

# Voronoi diagrams generated by regressing edges of precipitation fronts

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Reaction-diffusion systems where one of the reagents (outer electrolyte) penetrates into a gel by diffusion and forms a precipitate with the other reagent (inner electrolyte) homogenized in the gel, are able to produce various complex precipitation patterns. The previously studied  $\text{NaOH} + \text{AgNO}_3$  and recently discovered  $\text{CuCl}_2 + \text{K}_3[\text{Fe}(\text{CN})_6]$  processes, (where the first reagent is the outer electrolyte and the other is the inner electrolyte homogenized in the gel), when reacted using the above mentioned method, are able to generate tessellations of a plane by a mechanism dependant on the dynamics of so-called regressing edges of the reaction fronts. The spontaneous partitioning of the reacted phases results in the construction of a pattern analogous to a Voronoi diagram or one of their generalizations. © 2004 American Institute of Physics. [DOI: 10.1063/1.1635358]

## I. INTRODUCTION

Problems related to spatial tessellations arise in almost all fields of science, where a space should be partitioned into “spheres of influence.” Finding the best facility location,<sup>1–3</sup> a description of aggregation territories of slime mold cultures,<sup>4</sup> investigating the geometry and growth of cells,<sup>5</sup> and modeling some animal coat patterns<sup>6,7</sup> requires tasks of tessellations to be solved. These can usually be achieved by constructing the *Voronoi diagram* of the problem.<sup>1,2</sup> The Voronoi diagram (in plane) is the nearest-neighbor map for a set of initially given points. Each region contains those points that are nearer to one input point than any other input point, while edges of regions are equidistant to them. A Voronoi diagram is sometimes also known as a Dirichlet tessellation. The cells are called Dirichlet regions, Thiessen polytopes, or Voronoi cells and the boundaries of the cells are termed the medial axes.

Several kinds of simple reaction-diffusion systems in gels are found to be able to generate Voronoi diagrams.<sup>8–11</sup> In the reaction-diffusion system presented in Ref. 10 some droplets of an appropriate *outer electrolyte* [e.g., ferric (III) chloride and potassium iodide] were put at distinct points on the surface of a thin gel sheet containing the *inner electrolyte* (e.g., potassium ferrocyanide or palladium chloride). Thus a precipitation reaction is initiated around the droplets. Because the process is diffusion limited, ahead of the reaction fronts there is a thin region, where the inner electrolyte is depleted. Just before the reaction fronts started from different droplets meet, the depleted regions overlap, and the precipitation ceases or is significantly reduced. Since the speed of the fronts started from different points varies (decreases)

with time in an identical manner, then the resulting pattern, consisting of precipitate regions and empty bands, represents the Voronoi diagram of the droplets. Chemical reactions of this type have been used as experimental chemical processors for solving shortest path problems,<sup>10</sup> as preprocessors for shape recognition via the skeletonization of a planar shape<sup>12</sup> and in the construction of experimental XOR logic gates.<sup>13</sup>

In this paper we discuss the ability of building Voronoi diagrams of the  $\text{NaOH} + \text{AgNO}_3$  or  $\text{CuCl}_2 + \text{K}_3[\text{Fe}(\text{CN})_6]$  processes in a “Liesegang setup,” where the inner electrolyte {like  $\text{AgNO}_3$  or  $\text{K}_3[\text{Fe}(\text{CN})_6]$ } is homogenized in agarose gel, while the other reagent, the outer electrolyte is layered on the gel. The patterns in these reactions are built up by a mechanism that involves the so-called *regressing edges* of the reaction fronts. Some of these kind of processes have been studied in detail,<sup>14–16</sup> but the reactions involving the potassium ferricyanide as inner electrolyte represent a new branch of this class of pattern-forming chemical systems.

## II. EXPERIMENT

Preparation of the gel environment for the reactions has been performed as follows:

Agarose gel of 2 w/w % was prepared by adding agarose powder to high-purity water at room temperature. Solubilization was achieved by stirring for 1–2 min at 70–80 °C. The inner electrolyte concentration was set by adding appropriate amounts of concentrated inner electrolyte solution at 50–60 °C to an agarose solution of 100 ml. Then, the mixture was made up to 200 ml using high-purity water at 50–60 °C. After vigorous shaking the above mixtures were

poured into Petri dishes of 87 mm internal diameter and 13 mm height to give a gel layer of about 6 mm, and they were left to cool to room temperature.

In the case of the system having  $K_3[Fe(CN)_6]$  as an inner electrolyte, cross-linking took place when the above mixtures were allowed to cool to room temperature. However, when a higher amount of  $AgNO_3$  was homogenized in the mixture, the gelation took much longer time, e.g., at 0.88 M  $AgNO_3$  it required approximately 1 day. Gels having inner electrolyte concentration above 1 M  $AgNO_3$  could not be prepared, since they failed to cross-link.

The reactions were started by pouring a layer of about 5 mm of outer electrolyte onto the gel. The chemicals used were of: agarose (SeaKen low EEO or Sigma, low EEO),  $AgNO_3$  (Reanal A.R.), NaOH (Reanal A.R.),  $CuCl_2$  (Reanal A.R.), and  $K_3[Fe(CN)_6]$  (Merck, Z.S.).

### III. RESULTS AND DISCUSSION

As the outer electrolyte is layered on the gel containing the inner electrolyte, it will penetrate into the gel through diffusion. Having a concentrated outer electrolyte (8.00 M NaOH or 2.93 M  $CuCl_2$ , respectively), three types of behavior have been observed as the inner electrolyte concentration is varied.

At low inner electrolyte concentrations {below 0.3 M  $AgNO_3$  or 0.03 M  $K_3[Fe(CN)_6]$ } a homogeneous precipitate forms in the regions reached by the outer electrolyte, irrespective of the condition of the gel surface. When the concentrations were approximately 0.64 M  $AgNO_3$  or 0.09 M  $K_3[Fe(CN)_6]$ , Voronoi diagrams could be formed in a controlled way: in this case the centers of the induced Voronoi cells were the points at which the gel surface had been deliberately marked e.g., by gently touching the gel surface with a pipette tip or thin glass stick. At these concentrations no natural Voronoi cells would be formed, and if the gel had not been marked, then a homogeneous precipitate would have resulted from the addition of the outer electrolyte.

At even higher inner electrolyte concentrations {e.g., 0.88 M  $AgNO_3$  or 0.15 M  $K_3[Fe(CN)_6]$ }, minor defects of the gel surface become the natural centers of the Voronoi cells. Thus, the pattern becomes uncontrollable.

The precipitate patterns resembling Voronoi diagrams are built up via the following sequence of events. The precipitation does not begin on the whole surface of the gel; in some points, where the surface is damaged, the reaction does not start at all [Fig. 1(A)]. As time evolves, and the diffusion front followed by the reaction front (where the precipitation occurs) sweeps through the gel, these points expand into empty cones, free of precipitate [Fig. 1(B)]. The precipitation continues only on the leaky-disklike reaction front, that will be referred to as the *active border* of the precipitate. Since the base of the empty cones grows as the reaction front progresses, the disk-shaped holes in the front will also grow in size. The circular margins of the holes will be referred to as the *regressing edges* of the active border. In spite of the presence of both reagents, the reaction does not proceed on the mantle of the cones that separate the already formed precipitate from the empty regions. These stationary surfaces

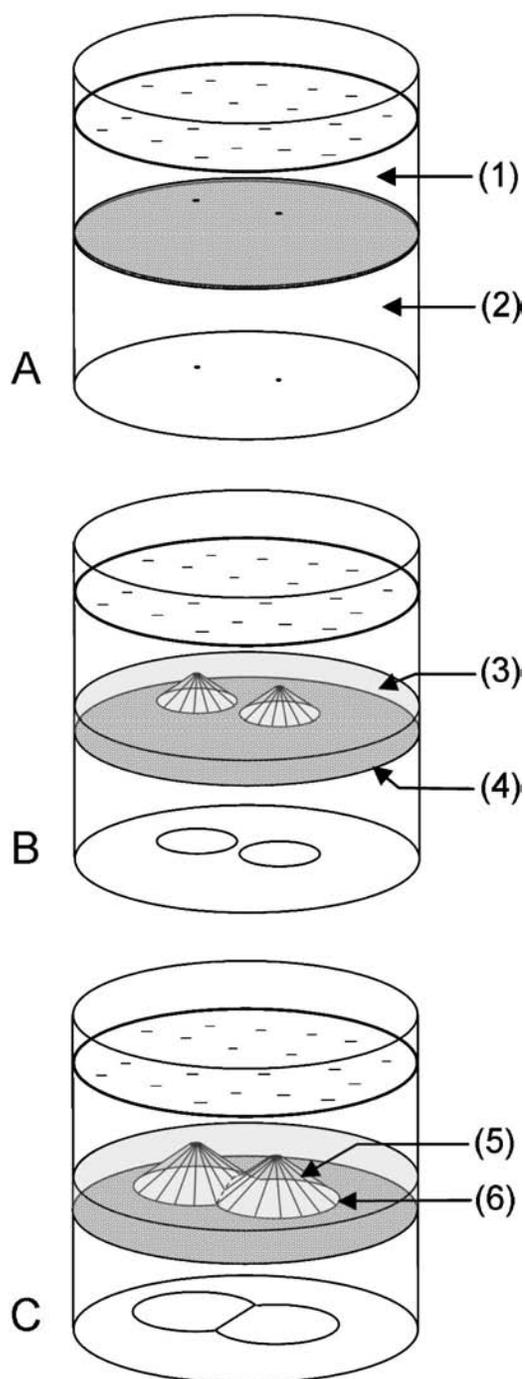


FIG. 1. Schematic representation of Voronoi diagram formation through the "regressing edge mechanism." (1) Outer electrolyte, (2) agarose gel containing the inner electrolyte, (3) precipitate, (4) reaction front (active border, represented by a dotted surface), (5) passive border, (6) regressing edge. The contours of the patterns are drawn on the bottom of the vessel. (A) The precipitation does not start at some points of the gel surface. (B) These points expand into precipitate-free cones as the front progresses. (C) The regressing edges meet on the line that is an equal distance from the tip of the empty cones.

will be referred to as the *passive borders* of the precipitate region.

At the points where the regressing edges of the fronts meet, the precipitation stops [Fig. 1(C)]. Seeing that the horizontal speed of the regressing edges changes in time in the same way, the locus of their meeting will draw the Voronoi

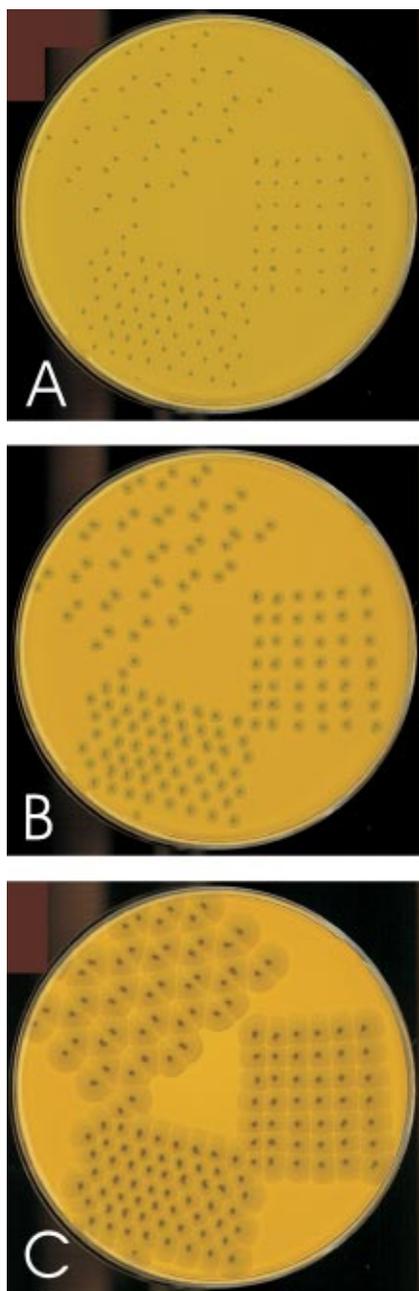


FIG. 2. Consecutive stages of development of a controlled Voronoi diagram, representing triangular, rectangular, and hexagonal arrangements. The centers of the cells were put by hand, therefore the pattern is not “true to type.” The outer electrolyte was of (2.93 M  $\text{CuCl}_2$ ), while the inner electrolyte was of (0.09 M  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ). Time elapsed from the start of the experiment was 43 s, 198 s, and 878 s at panels (A), (B) and (C), respectively. The diameter of the Petri dishes is 87 mm.

diagram of the points where the precipitation did not start. The Voronoi polygon appears as a local minimum of the precipitate region’s lower surface. Note that in most cases the precipitate does not restart in the empty cones, and the reactions are over after the active surface has vanished. All of these stages can be observed in Figs. 2 and 3 representing the formation of controlled and spontaneous patterns in the  $\text{CuCl}_2 + \text{K}_3[\text{Fe}(\text{CN})_6]$  and  $\text{NaOH} + \text{AgNO}_3$  experimental systems, respectively.

If some of the cones start to develop at this later stage,

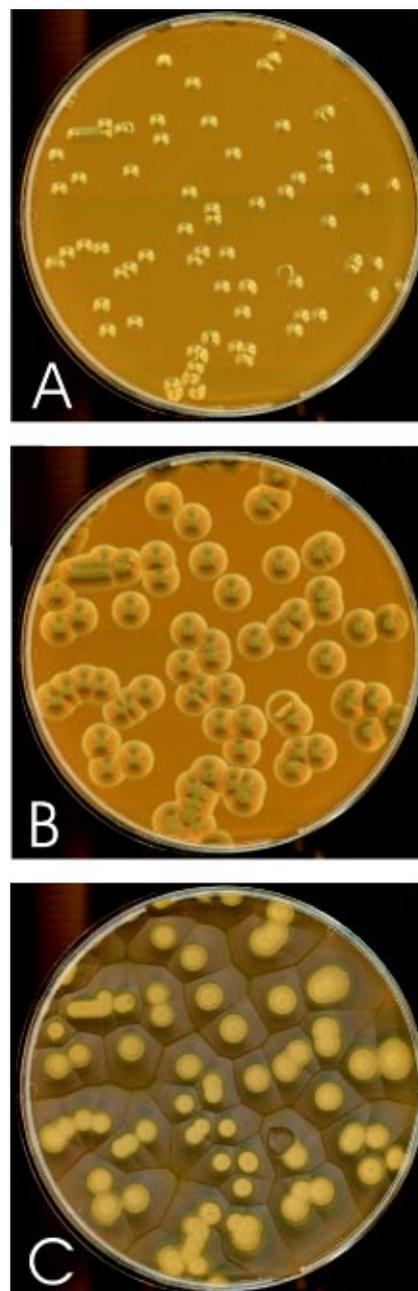


FIG. 3. Consecutive stages of development of a spontaneous Voronoi diagram. The outer electrolyte was of (8 M  $\text{NaOH}$ ), while the inner electrolyte was of (0.882 M  $\text{AgNO}_3$ ). Time elapsed from the start of the experiment was 35 s and 138 s at panels (A) and (B). The figure represented at panel (C) was taken after the termination of the reactions. The diameter of the Petri dishes is 87 mm.

the resulting polygon will not be of the ordinary Voronoi-type, since the “belated” cones will be able to expand only in a smaller area. The tessellation generated corresponds to a generalization of a Voronoi diagram more specifically to a type known as an additively weighted Voronoi diagram (AWVD). The AWVD differs from the ordinary Voronoi diagram in that where fronts initiated at different times collide they no longer form straight line bisectors but instead meet at hyperbolic segments. AWVD are employed in urban planning and the natural sciences, for example in modelling crystal growth.<sup>1</sup>

The key for understanding the pattern forming processes is the comprehension of the appearance and dynamics of regressing edges. Here we present a synopsis of the possible explanation described in Ref. 16.

The main assumption of the phenomenological explanation is that the sharp reaction front—the active, growing border of the already formed precipitate—acts as a catalytic surface, where the outer and inner electrolytes react, and a diffusive intermediary compound (DC) is formed. It is also supposed that the formation of the precipitate, and thus the progression of the reaction front require a critical concentration of the DC. If this concentration is reached on a portion of the active border, a new layer of precipitate will be formed, and the active border will be shifted. Otherwise, no new precipitate will form on that section of the front. Moreover, it is possible that the critical concentration of the DC on a section of the front is not reached within a certain time  $\tau$ , counted from the formation of the precipitate layer that is the actual front. In this case, the section of the active border is supposed to lose its catalytic properties, and becomes part of the stationary, passive border.

In order to understand the dynamics of regressing edges, the concentration of the DC has to be assumed to be smaller in the immediate vicinity of the front margins, than the constant value far from the edges. Computer simulations showed that this circumstance is typical.<sup>16</sup> If the critical concentration of the DC is smaller than the value far from, but larger than the value near the front margins, the next layer of precipitate (the new reaction front) will be smaller in surface than the actual front. For the shrinking to occur, the uncovered portions of the antecedent reaction front cannot remain reactive too long after the formation of a new layer of precipitate.

Initiation of empty cones happens either at the top of the gel, where an impurity is present or the surface is damaged, as well as when the front reaches an impurity or inhomogeneity present in the gel. At these points the reaction front is damaged, and may lose its catalytic property. As a consequence, the concentration of the DC will locally be reduced, and passive borders appear as described above. Note that the emergence of the active surface is not included in this phenomenological explanation.

#### IV. CONCLUSIONS

In this paper, we have shown that some reaction-diffusion systems, belonging to the class of pattern-forming chemical reactions first reported in Ref. 14, are able to produce Voronoi diagrams in the plane.

In addition, the dynamics of the systems are such that tessellations of the plane pertaining to generalizations of Voronoi diagrams will be formed where the regressing edges at some points of the reactor are initiated at a later stage of the diffusion fronts advance.

It is remarkable that a new chemical process {CuCl<sub>2</sub> outer electrolyte + K<sub>3</sub>[Fe(CN)<sub>6</sub>] loaded gel} reported in this paper has chemically very different outer and inner electrolytes from the cases previously reported in Refs. 14–16. Thus, this class of inorganic based nonlinear chemical reactions is much broader than believed up to this time, and their interesting properties will be the subject of further research. At present the chemical composition of the DC has not been identified. Work is continuing to ascertain the exact underlying mechanisms especially in light of the new chemical system described in this paper.

The work has also highlighted that by careful control of the initial reaction conditions it is possible to obtain controllable (programmable) pattern formations. The system we report in this paper has some inherent advantages over previously published systems<sup>10,12,13</sup> in that the reaction dynamics are faster, and the Voronoi cells can be initiated from a point rather than a drop of outer electrolyte applied to the gel surface. Thus the minimum area of an induced Voronoi cell can be greatly reduced using the current methodology.

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<sup>1</sup>A. Okabe, B. Boots, K. Sugihara, and S. N. Chiu, *Spatial Tessellations: Concepts and Applications of Voronoi Diagrams* (Wiley, Chichester, 2000).

<sup>2</sup>F. Aurenhammer, *Comput. Surv.* **23**, 345 (1991).

<sup>3</sup>A. Okabe and A. Suzuki, *Eur. J. Oper. Res.* **98**, 445 (1997).

<sup>4</sup>S. C. Müller, T. Mair, and O. Steinbock, *Biophys. Chem.* **72**, 37 (1998).

<sup>5</sup>M. Tanemura, H. Honda, and A. Yoshida, *J. Theor. Biol.* **153**, 287 (1991).

<sup>6</sup>K. J. Painter, in *Mathematical Models for Biological Pattern Formation, The IMA Volumes in Mathematics and Applications*, edited by P. K. Maini and H. G. Othmer (Springer, New York, 2001), Vol. 121, pp. 59–81.

<sup>7</sup>D. C. Bottino, in *Mathematical Models for Biological Pattern Formation, The IMA Volumes in Mathematics and Applications*, edited by P. K. Maini and H. G. Othmer (Springer, New York, 2001), Vol. 121, pp. 295–314.

<sup>8</sup>O. Steinbock, *Path Optimization in Chemical and Biological Systems on the Basis of Excitation Waves*, *Lect. Notes Phys.* **503**, 179 (1998).

<sup>9</sup>D. Tolmachieff and A. Adamatzky, *Adv. Mater. Opt. Electron.* **6**, 191 (1996).

<sup>10</sup>A. Adamatzky and B. de Lacy Costello, *Chaos, Solitons Fractals* **16**, 727 (2003).

<sup>11</sup>A. Adamatzky and B. de Lacy Costello, *Phys. Lett. A* **309**, 397 (2003).

<sup>12</sup>A. Adamatzky, B. de Lacy Costello, and N. M. Ratcliffe, *Phys. Lett. A* **297**, 344 (2002).

<sup>13</sup>A. Adamatzky and B. de Lacy Costello, *Phys. Rev. E* **66**, 046112 (2002).

<sup>14</sup>P. Hantz, *J. Phys. Chem. B* **104**, 4266 (2000).

<sup>15</sup>P. Hantz, *Phys. Chem. Chem. Phys.* **4**, 4 (2002); **4**, 1262 (2002).

<sup>16</sup>P. Hantz, *J. Chem. Phys.* **117**, 6646 (2002).