Structure Formation During Precipitation Reaction in Gels

New Liesegang Patterns

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The paper reports on an investigation carried out into one- to three-dimensional Liesegang systems (test tube arrangement) composed of different concentrations of lead nitrate in Agar gel with either potassium iodide or potassium dichromate as the precipitation reagent. A rich variety of different structure formations, including screw formations of the weakly soluble reaction product is documented.

Measurements of the progression of the precipitation front show a dependence of the diffusion path on time that which deviates from the Einstein-Smoluchowski root mean square displacement. The measured exponent n of the displacement $x^n = f(t)$ is discussed in detail and interpreted as the dynamic dimension d_w of the diffusion through the fractal medium of the gel, the backbone dimension of which could be estimated. A cellular automaton model is used to describe the DLA cluster formation of the precipitate as well as the geometrical shape of the Liesegang patterns.

Introduction

R.E. Liesegang published his first papers on pattern formation in gelatine in 1896 [1–3]. In general, the experimental preparation runs as follows: a gel is prepared which contains an ionic species that can later be precipitated by a suitable counterion.

The experiment is usually carried out in a one- or two-dimensional arrangement, e.g. in a test tube or in a Petri dish; the precipitation reagent is then placed as a solid or in concentrated solution onto the gel column or in the middle of the gel layer respectively.

During the diffusion of the counterion into the gel, the precipitation reaction occurring sometimes produces concentric rings or sharp disks of precipitate. These structures are commonly referred to in the literature as Liesegang rings.

The classification of the experimental arrangement in terms of integer dimensions is meant to emphasize the main direction of the diffusion. It does not imply that the process can be explained by solving a system of reaction-diffusion equations for one or two dimensions, since accidentally macroscopic screw dislocations of precipitated material appear (Fig. 1). Liesegang was one of the first to notice this, without giving an explanation [4].

Liesegang's discovery induced much experimental and theoretical work, including many papers and monographs by himself [1–6]. The attempt at a theoretical interpretation followed as early as 1897 by Wi. Ostwald and his supersaturation theory [7].

Much of Liesegang's early work is restricted somewhat to gelatine jellies, while A.C Chatterji and N.R. Dhar [8] used other types of gel-forming materials such as Agar, starch and silicia gel. The authors claimed any reaction giving an insoluble product to be capable of Liesegang structure formation under certain conditions. K. Kant [9] and J.M. Garciá-Ruiz [10] reported some experimental work concerning the formation of lead iodide in Agar. Garciá-Ruiz investigated in particular the role of gravity in the formation of Liesegang patterns. A tracer study which gives the density profile of the precipitation product is reported by H.J. Arnikar and D. Meenamani [11]. An extensive bibliography concerning crystal growth in gels was published by H.K. Henisch 1988 [12].

It should be noted that macroscopic structure formation can occur in the absence of a gel whose primary function is to surpress convection and sedimentation. Precipitation patterns are reported to occur both in gas phase reactions (interdiffusion of HCl and NH_3) [13, 14] and in pure water under carefully controlled conditions in capillary tubes [15].

A modern approach is provided by J. Ross and other groups, in various theoretical and experimental articles commencing in the 1970s [16–23]. The attempt at a theoretical description of the Liesegang phenomenon is based on nonlinear reaction diffusion equations and on nucleation kinetics leading to chemical instabilities. Nucleation kinetics, especially, are discussed at length in this literature. A very instructive computer simulation of simple Liesegang patterns has been carried out by B. Chopard et al. [24].

What all these articles have in common is that no special consideration is given to the role of the gel media with the precipitate as the diffusion space. Nevertheless, Fick's second law is usually used for the description of the diffusion process. This is the starting point of our investigation. Following some earlier ideas one of us had [25], it is doubtful that the diffusion of ionic species in gels can be explained by Fick's second law, which is derived by Einstein in a theoretical way by considering non-interacting particles in homogeneous Euclidian space. Einstein found that the average displacement of a random

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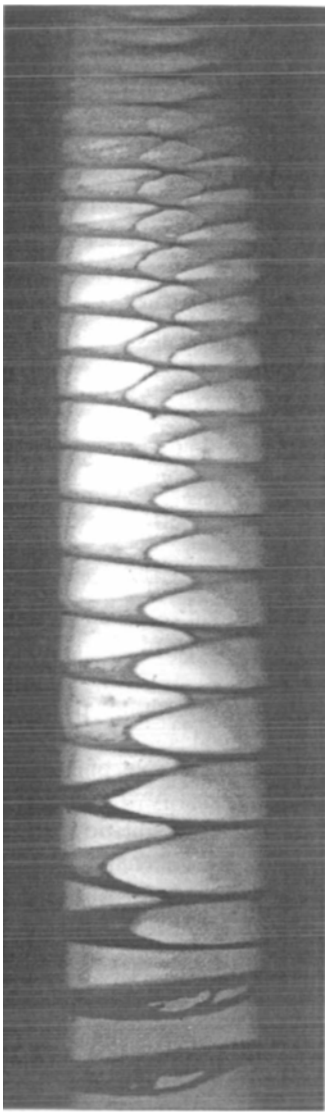

Fig. 1
Formation of Liesegang double and single screw surfaces and discs during the precipitation of lead chromate in Agar gel. This experiment was carried out by W. Jacobi in a "one"-dimensional arrangement in a test tube of normal size

walker relative to the x-direction is proportional to the square root of the time [26], where d_{top} is the topological dimension of the space in which the diffusion takes place.

$$\bar{x}^2 = 2\, d_{\text{top}}\, Dt$$

Rewriting this equation in logarithmic form gives

$$\log t = 2 \log \bar{x} - \log (2\, d_{\text{top}}\, D)\,.$$

The validity of the logarithmic equation can be examined by experimental determination of x and t.

Experimental Set-up

All experiments were performed in a constant temperature water bath. The temperature was controlled to ±0.1 °C precision. (Ultra-Kryostat Type UK 40 D, Fa. Lauda). The influence of light was excluded to a large extent.

A highly concentrated solution of the outer electrolyte was used to minimise the loss of concentration in this solution during the experiment. In the case of the test tube experiments, this solution was put on the upper surface of the gel, whereas it was placed in the centre of the gel by a capillary in the 3D-experiments. In the latter case, we took care that no convection flow of the outer electrolyte into the gel took place. For the formation of the aqueous gel we used a 0.75% by weight concentration of Agar (Agar in filaments, DAB 6 and 7, Riedel de Häen).

One of the reasons for using the $KJ/Pb(NO_3)_2$ in Agar system as an object to study was the fact that the bright yellow PbJ_2 is easily detected visually. This system is also known to form sharp distinct bands, and experimental work on it is available in the literature [9, 18, 20].

Results

1. Double Screw Surfaces

Screw surfaces have already been observed in test tube experiments [4, 18, 23]. In older literature they are named "spiral bands", although this term does not reflect exactly the mathematical function which describes this Liesegang pattern. Fig. 1 shows a double screw surface occurring during the precipitation of lead chromate in Agar gel. At higher concentration gradients of the chromate in the upper regions of the test tube, one can observe double screw surfaces which change into single screw surfaces for lower concentration gradients. Furthermore, if the concentration gradient is decreased, the winding of the single screw enlarges and suddenly the screw surface falls apart into a sequence of single slices.

We would point out that the screw surface is fixed by a helix to the test tube. This enables a second screw surface to be anchored at the same helix. These double screw surfaces represent a new type of Liesegang pattern (Fig. 1) that has not been reported before.

2. Fractal Precipitation Discs

As mentioned above, the screw surface falls apart to form single discs with decreasing concentration gradient. Surprisingly, however, these discs possess holes of different sizes. Cutting out slices of the gel, one can easily recognise the fractal character of the precipitation pattern (see Fig. 2). This may provide a hint with regard to the selection of a proper model. This type of pattern formation should be described by means of a diffusion-limited aggregation process. The pure geometrical macroscopic patterns should be the outcome of such a DLA process, which usually creates a fractal object. So we need to look for a model that creates classical geometrical objects such as screw surfaces and discs with an internal fractal substructure.

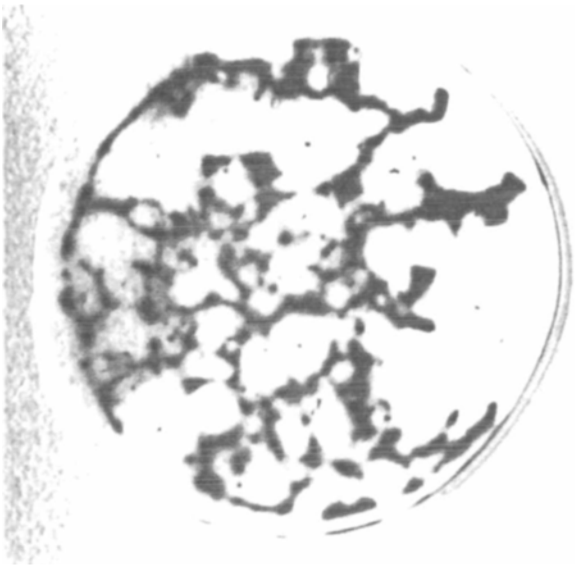

Fig. 2
A typical fractal DLA-structure of the PbJ_2 precipitate obtained from cutting the Agar gel column into narrow slices (approx. 1 mm thick and 14 mm in diameter)

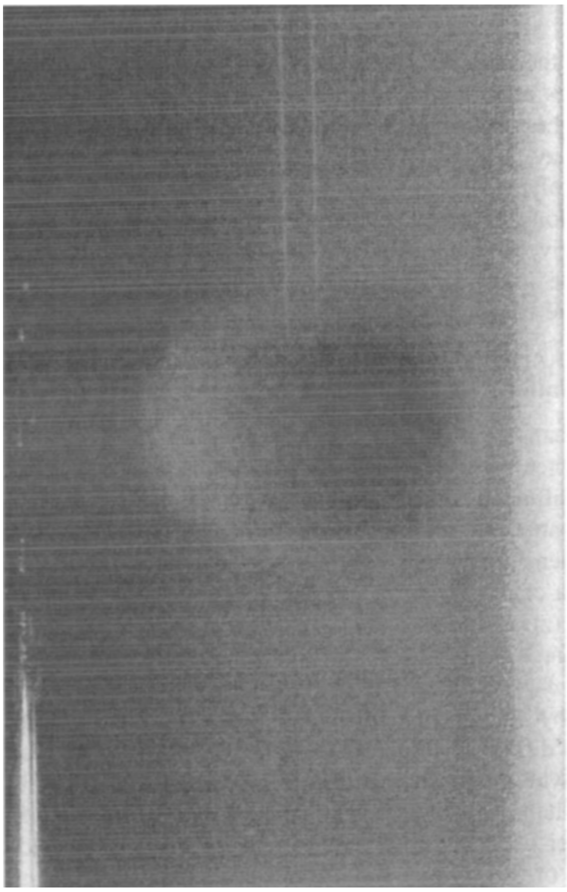

Fig. 3
The Liesegang ball formed by PbJ_2 in a "three"-dimensional arrangement using a capillary as a point source for the outer electrolyte. This experiment was carried out by S. Hollatz and T. Plikat

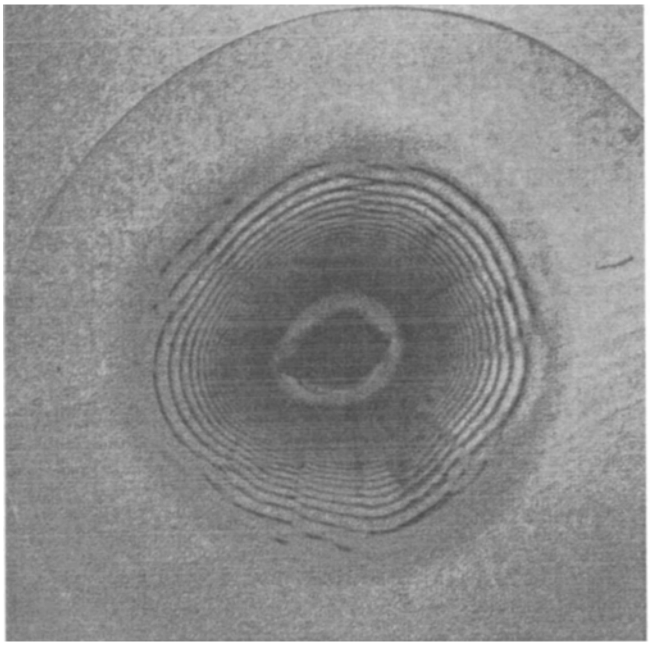

Fig. 4
A gel slice containing the centre of the Liesegang ball. This pattern greatly resembles the typical "two"-dimensional Liesegang structures. This experiment was carried out by S. Hollatz and T. Plikat using a small soluble capsule filled with solid KJ

3. Liesegang Balls

Executing the Liesegang experiment in a sufficiently large test tube with a point source of the outer electrolyte, as first performed by S. Hollatz and T. Plikat, one can observe 3D-Liesegang ball structured patterns (Fig. 3). This Liesegang ball is strongly suggestive of an onion-type structure.

Cutting out slices of the gel containing the centre of the ball (Fig. 4), one obtains Liesegang patterns that are well known from the 2D-experiments in Petri dishes. One can observe parts of circles of the precipitate, which are connected by zigzag lines or some undefined distortions starting from the centre.

However, cutting out gel slices containing ball sockets of the outer parts of the Liesegang ball (Fig. 5), one immediately recognizes the fractal structure of this onion skin, which is known to us from the gel slices in the test tube experiments (Fig. 2).

We can now combine both types of intersections to construct a 3D representation of the Liesegang ball. The precipitation forms fractal segments of ball sockets, which surround the centre like onion skins. They are interconnected with screw surfaces which emerge radially from the centre. The screw surfaces are strongly suggestive of winding stairs, since they possess the possibility to step out after $n\pi$ turns onto another fractal onion skin of the precipitation pattern.

The zigzag lines as well as the undefined radial distortions in the 2D experiments are nothing other than arbi-

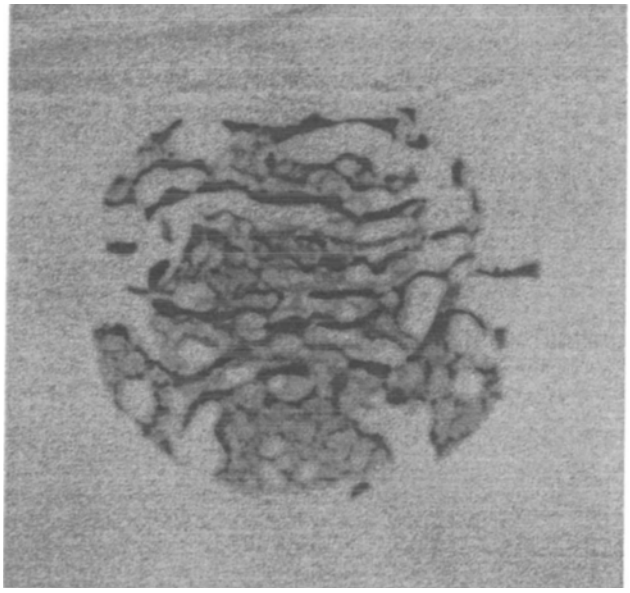

Fig. 5
A gel slice containing ball sockets of the outer part of the Liesegang ball, showing the typical fractal structure of the spheres of the precipitate surrounding the centre of the ball like onion skins. This experiment was carried out by S. Hollatz and T. Plikat

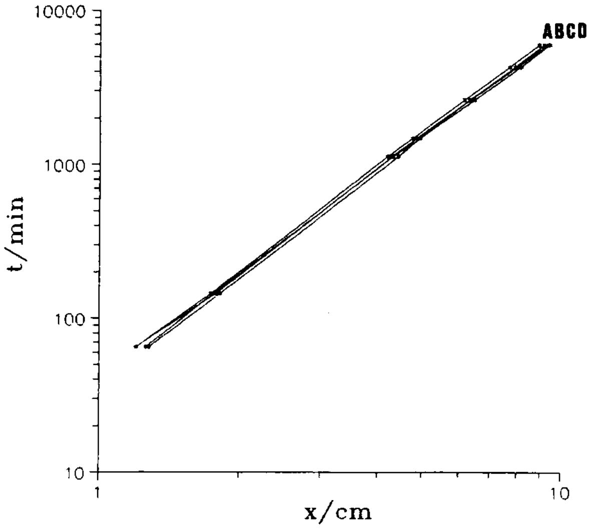

Fig. 6
Logarithmic plot of the progression of the lead iodide formation front in the Agar gel at 20 °C. Lead nitrate concentration in the gel: A) to D): 5 mM, 6 mM, 8 mM, and 9 mM. From the slopes of these lines, the dynamic dimension d_w is estimated

trary intersections of the gel slices with the radial screw surfaces discussed above.

4. Measurement of the Fractal Dimension

The position of the visible boundary of precipitate moving downward in the test tube is measured. It is assumed that this boundary occurs at a specific point in the concentration profile along the x-axis of the test tube. As long as the concentration of the outer electrolyte, which penetrates into the gel, is large compared to the concentration of the electrolyte present in the gel, an experimental set-up may be used in which the concentration of the outer electrolyte can be taken as constant at $x=0$ for sufficiently long times. Thus, a plot of log t versus log x should give a straight line with slope 2. This is not found to be the case. Instead, lines with slopes usually larger than 2 are found (Fig. 6).

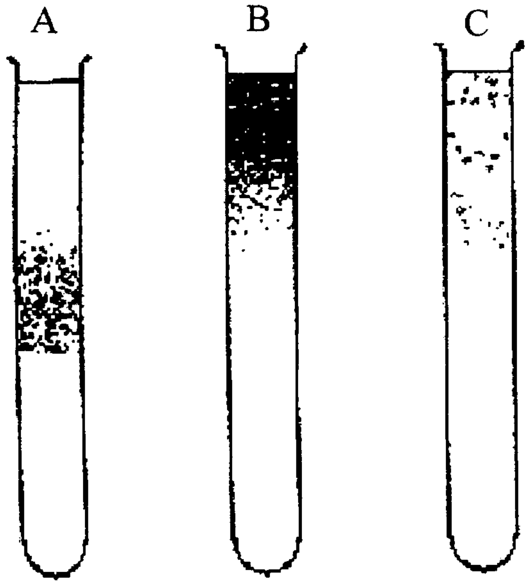

Fig. 7
Simulation of diffusion, reaction and aggregation in the Liesegang experiment by means of a cellular vector automaton; A) the distribution of the diffusing lead ions in the test tube; the lower part of the test tube is not coloured; B) the distribution of the iodide starting from the upper level of the gel in the test tube; C) the pattern formation of the PbJ_2 nuclei as a consequence of a DLA process

5. Simulation – A Cellular Vector Automaton Model

By means of a cellular vector automaton [27, 28] with three vector components, it is possible to describe the reaction diffusion nucleation process underlying the observed pattern formation in the Liesegang systems. In a two dimensional model with cylindrical boundaries, the state of a cell at time t in position i, j is given by the vector $z_{i,j}=(z(J), z(Pb), z(PBJ_2))$, where $z(J)$, $z(Pb)$ and $z(PbJ_2)$ are integer numbers representing the concentrations of J^-, Pb^{2+} and PbJ_2 in the elementary space described by the mathematical cell. All three components undergo diffusion. $\min\{z(J), z(Pb)\}$ is the number of $z(PbJ_2)$ which is created in the cell at time t. If $z(PbJ_2)$ is smaller than a given threshold, there is a probability that the nuclei will decay. If $z(PbJ_2)$ oversteps this threshold, the state of the components becomes stable, which means that the nuclei cannot be dissolved again. Moreover, this state becomes fixed in the lattice. The stable nucleus cannot diffuse any more and becomes an obstacle for all the diffusing states. In this way, it becomes a core of a DLA-cluster created by diffusing unstable nuclei. Fig. 7 shows the distributions of the states $z(\mathrm{Pb})$, $z(\mathrm{J})$ and $z(\mathrm{PbJ_2})$ after several time steps. One may recognise that there is a band structure in the accumulation of DLA clusters, which tends to develop into a spiral form. New nuclei are only formed in the small area where we have low numbers of $z(\mathrm{J})$ as well as $z(\mathrm{Pb})$ states. These nuclei in the nascent state can diffuse, and are thus responsible for the structure formation.

Discussion

The analysis of the measurements clearly shows that the time t for the displacement of the diffusing particles scales as

$$x^n \propto t\,.$$

As is well known, the Einstein-Smoluchowski relation for the diffusive Brownian motion can be interpreted in terms of a random walk in a homogeneous space or on a Euclidian lattice [29]. The fractal dimension d_w of the random walk

$$d_w = 2$$

is independent of the dimension $d = 1, 2, 3, \ldots$ of the homogeneous or discrete Euclidian space [30].

Assuming that the random walk takes place on a random fractal of dimension d_f like a DLA cluster or a percolation cluster, then d_w should be considerably larger than two:

$$d_w \geq 2$$

In the case of a percolation cluster at the percolation threshold, d_w depends on the dimension d_{top} of the space in which this cluster is embedded [30].

Assuming the Agar gel forms a network which is penetrated by a percolation cluster of water beyond its percolation threshold, then the mean square displacement for a random walk of the nuclei of the precipitate in the water cluster should scale with time as [31]:

$$x^2 \propto \begin{cases} t^{2/d_w}\,; & \text{if } x < \xi \\ t\,; & \text{if } x > \xi \end{cases}$$

For $x < \xi$, the percolation cluster possesses a fractal character, where ξ is the mean linear size of two sites belonging to the same cluster. A random walk on such a cluster is characterised by the dimension $d_w > 2$.

At the percolation threshold, ξ tends to infinity: $\xi \rightarrow \infty$ and $x^2 \propto t^{2/d_w}$ holds for all length scales.

This relation can be rewritten in the form:

$$x^{d_w} \propto t$$

In most cases we estimate $d_w \approx 2.27$ for the lead iodide experiments on average to be independent of the preparation of the Agar gel. For the dimensions $1 < d_{top} < 6$ the Alexander-Orbach conjecture [32] states that $d_s = 4/3$, while the spectral dimension is $d_s = 2\ d_f/d_w$ for fully developed percolation clusters.

The fractal dimension for the assumed water percolation cluster is thus found to be about $d_w \approx 1.5$ which is far too small with respect to $d_f = 1.896$ if $d_{top} = 2$, or $d_f = 2.5$ if $d_{top} = 3$, which are the fractal dimensions for infinite percolation clusters [31, 33] in one or two dimensions respectively. The dimension $d_f = 2.5$ is just in the order of the magnitude of the dimension of the backbone of a three dimensional ($d_{top} = 3$) percolation cluster [34].

We can now conclude that the Liesegang patterns are created by the nuclei of the precipitate forming DLA clusters. The diffusion of the ions of the electrolytes is not at all responsible in the first place for the pattern formation. However, the restricted diffusion of the very small nuclei, which happens on the water percolation cluster partially clogged with the DLA clusters, is most important. This diffusion takes place almost without any exception in the narrow area where the nuclei are formed between the moving diffusion fronts of the electrolytes.

We are greatly obliged to W. Jacobi for making his experiments on screw surfaces available to us. Furthermore, we are indebted to S. Hollatz and T. Plikat for placing their three-dimensional experiments at our disposal.

References

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

[2] R.E. Liesegang, Liesegangs photographisches Archiv. No. 801. Düsseldorf, 1 November 1896, Issue no. XXI.

[3] R.E. Liesegang, Z. Anorg. Chem. *48*, 364–366 (1906).
[2] und [3] are also available as a reprint in: Oswalds Klassiker der exakten Wissenschaften, Vol. 272. "Selbstorganisation chemischer Strukturen" Akademische Verlagsgesellschaft Geest & Portig K.-G. Leipzig, 1987.

[4] R.E. Liesegang, Über die Schichtung bei Diffusionen, Düsseldorf, 1907.

[5] R.E. Liesegang, Chemische Reaktionen in Galterten. 2nd edition, Dresden, Leipzig, 1924.

[6] R.E. Liesegang, Spezielle Methoden der Diffusion in Gallerten, in: Handbuch der biologischen Arbeitsmethoden Abt. III, Teil B, ed. by F. Abderhalden, Berlin, Schwarzenberg-Verlag, 1929.

[7] Wi. Ostwald, Lehrbuch der allgemeinen Chemie, Leipzig, 1887.

[8] A.C. Chatterji and N.R. Dhar, Kolloid Z. *11* (2), 97–112 (1926).

[9] K. Kant, Koll. Z. *189* (2), 151–156 (1963).

[10] J.M. Garciá-Ruiz, D. Rondón, A. Garciá-Romero, and F. Otálora, J. Phys. Chem. *100*, 8854–8860 (1996).

[11] H.J. Amikar and D. Meenamani, Kolloid Zeitschrift. Z. Polym. *189* (1), 57–59 (1963).

[12] H.K. Henisch, Crystals in Gels and Liesegang Rings. Cambridge, 1988.

[13] E.C. Spotz and J.O. Hirschfelder, J. Chem. Phys. *19*, 1215 (1951).

[14] L. Senf, Z. Phys. Chem. Leipzig *270* (5), 1020–1022 (1989).

[15] Wo. Ostwald, Koll. Z. *40*, 144 (1926).

[16] D. Feinn, P. Ortoleva, W. Scalf, S. Schmidt and M. Wolff, J. Chem. Phys. *69* (1), 27–39 (1978).

[17] G. Venzl, J. Ross, J. Chem. Phys. *77* (3), 1302–1307, and 1308–1313 (1982).

[18] S.C. Müller, S. Kai and J. Ross, J. Phys. Chem. *86* (20), 4078–4087 (1982).

[19] G. Venzl, J. Chem. Phys. *85* (4), 2006–2011, (1986).

[20] G.T. Dee, Phys. Rev. Lett. *57* (3), 275–278 (1986).
[21] J. Ross, Chemical Waves and Periodic Precipitation Processes, in: Springer Series in Synergetics, Vol. 41, p. 90–99, Propagation in Systems far from Equilibrium, 1988.
[22] A. Büki, E. Kárpáti-Smidrócski, and M. Zrínyi, J. Chem. Phys. *103* (23), 10387-10392 (1995).
[23] D.S. Chernovskii, A.D. Polezhaev, and S.C. Müller, Physica D54, 160–170 (1991).
[24] B. Chopard, P. Luthi, and M. Droz, J. Stat. Phys. *76* (1/2), 661-677 (1994).
[25] P.J. Plath and H. Engel-Herbert, Liesegangsche Spiralen. Lecture at the Winterseminar at Zeinisjoch, 24. 2. 1988.
[26] A. Einstein, Ann. Phys. 4th Series XVII, 549-560 (1905).
[27] P.J. Plath, J.K. Plath, and J. Schwietering, Discrete Dynamics in Nature and Society *1*, 57–76 (1997).
[28] M. Gerhardt, H. Schuster, and J.J. Tyson, Physica D46, 392–415 (1990).
[29] L. Peliti, in: Fractals in Physics, pp. 73–81, eds. by L. Pietronero and E.Tosatti, North-Holland, Elsevier Science Publishers B.V., Amsterdam, 1986.
[30] H.E. Stanley, in: On Growth and Form, Fractal and Non-Fractal Patterns in Physics, pp. 21–53, ed. by H.E. Stanley and N. Ostrowsky, Matinus Publishers, Dordrecht, 1986.
[31] Sh. Havlin, in: The Fractal Approach to Heterogeneous Chemistry, pp. 251–269, ed. by D. Avnir, J. Wiley & Sons, Chichester New York Brisbane Toronto Singapore, 1989.
[32] S. Alexander and R. Orbach, J. Phys. Lett. (Paris) *43*, L625 (1982).
[33] G.H. Weiss and S. Havlion, J. Stat. Phys. *37*, 17 (1984).
[34] A. Chhabra, H.J. Hermann, and D.P. Landau, in: Fractals in Physics, pp. 129–131, eds. by L. Pietronero and E. Tosatti, North-Holland, Elsevier Science Publishers B.V., Amsterdam, 1986.

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