Chemical Formation of Spatial Patterns Induced by Nonlinearity in a Concentration-Dependent Diffusion Coefficient

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Studies of pattern growth through coupling of reaction/diffusion have concentrated so far on strong nonlinearities in reaction kinetics. We report that pattern growth can be induced by nonlinearity in a concentration-dependent diffusion term, coupled to weakly nonlinear simple reaction schemes (A + B → C). According to the model the diffusion coefficient is constant at low concentration. However, there is a smooth transition to reciprocal dependence on the concentration at higher values; i.e., the diffusion becomes slower as concentration increases. Fast Fourier transform algorithms are used for two-dimensional numerical solutions of the kinetics equations.

1. Background

The study of spatial pattern formation driven by the coupling of reaction with diffusion has been confined, by and large, to strong nonlinearities in the chemical kinetics terms. The aim of this report is to demonstrate that if nonlinearity is introduced into the diffusion term, patterns evolve through coupling with even simple chemical reactions (which otherwise show no patterning). The nonlinearity chosen originates from a dependency of the diffusion coefficient on the concentration. This assumption stands on solid fusion rates on stability and bifurcation properties of the model and for its physical justification.

We present now a heuristic argumentation for the choice of that force

\[ \nabla \mu = RT \nabla \ln C = RT \frac{\nabla C}{C} \]

and the rate of concentration change at any given point is

\[ \frac{dC}{dt} = -\nabla J = \sqrt{\frac{RT}{C} \nabla C} = \sqrt{\nabla (DC)} \]

flow in the direction x, of decreasing \( \mu \). Only the direct coefficients \( \mu \) are considered. \( \mu \) is the phenomenological cross-diffusion coefficients are not considered here).

A small change in the chemical potential with distance is given by

\[ \mu = RT \nabla \ln C \]

i.e., (3):

\[ J = \frac{LRT}{C} \nabla C \]

and gravity. The role of the latter as driving force for patterning of unstable density gradients formed by (simple) chemical reactions has been investigated in our laboratory and in others.

2. The Model

Our concentration-dependent diffusion term has the form

\[ D(C) = (C + \alpha)^{-1} \]

in which \( C \) is concentration and \( \alpha \) is a constant, also of concentration units, whose physical meaning will shortly become clear. We present now a heuristic argumentation for the choice of that model and for its physical justification.

Our starting point is the Onsager classical relation which relates flux \( \mathbf{J} \) to force \( \mathbf{F} \) through a coefficient \( L_i 

\[ \mathbf{J} = L_i \mathbf{F} \]

A specific example is diffusion, in which \( \mathbf{J} \) (moles per area per time) of a solute C is related to its chemical potential gradient \( \mu \) through

\[ \mathbf{J} = L_i \nabla \mu \]

in which

\[ \mu = \mu_0 + RT \ln C \]

(where \( RT \) is defined as usual. The minus sign in (3) indicates

Dedicated to Prof. R. M. Noyes on the occasion of his 70th birthday.
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Figure 1. Concentration-dependent diffusion coefficient for \( D(C) = aD_0(\alpha + C) \), where \( D_0 = 0.2 \, \text{cm}^2/\text{s} \) and \( \alpha = 10^{-4} \, \text{M} \).

where \( D \) is the diffusion coefficient.

At high dilution where the interaction between the solute molecules is negligible, the diffusion coefficient should not be concentration dependent. This is taken care of usually by assuming linear dependence of \( L \) on \( C \), thus canceling the \( 1/C \) term in \( D \) and getting Fick's second law of diffusion:

\[
\frac{dL}{dt} = D(C) \nabla^2 C
\]

where \( D \) is here concentration independent. At higher concentrations, the effects of solute-solute interactions and changes in the solvent properties due to solute-solvent interactions are not negligible and the diffusion becomes concentration dependent.

Yet, the practice for small changes of \( C \) in an average concentration, is negligible and the diffusion becomes concentration dependent. Consequently, Fick's law cannot hold over a wide range of concentrations, and hence the need to specify \( C_0 \) when \( D \) is reported.

Our concentration-dependent diffusion coefficient is therefore valid for all concentrations as follows:

\[
\frac{dC}{dt} = D(C) \nabla^2 C
\]

where, as mentioned before, \( \alpha \) is a constant with concentration units. Adding \( \alpha \) to the denominator cancels the singularity at \( C = 0 \) and expresses the fact that at high dilution (\( C \ll \alpha \)) the diffusion coefficient is a constant. \( \alpha \), therefore, defines the range of solute concentration at which the solute interactions are still negligible and is a characteristic parameter of the solute-solvent system. Our concentration-dependent diffusion coefficient is therefore defined as

\[
D(C) = LRT(C + \alpha)^{-1}
\]

and for \( C \to 0 \):

\[
D_0 = LRT/\alpha
\]

We rewrite \( LRT \) as \( aD_0 \) and reach the final form of our model:

\[
D(C) = aD_0 \frac{C + \alpha}{C + \alpha}
\]

Its properties are demonstrated in Figure 1, where \( D \) is shown as function of \( C \) for \( \alpha = 10^{-4} \, \text{M} \). It is seen that for \( C \ll \alpha \), \( D \) is quite constant, and that beyond the "critical" value of \( C = \alpha \) it becomes reciprocally dependent on \( C \). This latter behavior reflects the physically feasible picture of solute interactions decrease the rate of diffusion as concentration increases.

For cases where a reaction produces \( C \), this model introduces a feedback loop: As more of a product is formed in the course of the reaction, its diffusion becomes slower. Feedback loops have been the source for nonlinearity leading to spatial and temporal patterning in many experimental and model reaction schemes; here we report that our model feedback loop induces patterning in simple reactions.

The nonlinear transport mode was coupled to the following \( C \)-producing reactions:

\[
2A \leftrightarrow C \quad (13)
\]

\[
A + B \leftrightarrow C \quad (14)
\]

\[
6A \leftrightarrow C \quad (15)
\]

\[
A \leftrightarrow C \quad (16)
\]

\[
A \leftrightarrow 6C \quad (17)
\]

In all cases only the diffusion of \( C \) was taken as concentration dependent, whereas \( A \) and \( B \) diffuse "normally".

The corresponding kinetic equations are demonstrated for reaction 13:

\[
\frac{dA}{dt} = -kA^2 + D_0 \nabla^2 A
\]

\[
\frac{dC}{dt} = kA^2 + \nabla \left( \frac{aD_0}{\alpha + C} \right) \nabla C
\]

3. The Computational Algorithm

3.1. The Derivative Operators. The algorithm used to solve (18) and (19) can be divided into two parts: (a) calculating the derivative operators in the right-hand side of (18) and (19); (b) propagating the concentrations in time starting from an initial concentration pattern.

The derivative operators are approximated by using the following considerations:

\[
\mathcal{F}(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ikx} \hat{f}(k) \, dk
\]

and its inverse

\[
\hat{f}(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx} f(x) \, dx
\]

A formal definition of the derivative operator becomes

\[
\frac{\partial f(x)}{\partial x} = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ikx} \hat{f}(k) \, dk
\]

and

\[
\frac{\partial^2 f(x)}{\partial x^2} = \frac{1}{2\pi} \int_{-\infty}^{\infty} -k^2 e^{-ikx} \hat{f}(k) \, dk
\]

A numerical implementation of this formula replaces the Fourier integral by a Fourier sum leading to the following approximations:

\[
\hat{f}(k) = \text{FFT}(f(x)) \quad i = 1, \ldots, N_x
\]

where the FFT stands for the fast Fourier transform algorithm of length \( N_x \). The derivative is approximated as

\[
\frac{\partial f(x)}{\partial x} = \text{FFT}(-ikFFT^{-1}[f(x)])
\]

and the second derivative becomes

\[
\frac{\partial^2 f(x)}{\partial x^2} \approx \text{FFT}(-k^2\text{FFT}^{-1}[f(x)])
\]

The extension to more than one dimension is straightforward. This

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method of calculation has exponential convergence characteristics with respect to the grid size. The high efficiency is the result of the FFT algorithm. The use of the FFT algorithm imposes the use of an evenly sampled grid on which the spatial dependence of the concentration was represented. In the examples presented below the one-dimensional examples used grids of 256 points and the two-dimensional examples were on grids of 64 × 64 or 128 × 128.

3.2. Time Propagation by the Explicit Euler Method. The time propagation of the spatial functions was by a linear, small time-step function since more accurate, higher orders are unstable. The time step is expressed as

$$\frac{\partial A(x,t)}{\partial t} = \frac{A(x,t+\Delta t) - A(x,t)}{\Delta t}$$

(27)

Solutions were always tested for numerical stability by reducing the size of the time step since if \( \Delta t \) were too large artifacts could result due to a breakdown of the discrete mapping of the differential function.

The algorithm is extremely flexible, allowing a wide range of diffusion-related "experiments" to be performed. The details of the simulation conditions (the fluctuation size, the \( k_a \) and \( D_0 \) values) are given in the captions of simulation figures.

4. Results

Pattern growth of initial fluctuations was observed for reactions 13–15. For reactions 16 and 17, which contain first-order reactions (\( k_A \) in (18) and (19)), no patterns evolved. However, it is not the nonlinearity in the reaction term (weak for (13) and (14); strong for (15)) which solely induces the pattern growth: under controlled conditions in which \( C \) diffuses "normally" (as in (18)) no patterns evolved.

In detail: Figure 2 shows a time sequence of a two-dimensional structure formation on a 64 × 64 grid from an initial double-line perturbation for reaction 13 (\( 2A \rightarrow C \)). Homogeneity of the product layer can be seen to break as the instability exhibits long-range effects reminiscent of the experimental observations.11,12 As in fracturing, growth occurred preferentially from the ends of the lines spreading outward. Without any clear boundary conditions it is not clear whether there is a predominant wavelength and what the influence of the distance between the initial lines has on the emerging pattern. The solution was checked for possible numerical artifacts. The time step was reduced by an order of magnitude with no apparent influence on the patterns. The grid was quadrupled to 128 × 128 units square; this too had no influence on the outcome. When the program was rerun with \( \alpha \) = 1.2–5.0 s. Below: time steps 20–200 s.

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Figure 2. Two-dimensional simulation of pattern growth in the concentration yield of \( C \) for the reaction \( 2A \rightarrow C \) with \( D_A = 0.2 \text{ cm}^2/\text{s}, \alpha = 10^{-4} \text{ M}, \) \( D_0 = 0.1 \text{ cm}^2/\text{s}, A_0 = 0.01 \text{ M}, \) and \( k = 10^3 \text{s}^{-1}. \) The initial fluctuation was a 5% increase in the concentration of \( A. \) Time frames are (a) \( t = 0, \) (b) \( t = 5000, \) (c) \( t = 18000. \)

Figure 3. Growth of \( C \) superimposed on \( A \) for \( 2A \rightarrow C \) in one dimension. Conditions: \( A_0 = 1 \text{ M}, k = 10^4 \text{s}^{-1}, D_A = 10^{-3} \text{ cm}^2/\text{s}, D_0 = 1 \text{ cm}^2/\text{s}, \) and \( \alpha = 10^{-3} \text{ M}. \) Fluctuations were generated with a random Poisson distribution ±2% of the critical concentration of \( A. \) Above: time steps 0.2–5.0 s. Below: time steps 20–200 s.

Figure 4. As in Figure 3, in two dimensions on a 64 × 64 grid.
Figure 5. Concentration of C with a center-perturbation of 1% in A for the oligomerization reaction 6A → C with α = 10^(-3) M, D₀ = 200 cm^2/s, D_A = 10 cm^2/s, k = 10^3 s^(-1), C₀ = 10^(-2) M.

The product, relatively high rate of diffusion can be seen to dampen out smaller fluctuations while allowing the more prominent to grow. This is shown explicitly by comparing the curve of the product to that of the overlaid starting material. Figure 4 shows a sequence in two-dimensional space for the reaction 2A → C that also started from random seeding. Reaction 14 (A + B → C) showed behavior similar to that seen in Figures 2–4 for 2A → C and is not shown here.

Figure 5 shows the result of an oligomerization reaction (6A → C) with a seeding perturbation at the center of the grid. This is an aggregation-type behavior.

5. Conclusion

We have demonstrated the concept that nonlinearities in the diffusion term can lead, when coupled to simple, weakly nonlinear reactions, to the evolution of patterns from initial fluctuations. The diffusion concentration dependency provides the necessary growth feedback loop through the assumption that the accumulation of product renders slower diffusion rates and provides a smooth transition to the low-concentration, constant D range. As in the well-studied case of spatial and temporal pattern formation through coupling of highly nonlinear reaction schemes with diffusion, the case we study emphasizes again the apparently paradoxical role that diffusion can play in nonequilibrium situations: Instead of being a mechanism for dissipation of concentration fluctuations, it becomes a source of pattern growth. The consequences of this report to the related areas of polymerization—aggregation and island formation phenomena are obvious and will be treated in future reports.

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Quasi-Periodicity and Chaos during an Electrochemical Reaction

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The dynamic behavior of the electrodissolution of copper in acidic chloride solution is studied. We show transitions from two- to one-band chaos and from a chaotic attractor to a torus. All the examples were observed during the course of a single experiment, and the transitions take place as the nature of the electrode surface changed slowly relative to the characteristic time of the dynamic behavior.

Introduction

Richard M. Noyes, with his co-workers Field and Körös, published in 1972 an analysis of the oscillatory behavior of the Belousov–Zhabotinski reaction. This seminal paper, along with the numerous other contributions of Professor Noyes, his students, and his colleagues, has led to an explosion in information on oscillating chemical reactions. His work has also led to a greatly improved understanding of the origin of oscillations in chemical reactions and to numerous examples of oscillatory behavior in homogeneous and heterogeneous chemical systems.

Oscillations can also occur during electrochemical reactions. Examples include both anodic and cathodic reactions which can be found in such diverse areas as electrocatalysis, electroplating, electropolishing, electromachining, and in the active-passive transitions of many metals.1–10


There have been several recent studies of the dynamics of oscillatory electrochemical reactions; these studies have produced numerous experimental examples of different types of dynamic behavior. Electrochemical reactions have several features, in addition to their interesting behavior, which facilitate such studies. First, the measurement of current or voltage is relatively straightforward. Second, the time scale of the oscillations under some conditions is short, both relative to the time scale of changes in the surface conditions so that data are taken under stationary conditions and absolutely so that large amounts of data can be obtained to use in data analysis.

Diem and Hudson11 have used methods such as the calculation of a correlation dimension12 to show the existence of simple and higher order chaotic structures during the electrodissolution of iron in H₂SO₄ at the limiting-current plateau. Copper electrodissolution in H₂PO₄ has been studied by Albahadily and Schell13

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