# Simple Chemomechanical Process for Self-Generation of Rhythms and Forms

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(Received 16 December 2002; published 7 May 2003)

We show that cross-coupling between the geometrical changes and the chemical reaction-diffusion regimes within a piece of gel embedded in a stationary reactive medium kept far from equilibrium can destabilize the trivial steady state and lead to spatiotemporal dissipative structures. The involved physical processes are the spatial bistability and the swelling properties of the gel. As an illustration of this morphogenetic process, we show that a sphere of gel immersed within such a medium with autocatalytic properties can exhibit periodic radius pulsations, the amplitude of which are controlled by chemistry.

DOI: 10.1103/PhysRevLett.90.188302 PACS numbers: 82.40.Ck, 82.33.Ln, 82.40.Bj, 89.75.Fb

Most rhythms and changes of shape in biological systems are governed by coupling of a mechanical system with chemical processes. A major objective in order to gain some insight in these phenomena and to devise biomimetics systems is to recognize elementary mechanisms that can generate self-induced motions in systems where sustained chemical reactions take place. Mechanically idle and chemically inert hydrogels are regularly used as supporting materials for the production of sustained reaction-diffusion patterns, including traveling waves [1–4], Turing patterns [5–7], or patterns controlled by front dynamics [8–12]. Most of these systems are fed with fresh reactants by diffusion from the gel boundaries. However, some types of gel may exhibit large volume changes as a function of the chemical composition of the solvent, e.g., the *p*H of the solution [13]. A swelling-deswelling mechanism naturally provides a coupling mechanism between the chemical processes operating within the gel and the geometrical characteristics of this gel. Recently, it was shown that oscillating reactions which exhibit large *p*H variations can induce periodic volume changes of a piece of polyelectrolyte gel immersed in the reacting solution [14,15]. A first theoretical model has been proposed by Dewel *et al.* [16]. Gel size oscillations were also obtained by making the Belousov-Zhabotinskii reaction to oscillate within a gel in which the catalyst was bound to the polymer network [17,18].

In all these experiments, the volume changes were slaved to the chemical oscillations, whether these occur in the surrounding medium or only within the gel. All these reactions can also oscillate in an homogeneous stirred medium. The mechanical oscillations are forced by the chemistry without introducing a destabilizing feedback. However, it has been shown that swelling can control the transfer of chemicals between two compartments through a gel membrane and facilitate oscillations in a biochemical reaction [19]. It was also shown that an elongated piece of gel, immersed in a stationary reactive medium that cannot exhibit oscillatory dynamics in homogeneous conditions, can display complex dynamical volume and shape changes [20]. It is an important challenge to find mechanisms by which the cross-coupling between the volume changes—more generally, geometrical changes—and a nonoscillating chemical reaction can cause an oscillatory instability leading to periodic changes of volume or shape. Here we show that the geometrical parameters can exert such direct feedback on the chemistry and report calculations on a model self-oscillatory medium.

In batch reactors, most systems controlled by autocatalytic steps present a more or less long induction time before the reaction speeds up. Consider a piece of gel immersed in a bath where such a reaction is kept in its initial stage by a sufficient flow of fresh reactants. If the size of the piece is small, the diffusive exchanges of the gel contents with the bath occur in a time shorter than the induction time so that they remain almost unreacted everywhere within the gel. If the size is large, the feed of fresh reactants cannot be sustained in the core of the gel so that the extent of the reaction is large except within a boundary layer. However, at intermediate sizes, both states can be stable since, if a sufficient amount of the autocatalytic species is initially present within the gel, the reaction is switched on. Then the extent of the reaction can remain large, even if the induction time is larger than the diffusion time. This defines a range of sizes for which the two states are both stable. We name them the "reacted state" and the "unreacted state." Transitions between states occur at the bistability limits with hysteresis. This phenomenon, known as "spatial bistability," has been extensively studied both theoretically and experimentally [3,4,21–23]. Consider a gel responsive to a species concentration $c$, which is small in the unreacted state (large in the reacted state) and assume that the gel shrinks for large $c$ (swells for small $c$). If we start with a swollen gel, the size of which is large enough for the unreacted state to be unstable, the system quickly switches to the reacted state and the gel begins to shrink. If the size becomes small enough to reach the lower bistability limit, the system switches back to the unreacted state. The gel stops shrinking and begins to swell. If the growing size now reaches the upper bistability limit, the system returns to the reacted state and shrinks again. Thus, for an appropriate initial size and a sufficient swelling-deswelling amplitude, the process repeats indefinitely, so that the gel exhibits periodic changes of volume. If the initial shape has a low symmetry, this can also lead to temporal shape changes.

To illustrate this idea, we solve numerically a model problem in the case of a spherical gel of radius $R$. The reaction involves two species $U$ and $V$ of concentrations $u$ and $v$, governed within the gel by the reaction-diffusion equation (in normalized space units)

$$\frac{\partial u}{\partial t} = -u^2 v^2 + \nabla^2 u, \qquad \frac{\partial v}{\partial t} = \frac{12}{7} u^2 v^2 + \nabla^2 v. \quad (1)$$

This system is often used as an oversimplified model of the chlorite-tetrathionate reaction, where the autocatalytic species $V$ is $H^+$, but will be here used as a toy model. To avoid ambiguities due to long range activation [4], the ratio of the two diffusion coefficients is fixed to 1. In these conditions, the reaction can never display oscillations or excitability. The concentrations in the unreacted surrounding medium will be fixed to $u_0 = 1$ and $v_0 = 0.05$ at the external radius of the sphere. This system was shown to exhibit spatial bistability in a flat film [4], but the extension to a spherical geometry is straightforward. Solving numerically Eq. (1), one finds that the system is bistable for $R_{\mathrm{inf}} = 4.48 < R < R_{\mathrm{sup}} = 5.42$. The two corresponding stable spatial concentration profiles $v(r)$, where $r$ is the distance to the center of the sphere, are given in Fig. 1 for $R = 5$. In the reacted state, concentration $v$ is large in the core of the sphere.

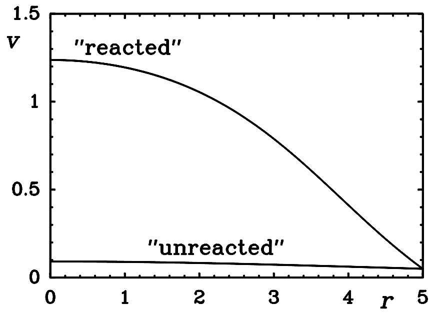

FIG. 1. Stable states: spatial dependence $v(r)$. $u_0 = 1$, $v_0 = 0.05$, $R = 5$.

Among dynamical approaches of the swelling process [24–29], we use, with minor adjustments, the theory of Bisschops *et al.* [28] and add the effects of the chemicals. This approach, based on Maxwell-Stefan (MS) equations [30], retains the essentials for our demonstration, ignoring complexities that would be unnecessary at this stage. Three types of constituent are considered: the solvent (the water), the solutes (the chemicals), and the polymer (organized in a network). To simplify the expressions, we do the following series of assumptions. The solutes are very dilute and their partial volume is negligible. The volume fraction $\phi$ of the polymer is small (typically a few percent in the experiments) so that, for the solutes, the gel appears as just water, both from the diffusional and the reactional standpoints. This assumption is commonly done without any problem in the study of chemical patterns. At worst, some constants would be slightly altered into effective values. To simplify expressions, one also assumes that a molecule of solvent occupies the same volume as a monomer. Finally, the dependence of network properties on a chemical concentration, here species $V$, is supposed to be contained only in the energy of interaction between the solvent and the polymer. The MS equations assert that at each point within the gel, a driving force $F_{\mathrm{tot}} = -\nabla(\Delta\mu)$, where $\Delta\mu$ is a generalized chemical potential including the contributions of the elastic forces, is equal to the friction force $F_{\mathrm{fr}} = \phi\, G(\phi)(\xi_S - \xi_P)$ applied to the solvent molecules, where $\xi_S$ and $\xi_P$ are the velocities of, respectively, the solvent and the polymer, and $G(\phi)$ is an increasing function of $\phi$. This function expresses the hydrodynamic increase of friction with the polymer density. Taking into account the spherical symmetry and the so-called "bootstrap" equation which expresses the mass balance

$$\xi_S(1 - \phi) + \xi_P \phi = 0, \quad (2)$$

one derives the following equation:

$$(\xi_P)_i = \frac{dr_i}{dt} = \frac{1 - \phi}{\phi\, G(\phi)} \left( \frac{\partial \Delta\mu}{\partial r} \right)_{r=r_i}, \quad (3)$$

where $r_i(t)$ is the radial coordinate of a given point $i$ attached to the network [28]. The expression of $\Delta\mu$ is given by the classical Flory-Rehner theory where the pure solvent is taken as the reference to calculate the mixing chemical potential. The mixing term is given by $\Delta\mu_{\mathrm{mix}} = RT[\phi + \ln(1 - \phi) + \chi\phi^2]$ and the elastic term by $\Delta\mu_{\mathrm{el}} = K_{\mathrm{net}} RT[(\phi/\phi_0)^{1/3} - (\phi/\phi_0)/2)]$, where constant $K_{\mathrm{net}}$ depends on the network properties and $\phi_0$ is the volume fraction in a reference state. The last term in the expression of $\Delta\mu_{\mathrm{el}}$ is controversial and could be dropped without changing our qualitative conclusions. According to our former assumption, $\Delta\mu = \Delta\mu_{\mathrm{mix}} + \Delta\mu_{\mathrm{el}}$ depends on the concentration $v$ through the energetic term $\chi = \chi(v)$. For a given uniform value of $v$, the equilibrium polymer volume fraction $\phi_{\mathrm{eq}}(v)$ is the solution of the equation $\Delta\mu = 0$. In Eq. (3), the function $G(\phi)$ is chosen in agreement with the model of Ogston *et al.* [31]

$$G(\phi) = \frac{RT}{D_0 \exp(-K_D \sqrt{\phi})}, \quad (4)$$

where the constant $K_D$ depends on the geometrical characteristics of the polymer and the solvent, and $D_0$ is the diffusion coefficient of the pure solvent. Given the function $\chi(v)$ and an initially uniform grid of $N$ points attached to the network, labeled $i$ for $0 \leq r_i(0) \leq R_0$, the evolution of the position $r_i(t)$ of these network points and concentration distributions $u(r, t)$ and $v(r, t)$ can be numerically computed by integrating the coupled set of Eqs. (1) and (3) in time. The boundary condition is given by the condition of local equilibrium on the surface of the sphere in contact with the bath ($i = N$), i.e., $u(r_N, t) = u_0$, $v(r_N, t) = v_0$ and $\phi(r_N) = \phi_{\mathrm{eq}}(v_0)$. The function $\chi(v, r, t)$ is slaved to the distribution $v(r, t)$. The radius of the sphere is a function of time given by $R(t) = r_N(t)$. This approach is limited to moderate swelling ratios. For large swelling ratios, the assumption that the driving force depends linearly on the gradient of the potential breaks down. Ignoring this limitation, the form of $\Delta\mu$ leads to an unstable deswelling process. In particular, the dynamics cannot be properly described when the gel exhibits a volumic phase transition.

In our computations, the reference state $\phi_0$ is taken at the equilibrium value that corresponds to the composition in the bath [$\phi_0 = \phi_{\mathrm{eq}}(v_0)$], i.e., the value at the boundary. We have used a sigmoidal function

$$\chi(v) = \frac{(\chi_{\min} + \chi_{\max})}{2} + \frac{(\chi_{\max} - \chi_{\min})}{2}\tanh[\alpha(v - v^*)]$$

that saturates at large $v$, as expected when all the sensitive network sites are activated (or deactivated). The parameters have reasonable values in regard to usual cases. For clarity, $K_{\mathrm{net}}$ and $\chi_{\min}$ were chosen so that the equilibrium at the bath concentration ($v = v_0 = 0.05$) is $\chi = \chi_0 = 0.20$ and $\phi = \phi_0 = 0.01$ (Fig. 2). In Fig. 3, we show the sphere radius and the concentration $v$ at the center as functions of time. The former is the signature of the geometrical (or swelling) state of the gel; the latter characterizes the chemical state (reacted or unreacted). The initial state corresponds to a sphere of radius $R_0 = 5.6$, density $\phi_0$, filled with chemicals at concentrations $u_0$ and $v_0$. Since $R_0 > R_{\mathrm{sup}}$, the system switches almost immediately to the reacted state, so that the gel begins to shrink and $R$ decreases down to $R = R_{\mathrm{inf}}$. Then the gel switches back to the unreacted state and starts swelling. The radius increases up to $R = R_{\mathrm{sup}}$ where the system switches again to the reacted state. The process repeats indefinitely, giving rise to relaxation oscillations of both the radius and the chemical composition. Other dynamical information, which will be reported in detail in a more extensive publication, can be obtained from this simple model. In particular, the swelling and deswelling processes are different. During deswelling, although the highest values of $\chi(v)$ are located deep in the core of the gel, a peak of polymer density that signs a high shrinking level forms inside a shell located close to the boundary. In fact, it results from Eq. (3) that the steepest changes of $\phi$ occur close to the maximum of the potential gradient, which is a complex combination of functions, and not close to the maximum of $\chi$. During swelling, the polymer density distribution becomes quickly smoother.

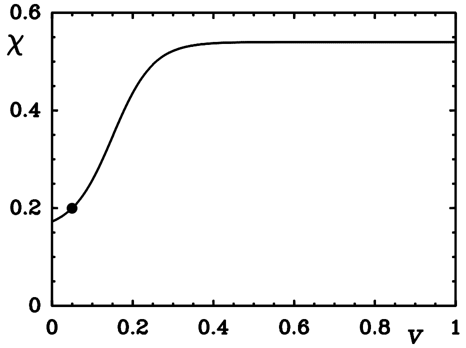

FIG. 2. Function $\chi(v)$. $\chi_{\min} = 0.154$, $\chi_{\max} = 0.54$, $\alpha = 10$, $v^* = 0.15$. The point corresponds to $\chi = \chi_0$.

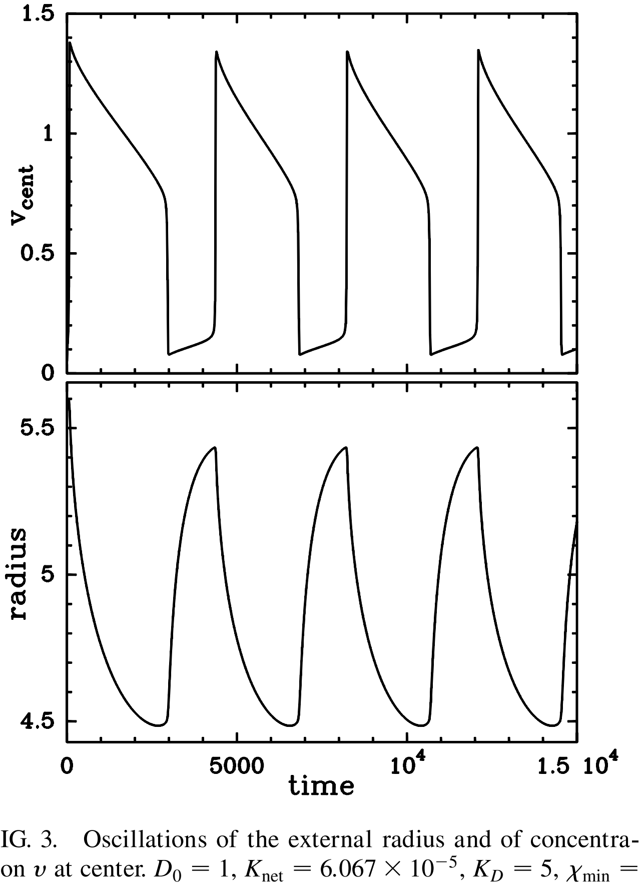

FIG. 3. Oscillations of the external radius and of concentration $v$ at center. $D_0 = 1$, $K_{\mathrm{net}} = 6.067 \times 10^{-5}$, $K_D = 5$, $\chi_{\min} = 0.154$, $\chi_{\max} = 0.54$, $\alpha = 10$, $v^* = 0.15$, $u_0 = 1$, $v_0 = 0.05$, $\phi_0 = 0.01$, $\chi_0 = 0.2$. All units are nondimensional.

We have shown that spontaneous mechanical pulsations can result from cross-coupling of a mechanically responsive medium with a chemical reaction which cannot produce oscillations by itself. The destabilization originates in the feedback of the system size (or geometry) on the chemical state within the system. The key is the hysteresis loop associated to the bistability generated by an autocatalytic reaction [32]. Such reactions are common in biological media and are observed in numerous other systems. Oscillations in Ref. [20] could enter this class, although excitability due to differential diffusion [4] could also play a role. The amplitude of the oscillations is controlled by chemistry which defines the bistability limits $R_{\mathrm{inf}}$ and $R_{\mathrm{sup}}$. Alternatively, the hysteresis loop could be provided by a volumic phase transition [13] and the feedback by a slow chemical reaction. Then the amplitude would be controlled by the properties of the gel. Although our model is adequate to describe the principles and the basic features of the phenomenon, improvements could be made in several directions. Many responsive gels are polyacids and charges are implied in the swelling. In this case, the transport of charges and, more generally, the transport in multicomponent systems should be accounted for [29]. Elasticity forces must be described explicitly to handle more complex geometries, such as cylinders or disks. Actually, due to the spherical symmetry, our model system exhibits only periodic volume changes, but no shape changes. Without this initial symmetry, one could expect to obtain stationary or unstationary shape changes, opening a new field for natural or artificial morphogenesis. In the same spirit, the possibility of additional instabilities which could spontaneously break the spherical symmetry should be considered.

We thank P. De Kepper, F. Gauffre, V. Labrot, E. Dulos, P. Borckmans, G. Dewel, and A. De Wit for useful and stimulating discussions. This work was supported by CNRS and région Aquitaine.

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