

MATHEMATISCHES FORSCHUNGSINSTITUT OBERWOLFACH

T a g u n g s b e r i c h t 29/1987

Mathematical Problems of Chemical Processes

5.7. bis 11.7.1987

Organizers: R. Aris, Minneapolis
P. C. Fife, Tucson

The participants assembled in the afternoon and evening of July 5, a few arriving early on the 6th. Those who had been to an Oberwolfach Conference before were uniformly delighted to be back and impressed on those who were here for the first time the excellence of the arrangements even though this was immediately clear to them. Of these "first-timers" there was a good proportion since this was the first time for the subject of mathematical problems arising very generally from chemistry and chemical engineering. There was a good mix between those who were primarily concerned with experimental studies and the mathematicians and others preoccupied with theory and modelling. This developed into a useful interaction for, not only was the level of sophistication in experimental measurement very high, but the methods of data analysis were equally advanced and computed derived quantities (power spectra, maximal Lyapounov exponents, etc.) which related the experiment rather immediately to the theoretical concepts and outlook of the mathematicians.

The diversity of interest at first sight presented a problem of time-talk arrangement to the organizers but certain coherent groupings began to emerge. For example,

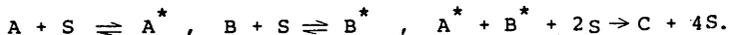
several speakers were concerned with problems involving diffusion and reaction and, though these were as diverse as dyeing and dead cores, they fitted together with a problem in combustion in which diffusion played a major role (Wednesday morning). Though there was a further problem in diffusion and reaction (Needham's) which would have fitted in here, it was linked to a discussion of oscillatory reactions in closed systems by being concerned with a closely similar chemical system (Scott's) and so these two formed a natural pair for an afternoon session. A group of four papers on combustion problems emerged as did another concerned with catalytic reactions. Wicke's presentation of his results on chaos in a reactor for the oxidation of carbon monoxide formed an admirable introduction to the latter and itself linked with Schneider's discussion of the distinction between deterministic chaos and amplified noise. Thus the following program evolved (to which the abstracts compiled by Hr. Heinze are appended): The sessions were well-attended and, with very few exceptions, provoked good discussing. Many other conversations took place on more specific topics.

Vortragsauszüge

Rutherford Aris

Aspects of Forced Oscillations in a Chemically Motivated System

A possible model for catalytic oxidation and other reactions is



This leads to a pair of differential equations for x and y the fractional average of the surface by A and B resp.

$$\begin{aligned} \dot{x} &= \alpha_1(1-x-y) - \gamma_1 x - xy(1-x-y)^2 \\ \dot{y} &= \alpha_2(1-x-y) - \gamma_2 y - xy(1-x-y)^2 \end{aligned}$$

where α_1 and α_2 are the dimensionless partial pressures of the reactant, and γ_1 and γ_2 are desorption constants. The autonomous behaviour of this system is discussed and a set of conditions in which there is a unique unstable steady state and a limit cycle. With $\bar{\alpha}_2$, the mean of α_2 , held in this region a resonance diagram in the plane of A und ω , where $\alpha_2 = \bar{\alpha}_2 + A \sin \omega t$, is described.

Thor A. Bak

Coagulation and Fragmentation Reactions in Infinitely Large Systems

I study a model for reversible aggregation in which all molecules (aggregates) are composed of the same kind of monomeric units, which are assumed to have f reactive sites. The rateconstant for coagulation between an i -mer

and a j -mer, K_{ij} is taken to be proportional to $\sigma_i \sigma_j$, where σ_k is the number of free reactive sites on a k -mer. The rateconstant for fragmentation of an $(i+j)$ -mer into an i -mer and a j -mer is λF_{ij} , where λ is a parameter which measures the relative strength of fragmentation and coagulation and F_{ij} is determined using detailed balance, K_{ij} and the equilibrium concentration C_k^{eq} , which is determined by a combinatorial argument.

It is shown that starting from pure monomer in an infinite system, $C_k(t)$ does not go to equilibrium as $t \rightarrow \infty$, unless λ is sufficiently large. Rather a state for which $\sum k^2 C_k$ diverges is reached in finite time. Corresponding to this the relaxation time for approach to equilibrium from a nearby state goes to infinity as $\lambda \rightarrow 0$.

This work was done in collaboration with Lu Bing Lin, Fushun Petroleum Institute, Liaoning, China.

Erich Bohl

Degradation of matter in anaerobic microbial ecosystems

A model for syntrophic associations between H_2 -producing acetogenic bacteria and H_2 -utilizing bacteria was presented. On a general basis for the ratefunctions the bifurcation diagram was developed. In a special case global convergence results were given. In general the local stability analysis at the steady states was discussed. Under certain inhibitory effects of the substrats and products on the bacteria populations involved the system can undergo hysteresis loops. In the region of bistability the second organism can be washed out of the system due to fluctuations. As a result degradation stops and the first organism cannot grow anymore.

Bruce Clarke

Extreme Currents in Chemical Network Theory

This talk would be basic "stoichiometric network analysis" as published in Advanced in Chemical Physics volume 43 (1980), but with more recent work as well. I would derive the general equation of motion for nonlinear stoichiometric systems and explain how it applies to many areas: the manifold of steady states, stability analysis, Lyapunov functions, sensitivity analysis, qualitative dynamics, mechanistic basis of instabilities.

Fritz Colonius

On Optimal Periodic Control of a CSTR near a Hopf Bifurcation Point

We analyse a simple model of a CSTR and ask, if it is possible to increase the average output by introducing (small) oscillations in the coolant flow rate and the states. It turns out that near a Hopf bifurcation point this is possible provided that the free periodic motion gives a (second order) direction of increase and a certain controllability condition holds.

J.W. Dold

Characterising Reaction Runaway

For sufficiently nonlinear reaction-rate functions $R(\phi)$ the equation $\dot{\phi} = v^2 \phi + R(\phi)$ (*) can lead to reaction runaway behaviour, for which $\phi(\underline{0}, t_I) = \infty$, $\phi(\underline{r}, t_I) < \infty$ for $\underline{r} \neq \underline{0}$ and $\phi(\underline{r}, t) < \infty$ for $t < t_I$. An additional physically sensible constraint is that ϕ should be bounded from below, $\phi > d > -\infty$. Local analysis of the runaway process shows that blowup has an asymptotic description as $(\underline{r}, t) \rightarrow (\underline{0}, t_I)$ of the form

$$\int_{\phi}^{\infty} \frac{d\phi}{R(\phi)} = t_I - t + A \frac{x^2/4}{\alpha + \xi} + \frac{y^2/4}{b + \xi} + \frac{z^2/4}{\gamma + \xi}$$

where $\xi = -\ln(t_I - t)$, $A = 1$ for $R = e^{\phi}$, $A = \frac{\mu-1}{\mu}$ for $R = \phi^{\mu}$ (with $\mu > 1$) and the constants $\alpha, \beta, \gamma \in \mathbb{R} \cup \{\infty\}$ are measures of supercriticality. This result contrasts with the expectation of similitude analysis that

$$\phi = f(t) + g(r/\sqrt{t_I - t}).$$

Conjecture (confirmed by numerical analysis and proven in some cases by J. Bebernes and W. Troy, A. Lacey): equation (*) possesses no solution of the form

$\phi = f(t) + g(r/\sqrt{t_I - t})$ which is bounded from below as $t \rightarrow t_I$. However, it is found that a boundary-layer ignition equation, $r\phi_t = \phi_{rr} + e^{\phi}$ does possess a realistic solution of the similarity form

$$\phi = -\frac{2}{3} \ln(t_I - t) + g(r/\sqrt[3]{t_I - t}).$$

This raises the question: For what class of convective functions $v(r)$ does the equation $v(\underline{r})\phi_t = \nabla^2 \phi + R(\phi)$, with ϕ bounded from below, possess a local description of blowup which takes the similitude form. It seems that $v = |\underline{r}|^{\sigma}$ as $r \rightarrow 0$ for $\sigma > 0$ falls within this class.

Andreas Dress

Some phenomenological models for oscillating catalytic processes on metal surfaces

A model of an ideal storage system is proposed in terms of the two equations

$$B(u+1) = B(u) + C - A(u) \cdot B(u)$$

$$A(u+1) = F(A(u) \cdot B(u)),$$

a discrete dynamical system in two variables A and B , where C is a positive control parameter and F is a monotonously increasing function, defined on the positive real numbers, with values in the open unit interval.

From the mathematical analysis of this model it follows that oscillations on catalytic surfaces could be understood as arising from a feed back mechanism, by which the "reactivity" A of the system is coupled in a monotonously increasing fashion to the fraction AB of reacting substance coming from the stored amount B of substance, while the storage is continuously refilled by a constant amount C .

In addition, peculiar dynamic features arising from coupling such systems in form of a cellular automaton are discussed.

Henrik Farkas

Use of Generalized Lotka-Volterra schemes in Modelling of the BZ-reaction

To modelize oscillatory chemical reactions, the Lotka-Volterra model is a good starting point. Its most serious shortcoming is that it provides "conservative" oscillations. To get limit cycle oscillation one should increase the complexity of the model. This can be accomplished by using more complex kinetics or increasing the dimension (Brusselator and three-dimensional Explodator resp.). We have constructed two-dimensional explodator cores from generalized Lotka-Volterra schemes. The generalized scheme contains five independent parameters, and includes stable, explosive and conservative systems.

Martin Feinberg

Chemical Reaction Network Structure and Multiple Steady States in Complex Isothermal CFSTRs

For isothermal continuous flow stirred tank reactors (CFSTRs), the steady states are determined by large sys-

tems of polynomial equations in many variables (the species concentrations in the reaction vessel). These equations contain many parameters (e. g., the residence time, the reaction rate constants, and the concentrations of the species in the feed stream). The polynomials themselves are determined (up to parameter values) by the underlying network of chemical reactions.

For a specified reaction network we can ask whether there are parameter values such that the corresponding steady state equations admit (at least) two distinct solutions for which all the species concentrations are positive. This question is generally difficult, but for many networks (even very intricate one) it can now be answered almost immediately. From the reaction network, one constructs a graph called the species-complex-linkage graph, which often carries decisive information about the possibility of multiple steady states. The determination is quite simple and can be taught to people with little mathematical training.

Paul C. Fife

Modeling complex chemistry in flames

Flames are exceedingly complex structures. The chemistry, in particular, is highly involved in most flames. It is important to be able, if possible, to rationally simplify known complex chemical networks to manageable proportions. This talk describes progress in developing a systematic procedure for doing this. The basic unknown quantities are average concentration levels in the reaction zone being studied, average reaction rates, and the allocation vector for the combustion process. The problem is formulated as finding solutions of a set of linear inequalities among the parameters. The procedure has been implemented for the H_2-O_2 network.

Marek Frankowicz

**Transient Evolution of Nonlinear Dynamical Systems:
Stochastic Approach**

The transient evolution of dynamical systems with well-separated time scales is studied. Several classes of models are considered: quadratic, cubic and cosine rate laws, thermal explosion. It is shown that stochastic effects due to distributed initial conditions, internal fluctuations, and/or external noises, can lead to the appearance of long tails or transient multimodality in the probability distribution. The differences between the stochasticity introduced by the spread in initial conditions and that caused by the effects of fluctuations during the evolution are pointed out. The possible applications in chemistry, biology and metallurgy are discussed.

Robert A. Gardner

Mach Stem Formation in Reacting Shock Fronts

We discuss a model equation which is used to predict the onset of Mach stem formation in planar detonation wave solutions of the equations of reactive gas dynamics.

Martin Gerhardt

A Cellular Automaton as a Description of Locally Interacting Processes in Heterogeneous Catalytic Systems

The dynamics of the oxidation of carbon monoxide, heterogeneously catalyzed by Palladium particles incorporated in

a zeolite matrix is described by a discrete mathematical model. It is assumed, that the complex oscillatory behaviour of the catalytic system is correlated to a spatially ordered structure caused by the interaction of neighboured reactive units.

This assumption is theoretically investigated by the numerical examination of a two-dimensional cellular automaton.

Tim Havel

Distance Geometry & Molecular Conformation

The theory of distance geometry, as developed by Karl Menger, provides a coordinate-free language for describing the conformational properties of molecules. The theory and some of its applications are described.

Steffen Heinze

Existence of Travelling Waves in Combustion Processes with Complex Chemical Networks

An existence proof of travelling waves for premixed laminar flames with complex chemistry is given under the following assumptions: 1) no viscosity, 2) zero Mach number, 3) all reactions are exotherm, 4) no cycles in the graph of the network. The method is to solve the equations in a bounded domain with suitable boundary condition. A priori bounds for the solution are obtained which allows one to pass to the infinite domain limit. The monotonicity of the temperature implies the existence of the limits at $\pm \infty$ which gives the result.

Niels I. Jaeger

Internal and External Forcing of Oscillating Heterogeneous Catalytic Oxidation Reactions

Experimental results obtained for heterogeneous catalytic oxidation reactions on supported metal catalysts will be presented. The experiments reveal in the case of the oxidation of ethanol that an autonomously oscillating region on a catalyst surface is able to entrain or force other even non-oscillating regions depending on the coupling strength between the areas. Entrainment can also be achieved by periodically varying concentrations of reactants fed into the reactor. This will be demonstrated for the catalytic oxidation of carbon monoxide.

As a prerequisite for the evolution of observable product oscillations in heterogeneous catalytic reactions the cooperation of large numbers of catalytically active centers is required. For the interpretation of the observed phenomena phase transitions on catalytic centers and their coupling via diffusive processes like mass or heat transfer are assumed.

Willi Jäger

Reactive flow through porous media

A mathematical model is derived, analyzed and simulated for the following chemical process. Within a fluid in a porous medium chemical species are transported, diffusing and reacting. Adsorption, reaction and diffusion is taking place on the surface of the pores. The chemical kinetics may be nonlinear and the reactive sites may be inhomogeneously distributed. Passing from a micro- to a macromodel by homogenization methods a system of integro-differential equations is obtained. Numerical results are presented for various assumptions on the chemical processes.

Coauthor of the paper reported is U. Hornung, (München).

Bengt Å. Månsson

Thermodynamics and Information Theory in Dynamic Chemical Systems

The first part treats a thermodynamic aspect of self-organizing chemical systems, the entropy production. This is studied in simple representative and reasonably realistic mathematical models. First, temporal structures, homogenous chemical systems performing regular or chaotic oscillations, are treated. The central issue is the time-average of the rate of entropy production, and the difference in it between a stable periodic mode and the corresponding unstable stationary state is analyzed. A derivation of a general analytical expression for this difference close to a Hopf bifurcation and simulation results for two typical models are shown. The results prove that a stationary state is not always favorable in terms of minimizing the entropy production, nor is the oscillating mode. Results of simulation of a model with periodic and chaotic modes and coexisting stationary states are shown. The second part treats spatial structures. Quantitative information-theoretical measures for structure are defined, and the connection to statistical mechanics concepts such as exergy (available work) is pointed out. Several information quantities, called 'contrasts' are decomposed with respect to correlation order, structure size and position in space. The concepts are applied to the evolution of structure in a model of a chemical self-organizing system.

Milos Marek

Pulse Forcing of Nonlinear Systems

Experimental studies of pulse concentration forcing of

single CSTR, coupled CSTR's and tubular reactor where autonomous limit cycle oscillations (or travelling pulse waves) occur have revealed existence of periodic, quasiperiodic and chaotic regimes. These regimes are analyzed by means of phase transition maps and rotation numbers. Definition of the rotation number for maps on the disc and the devil's staircase-like dependence of the rotation number on the forcing frequency were discussed. Results of the numerical analysis of Arnold tongues for several models considering pulse forcing in the parameter plane "forcing frequency-forcing amplitude" (arclength continuation methods of the construction of invariant manifolds were used) revealed that Arnold tongues are generally bounded and possess an intricate structure of higher codimension bifurcations.

D. J. Needham

Reaction-Diffusion in a Simple Pooled Chemical System

The reaction scheme based on the cubic autocatalator: $A + 2B \rightarrow 3B$, $B \rightarrow C$ is considered in a closed vessel with the reactant A being replenished by the slow decay of a precursor P via the simple step $P \rightarrow A$. The concentration of P is assumed to be very much larger than that of the intermediates A and B so that the pooled chemical approximation can be made. Spatial variations are allowed for within the vessel and it is assumed that initially the vessel contains only the reactant P and that at time $\bar{t}=0$ a quantity of B, characterised by the parameter β_0 , is introduced into some localised region. The long-time behaviour is discussed and it is shown that this depends on the parameters β_0 and μ (where μ is a nondimensional parameter representing the reaction rates) with the value of the diffusion parameter λ effectively controlling the form of the transient path leading to the final behaviour. Analytic solutions are derived for the cases when β_0 is small and λ is large. These are complimented by numerical solutions for general values of the parameters. It is found that there are three possibilities:

a finite equilibrium may be reached with A and B having constant concentrations, the concentrations of A and B may oscillate or B may die away leaving just the conversion of P to A. In the first two cases it is found that this behaviour is left behind a propagating reaction-diffusion front. The nature of this front is analysed in detail.

Peter J. Plath

Selected Aspects of the Heterogeneously Catalyzed Oxidation of Alcohols

A family of catalytic reactions: the oxidation of alcohols by palladium particles distributed on an inert and amorphous carrier has been characterized. Taking the example of the ethanol oxidation its dynamics was studied experimentally using a flow reactor. The exothermic reaction was followed by its temperature production ΔT and by mass-spectroscopy of the products. Since the functions of time $\Delta T(t)$ and $C_{CO_2}(t)$ are in phase, the reaction could be characterized easily only by following $\Delta T(t)$. Points of interest are the thermal coupling among the catalyst and the bifurcation behaviour of the reaction.

Using a partially decoupled system the internal entrainment of the subsystems has been shown.

To study the bifurcation diagrams a fully synchronized catalyst was used.

All states and bifurcations have been observed which are possible in a two variable system. Because of the relaxation-type shape of the oscillation and the set of bifurcations and states, it was proposed to describe this reaction by two differential equations

$$dx_1/dt = \epsilon f_1(x_1, x_2) \quad \epsilon \ll 1$$

$$dx_2/dt = f_2(x_1, x_2)$$

Expanding the functions f_1 into polynomials f_1 should be of degree five at least, whereas f_2 should be of degree

three. Up to now chemical or physical explanation can be given neither for the variables nor for the parameters. But there are good reasons not to believe, that both modes x_1 and x_2 can simply be interpreted by chemical intermediates. This work is based on the thesis of Mr. R. Ottensmeyer whom I am indebted very much.

W. Harmon Ray

Process Dynamics and Stability of Particulate Systems -
Mathematical Methods and Results

Particulate systems arise throughout the process industry and involve crystallization, polymerization, and other chemical processes. In this talk, a general form of models for such processes will be defined and mathematical approaches for analysis of process dynamics and stability will be discussed. A common characteristic of these systems is that system dynamics and process stability depend critically upon the particle growth process and the dynamic particle size distribution. Thus the model equations are usually integro-partial differential equations. Examples will be used to illustrate how experimental observations of multiple steady states and oscillatory behaviour can be explained through model analysis.

O. E. Rössler

Chemical Dissipative Structures from Hamiltonian Chaos

An explicit Hamiltonian from a formally 1-D gas is indicated. It produces "maximal chaos", that is, contains $n-1$ positive Lyapunov characteristic exponents (of equal magnitude)¹. It can be used to support "color coded" chemical reactions of quadratic mass action type. In this way for example a limit cycle oscillation can be simulated, that is, realized from first principles¹. While partial

results in this direction are known (see F. Schneider's abstract), or are in progress (A. L. Kawczyński, Warsaw; personal communication of M. Frankowicz), an artificial universe containing a dissipative structure like a limit cycle or an excitable system has apparently never been written down. Since the system is 1-D, a molecular dynamics simulation is actually feasible. New types of questions can be asked in principle, perhaps¹.

¹O. E. Rössler, A chaotic 1-D gas: Some implications. Lect. Notes in Phys. 278, 9-11 (1987).

Bernd Rogg

Deflagration Regimes of Laminar Flames Modeled after the Ozone Decomposition Flame

Methods of activation-energy asymptotics are employed to investigate regimes of combustion of steady, planar, adiabatic deflagrations involving a four-step kinetic mechanism modeled after that of the ozone decomposition flame. In addition to previously known regimes having flame structures that involve a nonreactive preheat zone followed by a narrow reactive-diffusive zone, in which a steady-state approximation for the reaction intermediary may or may not apply and downstream from which a recombination zone may or may not exist, a new regime is identified having a two-zone flame structure in which the intermediary is generated in a downstream zone that obeys a steady state approximation for temperature and diffuses into an upstream zone where the primary heat release occurs. In this regime convection, diffusion and reaction all are important in both zones, and heat release persists in the preheat zone all the way to the cold boundary.

Franz Rothe

Gradient-like Flows without Global Attractor

A reaction-diffusion equation $u_t = \Delta u + f(u)$ generates a local semiflow ϕ in a function space $C(\Omega)$. As Hale points out, this semiflow gives rise to a two-sided global flow on the maximal compact invariant set $S \subset C(\Omega)$, the existence of which is proven for pointwise dissipative systems. Pointwise dissipativity means "stability in the large". It excludes blow-up and holds e. g. for the Chafee-Infante problem $u_t = \Delta u + \lambda u(1-u^2)$.

On the other hand, systems from combustion theory as e. g. $u_t = \Delta u + \lambda e^u$ do give rise to blow-up for a subset of initial data A_∞ . Even for such systems with blow-up, we give an assumption - boundedness of approximate equilibria - under which the maximal compact invariant set S exists. Hence by results of Rybakowski, the Conley-Index $h(S)$ is well-defined for this type of systems, which do not admit a priori bounds.

F. W. Schneider

Distinction between Chaos and Amplified Fluctuations in Chemical Reaction Models and in the Belousov-Zhabotinsky Reaction

We have done numerical integrations of the Brusselator, Lorenz and Rössler models in their respective periodic and chaotic regions. Of interest are some invariant measures for deterministic chaos such as the maximum Lyapounov exponent (λ_{\max}) and the correlation dimension (D_{cor}). They were calculated as a function of the amplitudes of random fluctuations which were imposed on the reaction variables (multiplicative noise). As a result, the positive λ_{\max} in-

creases further with increasing fluctuations for chaos. Surprisingly, $\lambda_{\max} > 0$ in the periodic region for large fluctuations. D_{cor} is obtained from a plot of the correlation integral versus sphere radius, where a sphere has been placed with the attractor inside. For chaos we obtained a uniform slope at high embedding dimensions whereas for noisy periodic oscillations a break occurred in the slope. The lower part gives the dimension of the amplified fluctuations whereas the upper part yields the dimension of the attractor itself. With these model calculations as a guide we investigated similar regimes in the experimental Belousov-Zhabotinsky reaction as conducted in a "noisy" stirred flow reactor. We assumed the macroscopic fluctuations in the reactor to be inversely proportional to the stirring rate. Experimentally, we found $\lambda_{\max} > 0$ even for periodic oscillations. However, extrapolation to very high stirring rates gave $\lambda_{\max} \rightarrow 0$ proving the importance of amplified fluctuations at low stirring rates. Furthermore, λ_{\max} was always positive and independent of stirring rate for experimental chaotic oscillations. This shows that an experimental variation of the macroscopic fluctuations must be made before one can conclude that chaos exists even if $\lambda_{\max} > 0$. Our experiments are also in agreement with the general model predictions for D_{cor} . The behavior of the Fourier spectra and the autocorrelation functions was also discussed as a function of fluctuation size and stirring rate. Finally, a new cell model was presented which shows the effect of a small number of reacting particles (1200-6000) on λ_{\max} for the Brusselator model. Even for periodic oscillations λ_{\max} became positive and it increased when the number of reacting particles was decreased. By comparison with our calculated reaction probabilities we arrived at the concept of an activity (coefficient) constant which becomes important in strongly nonlinear mechanisms like the Brusselator at high concentrations.

Heike Schuster

A Discrete Mathematical Model for the Dynamics of the Methanol Oxidation at a Pd supported catalyst

The dynamics of the methanol oxidation on a Pd-supported catalyst is described by a discrete dynamical system including a phase transition of the catalytic system. A possible synchronization of the not uniformly acting catalyst by an heat transfer between neighboured Pd-crystallites is studied by coupling several dynamical systems.

S. K. Scott

Modelling Oscillatory Reactions in Closed Systems

Analyses of chemical reaction models for closed systems are often made easier by the 'pool chemical approximation'. By neglecting the consumption of initial precursor or reactant species, the system is artificially constrained away from its chemical equilibrium state. The resulting stationary-states can then be investigated by traditional local stability and Hopf methods. It is then assumed that the real system, with perhaps a slow decay of the pool chemical concentrations will exhibit similar pseudo-steady behaviour. This is not, however always the case. Here the simplest model for isothermal oscillations is shown rigorously to follow this approximation, to leading order. Most important features emerge algebraically. An extension of the model also exhibits forced chaotic solutions.

René Sperb

Some Mathematical Questions in Reactive Dyeing

Reactive dyeing may be modeled by the solution of

$$(1) \quad (1+\kappa) \frac{\partial u}{\partial t} = \Delta u - \phi^2 u \quad \text{in } \Omega$$

$$(2) \quad u = \hat{u}(t) \quad \text{on } \partial\Omega \quad \text{with}$$

$$\frac{d\hat{u}}{dt} = -\alpha\phi^2\hat{u} - \beta \int_{\partial\Omega} \frac{\partial u}{\partial n} ds + \gamma\phi^2$$

and given initial distribution. Here ϕ^2 is the Thiele modulus and $\kappa, \alpha, \beta, \gamma$ dimensionless constants. The quantity of interest in this problem is the efficiency E defined as

$$(3) \quad E = \frac{\int_{\Omega} u dx}{\kappa_1 \int_{\Omega} u dx + \kappa_2 v}, \quad v = \text{const.}$$

for $\gamma > 0$ and u being the solution of the steady state problem. For $\gamma = 0$ E is defined as

$$(4) \quad E = \frac{\int_{\Omega} \int_0^{\infty} u dx dt}{\kappa_1 \int_{\Omega} \int_0^{\infty} u dx dt + \kappa_2 v \int_0^{\infty} \hat{u} dt}$$

In this talk the efficiency is related to the effectiveness factor η and some questions related to the estimation of E are discussed.

Ivar Starkgold

Dead Cores in Reaction-Diffusion

When a reaction takes place in a domain Ω , it is possible for the concentration of the principle reactant to vanish in finite time over a part of Ω . Such a region is known as a dead core. An interesting and perhaps unexpected feature is that this phenomenon can occur even if the

reactant is continuously supplied through the boundary.

Examination of the steady-state problem

$$\Delta u = \lambda u_+^m, \quad x \in \Omega; \quad u(\partial\Omega) = 1$$

shows that a dead core occurs if and only if $m < 1$ and λ exceeds a certain critical value. The boundary of the dead core lies at a distance $O\left(\frac{1}{\sqrt{\lambda}}\right)$ from $\partial\Omega$.

Next, the evolution problem

$$u_t - \Delta u = -\lambda u_+^m \quad \text{in } \Omega \times [0, \infty); \quad u(x, 0) = 1, \quad u(\partial\Omega, t) = 1$$

is considered. If x_0 is in the interior of the steady dead core corresponding to λ , then it is shown that $u(x_0, t) = 0$ when $t \geq t_0$ with a simple explicit expression for t_0 . Recent results on related problems are also presented.

David Terman

Traveling Wave Solutions Arising from a Two-step Combustion Process

The combustion process $A \rightarrow B \rightarrow C$ may give rise to different traveling wave solutions which move at different velocities and may interact with each other. The first reaction, $A \rightarrow B$, produces a flame, F_1 , which converts the initial state to a partially burned state. The second reaction, $B \rightarrow C$, then converts the partially burned state to a final state producing a second flame F_2 . If F_1 is faster than F_2 , then one expects the waves to separate. However, if F_1 is slower than F_2 , then the back wave F_2 will catch up to the forward flame, F_1 . One can then imagine that what eventually evolves is a third wave which connects the initial state to the final state. It is demonstrated that if F_1 is slower than F_2 , then a third wave does indeed exist.

John T. Tyson

Spiral Waves and Scroll Waves in the Belousov-Zhabotinskii Reaction

Thin unstirred layers of BZ reagent propagate waves of oxidation in the form of expanding target patterns or rotating spiral waves. Thicker layers support fascinating three-dimensional structures called scroll waves which rotate around an axis which is a one-dimensional curve in three-space. The axis may terminate at a boundary of the medium or it may be closed in a loop which itself might be twisted and/or knotted. Furthermore, the axis of a scroll wave cruises through three-space in characteristic ways.

To understand the propagation of chemical waves in two and three spatial dimensions, one must combine the notion of dispersion of nonlinear traveling waves with the effects of wavefront curvature on the speed of propagation of the wave. The theory can account in quantitative as well as qualitative detail for the properties of traveling waves in the BZ reaction, and it can also be applied to similar waves in other excitable media: aggregation of slime mold amoeba, waves of contraction in the heart, and stimulus patterns in neural networks.

Ewald Wicke

Periodicity and Chaos in a Catalytic Packed Bed Reactor for CO Oxidation

A packed bed of catalyst pellets for CO oxidation can be taken as an assembly of reaction rate oscillators, covering a certain range of frequencies and amplitudes, and coupled by heat conduction between the pellets. Collective effects of the oscillations can be observed in the bifurcation range only, that is between the monostable regime at high gas flow rates and the bistable regime at low rates. In

this range reaction rate maxima at single pellets in the entrance cross section give rise to chemical waves that accumulate to large fluctuations of temperature and concentration at the bed exit. An analysis revealed a positive value of the Ljapunow exponent, indicating deterministic chaos. Entrainment as well as sub- and superharmonics could also be observed. The strength of the coupling between neighbouring pellets is decisive for the type of behaviour: periodic, quasiperiodic or chaotic, as can be demonstrated with arrangements of few pellets already. The system represents an interesting model case for the interaction of single oscillators to produce collective periodic and chaotic phenomena.

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