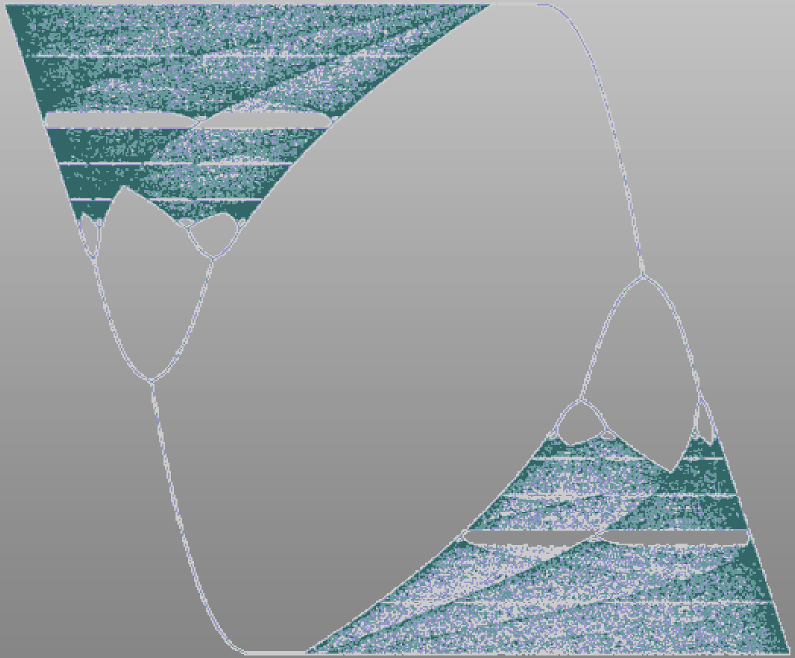
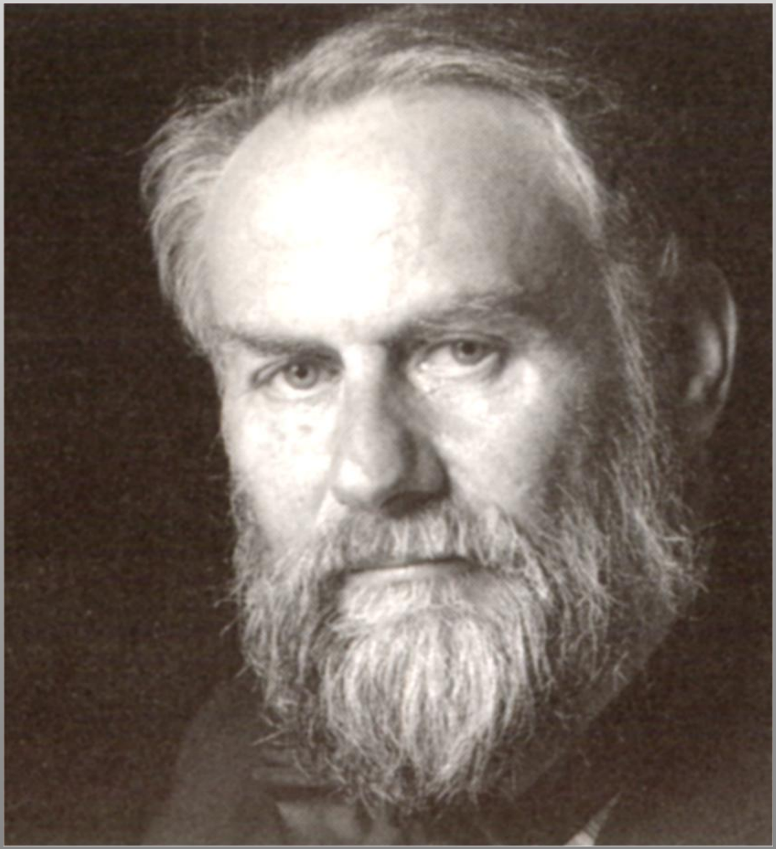
Synergetic Impact of Synergetics
- Remembrances of a Chemist -

Peter J. Plath



Hermann Haken
father of synergetics

What means synergetics ?



Zitat: H.Haken zur Synergetik:

"Was wir untersuchen, ist das **gemeinsame Wirken vieler Untersysteme**, das derart verläuft, daß es Strukturen und Funktionen auf einer makroskopischen Skala erzeugt."

What we are looking for that is the action of many sub-systems in common, creating structures and new functions on a macroscopic scale.

H. Haken; Synergtik – eine Einführung, Springer–Verlag Berlin, Heidelberg, ... (1990) Vorwort 1976

Convection Instability / Bénard-Instability I

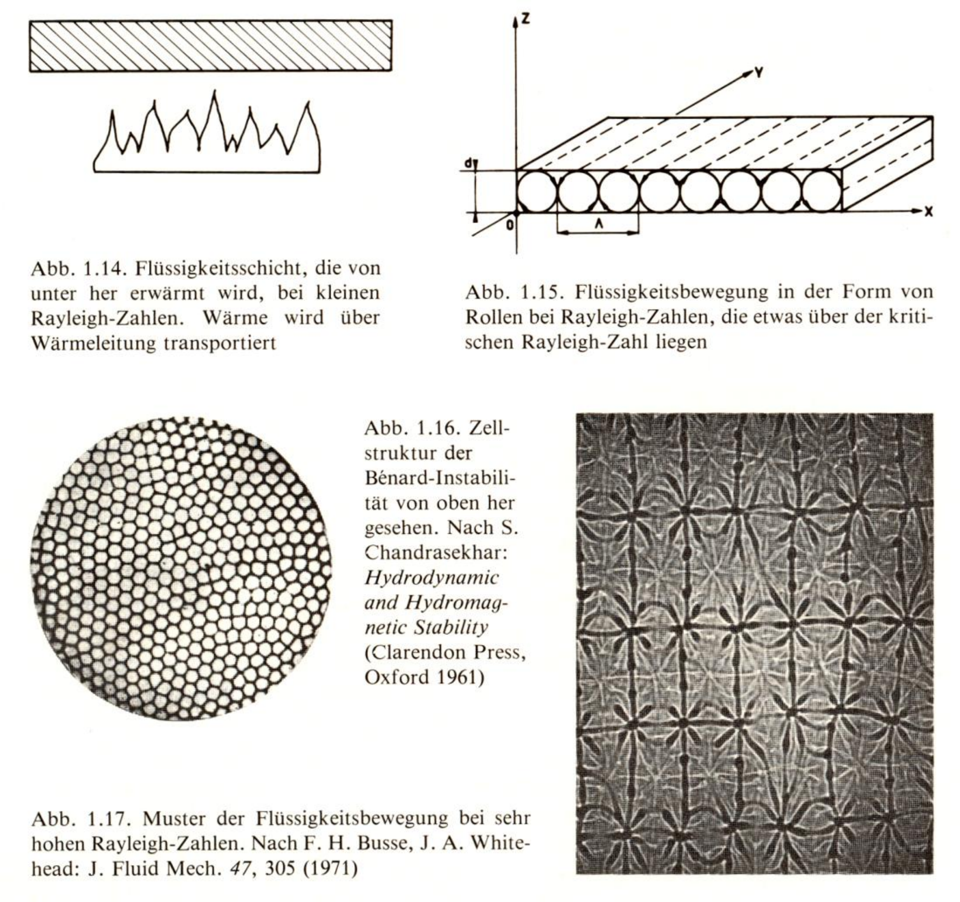


Abb. 1.14. Flüssigkeitsschicht, die von unter her erwärmt wird, bei kleinen Rayleigh-Zahlen. Wärme wird über Wärmeleitung transportiert

Abb. 1.15. Flüssigkeitsbewegung in der Form von Rollen bei Rayleigh-Zahlen, die etwas über der kritischen Rayleigh-Zahl liegen

Abb. 1.16. Zellstruktur der Bénard-Instabilität von oben her gesehen. Nach S. Chandrasekhar: *Hydrodynamic and Hydromagnetic Stability* (Clarendon Press, Oxford 1961)

Abb. 1.17. Muster der Flüssigkeitsbewegung bei sehr hohen Rayleigh-Zahlen. Nach F. H. Busse, J. A. Whitehead: J. Fluid Mech. *47*, 305 (1971)

low temperature gradient

$$\frac{\partial T}{dt} = \kappa \nabla^2 T; \qquad \kappa > 0$$

Fourier law

subsystem: „molecule“

large temperature gradient

convection cells

subsystem: „droplets“

mesoscopic areas of the liquid

Bénard Instabilities II

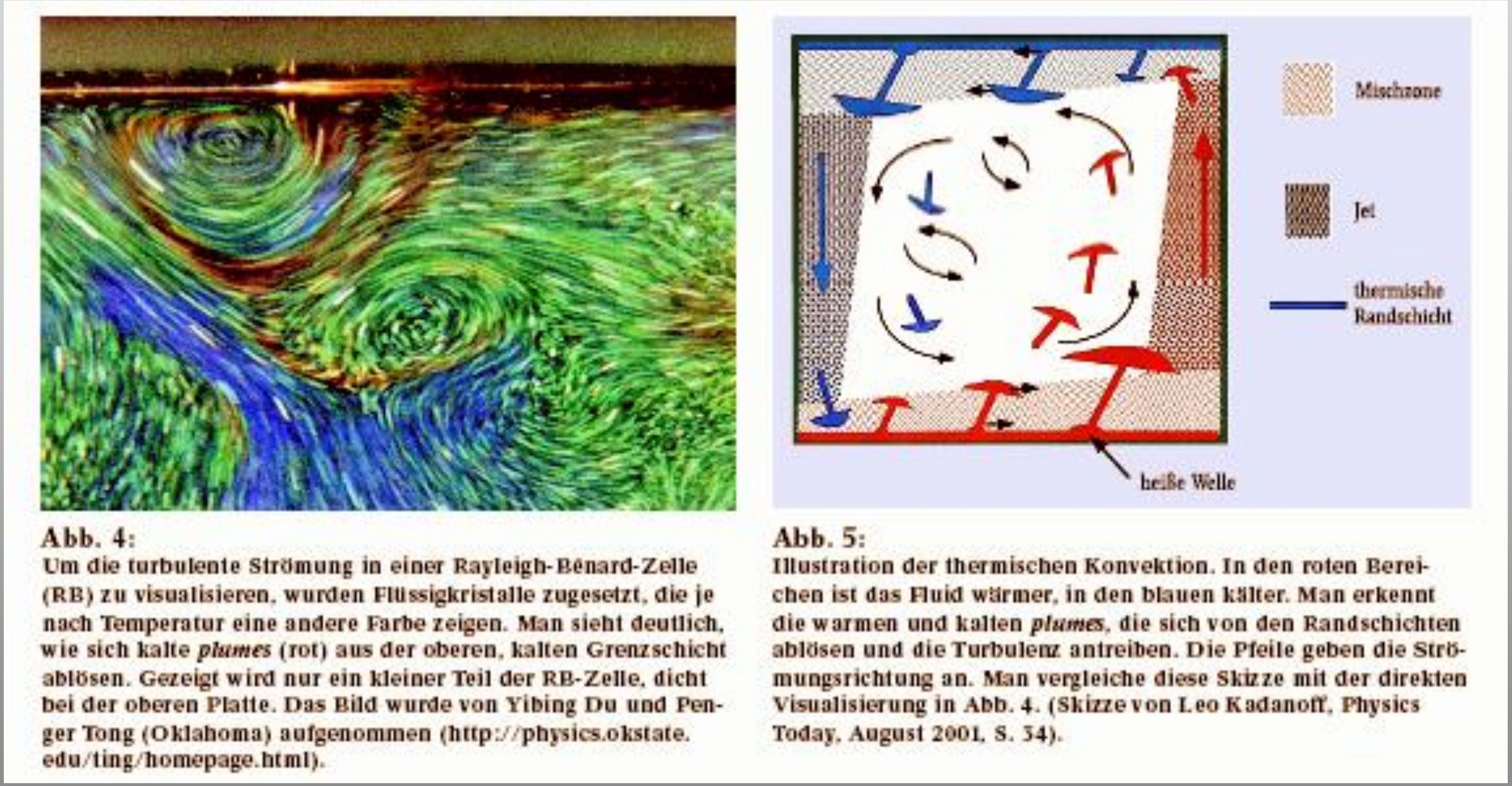


Abb. 4:
Um die turbulente Strömung in einer Rayleigh-Bénard-Zelle (RB) zu visualisieren, wurden Flüssigkristalle zugesetzt, die je nach Temperatur eine andere Farbe zeigen. Man sieht deutlich, wie sich kalte *plumes* (rot) aus der oberen, kalten Grenzschicht ablösen. Gezeigt wird nur ein kleiner Teil der RB-Zelle, dicht bei der oberen Platte. Das Bild wurde von Yibing Du und Penger Tong (Oklahoma) aufgenommen (http://physics.okstate.edu/ting/homepage.html).

Abb. 5:
Illustration der thermischen Konvektion. In den roten Bereichen ist das Fluid wärmer, in den blauen kälter. Man erkennt die warmen und kalten *plumes*, die sich von den Randschichten ablösen und die Turbulenz antreiben. Die Pfeile geben die Strömungsrichtung an. Man vergleiche diese Skizze mit der direkten Visualisierung in Abb. 4. (Skizze von Leo Kadanoff, Physics Today, August 2001, S. 34).

G. Ahlers, S. Großmann, D. Lohse;

Physik Journal 1 (2002) 31 - 37

Chemical Front Instabilities fractal fronts in Runge pictures

Ferdinand Runge
1794 - 1867

Musterbilder
1850

Bildungstrieb
1855

$D(\alpha) = 0.9331$

$$D(\alpha) = \frac{\ln \sum_{n=1}^{i} \sqrt{r_{i-1}^2 + r_i^2 - 2r_{i-1}r_i \cos s} - \ln k}{\ln(1/s)}$$

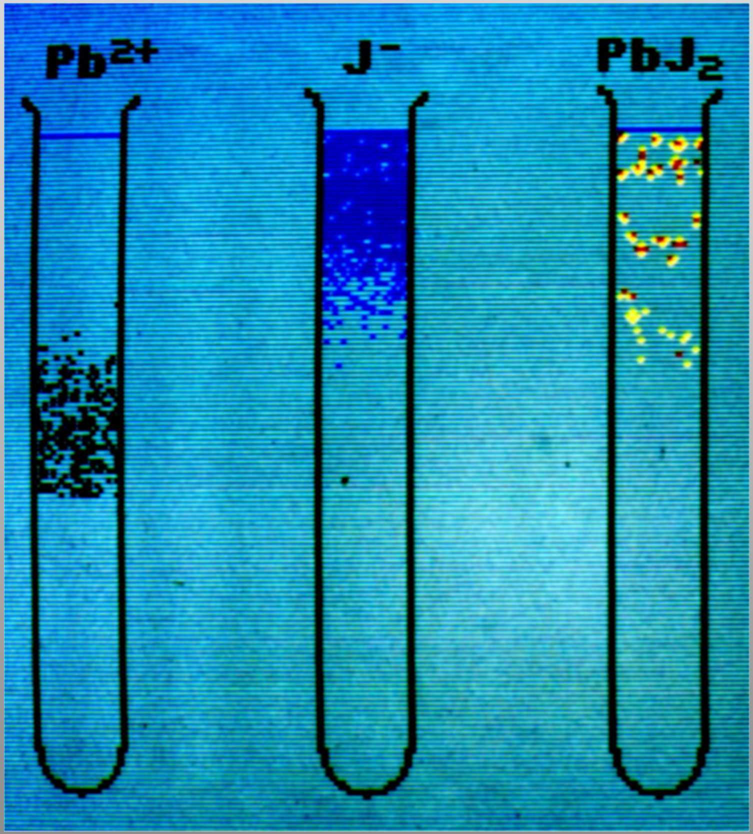
F.F. Runge; Zur Farbenchemie – **Musterbilder** für Freunde des Schönen, und zum Gebrauch für Zeichner, Maler und Zeugdrucker, Berlin (**1850**)

Synergetic Impact of Synergetics

Liesegang Structures

Raphael Liesegang
1869 -1947

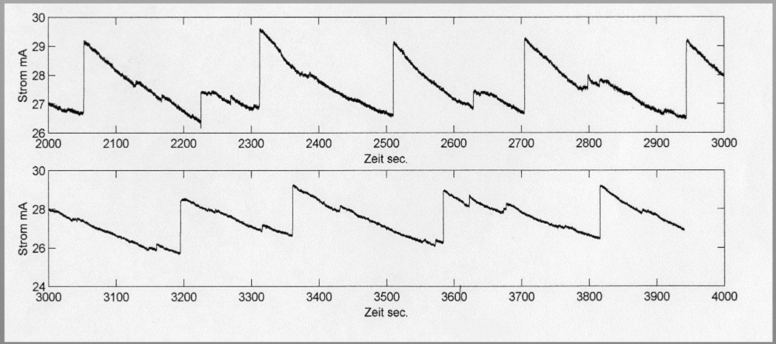
Liesegangs Photographisches Archiv,
Nr. 801; Düsseldorf, 1.Nov. **1896**; Heft XXI



Precepitation reactions in Gels

2D simulation on a cyclically closed cellular automaton

Wilhelm Ostwald‘s Swinging Chromium



“Periodische Erscheinungen bei der Auflösung des Chroms in Säuren”

Z. phys. Chemie 35 (1900) 33 - 76
Z. phys. Chemie 35 (1900) 204 - 256

Lotka – Volterra – Model

Alfred James Lotka
(1880-1949)

Chemist, mathem. Biologist

Chemical equation

$$A + X_1 \xrightarrow{k_1} 2X_1$$

$$X_1 + X_2 \xrightarrow{k_2} 2X_2$$

$$X_2 \xrightarrow{k_3} F$$

$$\overline{\quad A \quad \rightarrow \quad F \quad}$$

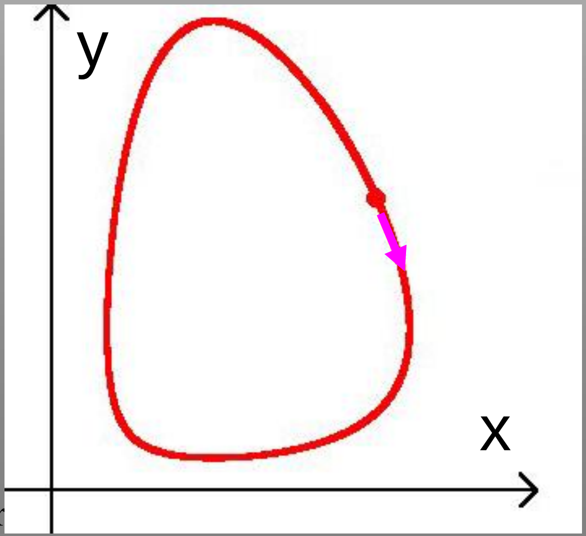
Kinetic equation

$$\frac{dc_1}{dt} = k_1' c_a c_1 - k_2' c_1 c_2$$

$$\frac{dc_2}{dt} = k_2' c_1 c_2 - k_3 c_2$$

Vito Volterra (1860 – 1940)

Mathematician, Physicist



A.J. Lotka; „Zur Theorie der periodischen Reaktionen“, Z. phys. Chemie **72** **(1910)** 508 - 511

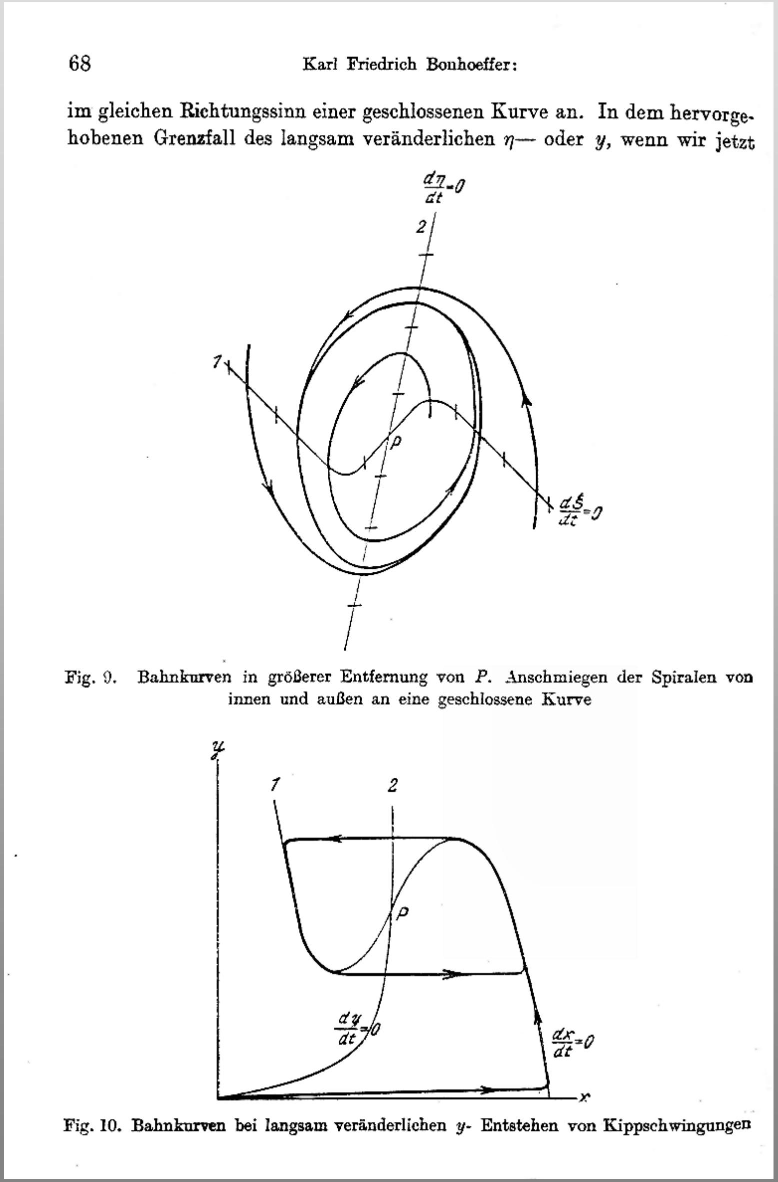
K.F. Bonhoeffer
Electro-chemical Oscillations

Karl Friedrich Bonhoeffer

(1899 – 1957)

Physical Chemist

K.F. Bonhoeffer; Ber. Verh. Sächs. Akad. Wiss. zu Leipzig math.-nat. wiss. Klasse 95, S. Hirzel (1943) 58 - 70



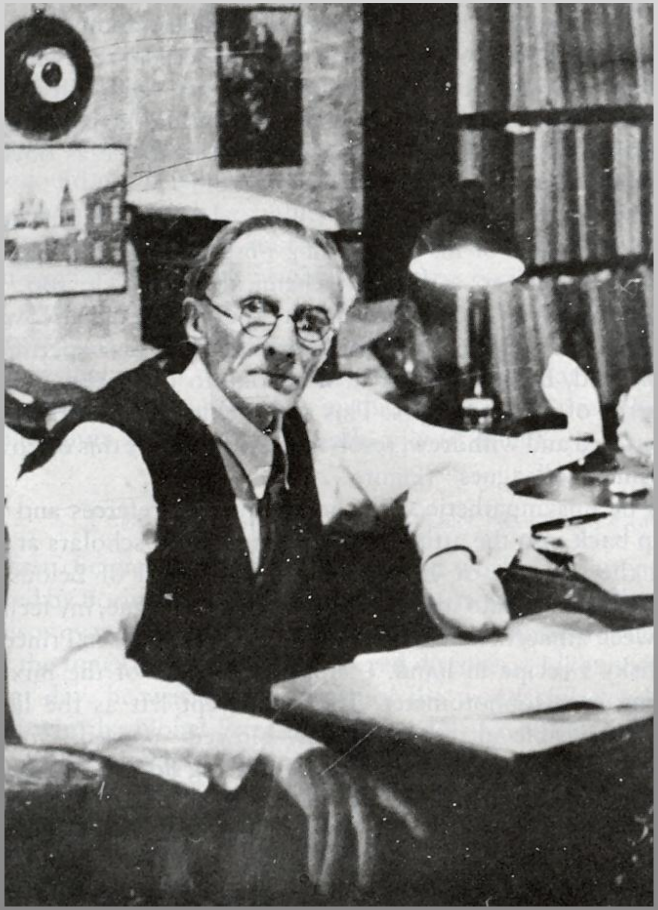
68 Karl Friedrich Bonhoeffer:

im gleichen Richtungssinn einer geschlossenen Kurve an. In dem hervorgehobenen Grenzfall des langsam veränderlichen η— oder y, wenn wir jetzt

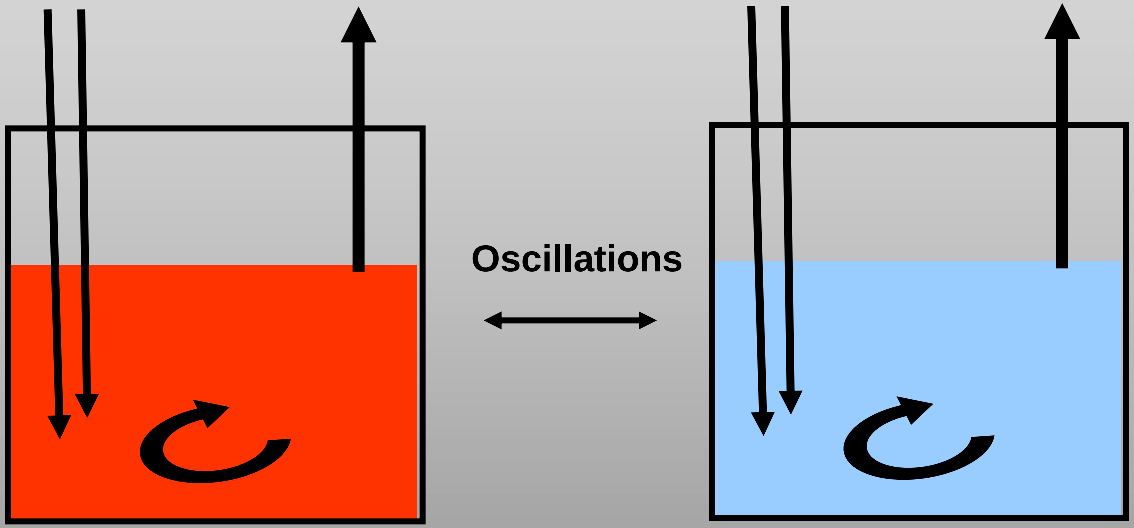
Fig. 9. Bahnkurven in größerer Entfernung von P. Anschmiegen der Spiralen von innen und außen an eine geschlossene Kurve

Fig. 10. Bahnkurven bei langsam veränderlichen y- Entstehen von Kippschwingungen

Reaction Instabilities / Chemical Oscillation



Boris Pawlowitsch
Belousov (1893 - 1970)



Cont. Stirred Tank reactor (CSTR)

Cer - catalysed Bromination of citric acid (1950 /1959)

A.T. Winfree; J. Chem. Educ.(1984) 661 - 663

Auto-Catalysis and Chemical Reaction 1967/68

Ilya Prigogine

1917 – 2003

Physical - Chemist

Chemical Equations

$$A \rightarrow X$$

$$2X + Y \rightarrow 3X$$

$$B + X \rightarrow Y + D$$

$$X \rightarrow E$$

Kinetic Equations

$$\frac{dX}{dt} = A + X^2Y - BX - X$$

$$\frac{dY}{dt} = BX - X^2Y$$

Ilya Prigogine, R.Lefever;

J. Chem. Phys. **48**,4 (1968) 1695 - 1700

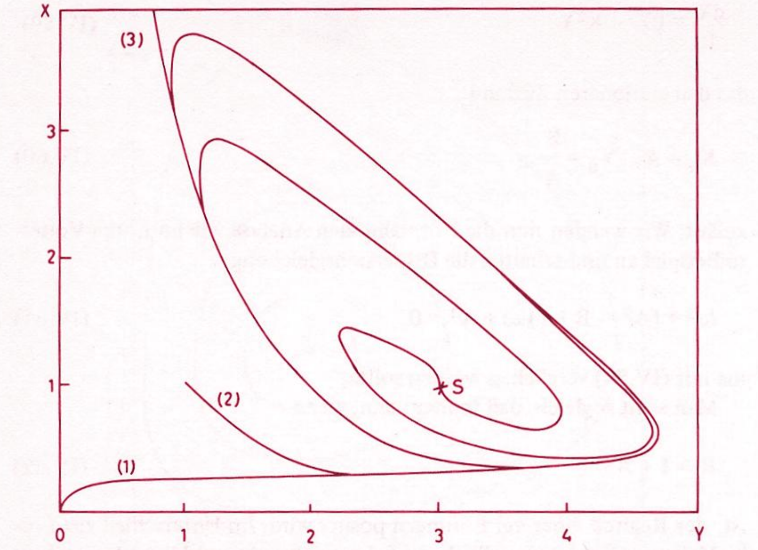
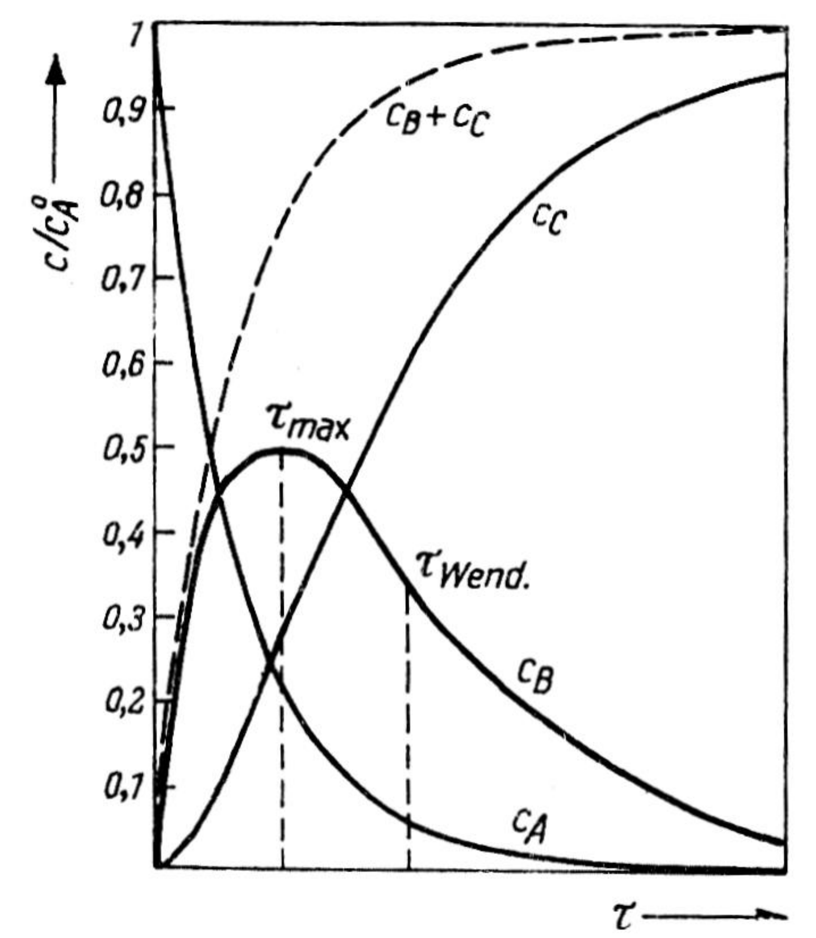


Abb. IV.8 Grenzzyklus-Verhalten des „Brüsselators“: Dieselbe periodische Trajektorie wird für verschiedene Anfangsbedingungen erhalten. (S bezeichnet einen instabilen stationären Zustand.)

Brusselator - Limit-Cycle

Synergetic Impact of Synergetics



Concentration of the substances in the consecutive reaction A→B→C

Consecutive Reaction

Non-equilibrium reaction

$$\mathrm{A} \rightarrow \mathrm{B} \rightarrow \mathrm{C} \rightarrow \ldots$$

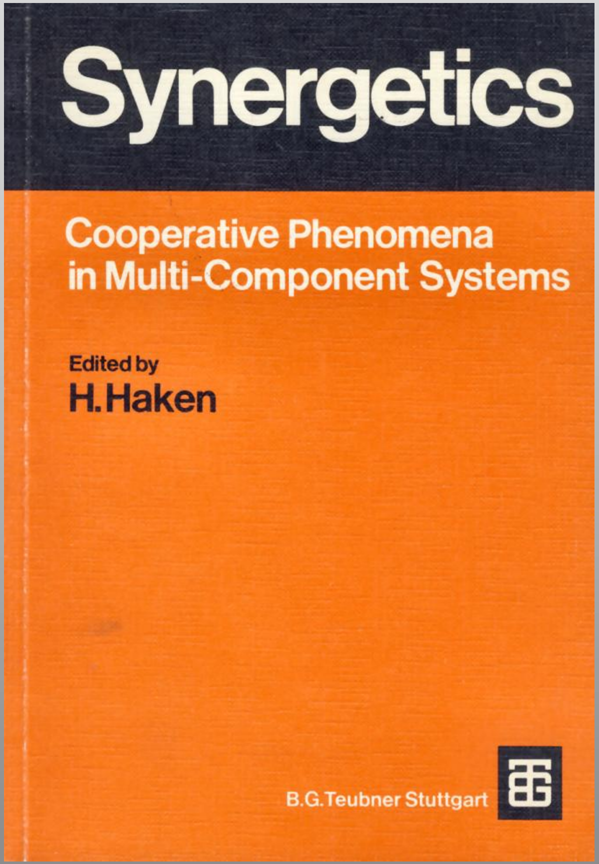
$$-\frac{dc_A}{dt} = k_1 c_A \qquad = k_1 c_A^0 e^{-k_1 t}$$

$$\frac{dc_B}{dt} = k_1 c_A - k_2 c_B \quad = k_1 c_A^0 e^{-k_1 t} - k_2 \frac{k_1 c_A}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

$$\frac{dc_C}{dt} = k_2 c_B \qquad = k_2 \frac{k_1 c_A}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

Text book example; R. Brdička, Grundlagen der Physikalischen Chemie (**1963**) 723

Synergetics



Synergetics

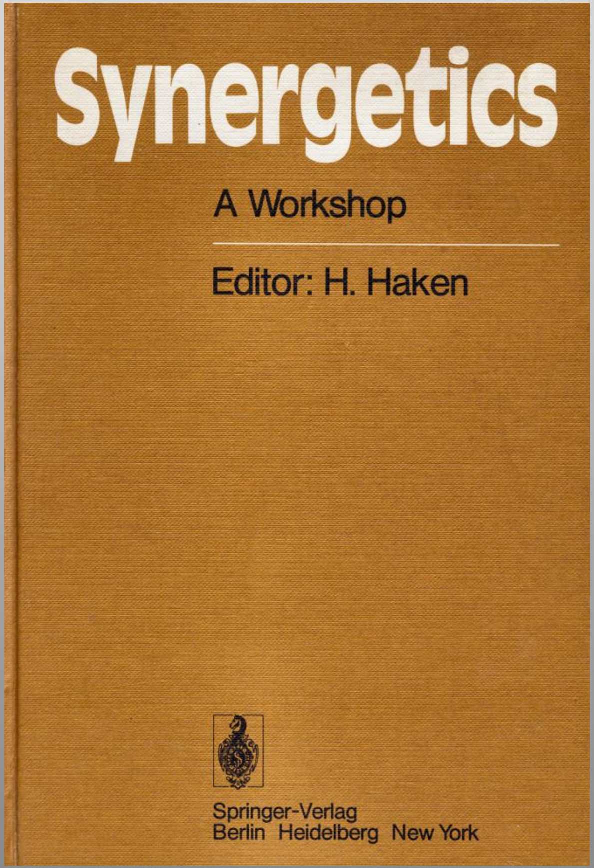
Cooperative Phenomena
in Multi-Component Systems

Edited by
H. Haken

B.G.Teubner Stuttgart

“Synergetics is a rather new field of interdisciplinary research which studies the self-organized behaviour of systems leading to the formation of structures functionings.”

Preface 1977; vol. 2



Synergetics

A Workshop

Editor: H. Haken

Springer-Verlag
Berlin Heidelberg New York

Schloß Elmau 1972

Schloß Elmau 1977

Synergetic Impact of Synergetics

U.F. Franck, E. Wicke, O.E. Rössler and many others

Franck: Feedback Kinetics in physico-chemical Oscillators

Wicke: Unstable and Oscilatory Behaviour in Heterogeneous Catalysis

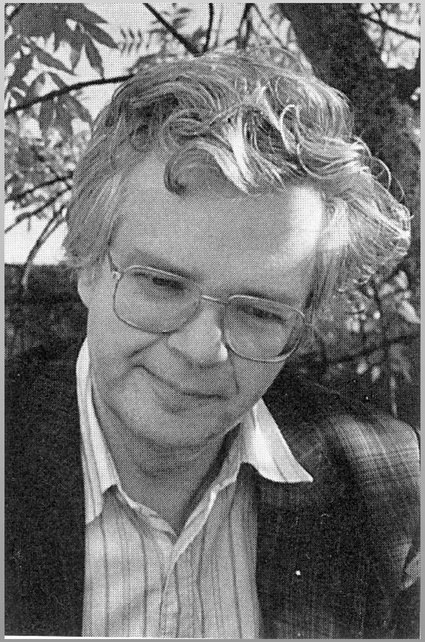
Zhabotinsky: Oscillating Bromide Oxidative Reactions

Gray: Thermokinetic Oscillations in Gaseous Systems

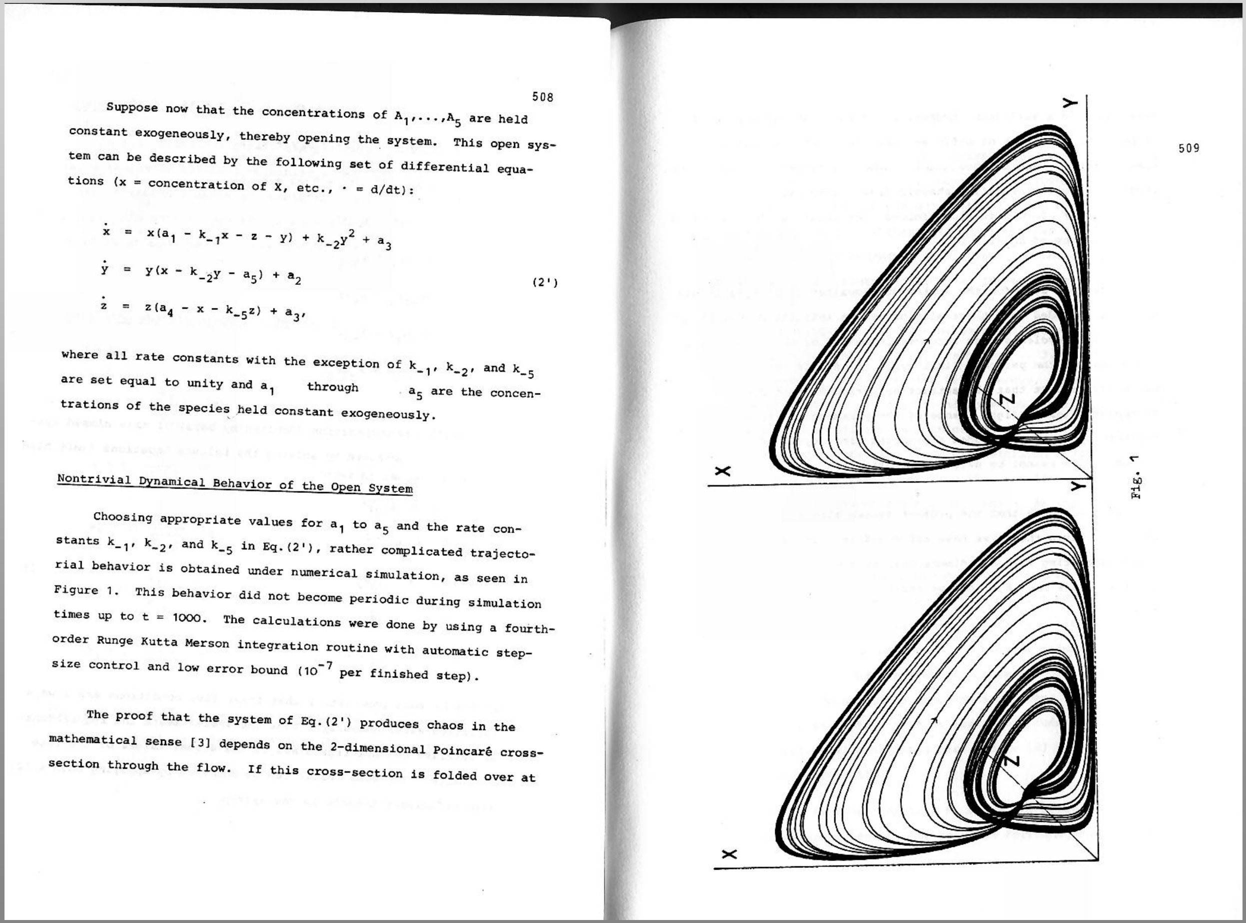
…

Bunsengesellschaft, Aachen 1979

O. Rössler 1979: “Chaos … can be realized in simple chemical systems.”



O.E. Rössler



508

Suppose now that the concentrations of $A_1, \ldots, A_5$ are held constant exogeneously, thereby opening the system. This open system can be described by the following set of differential equations (x = concentration of X, etc., $\cdot = d/dt$):

$$\begin{aligned} \dot{x} &= x(a_1 - k_{-1}x - z - y) + k_{-2}y^2 + a_3 \\ \dot{y} &= y(x - k_{-2}y - a_5) + a_2 \\ \dot{z} &= z(a_4 - x - k_{-5}z) + a_3, \end{aligned} \tag{2'}$$

where all rate constants with the exception of k_{-1}, k_{-2}, and k_{-5} are set equal to unity and a_1 through a_5 are the concentrations of the species held constant exogeneously.

<u>Nontrivial Dynamical Behavior of the Open System</u>

Choosing appropriate values for a_1 to a_5 and the rate constants k_{-1}, k_{-2}, and k_{-5} in Eq. (2'), rather complicated trajectorial behavior is obtained under numerical simulation, as seen in Figure 1. This behavior did not become periodic during simulation times up to $t = 1000$. The calculations were done by using a fourth-order Runge Kutta Merson integration routine with automatic step-size control and low error bound (10^{-7} per finished step).

The proof that the system of Eq. (2') produces chaos in the mathematical sense [3] depends on the 2-dimensional Poincaré cross-section through the flow. If this cross-section is folded over at

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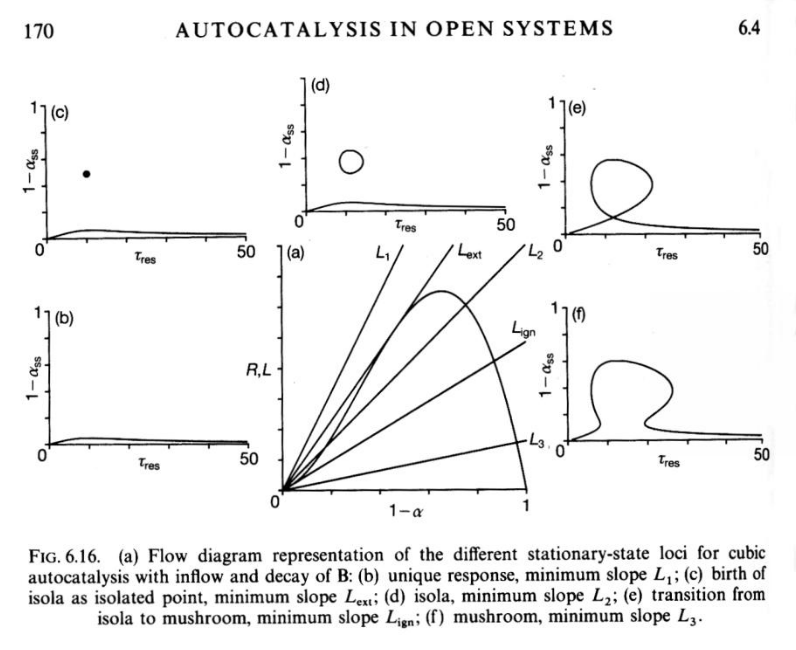
Fig. 1

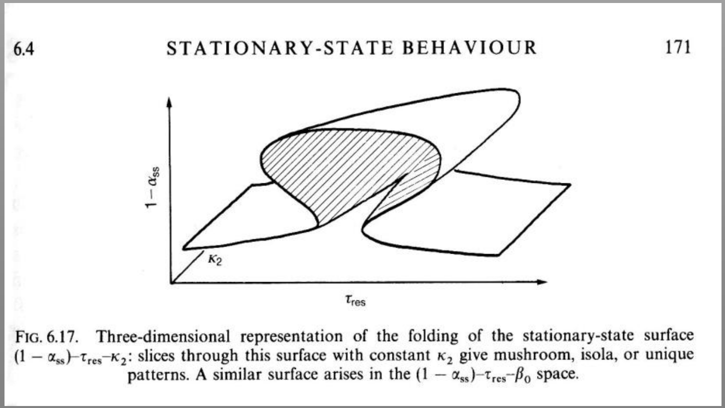
Auto-Catalysis – Classification of Static Instabilities



170 AUTOCATALYSIS IN OPEN SYSTEMS 6.4

FIG. 6.16. (a) Flow diagram representation of the different stationary-state loci for cubic autocatalysis with inflow and decay of B: (b) unique response, minimum slope L_1; (c) birth of isola as isolated point, minimum slope L_{ext}; (d) isola, minimum slope L_2; (e) transition from isola to mushroom, minimum slope L_{ign}; (f) mushroom, minimum slope L_3.

Peter Gray in discussion, Aachen 1979

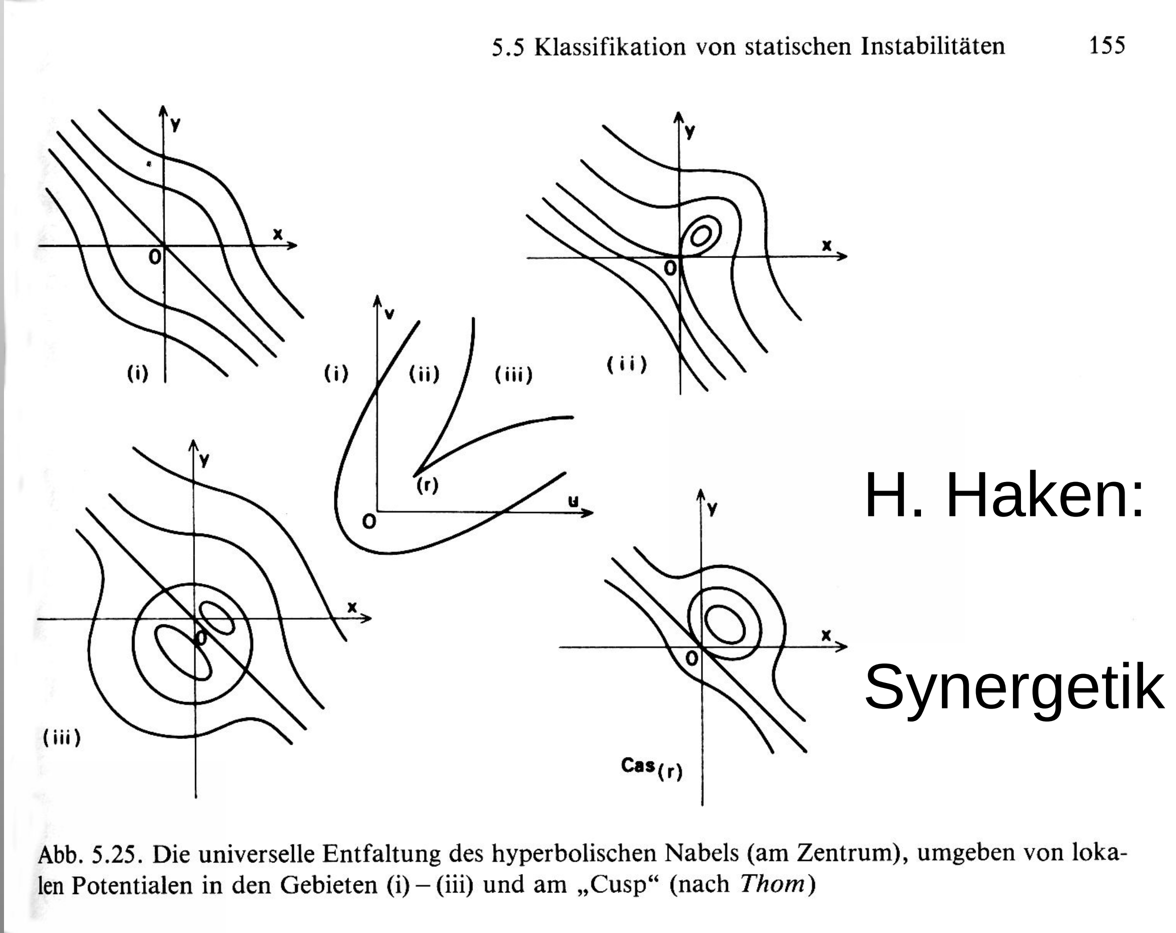


6.4 STATIONARY-STATE BEHAVIOUR 171

FIG. 6.17. Three-dimensional representation of the folding of the stationary-state surface $(1-\alpha_{ss})$–τ_{res}–κ_2: slices through this surface with constant κ_2 give mushroom, isola, or unique patterns. A similar surface arises in the $(1-\alpha_{ss})$–τ_{res}–β_0 space.

P. Gray , St. Scott; Chemical Oscillations and Instabilities; Clarendon Press - Oxford (1990)
P. 170 /171

Elementary Approach to Thom‘s Catastrophy-Theory



5.5 Klassifikation von statischen Instabilitäten 155

Abb. 5.25. Die universelle Entfaltung des hyperbolischen Nabels (am Zentrum), umgeben von lokalen Potentialen in den Gebieten (i) – (iii) und am „Cusp“ (nach *Thom*)

René Thom

H. Haken: universal unfolding of a hyperbolic umbilic;

Synergetik - Eine Einführung S.155

Heterogeneously catalysed

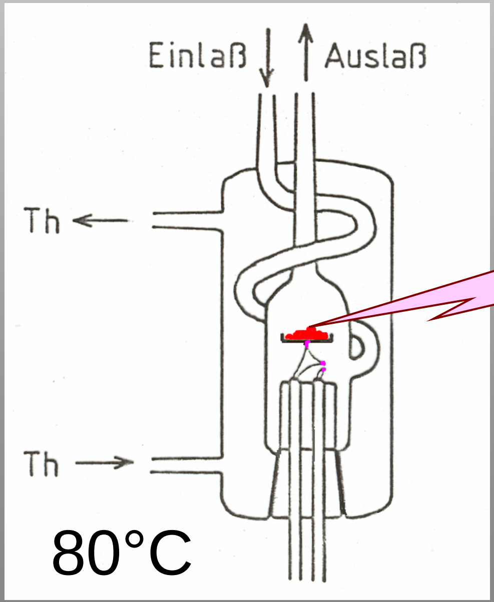
Methanol oxidation

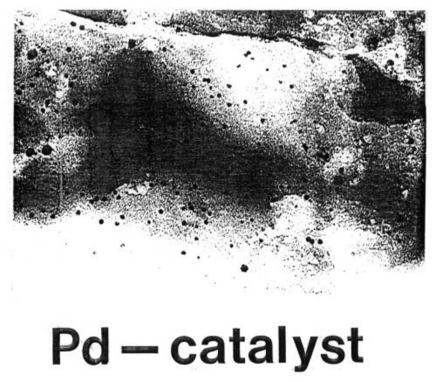
$2\ CH_3OH + O_2 \rightarrow HCOOCH_3 + 2\ H_2O + \Delta H_1$

$\mathbf{CH_3OH + 3/2\ O_2 \rightarrow CO_2 + H_2O + \Delta H_2}$

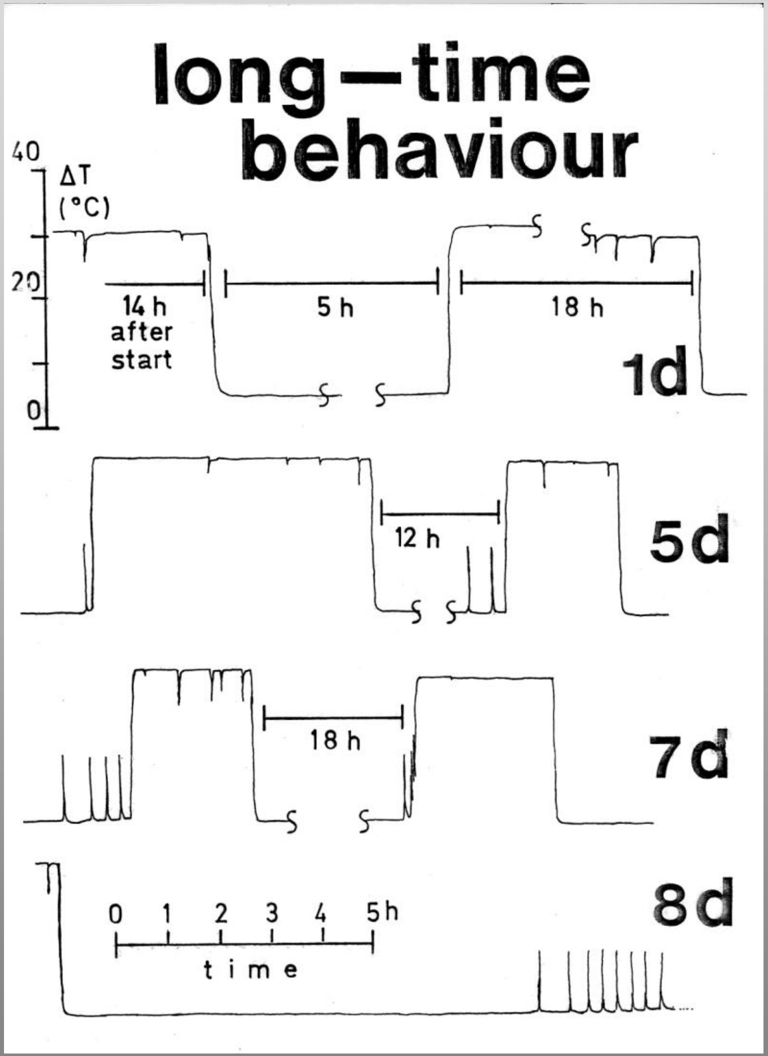
open system

Pd – support catalyst





Synchronous behaviour of Pd catalyst particles



A. Th. Haberditzl , Diplom Thesis 1982

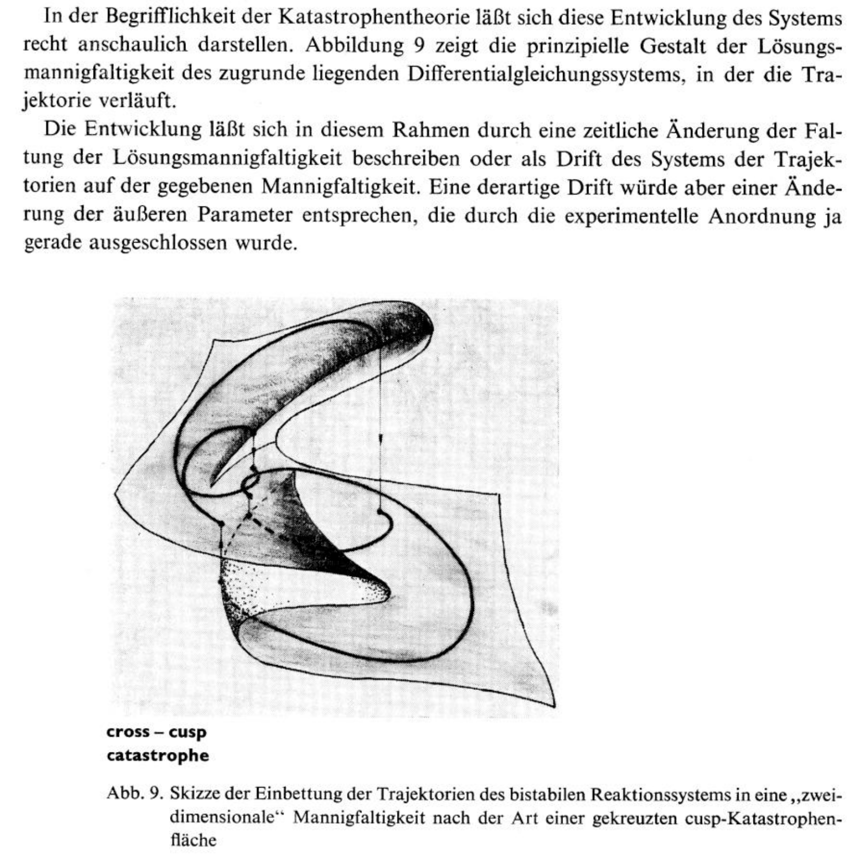
Methanol Oxydation – Catastrophy Theory

Classifikation of static Instabilities – an elementary approach to Thom‘s Catastrophy Theorie

H. Haken Synergetik - Eine Einführung S. 145

$2\ CH_3OH + O_2 \rightarrow HCOOCH_3 + 2\ H_2O$

$CH_3OH + 3/2\ O_2 \rightarrow CO_2 + H_2O$



In der Begrifflichkeit der Katastrophentheorie läßt sich diese Entwicklung des Systems recht anschaulich darstellen. Abbildung 9 zeigt die prinzipielle Gestalt der Lösungsmannigfaltigkeit des zugrunde liegenden Differentialgleichungssystems, in der die Trajektorie verläuft.

Die Entwicklung läßt sich in diesem Rahmen durch eine zeitliche Änderung der Faltung der Lösungsmannigfaltigkeit beschreiben oder als Drift des Systems der Trajektorien auf der gegebenen Mannigfaltigkeit. Eine derartige Drift würde aber einer Änderung der äußeren Parameter entsprechen, die durch die experimentelle Anordnung ja gerade ausgeschlossen wurde.

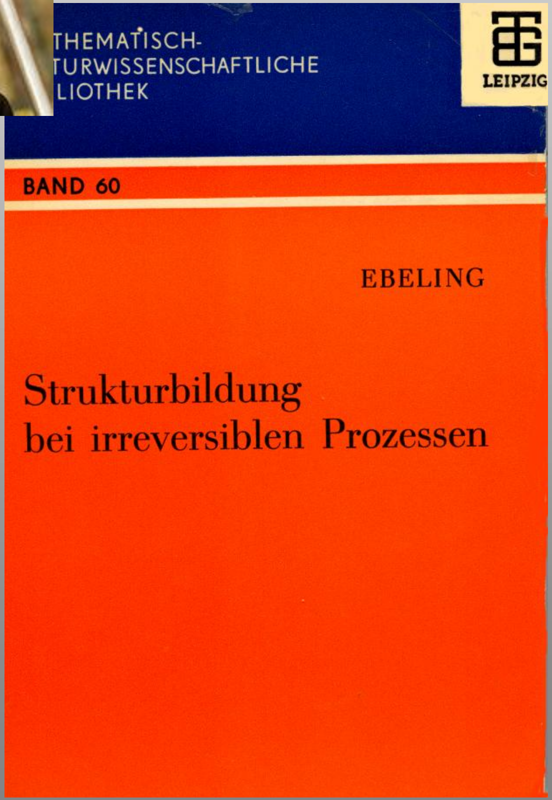
cross – cusp catastrophe

Abb. 9. Skizze der Einbettung der Trajektorien des bistabilen Reaktionssystems in eine „zweidimensionale“ Mannigfaltigkeit nach der Art einer gekreuzten cusp-Katastrophenfläche

A.Th.Haberditzl; N.I. Jaeger; P.J.Plath; Z. phys. Chemie, Leipzig 265 (1984) 449 -463

The non-moleculare perception

Chemistry – far from equilibrium



THEMATISCH-
TURWISSENSCHAFTLICHE
LIOTHEK

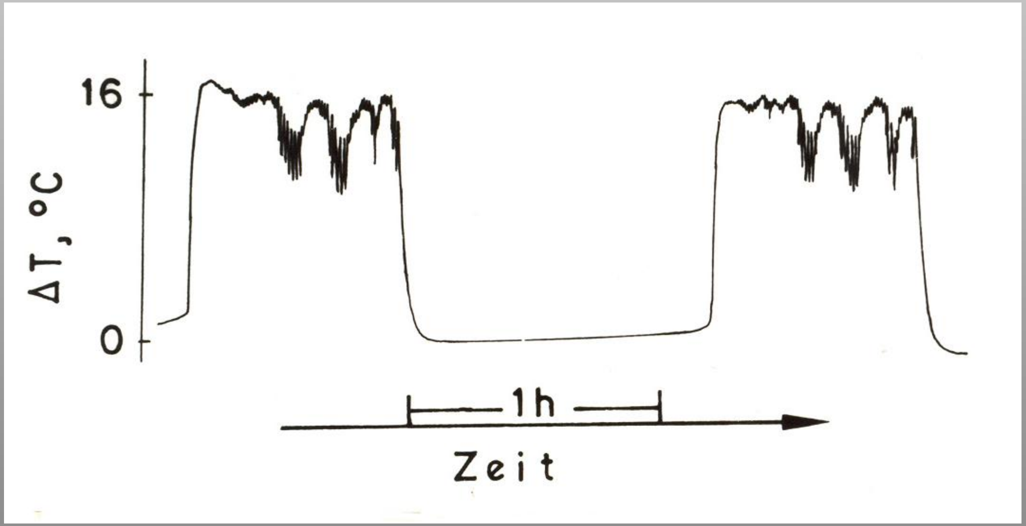
LEIPZIG

BAND 60

EBELING

Strukturbildung
bei irreversiblen Prozessen

1976



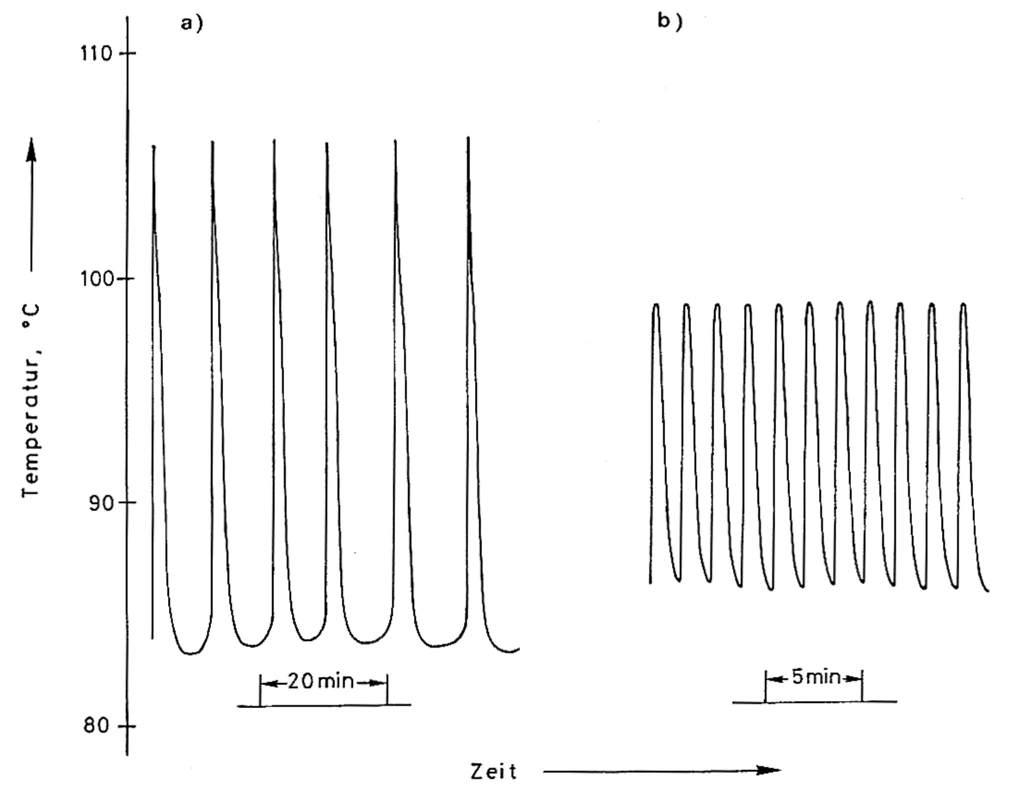
Pd-catalysed
CH_3OH -Oxydation

Oscillating Methanol-Oxidation

Critical values and trajectories in phase-space

limit cycles

Edith van Raaij



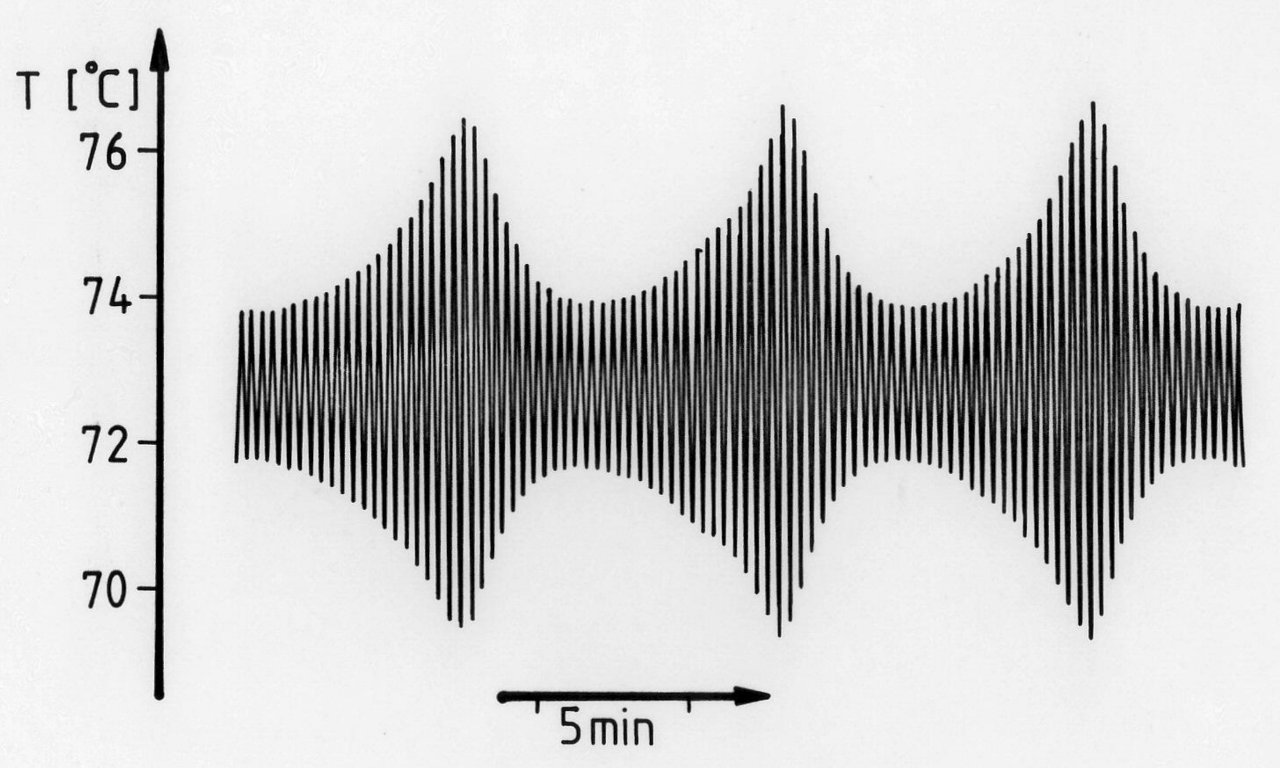
a) Methanol 1,9 Vol % / Oxygen; 41 ml/min

b) Methanol 1,9 Vol % / air; 19 ml /min

E. van Raaij , Diplom Thesis 1980

Toroidal Oscillations of the catalytic Methanol-Oxidation

Peter Svensson
1985

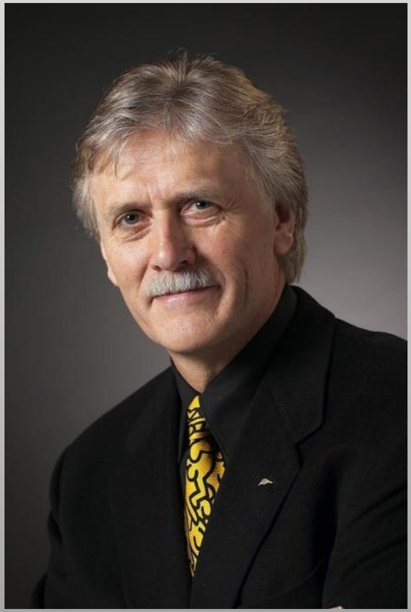


Synergetic Impact of Synergetics

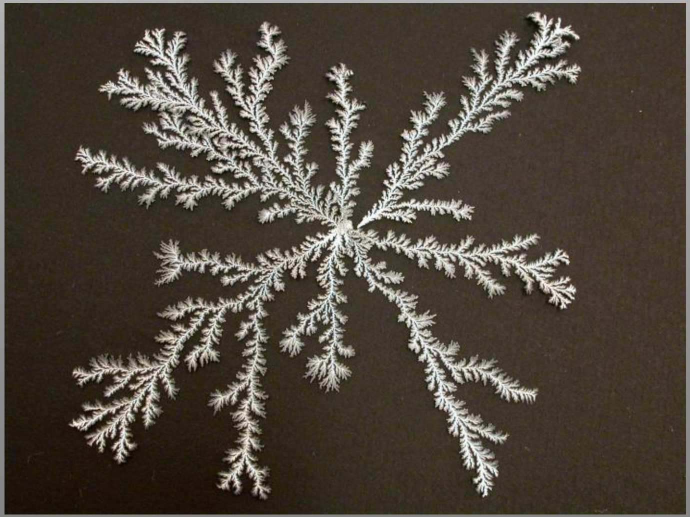
Fractals

Dimension: rat. numbers

Benoit
Mandelbrot

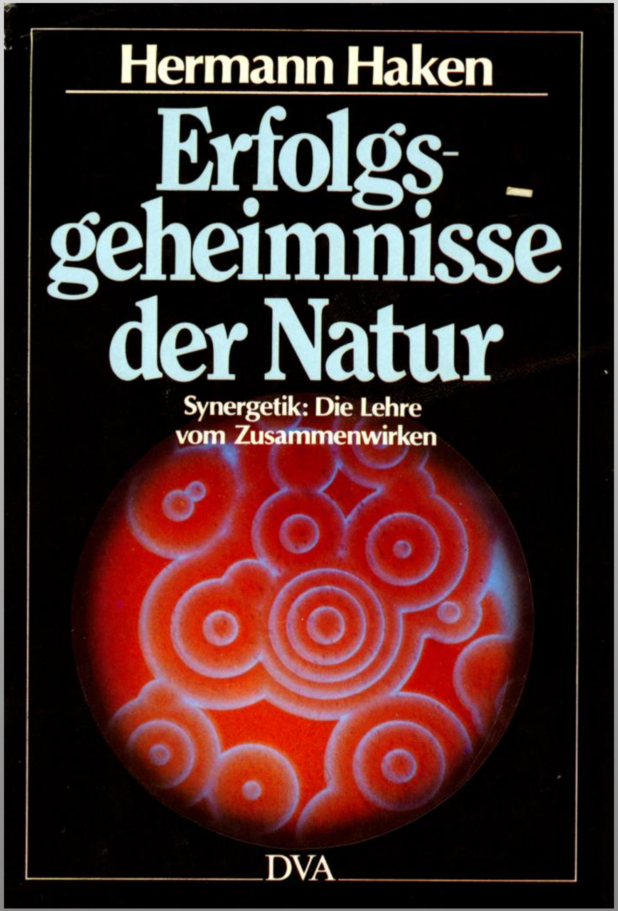


Heinz Otto
Peitgen



Elektro-chemical
deposition of Zinc

Chemical Waves



Hermann Haken
Erfolgsgeheimnisse der Natur
Synergetik: Die Lehre
vom Zusammenwirken
DVA

A local oscillation in an excitable medium becomes a chemical wave by diffusion

$$\frac{\partial c}{\partial t} = D\nabla^2 c; \quad D > 0$$

2nd Fick‘s law

Reaction-Diffusion-Equations

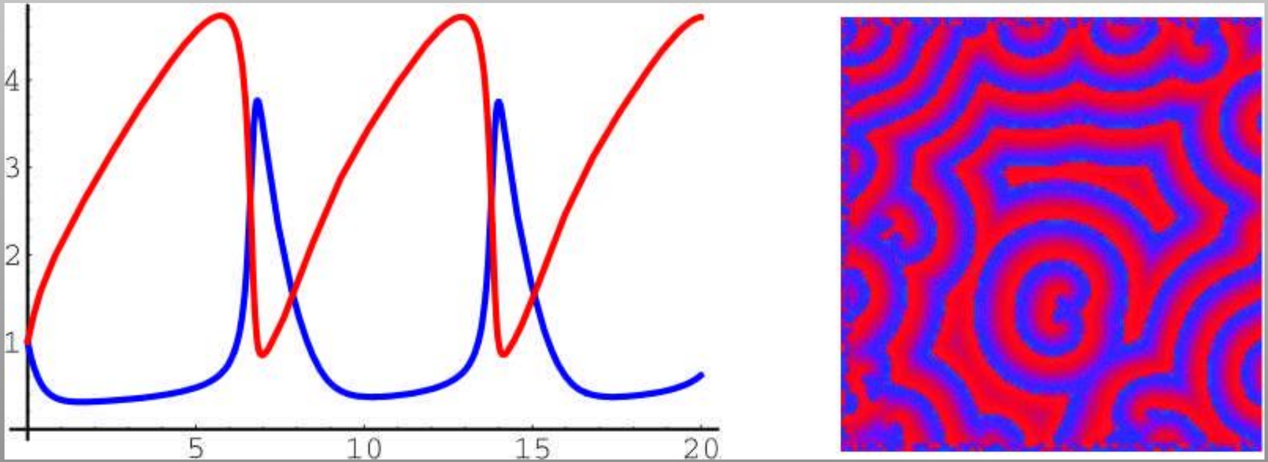
$$\frac{\partial c_i}{\partial t} = f_i(c_1, c_2, \cdots, c_n) + D_i \nabla^2 c_i$$

Belousov – Zhabotinsky Reaction
- BZR -

$$\frac{dX}{dt} = k_1 A - k_2 B X + k_3 X^2 Y - k_4 X$$

$$\frac{dY}{dt} = k_2 B X - k_3 X^2 Y$$

Self-organisation in spatially expanded media



$$\frac{\partial X(\vec{x},t)}{\partial t} = D_X \cdot \nabla^2 X(\vec{x},t) + k_1 A - k_2 B X(\vec{x},t) + k_3 X^2(\vec{x},t) Y(\vec{x},t) - k_4 X(\vec{x},t$$

$$\frac{\partial Y(\vec{x},t)}{\partial t} = D_Y \cdot \nabla^2 Y(\vec{x},t) + k_2 B X(\vec{x},t) - k_3 X^2(\vec{x},t) Y(\vec{x},t$$

Synergetic Impact of Synergetics

CO-Oxidation on Pt (100) single crystal surfaces

G. Ertl

1936- …

Physicist, Physical Chemist

Spirals during single crystal catalysis of CO-oxidation on Pt(100)

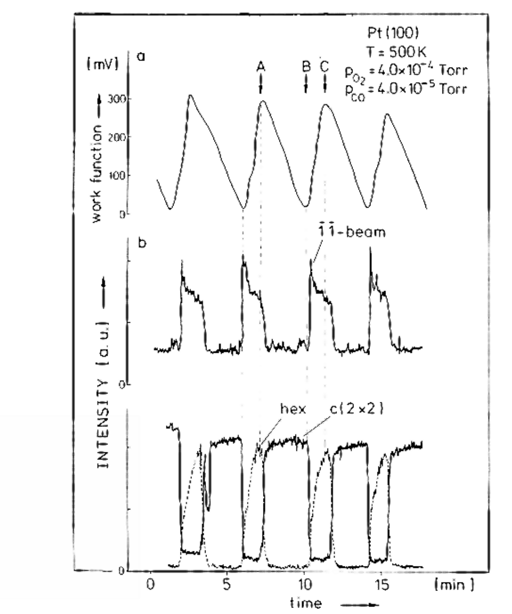
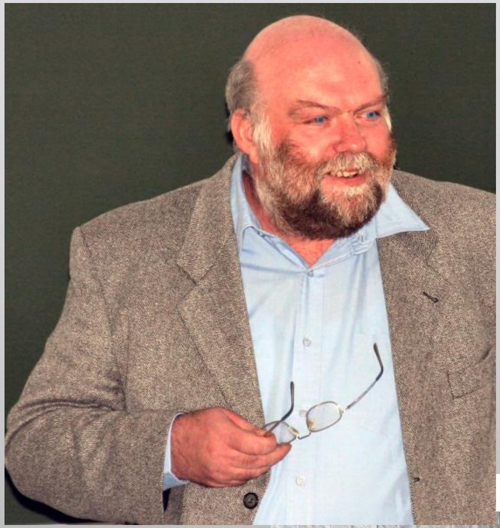
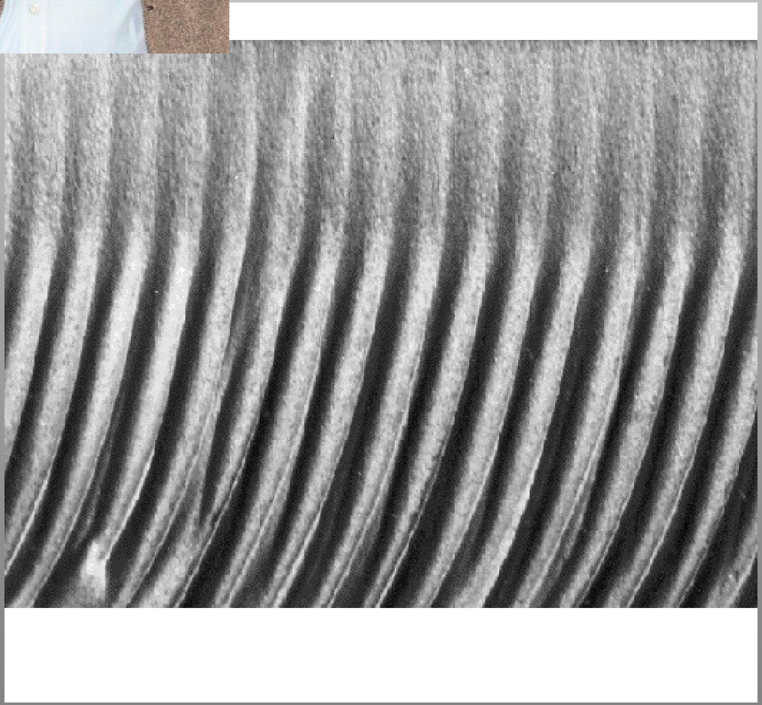


Fig. 2. Kinetic oscillations at $T = 500$ K, $p_{O_2} = 4\times10^{-4}$ Torr, $p_{CO} = 4\times10^{-5}$ Torr: (a) periodic variation of the work function; (b) intensities of various LEED spots as a function of time: $(\bar{1}\bar{1}) \hat{=}$ substrate lattice, $(\frac{1}{2}\frac{1}{2}) \hat{=}$ c2×2 − 1×1 structure, $(\frac{3}{5}\bar{1}) \hat{=}$ hex structure.

Cox, Ertl, Imbihl, Rüstig; Surface Science 134 (1983) I.517- I.523

Synergetic Impact of Synergetics



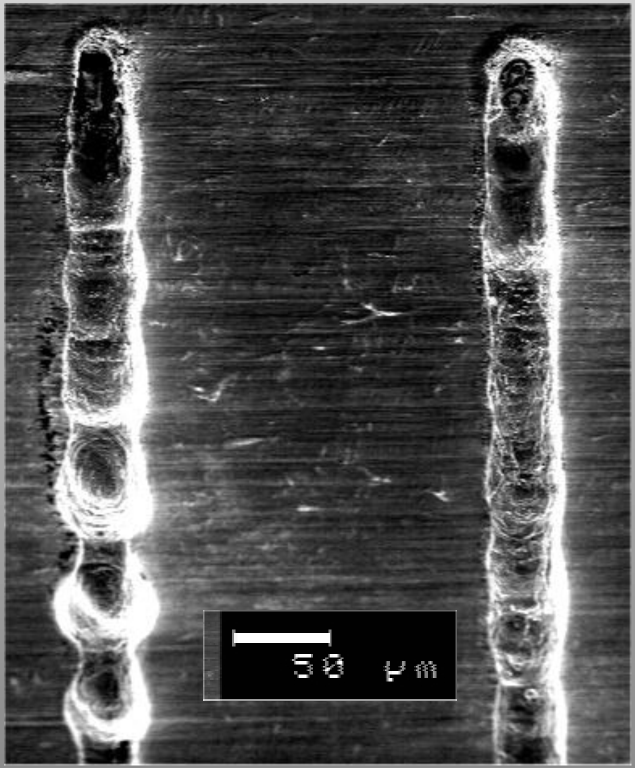


Ripples occuring during abrasive water-jet-cutting

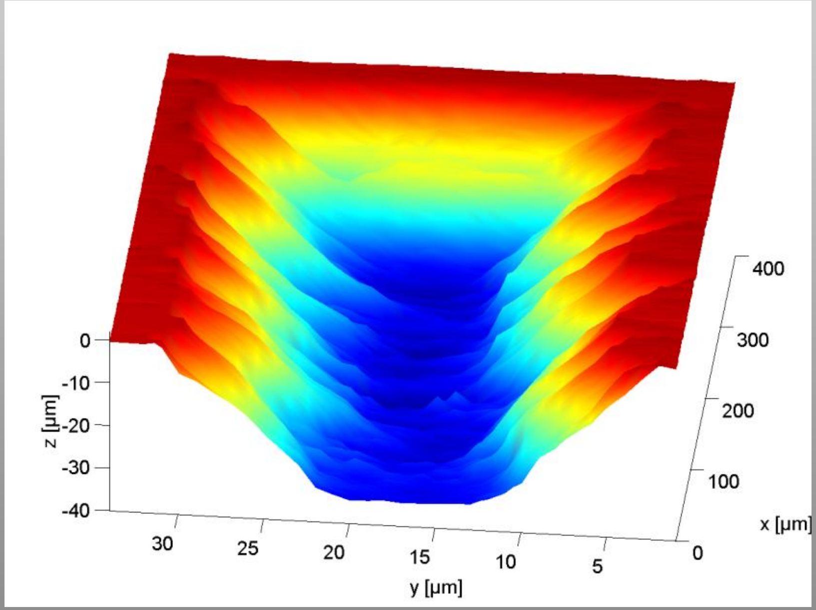
G. Radons, R. Friedrich
et al. 2003

Formation of ripples during laser-jet etching

Thomas Rabow



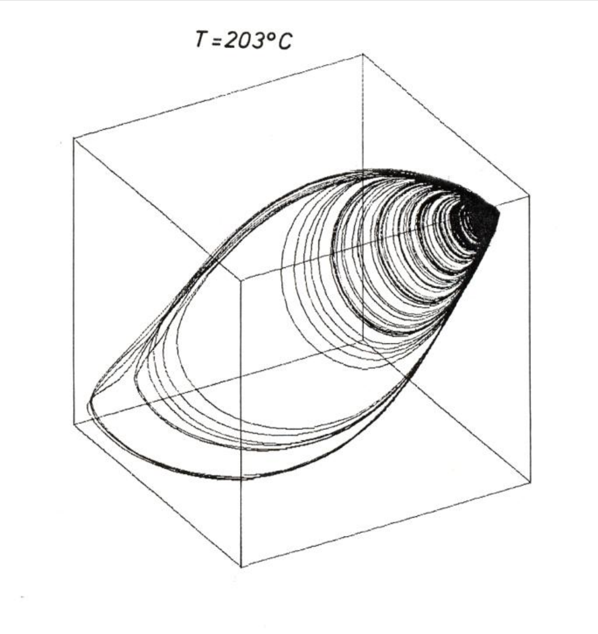
different rates of feed



Laser Scan surface profile

Chaos during the Catalytic CO-Oxidation

Prof. Dr. Nils Jaeger



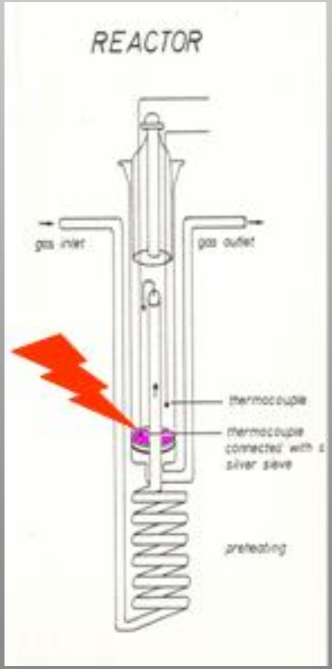
Chaotic attractor of Pd-catalysed CO-Oxidation

Dr. Karin Möller

The Real Catalytic System

$$CO + \frac{1}{2}O_2 \xrightarrow{Pd\,/\,X} CO_2 + \Delta H;\quad \Delta H < 0$$

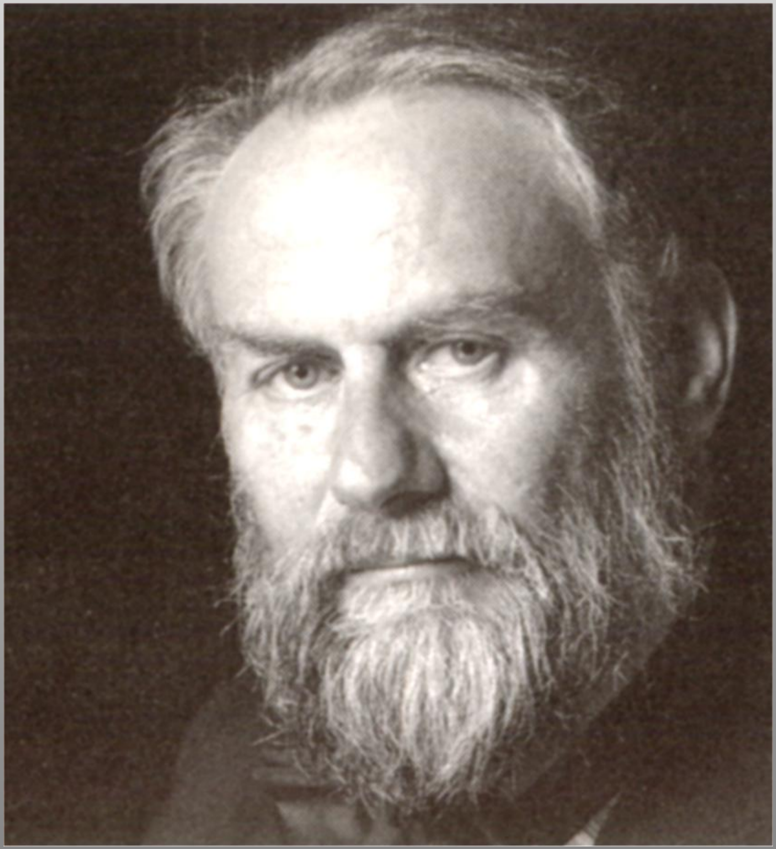
exothermic reaction



Control parameter

- CO concentration in a N_2/O_2 mixture (synthetic air): 0,39 Vol %
- catalyst composition: Pd/X catalyst i.e. X-type zeolite with variable Pd content, for example: 0.5 weight % Pd
- V_{eff} = 8 ml effective reactor volume
- dv/dt = 50 to 250 ml / min flowrate: τ_{res} = 1 to 10 sec residence time
- T_O reactor/oven temperature: 175 – 250 °C

What means synergetics ?



Zitat: H.Haken zur Synergetik:

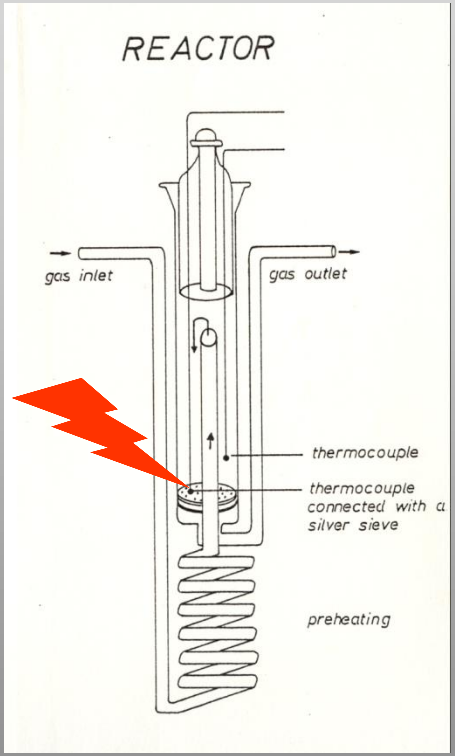
"Was wir untersuchen, ist das **gemeinsame Wirken vieler Untersysteme**, das derart verläuft, daß es Strukturen und Funktionen auf einer makroskopischen Skala erzeugt."

What we are looking for that is the action of many sub-systems in common, creating structures and new functions on a macroscopic scale.

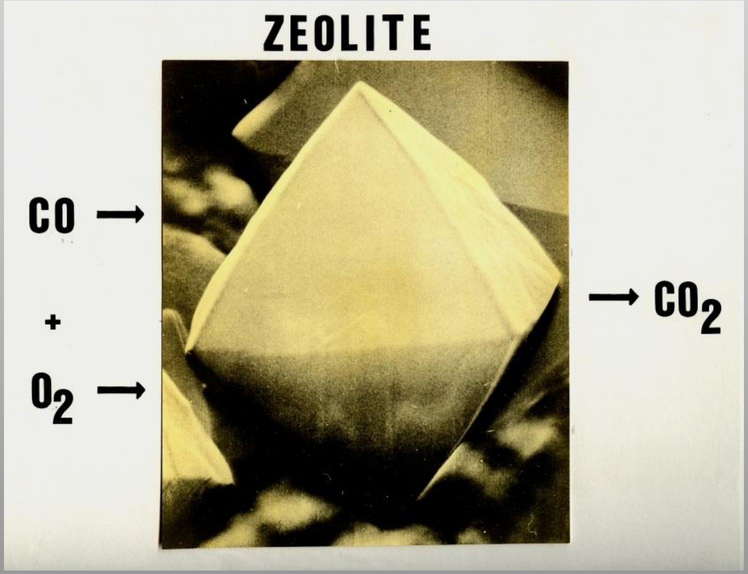
H. Haken; Synergtik – eine Einführung, Springer–Verlag Berlin, Heidelberg, ... (1990)

Heterogeneously Catalysed CO-Oxidation

Level of description?



catalyst in the reactor
diameter 1,5 cm; 20 mg

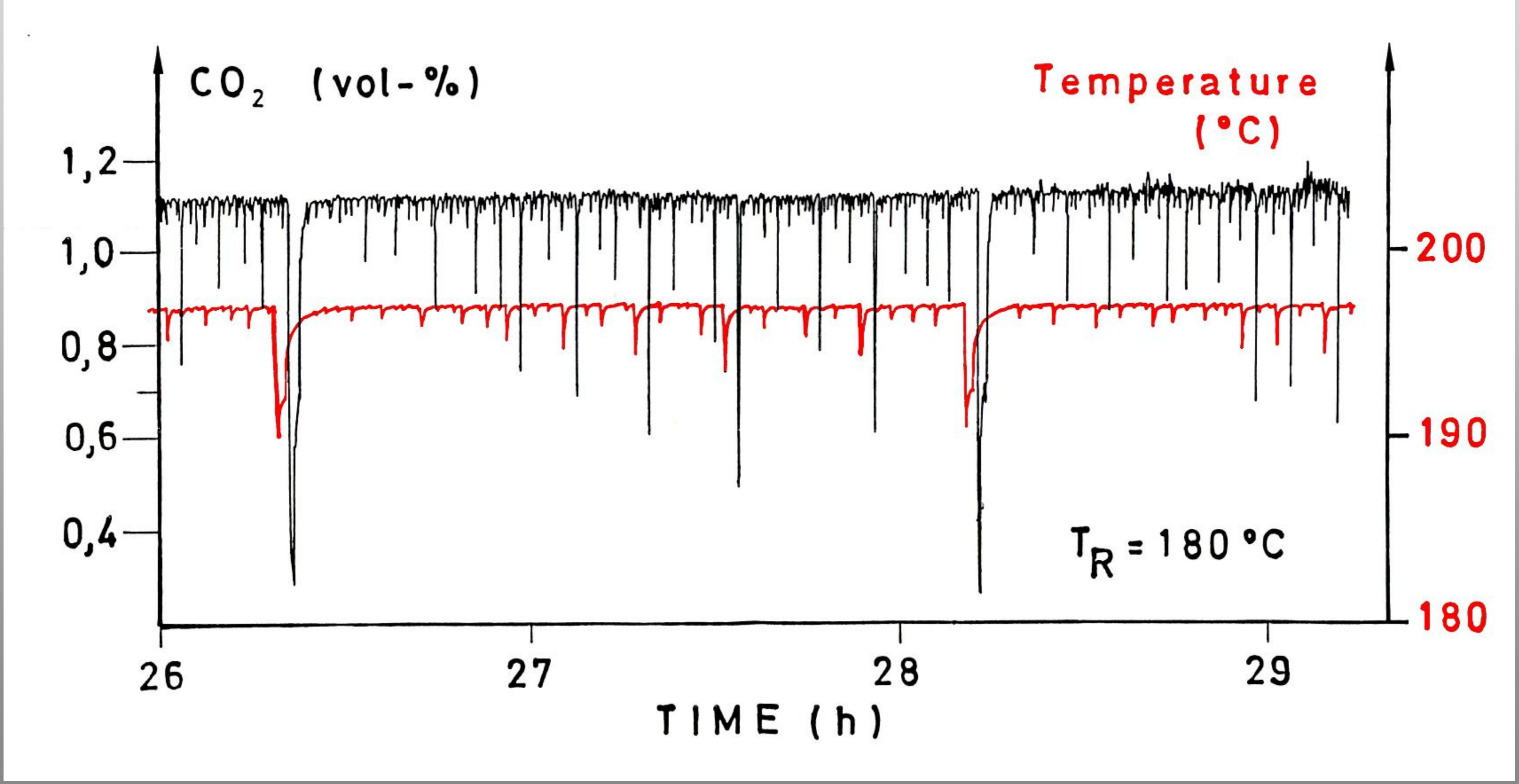


X-type zeolite – single-crystal
20 µm

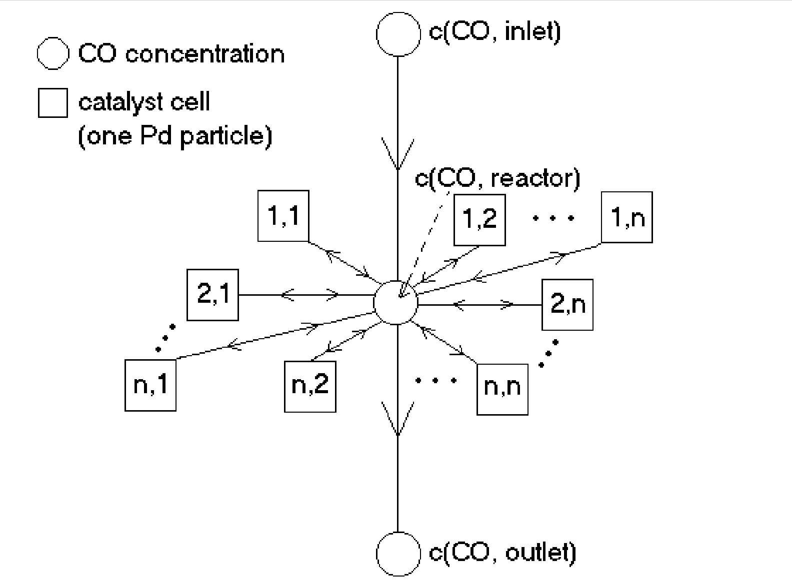
Palladium crystals 3 nm in the
zeolite-single-crystal

~$3 \cdot 10^{13}$ Pd-particle in the catalyst

Oscillation of CO_2 - Concentration and Temperature



Sub-system: Elementary reactor



Elementary reactor:
~ 3·10^{11} Pd-particles

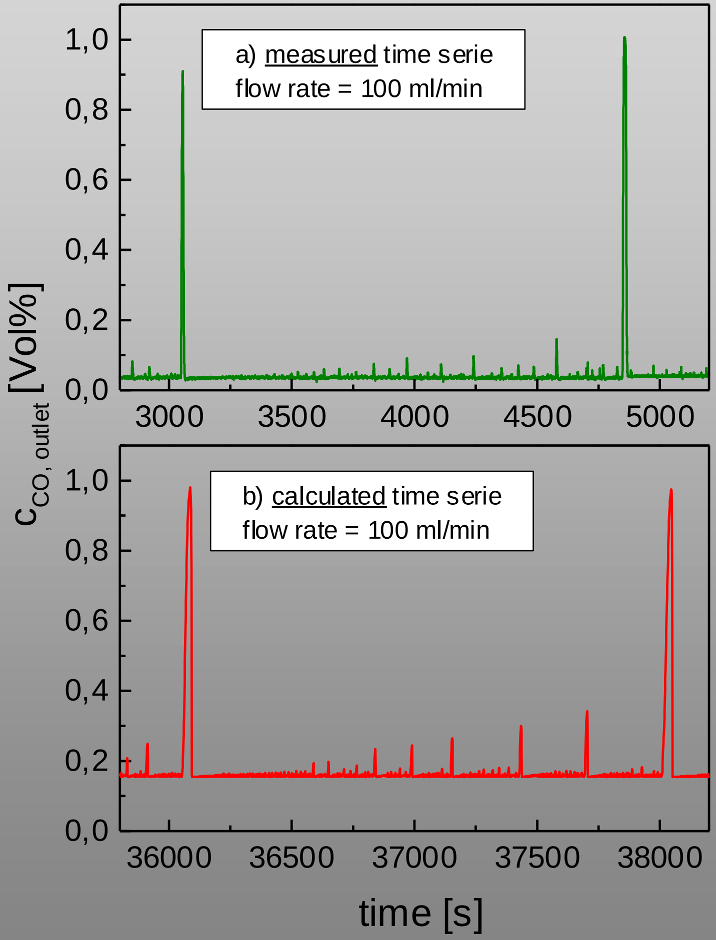
Temporal fractal structure formation

Experiment

CO-oxidation in a micro-reactor

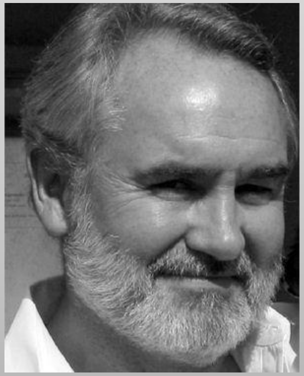
Modell

100 coupled elementary-reactors



Synergie der Synergetik - Beispiele

Michael Stadler
Psychology



J.A.S. Kelso

brain research

Alexander Mikhailov
PC – Bio-molecules

Wolfgang Wildgen
Linguistics

Ludger Rensing
Cell-biology

Synergetic Impact of Synergetics

The right view on our world

H. Haken

P. Plath

Synergetic Impact of Synergetics

„Das mußte doch `mal gesagt werden!“

“One already had to say it!“

Thank you

for your attention

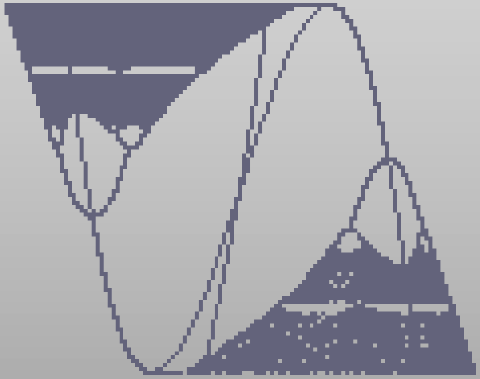
Rudolf Friedrich

in 2007

Blick zurück im Glück (Elisabeth Swart)

View Back in Luck

Peter J. Plath
in 2007



Wirrwarr-Attraktor

Hurly-burly attractor

Hurly burly: a complex system,
i.e. an attractor without only one trajectory

$$x(t+1) = b_1 x^3(t) + b_2 x(t) - y(t) + x(t)$$

$$y(t+1) = a_1 x^2(t+1) + a_2 x(t+1) - a_3$$