inhibitor V (gray) are shown in a horizontal cross section. A partial collision of the activator front with the inhibitory tail of the adjacent wavefront originates the first wave break (height = 0.55 mm).

above them, causing breakup of the latter. Wave breaks occur first in the vicinity of a spiral tip. Such a disruption promotes further wave breaks, expanding outwards from the center until they cover the whole medium. Note that the particular snapshots in Fig. 5 were chosen so as to give a clear description of the breakup process. We must point out, however, that a full understanding can only be obtained by considering the three-dimensional geometry of the scroll waves. Furthermore, one should consider in future simulations that the $[\text{Me}]$ gradient is not strictly independent on time and not constant in space within the temporal range considered here. A more detailed (three-dimensional and time-dependent) description is left to future work.

Note that a development of turbulence from the tip outwards was also obtained in the model in Ref. [20]. Note also that, besides that model, some other mechanisms for spiral breakup have been proposed [21–23]. However, the breakups described in these models (Refs. [20–23]) occur in two dimensions. In contrast, the third, vertical direction plays an essential role in the present case because of the methanol gradient in this direction.

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- [1] J.M. Davidenko, A.M. Pertsov, R. Salomonsz, W. Baxter, and J. Jalife, *Nature (London)* **355**, 349 (1992).
 [2] J. Lechleiter, S. Girard, E. Peralta, and D. Clapham, *Science* **252**, 123 (1991).

- [3] A. Gorelova and J. Bures, *J. Neurobiol.* **14**, 353 (1983).
 [4] F. Siegert and C.J. Weijer, *Proc. Natl. Acad. Sci. U.S.A.* **89**, 6433 (1992).
 [5] G.E. Ertl, *Science* **254**, 1750 (1991).

- [6] A.T. Winfree, *Science* **175**, 634 (1972).
- [7] M. Markus, Zs. Nagy-Ungvarai, and B. Hess, *Science* **257**, 225 (1997).
- [8] M. Markus, G. Kloss, and I. Kusch, *Nature (London)* **371**, 402 (1994).
- [9] V.S. Zykov, *Simulation of Wave Processes in Excitable Media* (Manchester University Press, Manchester, 1988).
- [10] *Nonlinear Wave Processes in Excitable Media*, edited by A.V. Holden, M. Markus, and H.G. Othmer (Plenum Press, New York, 1991).
- [11] J.J. Tyson, in *Oscillations and Traveling Waves in Chemical Systems*, edited by R.J. Field and M. Burger (J. Wiley, New York, 1985), pp. 93–144.
- [12] M. Markus and B. Hess, *Nature (London)* **347**, 56 (1990).
- [13] N. El-Sherif, R. Mehra, W.B. Gough, and R.H. Zeiler, *Circ. Res.* **51**, 152 (1982).
- [14] A.V. Panfilov, *Chaos* **8**, 57 (1998).
- [15] J. Abe, K. Matsuda, T. Masakazu, and S. Yasuo, *Chem. Phys. Lett.* **245**, 281 (1995).
- [16] H.D. Försterling, H.J. Lamberz, and H. Schreiber, *Z. Naturforsch. A* **38a**, 483 (1983).
- [17] T. Turányi, L. Györgyi, and R.J. Field, *J. Phys. Chem.* **97**, 1931 (1993).
- [18] W.H. Press, S.A. Teukolsky, W.T. Vetterling, and B.P. Flannery, *Numerical Recipes in C*, 2nd ed. (Cambridge University Press, Cambridge, 1992).
- [19] T. Yamaguchi, L. Kuhnert, Zs. Nagy-Ungvarai, S.C. Müller, and B. Hess, *J. Phys. Chem.* **95**, 5831 (1991).
- [20] M. Bär and M. Eiswirth, *Phys. Rev. E* **48**, R1635 (1993).
- [21] A. Hagberg and E. Meron, *Phys. Rev. E* **57**, 299 (1998).
- [22] H. Ito and L. Glass, *Phys. Rev. Lett.* **66**, 671 (1991).
- [23] A.F.M. Marée and A.V. Panfilov, *Phys. Rev. Lett.* **78**, 1819 (1997).