DISCUSSION PAPER: BIFURCATIONS AND PERTURBED ATTRACTORS IN PHYSICOCHEMICAL SYSTEMS

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The Search for and Extension of Elementary Attractors

As a concrete example for discussion let us consider a reacting diffusing system. We introduce an N dimensional column vector: Ψ of concentrations which is taken to obey the continuity equation

$$\frac{\partial \Psi}{\partial t} = \mathfrak{D} \nabla^2 \Psi + \mathfrak{F} [\Psi] \quad (1)$$

where $\mathfrak{D}$ and $\mathfrak{F}$ are the matrix of diffusion coefficients and column vector of chemical rates, respectively. One approach that has been used to analyze this prototype equation is to seek various attracting subspaces in the N-dimensional concentration space embedded in the rate law $\mathfrak{F} [\Psi]$.

Consider the associated ordinary differential equation to (**1**) corresponding to homogeneous evolution $\Psi_h(t)$,

$$\frac{\mathrm{d}\Psi_h}{\mathrm{d}t} = \mathfrak{F} [\Psi_h]. \quad (2)$$

Let M be the dimension of the attracting subspace. Examples of attracting subspaces are the stable steady state ($M = 0$), the limit cycle ($M = 1$) and the invarient torus ($M = 2$). Orbits within the M dimensional subspace may by definition be determined by M characteristic parameters $\zeta = \{\zeta_1, \zeta_2, \ldots, \zeta_M\}$. In the absence of diffusion, $\mathfrak{D} = 0$, it is clear that there are inhomogeneous solutions with the parameters ζ_i varying from point to point. The question then arises regarding the possibility of new phenomena due to the presence of "weak diffusion" such that at each point $\underline{r}$, Ψ is close to some point on the attractor $\mathfrak{A}$ embedded in (**2**). This concept has been applied for limit cycles using the method of constrained coordinates,[1-3] singular perturbation theory for plane waves,[3] frequency renormalization for periodic solutions[3] and multiple time scales[4] and integral equations.[5] We adopt a multiple time scale procedure here since it appears to be the most elegant and contains the flexibility afforded by most of the other procedures.

A complete weak diffusion picture involves the consideration of appropriate lengths to scale the effect of diffusion. We introduce a characteristic diffusion coefficient D_c and a reaction time T_c and let $\mathfrak{D} = D_c D$ and $\mathfrak{F} = T_c^{-1} F$. With this we may construct the characteristic reaction-diffusion length L_c such that $L_c^2 \equiv D_c T_c$. Now we may rewrite (**1**) in scaled form by using dimensionless time

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$t'(t = T_c t')$ and position $\underline{r}'(\underline{r} = L\underline{r}')$ for a class of phenomena varying in space on a scale L. With this we obtain (letting ∇^2 denote the Laplacian with respect to $\underline{r}'$)

$$\frac{\partial \Psi}{\partial t'} = \epsilon D \nabla^2 \Psi + F[\Psi], \tag{3}$$

where the length scale ratio ϵ is defined by

$$\epsilon = (L_c/L)^2. \tag{4}$$

With such a scaling argument the quantity ϵ presents itself as a natural smallness parameter, which may be used to develop asymptotic solutions for weakly inhomogeneous phenomena, $\epsilon \ll 1$. The key assumption is that the *only* length scale in the solution is L (an ansatz that is known to breakdown in certain wave and multiple scale phenomena[7]).

To properly carry out such a procedure we must recognize that even within the context of the assumption that the class of phenomena is on one (long) length scale, we must be able to account for many possible time scales. This manifests itself, for example, in the wavevector dependence of the frequency (dispersion relation) for plane chemical waves.[1-5] Thus we introduce a sequence of time scales τ_n such that $\tau_n = \epsilon^n t'$. If the attractor $\mathcal{Q}$ is to characterize the solutions as $\epsilon \to 0$ then the spatio-temporal extensions of the characteristic parameters ζ_i must only vary on the slower times τ_n, $n \geq 1$. Otherwise the leading term $\Psi_{(0)}$ in Ψ in an expansion of the form

$$\Psi = \sum_{n=0}^{\infty} \Psi_{(n)} \epsilon^n \tag{5}$$

will not obey the scaled homogeneous equation

$$\partial \Psi_{(0)} / \partial \tau_0 = F[\Psi_0], \tag{6}$$

guaranteeing that $\Psi_{(0)}$ is on $\mathcal{Q}$. Denoting an arbitrary orbit on the attractor as $\phi(\tau, \zeta)$, where again ζ are the parameters fixing the orbit, we have $\Psi_{(0)} = \phi(\tau_0, \zeta_0)$ to lowest order.

To first order in ϵ one obtains (making developments for ζ similar to that in (5)

$$L \Psi_{(1)} = D \nabla^2 \Psi_{(0)} - \partial \Psi_{(0)} / \partial \tau_1, \tag{7}$$

where the linear operator L is $\partial/\partial \tau_0 - \Omega(\Psi_{(0)})$ and $\Omega(\Psi)$ is $\partial F / \partial \Psi$. Both terms on the RHS of (7) are not zero since $\Psi_{(0)}$ implicitly depends on $\tau_{n \geq 1}$ and $\underline{r}'$ via the characteristic parameters $\zeta(\underline{r}', \tau_1, \tau_2, \ldots)$, e.g.,

$$\partial \Psi_{(0)} / \partial \tau_1 = \sum_{i=1}^{M} \left(\frac{\partial \phi}{\partial \zeta_{(0)i}} \right) \frac{\partial \zeta_{(0)i}}{\partial \tau_1}, \tag{8}$$

and similarly for $D \nabla^2 \Psi_{(0)}$. A key observation that one now must make is that the quantities $\partial \Psi_{(0)} / \partial \zeta_{(0)j}$ are in the null space of the operator L (as can be easily seen by taking the derivative of (6) with respect to $\zeta_{(0)j}$). Thus in order that (7) may be solved the RHS must be orthogonal to this null space. This introduces M

orthogonality conditions, which are indeed partial differential equations for $\zeta_{(0)}$. This program has been carried out successfully for the case of the limit cycle[4] (a one dimensional attractor). For the limit cycle the single parameter ζ is the phase of the oscillation. The theory has been used to study a variety of wave phenomena in systems with a homogeneous oscillation.[1-5] The theory has also been applied to multiply periodic attractors such as the invarient torus ($M = 2$).[6]

The Polarator—A Soluble Model of Multiply Periodic Spatio-Temporal Evolution

A class of three variable model systems has been introduced to which exact multiply periodic spatio-temporal solutions have been found.[6] It demonstrates some of the general features of certain multiple dimension ($M \geq 2$) attractors, i.e., the existence of multiparameter families of solutions. Consider the polar variables R, θ, ϕ to evolve according to the homogeneous dynamics $\dot{R} = RB(R)$, $\dot{\theta} = T(R)$, $\dot{\phi} = P(R)$ ($\cdot \equiv d/dt$). A model reacting-diffusing system has been constructed by transforming to Cartesian variables ($X = R \sin\theta \cos\phi$, $Y = R \sin\theta \sin\phi$, $Z = R \cos\theta$) and letting the "chemical species" X, Y, Z also diffuse via Fick's law. Exact solutions of these reaction diffusion equations have been presented. For example in the case where the diffusion coefficients of X, Y, and Z are all equal one may show that solutions of the form of two copropagating waves with different frequencies. In this case $X(r,t)$ (r being the spatial coordinate for a one dimensional infinite system) takes the form

$$X(r,t) = \tfrac{1}{2}R_k[\sin(\alpha_+ + w_+t + kr) + \sin(\alpha_- + w_-t + kr)],$$

where $\alpha_\pm$ are constant phases, $w_\pm(k^2) = T(R_k) \pm P(R_k)$ and R_k is the solution of $B(R_k) = k^2D$, D being the diffusion coefficient. This phenomena represents a two parameter family $(k, \alpha_+ - \alpha_-)$ of solutions, corresponding to the fact that the system has a 2-dimensional multiply periodic attractor (the sphere at $B(R) = 0$) in the homogeneous kinetics. (There is, of course, a third trivial parameter corresponding to the translational invarience of space.)

Chaotic Attractors

For a chaotic attractor (see several articles in this volume) trajectories for homogeneous evolution on the attractor which initially differ by an arbitrarily small amount separate to a distance of order of the dimensions of the attractor as $t \to \infty$. Hence the derivatives such as $\partial\phi/\partial\zeta_{(0)i}$ for some ζ_i (the "secular characteristic parameters") that appear in the theory become unbounded as $\tau_0 \to \infty$. Thus if we are to have weakly inhomogeneous extensions then these ζ_{0i} must be constant since the slow times $\tau_{n\geq 1}$ cannot keep up with τ_0. Alternatively, the weakly distorted attractor pictures must be modified for chaotic attractors. For "weakly chaotic" attractors, where the separation of nearby orbits occurs on a slow time scale, then weakly inhomogeneous solutions might be constructed as bifurcations. Thus consider systems such that as a parameter of the homogeneous kinetics F is varied multiply periodic orbits become chaotic with the time scale for the separation of initially close orbits that diverges as this parameter passes through a critical value, multiple periodicity bifurcating to weak chaos. In this case a bifurcation analysis for inhomogeneous evolution may be possible. This approach is presently being investigated.

For chaotic attractors which do not arise as a continuous bifurcation from multiple periodicity to weak chaos, a weakly perturbed attractor class of solutions for persistent spatio-temporal evolution with nonconstant secular characteristic parameters does not seem possible. In this case steep spatial gradients will build up and jumping from segment to segment of the chaotic attractor seems iminent. This would lead to the possibility of rapidly propagating transition layers for systems such as the Lorenz attractor where the time scale to relax to the attractor is much shorter than that of the evolution within it for certain ranges of parameters. Clearly inhomogeneous phenomena in systems with chaotic attractors are yet to be well understood and present themselves as interesting and challenging problems.

Catastrophe Theory and Jumping Between Kinetic Behavior Surfaces

The characteristic length and time scales embedded in a phenomonological continuity equation such as (1) may vary over several orders of magnitude. For example let the first f species in the column vector Ψ participate in a sequence of reactions that occur on a time scale t_f that is much shorter than the characteristic time $\overline{T}$ of all other reactions. We may make this fact explicit by writing

$$\mathfrak{F} = \epsilon^{-H} F_s, \quad \epsilon \equiv t_f/\overline{T} \ll 1, \tag{9}$$

where F_s contains only slow time scale processes (i.e., rate parameters of order $\epsilon^0 = 1$ in the time scale ratio ϵ. The diagonal matrix H has all elements zero except the first f elements, which are for simplicity all unity. With this (9) becomes

$$\frac{\partial \Psi}{\partial t} = \mathfrak{D} \nabla^2 \Psi + \epsilon^{-H} F_s[\Psi]. \tag{10}$$

For small ϵ it is clear that Ψ must either (1) vary rapidly in space or time or (2) Ψ must lie near one of the attracting intersections of the "behavior surfaces"

$$F_{s,i}[\Psi] = 0, \quad i = 1, 2, \ldots f$$

in concentration (Ψ) phase space. Thus the spatio-temporal evolution of the system consists of a finite or infinite sequence of rapid transitions between attracting branches of the intersection of the surfaces $F_{s,i} = 0$ separating smooth space-time variations on these intersections.

The question immediately arises as to how we may make general classifications of the phenomena that can occur in such systems. First we must be able to categorize the general topologies of these behavior surfaces and a start in this direction has been made using catastrophe theory.[7] Next we must be able to construct solutions to the problem in both the rapidly varying jumps between branches of the behavior surface and the constrained evolution lying on points in phase (Ψ) space near the attracting branches of the behavior surface. The technique of matched asymptotic expansions has been used to study these phenomena in reaction diffusion systems by a number of authors (see the citations in Reference 7).

Preliminary work combining catastrophe theory and matched asymptotic techniques to classify and predict phenomena appears to be a very promising direction in the future. From the preliminary studies[7] it is clear that for one fast variable ($f = 1$) and four or fewer slow variables ($N \leq 5$) that the four cuspoid catastrophes of Thom characterize all the basic features that can arise on the behavior surface. Some results for multiple fast variables, $f \geq 2$, have been obtained using the umbilic catastrophies. The approach thus far has led to the classification or discovery of a variety of propagating chemical wave phenomena such as the pulse, the finite train of pulses, the single jump pulse with smooth return, front multiplicity, wave train encroachment, and a variety of other phenomena (details and references are to be found in Reference 7).

Diffusional Behavior Surfaces

Multiple scales in diffusion are not uncommon. Let this be emphasized, for example, by introducing a factor $\epsilon^{\tilde{H}}$ ($\tilde{H}$ is similar in structure to H of the previous section) in the diffusion matrix, $\mathfrak{D} = \epsilon^{\tilde{H}}\tilde{D}$, where all the elements in $\tilde{D}$ are of order unity in ϵ and by proper choice of Ψ we can take $\tilde{D}$ to be diagonal. With this (1) becomes

$$\frac{\partial \Psi}{\partial t} = \epsilon^{\tilde{H}}\tilde{D}\nabla^2\Psi + \mathfrak{F}[\Psi]. \tag{11}$$

It is assumed that there is only one time scale in $\mathfrak{F}$.

A consideration of steady states $\Psi^*(\underline{r})$ in such systems shows how multiple diffusion scales ($\epsilon \rightarrow 0$) bring out "diffusional behavior surfaces" in $\mathfrak{F}$. Multiplying (11) by $\epsilon^{-\tilde{H}}$ and noting that Ψ^* is independent of time we obtain

$$\tilde{D}\nabla^2\Psi^* + \epsilon^{-\tilde{H}}\,\mathfrak{F} = 0. \tag{12}$$

Clearly as $\epsilon \rightarrow 0$ the spatial profile $\Psi^*(\underline{r})$ either varies rapidly in space or lies on attracting branches of the diffusional behavior surfaces

$$\mathfrak{F}_i[\Psi] = 0, \quad i = 1, 2, \ldots d, \tag{13}$$

for the d species $i = 1, 2, \ldots d$ with small diffusion coefficients $\epsilon\tilde{D}_i$. Here, as in the case of multiple time scales discussed in the previous section, a combined program of catastrophe theory and matched asymptotic expansions has been suggested.[7] A very complete and elegant treatment of the multiple diffusion approach for two species ($N = 2$) systems has been carried out by Fife who also considered the possibility of simultaneous multiple scaling of diffusion and rate processes.[7] The combined program of catastrophe theory and matched asymptotic expansions for classification or prediction of qualitatively new of phenomena is certain to unfold a great richness of possibilities.

BIFURCATION FROM UNSTABLE SUBSPACES

Bifurcation theory has been used in the study of the onset of new states that arise when one state of the system loses its stability. Indeed many beautiful examples of this have been given in this conference. The possibility of bifurcation of new states from unstable states of physicochemical systems brings about a variety of interesting phenomena. For example the loss of stability of an oscillatory system has been considered.[3] When one or more of the Floquet exponents (that determine the stability of the limit cycle to small inhomogeneous perturbations) has a real part that transverses the origin, new inhomogeneous and possibly aperiodic states of evolution may arise. In this context it would be interesting to develop these ideas for the bifurcation from more complex states such as similarly weakly unstable aperiodic or chaotic subspaces.

PADÉ APPROXIMANTS AND CENTER WAVES

Recently it has been shown that Padé approximants may be used to construct center waves (circular and spiral) that are either periodic or *aperiodic.*[13] The scheme involves a well-defined ordering scheme for coupling the wave center (core) to the plane-wave-like outer regions. The parameters of the Padé's are generated as solutions of simple differential equations.

SELECTED PHYSICOCHEMICAL BIFURCATIONS

Perhaps it would be of interest to point out a number of physicochemical phenomena which have not received a great deal of attention in the context of bifurcation theories.

Insect Flight. Many insects (for example flies) have a wing beat rate that exceeds the maximum nerve repetitive firing rate. Thus the individual wing beats cannot be triggered by individual nervous signals. However, it is known that the wing-thorax system is to a good approximation, a damped oscillator with a frequency of the correct order of magnitude. Furthermore flight muscle has the interesting property that when stretched it tends to contract (in excess of the elastic force!) presumably due to the contraction chemical kinetics. Using a simple model of a damped oscillator coupled to a simple contractile chemical kinetics it has been shown that such a system can enter a state of auto-oscillation.[4]

Fucus Egg Symmetry Breaking. In the very beautiful experiments of Jaffe and others it has been shown that the state of spherically symmetric membrane potential makes a transition to an asymmetric state with a net north-south polarity. This is believed to be the essence of the asymmetric cell differentiation responsible for the root/leaf differentiation that characterizes the subsequent biomorphogenesis. Introducing a set of electrophysiological equations and a simple model it has been shown that the polarized states may bifurcate from the spherically symmetric solutions.[8]

Spontaneous Pattern Formation in Precipitating Systems. It has been shown experimentally that the state of uniform precipitation from a supersaturated phase may spontaneously make a symmetry breaking (pattern forming) transition.[9,10] A simple theory based on diffusion and the competition of small and large particles for the growth material has been presented and describes many of the features of this phenomena.[10]

Nonlinear Phenomena at Local Sites of Reaction. It has become clear that a great variety of phenomena (including multiple states, oscillations, propagating waves and chaotic evolution) may occur in reacting diffusing systems with bulk kinetics. Studies on systems where reactions are localized to membranes or catalytic walls have indicated that this variety also exists in systems with heterogeneous kinetics.[11] When many local sites are present cooperative phenomena, in analogy to equilibrium phase transitions, may arise.[11] The description of these systems may often be reduced to sets of coupled nonlinear integral equations. Many of the mathematical methods used to describe nonlinear phenomena in systems with homogeneous kinetics, including bifurcation and attractor perturbation theory, have been applied to the analysis of these systems.[4]

Electrochemical Waves. In the best known example of chemical wave propagation, the Belousov-Zaikin-Zhaboutinsky reaction, most important chemical species are ionic yet the strong tendency toward charge neutrality that couples ionic motions has been neglected in most theories of these waves. Recently full account of the electrochemical nature of chemical waves in ionic media has been taken.[12] It has been shown that, in the presence of imposed fields, chemical waves in such media can be forced to remain stationary and even breakdown, making a transition to qualitatively new modes of wave propagation.[12]

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