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LETTERS

Simulation of Liesegang pattern formation using a discrete stochastic model

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Abstract

Simulations of the Liesegang pattern formation are presented that are based on a discrete stochastic model. The diffusion term was modeled by random walk using transition probabilities referring to one and two steps. A semi-stochastic model of the precipitation process was created, using Ostwald's supersaturation theory. The calculated variance of zone positions and formation time is in good accordance with the experimental observations of Müller et al. © 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

A well-known example of spatiotemporal pattern formation in reaction–diffusion systems is the Liesegang phenomenon [1]. The pattern formation occurs due to a precipitation reaction between a certain chemical reactant, which diffuses into a gel matrix and another reactant, which is in the gel. Mean field models of Liesegang pattern formation usually focus on the concentrations $\alpha(t,x)$, $\beta(t,x)$ of the two reactants, where α is the concentration distribution of the outer electrolyte while β is that of the inner electrolyte. In these models, chemical reaction and diffusion of the electrolytes as well as

nucleation and aggregation of the precipitate particles are taken into account [2–8]. Other effects, like fluctuation of concentrations, usually caused by heat anomalies or contaminations present in the gel, are completely ignored. However, there are some phenomena that are usually attributed to the existence of such randomizing impacts [9–11]. In the literature only a few trials to incorporate stochastic effects into mathematical descriptions of Liesegang patterning can be found. Chopard et al. [12,13] developed and applied a reaction–diffusion cellular automata model. Antal et al. [14] have studied a different model based on a Cahn-Hilliard type phase separation. They used a kinetic Ising model, which incorporated microscopic fluctuations.

In the present Letter we introduce a new *stochastic* description of Liesegang pattern formation in which all of the previously mentioned effects are

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taken into account. Although Liesegang patterns have four scaling laws, in our Letter only three of them will be examined. These so-called time, spacing and width laws are known for a long time and were formerly extensively studied by many experimentalists. Let us denote by X_n the position of the nth precipitate zone measured from the junction point of electrolytes and by τ_n the time elapsed until its formation. According to the time law of Liesegang patterning, these two quantities always correspond to the following relation: $X_n = c_1 \tau_n^{1/2}$ [15], where c_1 is a constant that depends on the experimental conditions. The so-called spacing law is a similar very simple relation that describes spatial development of these chemical patterns. If n is large enough then ratio X_{n+1}/X_n approaches a constant value, called spacing coefficient, and usually denoted by P [16]. Note that according to this scaling law positions of precipitate zones are members of a geometrical series which is probably the most surprising regularity of these patterns. Finally, according to the width law the thickness of zones increases with their positions, that is $w_n = c_2 X_n^{\alpha}$, where w_n is the width of the nth band, c_2 and α are positive constants [9,17,18].

In this Letter we present numerical simulations performed with a newly developed *discrete* model. Discretization of phase space – that is a microscopic approach of the problem – is an easy way to construct a graphic model. This way we can even avoid many difficulties emerging when stochastic partial differential equations in a continuous phase space are solved numerically. Application of time discretization with constant step length makes easy to program the problem even in this case, although this type of discretization often emerges also in the solution of continuous PDEs. Micro-level mathematical or numerical description of reaction–diffusion systems usually means application of a cellular automata [12,13]. Although this is a usual approach, it cannot be considered realistic because of the underlying artificial simplifying assumptions encoded into rules of the cellular automata. In contrast to the method applied by Chopard et al. [12,13] we were able to avoid these artificial constraints applied to movement and reaction of particles, which probably makes our model more

realistic. Although chemical reactions are usually modeled by Markov chains [20,21], in our case this approach was not enough, because development of a Liesegang pattern cannot be described simply by accounting the number of different particles.

2. The model

We investigate a simple Liesegang patterning. There is only one chemical reaction between two dissolved electrolytes according to reaction: $A(aq) + B(aq) \rightarrow AB(s)$. In the following, $A(aq)$ will denote the outer while $B(aq)$ the inner electrolyte. $AB(s)$ is the precipitate, which contains equal amounts of the two reactants. However, there are more complex pattern evolutions in case of redissolution of the precipitate due to complex formation [22–24]. In a continuous model of this system, the phase space is a stage with a given precipitate distribution function. According to our method, this space is discretized into N small segments in which values of the distribution function are represented by particle numbers. Thus, coordinates of the reaction space correspond to a set of positive integers $\{1, 2, \ldots, N\}$, while characteristics of the system can be described with the state vector $M_A(t)$ ($M_B(t), M_{AB}(t)$, respectively) of length N at any time, where the ith component of a vector i.e., $M_A(t)[i]$ corresponds to the number of A particles at time t at the ith space position.

In order to describe evolution of the chemical pattern, we have to define an operator F that contains joint effect of *diffusion* and *precipitation reaction*, and transforms distribution function in every time step in the proper way. Formally the task to be performed can be described by the following equations:

$$F : [\mathbf{R}^N]^3 \rightarrow [\mathbf{R}^N]^3 \text{ such that}$$

$$\begin{aligned} F(M_A(t), &M_B(t), M_{AB}(t)) \\ &= (M_A(t+h), M_B(t+h), M_{AB}(t+h)), \end{aligned}$$

where h is the length of a time step.

The *diffusion* term has been modeled by random walk [21] using controllable parameters. This process is defined as product $D_A M_A(t)$, where D_A is

a transition probability matrix [20,21] corresponding to species A. Matrix element $D_A[i][j]$ gives the probability of the passage that a particle residing at position i moves to position j within one time step. Generally most of the particles residing at a given position do not move at all. They are described by *zero* step. Certainly diffusive movement of the inner electrolyte can be described by a similar operator equation with a different diffusion matrix: in the same way $F_d M_B(t) = D_B M_B(t)$. However, in our simulations we applied only one diffusion matrix, that is diffusion constants of the two electrolytes were taken to be equal: $D_A = D_B$. We have used two slightly different types of diffusion models. In the first type (let us call it 'one-step model'), every particle can jump only to a neighboring segment, that is the length of an elementary step can only be 1, −1 or 0. In the second case ('two-step model') maximum length of an elementary step was 2, that is the possible steps are −2, −1, 0, 1 and 2. If the moving and reacting species are small (e.g., small molecules or hydrated ions), their stochastic behavior will correspond to a simple Brownian motion which is a usual mathematical model of such processes [21]. A consequence of the Brownian motion is that probability of the step length has a normal distribution. Since we permitted only three or five possible step lengths, we chose the probabilities according to the density function $\Phi(x) = \frac{1}{\sqrt{2\pi}} \exp\{-x^2/2\}$ of the standard normal distribution. In the 'one-step model' $P(\text{step} = 1) = P(\text{step} = -1) = 0.3085 \approx \int_{-\infty}^{-0.5} \Phi(x)\,dx$ and $P(\text{step} = 0) = 0.383 \approx \int_{-0.5}^{0.5} \Phi(x)\,dx$. In the 'two-step model' $P(\text{step} = 2) = P(\text{step} = -2) = 0.0668 \approx \int_{-\infty}^{-1.5} \Phi(x)\,dx$, $P(\text{step} = 1) = P(\text{step} = -1) = 0.2417 \approx \int_{-1.5}^{-0.5} \Phi(x)\,dx$ and $P(\text{step} = 0) = 0.383 \approx \int_{-0.5}^{0.5} \Phi(x)\,dx$. As the reaction product (AB) cannot diffuse in a gel, D_{AB} is the identity matrix. In real systems, diffusion of the electrolytes can be time dependent. Such effect can be caused by some changes in the environment (e.g., uneven or continuously changing temperature). Similarly, external fields like electric potential or different physical properties of the species can cause nonsymmetric particles movement. In our approach these effects can be described by time dependent or nonsymmetric diffusion matrices.

Description of the *precipitation reaction* was deterministic and was modeled by Ostwald's supersaturation theory [19]. First, we computed the number of particles A and B at every spatial positions taking into account those entities only that move across the given segment in the given time step. Let us denote these concentrations by $\text{SU}M_A[i](t)$ and $\text{SU}M_B[i](t)$. This way we have supposed that particles can react with each other even 'in-flight'.

If $M_{AB}[i](t)$ was zero (that is there was not any precipitate in the ith segment) then

$$\Delta[i](t) = \delta[i](t)\Theta(\text{SU}M_A[i](t)^*\text{SU}M_B[i](t) - K_s)$$

and if $M_{AB}[i](t) \neq 0$ (there is some precipitate in the ith segment) then

$$\Delta[i](t) = \delta[i](t)\Theta(\text{SU}M_A[i](t)^*\text{SU}M_B[i](t) - L)$$

is the precipitation reaction term [5] and

$$\delta[i](t) = 0.5[(\text{SU}M_A[i](t) + \text{SU}M_B[i](t))$$
$$- [(\text{SU}M_A[i](t) + \text{SU}M_B[i](t))^2$$
$$- 4 * (\text{SU}M_A[i](t) * \text{SU}M_B[i](t) - L)]^{1/2}]$$

is the amount of precipitate, which can form. Here L is the solubility product, K_s is the nucleation product and Θ is the Heaviside step function. The basic idea of the supersaturation model is that the reaction of the electrolytes is preceded by a supersaturated state of the system. At a clear region of the reaction media, precipitation does not start until the product of the reactant concentrations reaches K_s. However, if previously formed precipitate is present it promotes the process and the product of the concentrations has to reach only a lower threshold L. Since the reaction product is a solid material, it will be trapped by the gel matrix and remains in the segment where it came to existence. Growth of the precipitate stops when $M_{AB}[i]$ reaches a maximal value ($M_{AB\,\text{max}}$) in a spatial segment. Although the above sketched mechanism is a deterministic model of the reaction term, the patterning process as a whole will be stochastic because of the stochastic diffusion terms.

The stochastic model included the transformation of particles into precipitate. This effect can be described by decreasing the number of diffusing

particles (denoted by $SUM_A[i](t)$ and $SUM_B[i](t)$) at positions where precipitate exists and its amount has not reached the above-mentioned critical value. Let the probability that a particle type of A is transformed to precipitate at time t in the ith segment be $q_A[i](t) = \Delta[i](t)/SUM_A[i](t)$. From a practical point of view the most simple solution is to incorporate this probability into the transition probability matrix D_A, which cannot model the disappearance of particles A. It means that the probability of transition across the ith segment has to be multiplied by $1 - q$ because particles A react with probability q and 'disappear' from the reaction–diffusion process. Certainly the same holds for the internal electrolyte B. Let us denote these modified transition matrices by D_{A*} and D_{B*} which contain both the diffusion and the reaction effects. The 'in-flight-reaction' effect means that the growing zones deplete their surroundings because they act as autocatalytic reaction centers. In the simulation program, stochastic effects were modeled through application of random numbers during multiplication with the transition probability matrix.

In the simulations the linear extent of the reaction space was $N = 300$ and the other parameters had the following values: $K_s = 1400$, $L = 300$ and $M_{AB\,max} = 1000$. These parameter values were chosen in accordance with a formerly proposed deterministic model [5]. No-flux boundary conditions were applied in the simulations. Simulations were carried out till time step 60 000. Initial values were $M_B[i](t = 0) = 100$, $M_{AB}[i](t = 0) = 0$ and $M_A[i](t = 0) = 0$, but $M_A[1](t) = 100$ at all times. The last of initial conditions results in continuous flow of species A into the reaction space.

3. Results and discussion

The presented results are the average of thirty independent calculations. Fig. 1 shows the verification of the time law mentioned in the introduction. Our results suggest that using any of the two diffusion models X_n depends linearly on $\tau_n^{1/2}$ which is in complete agreement with experimental findings. Variance of both the zone positions and the square root of formation time increases continu-
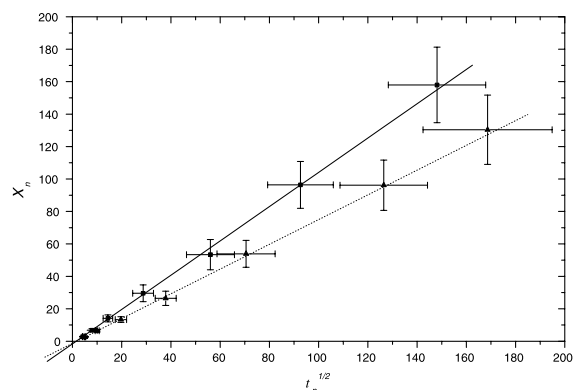

Fig. 1. Simulated dependence of the distance of bands (measured from the top of diffusion column) on the square root of formation time. The symbols (▲) and (■) represent the one- and two-step models, respectively. The solid and dotted lines are the fitted linear curves for each case. The spatial and square root time errors refer to the 95% confidence level.

ously during of development of patterns. These results coincide with experimental observations of Müller et al. [9–11]. In these works, they investigated the reproducibility of Liesegang patterns and gave a statistical analysis of measured bands using Gaussian distribution. They found that the average value of nth band location with their width is an increasing function of n. Although it is not surprising, it is important to note that the two-step model exhibits smaller average deviations in all respects than the other one-step description. Now let us turn to the spacing law. As Fig. 2
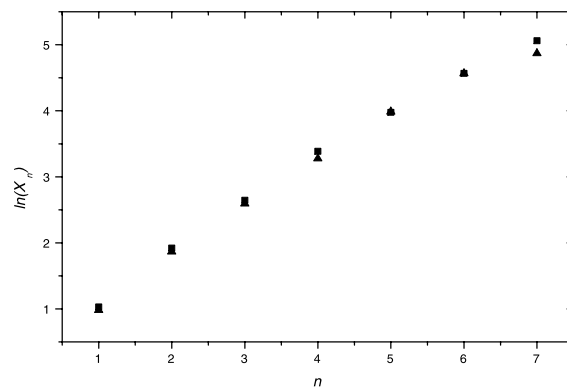

Fig. 2. Logarithm of the distance of bands (measured from the top of diffusion column) as a function of band number. Symbols (▲) and (■) represent one- and two-step models, respectively.
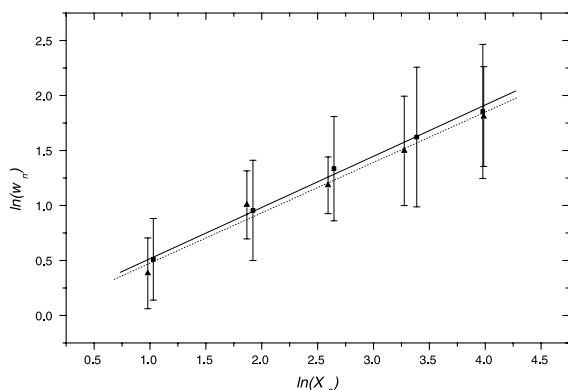
Fig. 3. Dependence of the width of the bands on their distance measured from the start of diffusion column for the one- (▲) and two-step (■) models, respectively. Solid and dotted lines represent the fitted linear curves for one- and two-step models, respectively. The spatial errors of the width of the bands refer to the 95% confidence level.

shows, dependence of $\ln(X_n)$ on n is almost linear, that is the spacing law of Liesegang patterning is reproduced by the model. We have also investigated variations of zone thickness with their position (see Fig. 3). In this case only the first five bands instead of all the seven were used, because development of the last two ones was not complete. Our simulation verified the validity of the width law proposed by Müller et al. [9]. Values of the exponent α were found to be $\alpha = 0.458$ and

$\alpha = 0.466$ for the one- and two-step models, respectively. These values are very close to those found by Chopard et al. [12,13] with cellular automata simulation. They obtained patterns, which exhibited width exponent α varying between 0.5 and 0.6. However, the experimental observations [17] and the deterministic model calculations [25] suggested a linear dependence of w_n on X_n. Fig. 4 shows spatial distribution of precipitate in our stochastic simulations. This picture demonstrates that results of our model are very similar to regular Liesegang patterns.

4. Conclusions

An advanced one-dimensional stochastic model for the description of reaction-diffusion systems has been developed and applied for the simulation of periodic precipitate patterns. Diffusion has been described by Brownian random walk, while the reaction term was based on Ostwald's supersaturation theory. This later was extended by stochastic precipitate formation and growth. Results of both the one- and two-step models show that this approach is successful for the description of regular Liesegang patterning as all of the important scaling laws of these chemical patterns were verified.
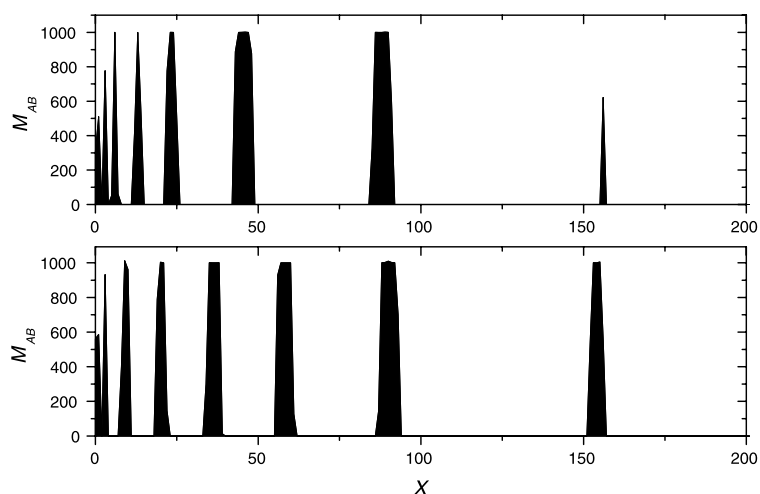

Fig. 4. Spatial distribution of the precipitate corresponding to the one-(top) and the two-step (bottom) models in one independent simulation.

Acknowledgements

References

[1] R.E. Liesegang, Naturwiss. Wochenschr. 11 (1896) 353.

[2] G. Venzl, J. Ross, J. Chem. Phys. 77 (1982) 1302.

[3] M.E. LeVan, J. Ross, J. Phys. Chem. 91 (1987) 6300.

[4] A.A. Polezhaev, S.C. Müller, Chaos 4 (1994) 631.

[5] A. Büki, É. Kárpáti-Smidróczki, M. Zrinyi, J. Chem. Phys. 103 (1995) 10387.

[6] A. Büki, É. Kárpáti-Smidróczki, M. Zrinyi, Phys. A. 375 (1995) 357.

[7] H-J. Krug, H. Brandtstädter, J. Phys. Chem.A. 103 (1999) 7811.

[8] I. Lagzi, Phys. Chem. Chem. Phys. 4 (2002) 1268.

[9] S.C. Müller, S. Kai, J. Ross, J. Phys. Chem. 86 (1982) 4078.

[10] S. Kai, S.C. Müller, J. Ross, J. Phys. Chem. 87 (1983) 806.

[11] S. Kai, S.C. Müller, Sci. Form 1 (1985) 9.

[12] B. Chopard, P. Luthi, M. Droz, Phys. Rev. Lett. 72 (1994) 1384.

[13] B. Chopard, P. Luthi, M. Droz, J. Stat. Phys. 76 (1994) 661.

[14] T. Antal, M. Droz, J. Magnin, A. Pekalski, Z. Rácz, J. Chem. Phys. 114 (2001) 3770.

[15] H.W. Morse, G.W. Pierce, Proc. Am. Acad. Arts Sci. 38 (1903) 625.

[16] K. Jablczynski, Bull. Soc. Chim. Fr. 33 (1923) 1592.

[17] K.M. Pillai, V.K. Vaidyan, M.A. Ittyachan, Colloid Polym. Sci. 258 (1980) 831.

[18] M. Droz, J. Magnin, M. Zrinyi, J. Chem. Phys. 110 (1999) 9618.

[19] W. Ostwald, Kolloid Zeit. 36 (1925) 380.

[20] A. Tamir, Application of Markov Chains in Chemical Engineering, Elsevier, Amsterdam, 1997.

[21] H.M. Taylor, S. Karlin, An Introduction to Stochastic Modeling, third ed., Academic Press, New York, 1998.

[22] M. Zrínyi, L. Gálfi, É. Smidróczki, Z. Rácz, F. Horkay, J. Phys. Chem. 95 (1991) 1618.

[23] R. Sultan, Phys. Chem. Chem. Phys. 4 (2002) 1253.

[24] M. Al-Ghoul, R. Sultan, J. Phys. Chem. A 105 (2001) 8053.

[25] G.T. Dee, Phys. Rev. Lett. 57 (1986) 275.