

# Cooperative instability phenomena in arrays of catalytic sites\*

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Cooperative instability phenomena are shown to arise in arrays of localized catalytic sites immersed in a bulk system. Nonlinear reaction mechanisms may occur on the catalytic sites; the reactions in the bulk are stable. From the partial differential reaction-diffusion equations for the total system we derive ordinary integral equations and obtain from these, by linearization, stability conditions as a function of catalytic site density. The theory is applied to one-dimensional lattices of catalytic sites with several model reaction mechanisms. For a product activated enzyme mechanism occurring on each catalytic site we show that there exist cooperative effects among sites due to the intersite coupling via the bulk reactions and diffusion. For given constraints, the number of stationary states available (one or three) depends on the density of catalytic sites, such that as the density increases, first three, then one, then three stationary states exist. For the Prigogine-Lefever mechanism critical concentrations necessary to produce chemical oscillations are shown to depend on the catalytic site density; the functional dependence has a maximum due to cooperative interactions among the sites. We study next a linear array of two types of alternating catalytic sites on which occur reactions of mutual activation of two species (a generalization of a model of Shymko and Glass). Multiple stationary states are found, and again the number of such states available depends on the site density.

## I. INTRODUCTION

Many studies have been reported recently on instabilities in systems in which coupled nonlinear chemical reactions and transport processes occur simultaneously.<sup>1</sup> Less is known about the behavior of systems with locally bound reactions. Most of the research in this direction has been concentrated on problems involving transport in membranes.<sup>2</sup> Some studies on the role played by heterogeneous catalysis in potentially unstable systems have also been reported.<sup>3-5</sup>

In an earlier paper<sup>5</sup> we discussed various instability phenomena which can occur in a system in which certain classes of reactions, localized to a wall or membrane site, interact by diffusion with bulk reactions. From the reaction-diffusion equations we derived integral equations and applied them to simple model kinetic schemes to show the occurrence of multiple steady states, local oscillations, and waves localized to the membrane surface. In the present work we generalize our considerations to systems with many centers of reactions. We focus our attention on systems in which relatively simple bulk reactions are coupled to locally bound nonlinear reactions which may lead to instability phenomena, such as transitions to new steady states or to limit cycle oscillations. In living organisms this may come about due to the presence of membrane bound enzymes. Alternatively, it may happen in chemical reactors with heterogeneous catalysis. For example, Hlavacek and Votruba<sup>6</sup> have shown that the transition

between different stable steady states in a heterogeneously catalyzed oxidation of CO depends significantly on the geometry of packing of the catalyst.

In the present work we investigate several models with localized sources of nonlinearity. We pay particular attention to cooperative behavior such as mutual interaction between sites and its dependence on distance between sites, as well as effects of the coupling efficiency (diffusion rate in the bulk) between the sites and of possible bulk reactions. In principle two main cases can be distinguished; (a) a regular distribution of sites, and (b) a random distribution of sites. Here we focus attention on the first case and study two possible models: a case where all the sites are taken to be equivalent, which we call the AA lattice, and a case where two different sites alternate in the regular array, the AB lattice. Using Fourier and Laplace transform techniques we investigate the stability of steady states and obtain conditions for stability as functions of the site and bulk reactions, of the intersite distance, and the reaction-diffusional coupling between the sites.

The general results are applied to some model systems. First we treat a system consisting of a periodic lattice with a product activated enzyme. We show that the number of steady states and the points of marginal stability depend on the rate and transport coefficients and on the density of catalytic sites. Our results on the lattice yield the expected behavior in the two known limiting cases: the continuum limit of homogeneous kinet-

ics<sup>1a</sup> and the limit of infinite separation between the local site which corresponds to the single site problem.<sup>5</sup> In a second application we use the model scheme introduced by Prigogine and Lefever<sup>7</sup> and study the site density dependence of the marginal stability point. In both systems cooperativity among the sites at intermediate site densities leads to unexpected behavior. Finally we apply the general equations to the model used by Shymko and Glass<sup>4</sup> in their treatment of a system with two reaction sites. For a model involving mutual activation of species on the two types of sites an exponential site density dependence of the steady state concentrations is found. The number of available stationary states depends strongly on the density of catalytic sites.

## II. GENERAL THEORY

Consider a one-dimensional array of localized catalytic sites. Physically this can be realized for a system of parallel planar membranes (or catalytic sheets or screens) located at points  $x_n$  along the  $x$  axis. The sites are taken to be infinitely thin and porous, and provide local sites of chemical reaction. For the purposes of formal development we start with the  $d$ -dimensional problem and specialize later to the one-dimensional case.

### A. Derivation of integral equations

The dynamic equations describing kinetics and transport in our system are taken to be<sup>3c</sup>

$$\frac{\partial \psi}{\partial t} = \mathbf{D} \nabla^2 \psi + \mathbf{F}[\psi] + \sum_m \mathbf{G}_m[\psi] \delta(\mathbf{r} - \mathbf{r}_m). \quad (\text{II. 1})$$

Here  $\psi(\mathbf{r}, t)$  represents a column vector of concentrations,  $\mathbf{D}$  a matrix of transport coefficients,  $\mathbf{F}[\psi]$  the rates of the bulk reactions, and  $\mathbf{G}_m[\psi]$  the rate terms due to reactions localized to the site at  $\mathbf{r}_m$ . We note that in systems of spatial dimensions greater than one, one encounters infinite concentrations using the formulation (II.1). Proper account of the finite size of the catalyst particles removes this problem (see Ref. 8 for details). We assume that in the absence of the local sites the system attains a stable homogeneous steady state. We also take the system to be isothermal and with no convective transport. Further we shall linearize the bulk system about the homogeneous steady state  $\psi_h$  defined by  $\mathbf{F}[\psi_h] = 0$  but retain the full nonlinearity of the kinetics at the local sites  $\mathbf{G}_m$ . Maintaining the bulk kinetics in a homogeneous nonequilibrium state may be experimentally realized by either the presence of a chain of feeder bulk reactions, as in the Belousov-Zaikin-Zhabotinsky reaction for a transient experiment or by the imposition of light [see Ref. 1(j)].

The set of partial differential equations (II.1) can be transformed into a set of ordinary nonlinear integral equations<sup>5</sup>:

$$\begin{aligned} \psi(\mathbf{r}, \{\mathbf{r}_m\}, t) = & \psi_h + \int d\mathbf{r}' \mathbf{Z}(\mathbf{r}, \mathbf{r}'; t) [\psi(\mathbf{r}', t=0) - \psi_h] \\ & + \sum_m \int_0^t dt' \mathbf{Z}(\mathbf{r}, \mathbf{r}_m; t-t') \mathbf{G}_m[\psi(\mathbf{r}_m, \{\mathbf{r}_i\}, t')]. \end{aligned} \quad (\text{II. 2})$$

The notation  $\{\mathbf{r}_i\}$  in the argument of  $\psi$  indicates the parametric dependence on the location of the local sites and will be omitted henceforth.  $\mathbf{Z}(\mathbf{r}, \mathbf{r}'; t)$  is the propagator for the bulk dynamics which satisfies the linearized bulk kinetics and a singular initial condition

$$\frac{\partial \mathbf{Z}}{\partial t} = (\mathbf{D} \nabla^2 + \mathbf{\Omega}) \mathbf{Z}, \quad (\text{II. 3})$$

$$\mathbf{Z}(\mathbf{r}, \mathbf{r}'; t=0) = \delta(\mathbf{r} - \mathbf{r}') \mathbf{1} \quad (\text{II. 4})$$

where  $\mathbf{\Omega}$  is the matrix of the linearized bulk reaction rates

$$\mathbf{\Omega} = \left( \frac{\partial \mathbf{F}}{\partial \psi} \right)_{\psi_h}. \quad (\text{II. 5})$$

Equation (II.2) is an important result since, if we put  $\mathbf{r} = \mathbf{r}_m$ , we have reduced our problem to a set of ordinary integral equations among the concentrations at the various sites.

### B. Steady states

The bulk system is taken to be stable so that

$$\mathbf{Z}(\mathbf{r}, \mathbf{r}', t) \underset{t \rightarrow \infty}{\sim} 0. \quad (\text{II. 6})$$

The steady state solution  $\psi^*(\mathbf{r})$  of Eq. (II.2) is obtained by replacing  $\psi(\mathbf{r}, t)$  on both sides by  $\psi^*(\mathbf{r})$  and taking  $t \rightarrow \infty$  in the right-hand side (rhs) of Eq. (II.2). We obtain the following algebraic equation for the steady states:

$$\psi^*(\mathbf{r}) = \psi_h + \sum_m \mathbf{Z}(\mathbf{r} - \mathbf{r}_m) \mathbf{G}_m[\psi^*(\mathbf{r}_m)], \quad (\text{II. 7a})$$

where

$$\mathbf{Z}(\mathbf{r} - \mathbf{r}_m) = \int_0^\infty dt \mathbf{Z}(\mathbf{r}, \mathbf{r}_m; t), \quad (\text{II. 8a})$$

and where we used the fact that the propagator  $\mathbf{Z}(\mathbf{r}, \mathbf{r}'; t)$  in an isotropic system depends only on  $(\mathbf{r} - \mathbf{r}')$ .  $\mathbf{Z}(\mathbf{r})$  can be obtained explicitly from Eqs. (II.3) and (II.4) by applying a Laplace transform in  $t$  and a Fourier transform in  $\mathbf{r}$ . Limiting our results now to one dimension ( $x$ ), we obtain

$$\mathbf{Z}(x) = \int \frac{dk}{2\pi} e^{ikx} (k^2 \mathbf{D} - \mathbf{\Omega})^{-1}, \quad (\text{II. 8b})$$

with which we may calculate the steady state concentration  $\psi^*$  satisfying

$$\psi^*(x) = \psi_h + \sum_m \mathbf{Z}(x - x_m) \mathbf{G}_m[\psi^*(x_m)]. \quad (\text{II. 7b})$$

From Eqs. (II.7) we obtain the steady state concentrations and then investigate their stability by linearization of the integral Eq. (II.2) in perturbations about these states.

For the AA lattice all sites are taken to be equivalent, so that  $\mathbf{G}_m = \mathbf{G}$ ; for the AB lattice the rates are taken to be  $\mathbf{G}_A$  at sites of type A and  $\mathbf{G}_B$  at sites of type B.

#### 1. Steady states of the AA lattice

Here we expect the possibility of a solution such that  $\psi^*$  is the same on all the sites. In general, of course, there may be other solutions corresponding to spatially

differentiated structures.<sup>1</sup>

Taking the lattice spacing to be (a), we place the sites on positions  $x_m$  given by

$$x_m = ma \quad (II.9a)$$

Since the concentration is taken to be the same at all sites, we put

$$\psi^*(x_m) = \bar{\psi} \quad (II.9b)$$

It is convenient at this point to introduce lattice Fourier transforms ( $m \rightarrow q$ ). For a quantity  $A$  taking on values  $A_m$  at site  $m$  in our infinite lattice, we define the lattice Fourier transform  $A_q$  by

$$A_q = \sum_m A_m e^{-iqma} \quad (II.10a)$$

$$A_m = \frac{a}{2\pi} \int_0^{2\pi/a} dq A_q e^{iqma} \quad (II.10b)$$

In association with these transformation and inversion formulas we have the completeness relations

$$\frac{a}{2\pi} \int_0^{2\pi/a} dq e^{iq(m-m')a} = \delta_{mm'} \quad (II.10c)$$

$$\frac{a}{2\pi} \sum_{m=-\infty}^{\infty} e^{i(\alpha - \alpha')ma} = \sum_{r=-\infty}^{\infty} \delta(q - q' - r\beta\kappa_a) \quad (II.10d)$$

The lattice vector  $\beta\kappa_a$  is defined as

$$\beta\kappa_a = 2\pi/a \quad (II.10e)$$

Using (II.7b), we can show that the steady states of equal concentration  $\bar{\psi}$  at each site are given by

$$\bar{\psi} = \psi_h + \mu G[\bar{\psi}] \quad (II.11)$$

where

$$\mu = \sum_{m=-\infty}^{\infty} Z(x_m) \quad (II.12a)$$

$$= \alpha^{-1} \sum_{m=-\infty}^{\infty} [(m\kappa_a)^2 \mathbf{D} - \Omega]^{-1} \quad (II.12b)$$

The last step in (II.12) is obtained using (II.10d). The summation formula<sup>9</sup>

$$2 \sum_{m=1}^{\infty} (y^2 - m^2)^{-1} = \frac{\pi}{y} [\cot(\pi y) - (\pi y)^{-1}] \quad (II.13a)$$

yields a closed form for  $\mu$ :

$$\mu = -\frac{a}{4\pi} \alpha^{-1} \cot(\pi\alpha) \mathbf{D}^{-1}, \quad \alpha^2 = (\beta\kappa_a^2 \mathbf{D})^{-1} \Omega \quad (II.13b)$$

Note that  $\alpha^2$  is a measure of the ratio of the time scales for diffusion on the length scale of the site separation  $(\beta\kappa_a^2 \mathbf{D})^{-1}$  to that of the bulk kinetics  $\Omega^{-1}$ . [Care must be taken in writing equations such as (II.13b) since quantities such as  $\mathbf{D}$ ,  $\Omega$ , and  $\alpha$  are matrices and hence the ordering of products is important.]

## 2. Steady states for the AB lattice

For this case the sites of type  $A$  are located at  $x_m = ma$  and those of type  $B$  at  $x'_m = ma + b$ . The steady state concentrations are then found to be

$$\psi^*(x) = \psi_h + \sum_m e^{-(m\beta\kappa_a x)} [(m\beta\kappa_a)^2 \mathbf{D} - \Omega]^{-1} \mathbf{G}_A[\psi(x_m)]$$

$$+ \sum_n e^{-in\beta\kappa_a(x-b)} [(n\beta\kappa_a)^2 \mathbf{D} - \Omega]^{-1} \mathbf{G}_B[\psi(x'_n)] \quad (II.14)$$

We let  $\bar{\psi}_A$  and  $\bar{\psi}_B$  be the values of the steady state concentrations on their respective site types, limiting ourselves to the case such that for any given site type ( $A$  or  $B$ ) the concentrations are the same on all sites of that type ( $\psi_A$  or  $\psi_B$ ). With this we obtain

$$\bar{\psi}_A = \psi_h + \mu^{(e)} \mathbf{G}_A[\bar{\psi}_A] + \mu^{(0)} \mathbf{G}_B[\bar{\psi}_B] \quad (II.15a)$$

$$\bar{\psi}_B = \bar{\psi}_h + \mu^{(0)} \mathbf{G}_A[\bar{\psi}_A] + \mu^{(e)} \mathbf{G}_B[\bar{\psi}_B] \quad (II.15b)$$

where

$$\mu^{(e)} = \alpha^{-1} \sum_{r_1=-\infty}^{\infty} [(r_1\beta\kappa_a)^2 \mathbf{D} - \Omega]^{-1} \quad (II.15c)$$

$$= -\frac{a}{4\pi} \alpha^{-1} \cot(\pi\alpha) \mathbf{D}^{-1} \quad (II.15d)$$

$$\mu^{(0)} = \alpha^{-1} \sum_{r_1=-\infty}^{\infty} e^{-ir_1\beta\kappa_a b} [(r_1\beta\kappa_a)^2 \mathbf{D} - \Omega]^{-1} \quad (II.15e)$$

We have been able to find a closed form for  $\mu^{(0)}$  in the special case  $b = a/2$ , for which we obtain

$$\mu^{(0)}(b = a/2) = -\frac{a}{4\pi} \alpha^{-1} \csc(\pi\alpha) \mathbf{D}^{-1} \quad (II.16)$$

These formulas will be used to study model systems later.

The concentrations  $\psi^*(x)$  at a general point  $x$  may be obtained via (II.7b) from the concentrations  $\bar{\psi}_A$  and  $\bar{\psi}_B$  on the sites. Thus our partial differential system has been reduced to a set of nonlinear algebraic equations, (II.15a) and (II.15b) and similarly for Eq. (II.11) in the AA lattice case.

## C. Stability of steady states

Consider the stability of the system to small perturbations  $\phi$  from the steady state concentrations  $\psi^*$ :

$$\psi(x, t) = \psi^*(x) + \phi(x, t) \quad (II.17)$$

Linearizing in  $\phi$  about the steady state  $\psi^*(x)$ , we have

$$\frac{\partial \phi}{\partial t} = [\mathbf{D} \nabla^2 + \Omega] \phi + \mathbf{L}(x) \phi \quad (II.18)$$

$$\mathbf{L}(x) = \sum_m \Gamma_m \delta(x - x_m) \quad (II.19)$$

$$\Gamma_m = (\partial \mathbf{G}_m / \partial \psi)_{\psi^*(x_m)} \quad (II.20)$$

In Eq. (II.20) the matrix  $\Gamma_m$  is evaluated at the steady state concentration  $\psi^*$ . Equation (II.18) can be transformed to the integral equation

$$\phi(x, t) = \mathbf{T}(x, t) + \sum_m \int_0^t dt' \mathbf{Z}(x - x_m, t - t') \Gamma_m \phi(x_m, t') \quad (II.21)$$

$$\mathbf{T}(x, t) = \int dx' \mathbf{Z}(x - x', t) \phi(x', 0) \quad (II.22)$$

Equation (II.21) is our starting point for investigating the asymptotic stability properties of the system.

### 1. AA lattice

We investigate the stability of the symmetric state  $\psi^*(x_m) = \bar{\psi}$  and hence  $\Gamma_m$  is independent of  $m$ ;

$$\Gamma_m = \Gamma \quad (II. 23)$$

Since  $\phi$  at arbitrary  $x$  may be obtained from  $\phi(x, 0)$  and  $\phi(x_m, t)$ , we focus our attention on  $\phi(x_m, t)$ . If we take Laplace transforms ( $t \rightarrow s$ ) and introduce the notation

$$\hat{\phi}(x, s) = \int_0^\infty dt e^{-st} \phi(x, t) \quad (II. 24)$$

then Eq. (II. 22) at site  $m$  takes the form

$$\hat{\phi}(x_m, s) = \hat{T}(x_m, s) + \sum_{m'} \mathbf{Z}(x_m - x_{m'}, s) \Gamma \hat{\phi}(x_{m'}, s) \quad (II. 25)$$

Equation (II. 25) is solved by lattice Fourier transform ( $m \rightarrow q$ ) introduced in (II. 10). Using the convolution theorem for these transforms, we see

$$\sum_m e^{-iama} \sum_{m'} \hat{\mathbf{Z}}(x_m - x_{m'}, s) \Gamma \hat{\phi}(x_{m'}, s) = \mathbf{Z}_q(s) \Gamma \hat{\phi}_q(s) \quad (II. 26)$$

and we obtain from (II. 25)

$$\hat{\phi}_q(s) = [I - \hat{\mathbf{Z}}_q(s) \Gamma]^{-1} \hat{T}_q(s) \quad (II. 27)$$

so that

$$\phi_q(t) = \int_{-i\infty+c}^{+i\infty+c} ds [I - \hat{\mathbf{Z}}_q(s) \Gamma]^{-1} \hat{T}_q(s) \quad (II. 28)$$

where the contour of integration is chosen, via  $c$ , to be to the right of all singularities of the integrand and where

$$\hat{\mathbf{Z}}_q(s) = \sum_{m=-\infty}^{\infty} \mathbf{Z}(x_m, s) e^{-iama} \quad (II. 29)$$

The stability of the system is determined by the location of the poles of  $\hat{\phi}_q(s)$  in the  $s$ -plane. In the absence of any local reactions,  $\Gamma = 0$ , these poles are seen to be identical with those of  $\hat{T}_q(s)$ . Since the bulk is assumed to be stable, we see that instability behavior, i.e., the presence of poles in  $\hat{\phi}_q(s)$  in the right half-plane, can only arise from the factor  $[I - \hat{\mathbf{Z}}_q(s) \Gamma]^{-1}$ . These poles  $s(q)$  are the solutions of

$$\det[I - \hat{\mathbf{Z}}_q(s) \Gamma] = 0 \quad (II. 30)$$

the characteristic equation for our system.

Let us now derive an explicit expression for  $\hat{\mathbf{Z}}_q(s)$ . First we note that we are using two types of Fourier transforms in this work. A continuous transform defined by

$$A(x) = (2\pi)^{-1} \int_{-\infty}^{\infty} dk A_k e^{ikx} \quad (II. 31)$$

$$A_k = \int_{-\infty}^{\infty} dx A(x) e^{-ikx} \quad (II. 31)$$

and the lattice Fourier transform defined by Eq. (II. 10). Applying continuous Fourier transform (FT) to Eqs. (II. 3) and (II. 4) and taking also the Laplace ( $t \rightarrow s$ ) transform, we obtain

$$\hat{\mathbf{Z}}(x, s) = (2\pi)^{-1} \int_{-\infty}^{\infty} dk e^{ikx} (s\mathbf{I} + k^2 \mathbf{D} - \Omega)^{-1} \quad (II. 32)$$

[Note that (II. 8b) is obtained as the  $s \rightarrow 0$  limit of this equation.] For  $x = x_n = na$  we obtain

$$\hat{\mathbf{Z}}(x_n, s) = (2\pi)^{-1} \int_{-\infty}^{\infty} dk e^{ikh} (s\mathbf{I} + k^2 \mathbf{D} - \Omega)^{-1} \quad (II. 33)$$

Taking the lattice FT of the last equation according to Eq. (II. 10), we get

$$\hat{\mathbf{Z}}_q(s) = (2\pi)^{-1} \int_{-\infty}^{\infty} dk (s\mathbf{I} + k^2 \mathbf{D} - \Omega)^{-1} \sum_n e^{(k-a)na} \quad (II. 34)$$

Here  $q$  is limited to no larger than  $K_a (= 2\pi/a)$  but  $k$  can take any value. Equation (II. 10) can then be used to show that

$$\hat{\mathbf{Z}}_q(s) = a^{-1} \sum_{r=-\infty}^{\infty} [s\mathbf{I} + (rK_a - q)^2 \mathbf{D} - \Omega]^{-1} \quad (II. 35)$$

which is the desired explicit form of  $\hat{\mathbf{Z}}_q(s)$ .

### 2. AB lattice

The stability analysis for this case is essentially the same as for the AA lattice and hence details will not be given here. If we define

$$\Gamma_A = \left( \frac{\partial G_A}{\partial \psi} \right)_{\psi_A} \quad (II. 36)$$

$$\Gamma_B = \left( \frac{\partial G_B}{\partial \psi} \right)_{\psi_B}$$

the stability of the system is determined by the sign of the real part of the roots  $s(q)$  of the characteristic equation

$$\det \begin{bmatrix} \mathbf{I} - \hat{\mathbf{Z}}_q(s|0) \Gamma_A & \hat{\mathbf{Z}}_q(s|b) \Gamma_B \\ \hat{\mathbf{Z}}_q(s|b) \Gamma_A & \mathbf{I} - \hat{\mathbf{Z}}_q(s|0) \Gamma_B \end{bmatrix} = 0 \quad (II. 37)$$

$$\hat{\mathbf{Z}}_q(s|b) = a^{-1} e^{-iqb} \sum_{m=-\infty}^{\infty} e^{-im\mathcal{X}_a b} [s\mathbf{I} - \Omega + (m\mathcal{X}_a - q)^2 \mathbf{D}]^{-1} \quad (II. 38)$$

Note that  $\hat{\mathbf{Z}}_q(s|b=0)$  is identical to  $\hat{\mathbf{Z}}_q(s)$  given in (II. 35), as arose in the discussion of the AA lattice.

### 3. Stability of uniform steady states to uniform perturbations: The continuum limit

In this section we consider the continuum limit where the lattice spacing  $a$  for a regular array vanishes. In particular we analyze the stability of such a system with respect to homogeneous perturbations, that is,  $\phi(x;0)$  is the same in every cell. For the AA lattice this case corresponds to setting  $q=0$  in Eq. (II. 35) and we write

$$\mathbf{Z}_0(s) = a^{-1} \sum_{m=-\infty}^{\infty} [s\mathbf{I} - \Omega + (m\mathcal{X}_a)^2 \mathbf{D}]^{-1} \quad (II. 39)$$

Uniform steady states are unstable to uniform perturbations if there are roots  $s$  of the equation

$$\det[\mathbf{I} - \mathbf{Z}_0(s) \Gamma] = 0 \quad (II. 40)$$

with  $\text{Re } s > 0$ . At a critical or marginal stability point we have at least one root with  $\text{Re } s = 0$ . To investigate deviations in the critical point from its value in the continuum limit we seek an expansion to solutions of the stability Eq. (II. 40). Formally the continuum limit is defined by

$$a^{-1} \mathbf{G} = \mathbf{g} \quad (II. 41)$$

$$a^{-1} \Gamma = \gamma \quad a \rightarrow 0 \text{ with } |\mathbf{g}|, |\gamma| < \infty$$

where  $a^{-1}$  is the number of the sites per unit length. From Eq. (II. 39) we have to order  $a^2$

$$a\hat{\mathbf{z}}_0(s) \underset{a \rightarrow 0}{\sim} (s\mathbf{I} - \mathbf{\Omega})^{-1} + a^2 \mathbf{D}^{-1}/12, \quad (\text{II. 42})$$

where we have used the relation

$$\sum_{m=1}^{\infty} m^{-2} = \pi^2/6. \quad (\text{II. 43})$$

Hence we find that in the continuum limit the stability condition Eq. (II. 40) can be written

$$\det[s\mathbf{I} - \mathbf{\Omega} - \gamma - (s\mathbf{I} - \mathbf{\Omega}) a^2 \mathbf{D}^{-1} \gamma / 12 + \dots] = 0. \quad (\text{II. 44})$$

If we let  $a \rightarrow 0$  in this equation we obtain the characteristic equation for the determination of the stability to homogeneous perturbations of a system with effective linearized kinetics  $(\mathbf{\Omega} + \gamma)$ . Let  $z_\alpha$ ,  $|\alpha\rangle$ , and  $\langle\alpha|$  be the eigenvalues and corresponding left and right eigenvectors of this stability matrix, i. e.,

$$\begin{aligned} (\mathbf{\Omega} + \gamma)|\alpha\rangle &= z_\alpha |\alpha\rangle, \\ \langle\alpha|(\mathbf{\Omega} + \gamma) &= \langle\alpha| z_\alpha. \end{aligned} \quad (\text{II. 45})$$

Then with nondegenerate perturbation theory we calculate the first order correction to the eigenvalues  $s_\alpha$  of Eq. (II. 40) as

$$s_\alpha(a) = z_\alpha + \frac{1}{12} \langle\alpha| \gamma \mathbf{D}^{-1} \gamma |\alpha\rangle a^2. \quad (\text{II. 46})$$

In the continuum system the critical point is determined by the condition  $\text{Re } z_\alpha = 0$  for at least one  $\alpha$ . Here the condition  $\text{Re } s_\alpha = 0$  implies a shift in the critical point which in the continuum limit  $a^{-1}G - \text{const}$  (1) is quadratic in  $a$ , the distance between the reactive sites, (2) is quadratic in the local reaction rate terms, and (3) explicitly involves the diffusion coefficient matrix. As expected, the shift vanishes with diffusive homogenization  $|\mathbf{D}| \rightarrow \infty$ . Indeed if we introduce the matrix  $\mathbf{K}_\gamma$  of inverse penetration lengths  $\mathbf{K}_\gamma^2 = -\mathbf{D}^{-1} \gamma$ , we see that the shift in critical point goes as  $(\mathbf{K}_\gamma a)^2$ , that is, as the ratio of the interparticle distance to the reaction-diffusion lengths corresponding to the time scale of the local kinetics.

### III. APPLICATIONS TO MODEL SYSTEMS

The equations derived in Sec. II are now applied to several model systems chosen to illustrate the cooperative and other aspects of local sites of reaction in a system maintained far from equilibrium.

#### A. Product activated enzyme localized on an AA lattice

In this section we consider a system consisting of a bulk reacting medium and a periodically distributed array of local sites of reaction. The local reactions involve a product activated enzyme step which couples to the bulk to yield a reaction mechanism with multiple steady states. This and other effects are possible because the bulk reactions are maintained out of equilibrium. The results are obtained in closed analytical form and hence describe the phenomena over the complete range of site densities.

We consider a model system with bulk reactions



In the scheme Eq. (III. 1) we have put all rate coefficients equal to  $k$  to simplify our analysis.

At lattice sites there occur the reactions



In Eq. (III. 2) only the concentrations of the species  $X$  and  $Y$  may diffuse. The three forms of the enzyme  $E$ ,  $E'$ , and  $E''$  are localized to the sites, and the total concentration at a given site  $(E'' + E' + E)$  remains constant. Assuming that the equilibration between the various forms of the enzyme is fast and that the total enzyme is low in concentration, then one can show that the overall rate of the processes (III. 2) takes the form  $\lambda X^2 Y$ , for low  $X$  concentrations;  $\lambda$  is a constant.<sup>2d</sup>

In the absence of the localized reactions, the bulk homogeneous steady states are [see Eq. (III. 1)]

$$\begin{aligned} X_h &= 0, \\ Y_h &= B. \end{aligned} \quad (\text{III. 3})$$

For our system the bulk reaction and diffusion matrices are given by

$$\mathbf{\Omega} = -k\mathbf{I}, \quad \mathbf{D} = \begin{bmatrix} D_x & 0 \\ 0 & D_y \end{bmatrix}. \quad (\text{III. 4})$$

Hence the steady state factor  $\mu$  given in Eqs. (II. 11) and (II. 13) is purely diagonal, with diagonal elements denoted  $\mu_x$  and  $\mu_y$ , and we obtain from Eq. (II. 11) the steady state equations

$$\bar{X} = \lambda \mu_x \bar{X}^2 \bar{Y}, \quad (\text{III. 5})$$

$$\bar{Y} = B - \lambda \mu_y \bar{X}^2 \bar{Y}, \quad (\text{III. 6})$$

where  $\lambda$  is the local rate constant. These equations are found to have the solution

$$\bar{X} = 0, \quad \bar{Y} = B \quad (\text{III. 7})$$

and a pair of solutions

$$\begin{aligned} \bar{X}_\pm &= \frac{1}{2} [(B\mu_x/\mu_y) \pm \sqrt{(B\mu_x/\mu_y)^2 - 4(\lambda\mu_y)^{-1}}], \\ \bar{Y}_\pm &= (\lambda\mu_x \bar{X}_\pm)^{-1}. \end{aligned} \quad (\text{III. 8})$$

The branches of steady states ( $\pm$ ) are strictly nonequilibrium states existing beyond a critical value  $B_c$  of  $B$  given by

$$B_c = 2(\mu_y/\lambda\mu_x^2)^{1/2}. \quad (\text{III. 9})$$

Let us now examine the site density dependence of  $B_c$  for the possibility of cooperative phenomena among the local sites.

From (II. 13b) we obtain

$$\mu_i = ak^{-1} \sigma_i \cot \sigma_i, \quad \sigma_i^2 = a^2 k / 4D_i. \quad (\text{III. 10})$$

Thus Eqs. (III. 9) and (III. 10) give the explicit dependence of  $B_c$  on  $a$ . In order to interpret this result we

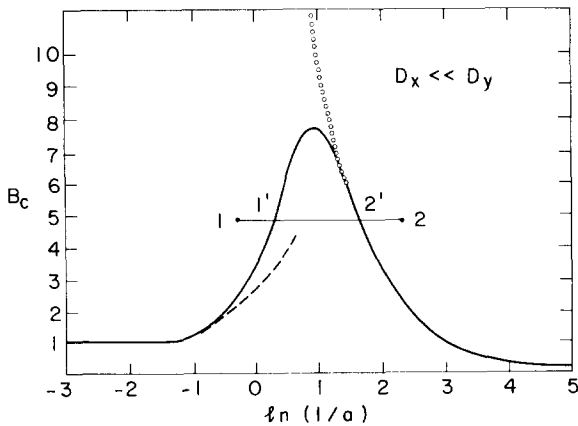


FIG. 1. Critical concentration  $B_c$  necessary for multiple steady states, plotted (full line) against the natural logarithm of the density of sites for model system (III.1) for the case  $D_x \ll D_y$ . Dashed and dotted lines are for the continuum limit and isolated site limit, respectively. Values of parameters used are  $D_x=0.01$ ,  $D_y=100$ ,  $k=4$ .

first calculate the extreme limits of low and high site density.

For the present problem the continuum limit takes the form  $a \rightarrow 0$ ,  $\lambda a^{-1} \rightarrow \text{const} < \infty$ . Putting (III.10) into (III.9) and retaining terms to order  $a^2$  we obtain

$$B_c \underset{a \rightarrow 0}{\sim} 2(ak/\lambda)^{1/2} [1 + a^2(k_y^2 - 2k_x^2)], \quad (\text{III.11})$$

where the bulk inverse penetration lengths  $k_i$  are given by

$$k_i = (k/D_i)^{1/2}. \quad (\text{III.12})$$

Equation (III.11) shows the interesting possibility that the discreteness of the sites, appearing there as a correction to the continuum limit, may increase/decrease the values of critical parameter depending on the nature of the site interaction ( $k_y^2 \gtrless 2k_x^2$ ).

In the low density limit  $a \rightarrow \infty$  we use Eq. (II.12a) as our starting point. For the present model the matrix  $\mathbf{Z}(x)$  [see (III.8a)] is diagonal and is easily calculated. Its diagonal elements  $Z_i(x)$  are given by

$$Z_i(x) = (2k_i D_i)^{-1} e^{-k_i |x|}. \quad (\text{III.13})$$

Using this result and Eq. (II.12a) we neglect terms of order  $(e^{-k_i a})^2$  and higher and obtain

$$B_c \underset{a \rightarrow \infty}{\sim} 2(4k D_x / \lambda^2 D_y)^{1/4} (1 + e^{-k_y a} - 2e^{-k_x a}). \quad (\text{III.14})$$

This result may be interpreted in terms of the expected cooperative aspects of the multiple site problem. As the intersite distance  $a$  decreases from infinity the sites begin to interact in that the autocatalytic nature of the process at each site is augmented by sharing the  $X$  molecules produced at neighboring sites. Thus as  $a$  decreases we expect that  $B_c$  will decrease. This effect is manifested by the  $-2e^{-k_x a}$  term in (III.14). However, if  $D_y \gg D_x$ , then before the cooperative sharing of  $X$  is sensed at a given site the cooperative depletion of  $Y$  at that site by its neighboring sites occurs and hence  $B_c$  first increases as the density  $a^{-1}$  increases from zero, as seen in the  $+e^{-k_y a}$  term in Eq. (III.14). Eventually, however, as  $a$  decreases (i.e., the density increases)

the cooperativity associated with the  $X$  species becomes dominant and thus  $B_c$  attains a maximum and then starts to decrease for the  $D_y \gg D_x$  case. These ideas are demonstrated in Figs. 1 and 2. In these figures we also graph the results for weakly interacting sites (III.14) and for the continuum limit (III.11) for comparison with the exact result [Eqs. (II.9) and (II.10)].

The case  $D_y \gg D_x$  allows for an interesting phenomenon. Figure 1 may be viewed as a phase diagram in the  $(B, \ln n)$  plane ( $n = a^{-1}$  is the density of sites). In the region  $B > B_c$  we may have three steady states (one of which,  $X_+$ , is probably unstable). If we look at the available states as a function of density for fixed  $B$  we may run into the possibility, as shown in Fig. 1 along the line 1-2, that as the density of sites increases from a given point labeled 1 there may be an intermediate region of density corresponding to that segment of the line (denoted 1'-2') where only one state is available, that of no  $X$ .

## B. Oscillatory scheme with localized Prigogine-Lefever reactions

In an earlier paper<sup>5</sup> we demonstrated the existence of marginal stability oscillations at a localized site by using for the reactions at that site a model mechanism proposed by Prigogine and Lefever.<sup>7</sup> We consider for the present case such reactions localized at all sites of the AA lattice and show how the marginal stability point varies as a function of the site density.

Consider an infinite system with no reactions in the bulk,  $\mathbf{F} \equiv 0$  [see Eq. (II.1)]. At the steady state  $\psi^*$  of our system with no bulk reactions, the net rate of change of all species at the site must vanish, i.e.,  $G[\psi^*] = 0$ ; this implies that the concentrations are uniformly distributed. For the nonreacting bulk with equal diagonal diffusion the propagator  $\hat{\Xi}(x_m; s)$  takes the form  $\Xi(x_m; s)\mathbf{I}$ . From (II.32) we have

$$\begin{aligned} \hat{\Xi}(x_m; s) &= \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{-ikx_m} (s + k^2 D)^{-1} \\ &= \frac{1}{2(sD)^{1/2}} e^{-(s/D)^{1/2} |x_m|}. \end{aligned} \quad (\text{III.15})$$

The  $q=0$  lattice Fourier transform  $\Xi_0$  [see (II.10a)] is given by

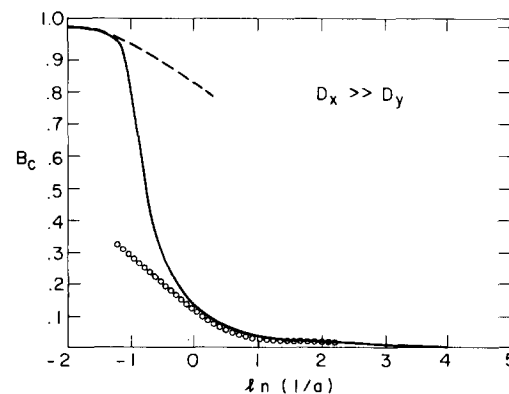


FIG. 2. Same as in Fig. 1 but for the case  $D_x \gg D_y$ , with  $D_x=100$ ,  $D_y=1$ ,  $k=4$ .

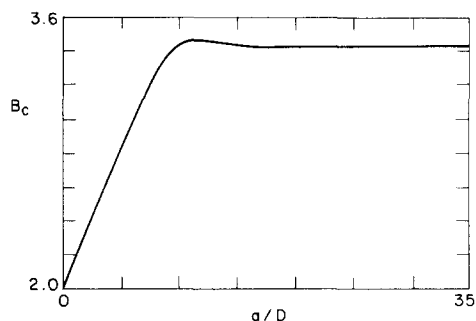


FIG. 3. Variation of marginal stability concentration  $B_c$  with  $a/D$  for model system (III. 22), with  $D_x = D_y = D$ ,  $\lambda = 1$ .

$$\hat{z}_0(s) = \frac{1}{2\sqrt{sD}} \frac{(1 + e^{-a\sqrt{s/D}})}{(1 - e^{-a\sqrt{s/D}})} \quad (\text{III. 16})$$

We now use this result for the analysis of the present mechanism.

At the local sites there occur the Prigogine-Lefever reactions<sup>7</sup>



This mechanism in a homogeneous phase, with  $A$ ,  $B$ ,  $D$ , and  $E$  kept constant, is known to give limit cycle oscillation in  $X$  and  $Y$ . Thus if this mechanism is localized at sites, we expect that cooperative effects among the sites will alter the conditions under which oscillation may occur. We keep  $A$ ,  $B$ ,  $D$ , and  $E$  constant in the present calculations and focus our attention on the species  $X$  and  $Y$ ,  $\psi = [X, Y]$ , which may diffuse and evolve in time. For the mechanism in Eq. (III.17) we have

$$\mathbf{G} = \lambda \begin{bmatrix} A - BX + X^2Y - X \\ BX - X^2Y \end{bmatrix}, \quad (\text{III. 18})$$

where we have set all rate coefficients to  $\lambda$ . The steady states for the system (bulk and sites) are obtained by setting  $\mathbf{G} = 0$ , which gives

$$\begin{aligned} X^* &= A, \\ Y^* &= B/A. \end{aligned} \quad (\text{III. 19})$$

For simplicity we take  $A = 1$ , in which case the matrix  $\mathbf{\Gamma}$  of the linearized local reactions becomes

$$\mathbf{\Gamma} = \lambda \begin{bmatrix} B - 1 & 1 \\ -B & -1 \end{bmatrix}. \quad (\text{III. 20})$$

The characteristic equation (II. 30) for the stability eigenvalue  $s$  may be written

$$\det[\hat{z}_0^{-1}(s) - \mathbf{\Gamma}] = 0. \quad (\text{III. 21})$$

Let  $\delta \pm i\omega$  be the eigenvalues of the matrix  $\mathbf{\Gamma}$ . Then for the simple case of equal and diagonal diffusion considered here we have

$$\hat{z}_0(s) = \delta \pm i\omega, \quad (\text{III. 22})$$

which from (III.16) is seen to be a transcendental equation for  $s$ . We seek the critical value of  $B$ , labeled  $B_c$  for marginal stability oscillations and hence the condition for which  $s$  is a pure imaginary number

$$s = i\omega_c. \quad (\text{III. 23})$$

For the mechanism Eq. (III.19) the quantities  $\delta$  and  $\omega$  are easily calculated by finding the eigenvalues of  $\mathbf{\Gamma}$  in (III.20) and we have

$$\begin{aligned} \delta &= \lambda(B - 2)/2, \\ \omega &= \pm \sqrt{(4B - B^2)}/2. \end{aligned} \quad (\text{III. 24})$$

Equation (III.22) with  $\delta$  and  $\omega$  given by Eq. (III.14) was solved numerically to obtain the critical value of  $B$ ,  $B_c$  (see Fig. 3). For  $a \rightarrow 0$  we obtain the result  $B_c = 2$  corresponding to the continuum value found previously.<sup>7</sup> For the independent site case  $a \rightarrow \infty$  we also find the previously obtained value  $B_c = 2 + \sqrt{2}$  for the isolated site.<sup>5</sup> The maximum in the calculated curve for the critical value of  $B$  is a result of the cooperativity among the catalytic sites. Calculations for unequal diffusion coefficients were not done; however for such cases we may expect similar findings as obtained for the product activated enzyme mechanism, of Sec. III.A, where pronounced peaks in the critical parameter were found.

### C. AB lattice

In this section we consider a system with two types of local sites of reaction. An interesting feature of such a system is that the isolated single sites of either type (for the mechanism chosen) do not sustain new far-from-equilibrium steady states, whereas the symbiotic relation between the two types of sites can bring about new steady states.

Consider the system to have two species  $X$  and  $Y$ . These undergo first order decay in the bulk medium and for simplicity we take the bulk rate constants equal to  $k$ ; hence  $\mathbf{\Omega} = -k\mathbf{I}$ . The species  $X$  and  $Y$  are synthesized at the local sites only and are chemically coupled such that each controls the production rate of the other. More explicitly the local rate expressions  $\mathbf{G}_A$  and  $\mathbf{G}_B$  on sites of type  $A$  and  $B$ , respectively, [see Eq. (II.14)] are taken to be of the form

$$\mathbf{G}_A = \lambda_A f_A(Y) \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad \mathbf{G}_B = \lambda_B f_B(X) \begin{bmatrix} 0 \\ 1 \end{bmatrix}. \quad (\text{III. 25})$$

This scheme was used by Shymko and Glass<sup>4</sup> for their treatment of two sites. In Eq. (III.25)  $\lambda_A$  and  $\lambda_B$  are production constants (products of a rate constant and substrate concentrations). Substituting the given forms of the  $\mathbf{G}$ 's in (II.15), we have

$$X_A^* = \mu^{(e)} \lambda_A f_A(Y_A^*), \quad (\text{III. 26a})$$

$$Y_A^* = \mu^{(0)} \lambda_B f_B(X_B^*), \quad (\text{III. 26b})$$

$$X_B^* = \mu^{(0)} \lambda_A f_A(Y_A^*), \quad (\text{III. 26c})$$

$$Y_B^* = \mu^{(e)} \lambda_B f_B(X_B^*). \quad (\text{III. 26d})$$

We see that the steady state concentrations  $X_A^*$ ,  $Y_B^*$  are determined by  $Y_A^*$  and  $X_B^*$  and that  $X_B^*$  and  $Y_A^*$  obey a closed set of equations (III.6b) and (II.6c). We now consider a few specific choices of  $f_A$  and  $f_B$  which yield new far-from-equilibrium states.

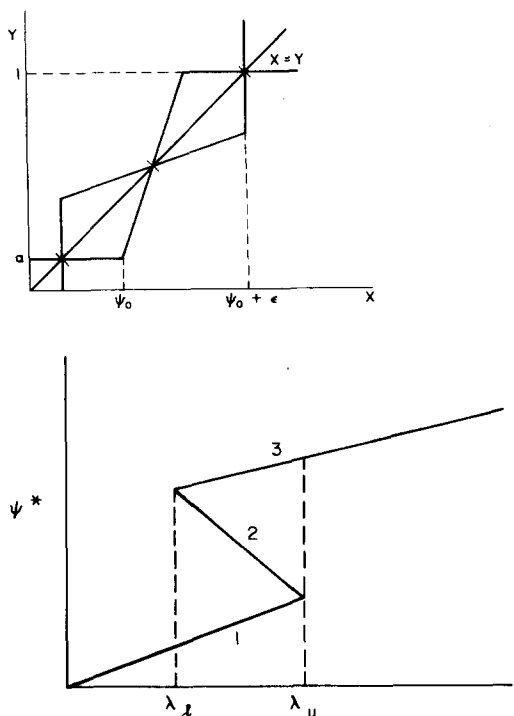


FIG. 4. (a) Schematic plot of Eqs. (III.25)–(III.27) showing that the solutions of Eqs. (III.25) and (III.26) lie on the line  $x=y$  and that there may be multiple solutions. (b) Steady states  $\psi^*(=x, y)$  plotted schematically as a function of the production constant  $\lambda$ . Note the existence of multiple steady state solutions in the region  $\lambda_l < \lambda < \lambda_u$ .

For the case of mutual activation we make the further simplification that  $f_A^*$  and  $f_B^*$  have the same functional form  $f$  and also that the production constants are equal,  $\lambda_A = \lambda_B = \lambda$ . Writing  $x = X_B^*$ ,  $y = Y_A^*$ , we see that Eqs. (III.26b) and (III.26c) become

$$x = \lambda \mu^{(0)} f(y), \tag{III.27}$$

$$y = \lambda \mu^{(0)} f(x). \tag{III.28}$$

where from (II.16)  $\mu^{(0)}$  is given for equal diagonal  $\Omega$  and  $D$  and for the case  $b = a/2$  by

$$\mu^{(0)} = [2(kD)^{1/2} \sinh(\frac{1}{2} a \sqrt{k/D})]^{-1}. \tag{III.29}$$

Shymko and Glass<sup>4</sup> considered a system of two localized sites in which they took the function  $f$  to be a Hill function. Such a control dependence has been observed in a number of different biochemical systems.<sup>10,11</sup> The qualitative dynamics of systems with rates given by such functions are insensitive to the detailed shape of the sigmoidal function  $f(\psi)$  and hence in our treatment we take  $f(\psi)$  to be a piecewise smooth function of the form

$$f(\psi) = \begin{cases} 1, & \psi > \psi_0 + \epsilon \\ f_0 + (\psi - \psi_0)(1 - f_0)/\epsilon, & \psi_0 < \psi < \psi_0 + \epsilon, \\ f_0, & \psi < \psi_0, \end{cases} \tag{III.30}$$

where  $f_0$ ,  $\psi_0$ , and  $\epsilon$  are constants [see Fig. 4(a)]. A plot of (III.27) and (III.28) in the  $x, y$  plane shows that the only solutions are symmetric,  $x=y$ . From Fig. 4(a) we see that there may be 1, 2, or 3 steady states.

For three steady state solutions the production constant  $\lambda$  must satisfy

$$\lambda_l < \lambda < \lambda_u, \tag{III.31}$$

where

$$\lambda_l = (\psi_0 + \epsilon) / \epsilon \mu^{(0)}, \tag{III.32}$$

$$\lambda_u = \psi_0 / f_0 \mu^{(0)}. \tag{III.33}$$

Figure 4(b) shows a schematic plot of the variation of the steady states with the production constant  $\lambda$ . Between the values  $\lambda_u$  and  $\lambda_l$ , there are three steady states. Choosing for example  $f_0 = 0.01$ ,  $\psi_0 = 1$ ,  $\epsilon = 0.1$ ,  $k = 1$ ,  $D = 1$ , and  $b = a/2$ , we use (II.16) in (II.32) and (II.33) to obtain

$$\lambda_u = 200 \sinh(a/2), \tag{III.34}$$

$$\lambda_l = 22 \sinh(a/2), \tag{III.35}$$

for the present case of equal diagonal reaction ( $\Omega = -kI$ ) and diffusion ( $D = DI$ ). A plot of  $\ln(\lambda_u)$  and  $\ln(\lambda_l)$  against the density of sites,  $a^{-1}$ , is shown in Fig. 5. This plot serves as a phase diagram for the system. Only the branch of steady states 1 [labeled in Fig. 4(b)] exists in region I and similarly for branch 3 in III. In region II the system may be found in either state 1 or 3 (state 2 is expected to be unstable). Thus we have here an analogous situation to that encountered for the product activated enzyme mechanism, Fig. 1. For given external constraints, here the quantity  $\lambda$  which depends on substrate concentration, the system has available one stationary state at low density of catalytic sites, three stationary states (two stable, one unstable) at intermediate densities, and one stationary state at high density. From (III.29) we see that as  $a \rightarrow \infty$ ,  $\mu^{(0)}$  vanishes exponentially and hence from (III.27) and (III.28) we see that the concentrations of  $X$  and  $Y$  thus also vanish exponentially according to

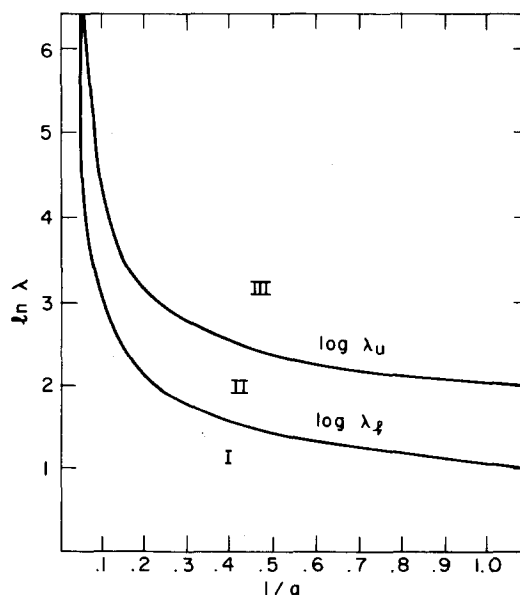


FIG. 5. A nonequilibrium phase diagram in the  $(\ln \lambda, a^{-1})$  plane. The demarcation lines defining the various regions,  $\ln \lambda_l$  and  $\ln \lambda_u$  are termination (or bifurcation) points for the various branches shown in Fig. 4(b).



$$X_B^* = Y_A^* a^{-\infty} \frac{\lambda f_0}{2\sqrt{kD}} e^{-1/2\sqrt{k/D}a} \quad (\text{III. 36})$$

This behavior is seen in the leftmost part of region I in Fig. 5 and is due to the strong interdependence of the two species because of the mutual activation of their rates of formation.

#### IV. DISCUSSION

In this paper we have analyzed the stability properties of systems with simple bulk reaction and transport and with local sites on which nonlinear chemical processes take place. We presented a general formulation of an approach to the stability analysis of such systems based on integral equations for the site concentrations in which a propagator describes the linear transport and reaction dynamics of the bulk. This general formalism was applied to simple one-dimensional systems for which we demonstrate that the marginal stability points depend in a nontrivial way on the density of local sites and bulk reaction-diffusional coupling between them. In the almost homogeneous limit the shift in the marginal stability points for a general system is given in Eq. (II. 46) and is inversely proportional to the diffusion matrix and to the square of density of sites. The homogeneous limit is taken by keeping the product of density and local rates constant as the density goes to infinity. This is the physically interesting limit since it leads to a finite rate contribution in the continuum limit. Note for example in Eq. (II. 44) how the term  $\gamma (= a^{-1} \Gamma$ , where  $\Gamma$  is the linearized local rate) plays the role of an effective bulk rate contribution as is expected in the continuum limit. This is discussed in greater detail in Ref. 8. (In that work the full three-dimensional aspects of catalyst particle dynamics is discussed and effective rate and transport properties are calculated.) Far from the continuum limit the shift in critical constraints may vary monotonically or can pass through extrema as the distance between sites is varied. As is seen clearly from the mechanism in Sec. II. A this type of behavior can depend qualitatively on the bulk properties such as the ratio of diffusion coefficients. For given constraints the number of available stationary states or the possibility for oscillation can be varied with changes in the density of catalytic sites.

The concept of localized reactions is important both in living organisms and in chemical reactor systems. Generally we see that interesting effects may arise in problems of heterogeneous catalysis when the arrangement of catalytic sites becomes a variable to be considered. This paper is a beginning in analyzing the far from equilibrium properties of such systems with particular emphasis on this variable. Further developments should involve application to three-dimensional systems<sup>8</sup> with attention given not only to the density of sites but also to the geometry of their packing.

A random distribution is typically the case for the dispersion of catalyst particles in a solution (although

experiments with styrofoam particles in water have shown that electrical effects can lead to a lattice structure). For a random distribution one might expect a local clustering to cause a local instability under conditions for which the periodic array is stable. The effects of the randomness of the catalyst site distribution is still an open question. An ensemble approach for dealing with such problems has been introduced in Ref. 8. Generally one expects that in nonlinear systems a random input to the problem would yield a change in the location and properties of a point of instability from the values of these quantities as predicted by averaged equations.

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