The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
and Cultural Organization

International Atomic
Energy Agency

Summer School on
Design and Control of Self-Organization in Physical, Chemical, and Biological Systems

25 July to 5 August, 2005

Miramare-Trieste, Italy

1668/25

Flow Distributed Oscillators

Stephen Scott
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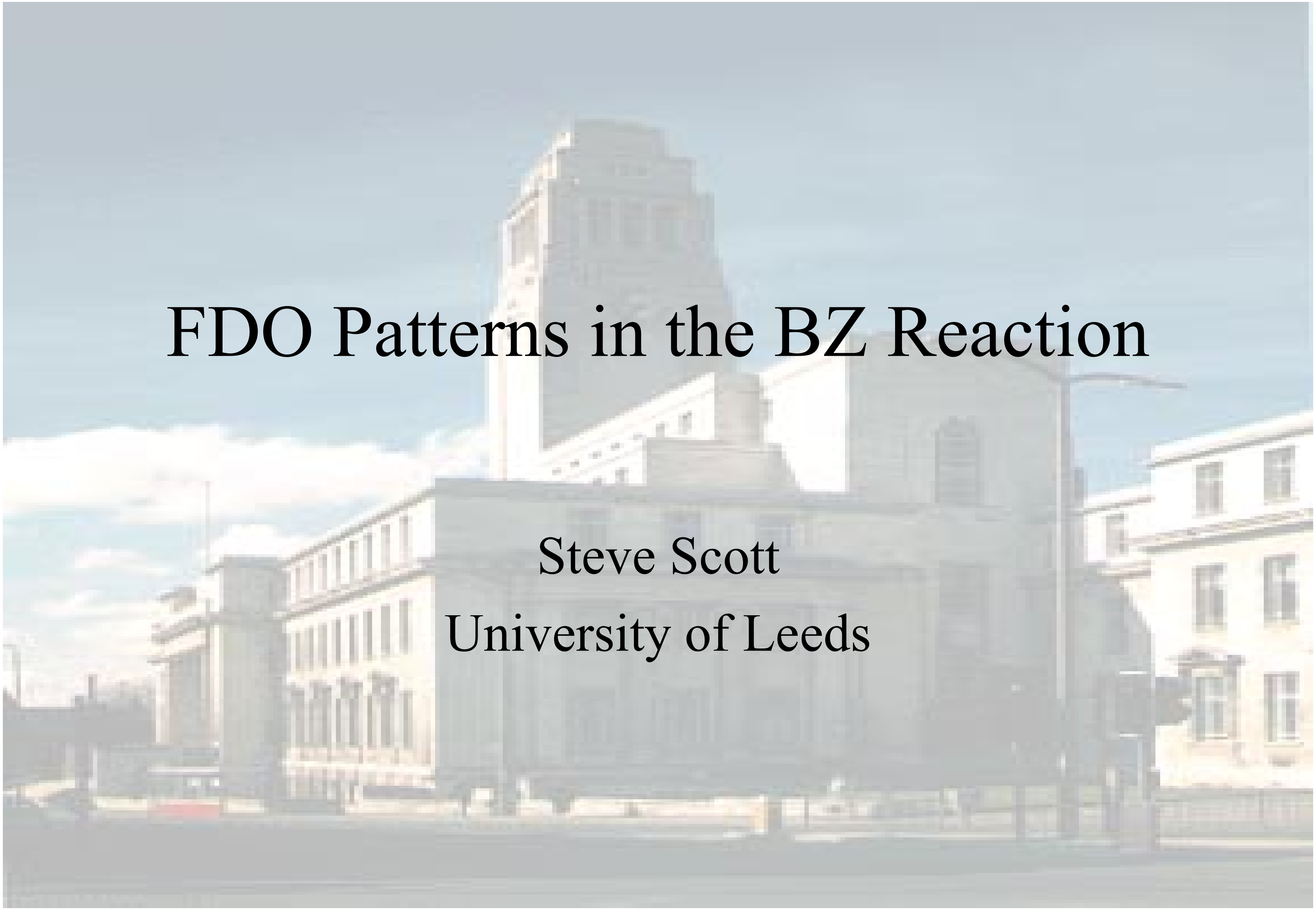
United Kingdom

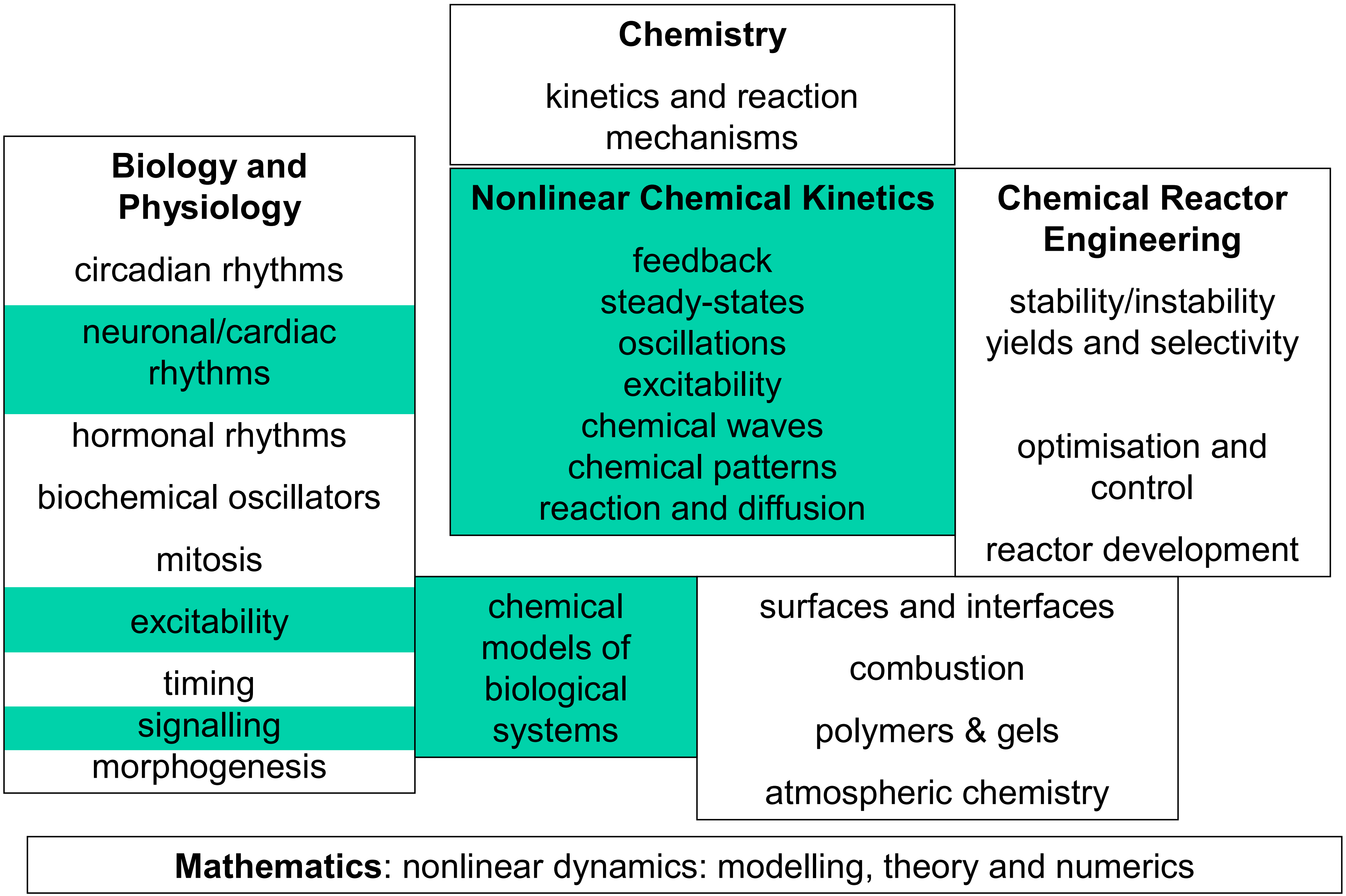
FDO Patterns in the BZ Reaction

Steve Scott
University of Leeds

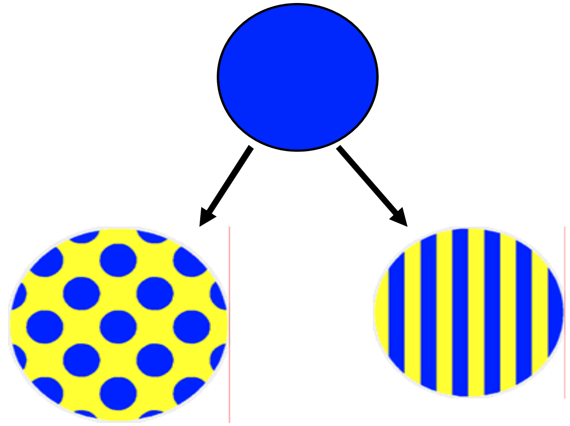


Chemical Models

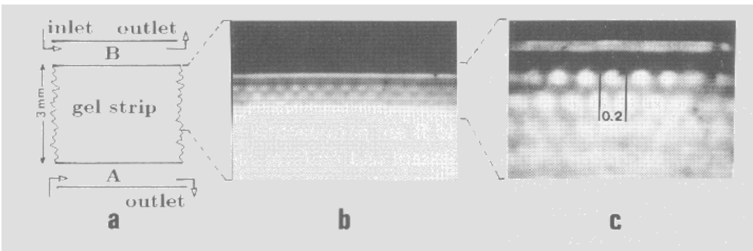
- Chemistry can provide “reduced model” of selected aspects of biological or engineering systems
- Chemical systems show feedback and excitability
- Convenient time and length scales
- Easily monitored
- Reaction and diffusion couple in rigorous and intuitive way (in most cases)
- Can begin with virtually homogeneous systems and then incorporate increasing extents of heterogeneity


Chemistry
kinetics and reaction mechanisms
Biology and Physiology
circadian rhythms
neuronal/cardiac rhythms
hormonal rhythms
biochemical oscillators
mitosis
excitability
timing
signalling
morphogenesis
Nonlinear Chemical Kinetics
feedback
steady-states
oscillations
excitability
chemical waves
chemical patterns
reaction and diffusion
Chemical Reactor Engineering
stability/instability
yields and selectivity
optimisation and control
reactor development
chemical models of biological systems
surfaces and interfaces
combustion
polymers & gels
atmospheric chemistry
Mathematics: nonlinear dynamics: modelling, theory and numerics

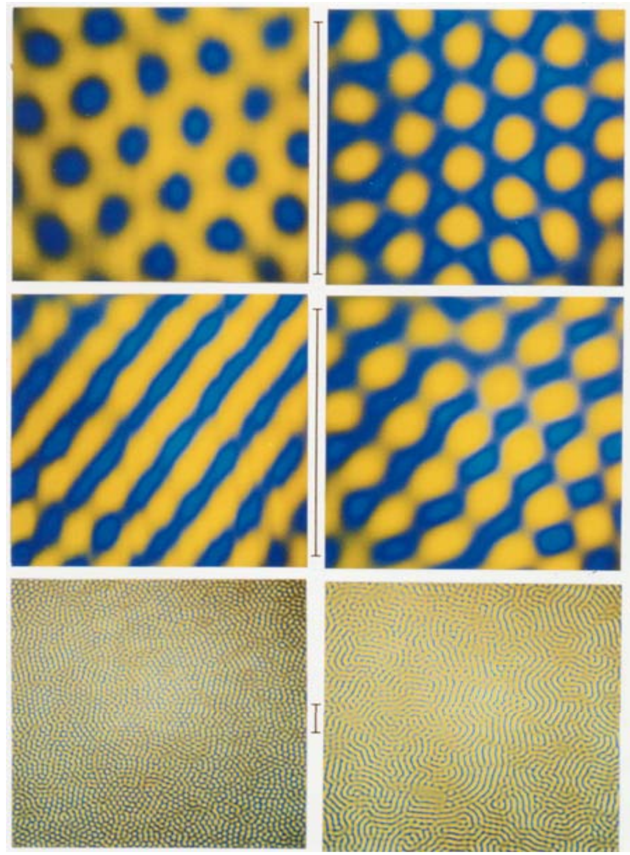
Turing Patterns



- Turing proposal for "morphogenesis" (1952)
- "selective diffusion" in reactions with feedback
- requires diffusivity of feedback species to be reduced compared to other reactants
- observed in chemical systems



Castets *et al*. Phys Rev. Lett 1990



Ouyang and Swinney, Chaos 1991

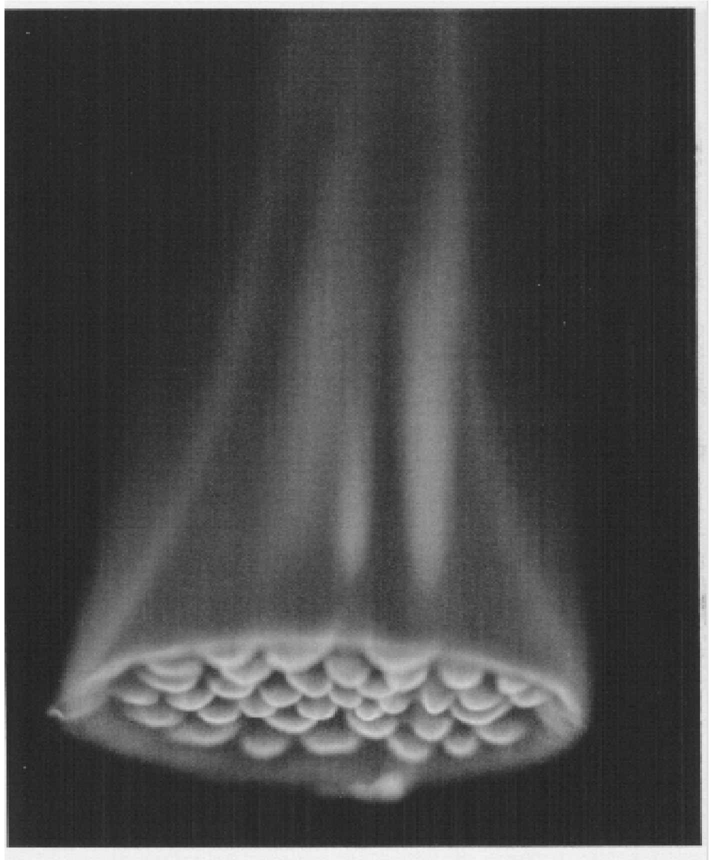
Experimental Realisation

- Chemical system that supports batch oscillations – but run under non-oscillatory conditions
- Arrange selective diffusion typically via complexing to immobilised species trapped in gel
- Open reactor configuration

“Turing Patterns” in flames

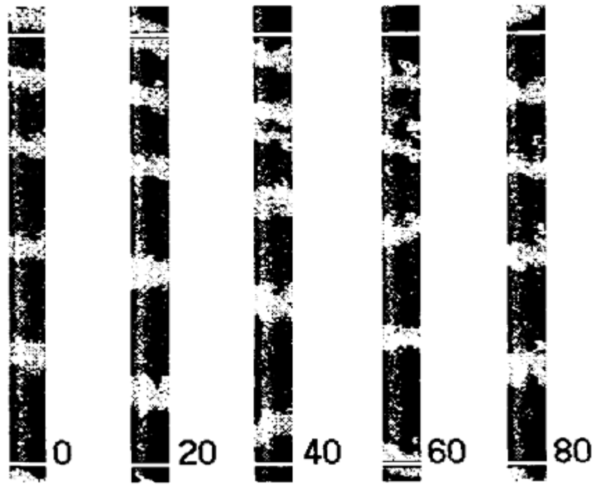
“thermodiffusive instability”
- first observed in Leeds
(Smithells & Ingle 1892)

requires thermal diffusivity <
mass diffusivity



DIFICI

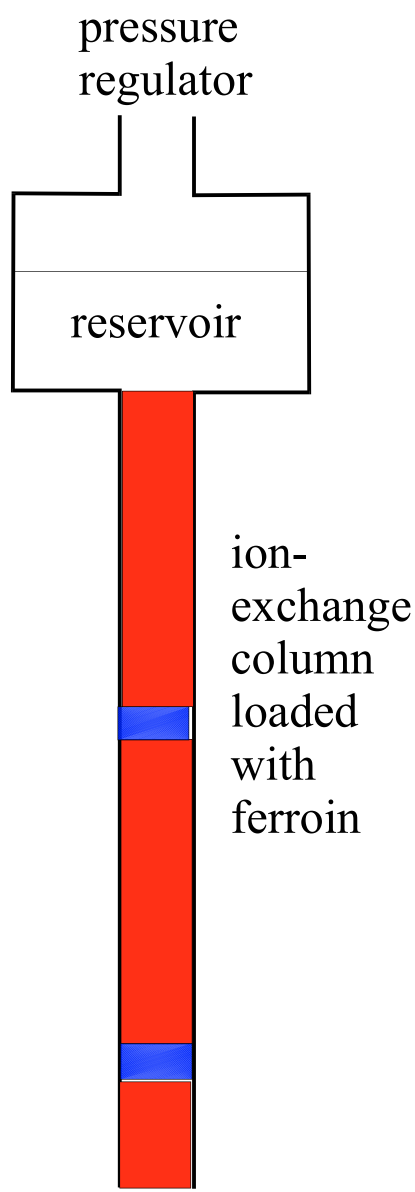
- differential-flow induced chemical instability
- requires selective diffusivity but can be ***any*** species



Menzinger and Rovinsky
Phys. Rev. Lett., 1992,1993

BZ reaction: DIFICI

- immobilise ferroin on ion-exchange resin
- flow remaining reactants down tube
- above a “critical” flow velocity, distinct “stripes” of oxidation (blue) appear and travel through tube



Experiment

$\lambda = 2.1$ cm

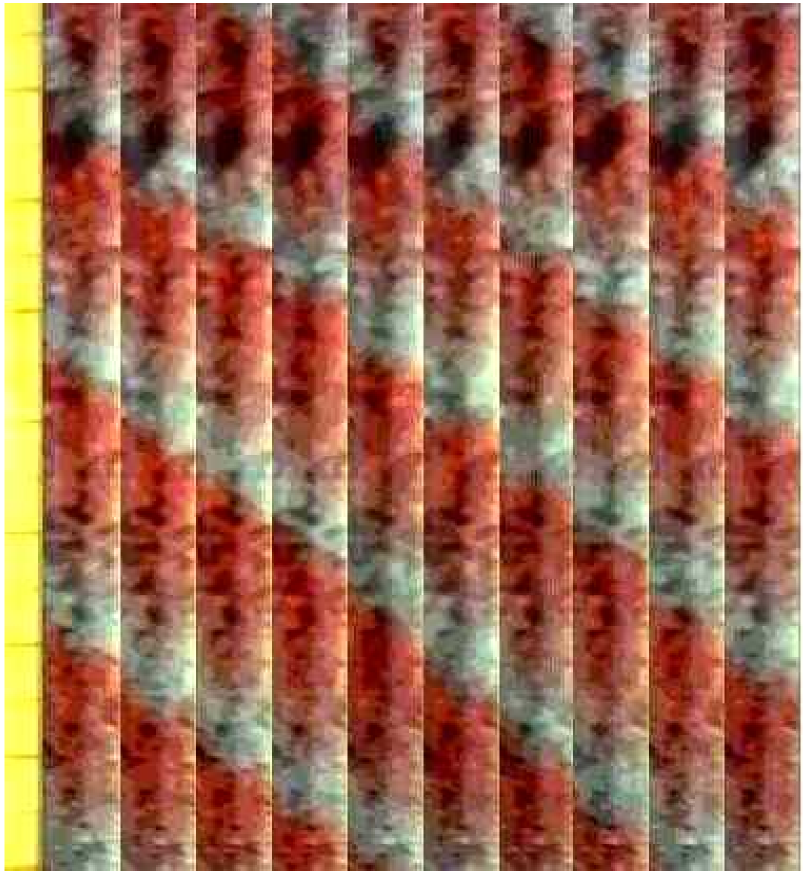
$c_f = 0.138$ cm s^{-1}

$f = 2.8$ s frame^{-1}

$[BrO_3^-] = 0.8$ M

[BrMA] = 0.4 M

$[H_2SO_4] = 0.6$ M

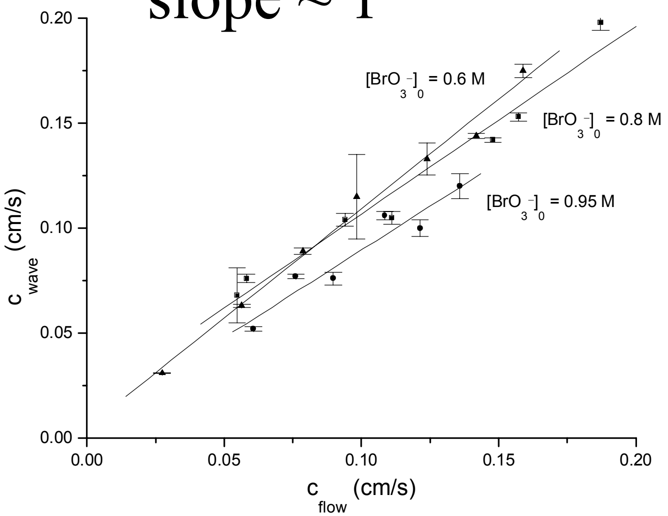


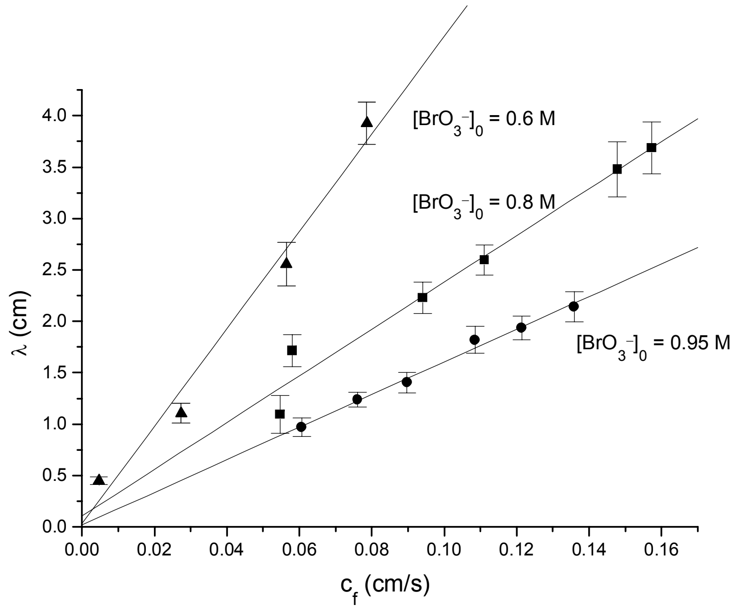
Rita Toth, Attila Papp (Debrecen), Annette Taylor (Leeds)

Experimental results

imaging system: vary “driving pressure”

slope ~ 1





Not possible to determine “critical flow velocity”

Theoretical analysis:

- Dimensionless equations

$$\varepsilon \frac{\partial u}{\partial t} + \phi \frac{\partial u}{\partial x} = \frac{\partial^2 u}{\partial x^2} + \left\{ u(1-u) - fv \frac{(u-q)}{(u+q)} \right\}$$

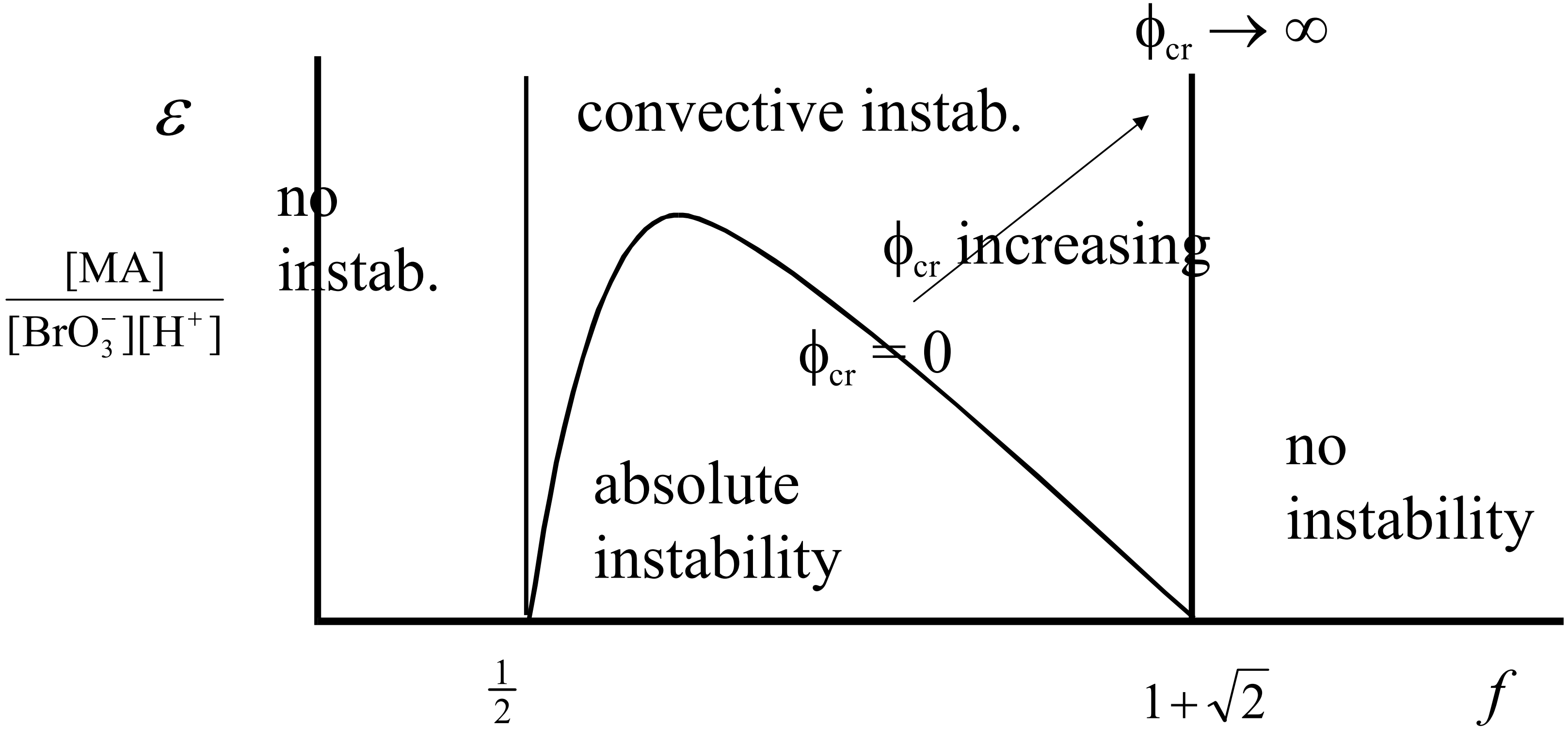
$$\frac{\partial v}{\partial t} + \delta\phi \frac{\partial v}{\partial x} = \delta \frac{\partial^2 v}{\partial x^2} + u - v$$

u = [$HBrO_2$], v = [M_{ox}] : take $\delta = 0$

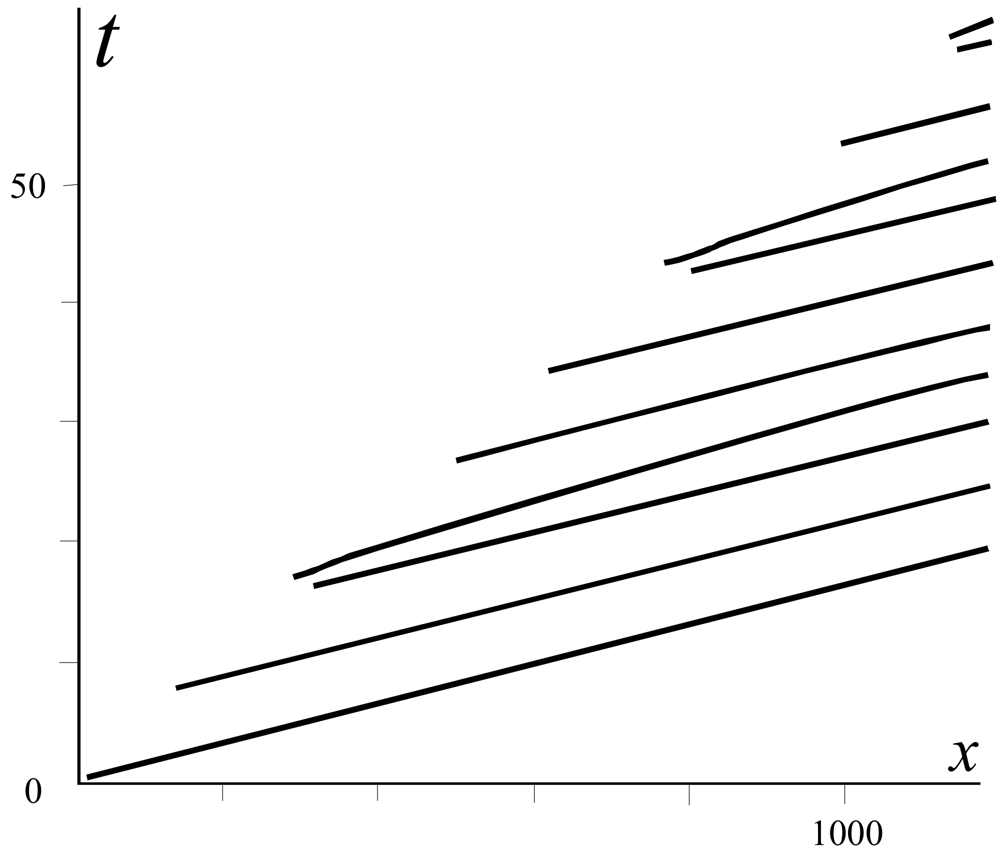
ε and f depend on initial reactant concentrations

main results

- DIFICI patterns in range of operating conditions separate from oscillations



Space-time plot showing position of waves



back to dimensional terms :

predict

$c_{f,cr} = 1.3 \times 10^{-2}$ cm s^{-1}

For
$c_{f,cr} = 2.4 \times 10^{-2}$ cm s^{-1}

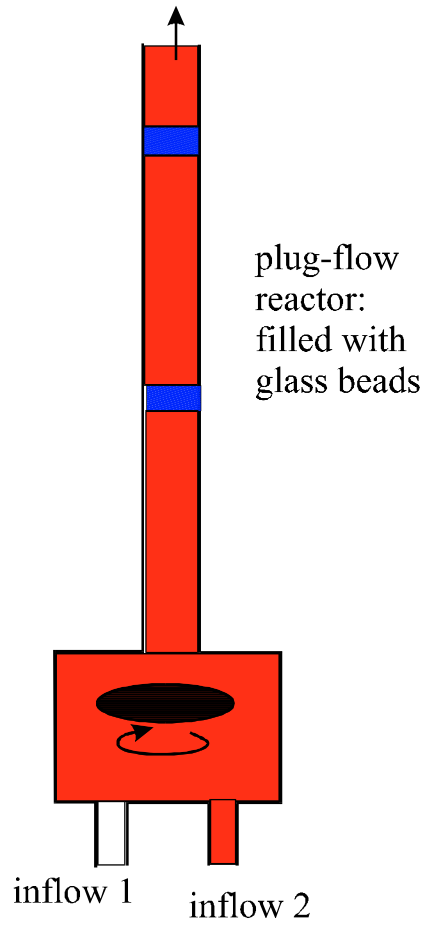
$\lambda = 0.42$ cm

note: initiation site moves down tube

Kuznetsov, Andresen, Mosekilde, Dewel, Borckmans

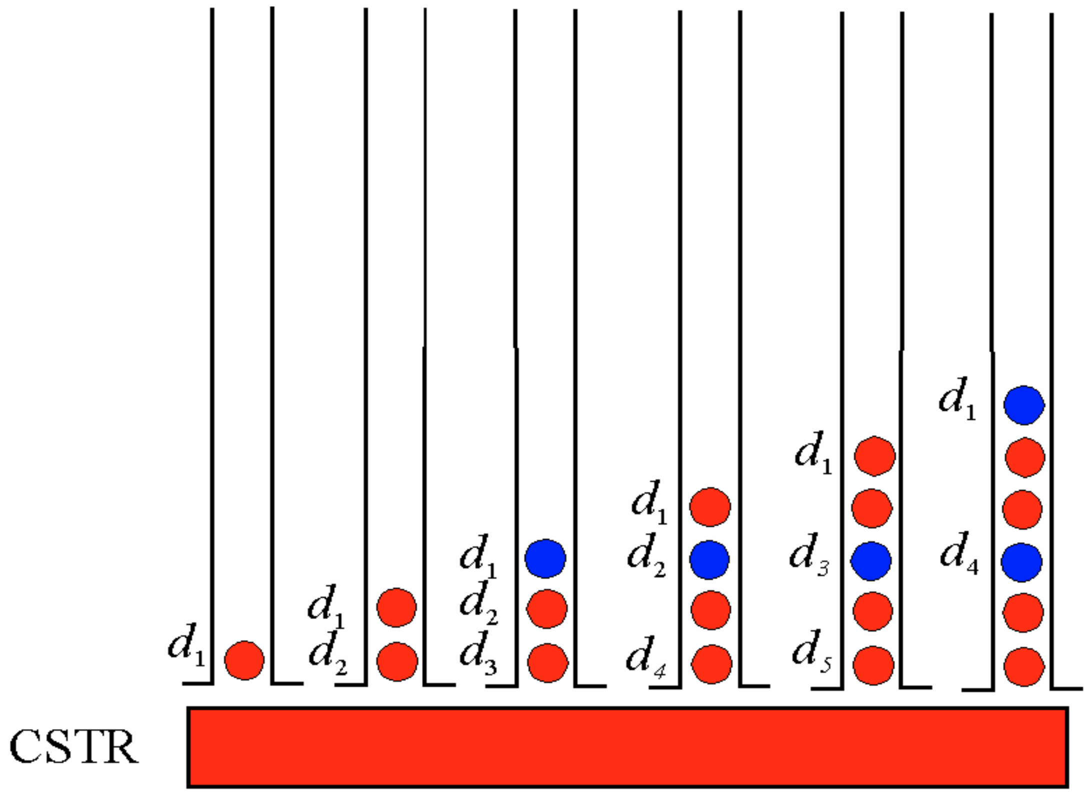
Flow Distributed Oscillations

- patterns without differential diffusion or flow
- Very simple reactor configuration:
  - plug-flow tubular reactor fed from CSTR
- reaction run under conditions so it is oscillatory in batch, but steady-state in CSTR



Simple explanation

- CSTR ensures each "droplet" leaves with same "phase"
- Oscillations occur in each droplet at same time after leaving CSTR and, hence, at same place in PFR



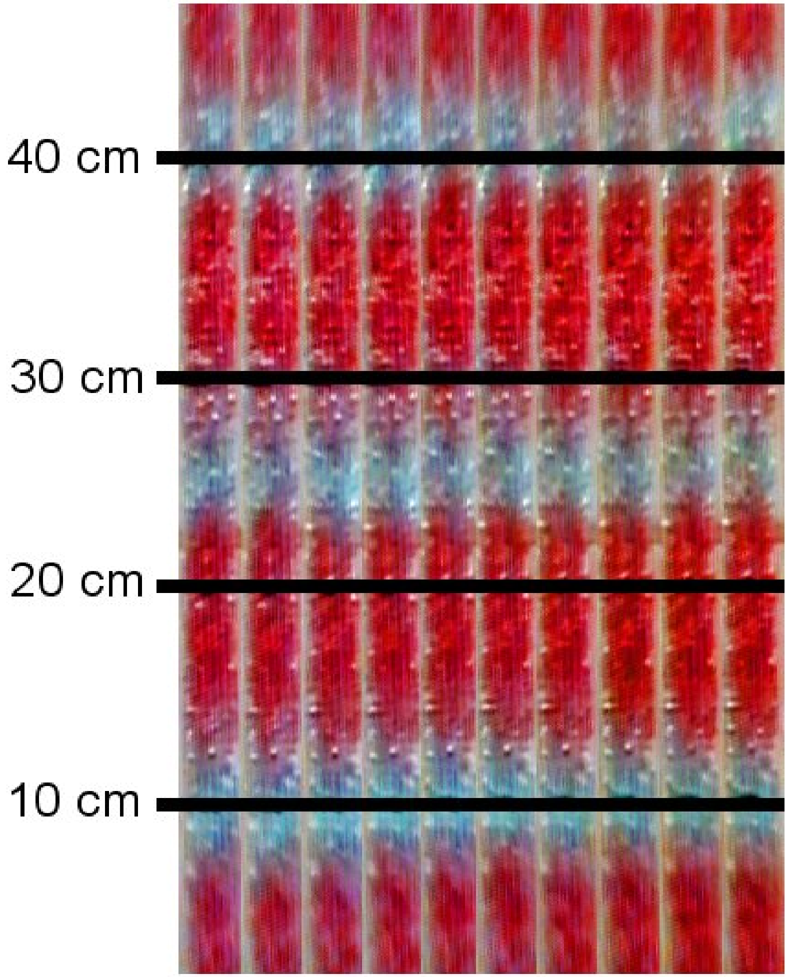
explains:

existence of stationary patterns

need for "oscillatory batch" reaction

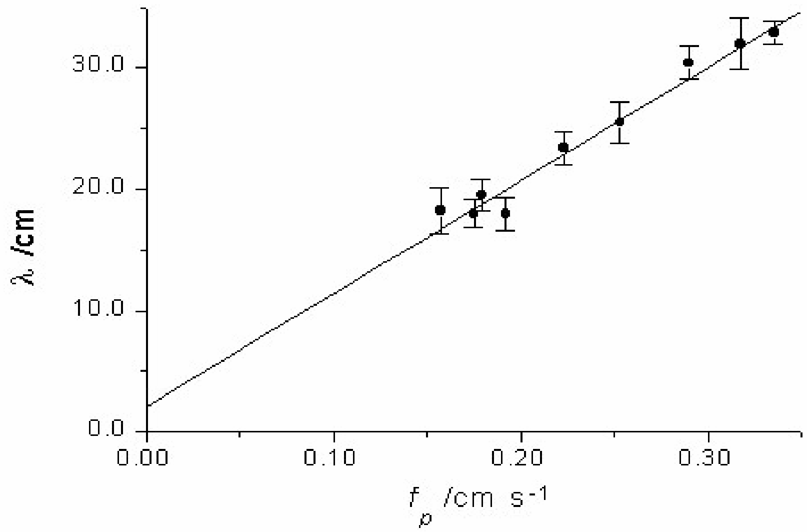
BZ system with $f = 0.17$ cm s^{-1}

$[BrO_3^-] = 0.24$ M, $H^+ = 0.15$M
[MA] = 0.4 M,
[Ferroin] = 7×10^{-4} M



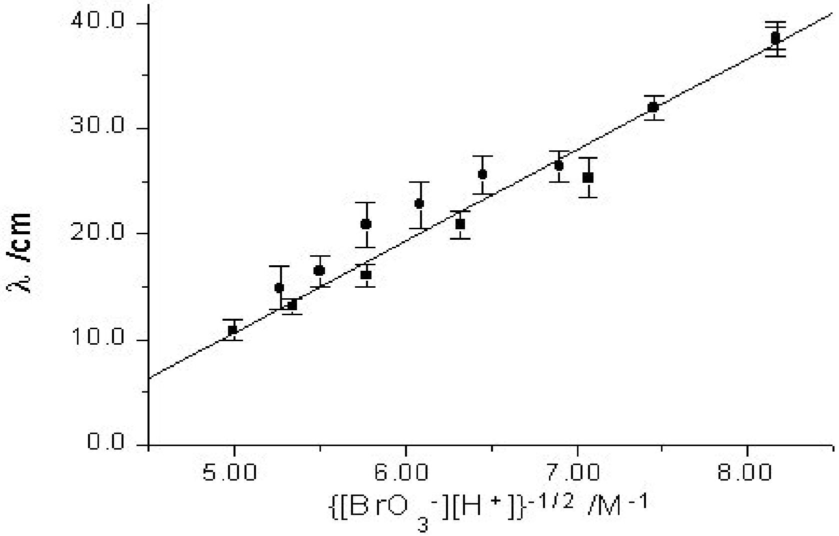
Images taken at 2 min intervals

wavelength = velocity × period



Using simple analysis of Oregonator model, predict:

$$\lambda \sim \frac{\phi}{[BrO_3^-]^{1/2}[H^+]^{1/2}}$$



Doesn't explain some key features

- critical flow velocity
- nonlinear dependence of wavelength on flow velocity
- other responses observed, especially the dynamics of pattern development

Modelling

- Oregonator model:

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} - \phi_P \frac{\partial u}{\partial x} + \frac{1}{\varepsilon}\left\{ u(1-u) - fv\frac{(u-q)}{(u+q)} \right\}$$

$$\frac{\partial v}{\partial t} = \frac{\partial^2 v}{\partial x^2} - \phi_P \frac{\partial v}{\partial x} + u - v$$

Initial Development of Stationary Pattern

- Oregonator model

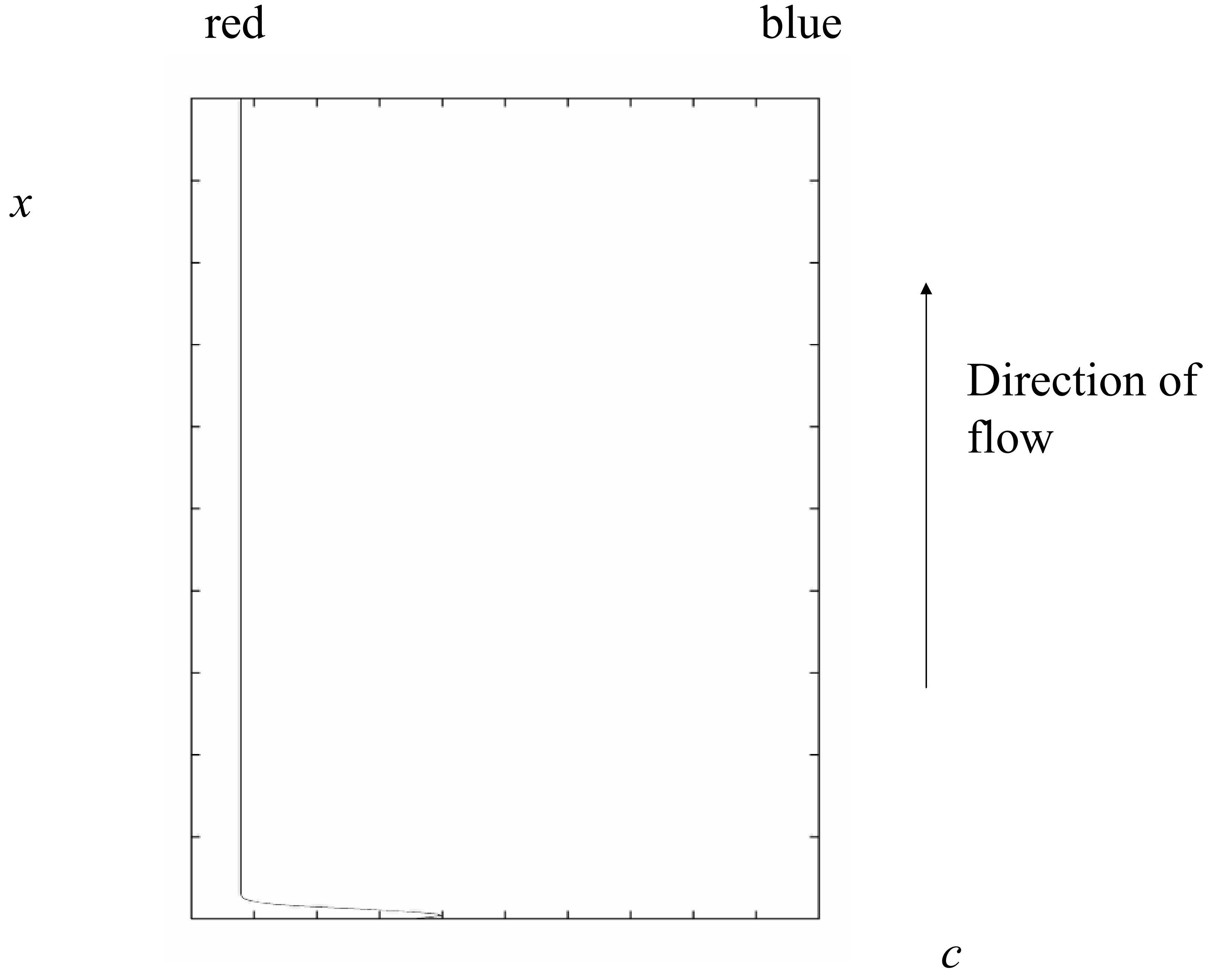
  $\varepsilon = 0.25$

  $f = 1.0$

  $q = 8 \times 10^{-4}$

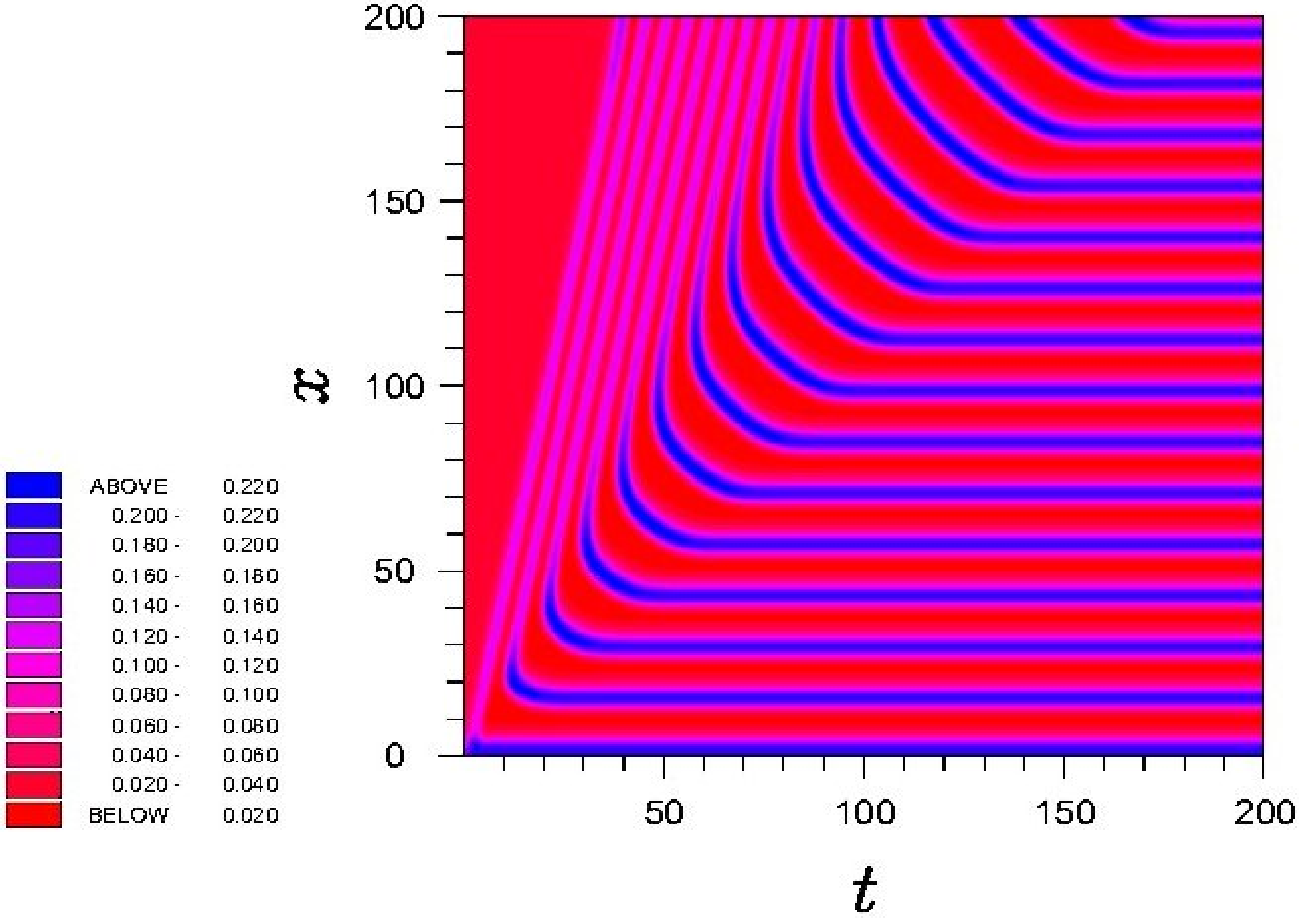
  $\phi = 2$

  0.4 time units per frame



red
blue
x
Direction of flow
c

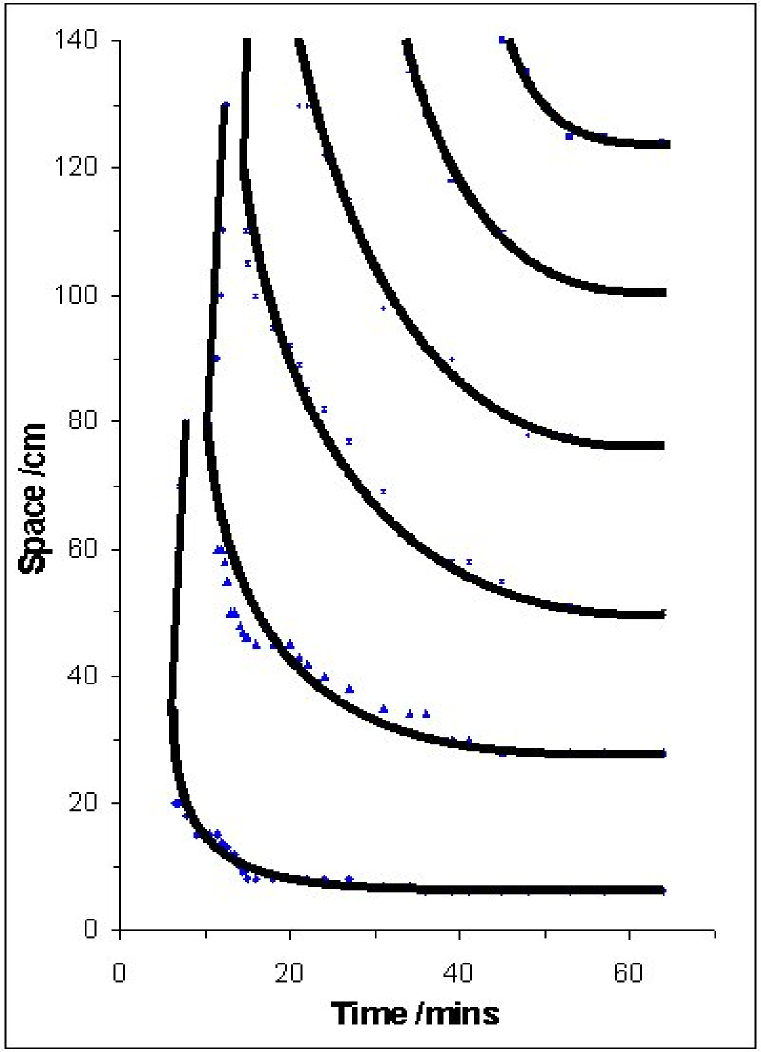
Space-time plot



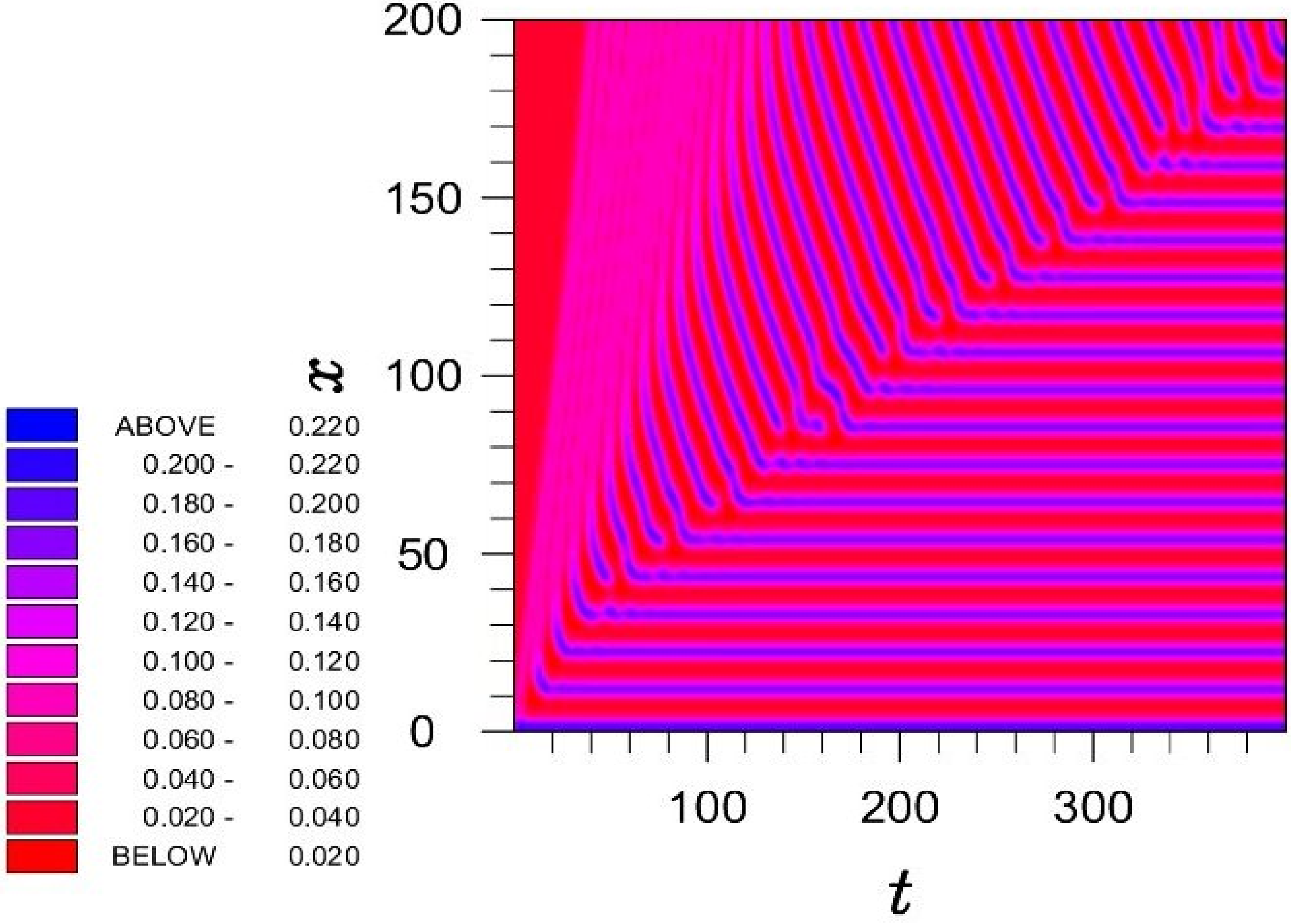
Experimental verification

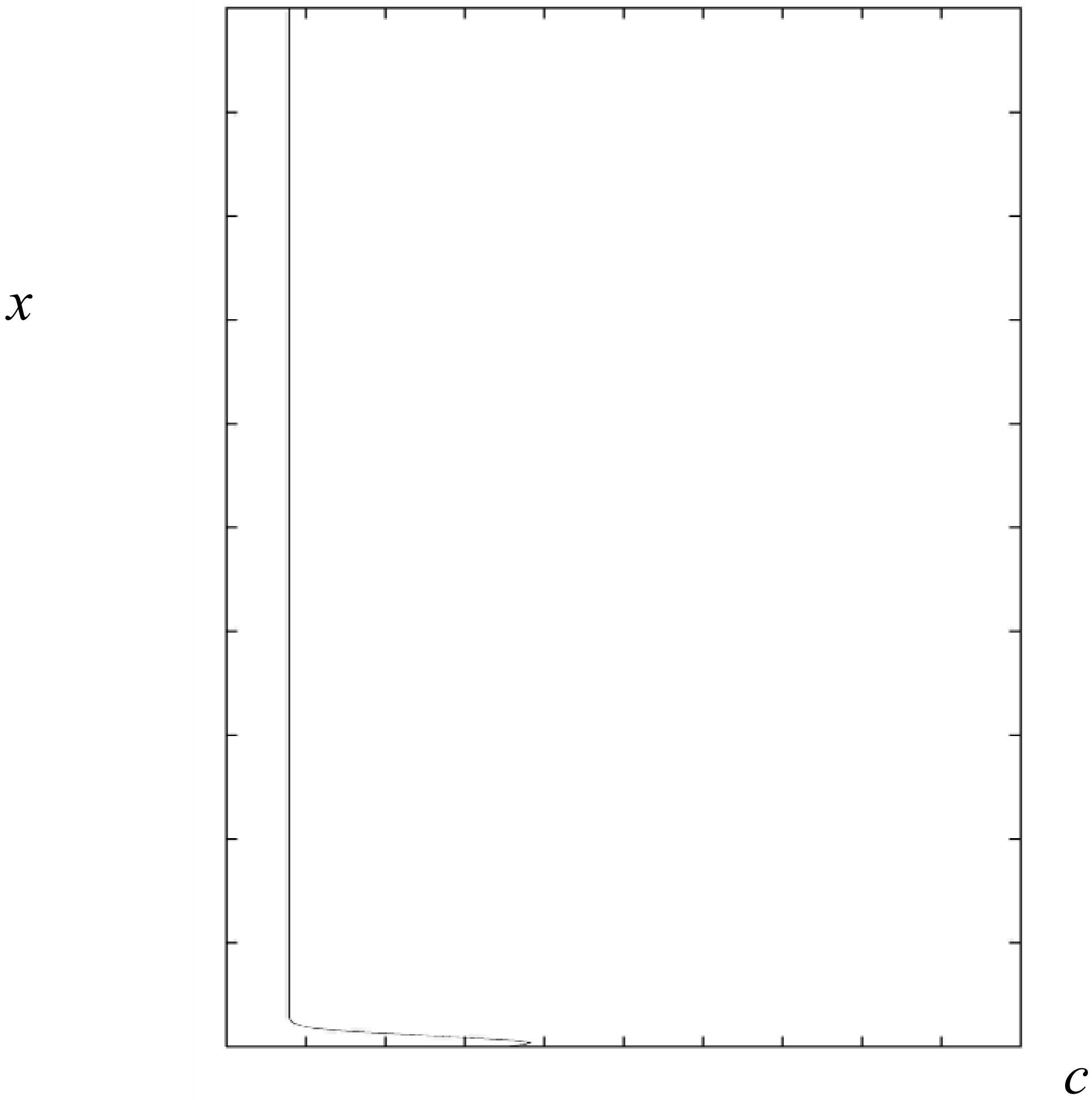
BZ system with
$f = 0.17$ cm s^{-1}
$[BrO_3^-] = 0.2$ M,
$H^+ = 0.15$M
$[MA] = 0.4$ M,
$[\text{Ferroin}] = 7 \times 10^{-4}$ M

Experimental space-time plot

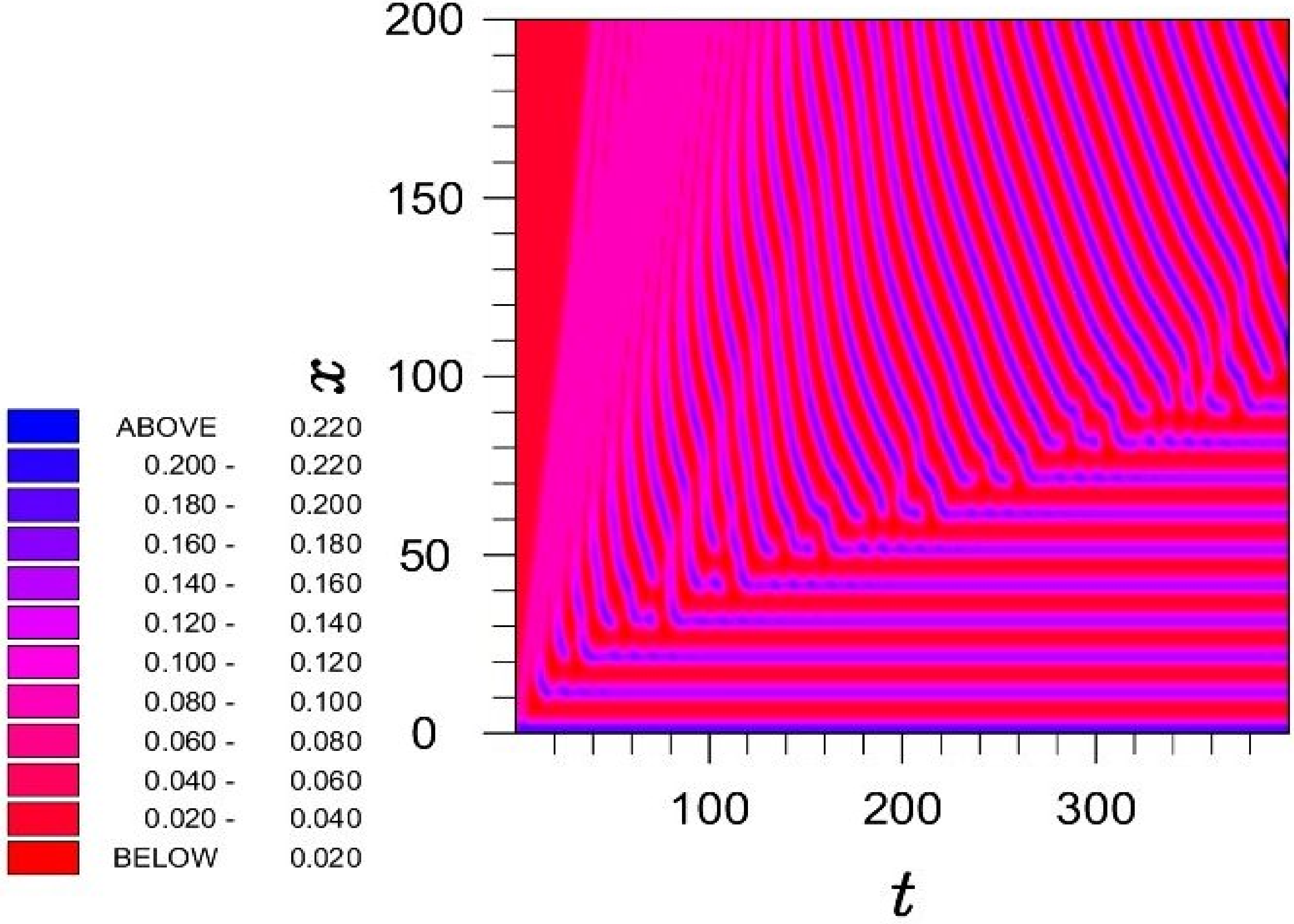


Complex Pattern Development



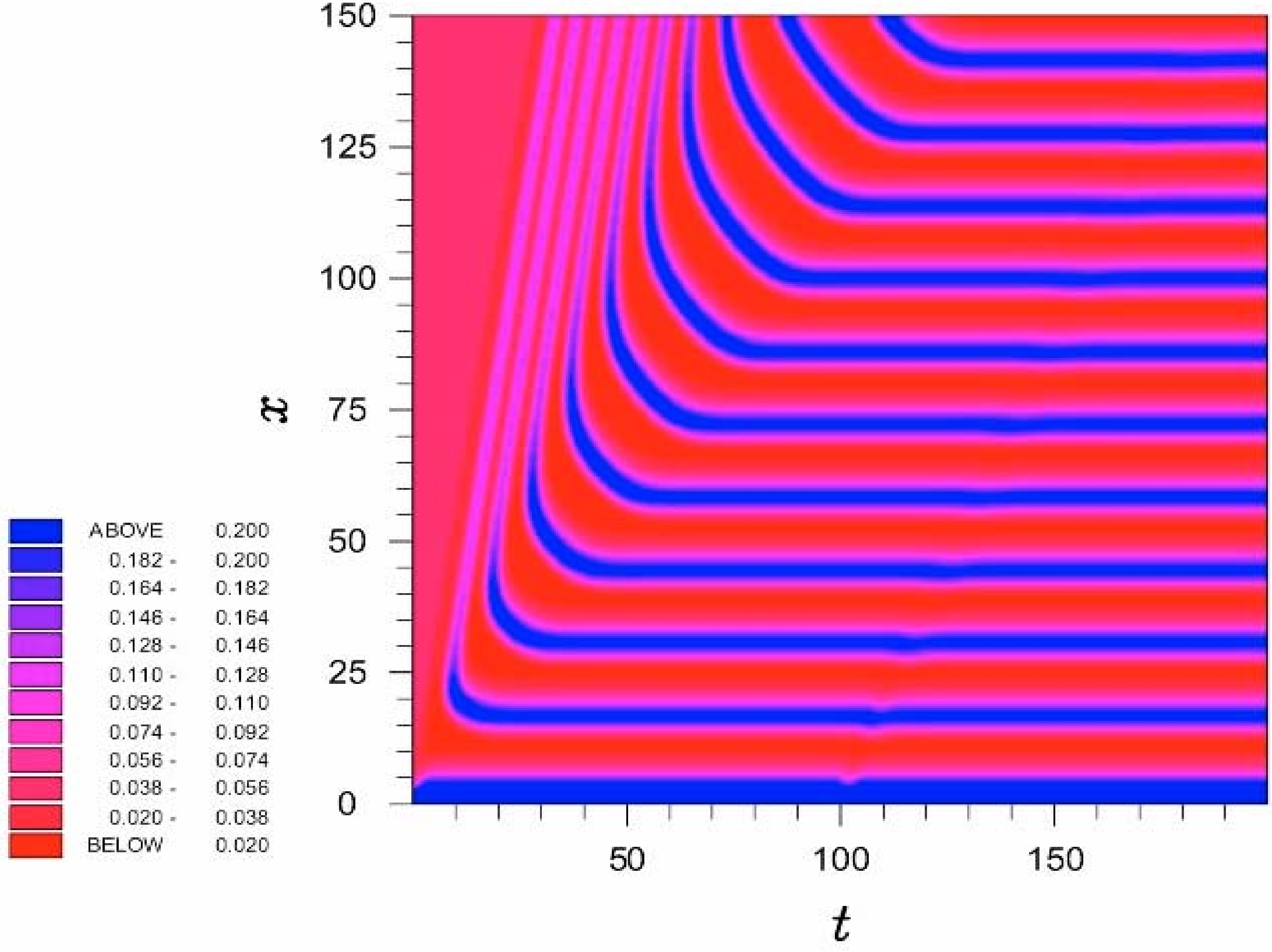

x
c

more complexity

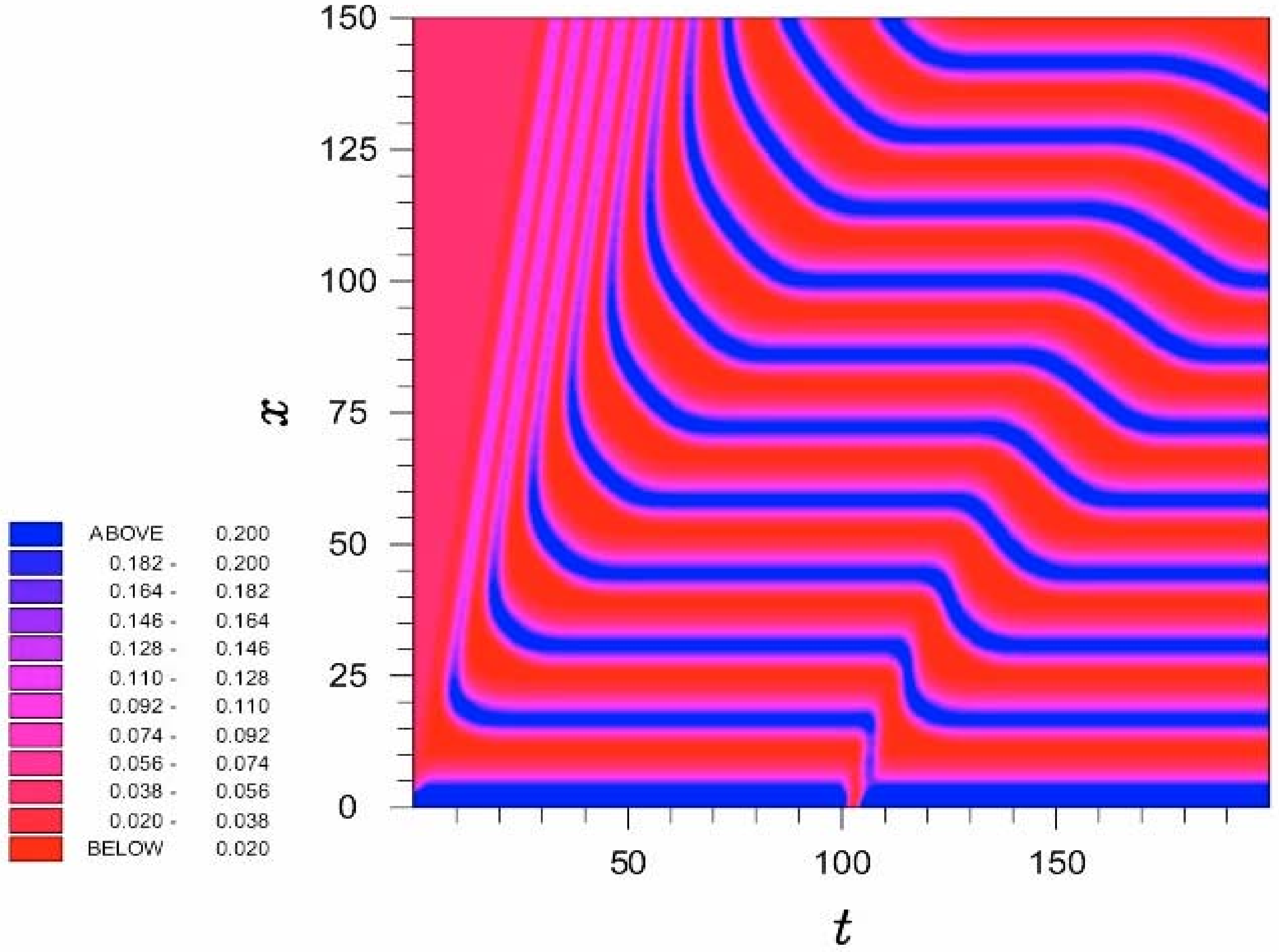


Perturbations to Boundary Conditions

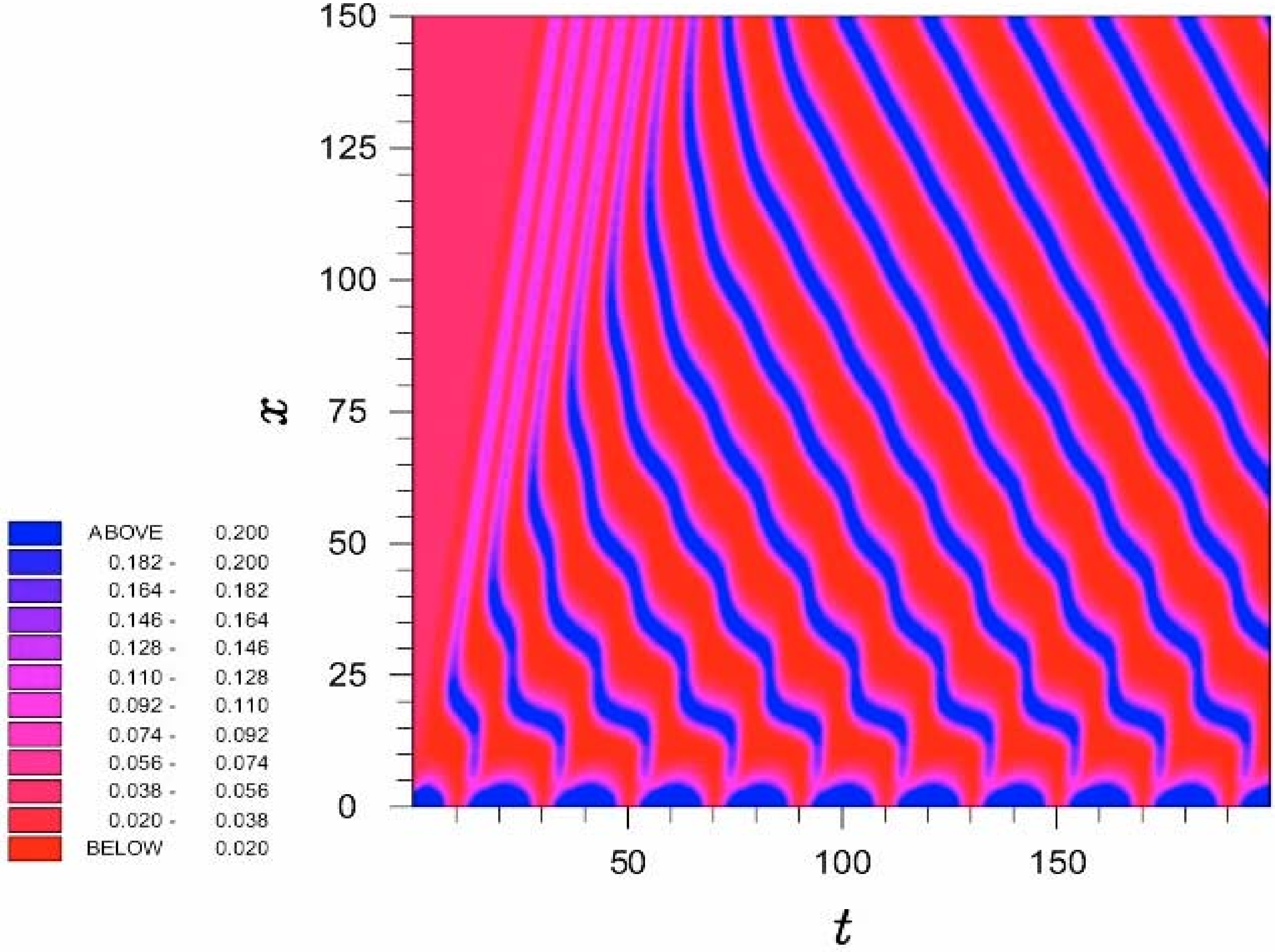
Decreasing *u,v* on boundary: time 100 - 101



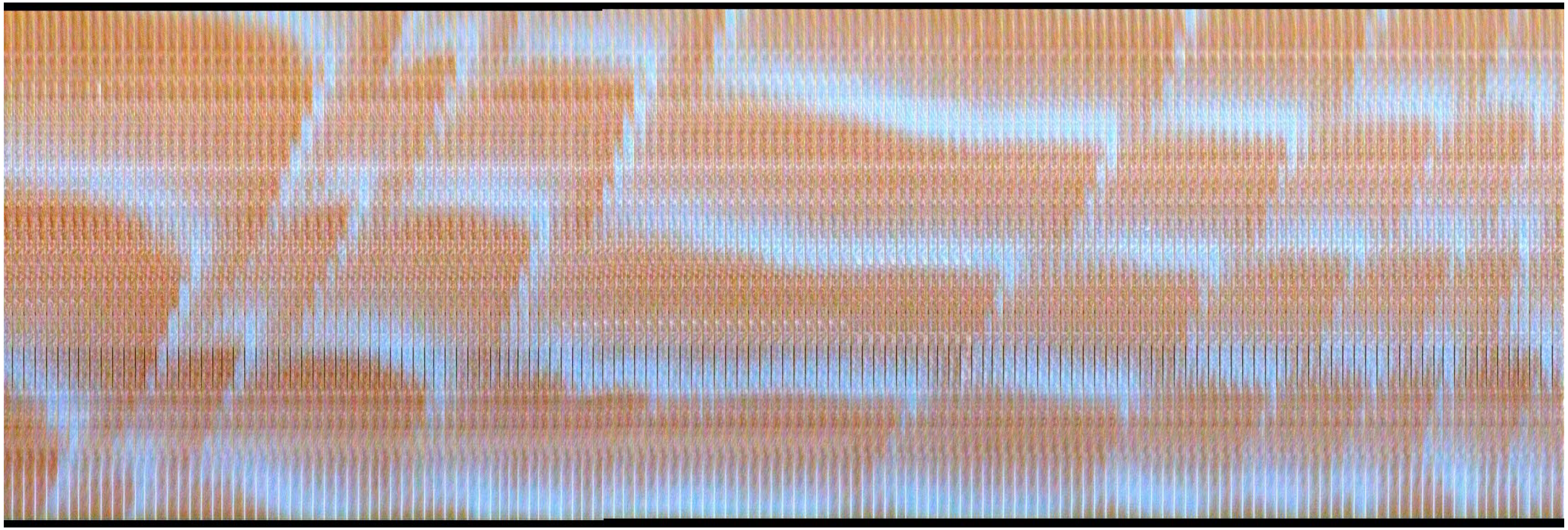
perturbation time 100 - 105



Oscillatory Perturbation



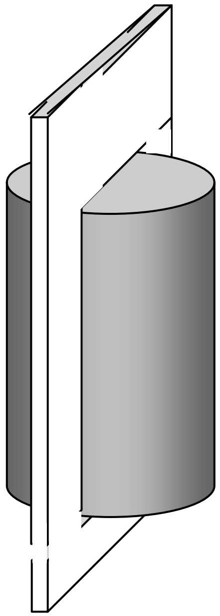
Experimental

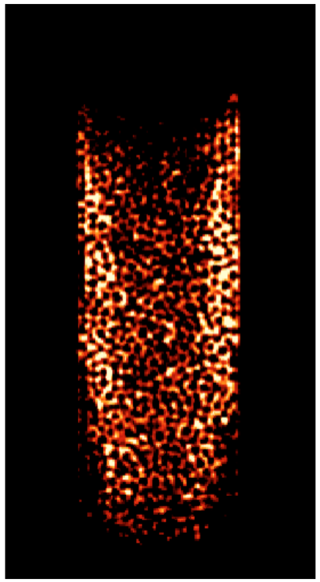


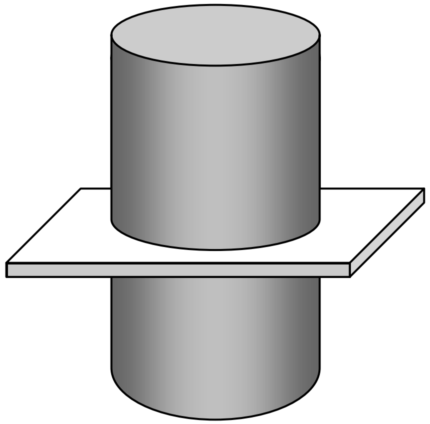
MRI studies of FDO patterns

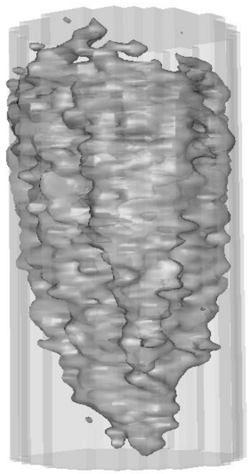
Use of BZ system as a model to investigate behaviour of reactor

Mn-catalysed BZ system: contrast from changes in H_2O relaxation times

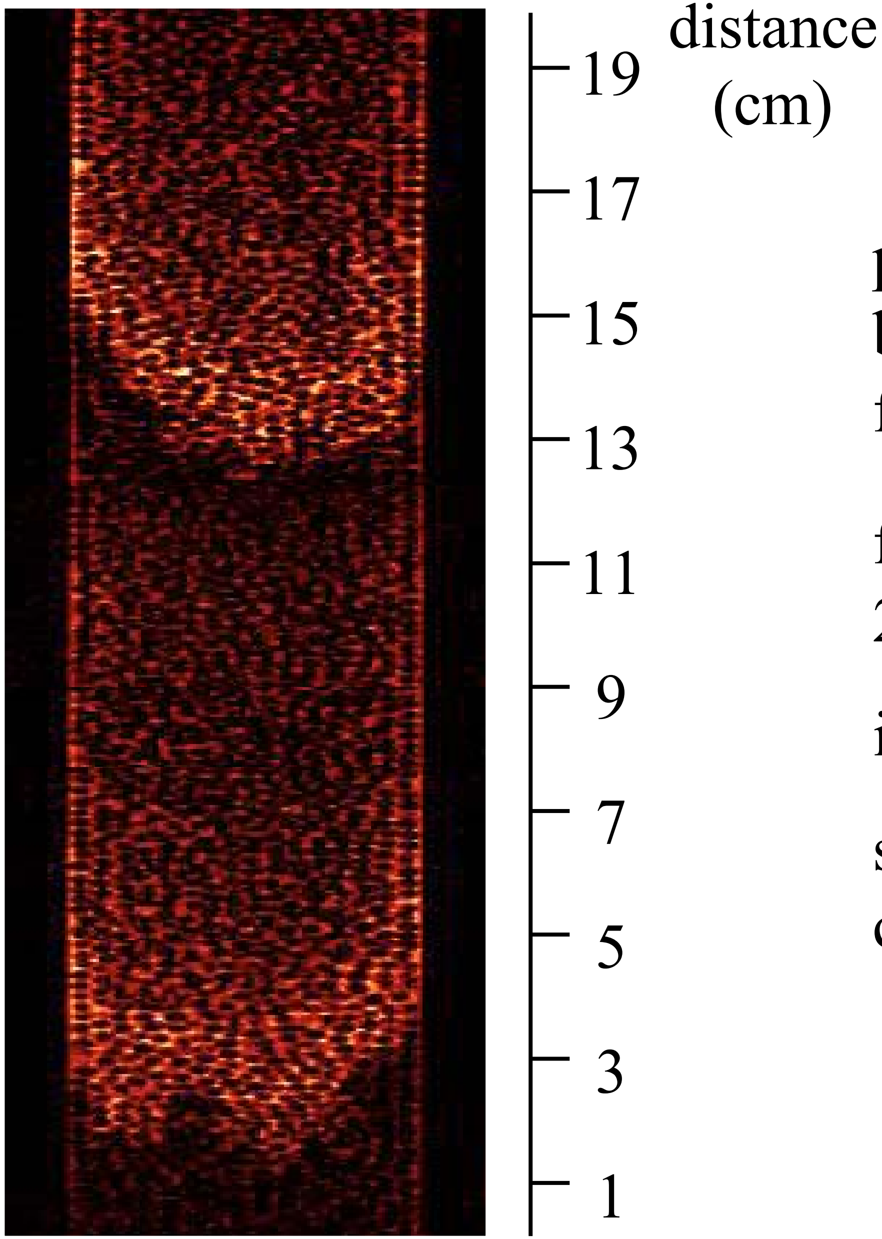








Imaging of stationary patterns



patterns formed in and above a packed bed of glass beads (tube of 20 mm i.d. filled with 1 mm beads)

field of view of single image was 44.5 x 25 mm, pixel size was 174 x 195 μm

image taken in the centre of the tube

sample moved through the magnet in 2 cm increments over a distance of 18 cm

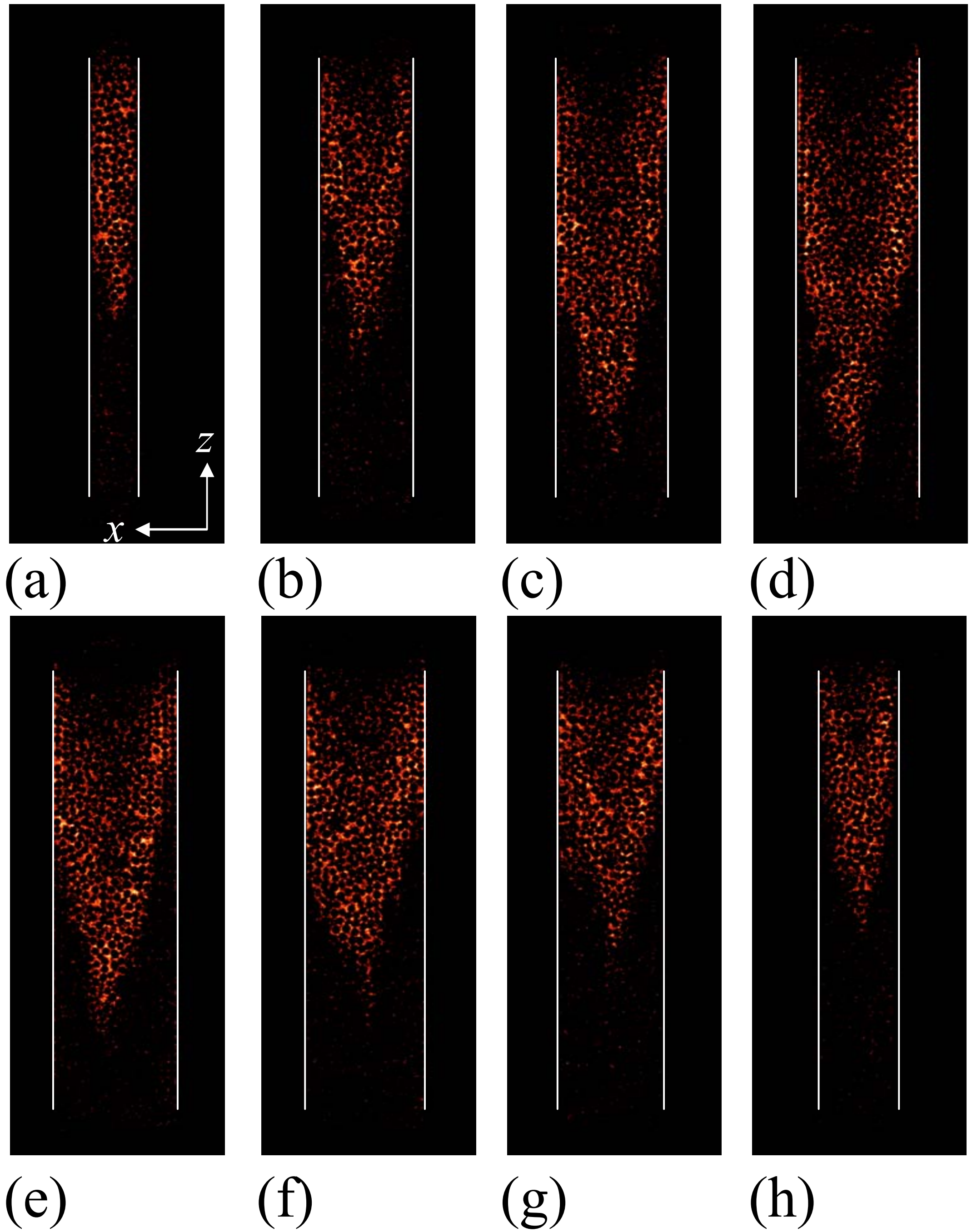


Figure C

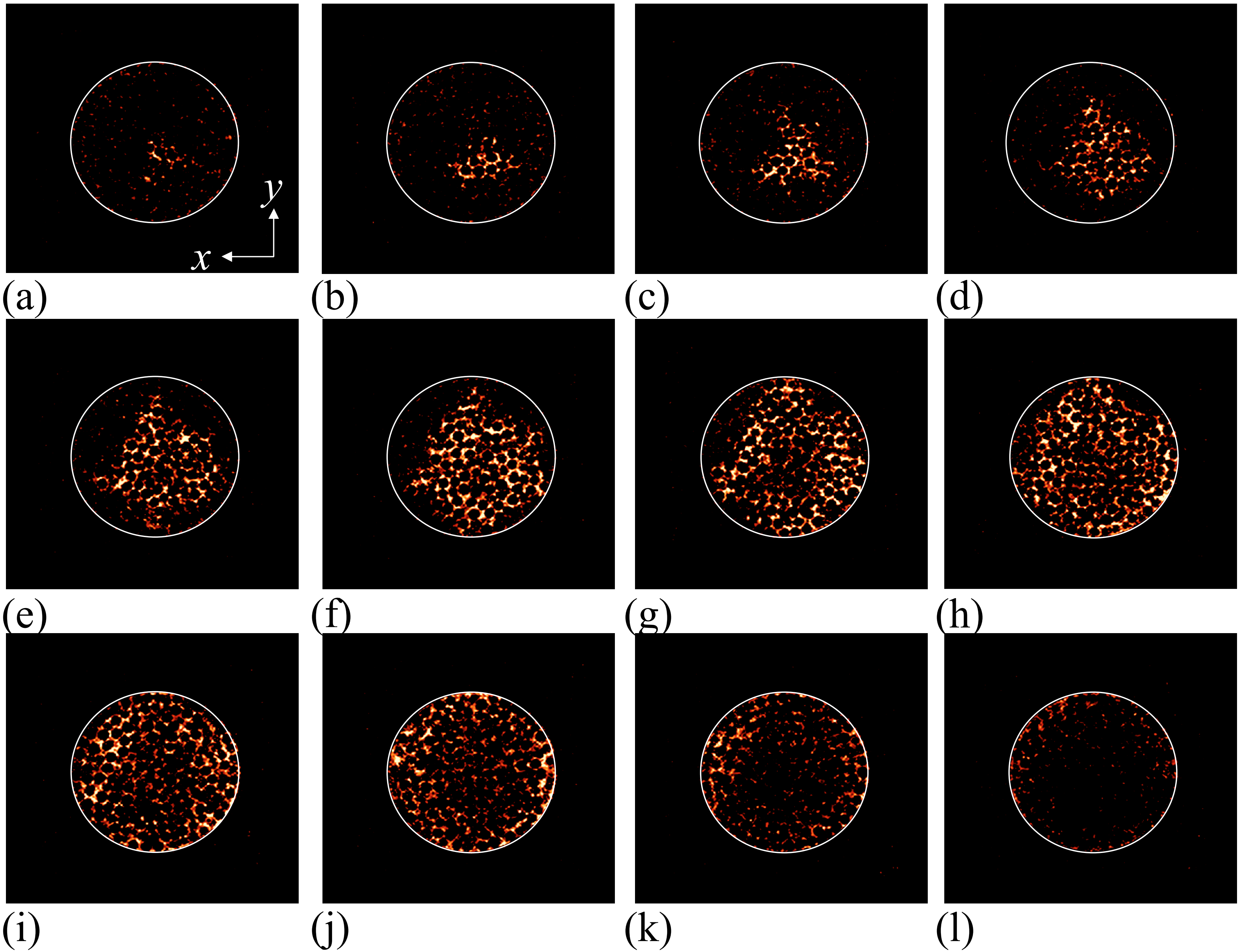
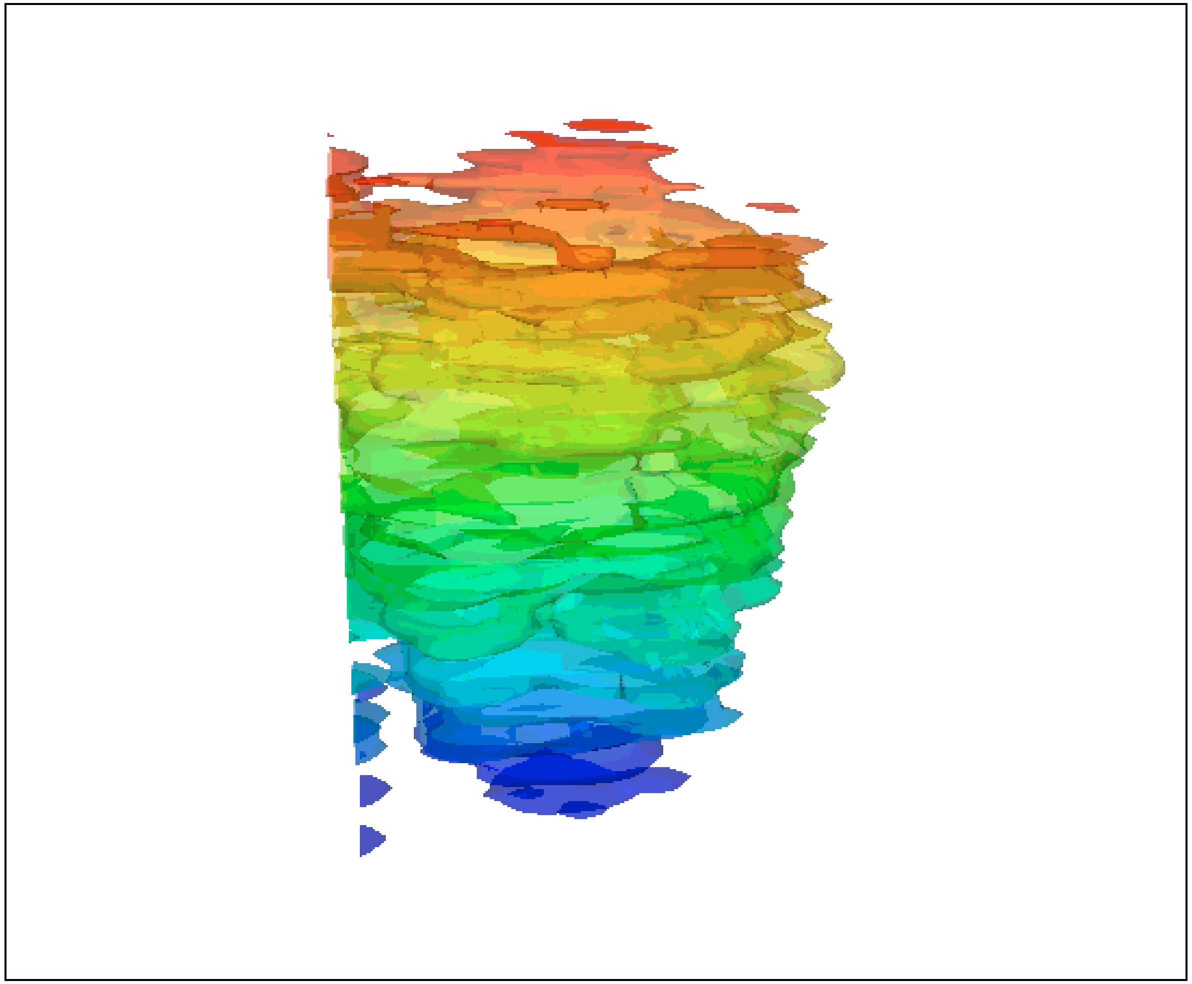
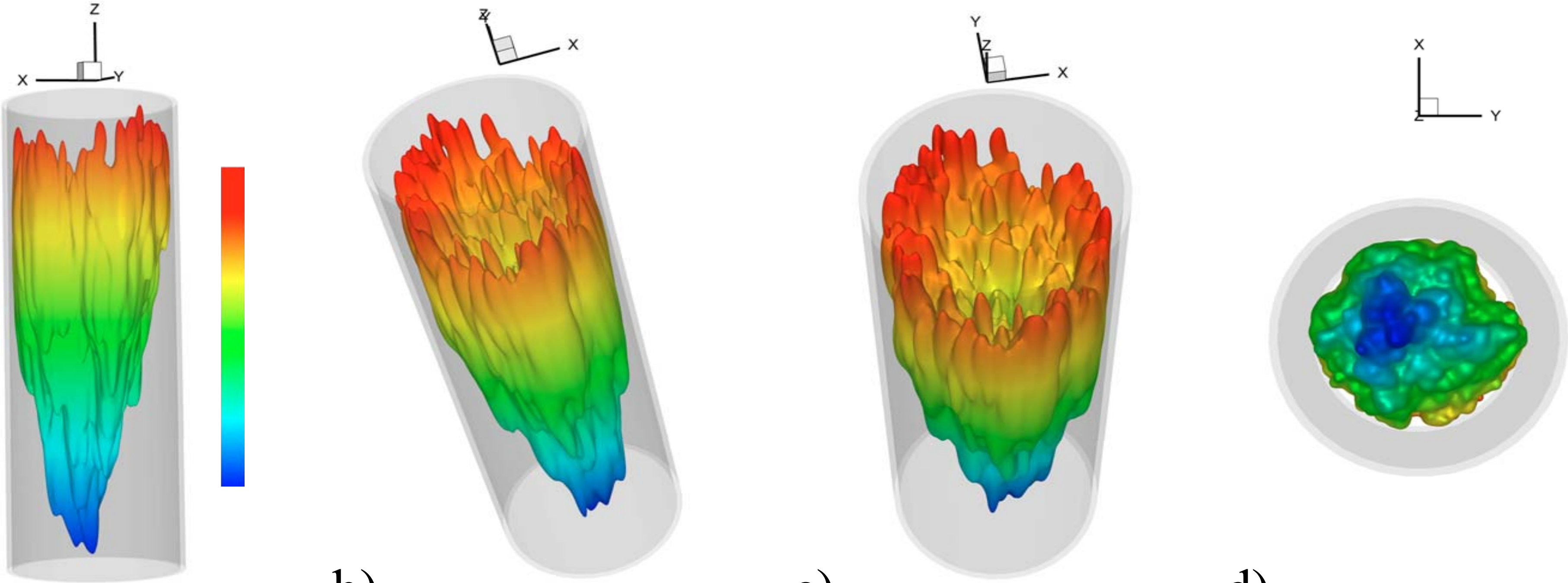
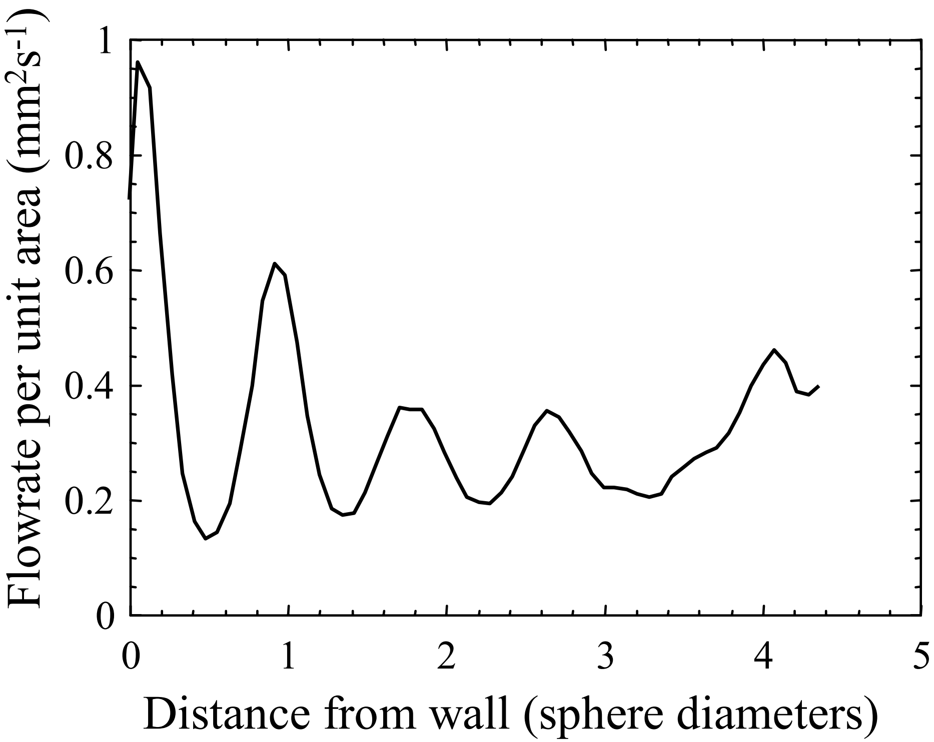


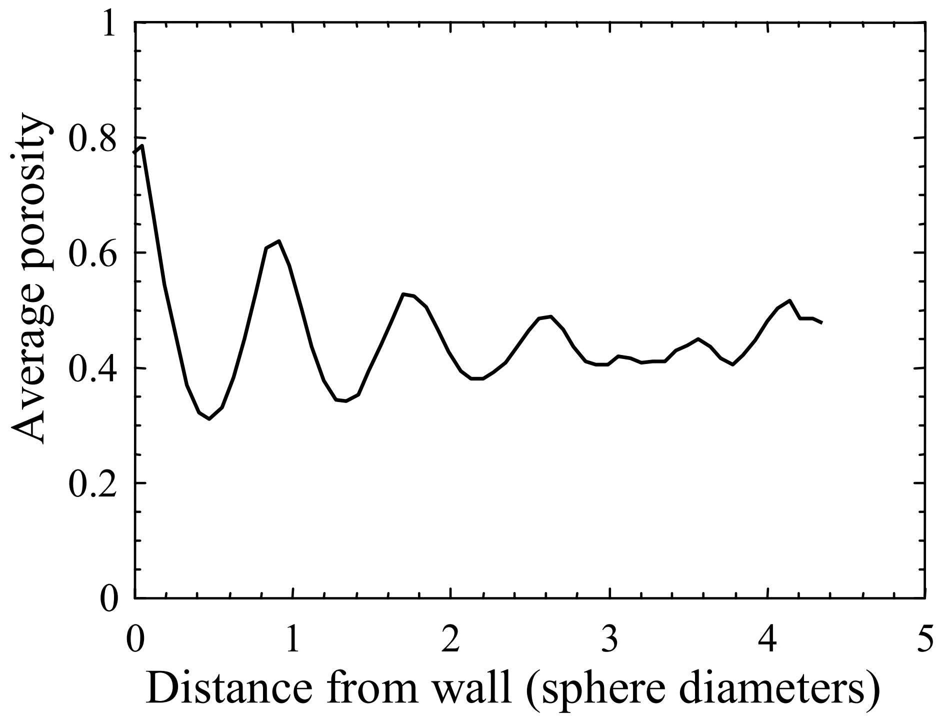
Figure D



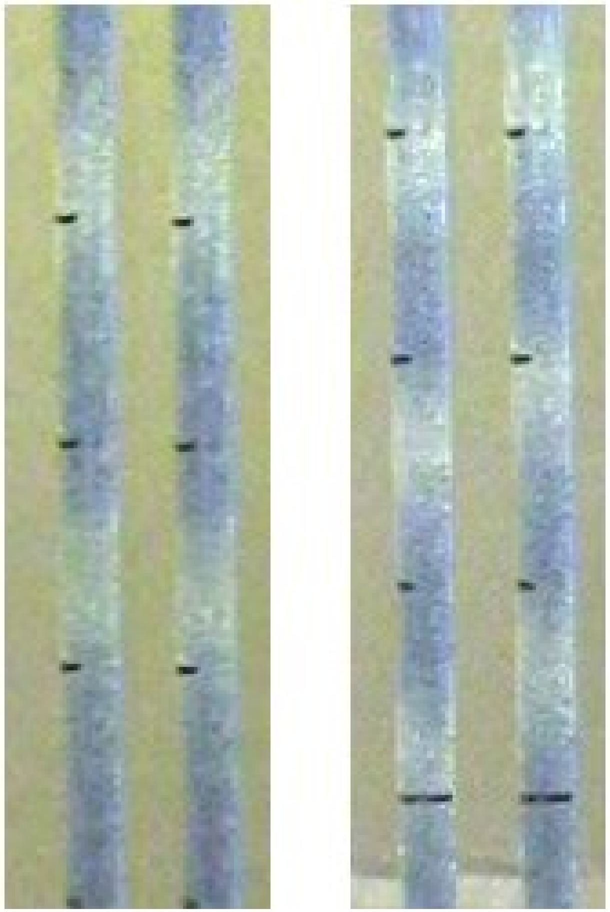


a) b) c) d)


Flowrate per unit area (mm2s-1)
0
0.2
0.4
0.6
0.8
1
0
1
2
3
4
5
Distance from wall (sphere diameters)


Average porosity
0
0.2
0.4
0.6
0.8
1
0
1
2
3
4
5
Distance from wall (sphere diameters)

CDIMA reaction



Patterns

but *unsteady*

Acknowledgements

- Annette Taylor (Leeds)
- Gavin Armstrong (Leeds)
- Rita Tóth (Debrecen/Leeds)
- Vilmos Gáspár (Debrecen)
- Melanie Britton (Birmingham)
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  Hungarian Academy of Science
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