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INSTABILITIES IN CHEMICALLY REACTING MIXTURES

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1. **Introduction.** We shall study two different types of instability which arise in the theory of chemical and biochemical reactions [1], [2] and in the study of heat and mass transfer in porous catalysts [3], [4]. Peculiar physical effects involving local regions of oscillation and local instability (in a sense to be explained below) are observed experimentally. For each of the two different types of phenomena we believe that we have identified one possible mechanism for such occurrences.

In § 2 we shall show that the sudden transition to localized temporal oscillation is reflected in a special situation first observed by N. Levinson [5]. The underlying chemistry and mathematics is introduced via a very simple initial value problem for a model system of reaction equations. A singular perturbation analysis clearly reveals the structure of the solution and also the mechanism which governs the occurrence of the oscillatory instabilities.

In § 3 we consider the phenomenon of localized steady spatial oscillation for general reaction-diffusion equations. By combining singular perturbation and generalized WKB type methods we present a general technique for studying this type of phenomenon.

2. **The initial value problem for reaction equations.** We shall consider the system of "reaction" equations given by

$$u' = v, \tag{2.1}$$

$$v' = w, \tag{2.2}$$

$$\epsilon^2 w' = f'(v)w - v, \qquad (0 < \epsilon \ll 1), \tag{2.3}$$

where the "rate function" f whose derivative appears in (2.3) satisfies the following conditions:

H-1: $f(v)$ is continuously differentiable for all v,
H-2: $f(v)$ is odd, $f(v) > 0$ for $v > 0$, and $f(v) \to 0$ as $v \to \infty$.

Note that properties H-1 and H-2 imply that there exists positive constants M and λ such that

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$$|f(v)| \leqq M, \tag{2.4}$$

$$f'(v) < 0 \quad \text{for} \quad v > \lambda > 0. \tag{2.5}$$

A typical function $f(v)$ is illustrated in Figure 1.

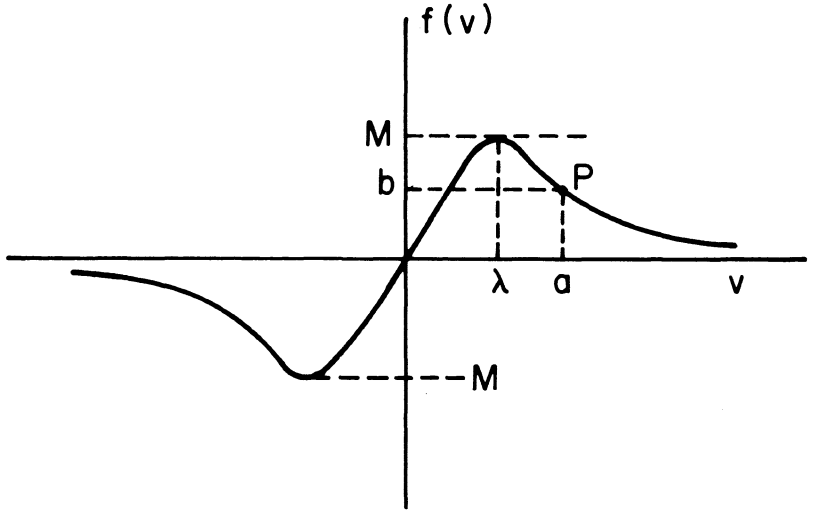

Fig. 1

The system (2.1)-(2.3) does not represent the kinetic equations for any known reaction. It is purely a mathematical model to illustrate the phenomena we shall derive. Nevertheless, as pointed out by Zhabotinsky and Zaikin [1] practically every kind of vector system of the form $\underline{X}' = \underline{F}(\underline{X})$ can be realized in a chemical system. Thus, our hope is that we have identified one type of possible functional dependence which controls the instabilities we discuss.

Upon eliminating v and w from the equations (2.1)-(2.3), we find that u satisfies

$$\epsilon^2 u''' - f'(u')u'' + u' = 0, \qquad (0 < \epsilon \ll 1). \tag{2.6}$$

Now, integrate once to find that u satisfies

$$\epsilon^2 u'' - f(u') + u = 0, \qquad (0 < \epsilon \ll 1). \tag{2.7}$$

We shall now study the initial value problem for (2.7) where f has the properties listed above and looks as illustrated in Figure 1. Levinson [5] studied the special case where $f(u') = 4u'/(3 + u'^4)$, and he pointed out that his result can be easily generalized for systems of

equations. Thus, our analysis here for the properties of solutions of (2.7) merely follows Levinson's ideas. Our goal is to go slightly further to investigate the bifurcation of the chemical instabilities.

We now consider the singularly perturbed initial value problem consisting of (2.7) and the initial values

$$u(0) = b = f(a), \tag{2.8}$$

$$u'(0) = a > \lambda. \tag{2.9}$$

Thus, point P in Figure 1 represents the initial values. If we assume that in some outer region (i.e., region where $\epsilon u''$ is negligible) the solution is given asymptotically by

$$u(t) \sim u_0(t) + \epsilon u_1(t) + \epsilon^2 u_2(t) + \cdots, \tag{2.10}$$

then clearly $u_0(t)$ satisfies the reduced problem

$$f(u_0') = u_0, \tag{2.11}$$

$$u_0(0) = b. \tag{2.12}$$

Note that the initial value $u_0'(0) = a$ is compatible with (2.12) and the equation (2.11) evaluated at $t = 0$. Thus, we examine the solution of (2.11) which starts with initial values $u_0{}^1(0) = a$, $u_0(0) = b = f(a)$. Since $u_0'(0) = a > 2$, the solution $u_0(t)$ increases from its initial value $u_0(0) = b$. Now, $f(v)$ is a decreasing function of v for increasing $v > \lambda$ so that when u_0 in (2.11) increases, u_0' must decrease. Thus, $u_0(t)$ increases with decreasing slope, and as $u_0(t) \to M -$, $u_0'(t) \to \lambda +$. Furthermore, $u_0(t)$ reaches the value M for a finite value of t, which we denote by t_1, because

$$t_1 = \int_0^{t_1} dt = \int_b^M \frac{du_0}{u_0'} < (1/\lambda) \int_b^M du_0 = (M - b)/\lambda. \tag{2.13}$$

Hence, $u_0(t_1) = M$ and $u_0'(t_1) = \lambda$. This solution *cannot* be continued beyond $t = t_1$ because if $u_0(t)$ were continued, it would have to increase since $u_0'(t_1) = \lambda > 0$. However, since $|f(u')| \leqq M$ for all real u, this is impossible. Therefore, we conclude that the solution $u_0(t)$ of the reduced problem exists only in the interval $0 \leqq t \leqq t_1$.

Let us now study the full problem (2.7)–(2.9). Obviously, fundamental existence and uniqueness theorems guarantee that the solution $u(t)$ is continuable from any finite values of u and u'. We shall see that $u(t)$ is very close to $u_0(t)$ for $0 \leqq t \leqq t_1$, and beyond the point $t = t_1$ the solution $u(t)$ goes into rapid oscillation of amplitude approximately M (actually increasing amplitude), and period $2\pi\epsilon$ as illustrated in Figure 2. The oscillatory part of the solution on $t > t_1$ can

be considered unstable since small changes in the initial conditions affect the phase.

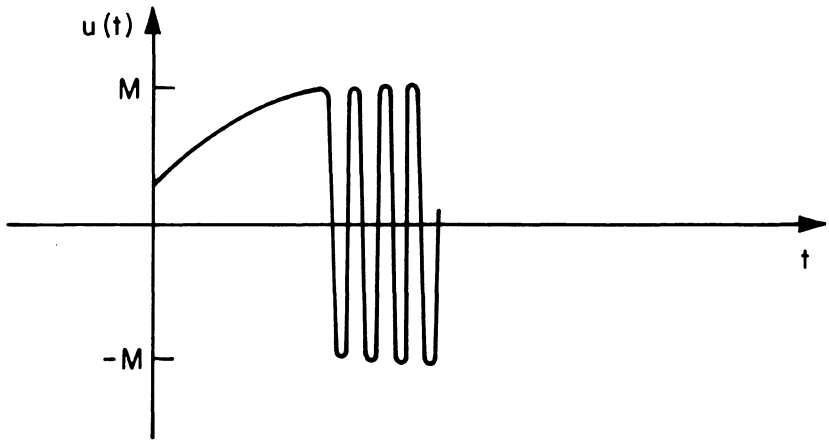

Fig. 2

In order to prove that $u(t)$ behaves as stated we shall study the (u, u') phase plane associated with (2.7). Let $v = u'$. Then (2.7) is equivalent to

$$\epsilon^2 v' = f(v) - v \tag{2.14}$$

$$u' = v \tag{2.15}$$

It will also be convenient to express (2.14) and (2.15) in polar coordinate variables r and θ given by

$$u = r\cos\theta, \qquad v = (1/\epsilon) r \sin\theta, \tag{2.16}$$

so that

$$r^2 = u^2 + \epsilon^2 v^2, \qquad \tan\theta = (\epsilon v/u). \tag{2.17}$$

In these variables equations (2.14), (2.15) become

$$\frac{dr^2}{dt} = 2vf(v) \gtreqless 0, \quad \frac{d\theta}{dt} = (1/\epsilon)\left(\frac{f(v)\cos\theta}{r} - 1\right). \tag{2.18}$$

Since $|f(v)| \leqq M$, we see that if $r > M$, then $d\theta/dt < 0$. This fact

together with the fact that $dr^2/dt \geqq 0$ implies that for $r > M$, a point (u, v) on the trajectory moves clockwise with r increasing. Now, the solution of our problem (2.7)–(2.9) starts at the point A of Figure 3 and proceeds along a trajectory from A to B very close to the curve $u = f(v)$. This is the part of the solution which is close to $u_0(t)$. Near point B the trajectory passes outside the ellipse $r^2 = u^2 + \epsilon^2 v^2 = M^2$. As we have just seen, for all points (u, v) outside the ellipse we have $dr^2/dt \geqq 0$, $d\theta/dt < 0$, and thus, once the trajectory reaches such a point it then moves clockwise with r increasing. Therefore, past point B (corresponding to $t > t_1$) the solution $u(t)$ of (2.7)–(2.9) represents an increasing oscillation. To prove that it is a rapid oscillation of amplitude approximately M for small ϵ and period $2\pi\epsilon$ requires certain precise estimates the details of which follow from the arguments in Levinson's paper [5].

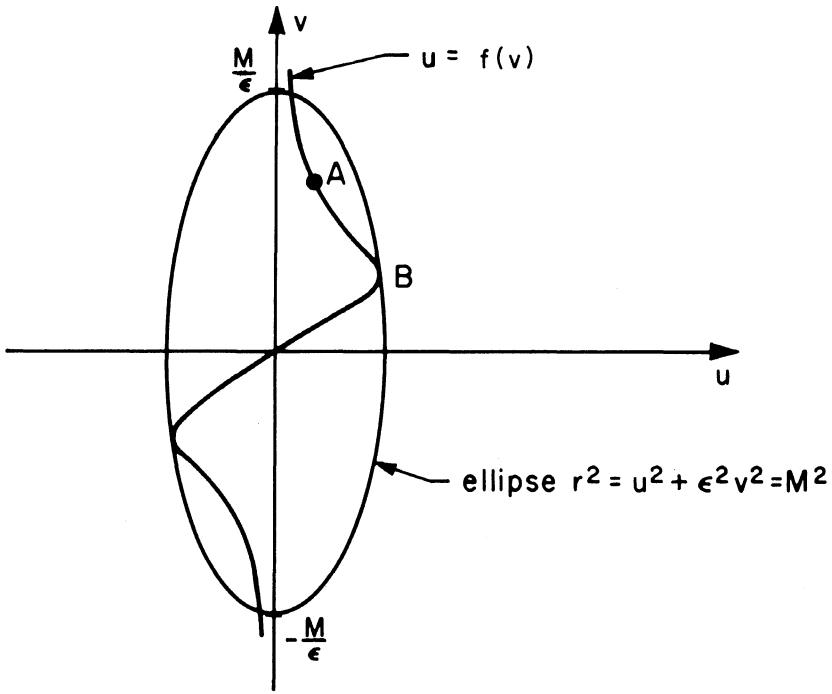

Fig. 3

To the author's knowledge, Levinson's paper [5] is the only study made of this type of situation, namely the case where the solution of the reduced problem does not exist on the entire domain where a solution of the original problem is sought. (It should be noted that this kind of problem is basically different from those involving relaxation oscillations, for example, where solutions of the reduced problem are discontinuous but nevertheless exist almost everywhere.)

We conclude that for the initial value problem involving the equations (2.1)–(2.3) an oscillatory instability is set up starting at time $t = t_1$. If we are interested in a shorter time interval (for example, if the reaction goes to completion before time $t = t_1$), then we observe only the stable situation represented by the solution before time $t = t_1$. Equation (2.13) provides us with a simple upper bound on t_1. A lower bound on t_1 can be established as follows: Since t_1 is the time to go from A to B in Figure 3, we have

$$t_1 = \int_0^{t_1} dt = \int_b^M \frac{du_0}{u_0'} > (1/a) \int_b^M du_0 = (M - b)/a.$$

Thus, if, for example, the reaction goes to completion before time $(M - b)/a$, then an unstable oscillation is not observed.

3. **Localized spatial instability.** We wish to account for situations whereby stable concentration and/or temperature profiles lose their stability via a localized spatial oscillation [1], [2]. Thus, before bifurcation the physical quantity U (chemical concentration or temperature) may look as illustrated in Figure 4, and after bifurcation (as a result of changing some parameter) the new stable state looks as illustrated in Figure 5. Our analysis which is generally applicable for reaction-diffusion equations with small diffusivities follows the method of J. A. Boa [6] and J. A. Boa and D. S. Cohen [7].

We consider an initial-boundary value problem involving the equations

$$U_t = \epsilon U_{xx} + F(x, U, V, \lambda), \tag{3.1}$$

$$V_t = \theta\epsilon V_{xx} + G(x, U, V, \lambda). \tag{3.2}$$

Here $0 < \epsilon \ll 1$, $\theta = O(1)$ in ϵ, and the equations are to be solved in the region $t \geqq 0$, $0 \leqq x \leqq 1$. The problem is to be completed with the specification of arbitrary initial conditions and standard linear boundary conditions (i.e., Dirichlet, Neumann, or Robin conditions on U and V at $x = 0$ and $x = 1$). The nonlinearities F and G are usually smooth positive functions containing the parameter λ.

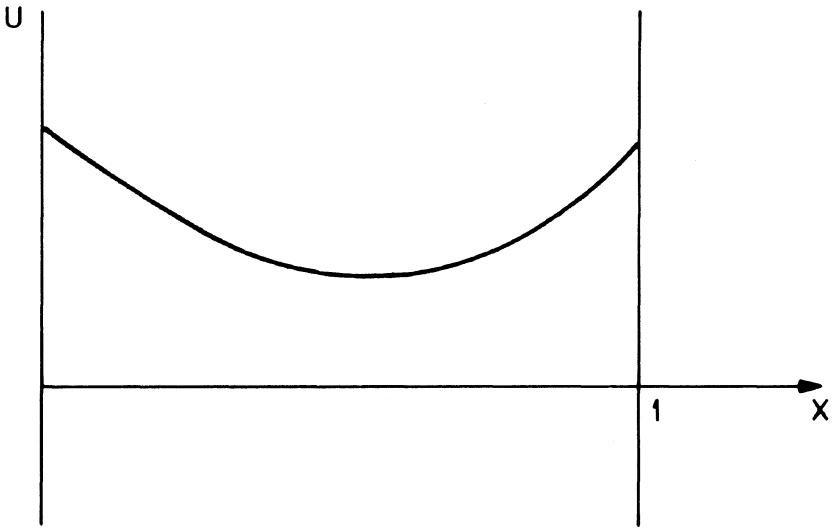

Fig. 4

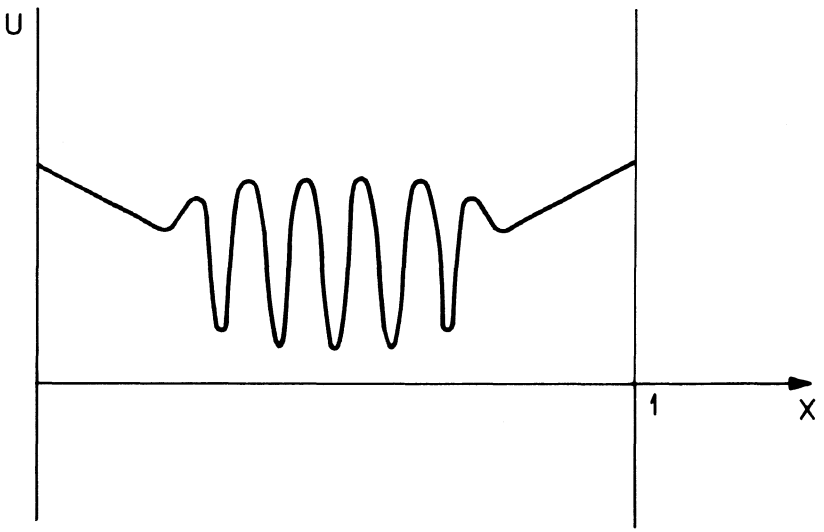

Fig. 5

Suppose that we can find a (not necessarily unique) steady state solution

$$U = U_0(x, \lambda), \qquad V = V_0(x, \lambda). \tag{3.3}$$

(In general, U_0 and V_0 will have to be constructed by singular perturbation methods. For the purposes of the present study we simply assume that we know U_0 and V_0 by some technique.) We now wish to study the stability of the steady state U_0, V_0 as a result of varying λ. First we carry out a standard linearized stability analysis. Hence, we consider the problem with initial conditions which are small perturbations of U_0 and V_0 and study the perturbations $u(x, t)$ and $v(x, t)$ to see whether or not they die out or grow in time. In the usual way we find that the perturbations u and v satisfy the linear equations

$$u_t = \epsilon u_{xx} + F_U(x, U_0, V_0, \lambda)u + F_V(x, U_0, V_0, \lambda)v, \tag{3.4}$$

$$v_t = \theta\epsilon v_{xx} + G_U(x, U_0, V_0, \lambda)u + G_V(x, U_0, V_0, \lambda)v. \tag{3.5}$$

By the standard separation of variable methods we know that the solution of (3.4), (3.5) is given by

$$\begin{pmatrix} u \\ v \end{pmatrix} = \sum_n c_n e^{\sigma_n t} \begin{pmatrix} \phi_n \\ \psi_n \end{pmatrix}, \tag{3.6}$$

where the σ_n and (ϕ_n, ψ_n) are the eigenvalues and eigenfunctions of

$$\sigma\phi = \epsilon\phi'' + F_U(x, U_0, V_0, \lambda)\phi + F_V(x, U_0, V_0, \lambda)\psi, \tag{3.7}$$

$$\sigma\psi = \theta\epsilon\psi'' + G_U(x, U_0, V_0, \lambda)\phi + G_V(x, U_0, V_0, \lambda)\psi. \tag{3.8}$$

Here, of course, the ϕ and ψ are subject to the same boundary conditions as U and V respectively. Hence, in the usual way we conclude that the steady state U_0, V_0 is stable if all eigenvalues are such that $\mathrm{Re}\{\sigma_n\} < 0$ and unstable if there is at least one σ_k such that $\mathrm{Re}\{\sigma_k\} > 0$.

Clearly, all eigenvalues σ_k depend on λ, and the stability boundary $\lambda = \lambda_0$ is determined by $\sigma_j(\lambda) = 0$ where σ_j is the first eigenvalue whose real part changes sign. As we cross the stability boundary, we expect the new state (i.e., the bifurcated solution or new branch) to be proportional to the eigenfunction corresponding to the eigenvalue whose real part changes sign. Thus, the new state will for small $\lambda - \lambda_0$ look like this eigenfunction, and since (3.7), (3.8) will not be self-adjoint in general, then this eigenfunction can contain many internal zeros. Therefore, in order to determine the structure of the bifurcating solution we study (3.7), (3.8) *at the stability boundary* for small ϵ. This is not a singular perturbation problem. However, in

analogy with the WKB method for single equations we expect that for small ϵ solutions of (3.7), (3.8) exist in the form

$$(3.9)\quad \begin{pmatrix} \phi \\ \psi \end{pmatrix} = e^{iw(x)/\epsilon}\left[\begin{pmatrix} \phi_0 \\ \psi_0 \end{pmatrix} + \sqrt{\epsilon}\begin{pmatrix} \phi_1 \\ \psi_1 \end{pmatrix} + \epsilon\begin{pmatrix} \phi_2 \\ \psi_2 \end{pmatrix} + \cdots\right].$$

Upon substituting (3.9) into (3.7), (3.8) and equating like powers of ϵ, we first find the equation for $w(x)$ which is analogous to the eikonal equation of geometrical optics. For many of the rate functions F and G corresponding to various chemical and biochemical reactions the equation for w possesses real solutions only on subintervals of $0 \leqq x \leqq 1$ and complex solutions elsewhere. The points of which the solutions change from real to complex are called turning points. The mechanism for localized oscillation is now clear; namely on one side of a turning point the solution will be real (exponentially decaying) while on the other side of the turning point the solution will be oscillatory (in space). Thus, the bifurcated solution has the structure sketched in Figure 5. WKB type connection formulae (analogous to the usual Airy function formulae) can be worked out to join the decaying parts to the oscillatory parts.

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