Compartmentalized reaction-diffusion systems

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Reaction-diffusion systems consisting of a collection of reactive domains separated by chemically inactive regions are considered. The reactive dynamics is governed by a multistep reaction mechanism and each reactive domain is specific to a particular elementary step or collection of elementary steps of the global reaction mechanism. Far-from-equilibrium situations where the global kinetics can give rise to complex states such as bistability or oscillations are studied. A general method for the calculation of the average concentration on each reactive domain is presented. The effects of compartmentalization are illustrated by a study of the influence of diffusion, reactive domain size, and domain distribution on the nature of the stationary states of the Schlögl model. Compartmentalization can drive the system into and out of the bistable regime of this reactive system.

I. INTRODUCTION

If a chemical reaction comprising several elementary steps takes place in a medium where the reacting species are uniformly dispersed on scales which are small compared to the diffusion length, one expects the mass action rate laws to describe the dynamics of the chemical concentrations. If instead the system is inhomogeneous and each elementary reaction step, or subset of elementary steps, takes place in a specific spatial region of the medium, modifications of the reaction dynamics may appear. Such compartmentalized reaction kinetics can arise from an inhomogeneous distribution of specific catalytic domains [1]; in biological contexts it might occur when reactions take place only in specialized organelles in the cell [2].

Some limiting cases will serve to illustrate the effects of compartmentalization. Suppose the domains that catalyze specific reaction steps are finely dispersed. In this circumstance the reactive domains in small coarse grained regions of the system will be coupled strongly by diffusion. All steps of the reaction mechanism will contribute and the dynamics will be described by the global reaction mechanism. Next, consider the case where the domains are large compared to the diffusion length in the system. In the interior of each catalytic domain one will observe behavior corresponding to the particular step of the reaction mechanism that takes place on the domain but the domains themselves will be coupled by diffusion. We investigate how reactive dynamics changes from that described locally by specific reaction steps to global behavior involving the full reaction mechanism.

Interesting situations may arise in autocatalytic reactions carried out under far from equilibrium conditions which have been studied extensively [3]. The effects of inhomogeneities have been the topics of recent investigations. For example, inhomogeneous illumination of the light-sensitive Belousov-Zhabotinsky reaction can cause certain steps of the reaction mechanism to occur at different rates inducing variable excitability in the medium [4,5]. Complexation reactions of starch are believed to play a role in Turing pattern formation in the chlorite-iodide-malonic acid reaction [6] and the effects of inhomogeneous distributions of complexing agents on Turing pattern formation have been investigated [7].

Effects of compartmentalization of the reaction mechanism on the qualitative dynamics of a system composed of reactive domains have been studied in the earlier [8]. For instance, it has been shown that changes in reactive domain separation can alter the stability of the steady state [9] and can influence the oscillatory dynamics of the system [10,11].

We consider how compartmentalized reaction kinetics can influence the behavior of reactions occurring under far from equilibrium conditions where complex kinetics may give rise to multiple steady states, oscillations and chaos. In Sec. II we present a general formulation of this problem and show how one may obtain a set of coupled equations for the mean concentrations on each domain. We examine regular and disordered distributions of domains. A specific model reaction mechanism, the Schlögl model [12], is considered in Sec. III. The reaction mechanism for this model consists of two steps and we suppose that the reactions corresponding to these steps occur in distinct spatial domains. Under far-from-equilibrium conditions the system may exhibit bistability in appropriate parameter ranges. We show how the steady state bifurcation structure is modified as a result of compartmentalized reaction kinetics. The calculations are carried out for various distributions of catalytic sites and for various boundary conditions. The conclusions of the study along with comments on other types of compartmentalized reaction dynamics are presented in Sec. V.

II. COMPARTMENTALIZED CHEMICAL REACTIONS

We consider a system with m chemically reactive species where the overall reaction mechanism consists of n elementary steps

$$\sum_{k=1}^{m} \nu_k^\alpha X_k \underset{k_{-\alpha}}{\overset{k_\alpha}{\rightleftharpoons}} \sum_{k=1}^{m} \bar{\nu}_k^\alpha X_k \quad (\alpha = 1, \ldots, n). \tag{1}$$

Here X_k ($k=1, \ldots, m$) are the m chemical species, ν_k^α and $\bar{\nu}_k^\alpha$ are the stoichiometric coefficients for reaction step α, and the forward and reverse rate constants for this step are k_α and $k_{-\alpha}$, respectively.
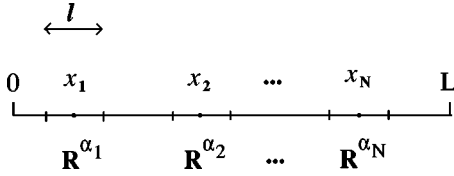
FIG. 1. A schematic illustration of a one-dimensional medium showing reactive domains centered at x_j where reactions R^{α_j} take place. The system length is L while the reactive domains have length l.

The reaction is assumed to take place in an s-dimensional medium consisting of N reactive domains centered at $\mathbf{r}_i$ ($i = 1, \ldots, N$), on which reactions corresponding to one or some subset of the elementary steps of the mechanism take place. We denote by Ω_i the region of space occupied by the reactive domain i. We suppose that reactions occur only within these domains and that chemical species freely diffuse throughout the medium. One may consider other situations where reactions also occur outside specific catalytic states [13]. A schematic illustration of such medium for one space dimension is shown in Fig. 1.

Such a system is described by a reaction-diffusion equation

$$\frac{\partial \mathbf{c}(\mathbf{r},t)}{\partial t} = \mathbf{D}\nabla^2 \mathbf{c}(\mathbf{r},t) + \mathbf{R}[\mathbf{c}(\mathbf{r},t)], \qquad (2)$$

subject to appropriate boundary and initial conditions. Here $\mathbf{c}(\mathbf{r},t) = \{c_k(\mathbf{r},t)\}$ is the vector of local concentrations for species $\mathbf{X} = \{X_k\}$ at time t, $\mathbf{D}$ is the diffusion coefficient matrix assumed to be constant and diagonal and $\mathbf{R}[\mathbf{c}(\mathbf{r},t)] = \{\mathcal{R}_k[\mathbf{c}(\mathbf{r},t)]\}$ is the vector of reaction rates whose elements can be written as

$$\mathcal{R}_k[\mathbf{c}(\mathbf{r},t)] = \sum_{i=1}^{N} R_k^{\{\alpha_i\}}[\mathbf{c}(\mathbf{r},t)]\Theta_i(\mathbf{r}). \qquad (3)$$

In this equation $R_k^{\{\alpha_i\}}$ is the reaction rate for species k corresponding to the elementary steps $\{\alpha_i\}$ that occur in domain i and $\Theta_i(\mathbf{r})$ is a characteristic function which is unity within domain i and zero otherwise,

$$\Theta_i(\mathbf{r}) = \begin{cases} 1 & \text{if } \mathbf{r} \in \Omega_i, \\ 0 & \text{otherwise.} \end{cases}$$

The formal solution of Eq. (2) is [14]

$$c_k(\mathbf{r},t) = \int G(\mathbf{r},t;\mathbf{r}_0,0)\phi_k(\mathbf{r}_0)d^s\mathbf{r}_0$$

$$+ \int_0^t \int G(\mathbf{r},t;\mathbf{r}_0,t_0)\mathcal{R}_k[c(\mathbf{r}_0,t_0)]d^s\mathbf{r}_0 dt_0$$

$$+ D_k \int_0^t \oint [G(\mathbf{r},t;\mathbf{r}_0,t_0)\nabla_{\mathbf{r}_0}c_k(\mathbf{r}_0,t_0)$$

$$- c_k(\mathbf{r}_0,t_0)\nabla_{\mathbf{r}_0}G(\mathbf{r},t;\mathbf{r}_0,t_0)]\cdot\hat{\mathbf{n}}dS_0 dt_0, \qquad (4)$$

where $G(\mathbf{r},t;\mathbf{r}_0,t_0)$ is the time-dependent Green function, $\phi_k(\mathbf{r})$ is the initial condition, $\hat{\mathbf{n}}$ is the unit vector normal to the boundary surface of the system, and dS_0 is a differential element of the surface area of the system. The first term in this equation represents the effect of the initial condition on the solution and the second term contains the reaction rates. The third term accounts for the effect of the boundary conditions on the solution. The third term vanishes if the concentrations or their gradients at the boundary are prescribed to be zero.

The solution of Eq. (4) is difficult to obtain in the general case. To study the bifurcation structure and to simplify the analysis, instead of computing the concentration fields at arbitrary space points, we focus on the reactive domains and construct a set of equations that show how the dynamics on the various domains is coupled through diffusion. For each reactive domain j, we consider the concentration field averaged over the domain,

$$c_{k,j}(t) = \frac{1}{V_j}\int c_k(\mathbf{r},t)\Theta_j(\mathbf{r})d^s\mathbf{r}, \qquad (5)$$

where V_j is the volume of domain j. The volume average of Eq. (4) leads to

$$c_{k,j}(t) = I_{k,j}^\phi + \sum_i^N I_{k,ji}^R + D_k I_{k,j}^B, \qquad (6)$$

where

$$I_{k,j}^\phi = \frac{1}{V_j}\int\int G(\mathbf{r},t;\mathbf{r}_0,0)\phi_k(\mathbf{r}_0)\Theta_j(\mathbf{r})d^s\mathbf{r}_0 d^s\mathbf{r}, \qquad (7)$$

$$I_{k,j}^B = \frac{1}{V_j}\int_0^t\int \oint [G(\mathbf{r},t;\mathbf{r}_0,t_0)\nabla_{\mathbf{r}_0}c_k(\mathbf{r}_0,t_0)$$

$$- c_k(\mathbf{r}_0,t_0)\nabla_{\mathbf{r}_0}G(\mathbf{r},t;\mathbf{r}_0,t_0)]\cdot\hat{\mathbf{n}}\Theta_j(\mathbf{r})dS_0 d^s\mathbf{r}dt_0, \qquad (8)$$

$$I_{k,ji}^R = \sum_i^N \frac{1}{V_j}\int_0^t\int\int G(\mathbf{r},t;\mathbf{r}_0,t_0)R_k^{\{\alpha_i\}}$$

$$\times[\mathbf{c}(\mathbf{r}_0,t_0)]\Theta_i(\mathbf{r}_0)\Theta_j(\mathbf{r})d^s\mathbf{r}_0 d^s\mathbf{r}dt_0. \qquad (9)$$

We have used Eq. (3) in order the obtain the form of the reaction contribution in Eq. (9). If the Green function is known, integrals (7) and (8) involve only known quantities and can be calculated. We concentrate on the reactive term (9). The integrals in this term can be interpreted as the effect of the reactions within domain i on the mean concentration in domain j. Exact calculation of these terms is in general not possible. However, if domain i is distant from domain j, we may compute $I_{k,ji}^R$ for $j \neq i$ by expanding the reaction rate in domain i in a multipole expansion

$$R_k^{\{\alpha_i\}}[c(\mathbf{r},t)]\Theta_i(\mathbf{r}) = \sum_{l=0}^{\infty} \frac{1}{l!}\left[\int d^s\mathbf{r}\, r^l\right.$$

$$\left.\times R_k^{\{\alpha_i\}}[\mathbf{c}(\mathbf{r},t)]\Theta_i(\mathbf{r})\right]\odot^l\boldsymbol{\nabla}^l\delta(\mathbf{r}-\mathbf{r}_i),$$

where $\odot^l$ signifies l tensor contractions. For widely separated domains we may retain only the monopole term $l=0$ in the above sum to obtain

$$R_k^{\{\alpha_i\}}[c(\mathbf{r},t)]\Theta_i(\mathbf{r}) \approx \left[\int d^s\mathbf{r}R_k^{\{\alpha_i\}}[\mathbf{c}(\mathbf{r},t)]\Theta_i(\mathbf{r})\right]$$

$$\times \delta(\mathbf{r}-\mathbf{r}_i) \quad (\mathbf{r}\in\Omega_j).$$

In general the reaction rates will be nonlinear functions of the concentration fields so the volume average will be difficult to compute exactly. If we neglect the spatial structure of the concentration field over a domain we may write

$$R_k^{\{\alpha_i\}}[\mathbf{c}(\mathbf{r},t)]\Theta_i(\mathbf{r}) = V_i R_k^{\{\alpha_i\}}[\mathbf{c}_i(t)]\delta(\mathbf{r}-\mathbf{r}_i). \quad (10)$$

In this approximation the terms for $j\neq i$ simply involve the computation of the volume average of the Green function over domain j evaluated at the location of the center of domain i, a quantity which is easily computed once the Green function is known.

The diagonal terms $i=j$ in Eq. (9) involve diffusive coupling of spatial points within a single domain and the multipole expansion cannot be used. However, as in the case of the off-diagonal terms, we may still approximate the reaction rate within a domain by its value at the mean concentration within the domain so that

$$R_k^{\{\alpha_j\}}[\mathbf{c}(\mathbf{r},t)] \approx R_k^{\{\alpha_j\}}[\mathbf{c}_j(t)], \quad (11)$$

which neglects reactive correlations within a domain. The diagonal terms then involve the double integral of the Green function over domain j, a quantity which is again easily computed if the Green function is known.

Using these approximations, Eq. (6) becomes

$$c_{k,j}(t) = I_{j,k}^\phi + D_k I_{k,j}^B + \sum_i^N \int_0^t \omega_{k,ji}(t,t_0) R_k^{\{\alpha_i\}}[\mathbf{c}_i(t_0)]dt_0. \quad (12)$$

The prefactors $\omega_{k,ji}$ are given by

$$\omega_{k,ji}(t,t_0) = \frac{1}{V_j}\int\int_{\Omega_j}G(\mathbf{r},t;\mathbf{r}_0,t_0)d^s\mathbf{r}_0 d^s\mathbf{r}\delta_{ji}$$

$$+\int_{\Omega_j}G(\mathbf{r},t;\mathbf{r}_i,t_0)d^s\mathbf{r}(1-\delta_{ji}). \quad (13)$$

Equation (12), together with Eqs. (7), (8), and (13), have recast the original reaction-diffusion problem into the form of a system of $N\times m$ integral equations. The complexity of this set of equations will depend on the number of domains and their spatial configurations. We shall explore the validity of this reduction in the sequel; however, before doing this we

may construct a further approximate solution which will allow one to consider complicated configurations of reactive domains.

Mean-field approximation. As a further simplification, particularly useful when the number of domains is large and randomly distributed, one can sum over all like domains to obtain their mean concentrations, i.e., $c_{k,j}=c_{k,\{\alpha_p\}}$ for all domains in which the set of $\{\alpha_p\}$ elementary steps take place. We obtain a system of $n\times m$ equations

$$c_{k,\{\alpha_p\}} = W_t + \sum_{s=1}^n \int_0^t W_{\{\alpha_p\},\{\alpha_s\}}(t,t_0)R^{\{\alpha_s\}}[c_{k,s}(t_0)]dt_0, \quad (14)$$

with

$$W_t = \frac{n}{N}\left[\sum_i^N I_{k,i}^\phi \delta_{\{\alpha_i\},\{\alpha_p\}} + D_k\sum_i^N I_{k,i}^B \delta_{\{\alpha_i\},\{\alpha_p\}}\right], \quad (15)$$

$$W_{\{\alpha_p\},\{\alpha_s\}} = \frac{n}{N}\sum_{i,j}^N \omega_{k,ji}(t,t_0)\delta_{\{\alpha_j\},\{\alpha_p\}}\delta_{\{\alpha_i\},\{\alpha_s\}}. \quad (16)$$

Such a description will be useful if we are not concerned with the details of the concentration fields for any specific configuration of reactive domains but only the behavior of like domains when averaged over realizations of the random distribution. The description will also be useful if there are symmetries that fix the concentrations of like domains to be identical. Equations (12) and (14) will form the basis for the analysis presented in the following sections.

III. AN EXAMPLE: SCHLÖGL MODEL

As an illustration of the above formalism we consider the Schlögl model [12]

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X,$$

$$B+2X \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 3X \quad (17)$$

in a one-dimensional medium consisting of N reactive domains of length l centered at positions x_i.

In this case $n=2$, $\alpha_i=1,2$, for $i=1,\ldots,N$. Furthermore, if A and B are pool species whose concentrations are constant, there is only one reactive species and we can drop the index k. Depending on the choice of kinetic parameters, the Schlögl model possesses either a single stable steady state or bistable steady states. To investigate such stable states we consider the time-independent form of Eq. (2) in one dimension

$$D \frac{\partial^2 c(x)}{\partial x^2} = -\mathcal{R}[c(x)], \qquad (18)$$

which supports kinklike solutions separating the two stable homogeneous states if $\mathcal{R}$ represents the reaction rate for the full mechanism (17). Instead, if we consider the compartmentalized inhomogeneous form of the Schlögl reaction-diffusion system, different types of behavior are possible. If D is small or the reactive domains are large, each domain will tend to reach the equilibrium concentration corresponding to the particular step of the reaction mechanism taking place in it. For example, type-1 domains, corresponding to the first step of mechanism (17), will tend to $c_j = k_1 a/k_{-1}$ while the type-2 domains will have $c_2 = k_2 b/k_{-2}$. As D increases or the domain size becomes small the system will tend to the bistable values of the homogeneous system. We now study this situation in detail.

For zero-flux boundary conditions or for $c(0) = c(L) = 0$, the third term of Eq. (4) vanishes and $I_j^B = 0$. If $c(0) = c(L) \neq 0$ this term reduces to a constant which we call c^0. Also, for one spatial dimension the characteristic function $\Theta_i(\mathbf{r})$ is the Heaviside function $\mathcal{H}(l/2 - |x_0 - x_i|)$. Thus, the formal solution, Eq. (4) reduces to

$$c(x) = \int G(x,x_0) \sum_i R^{\alpha_i} c(x_0) \mathcal{H}\left(\frac{l}{2} - |x_0 - x_i|\right) dx_0 + c^0. \qquad (19)$$

The reaction rates corresponding to the mechanism (17) are

$$R^1[c(x)] = k_1 a - k_{-1} c(x),$$

$$R^2[c(x)] = k_2 b c(x)^2 - k_{-2} c(x)^3, \qquad (20)$$

where a and b are the constant concentrations of species A and B, respectively.

Integration over any particular domain j yields

$$c_j = \frac{1}{l} \sum_i \int \int G(x,x_0) R^{\alpha_i}[c(x_0)] \mathcal{H}\left(\frac{l}{2} - |x_0 - x_i|\right)$$
$$\times \mathcal{H}\left(\frac{l}{2} - |x_0 - x_j|\right) dx_0 dx + c^0, \qquad (21)$$

which we rewrite in the form

$$c_j = I_{jj} + \sum_{i \neq j} I_{ji} + c^0. \qquad (22)$$

Since the first step of the Schlögl model is linear in the concentration of species X, the volume average of this reaction rate involves no approximation. Equations (10) and (11) take the form

$$R^{\alpha_i}[c(x)] \mathcal{H}\left(\frac{l}{2} - |x_0 - x_i|\right) = l R^{\alpha_i}(c_i) \delta(x - x_j) \qquad (23)$$

and

$$R^{\alpha_j}[c(x)] = R^{\alpha_j}(c_j). \qquad (24)$$

Using these approximations we arrive at the solution

$$c_j = \sum_{i=1}^N \omega_{ji} R^{\alpha_i}(c_i) + c^0, \qquad (25)$$

where the prefactors are given by

$$\omega_{ji} = \frac{1}{l} \int \int_{\Omega_j} G(x,x_0) dx_0 dx \, \delta_{ji} + \int_{\Omega_j} G(x,x_i) dx (1 - \delta_{ji}), \qquad (26)$$

and the integrals are evaluated over the interval $\Omega_j = \{x : x_j - l/2 \leq x \leq x_j + l/2\}$.

Next, we apply the mean field approximation described in Sec. II A to this model. Let the average concentrations in all domains where the first and second elementary steps of the Schlögl mechanism are active be c_1 and c_2, respectively. We obtain the following system of two algebraic equations:

$$c_1 = W_{11} R^1(c_1) + W_{12} R^2(c_2) + c^0,$$

$$c_2 = W_{22} R^2(c_2) + W_{21} R^1(c_1) + c^0, \qquad (27)$$

where

$$W_{11} = \frac{2}{N} \sum_{ij} w_{ji} \delta_{\alpha_i,1} \delta_{\alpha_j,1},$$

$$W_{22} = \frac{2}{N} \sum_{i,j} w_{ji} \delta_{\alpha_i,2} \delta_{\alpha_j,2},$$

$$W_{12} = W_{21} = \frac{1}{N} \sum_{i,j} w_{ji} (1 - \delta_{\alpha_i,\alpha_j}). \qquad (28)$$

These equations are valid for any reaction scheme provided it can be decomposed into two elementary steps. The information pertaining any specific case is contained in the Green function and c^0. We now evaluate the prefactors w_{ji} for two particular cases in a finite domain: fixed concentrations at the boundaries and zero-flux boundaries.

A. Fixed concentrations at the boundaries

If $c(0) = c(L) = c_{BO}$, the Green function is [14]

$$D \, G(x,x_0) = \begin{cases} (1 - x_0/L)x & \text{if } x \leq x_0, \\ x_0(1 - x/L) & \text{if } x \geq x_0. \end{cases}$$

For this case, since $G(0,x_0) = 0$, we have $c^0 = c_{BO}$, the concentration at the boundaries. In general, c_{BO} is an externally fixed parameter; however, if we set

$$c_{BO} = c_1 \frac{L - x_N}{x_1 + L - x_N} + c_N \left(1 - \frac{L - x_N}{x_1 + L - x_N}\right),$$

the system has periodic boundary conditions. In this case c_{BO} takes the form of a weighted average of the concentrations of the last and the first domains, depending on their distances to the boundaries, and is a consequence of the linearity of the interdomain concentration profile.

The prefactors can be readily evaluated:

$$D\,w_{ji} = \begin{cases} \left(1-\dfrac{x_j}{L}\right)x_j l - \dfrac{l^2}{6} & \text{if } x_i = x_j, \\[2mm] \left(1-\dfrac{x_i}{L}\right)x_j l & \text{if } x_j < x_i. \end{cases}$$

It can also be shown that $w_{ji} = w_{ij}$. This expression, along with the equation for the concentrations at the boundaries and the positions of the N domains, (the set of values of the $N\ x_i$) allows the calculation of all c_j from a set of N simultaneous equations.

B. Zero-flux boundary conditions

Physically, zero-flux boundary conditions correspond to an isolated system, thus, for a stationary state solution to exist the net production of material in the system must be zero. Mathematically this is represented by the so-called Fredholm alternative. In order for a solution to exist it is necessary that

$$\int \mathcal{R}[c(x)] = 0,$$

where the integral is taken over the entire medium. We can follow the procedure of the previous section if we use a modified Green function [14] which, apart from an additive constant, has the form

$$D\,G_m(x,x_0) = \begin{cases} \dfrac{x^2+x_0^2}{2L} - x_0 & \text{if } x \leq x_0, \\[2mm] \dfrac{x^2+x_0^2}{2L} - x & \text{if } x \geq x_0. \end{cases}$$

This form satisfies the boundary conditions

$$\frac{dc}{dx}(0) = \frac{dc}{dx}(L) = 0.$$

After performing the required integrations and subject to the same approximations we arrive at

$$D\,w_{ji} = \begin{cases} \dfrac{l^3}{12L} - \dfrac{l^2}{6} - \left(1-\dfrac{x_j}{L}\right)x_j l & \text{if } x_i = x_j, \\[2mm] \dfrac{l}{L}\left(\dfrac{l^2}{24} + \dfrac{x_j^2}{2}\right) - \left(1-\dfrac{x_i}{2L}\right) & \text{if } x_j < x_i, \end{cases}$$

with $w_{ji} = w_{ij}$. If we substitute these results into Eq. (25), the resulting equation may not naturally satisfy the Fredholm condition, unless c^0, which arises from the additive constant in the Green function, is suitably chosen.

To determine the appropriate value of c^0 we sum Eqs. (25) to obtain

$$\sum_j c_j = \sum_{i,j} w_{ji} R^{\alpha_i}(c_i) + Nc^0.$$

If in this equation we set

$$c^0 = \frac{1}{N}\sum_j c_j + \sum_i R^{\alpha_i}(c_i)\left(\sum_j w_{jk} - \sum_j w_{ji}\right), \quad (29)$$

we arrive at the desired condition

$$\sum_i R^{\alpha_i}(c_i) = 0.$$

As an example, if we apply Eq. (29) to calculate the value of c^0 in Eq. (27) we obtain

$$c^0 = \frac{1}{2}(c_1 + c_2) + R^2(c_2)(W_{11} - W_{22}).$$

In the above expressions for both boundary conditions the ω_{ji} factors embody all geometrical information about the distribution and sizes of the reactive domains. The parameters characterizing the intrinsic reaction kinetics reside in the $R^{\alpha_i}(c_i)$.

IV. RESULTS FOR SCHLÖGL MODEL

The behavior of this model in a homogeneous medium is well known. The stationary states can be found from the equation

$$k_{-2}c^3 - k_2 bc^2 + k_{-1}c - k_1 a = 0, \quad (30)$$

or using scaled concentration variables $c = x\sqrt{k_1 a/k_2 b}$, from $\alpha x^3 - x^2 + \beta x - 1 = 0$, where

$$\alpha = \frac{k_{-2}}{k_1 a}\left(\frac{k_1 a}{k_2 b}\right)^{3/2}, \qquad \beta = \frac{k_{-1}}{k_1 a}\left(\frac{k_1 a}{k_2 b}\right)^{1/2}.$$

The cusp-shaped bistability region in the α-β parameter plane is shown in Fig. 2.

We investigate the effect of the sizes and distribution of the reactive domains on the nature of the stationary states. We assume that the Schlögl reaction occurs on a substrate consisting of a collection of domains of types 1 and 2 of length l: only the first reaction step can occur on type-1 domains while type-2 domains support the second reaction step.

A. Two-domain case

Simple analytical results can be obtained for a medium of size L with one type-1 domain centered at $x_1 = L/4$ and one type-2 domain centered at $x_2 = 3L/4$. Thus, the distribution is completely defined by the values of l and L or, alternatively, by l and $d = x_2 - x_1$.

Setting $c^0 = (c_1 + c_2)/2$, from Eq. (25) we arrive at
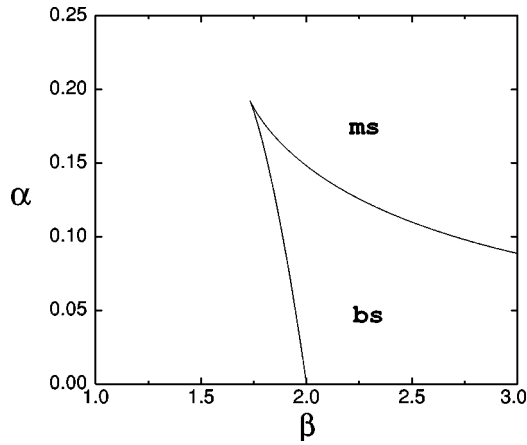
$$R^1(c_1) + R^2(c_2) = 0, \quad (31)$$

FIG. 2. Phase diagram for the homogeneous Schlögl model in the space of reduced parameters α and β, showing the regions of bistability (bs) and monostable states (ms). The cusp point is located at $\alpha_c = 3^{1/2}/9$ and $\beta_c = 3^{1/2}$.

$$\frac{1}{2\gamma}[R^1(c_1) - R^2(c_2)] = c_1 - c_2,$$

where R^1 and R^2 are given by Eq. (20). This set of equations is valid for both fixed-concentration and zero-flux boundary conditions (BC) with

$$\gamma = \begin{cases} \dfrac{6D}{3dl - 2l^2}, & \text{fixed-concentration BC,} \\[3mm] \dfrac{24dD}{l(24d^2 + l^2 - 8dl)}, & \text{zero-flux BC.} \end{cases}$$

Notice that γ, which is proportional to D, incorporates all of the nonkinetic parameters of the system, including all the parameters that describe the spatial characteristics of the medium. In these equations $l \leqslant d$, since we are only concerned with nonoverlapping domains.

The solution of these equations for the Schlögl model can be found easily. We obtain

$$c_1 = \frac{\gamma c_2 + k_1 a}{\gamma + k_{-1}},$$

and c_2 is the root of

$$k_{-2}c_2^3 - k_2 b c_2^2 + \left(\frac{\gamma k_{-1}}{\gamma + k_{-1}}\right)c_2 - \frac{\gamma k_1 a}{\gamma + k_{-1}} = 0. \quad (32)$$

This equation has exactly the same form as Eq. (30) for a simple homogeneous substrate, except for the factor $\gamma k_{-1}/(\gamma + k_{-1})$ in the terms linear and independent of c_2. If the polynomial for c_2 is cast in the form $\alpha_s x^3 - x^2 + \beta_s x - 1 = 0$, the coefficients are given by

$$\alpha_s = \alpha \sqrt{\frac{\gamma}{\gamma + k_{-1}}}, \quad \beta_s = \beta \sqrt{\frac{\gamma}{\gamma + k_{-1}}}.$$

Thus, if the reaction occurs in compartmentalized domains the steady states can be related to those for a homogeneous
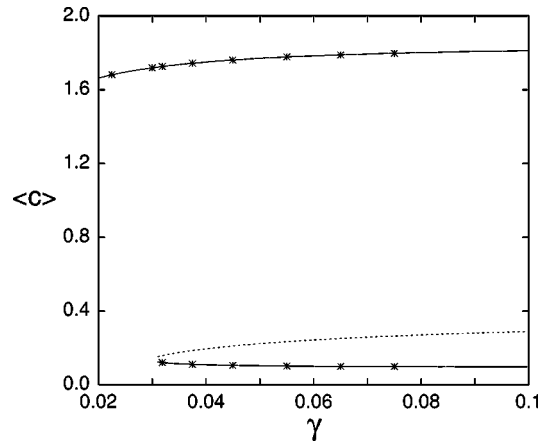

FIG. 3. Bifurcation diagram for the Schlögl model for a compartmentalized one-dimensional medium. Solid lines represent the solution from Eq. (31). Stars are numerical solutions of the reaction-diffusion equation. The ordinate is the concentration averaged over the entire medium. The kinetic parameters are $k_{-1} = 0.014$, $k_1 a = 0.001$, $8/3 k_2 b = 0.095$, $16 k_{-2} = 0.24$ and correspond to a point in the bistable region of the homogeneous system. The dotted line represents the unstable state.

medium through a rescaling of the kinetic parameters α and β by the factor $\sqrt{\gamma/(\gamma + k_{-1})} < 1$. This factor tends to 1 as $D \to \infty$.

We have compared these analytical results to results from numerical solutions of the reaction-diffusion equation for several cases and found excellent agreement. We have constructed bifurcation diagrams using the diffusion coefficient D as the control parameter (keeping the other parameters constant). If the kinetic parameters are chosen so that the system is bistable for a homogeneous medium, the following behavior is observed: for high values of the diffusion constant the system exhibits bistability; for low values there exists only one solution. The bifurcation occurs at some intermediate D^*, which can be predicted from Eq. (32). A comparison of the analytical and the numerical solutions is shown in Fig. 3.

B. Regular and random distributions of N domains

An interesting special case is a system with periodic boundary conditions where the N reactive domains are placed regularly such that the distance between any adjacent pair is the same throughout the medium. Physically this situation may be realized in a reactive medium in the form of a thin ring, large enough so curvature effects can be neglected. The behavior for this reactive domain distribution can be determined from that in a unit cell with two domains, similar to that described in the previous section for fixed concentration boundary conditions, by taking $c_{BO} = (c_1 + c_2)/2$.

For such a regular domain distribution the equations for the zero-flux case also take a simple form since in this circumstance Eq. (29) reduces to $c_0 = (c_1 + c_2)/2 = c_{BO}$ due to the symmetry of the distribution. For any particular distribution of reactive domains the average concentration in each domain can be obtained by solving the system of equations
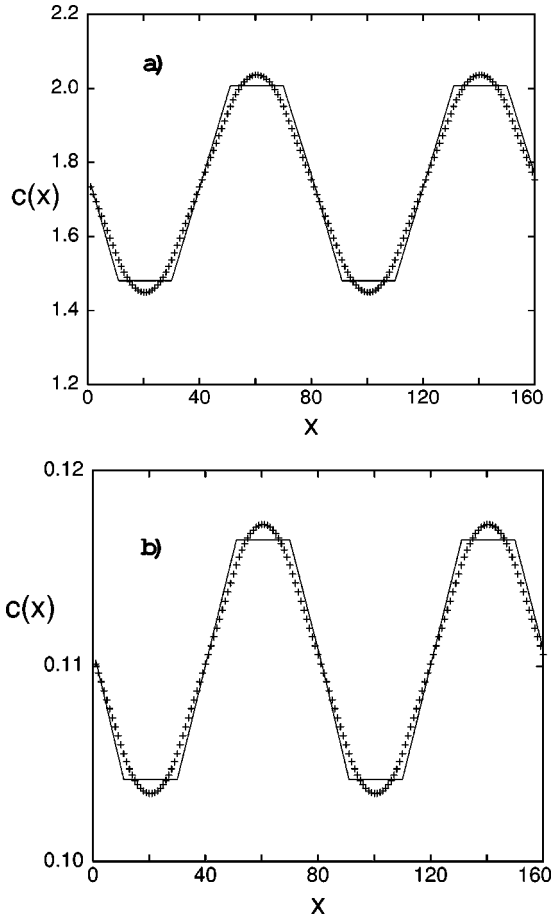
FIG. 4. Bistable regime. Solid line: reconstructed concentration profile calculated from Eqs. (25) with periodic boundary conditions. Crosses: numerical solution of the reaction-diffusion equation. (a) High concentration solution, (b) low concentration solution. The medium in this case has four reactive domains (two type-1 and two type-2) of length $l=20$ with centers at $x_i=20, 60, 100, 140$. All kinetic parameters are the same as in Fig. 3.
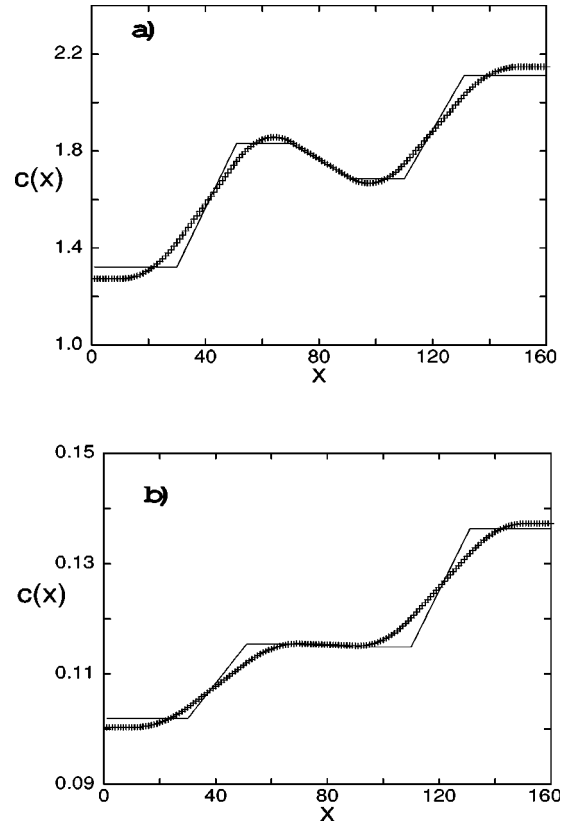

FIG. 5. Bistable regime. Solid line: reconstructed concentration profile calculated from Eqs. (25) with zero-flux boundary conditions. Crosses: numerical solution of the reaction-diffusion equation. (a) High concentration solution, (b) low concentration solution. The medium and kinetic parameters are the same as in Fig. 4.

(25). The geometric data defining the distribution is contained in the prefactors w_{ji}. Furthermore, since no chemical reaction occurs in the parts of the medium separating the reactive domains the interdomain concentration profile is linear to a good approximation. In this manner a concentration profile can be reconstructed for the spatially extended medium and compared to results from numerical solutions of the reaction-diffusion equation. Such a comparison is presented in Figs. 4 and 5 in the bistable regime for fixed concentration and zero-flux BC, respectively. The analytical solutions capture the gross features of both the monostable and bistable regimes but the concentration profiles differ in detail since the reactive domain size is not much greater than the diffusion length and the analytical solution contains information only about the average concentration within each of the domains.

If the number of reactive domains is large and the domains are randomly distributed one must solve a large set of coupled equations. In this circumstance the mean-field approximation, Eq. (14), provides a means to study the bifurcation structure. As an illustration we have considered a sys-

tem of size $L=1000$ with $N=50$ and $l=10$. Since the mean-field approximation is expected to be valid only in a statistical sense and not for any particular realization we have calculated the average concentrations over 10 realizations of the distribution of reactive domains. Figure 6 compares the mean field and simulation results for periodic boundary conditions. Similar results were obtained for zero-flux boundary conditions.

The results show that mean-field theory is able to accurately reproduce the bifurcation diagram obtained from simulations averaged over realizations of the distribution of reactive sites. The results also show that if the kinetic parameters are fixed so that the homogeneous system is bistable, then for any distribution of reactive domains there is a critical diffusion constant D^* above which bistability is observed. Below D^* only the high concentration solution exists.

The effect of the length of the domains l and of the interdomain distance d can be elucidated by examining Eq. (32) and the definition of γ; γ decreases monotonically with d and, thus, increasing d has an effect qualitatively similar to that of decreasing D. As a consequence, the system can undergo a bifurcation by changing the separation of the domains.

If the domain size is large compared to the diffusion length the interiors of the domains will be effectively decoupled from the rest of the system and higher values of D will
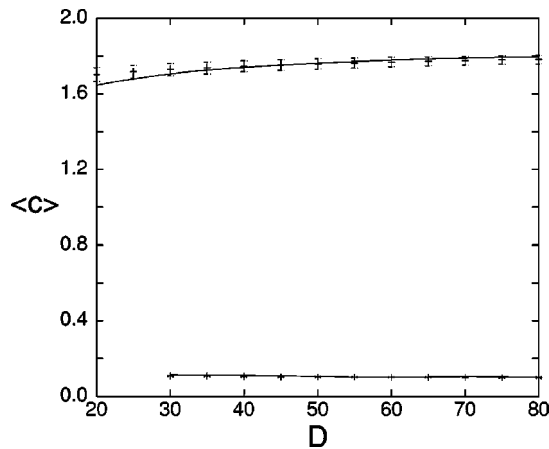
FIG. 6. Bifurcation diagram constructed from an average over ten realizations of the distribution of reactive domains with periodic boundary conditions. Solid lines: results from Eqs. (27). Crosses: numerical solution of the reaction-diffusion equation. The ordinate is the concentration averaged over the entire medium and realizations. All kinetic parameters are the same as in Fig. 3.

FIG. 8. Bifurcation diagram corresponding to a system which is at point A for the homogeneous medium. At high diffusion (high γ) it is monostable; at intermediate D it becomes bistable and again monostable at low values of D (low γ). $\langle c \rangle$ is the concentration averaged over the entire medium. All parameters as in Fig. 3 with $k_{-1}=0.024$. Dotted line is the unstable state.

be required to observe bistability. Thus, the system undergoes a bifurcation from bistability to monostability as l is increased. However, if the inter-domain distance is kept constant as l is increased, effectively the domains get closer to each other and this could lead again to bistability as $l/d \rightarrow 1$. This behavior of the stationary state is supported by our model and has been confirmed by numerical simulations. Although these results were obtained for the Schlögl mechanism similar conclusions apply to a general chemical system.

A feature of this study is the possibility of inducing bistability from compartmentalization in a range of kinetic parameters for which the homogeneous system is monostable. This is illustrated by point A of Fig. 7. We have shown that for a regular distribution of reactive domains the compartmentalization of the medium is equivalent to a contraction of

kinetic parameters. For infinite diffusion, for any given substrate, the contraction factor $\sqrt{\gamma/(\gamma+k_{-1})}$ is equal to 1 and we recover the homogeneous substrate case: point A. As diffusion is decreased, or equivalently as l is increased, the state of the system is found on the line connecting point A with the origin. First, the system will undergo a bifurcation to bistability at point B, and finally, at point C, it will become monostable again. Figure 8 shows the bifurcation diagram under such circumstances. The range of values of γ for which bistability exists can be calculated from the definitions of α and β.

It is also clear from Fig. 7, that systems located in the quadrant defined by $\beta<\beta_c$ and $\alpha>\alpha_c$ will remain monostable since variations of γ will not cause the system to enter the cusp bistable region.

V. DISCUSSION

The results in this paper show that there is a nontrivial interplay between the diffusion process and compartmentalized reaction dynamics. For sufficiently large diffusion constants the behavior of the system depends weakly on the spatial characteristics of the medium since diffusion is able to homogeneize the concentration field among the reactive domains. In this limit the compartmentalized system behaves like a homogeneous system. For lower values of the diffusion coefficient or larger reactive domains, concentration gradients begin to form and lead to behavior qualitatively different from that of the homogeneous system. Finally, in the limit of very low diffusion each domain acts independently and the concentrations attain values characteristic of the steady states determined by reaction steps which take place on the domains.
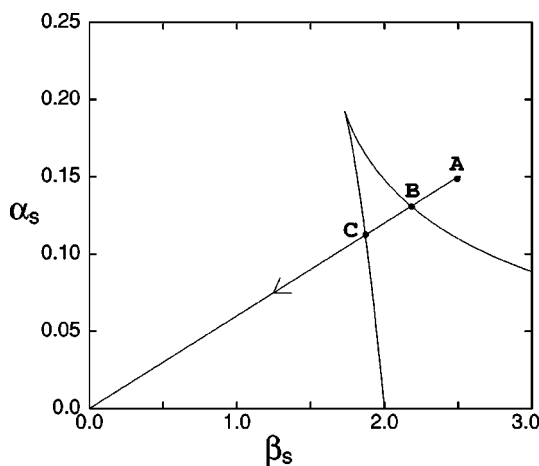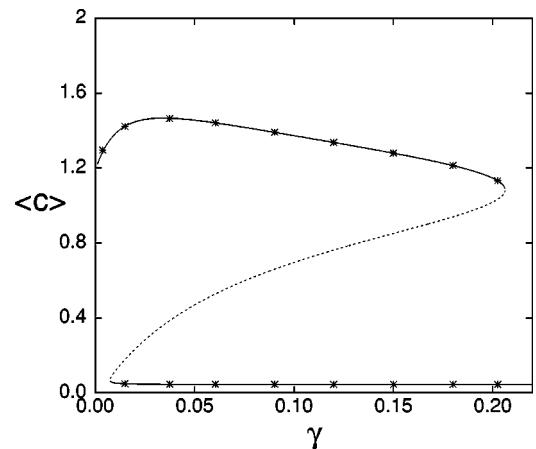

FIG. 7. Phase diagram for the Schlögl model. At infinite diffusion the inhomogeneous medium case is equivalent to the homogeneous case. As γ is decreased (by decreasing D or increasing l) the system moves on the straight line toward the origin; it becomes bistable at B and again monostable at C.

We have considered only a few of the possibilities even for the rather simple Schlögl model. For example, one may also study situations where both reaction steps occur on the same reactive domain. In such a case, for $D=0$, each domain

can attain a steady state concentration independent of the other domains. If the kinetic parameters lie within the bistable regime, the compartmentalized system will exhibit several solutions corresponding to all posible combinations of the two stable steady state solutions. When $D > 0$ but sufficiently small, or interdomain distance is large, a large variety of inhomogeneous solutions with different domains in different stable states are found to persist. Similar situations arise if the domains support only certain reaction steps. For example, suppose one has a sequence of domains where the two steps of the reaction mechanism alternate from one domain to the next but the distance of a domain to its right neighbor is much greater that to its left neighbor. On a large scales this distribution is equivalent to that of a sequence of domains that support both reaction steps separated by large interdomain distances.

The methodology developed here is not restricted to time-independent states. In this context, Eq. (6) provides a means to study the effect of compartmentalization on the properties of oscillatory or chaotic systems in one or more spatial dimensions. One may consider applications to specifically designed arrays of catalytic sites to probe reaction mechanisms or to study how aspects of the reaction mechanism affect chaotic synchronization processes [15].

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