

# SELFORGANIZATION IN NONEQUILIBRIUM SYSTEMS



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## MODELS OF PRECIPITATION PATTERN FORMATION IN AN ELECTRIC FIELD

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### Abstract

We studied the effect of an electric field on the evolution of Liesegang pattern formation. Our aim was to describe quantitatively the changes of the scaling regularities compared with the electric field-free case. We applied a modified deterministic (Ostwald's supersaturation) model to this case and a stochastic model, which also reflects the weak reproducibility of the phenomenon.

### Introduction

Formation of precipitation patterns has been observed in a wide range of coupling chemical reactions with diffusion. A typical example is the Liesegang phenomenon studied by R. E. Liesegang for the first time in 1896 [1,2]. In a usual experimental setup an electrolyte (called outer electrolyte) diffuses into a reaction medium, which contains another electrolyte (called inner electrolyte), the precipitation reaction between them produces a quasiperiodic precipitate distribution.

Liesegang patterns exhibit some regularities, which make connection between the macroscopic quantities of the system:  $X_n$  is the distance of the  $n$ th band measured from the junction point of the two electrolytes,  $t_n$  is the formation time of the  $n$ th band and  $w_n$  is the width of the  $n$ th band.

The *spacing law* [3] can be formalized as

$$\lim_{n \rightarrow \infty} \frac{X_{n+1}}{X_n} = P, \quad (1)$$

where  $P$  is the so-called spacing coefficient, which depends on the initial concentration of the outer and the inner electrolytes (Matalon-Packter law [4-5]).

According to the *time law* [6]

$$X_n = a_0 t_n^{1/2} + c_0,$$

where  $a_0$  and  $c_0$  are constants.

The less precise scaling law is the *width law* [7-9] due to the inaccurate definition of the band thickness in experiments:

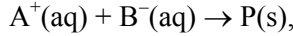
$$w_n \propto X_n^\alpha,$$

where  $\alpha$  has been found equal to *one*.

The aim of this paper is to investigate how a constant electric field modifies the regularities above. Since precipitates in Liesegang experiments are formed by ions, an electric field is expected to have a significant effect on the evolution of patterns.

## Results and Discussion

We studied the effect of an electric field using two models: a deterministic [10] and a stochastic [11,12] one. The models incorporate a simple chemical reaction between two electrolytes



where  $A^+(aq)$  and  $B^-(aq)$  are the ionic species and  $P(s)$  is the precipitate. In both models we applied a most popular description of precipitate formation (ion-product supersaturation theory based on Ostwald's idea [13]) driven by two thresholds:  $K$  is the nucleation product and  $L$  is the solubility product. Precipitation occurs only if the product of the local concentrations of the electrolytes reaches  $K$ . The previously formed precipitate promotes the precipitation process, and the former mentioned product has to reach only a lower threshold  $L$  [14,15].

### *Deterministic (mean-field) model*

In 1D the evolution of the system is described by the following partial differential equations

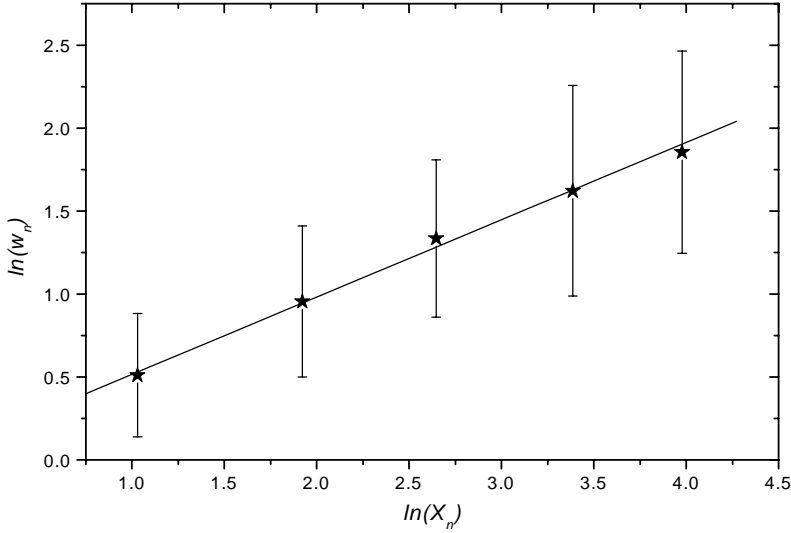
$$\begin{aligned} \frac{\partial a}{\partial t} &= D_a \frac{\partial^2 a}{\partial x^2} - z_a \varepsilon \frac{\partial a}{\partial x} - \delta(ab, K, L), \\ \frac{\partial b}{\partial t} &= D_b \frac{\partial^2 b}{\partial x^2} - z_b \varepsilon \frac{\partial b}{\partial x} - \delta(ab, K, L), \\ \frac{\partial p}{\partial t} &= \delta(ab, K, L), \end{aligned} \quad (2)$$

where  $a = a(x, t)$  and  $b = b(x, t)$  are the concentrations,  $D_a$  and  $D_b$  are the diffusion coefficients,  $z_a$  and  $z_b$  are the charges of ions  $A^+(aq)$  and  $B^-(aq)$ , respectively.  $\varepsilon$  corresponds to the electric field strength.  $p$  is the amount of the precipitate and  $\delta(ab, K, L)$  describes the precipitation reaction. Equations (2) were solved numerically using "method of lines", which based on spatial discretization (finite difference method on a rectangular grid) and time integration (second order Runge- Kutta method).

### *Stochastic (discrete) model*

In this discrete model we proceed with each of particles in a discretized phase space. We give the number of particles in each "space segment" in every time step. We described the evolution of the system with transition probabilities: we allow a "jump" at most of two segments, and assumed that the precipitate does not diffuse.

The precipitation reaction is supposed to be deterministic. However, the motion is driven by a random walk, which makes the whole system stochastic. We explain the weak reproducibility in the real experiments in this way.



**Figure 1.** Dependence of the width of the bands on their distance measured from the junction point of the two electrolytes in the presence of an electric field (stochastic model). We fitted a linear curve for two steps model in a logarithmic scale.

In the model all segments where band formation occurs “catch” some moving particles. The effect of an electric field (we denote its strength with  $\varepsilon_+$  if it promotes the ion-transport) can be modeled by taking non-symmetric random walk. Started from normally distributed deviations, we used the transition probabilities:

$$p_{-2} = p_2 = 0.0668, \quad p_{-1} = p_1 = 0.2417 \quad \text{and} \quad p_0 = 0.383,$$

where  $p_i = P(\text{step} = i)$  for  $i = -2, -1, 0, 1, 2$ .

The effect of the electric field was incorporated by a modification of the transition probabilities  $p_i^{\varepsilon_+}$  as follows:

$$p_i^{\varepsilon_+} = p_{i-1}^{\varepsilon_+} + p_i(1 - \varepsilon_+) \quad \text{for} \quad i = -1, 0, 1, 2 \quad \text{and} \quad p_{-2}^{\varepsilon_+} = p_{-2}(1 - \varepsilon_+).$$

We modified the transition probabilities similarly, if the electric field retards the diffusion of ions.

## Discussion

*Spacing law:* The simulation results showed that in the presence of an external electric field the  $X_{n+1}$  is still linear proportional to  $X_n$ . At the same time, the spacing coefficient  $P$  in eq. (1) decreases with increasing field strength [10,11].

*Time law:* In both cases were found that in presence of an electric field the position of bands, measured from the junction point of electrolytes can be characterized by the function  $X_n = a(\varepsilon)t^{1/2} + b(\varepsilon)t + c(\varepsilon)$ , where  $a(\varepsilon)$ ,  $b(\varepsilon)$  and  $c(\varepsilon)$  depend on electric field strength. Taking the limit  $\varepsilon_+ \rightarrow 0$  or  $\varepsilon_- \rightarrow 0$ , results in  $a(\varepsilon) \rightarrow a_o$ ,  $b(\varepsilon) \rightarrow 0$  and  $c(\varepsilon) \rightarrow c_o$  [10,11,16,17].

*Width law:* We have proposed an extended form of the width law (Figure 1), which takes into account the effect of a constant electric field. The general form of this scaling law is  $w_n \propto X_n^{\alpha(\varepsilon)}$ , where  $\alpha(\varepsilon)$  is a decreasing function of its argument [11]. We have carried out real experiments to validate our numerical results in AgNO<sub>3</sub>/K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/gelatine system [10,11]. The formation of precipitation bands was monitored by a CCD camera, connected to a computer-controlled imaging system. Our findings are in a good agreement with the results of the numerical simulations described above. All these results show that the stochastic and the deterministic approaches presented here are effective methods to simulate the formation and dynamics of the regular Liesegang patterns even in an external electric field. Our approach based on the supersaturation model is not eligible for the description of the precipitation pattern formation in many situations: e.g. in case of various boundary and initial conditions [2].

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