

5 Complexity and Self-Organization in Chemical Reactions

It has been illustrated in Sect. 1 that mechanical systems with several *coupled degrees of freedom* have a variety of modes, only some of which settle down in time to a stable, steady state. In other conditions, defined by the magnitude of system parameters, such a system is capable of oscillatory motion or even random, chaotic behavior. In the light of the previous discussion of mechanical systems, one wonders, how some complex chemical reactions behave. In fact, even many "simple" chemical reactions usually involve several, interrelated steps. Consider, e.g., the reaction



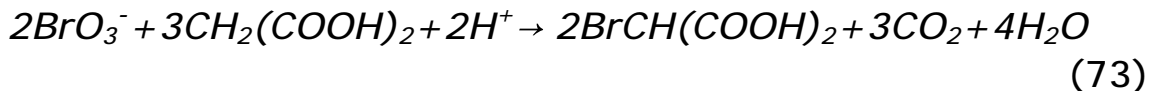
Actually, this *stoichiometric equation summarizes* the following 3 intermediate processes:



Obviously, the reaction rates for the second and third processes depend on the availability of atomic *Br*. On the other hand, depleting the system of atomic *Br* will effectively speed up the dissociation of *Br*₂. Hence, there is a *feedback* between the different reactions above, and therefore, one suspects that chemical systems may behave in different, orderly, oscillatory, or chaotic ways. This suspicion is actually borne out in reality, in particular in complex, often catalytic, reactions.

A reaction that has been studied in some detail is the *Belousov-Zhabotinski (BZ) Reaction*, where an organic molecule is oxidized by bromate ions, which leads to an oscilla-

tory concentration change between colorless Ce^{3+} and yellow Ce^{4+} ions. The overall reaction is



but more than 20 individual reactions are actually involved in the process. The Ce ions are not explicitly noted in Equ. 73; because of their catalytic function, their overall concentration does not change.

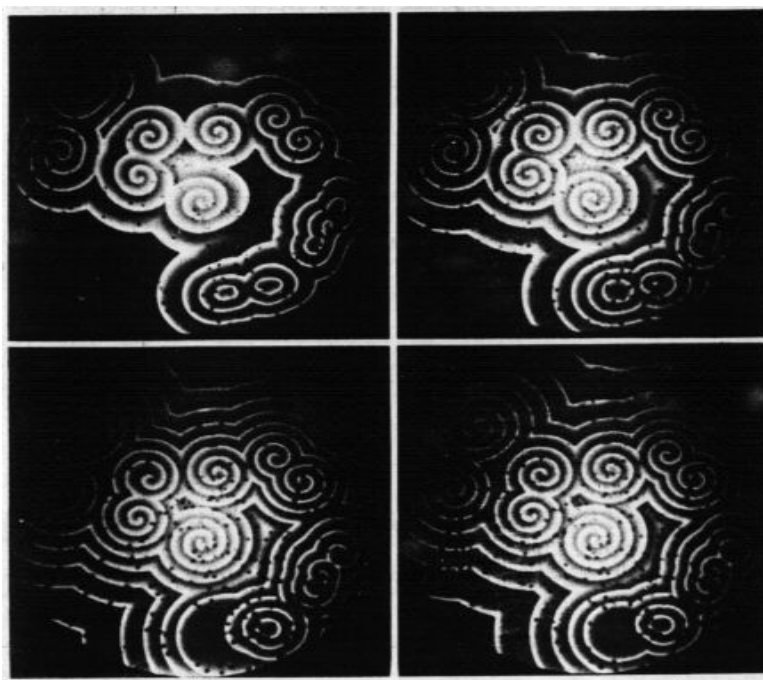


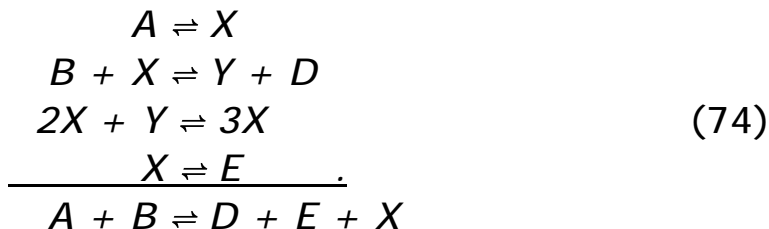
Figure 28: Brusselator concentration patterns for different times.

a shallow layer of a *BZ* mixture. Curiously, adjacent spirals rotate in opposite direction. This behavior is obviously not what is generally understood to reflect a *steady-state, time-independent chemical equilibrium*.

To describe a reaction system such as the *BZ* reaction in mathematical detail is somewhat laborious. The so-called "*Brusselator*" reaction is a much simpler reaction, since it involves only *two reactive variables*, the concentrations $X = X(t)$ and $Y = Y(t)$ of one final and one intermediate prod-

The figure on the left shows the time evolution of the color scheme, reflecting the Ce^{4+} concentration, as observed with

uct, respectively. The individual steps in the *Brusselator* reaction are



In the process, the initial concentrations A and B of the reagents and the product concentrations D and E are held constant, by external regulation, at values very far away from chemical equilibrium. Under such conditions, *equations of motion* describing the time (t) evolution can be derived for the concentrations X and Y . They are only quoted here (see, e.g., Babloyantz):

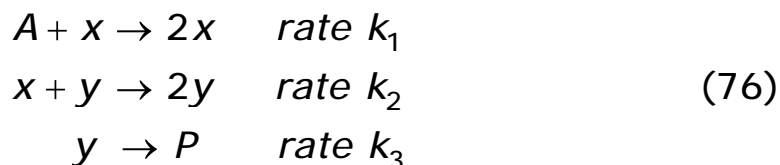
$$\begin{aligned} \frac{\partial X}{\partial t} &= A - (B+1)X + X^2Y + D_x \frac{\partial^2 X}{\partial r^2} \\ \frac{\partial Y}{\partial t} &= BX - X^2Y + D_y \frac{\partial^2 Y}{\partial r^2} \end{aligned} \quad (75)$$

For a realistic treatment, the *spatial diffusion* of the molecules along has to be taken into account. For a very long and thin chemical reactor, the diffusion is important only along a linear degree of freedom (r). The *diffusion coefficients* D_x and D_y depend on the different *mobilities* of substances A and B . These equations (75) are somewhat reminiscent of Lorenz' weather equations (see Equ. (1)) and should, therefore, show a similar rich dynamics of the chemical system. This fact has been demonstrated in class, even for two spatial dimensions, with a *BASIC* code [Koonin:BRUS.BAS](#) (load [GWBASIC](#)). It was shown in these simulations, how the time-dependent *chemical-wave patterns* of (surface) concentrations appear and disappear for some values of the

concentrations, but not for others. Unexpectedly, the effect of spatial diffusion does not suppress this *cooperative behavior* of a chemical system. The Brusselator system can actually be studied theoretically in considerable detail, a project that is feasible and requires only little background in the calculus of differential equations.

A simpler example is the catalytic Lotka-Volterra reaction. It is also subject of a homework project.

Catalytic reactions represent chemical examples of non-linear feed-back processes, which are capable of a range of behavior. Consider the Lotka-Volterra process, where the overall reaction $A \rightarrow P$ is a superposition of the following three reactions:



with the corresponding reaction rates k_i given in some time units characteristic for the overall reaction. Here, the substances x and y are catalysts, which are supplied with the initial concentrations

$$\begin{pmatrix} y_0 \\ x_0 \end{pmatrix} \quad (77)$$

The reagent is supplied continuously to the reaction vessel with a constant concentration A .

An analysis of the reaction pattern would consist in *a)* Writing down the rate equations ($dx/dt=...$, etc.) for all intermediate reactions, and *b)* an analytical or numerical solution of the time dependent DEqs. for the product P as a function of the concentration of the reagent A provided externally and

the concentrations of the catalysts x and y . One would then plot the solutions graphically to demonstrate different influences of catalyst on stability and behavior of the reaction.

Project: Write a *MATCAD* program to explore (and discuss) the time evolution of the reaction for different concentrations of the reagent (for example $A = 0.01, 0.05, 1.0$, etc.).

Use vector notation for the simultaneous iteration of the concentrations x_i, y_i , and P_i , in the time intervals $t_i = i dt$, where the time step is $dt = 0.01$ in the above time units.

Plot (a) the concentrations of catalyst x and product P vs. time t_i (or index i) and (b) the "limit cycle" of P vs. x .

Summary

In summary, the discussion in this chapter has demonstrated that dynamical systems, even relatively simple ones following very simple laws of motion, are capable both of orderly and of chaotic motion, depending on some system scaling (amplification) parameters and the initial conditions. These systems include the laser amplifier, whose *non-linear dynamics* was discussed in some detail in terms of the logistic map. It was possible to "*understand*", i.e., to predict, conditions under which a laser works in a stable mode, when it will extinguish, when it will operate in a bi-stable pulsed mode, and when it will behave chaotically, delivering pulses of randomly different intensities. Other examples comprise various types of mechanical, electrical, or other oscillators (e.g. the heart).

Further, different types of non-chaotic, quasi-stable or *oscillatory (cooperative) behavior of chemical reac-*

tions were briefly mentioned. While orderly behavior is usually desired for mechanical systems, chemical reactions are most efficiently used when the interacting reagents and products, forming a complex feed-back system, follow a completely random, chaotic mode. Finally, combinations of iterative maps were employed to simulate some interesting *fractal growth patterns* found, not only in crystallization processes, but also in the living nature. While it is not clear that nature has proceeded in this fashion along its route of the evolution of life, these very simple iterative processes steered by genes offer that possibility.

A large class of complex systems, naturally capable of chaotic motion, include systems of *more than 2 interacting particles*, such as gases or liquids, or mixtures thereof, all systems whose individual constituents follow *linear dynamics*.

*Sensitivity to initial Conditions
in Molecular Scattering*

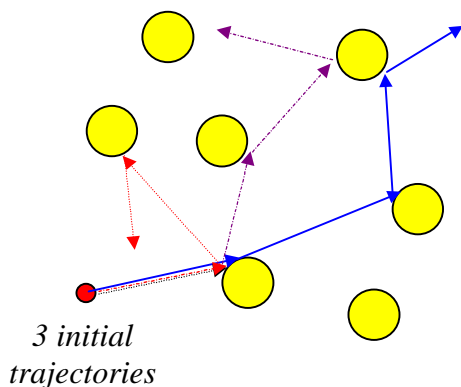


Figure 29: Complexity via multiple scattering

Here, chaoticity is due to the complexity of the system, which is described by a system of coupled differential equations leading to non-linear feed-back effects on the motion of the individual particles and *extreme sensitivity to initial conditions*. This type of system includes multi-particle systems which will be discussed in more detail later ([animation](#)).

Chaotic motion is, for fundamental reasons, essentially unpredictable. For certain systems, one can give general conditions for the occurrence of chaos or order. However, chaotic motion along a certain degree of freedom changes directions in a more or less random, stochastic fashion.

Chaotic trajectories can cover the whole accessible space uniformly. Waiting long enough, every point will be visited. Therefore, in the limit, every point has the same significance for the system, it has an *equal a priori probability*, equal to that of any other point. This principle underlies the framework of the *microscopic theory of Statistical Mechanics*, which governs the observable *thermodynamic behavior of macroscopic systems* such as gases or liquids.

Further Reading:

The New Physics, Paul Davis (Editor), Cambridge University Press New York, 1989.

D. Kondepudi and I. Prigogine, *Modern Thermodynamics*, Wiley-Interscience Publ., New York 1998

A. Babloyantz, *Molecules, Dynamics, and Life; An Introduction to Self-Organization of Matter*, Wiley-Interscience Publ., New York 1986

H. O. Peitgen, H. Jürgens, D. Saupe, *Chaos and Fractals – New Frontiers of Science*, Springer Verlag New York, 1992.

G.L. Baker and J.P. Gollub, *Chaotic Dynamics, an Introduction*, Cambridge University Press, Cambridge 1996.

C. Beck and F. Schlögl, *Thermodynamics of chaotic systems*, Cambridge University Press, Cambridge 1993.

F. Scheck: *Mechanics, From Newton's Laws to Deterministic Chaos (Ch. 6.4)*, Springer Verlag Berlin 1990.

R. Dawkins: *The Blind Watchmaker*, W.W. Norton&Co., New York 1986