Designed Patterns: Flexible Control of Precipitation through Electric Currents

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Understanding and controlling precipitation patterns formed in reaction-diffusion processes is of fundamental importance with high potential for technical applications. Here we present a theory showing that precipitation resulting from reactions among charged agents can be controlled by an appropriately designed, time-dependent electric current. Examples of current dynamics yielding periodic bands of prescribed wavelength, as well as more complicated structures are given. The pattern control is demonstrated experimentally using the reaction-diffusion process $2AgNO_3 + K_2Cr_2O_7 \rightarrow \underline{Ag_2Cr_2O_7} + 2KNO_3$.

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Spontaneous pattern formation can be observed at all length scales [1] and much effort has been devoted to gaining insight into the dynamics of theses processes [2]. One of the aims of these studies is to reproduce and control the emerging patterns, thereby opening possibilities for applications such as, e.g., the downsizing of electronic devices [3]. For practical purposes, reaction-diffusion processes which yield bulk precipitation patterns [4] are especially important since they are building blocks for the so-called *bottom-up* or *bulk* approach to structure design (to be contrasted with *top-down* methods where material is removed to create structures, as in case of lithography). The use of precipitation processes, however, is limited due to problems over their control. Indeed, precipitation can be influenced by appropriately chosen geometry [5], by boundary conditions [6], or by a combined tuning of the initial and boundary conditions [7,8], but all the above methods are unwieldy, and developing more flexible approaches would be clearly valuable.

Here we introduce a general and easily realizable tool of control based on employing predesigned electric currents for regulating the dynamics of the reaction zones in the system. The method originates in two observations. First, precipitation patterns are often formed in the wake of moving reaction fronts whose reaction dynamics specifies where and when precipitation thresholds are crossed [2,4]. Hence control over precipitation should be realized through controlling the reaction front. Second, the reacting species are usually oppositely charged ions. Hence the details of the control: An appropriately directed electric field or current strongly affects the concentration of reagents in the reaction zone and, consequently, it can be used to govern the crossing of precipitation thresholds and thus the location of the precipitate.

The details of our method will be described below on the specific example of Liesegang patterns [4]. Then we shall demonstrate how the control works in experiments by producing periodic precipitation patterns with controlled spacing, as well as obtaining a more complex, predesigned structure.

In a somewhat generic description, Liesegang patterns emerge from the reaction $A^+ + B^- \rightarrow C$ of the ions of two electrolytes $A \equiv (A^+, A^-)$ and $B \equiv (B^-, B^+)$, followed by the precipitation of the reaction product C. The electrolytes are initially separated (see Fig. 1 for a typical experimental setup) with the inner electrolyte B homogeneously dissolved in the gel inside a tube. The outer electrolyte A is in an aqueous solution which is brought into contact with the gel at the start of the experiment. The initial concentration a_0 of A is much larger than that b_0 of B and, consequently, A invades the gel and a *reaction front* forms and moves along the tube.

The relevant properties of this front in the absence of an electric field are well-known [9,10]: (i) The width of the front is practically negligible. (ii) The front moves diffusively; i.e., its position along the tube is given by $x_f(t) = \sqrt{2D_f t}$, with the diffusion coefficient D_f determined by a_0, b_0, and by the diffusion coefficients of the reagents.

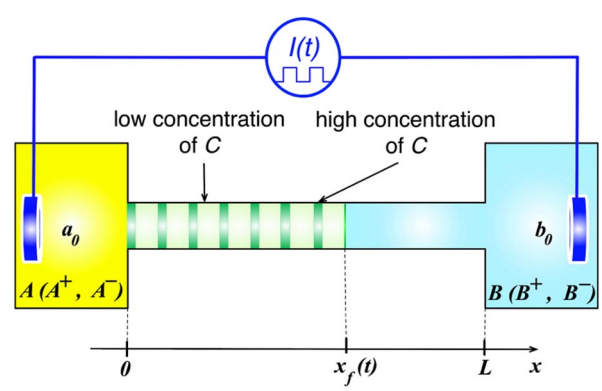

FIG. 1 (color online). Experimental setup for producing Liesegang precipitation patterns as described in the text. The controlling agent is the generator providing electric current $I(t)$ with a prescribed time dependence.

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(iii) The concentration c of the reaction product C left in the wake of the front is constant, $c = c_0$. The value of c_0 depends on a_0, b_0, the diffusion coefficients, and on the rate k of the reaction $A^+ + B^- \xrightarrow{k} C$.

The pattern formation, namely, the phase separation of the C-s, takes place only if their local concentration c is above a precipitation threshold, $c > c^*$; thus, $c_0 > c^*$ is chosen in experimental setups. The precipitation pattern itself results from a complex interplay of the production of C-s in the front and the ensuing phase-separation dynamics in the wake of the front. Namely, the front produces a precipitation band at the beginning since $c_0 > c^*$ just behind the front. This band acts as a sink for the newly produced C-s and thus their concentration in the front decreases below c^*. As the front moves far from the existing band, the depletion effect diminishes and the c in the front can again exceed c^* thus leading to the formation of the next band. A quasiperiodic reiteration of the above process yields the Liesegang patterns (lowest panel in Fig. 4). The positions x_n ($n = 0, 1, \ldots$) of the bands obey the spacing law; i.e., they form a geometric series $x_n \sim (1 + p)^n$ ($p > 0$), as observed in experiments and reproduced by various theories [10,11].

Since the precipitation is always initiated in the front, the position of the band x_n and its time of formation t_n are related by the so-called *time-law*,

$$x_n = \sqrt{2D_f t_n}. \tag{1}$$

From this equation one concludes that the positions x_n of the precipitation bands can be regulated either by modifying the time-law, or by controlling the t_n-s.

The first attempts to change the functional form of the time-law were based on the idea that the reaction takes place between ions $A^+ + B^- \rightarrow C$; therefore, the motion of the front is potentially affected by applying a constant external electric field [12–17]. These investigations indicate however that for a wide range of electric field intensities (for specifics see [16,17]) neither the locality (i), nor the diffusive nature (ii) of the front, which implies the time-law (1), are altered. Nevertheless, the electric field has an important effect on (iii) the production of C-s [16]. Namely, for a *forward field* (i.e., a field that drives the ionic reagents towards each other), the concentration c increases in the direction of the front motion, while a *backward field* yields a decreasing concentration of C-s, eventually till the complete extinction of the reaction.

One can alternatively use a *current generator* (Fig. 1) to produce constant backward and forward currents. The above conclusions hold also for a wide range of current intensities (when current and electric field are proportional to each other), to which we shall limit our studies hereafter. Figure 2 illustrates the C-production in these situations. The new results obtained from Eqs. (2)–(6) are represented by the continuous curve and concern the case when the applied current is constant in absolute value, but changes sign quasiperiodically at times $\tau n^2/2$, with τ giving a time scale and $n = 0, 1, 2, \ldots$. These results were obtained by numerical simulations of the model described below.

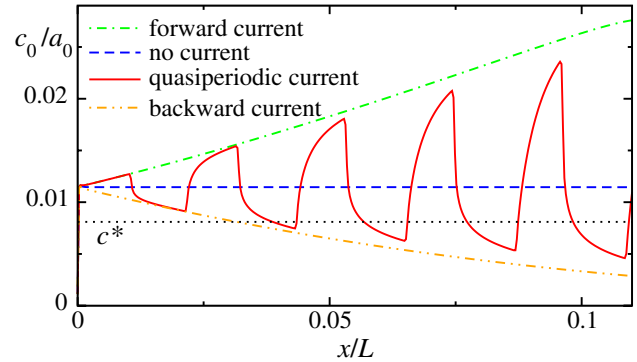

FIG. 2 (color online). Concentrations of the reaction product in the wake of the front, in the absence of a current, respectively, when a constant forward or backward current, or a quasiperiodic current (changed at times $\tau n^2/2$) is switched on [19].

Figure 2 together with the time-law (1) provide us the key to create precipitation bands at arbitrarily predefined locations, by using an appropriately-designed time-dependent current $I(t)$. Indeed, given a set of prescribed band positions x_n, one switches on the forward current at times $t_n = x_n^2/2D_f$. This increases the concentration of C-s to cross the precipitation threshold and thus a band forms at x_n. In order to avoid spontaneous formation of spurious bands one must switch on a backward current at some intermediate time between t_n and t_{n+1}.

The above protocol works, in particular, for producing the much sought after *periodic Liesegang pattern*. One can obtain a controlled wavelength d such that $x_n = dn$ by switching on the forward current at $t_n = (2n)^2\tau/2$, where $\tau = d^2/2D_f$. If the desired period d is smaller than half the *local wavelength* of the Liesegang pattern, then the spurious bands can be avoided by switching on the backward current when the front is halfway between x_n and x_{n+1}, i.e., at times $(2n + 1)^2\tau/2$.

In order to put the above arguments on a more solid foundation, we extended our model of the formation of Liesegang patterns in an electric field [16,17] to the case of a time-dependent current flowing through the system. The first stage of the process is described by the evolution equations for the ion concentrations $a^\pm(x, t)$ and $b^\pm(x, t)$, with the underlying electroneutrality hypothesis. These equations take a relatively simple form for the case of monovalent ions with equal diffusion coefficients,

$$\partial_t a^+ = D\partial_x^2 a^+ - j(t)\partial_x(a^+/\Sigma) - ka^+b^-, \tag{2}$$

$$\partial_t b^- = D\partial_x^2 b^- + j(t)\partial_x(b^-/\Sigma) - ka^+b^-, \tag{3}$$

$$\partial_t a^- = D\partial_x^2 a^- + j(t)\partial_x(a^-/\Sigma), \tag{4}$$

$$\partial_t b^+ = D\partial_x^2 b^+ - j(t)\partial_x(b^+/\Sigma). \tag{5}$$

Here $j(t) = I(t)/\mathcal{A}$ is the externally controlled electric

current density flowing through the tube of cross section $\mathcal{A}$, $\Sigma = q(a^+ + a^- + b^+ + b^-)$ with q being the unit of charge, and D is the diffusion coefficient of the ions. The reaction rate k is usually large resulting in a reaction zone of negligible width.

The second stage of the process is the phase separation of the reaction product C, modeled by the Cahn-Hilliard equation with a source term describing the rate of production of C-s in the reaction zone [11,17]. The free energy underlying the thermodynamics is assumed to have a Ginzburg-Landau form with minima at some low (c_l) and high (c_h) concentrations of C. Using then a shifted and rescaled concentration $m = (2c - c_h - c_l)/(c_h - c_l)$, yields the following equation

$$\partial_t m = -\lambda\Delta(m - m^3 + \sigma\Delta m) + S(x, t), \qquad (6)$$

where $S(x, t) = 2ka^+b^-/(c_h - c_l)$ is the source term coming from the Eqs. (2)–(5) of the first stage. The parameters λ and σ can be chosen so as to reproduce the correct time and length scales in experiments [17–19].

Equations (2)–(6) constitute the mathematical formulation of the problem. They can be solved numerically and examples of emerging patterns in case of quasiperiodic current (periodic pattern) or without current (standard Liesegang pattern) are shown in Fig. 3 [20].

The theory is tested on a much-studied case where a precipitate of silver dichromate ($Ag_2Cr_2O_7$) is formed due to the reaction of silver nitrate ($AgNO_3$) and potassium dichromate ($K_2Cr_2O_7$) in a gelatine gel. Our experiments were carried out in vertical glass tubes (diameter: 1 cm, length: 20 cm) containing a gelatine gel column (length: 13 cm) closed by agarose gel stoppers (length: 1.5 cm). The inner electrolyte was dissolved in the gel [3.0 g gelatine (Reanal) added to 50 cm^3 of 0.0036 mol/dm^3 $K_2Cr_2O_7$ (Reanal) solution] while the outer electrolyte [2 cm^3 of $AgNO_3$ solution (Reanal, 2.50 mol/dm^3)] was placed on top of the gel at the start ($t = 0$) of the experiments. Ni electrodes were fixed at the top and the bottom of the gel and the current was supplied by a programmable current generator. Starting with a forward current (the upper electrode in the $AgNO_3$ solution was positive), the direction of the current was changed from forward to backward and vice-versa at times $\tau n^2/2$. As the outer electrolyte diffused into the gel and the reaction front advanced along the tube, one could observe a brown $Ag_2Cr_2O_7$ precipitate emerging in the form of bands. The experiments were run usually for two days, followed by taking pictures of the resulting pattern in transmitted light.

Three sets of experiments were performed. First, in the absence of electric current, usual Liesegang bands were produced (lowest panel of Fig. 4). Second, the direction of an electric current of a few hundred μA amplitude was switched at times $\tau n^2/2$, resulting in periodic patterns shown for various τ-s on Fig. 4. We found that the wavelengths d of the patterns obey $d \sim \sqrt{\tau}$ (Fig. 5) and, furthermore, d is unaffected by the intensity of the electric current used in the experiments (250, 500, and 1000 μA). All these observations are in accord with our theory. The only unexplained feature of the experiments is the occasional emergence of secondary patterns with a wavelength an order of magnitude smaller than d (see the first three band gaps in the upper panel of Fig. 4). It is not clear which experimental conditions induce these secondary patterns, the only trend we observed is that they appear more frequently for larger d.

The third set of experiments was carried out to prove the feasibility of creating more complex patterns. Figure 6 shows an example where equidistant bands are followed by a predesigned structure consisting of groups of 2, 3, and 2 bands separated by voids. This "2-3-2" pattern was generated by making two modifications in the protocol

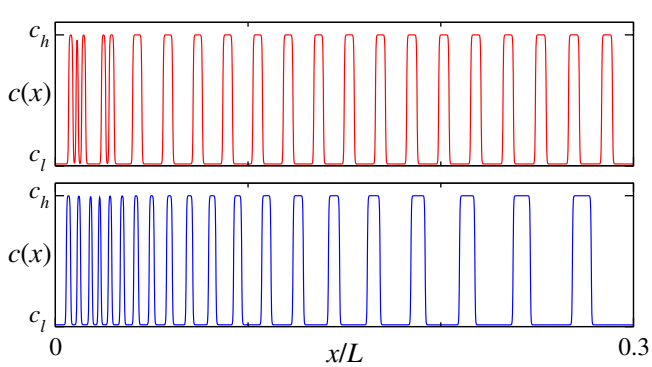

FIG. 3 (color online). Theoretical precipitation patterns. The periodic pattern emerging in the presence of a quasiperiodic current (upper panel) as compared to the usual Liesegang bandstructure obtained in the absence of current (lower panel). The values c_h and c_l are the stable concentrations of C [19].

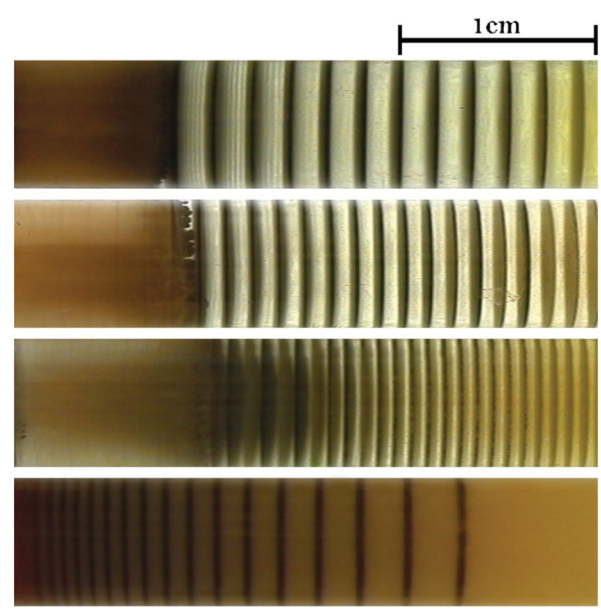

FIG. 4 (color). Experimental precipitation patterns. A quasiperiodic current of amplitude 500 μA was used with $\tau = 4$, 2, and 1 min, respectively, as going down the panels. Lowest panel illustrates the usual Liesegang bands.

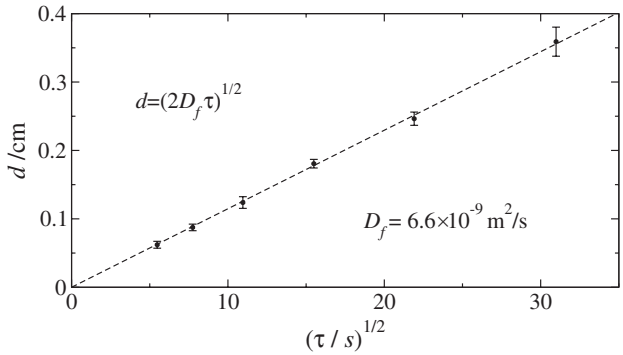

FIG. 5. Characteristic wavelength d of the pattern generated experimentally by switching the current forward and backward at times $\tau n^2/2$. The front diffusion coefficient D_f is the result of a linear fit.

for a periodic pattern. Namely, voids were generated by substituting the forward with a backward current and, furthermore, the amplitude of the backward current was always half of the forward one. Here again, the experimental results are in excellent agreement with the theoretical predictions (Fig. 6).

One of the motivations for controlling precipitation is the possible application to small-scale design. Figure 5 shows no indication that a lower limit on d exits. One should note, however, that the reaction-zone width and the thermal fluctuations are expected to limit the downsizing of the patterns. While this problem remains to be understood and evaluated, recent experiments on precipitation patterns [21] suggest that the submicron range can indeed be reached.

Our results on the control of precipitation patterns have important theoretical as well as practical implications. From a theoretical point of view, they demonstrate the predictive power and, implicitly, the correctness of our phase separation in the presence of a moving source scenario for Liesegang pattern formation [11]. Indeed, these are the first experiments which test intricate details of the theory and the agreement is excellent.

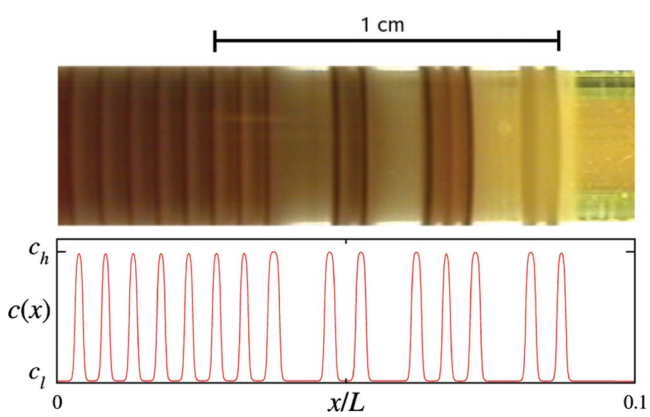

FIG. 6 (color). An example of a predesigned pattern. The protocol described in the text for generating the "2-3-2" structure is shown to work both in the experiment (upper panel) and in the theory (lower panel) [19].

From a practical point of view, the electric-current control of the patterns we developed is a flexible and generic tool. Indeed, it should be useful whenever the patterns emerge from reactions between charged particles (ions, nano- or colloid particles). Combining this tool with traditional ones (choice of geometry, initial concentrations, boundary conditions) opens up a wide range of new possibilities for control and design of structures.

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[1] T. Shinbrot and F. J. Muzzio, Nature (London) **410**, 251 (2001).
[2] For a review, see M. C. Cross and P. C. Hohenberg, Rev. Mod. Phys. **65**, 851 (1993).
[3] W. Lu and C. M. Lieber, NATO ASI Series, Series E Diffusion of Materials, 1990 **6**, 841 (2007).
[4] H. K. Henisch, *Periodic Precipitation* (Pergamon Press, New York, 1991).
[5] O. Giraldo *et al.*, Nature (London) **405**, 38 (2000).
[6] I. T. Bensemann, M. Fialkowski, and B. A. Grzybowski, J. Phys. Chem. B **109**, 2774 (2005).
[7] M. I. Lebedeva, D. G. Vlachos, and M. Tsapatsis, Phys. Rev. Lett. **92**, 088301 (2004).
[8] T. Antal *et al.*, Phys. Rev. E **76**, 046203 (2007).
[9] L. Gálfi and Z. Rácz, Phys. Rev. A **38**, 3151 (1988).
[10] T. Antal *et al.*, J. Chem. Phys. **109**, 9479 (1998).
[11] T. Antal, M. Droz, J. Magnin, and Z. Rácz, Phys. Rev. Lett. **83**, 2880 (1999).
[12] I. Das, A. Pushkarna, and A. Bhattacharjee, J. Chem. Phys. **94**, 8968 (1990).
[13] R. Sultan and R. Halabieh, Chem. Phys. Lett. **332**, 331 (2000).
[14] I. Lagzi, Phys. Chem. Chem. Phys. **4**, 1268 (2002).
[15] T. Unger and Z. Rácz, Phys. Rev. E **61**, 3583 (2000).
[16] I. Bena, F. Coppex, M. Droz, and Z. Rácz, J. Chem. Phys. **122**, 024512 (2005).
[17] I. Bena, M. Droz, and Z. Rácz, J. Chem. Phys. **122**, 204502 (2005).
[18] Z. Rácz, Physica (Amsterdam) **274A**, 50 (1999).
[19] The parameter values in our numerical simulations are $b_0/a_0 = 0.01$, $c_h/a_0 = 0.0365$, $c_l/a_0 = 5 \times 10^{-4}$, $D = 1.22 \times 10^{-9}$ m^2/s, $|j| = 10$ A/m^2, $\sigma = 10^{-8}$ m^2; $\lambda = 0.3 \times 10^{-9}$ m^2/s for Figs. 2 and 3, and $\lambda = 0.1 \times 10^{-9}$ m^2/s for Fig. 6.
[20] The beginning of the pattern is irregular, since the local wavelength of the Liesegang pattern is smaller than d and our protocol cannot prevent spurious band formation.
[21] C. Mohr, M. Dubiel, and H. Hofmeister, J. Phys. Condens. Matter **13**, 525 (2001).