Reaction-Diffusion Cellular Automata Model for the Formation of Liesegang Patterns

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Cellular automata models for the formation of Liesegang structures are proposed. This novel approach, which takes into account the fluctuations for the first time, describes the problem at a microscopic scale, in terms of reaction, diffusion, nucleation, and aggregation processes. We present large scale numerical simulations which provide clear verifications of the time and spacing laws and predict a novel behavior for the widths of the patterns. We show that two different microscopic reaction schemes are possible for producing Liesegang structures and we propose a phase diagram showing the different types of possible patterns.

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Pattern formation in reaction-diffusion systems is frequently encountered in nature. A particular example is the formation of the so-called Liesegang rings or bands [1] that were discovered at the end of the past century. These patterns are produced by precipitation in the wake of a moving reaction front. Many experiments exhibiting such a pattern formation consist of a test tube containing a gel in which a chemical species B (for example, $AgNO_3$) is uniformly distributed with concentration b_0. Another species A, with concentration a_0 (for example, HCl), is allowed to diffuse into the tube from its open extremity and chemically react with B. As this reaction goes on, formation of consecutive bands of precipitate (AgCl in our example) is observed in the tube, provided that the concentration a_0 is large enough compared to b_0.

A striking feature of this process is that, after a transient time, these bands appear at some positions x_i and times t_i that obey simple laws. More precisely, it is first observed that the center position x_n of the nth band is related to the time t_n of its formation through the so-called time law $x_n \sim \sqrt{t_n}$. Second, the ratio $p_n \equiv x_n/x_{n-1}$ of the positions of two consecutive bands approaches a constant value p for large enough n. This last property is known as the Jablczynski law [2] or the spacing law. Finally, the width w_n of the nth band is an increasing function of n.

The presence of bands is related to the geometry of the experiment, i.e., the use of a test tube with axial symmetry. In more complicated situations, different shapes may be obtained. A well known example are the rings formed in agate rocks [1–3].

The formation of Liesegang patterns has been investigated by many researchers. The models proposed so far belong to three categories [4]: sol coagulation models, competitive particle growth models, and supersaturation models. Although none of these models is able to account for all experimental observations (like inverse banding [5]), we believe, following Prager [6], Zeldovitch *et al.* [7], Smith [8], Dee [9], and Le Van and Ross [10], that the supersaturation mechanism based on Ostwald's ideas [11] plays a crucial role in the band formation.

Within this framework, two scenarios have been studied. In the first one [4, 6–8], the A and B species coexist in the gel until the solubility product ab reaches a critical value k_{sp}, above which nucleation occurs according to the reaction $A+B \rightarrow AB(\text{solid})$. Using *ad hoc* boundary conditions and crude nucleation law, the spacing laws can be established analytically [8].

In the most recent scenario [9], the two species A and B react to produce a new species C which also diffuses. When the local concentration of C reaches some threshold value, nucleation occurs. The nucleated particles D at the reaction front deplete their surroundings of the reaction product. As a result, the level of supersaturation drops dramatically and the nucleation process stops. After some time, the reaction front has moved away and the concentration of product at the moving front reaches a large enough value, allowing the nucleation to occur again, and separated bands will appear.

This process is described in terms of rate equations for the local densities of A, B, and C. In appropriate units, they read

$$\partial_t a = \partial_x^2 a - \kappa ab, \tag{1}$$

$$\partial_t b = \left(\frac{D_b}{D_a}\right) \partial_x^2 b - \kappa ab, \tag{2}$$

$$\partial_t c = \left(\frac{D_c}{D_a}\right) \partial_x^2 c + \kappa ab - u, \tag{3}$$

where D_i is the diffusion constant for the species i, κ is the reaction constant, and u the nucleation and aggregation term. Because of diffusion, the reaction front position $x_f(t)$ obeys the relation $x_f(t) \sim \sqrt{t}$, with an amplitude depending on the difference of the concentrations

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a and b [12]. This is the origin of the well understood time law.

Different expressions for u obtained from the theory of homogeneous nucleation and droplet growth have been used by Dee [9] and Le Van and Ross [10], leading to a system of coupled nonlinear partial differential equations. When solved numerically, these equations exhibit oscillatory solutions for the density of precipitate, which are interpreted as bands.

In the approach of Dee [9] and Le Van and Ross [10], only very few bands are produced from the numerical solution. Accordingly, the verification of the spacing law is not convincing and little can be said about the existence of a width law. In addition, their approach is mean field in essence. It is impossible to describe patterns, such as spirals, in which there is a symmetry breaking due to the presence of local fluctuations [13]. Moreover, it is well known that even without symmetry breaking the fluctuations may play a very important role in the kinetics of some reaction-diffusion processes [14].

Accordingly, an approach based on a microscopic model in which the essential features of the kinetics are included would provide a better description of the formation of Liesegang structures and, in particular, of their microscopic structure (fractal dimension, for instance).

In this Letter, we propose a novel and promising microscopic approach to the Liesegang phenomenon in terms of a cellular automata [15]. The essential mechanisms are modeled in a simple way, without *a priori* discontinuities in the boundary conditions. We propose simple cellular automata rules for controlling nucleation and aggregation in terms of two free parameters.

When these control parameters are suitably chosen, Liesegang bands emerge naturally from our model and well obey the time law and the spacing law. We show that the widths w_n of the bands grow with n according to a power law $w_n \sim x_n^\alpha$ and that all these properties can be obtained in both Prager-Zeldovitch and Dee scenarios. The same model can also be used to study other situations, such as the formation of rings in two-dimensional gels where the A species diffuses from a point source. Preliminary results [13] for cylindrical-like geometries show that spiral-like patterns breaking the cylindrical symmetry can emerge in our model, due to the presence of local density fluctuations. This situation is in perfect agreement with experimental facts.

Our model is defined on a two-dimensional square lattice. Particles of types A, B, and C perform a simultaneous random walk as described in Ref. [16]. When an A and a B particle meet at the same site, they disappear and produce a C particle with probability κ [17, 18]. At the initial time, the left part of the system ($x \leq 0$) is randomly occupied by A particles with a density a_0 and the right part ($x > 0$) is filled with B particles with a density b_0. The initial densities a_0 and b_0, the diffusion constants, and the reaction constant κ are free parameters.

The new ingredients in the model concern the nucleation and aggregation mechanisms. On general grounds, based on local supersaturation theory [19], we have implemented the precipitation as follows: once the local density of C particles (computed as the number of particle in a small neighborhood) reaches the threshold value K_{sp}, they spontaneously precipitate and become D particles at rest (nucleation). The C particles located in the vicinity of precipitate D particles will aggregate, provided that their density is larger than an aggregation threshold $K_p < K_{sp}$. If a C sits on top of a D it always becomes a D. The parameters K_p and K_{sp} are the two main control parameters of the model. The introduction of these critical values refers to the qualitative models of solidification theory, relating supersaturation and growth behavior [4].

Our model has been implemented on 8k processors Connection Machine CM-2. Results of simulation (taking 10 h of CPU time) for systems composed of 64 layers with 512 sites along the direction of motion of the front (x axis) and 64 sites along the perpendicular direction are shown in Fig. 1. After a transient regime, well defined bands are formed, which obey the expected laws. The law $x_n \sim \sqrt{t}$ is well satisfied, as a signature of the diffusion process. The spacing law, $x_n/x_{n-1} \to p$, is clearly verified already for small n, as shown in Fig. 2. From these data, one finds $p = 1.08$, a value well in the range of the experimental findings (typically, one observes $1.05 \leq p \leq 1.15$ for different cases).

Liesegang bands are only obtained for a narrow interval of the parameters. The same difficulty is present in real experiments [4]. Outside of this region, other types of patterns are produced, as shown in the qualitative phase diagram given in Fig. 3. We named these patterns homogeneous clustering, amorphous solidification,

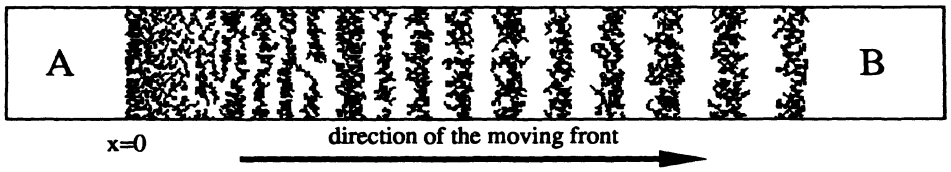

FIG. 1. Example of Liesegang bands as obtained from the simulations of our cellular automata model. The values of the parameters are $b_0/a_0 = 0.01$, $D_b/D_a = D_c/D_a = 0.1$, $k_{sp}/a_0 = 1.39 \times 10^{-2}$, and $k_p/a_0 = 6.07 \times 10^{-3}$.

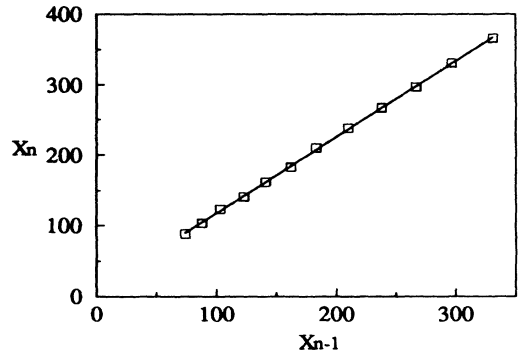

FIG. 2. Verification of the spacing law for the situation shown in Fig. 1. The Jablczynski coefficient is found to be $p = 1.08$.

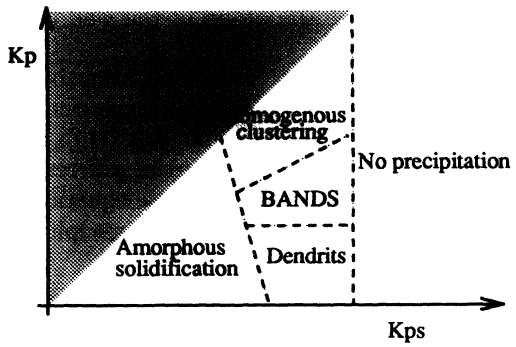

FIG. 3. Phase diagram showing the different possible patterns that can be obtained with our cellular automata model, as a function of the values of k_{sp} and k_p.

and dendrites, in agreement with the usual classification [17, 20], and several examples of them will be given in a forthcoming publication [13].

The control parameter K_{sp} is directly related to the critical supersaturation, while K_p influences the growth rate of the bands in a way which can be found through numerical simulations. The precise dependence is currently under investigation.

The need for investigating larger systems and reducing statistical noise led us to speed up our algorithm. In order to keep the advantages of our microscopic description we have adapted to our problem the Boltzmann lattice-gas technique [21]. To restore the fluctuations suppressed in the lattice Boltzmann approach, the nucleation and aggregation processes take place only with a given probability when the concentration reaches the critical value k_{sp} or k_p. We have verified that this noisy version of the Boltzmann approach is able to reproduce the generic laws of the Liesegang structures. This strategy allows us to gain a factor 100 in the speed of the simulation and to produce up to 30 consecutive bands for systems of sizes 1024×64. All the results obtained (time law, spacing law) are similar to the ones given by the cellular automata model, up to a renormalization of $K_{sp} \to k_{sp}$ and $K_p \to k_p$.

An interesting property of these bands is the behavior of the width w_n. Little is known about its dependence on n. Experimental data [22] and numerical predictions [9] suggest a linear dependence. However, the number of bands considered to support this claim is too small to be conclusive and the experimental data have large error bars. Because of the large number of bands obtained with our method, we have been able to extract a more accurate behavior which can be expressed by the following new law:

$$w_n \sim x_n^{\alpha}. \tag{4}$$

We found that α is independent of k_{sp}, but depends on the initial concentration b_0 and a_0. We have obtained values of α which are clearly smaller than 1 and are in the range 0.5–0.6, as shown in Fig. 4. From relation (4), it follows that the width law can be written as $w_n/w_{n-1} \to p^{\alpha}$.

The scenario due to Prager and Zeldovitch is still of importance for reactions in which the existence of the diffusing C species cannot be established. We have implemented this scenario in a lattice Boltzmann model with, in addition to the previous diffusion dynamics for A and B, the following rules: (i) $A+B \to AB$(solid) if the solubility product $ab > k_{sp}$; (ii) in the vicinity of precipitate, A and B aggregate if $ab > k_p$; (iii) on the top of a precipitate particle, A and B aggregate provided that $ab > k$; k and k_p are such that $k < k_p < k_{sp}$. The depletion of A and B resulting either from nucleation or aggregation lowers the solubility product to the stationary value $ab = k$. The simulations resulting from this approach also lead to bands of precipitate [13], obeying the same formation laws as described previously.

In conclusion, our approach is able to reproduce the main experimental features of the Liesegang structures and go beyond. As shown by our phase diagram, it pro-

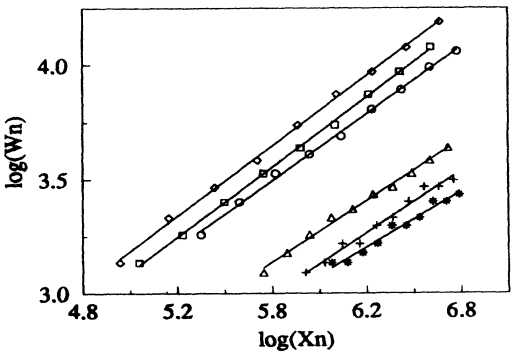

FIG. 4. Dependence of the width w_n of the Liesegang bands as a function of their position x_n, for various values of $a_0 - b_0$ with $a_0 \times b_0 = 0.01$. From left to right, the lines correspond to $b_0 = 0.0094$, 0.0096, 0.0098, 0.012, 0.014, and 0.016. One obtains $w_n \sim x_n^{\alpha}$ with α decreasing from 0.61 to 0.49.

vides a unified framework for understanding the role of the supersaturation values in producing other precipitation patterns encountered in solidification processes. We have confirmed on large scale simulations that the essential microscopic mechanisms leading to these patterns were the interplay between a moving reaction-diffusion front and the rate of the nucleation-aggregation processes. We have proposed a simple mechanism, much in the spirit of theoretical growth models, for controlling precipitation. Our approach, based on Ostwald supersaturation arguments, shows clearly that models with or without C both give a consistent description of the Liesegang phenomenon, as opposed to what is claimed in the literature [23]. Experimental tests of the width law we have predicted here would give an additional confirmation of the validity of our models.

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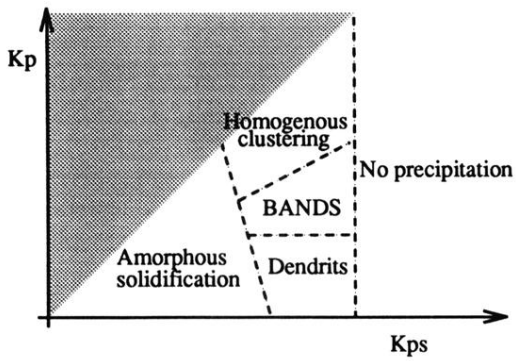

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