Synchronization and Spatiotemporal Dynamics in Chemical Systems

Hands-on Research in Complex Systems
Winter School
Universidade Federal do ABC, Sao Paulo, Brasil
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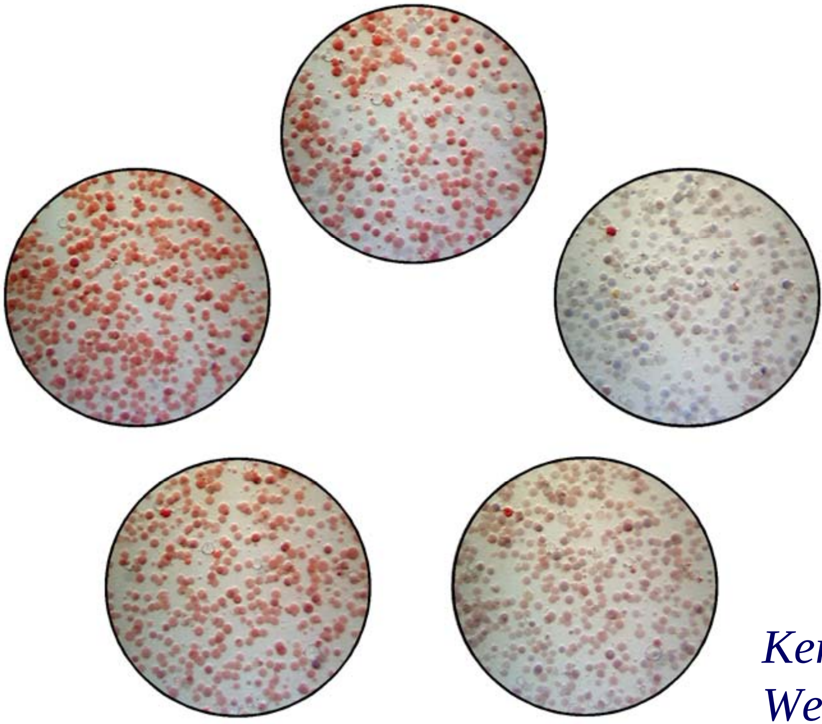


Funding:
National
Science
Foundation

Kenneth Showalter
West Virginia University

AUTOCATALYSIS - Positive Feedback

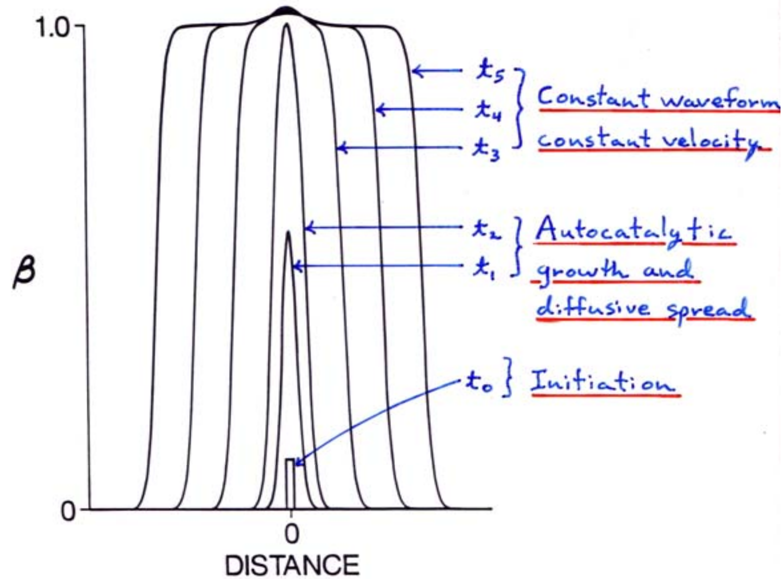
$$A + 2B \rightarrow 3B$$

Kinetics

$$-da/dt = db/dt = ab^2$$

Propagating Reaction-Diffusion Front

$$(\partial b/\partial t)_x = D\,(\partial^2 b/\partial x^2)_t + (a_0 - b)b^2$$

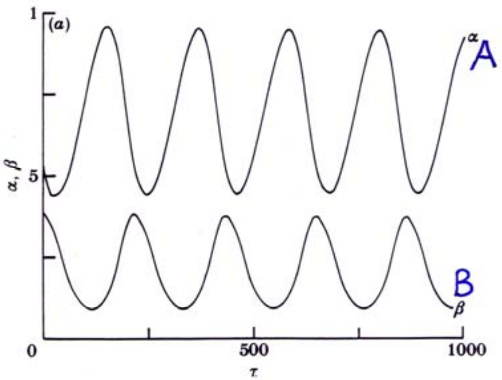


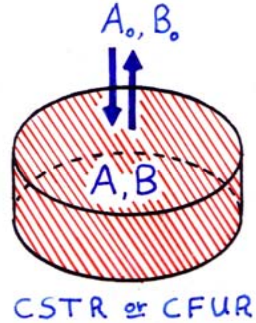
AUTOCATALYSIS - With Catalyst Decay

$$A + 2B \rightarrow 3B$$

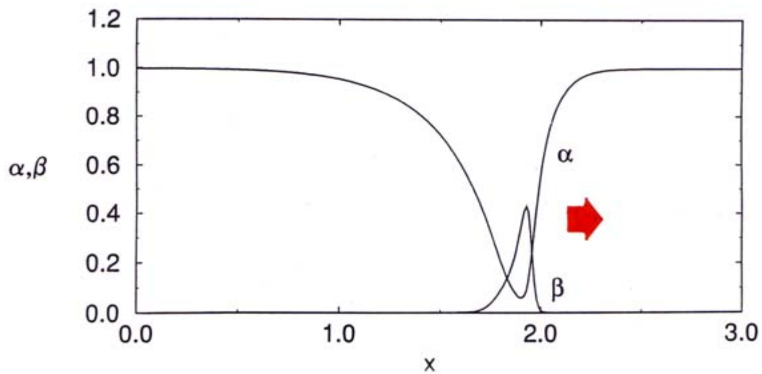
$$B \rightarrow C$$

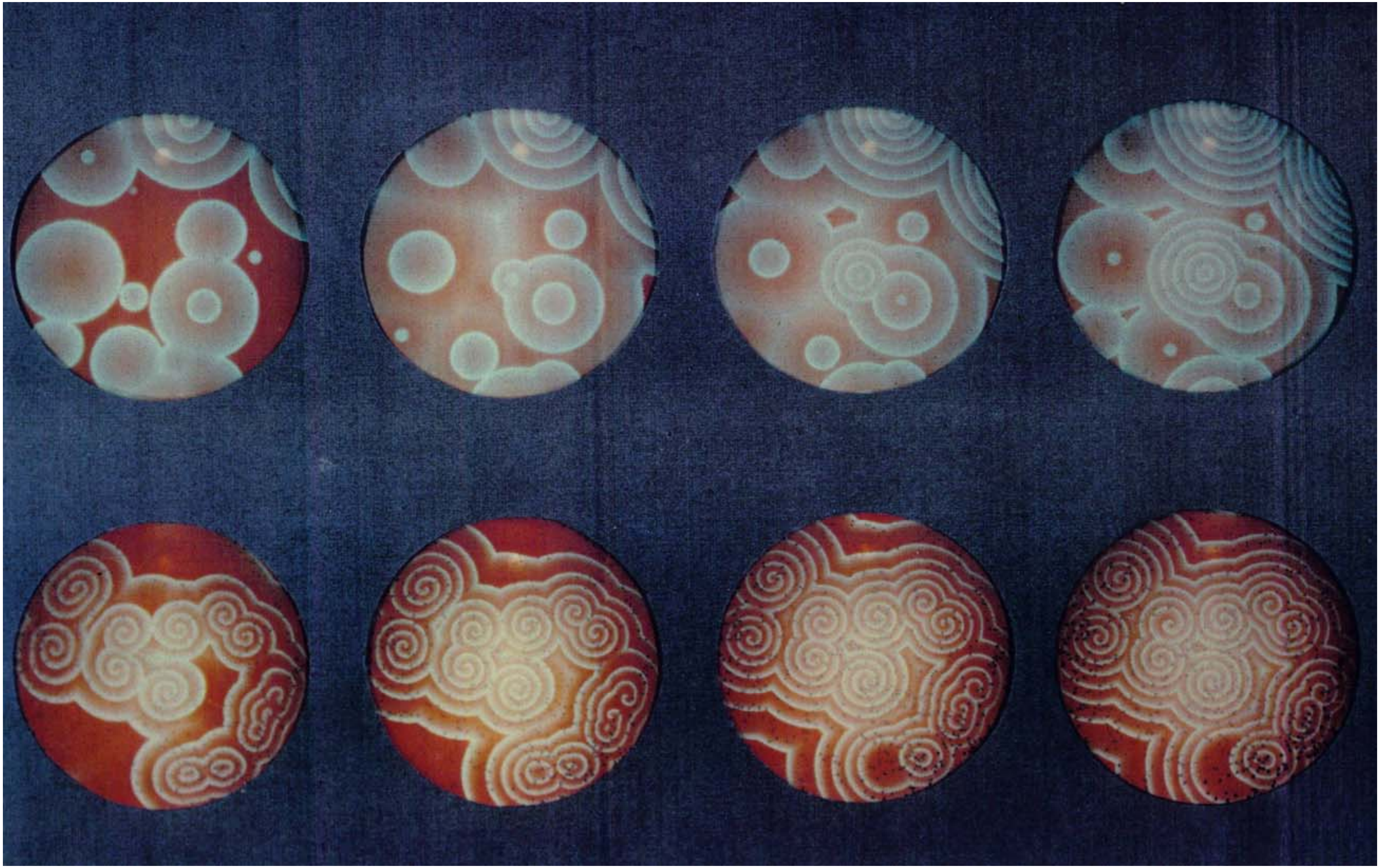
Open System - Oscillatory (Gray-Scott)





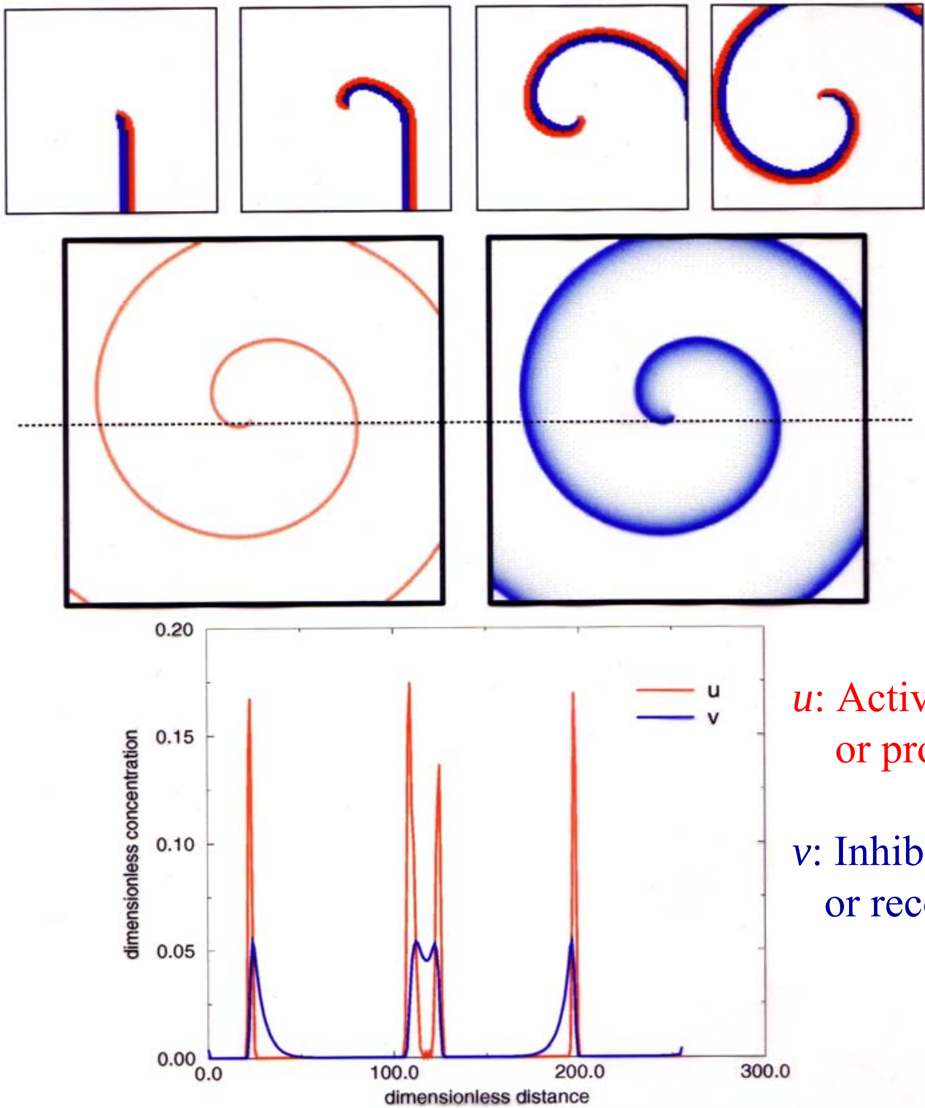
Unstirred System - Propagating Waves





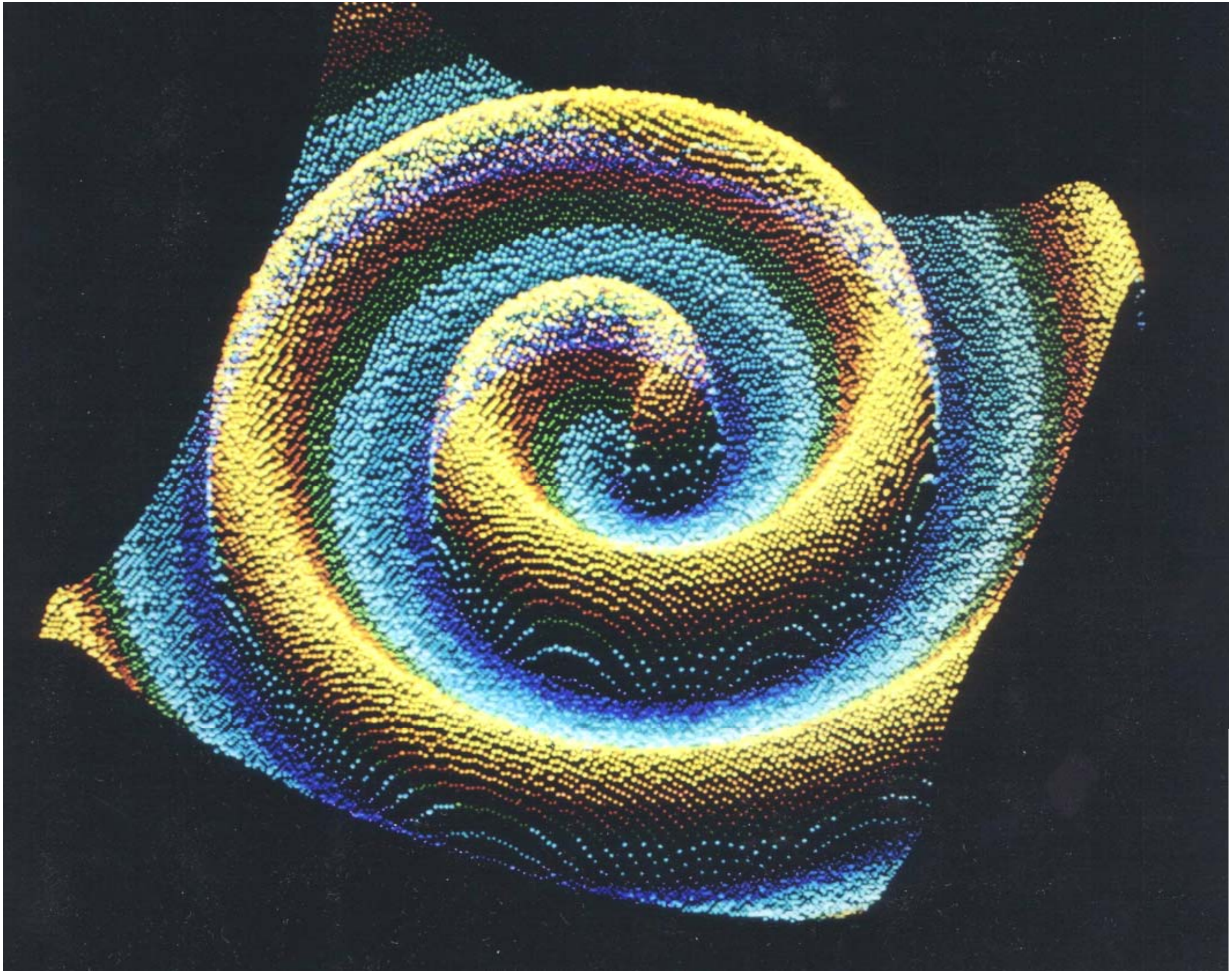
Art Winfree

Spiral Wave Formation



u: Activator
or propagator variable

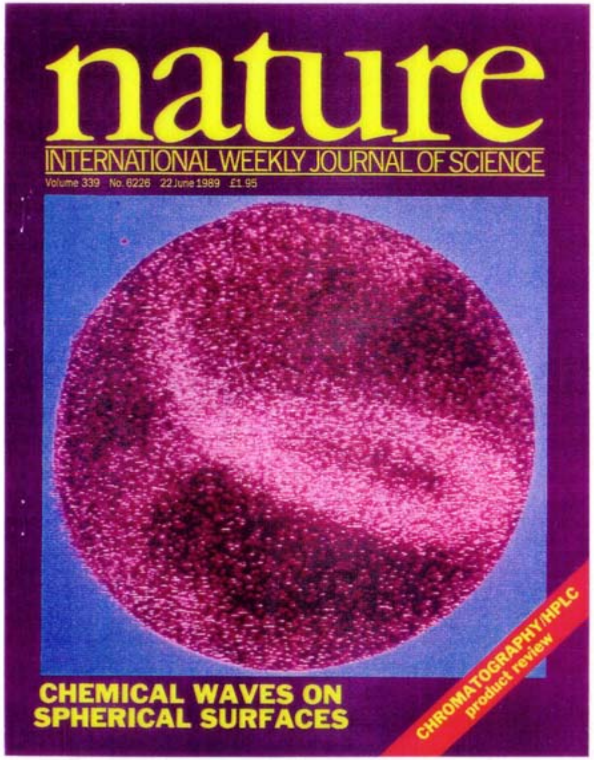
v: Inhibitor
or recovery variable

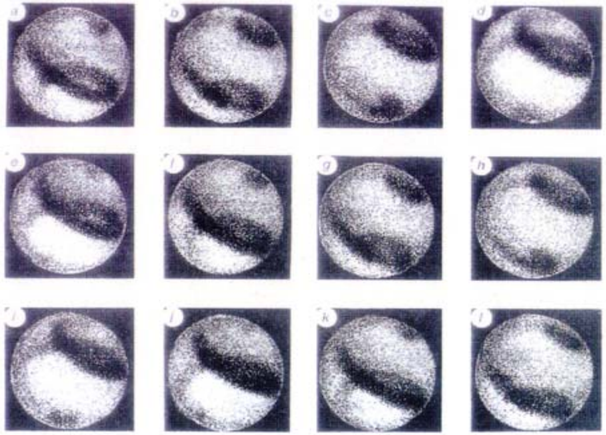


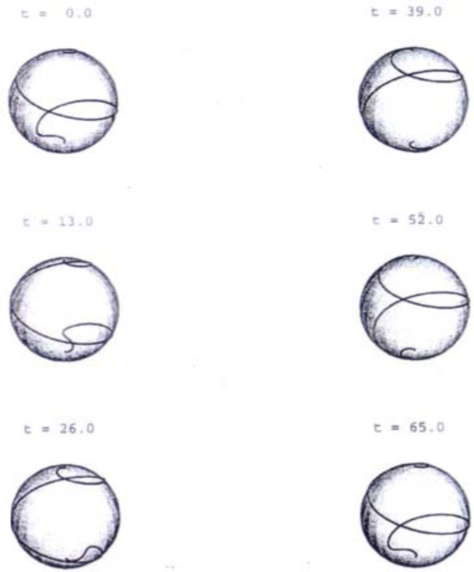
Stefan Müller

Sphere Waves

Diameter: 1.39 mm
Time interval: 12.8 s





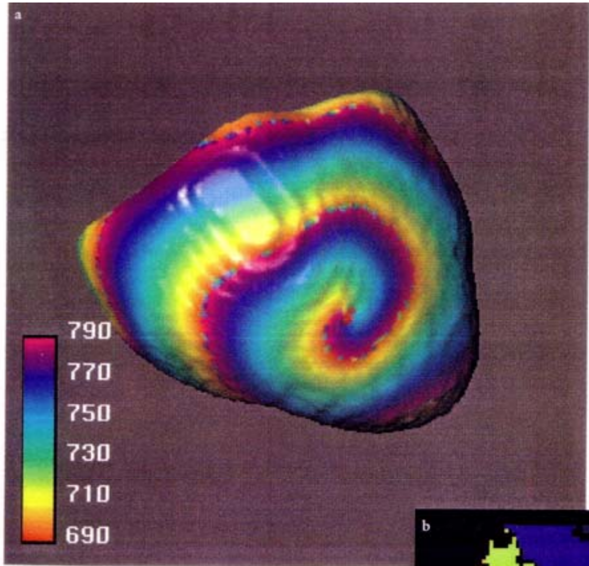


P. McQuillan and J. Gomatam,
J. Phys. Chem. 100, 5157 (1996).

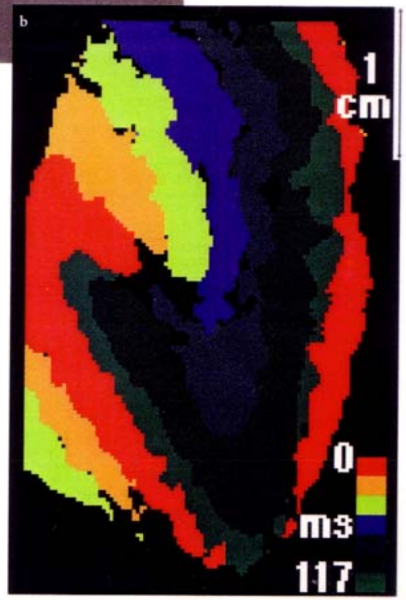
J. Maselko and K. Showalter, Nature ***339****, 609 (1989).*

Heart Waves

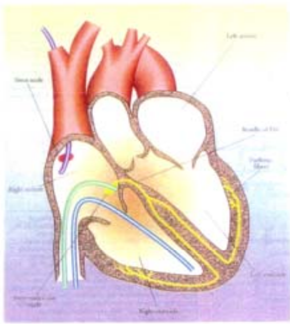
L. Glass, Physics Today, August 1996, p. 40.



A. Panfilov
Dog Heart: 3D model
FitzHugh-Nagumo

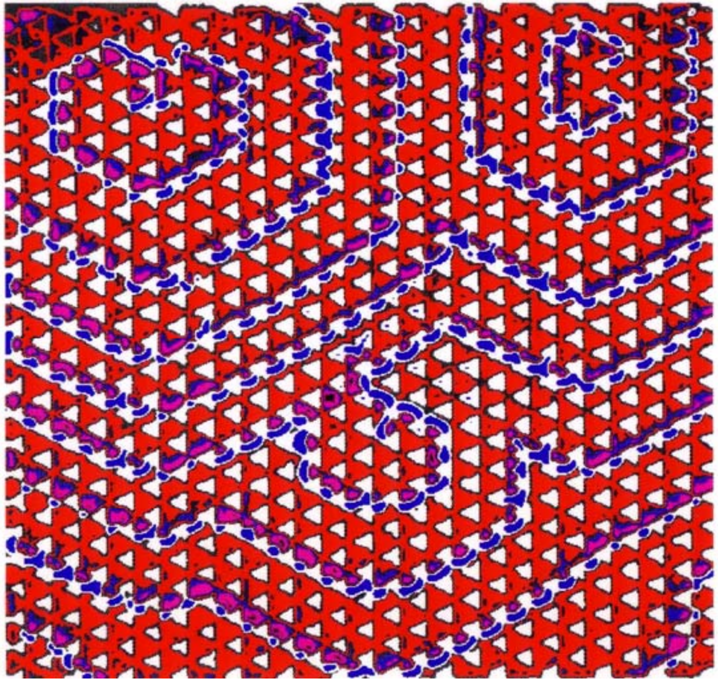


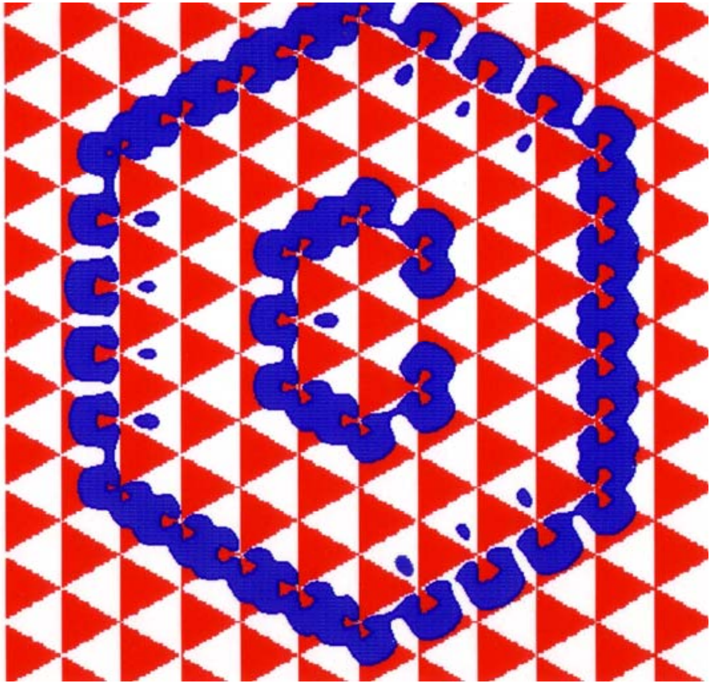
J. Jalife
Rabbit Heart:
Voltage sensitive dyes



Patterned Excitable Media

BZ catalyst (shown in red) printed on membrane using an injet printer.



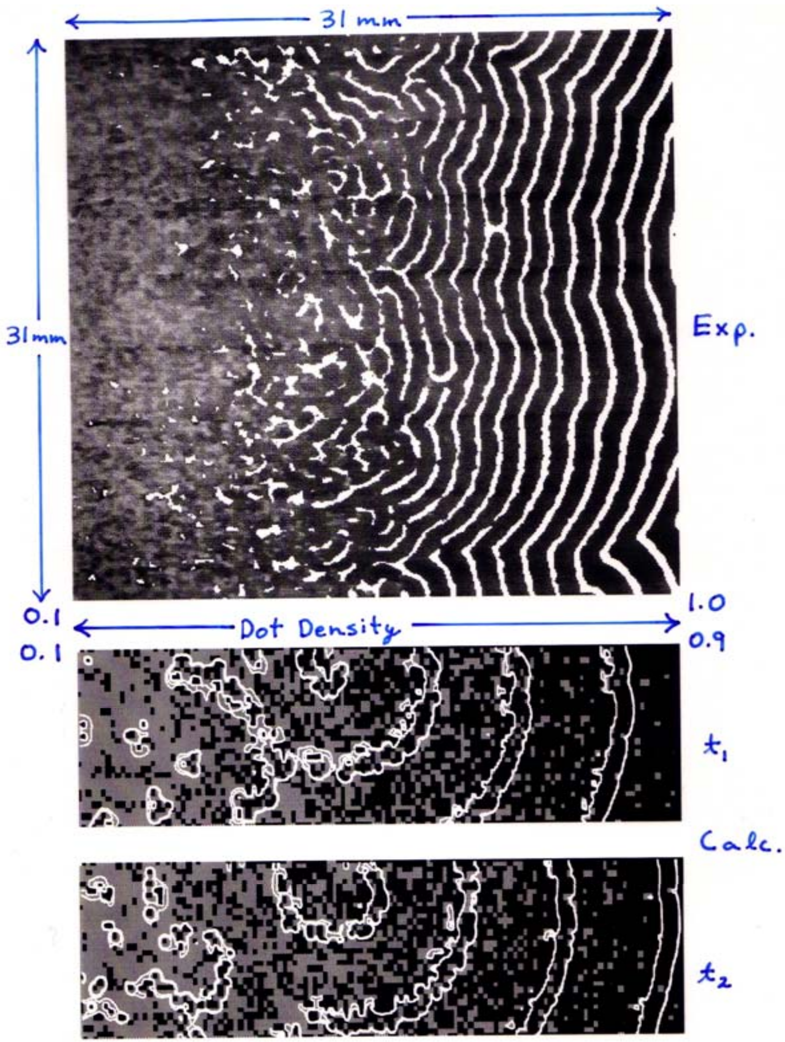


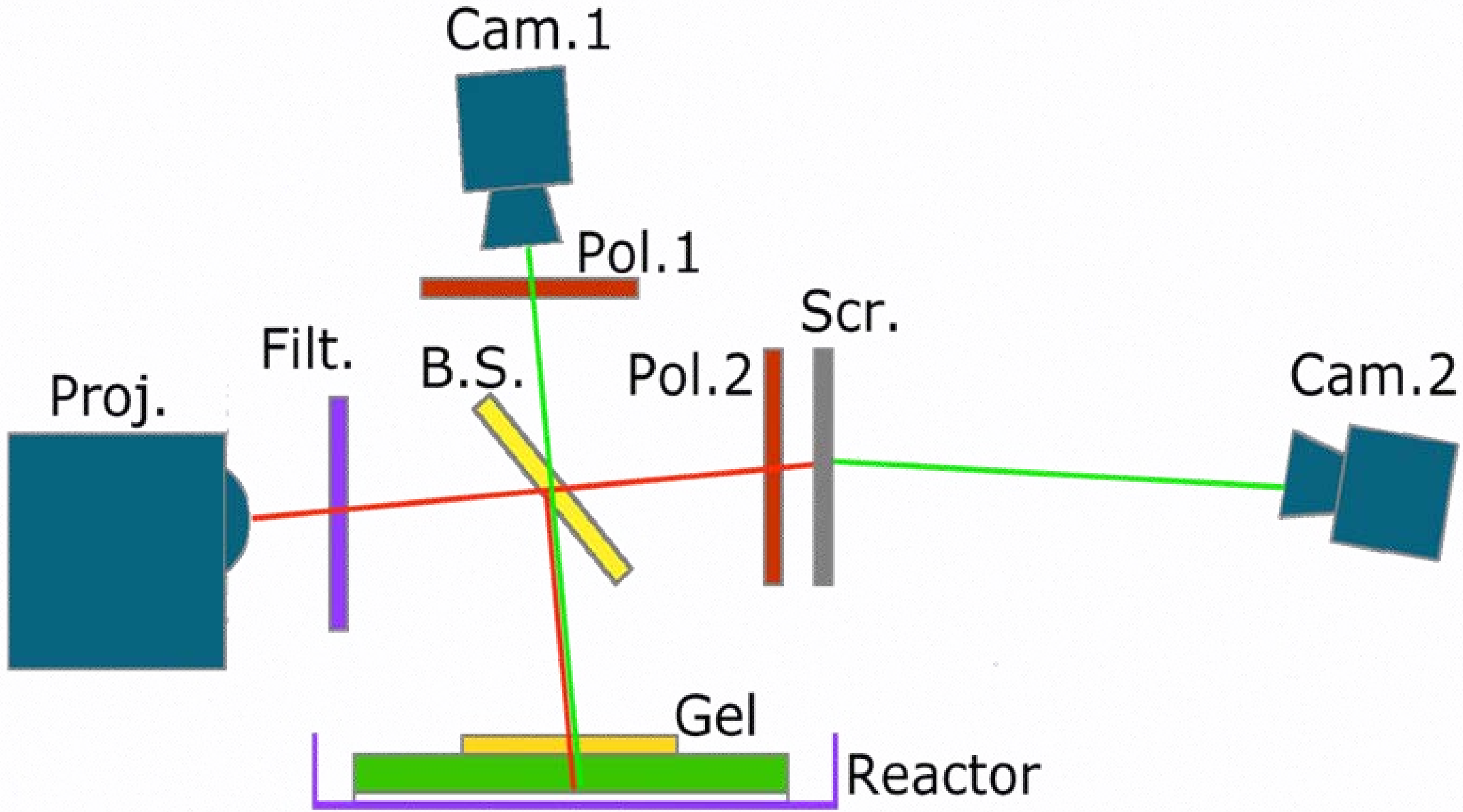
Experiment: Wavefront blue; waveback violate.

Calculation: Autocatalyst $HBrO_2$ shown in blue.

O. Steinbock, P. Kettunen, and K. Showalter, Science ***269****, 1857 (1995).*

Random Heterogeneities





$$Ru(bipy)_3^{2+} + BrMA + h\nu \rightarrow Br^-$$

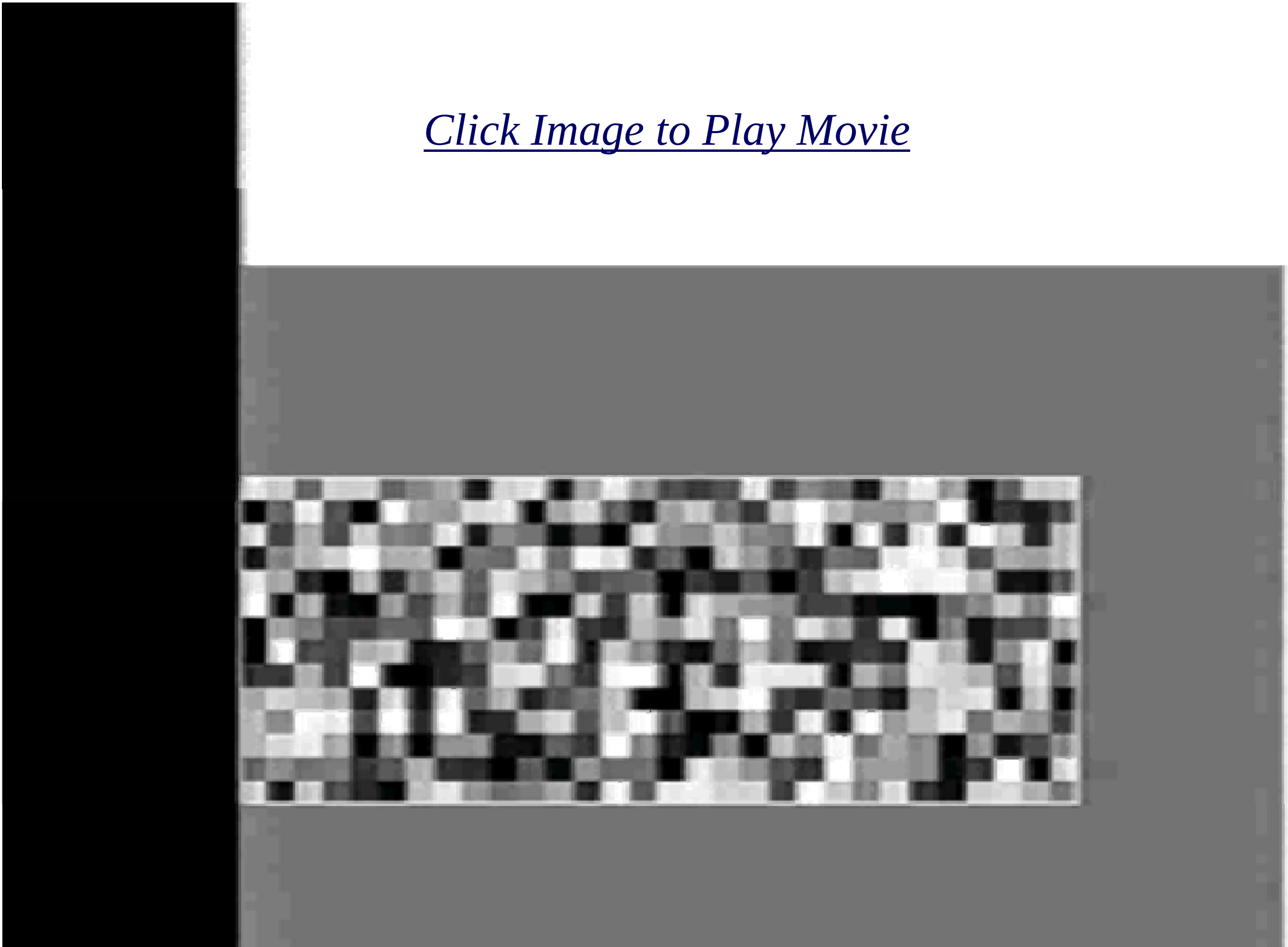
Imposed Spatiotemporal Noise

Black: wave initiation zone

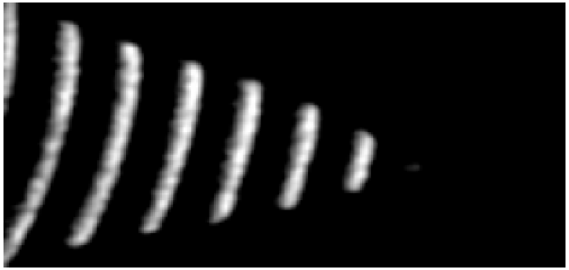
Gray: reference intensity boundary

Noise: zero mean amplitude

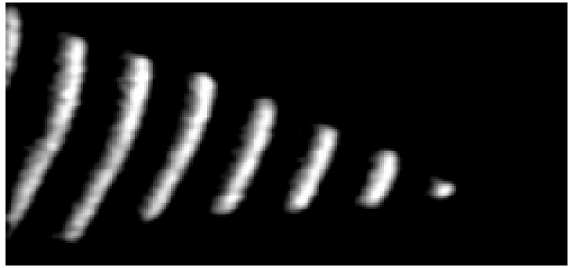
Click Image to Play Movie



Noise Supported Waves



15 mm



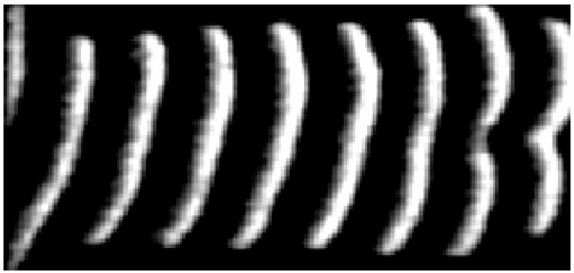
5 mm

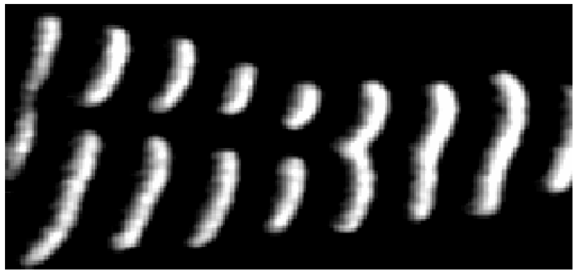
Noise level = 0

(Subexcitable)

Noise level = 30%

Click Image to Play Movie



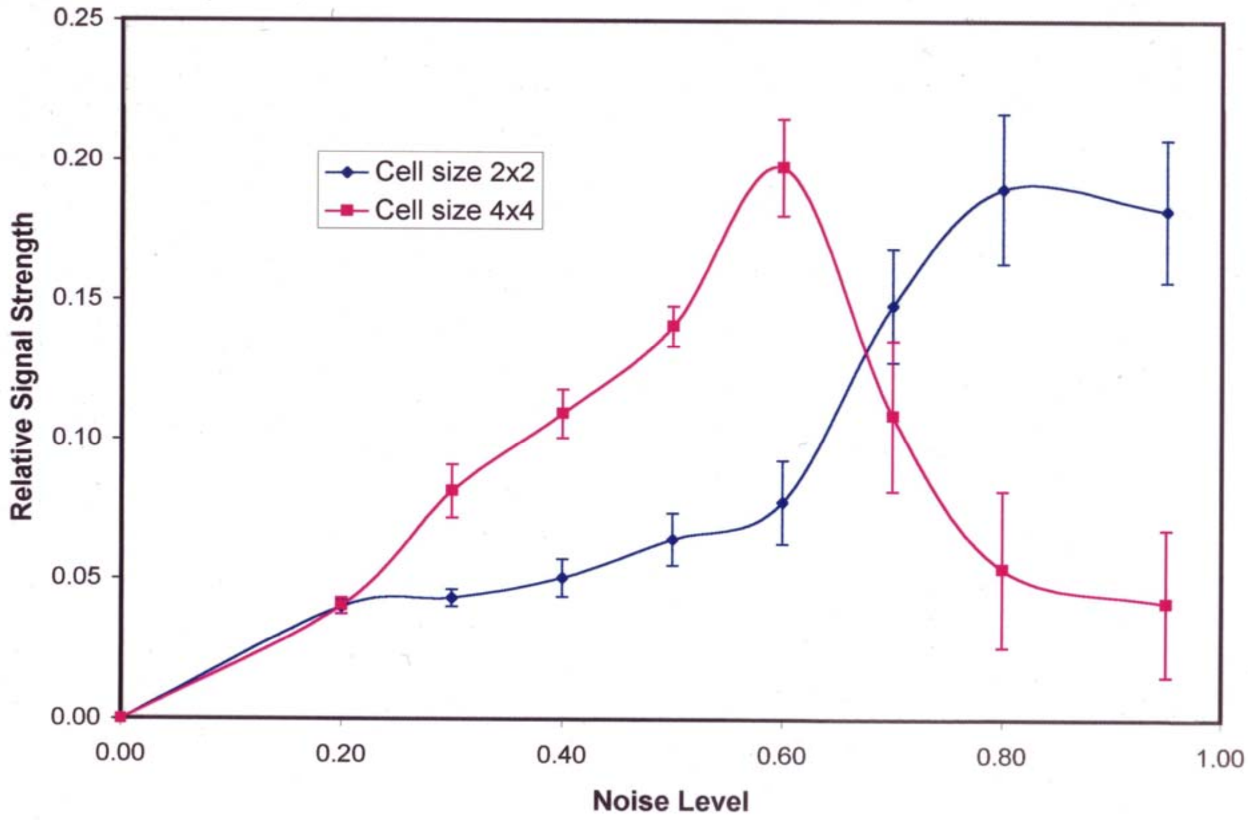


Noise level = 60%

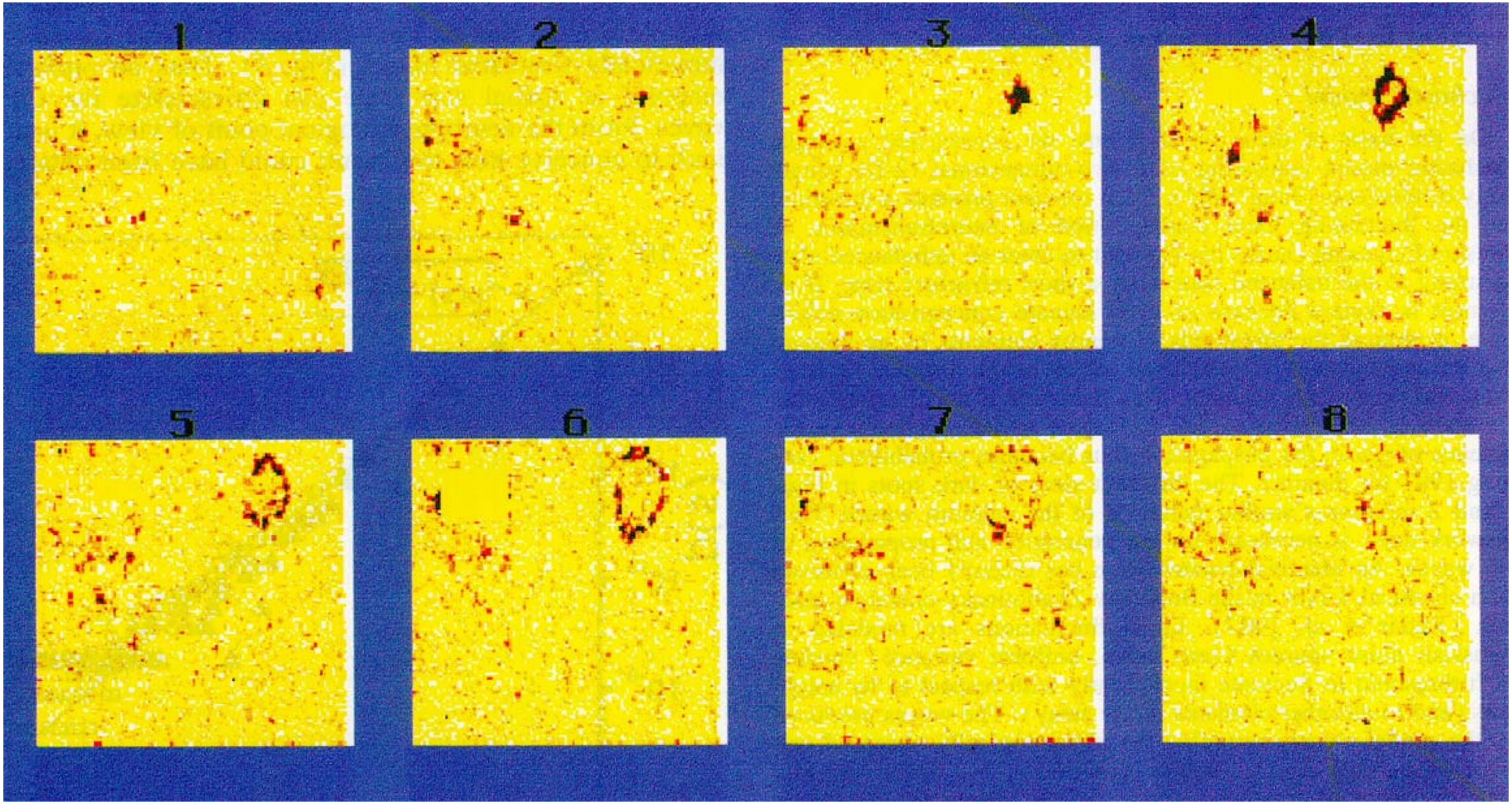
Noise level = 100%

S. Kádár, J. Wang, and K. Showalter, Nature ***391****, 770 (1998).*

Signal Strength vs Noise Level



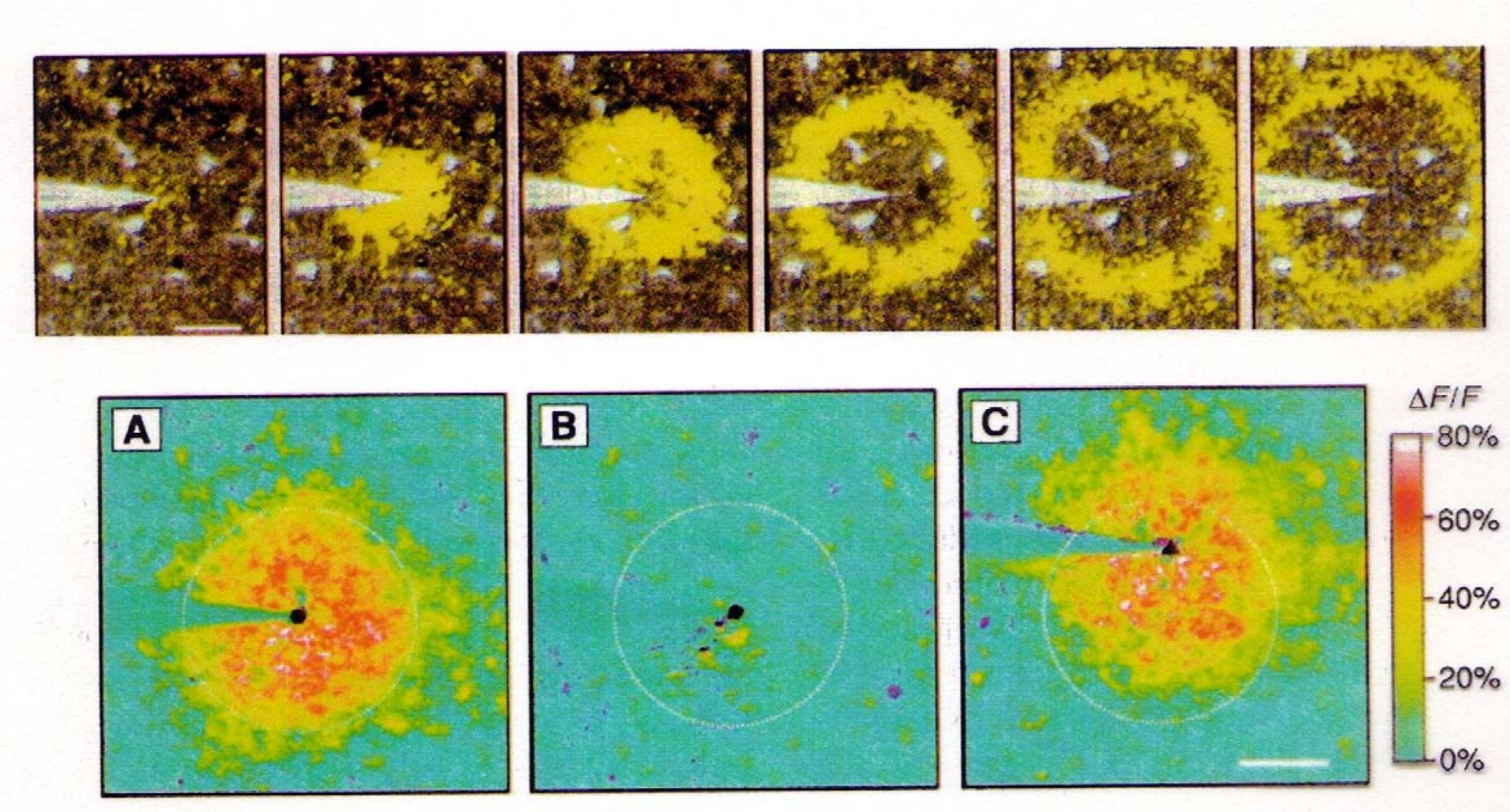
Noise Mediated Waves in Cultured Glial Cells



50 mM kainate; frames at 1.0 s intervals

P. Jung, A. Cornell-Bell, K.S. Madden, F. Moss, J. Neurophysiol. 79, 1098 (1998).

Calcium Waves in Retinal Glial Cells



Top: Calcium wave initiated by mechanical stimulus. Time interval: 0.93 s.

Bottom: Average activity following stimulation at 0, 180, and 270 s.

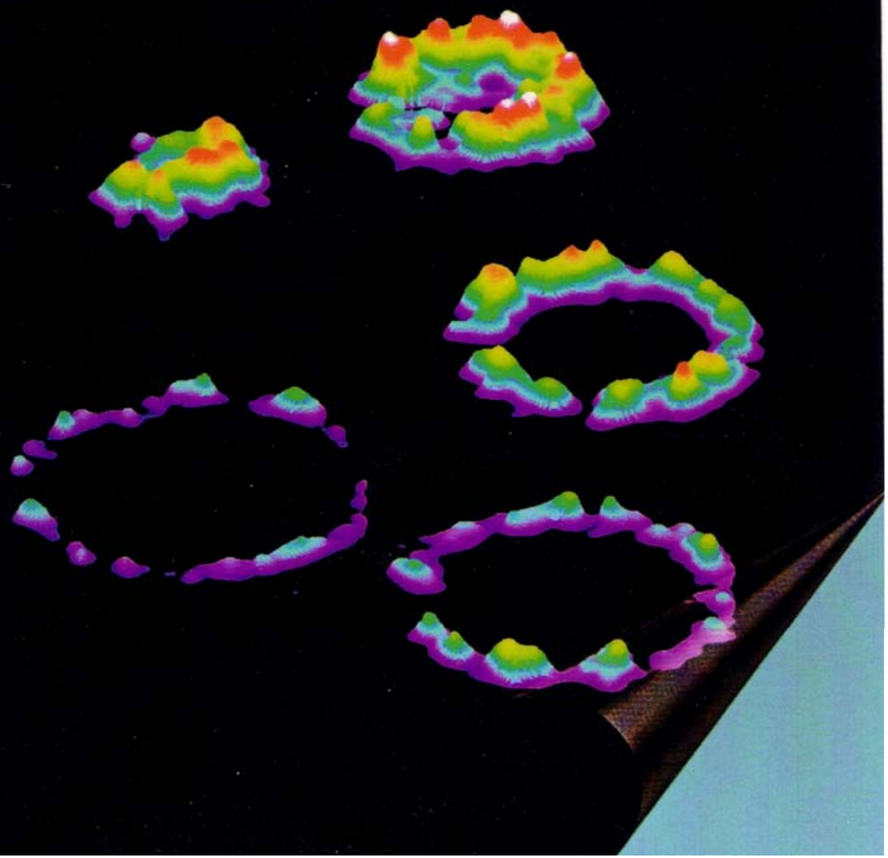
E. A. Newman and K. R. Zahs, Science 275, 344 (1997).

American
Association for the
Advancement of
Science

Science

7 February 1997
Vol. 275 • Pages 721–892

$7.00



Wave Propagation in Subexcitable Media

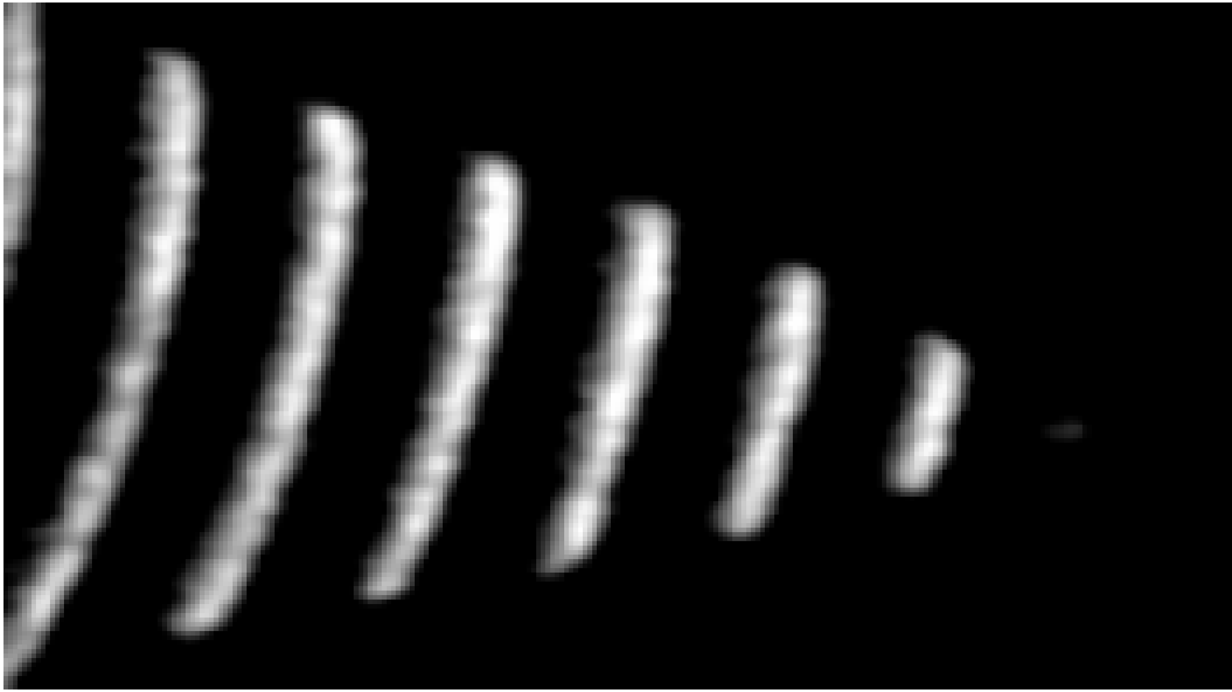
15 mm

Click Image to Play Movie

5 mm

At low excitability waves with free ends contract tangentially.

Medium does not support sustained wave propagation; hence, subexcitable.

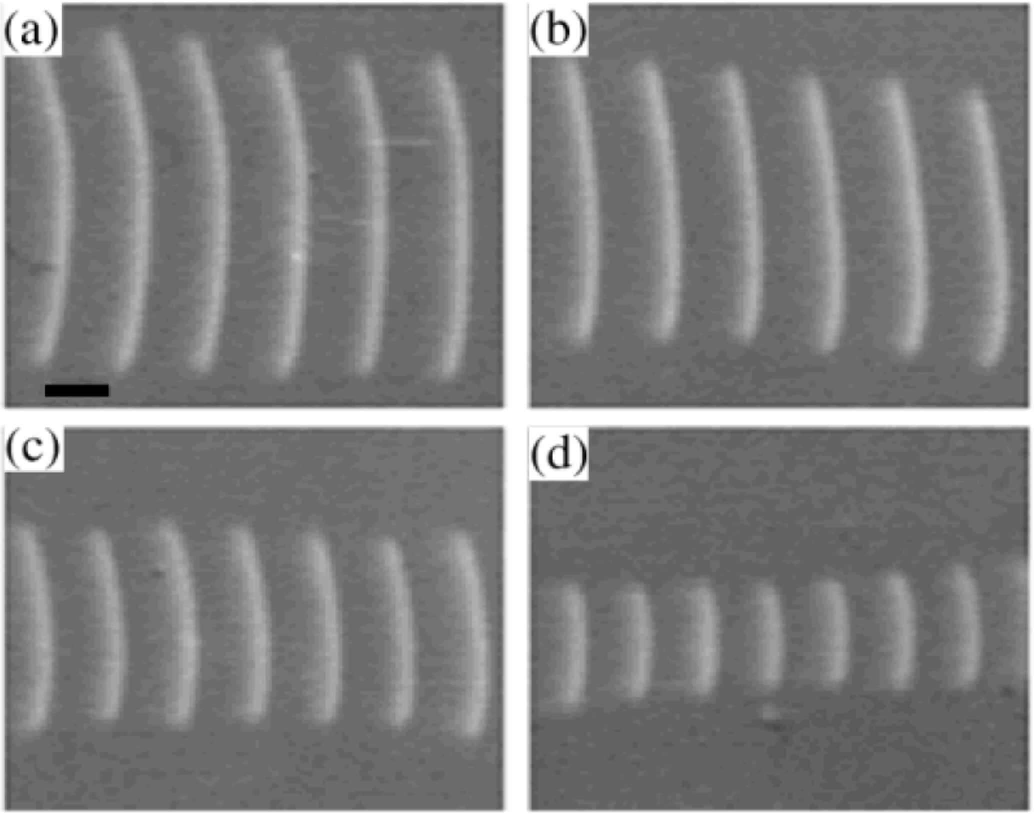


Superimposed images at equal time intervals

Nature ***391***, *770-772 (1998).*

Feedback Stabilized Waves

$$\phi(x, y) = a \cdot A + b$$



A = area
a = gain
b = offset

Excitability is determined by offset:

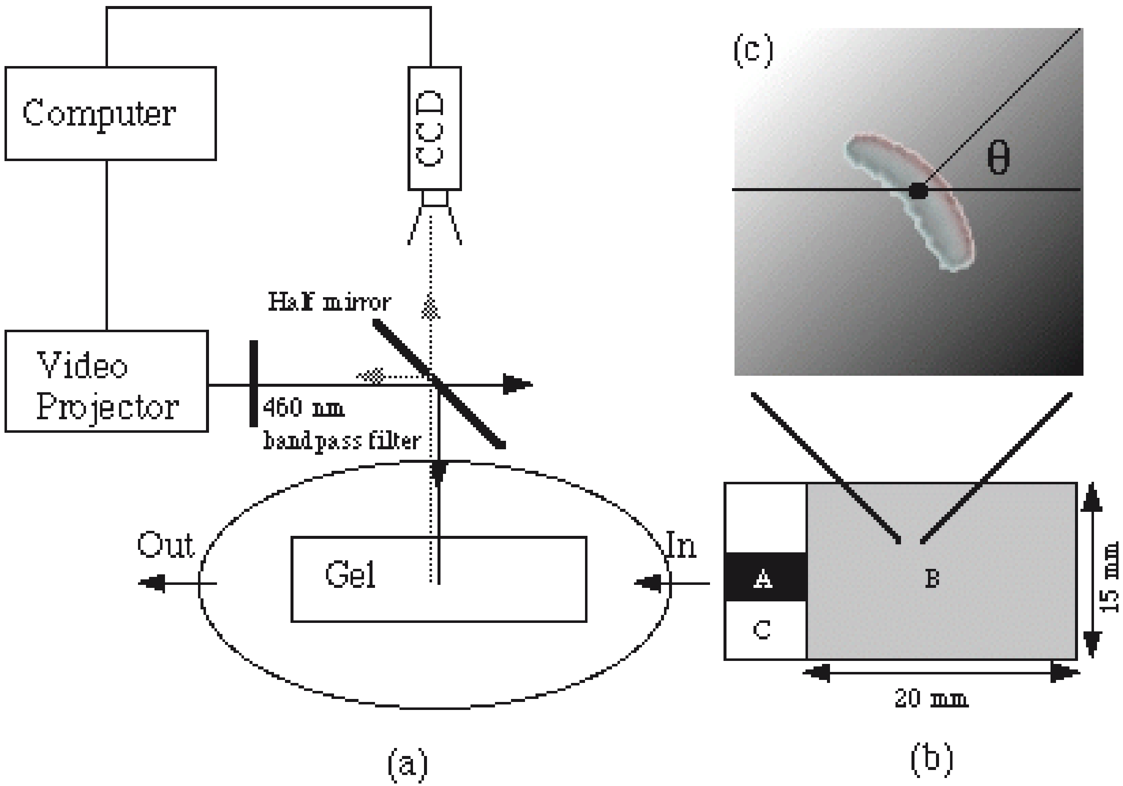
b = -0.0744 (a)
-0.0248 (b)
0.0248 (c)
0.0744 (d)
mW/cm^2

Phys. Rev. E ***65****, 065602 (2002).*
Phys. Rev. Lett. ***94****, 068302 (2005).*

Directing Stabilized Waves with Excitability Gradients

$$\phi(x,y) = a \cdot A + b + c \cdot G(x,y)$$

$$A = \sum_{x,y} \Theta(p(x,y) - p_{th})$$



Controlling Particle-Like Waves

$$X = (\alpha - \beta)\cos(\theta) + \gamma\cos((\tfrac{\alpha}{\beta} - 1)(\theta))$$

$$Y = (\alpha - \beta)\sin(\theta) - \gamma\sin((\tfrac{\alpha}{\beta} - 1)(\theta))$$

Circular trajectories:

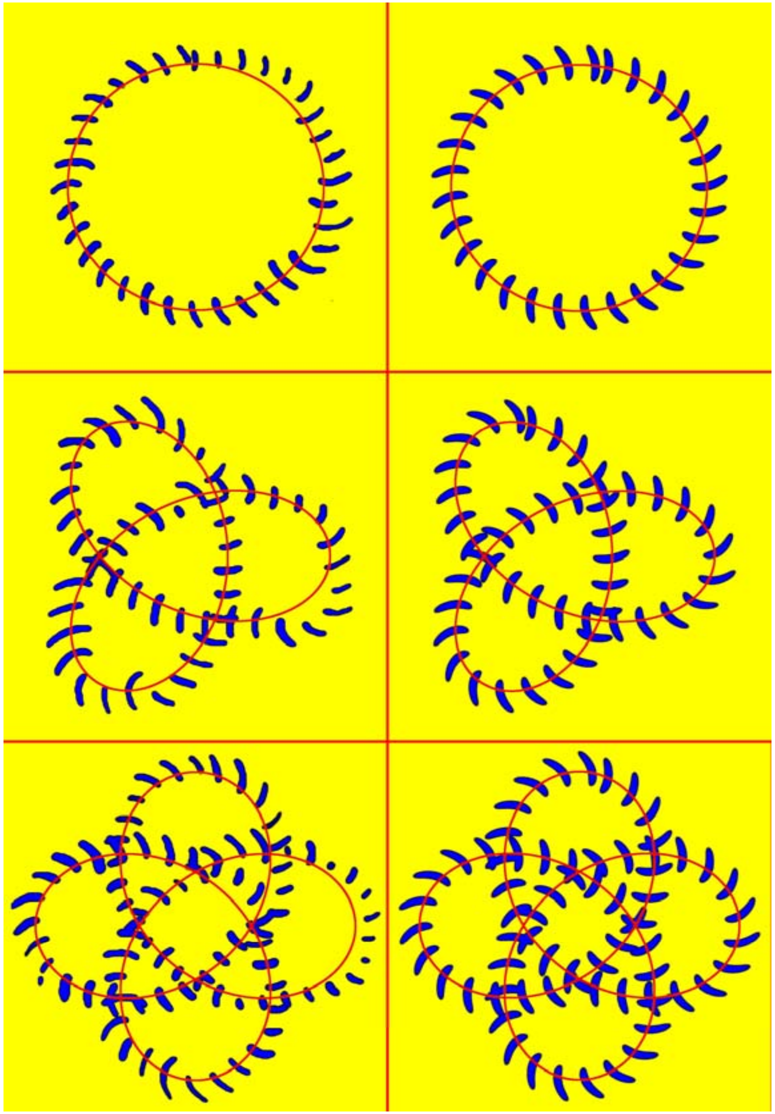
$\alpha = \gamma = 0,\ \beta = 100$

Three-lobed trajectories:

$\alpha = 60,\ \beta = 20,\ \gamma = 80$

Four-lobed trajectories:

$\alpha = 60,\ \beta = 15,\ \gamma = 80$

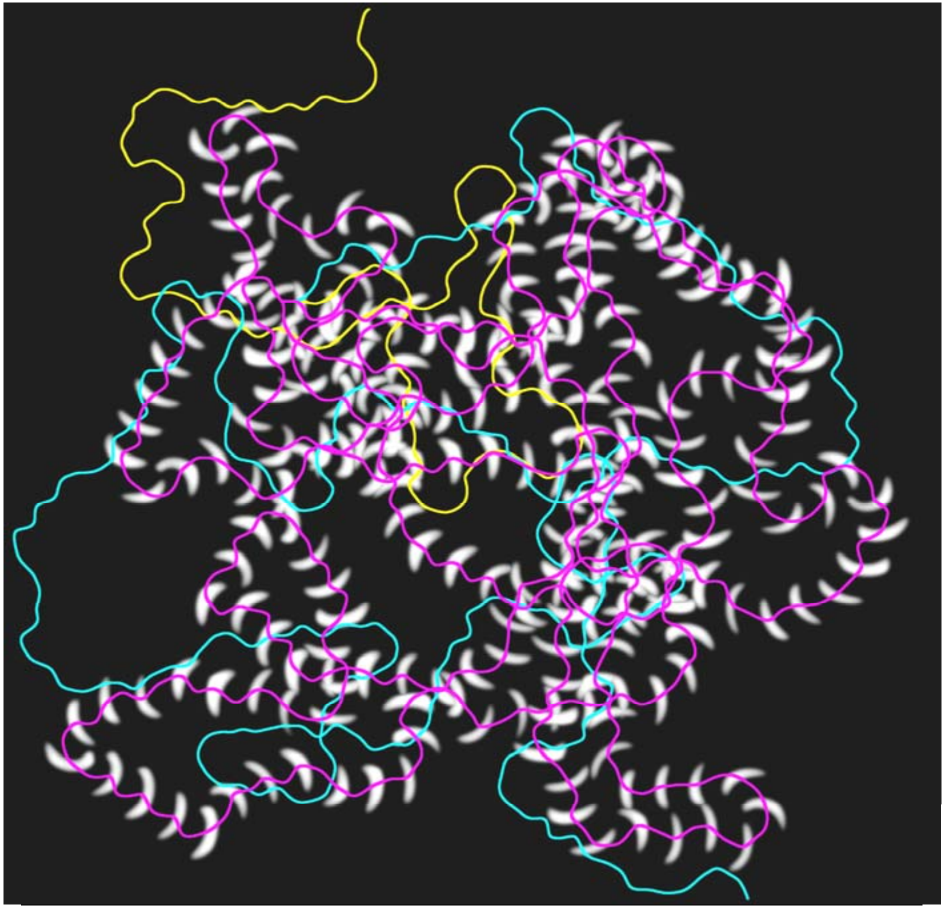


T. Sakurai, E. Mihaliuk, F. Chirila, and K. Showalter, Science ***296****, 2009 (2002).*

Waves Undergoing Random Walks

The slope of *G* randomly selected from a uniform probability distribution between -0.002 and 0.002.

Three different random walk trajectories, all starting at the same point, shown in red, blue and yellow.



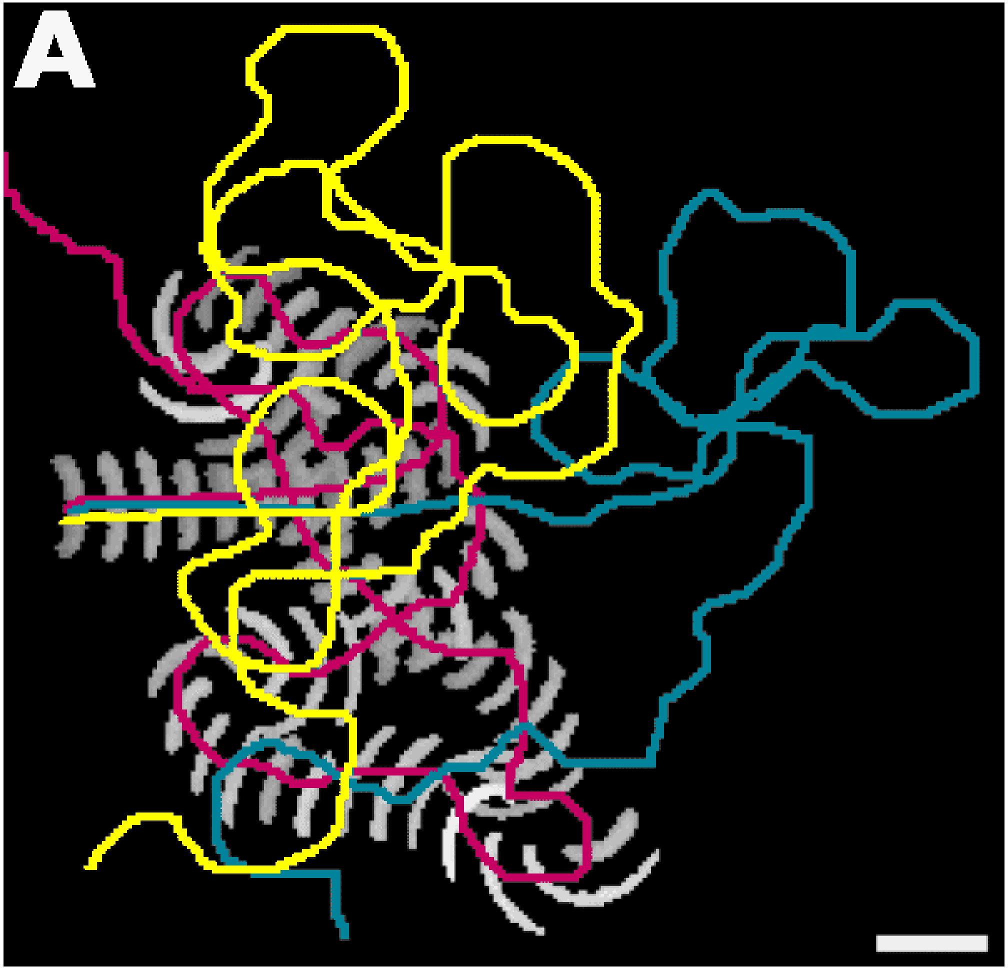
Click Image to Play Movie

Experimental Waves Undergoing Random Walks

Three different random walk trajectories, each starting at the same point.

Slope of G randomly selected from a uniform probability distribution between -2.5 and 2.5.

Scale bar: 2.0 mm.



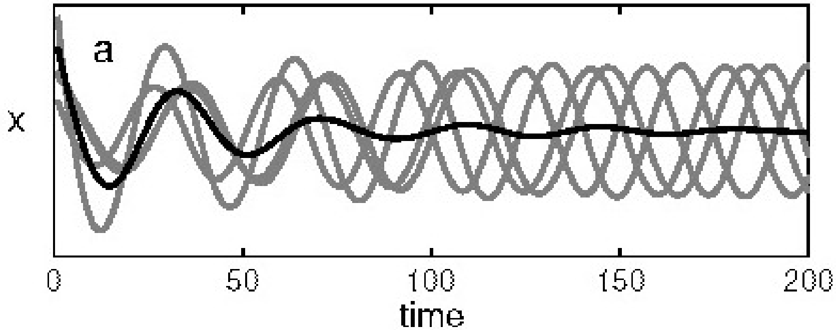
Dynamical quorum sensing: population density encoded in cellular dynamics

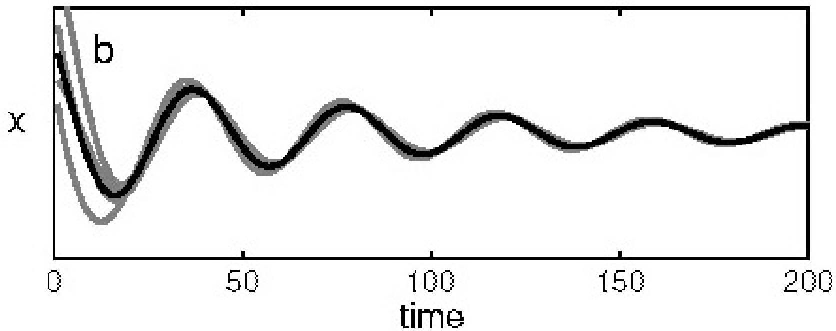
Silvia De Monte*†, Francesco d'Ovidio ‡, Sune Danø §, and Preben Graae Sørensen ¶

†Laboratoire "Fonctionnement et Evolution des Systèmes Ecologiques", UMR 7625, Ecole Normale Supérieure, Paris, France, ‡Laboratoire de Meteorologie Dynamique, Ecole Normale Supérieure, Paris, France, §Department of Biomedical Sciences, University of Copenhagen, Denmark, and ¶Department of Chemistry, University of Copenhagen, Denmark

Submitted to Proceedings of the National Academy of Sciences of the United States of America

S. De Monte F. d'Ovidio, S. Danø, and P. G. Sørensen, Proc. Nat. Acad. Sci. 104, 18377 (2007).



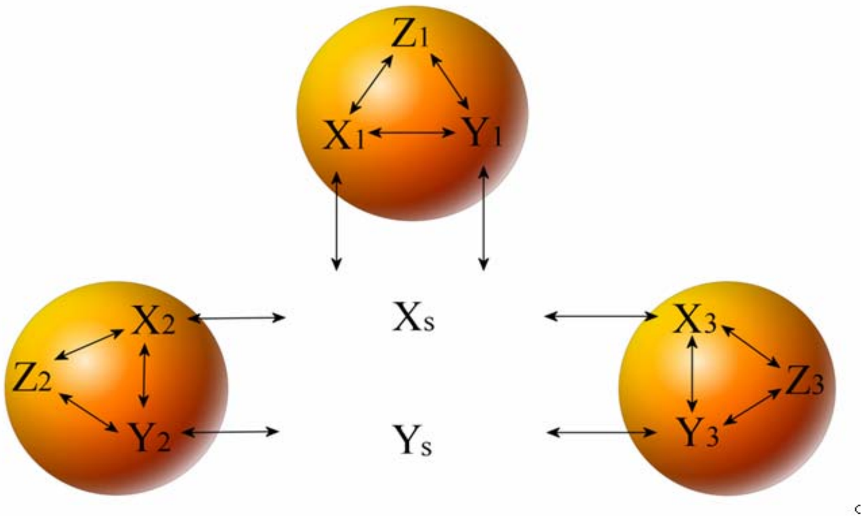


As the density of the population of yeast cells is decreased, a transition from oscillatory to nonoscillatory behavior of the overall population is observed.

J. Aldridge and E. K. Pye, Nature 259, 670-671 (1976).

<u>Quorum-sensing</u>: Appearance of bioluminescence in *Vibrio fischeri* and biofilm formation in *Pseudomonas aeruginosa*.

Catalyst-Loaded Beads in Catalyst-Free BZ Solution



Exchange species:
$X = HBrO_2$
$Y = Br^-$

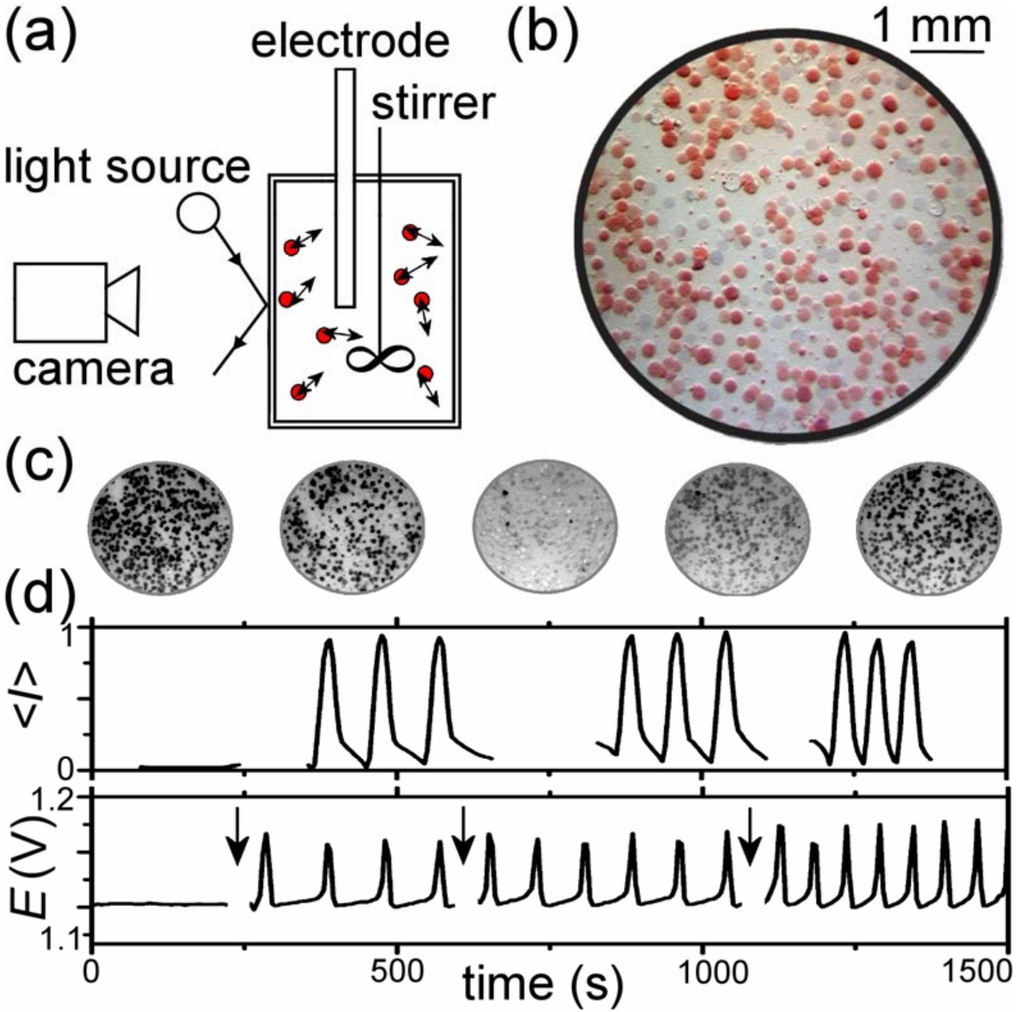
Immobilized:
$Z = Fe(phen)_3^{3+}$

Desynchronization transition with decreasing density for a particular exchange rate: globally oscillatory to globally nonoscillatory (with oscillatory individuals).

R. Toth, A. F. Taylor, and M. R. Tinsley, J. Phys. Chem. B 110, 10170 (2006).
J. Maselko and K. Showalter, Nature 339, 609 (1989)

Large populations! A cuvette 1.8 cm × 1.8 cm allows a population of about 100,000 catalyst-loaded ~200 μm beads.

Experimental Setup



Stirred suspension of catalyst-loaded particles in catalyst-free solution

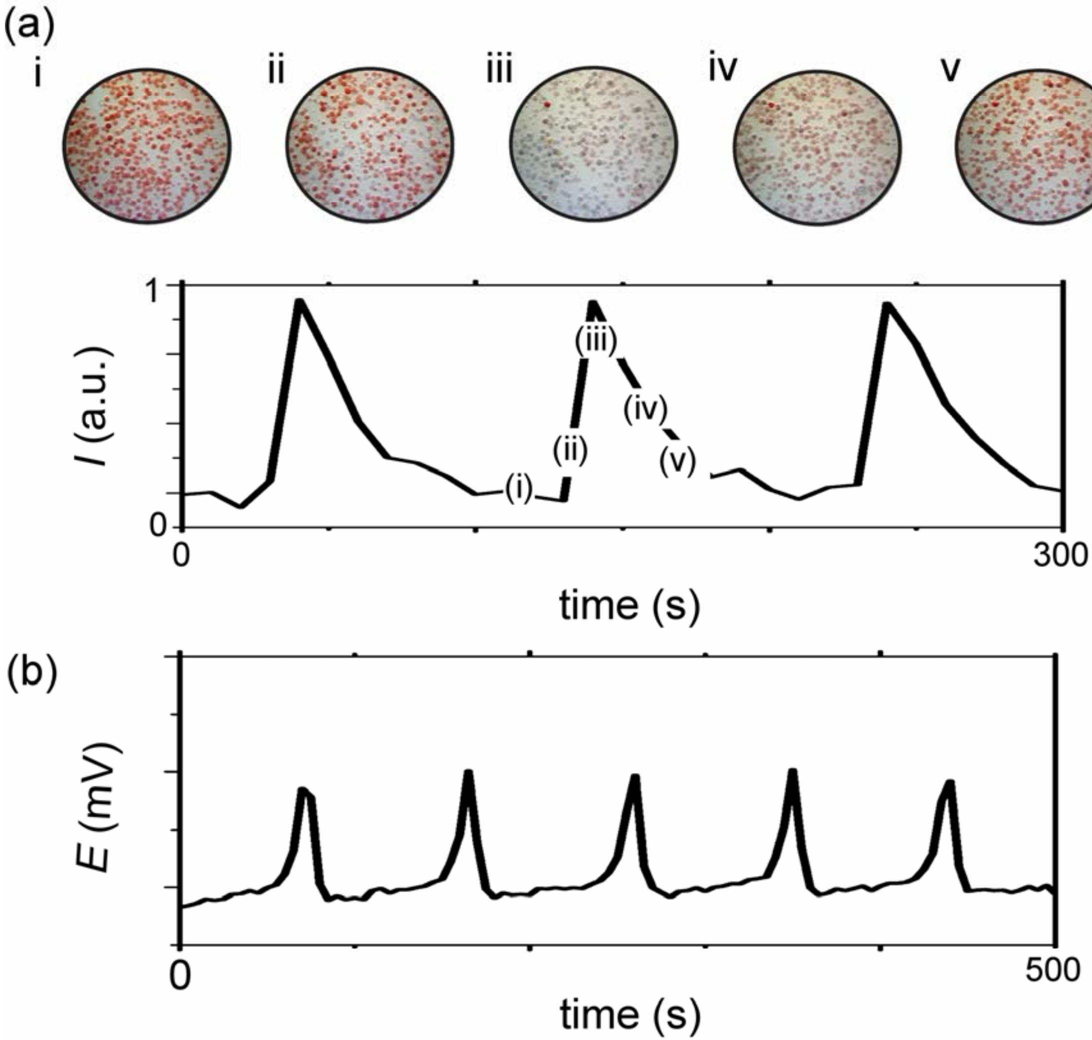
Particle size: ~200 μm
Stirring rate: 300 – 600 rpm
Shutter speed: 0.4 ms
Frame rate: 1 s

Video

Pt electrode

A. F. Taylor, M. R. Tinsley, F. Wang, Z. Huang, and K. Showalter, Science 323, 614 (2009).

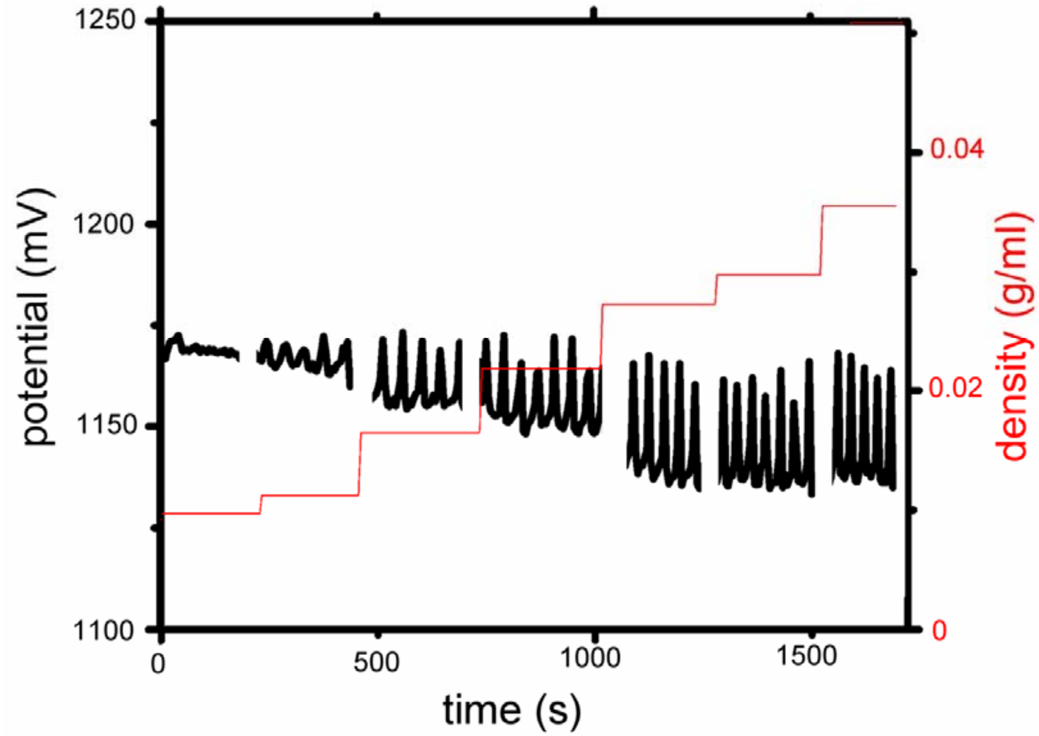
Monitoring Solution and Catalyst Particles

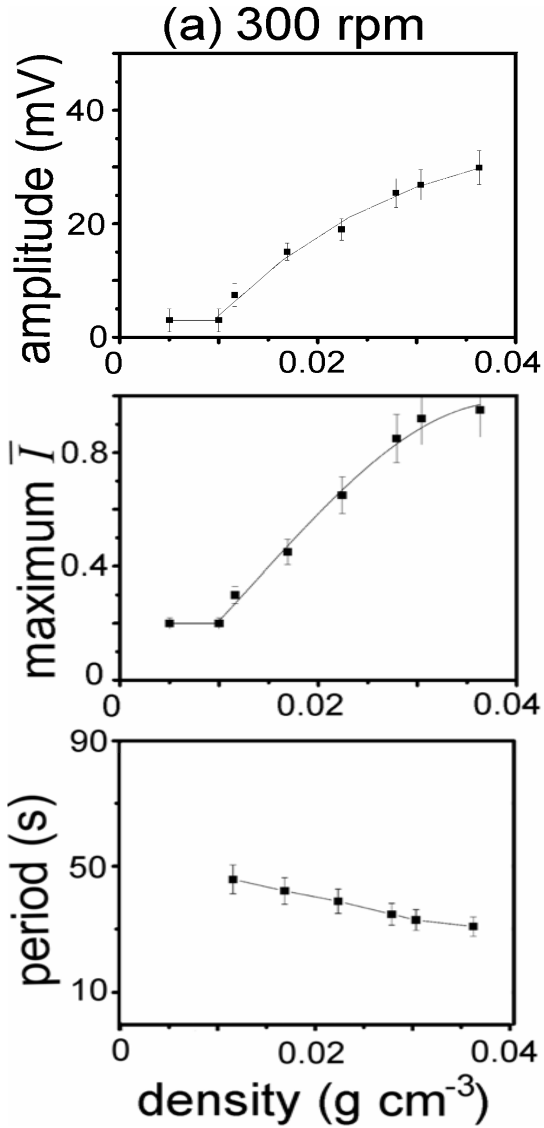


Intensity normalized with respect to the maximum excitation (iii).

Particle size: ~200 μm
Stirring rate: 300 – 600 rpm
Shutter speed: 0.4 ms
Frame rate: 1 s

Transition at Low Exchange Rate





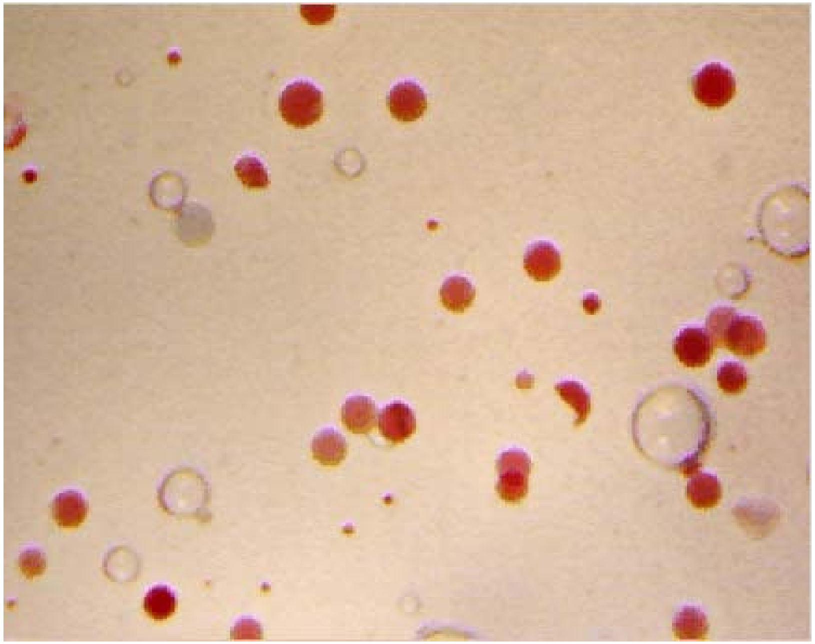
Stirring speed: 300 rpm

Catalyst particle density

0.010 g/ml, 0.0116 g/ml, 0.0136 g/ml, 0.0169 g/ml, 0.0224 g/ml, 0.0251 g/ml, 0.0363 g/ml.

Low Particle Density – Low Exchange Rate

Click Image to Play Movie



Bead density = 0.0116 g/ml

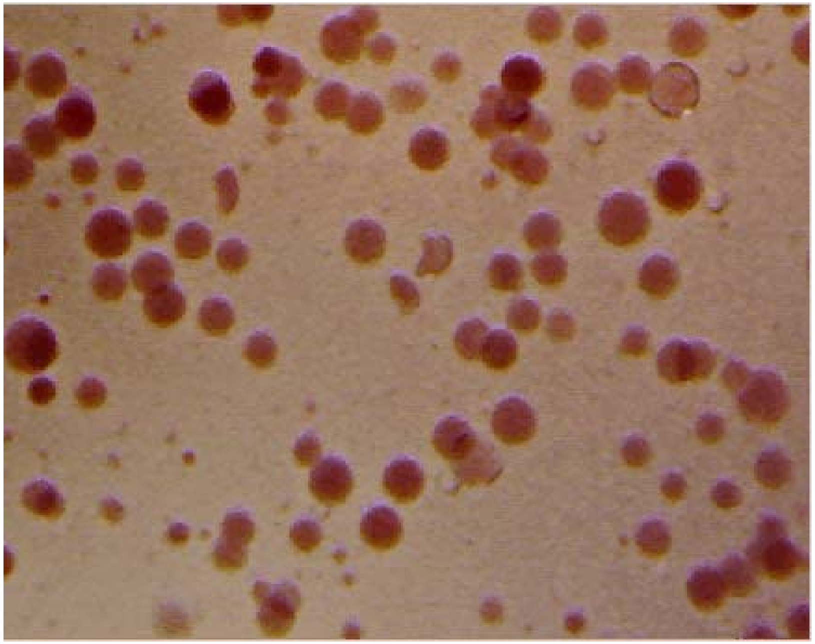
Stirring speed: 300 rpm

[NaBr] =0.07 M, [MA] =0.14 M, $[NaBrO_3]$ = 0.49 M, $[H_2SO_4]$ =0.67 M

Particles are loaded with ferroin at 1.7 x 10^{-5} mol/g

High Particle Density – Low Exchange Rate

Click Image to Play Movie



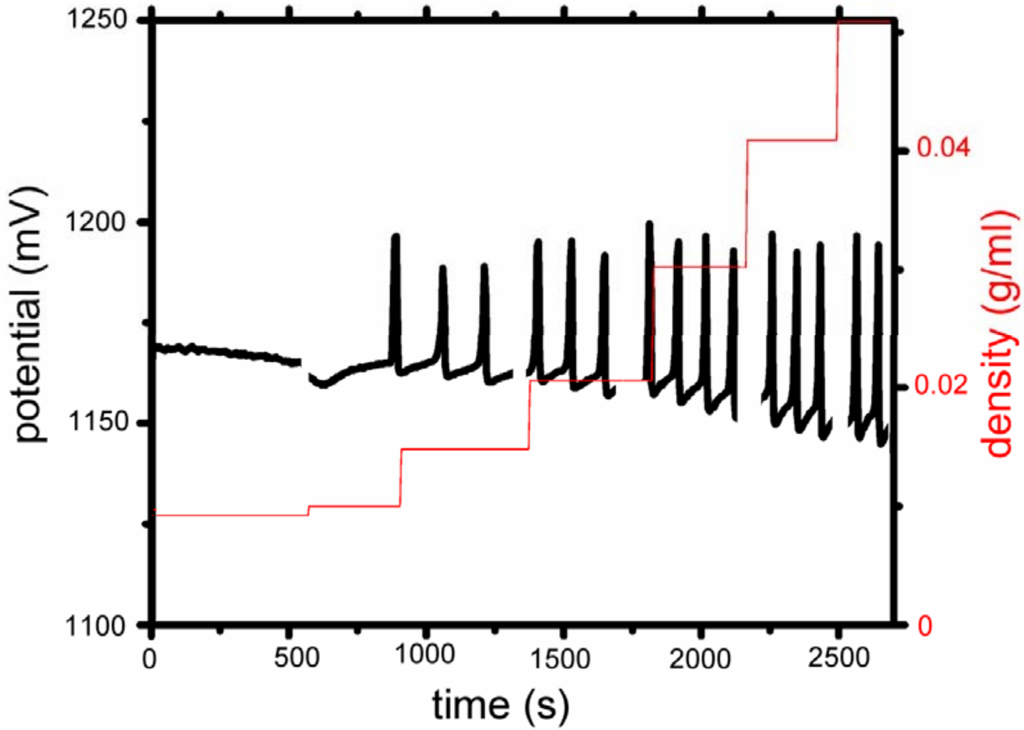
Bead density = 0.0363 g/ml

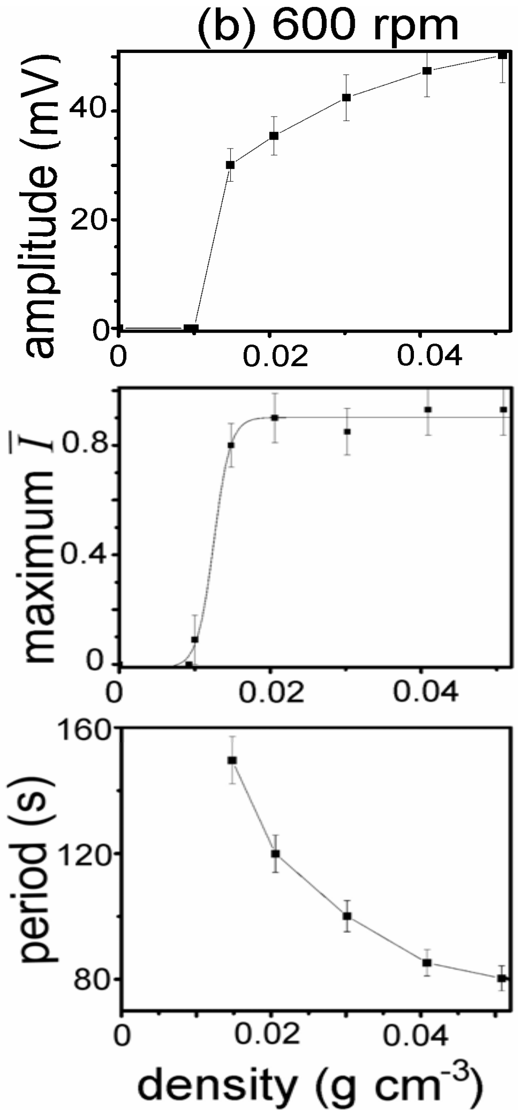
Stirring speed: 300 rpm

[NaBr] =0.07 M, [MA] =0.14 M, $[NaBrO_3]$ = 0.49 M, $[H_2SO_4]$ =0.67 M

Particles are loaded with ferroin at 1.7 x 10^{-5} mol/g

Transition at High Exchange Rate



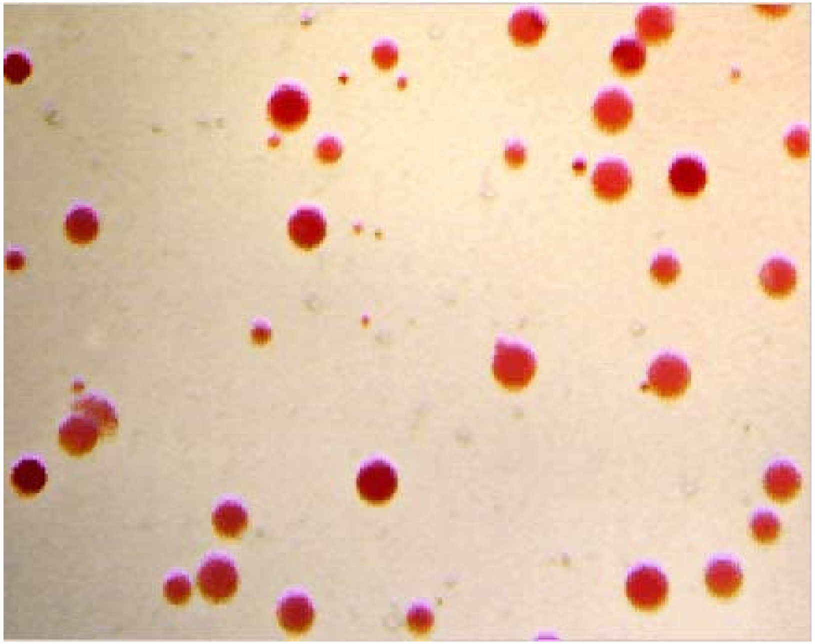


Pt electrode potential vs time

Stirring rate = 600 rpm

Low Particle Density – High Exchange Rate

Click Image to Play Movie



Particle density = 0.0093 g/ml

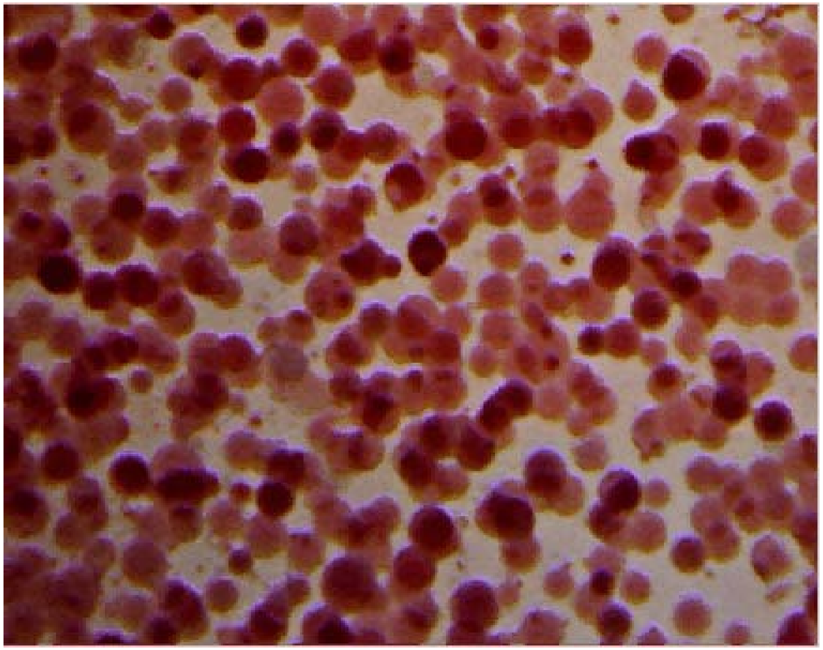
Stirring speed: 600 rpm

[NaBr] =0.07 M, [MA] =0.14 M, [$NaBrO_3$] = 0.49 M, [H_2SO_4] =0.67 M

Particles are loaded with ferroin at 1.7 x 10^{-5} mol/g

High Particle Density – High Exchange Rate

Click Image to Play Movie



Particle density = 0.123 g/ml

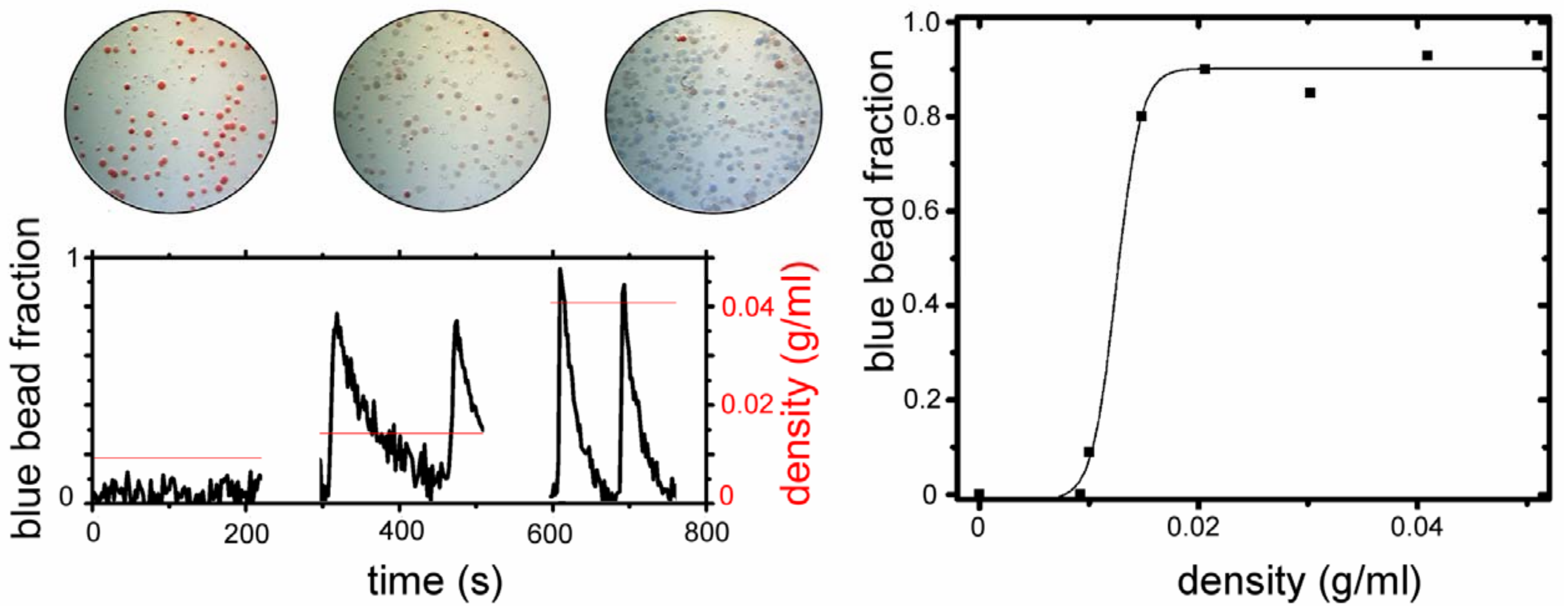
Stirring speed: 600 rpm

[NaBr] =0.07 M, [MA] =0.14 M, $[NaBrO_3]$ = 0.49 M, $[H_2SO_4]$ =0.67 M

Particles are loaded with ferroin at 1.7 x 10^{-5} mol/g

Maximum Fraction of Excited Catalyst Particles

High Exchange



Stirring rate = 600 rpm

Catalyst particle density

0.0092 g/ml, 0.0148 g/ml, 0.0409 g/ml

[NaBr] =0.07 M, [MA] =0.14 M, [$NaBrO_3$] = 0.49 M, [H_2SO_4] =0.67 M

Fraction = (grayscale - grayscale (all red)) / (grayscale (all blue) - grayscale (all red))

Model for Catalyst-Loaded Particles in Catalyst-Free Solution

variables	X (U_{ss})	$HBrO_2$ activator ($HBrO_2^{+}$)
	Y	Br^-, inhibitor
	Z	oxidized catalyst

For $i = 1, \ldots N$ particles:

$$\frac{dX_i}{dt} = -k(X_i - X_s) - k_2 h_0 X_i Y_i + k_3 h_0 A Y_i - 2k_4 X_i^{\,2} - k_5 h_0 A X_i + k_{-5} U_{ss}^{\,2} + k_6 U_{ss}(C - Z_i) - k_{-6} X_i Z_i$$

$$\frac{dY_i}{dt} = -k(Y_i - Y_s) - k_2 h_0 X_i Y_i - k_3 h_0 A Y_i + q_i \frac{k_7 k_8 B Z_i}{k_{-7} h_0 (C - Z_i) + k_8} + k_9 B$$

$$\frac{dZ_i}{dt} = k_6 U_{ss}(C - Z_i) - k_{-6} X_i Z_i - \frac{k_7 k_8 B Z_i}{k_{-7} h_0 (C - Z_i) + k_8}$$

For solution:

$$\frac{dX_s}{dt} = \frac{<V_i>}{V_s} \sum_i^N k(X_i - X_s) - k_2 h_0 X_s Y_s + k_3 h_0 A Y_s - 2k_4 X_s^{\,2} + k_{-5} U_{ss}^{\,2}$$

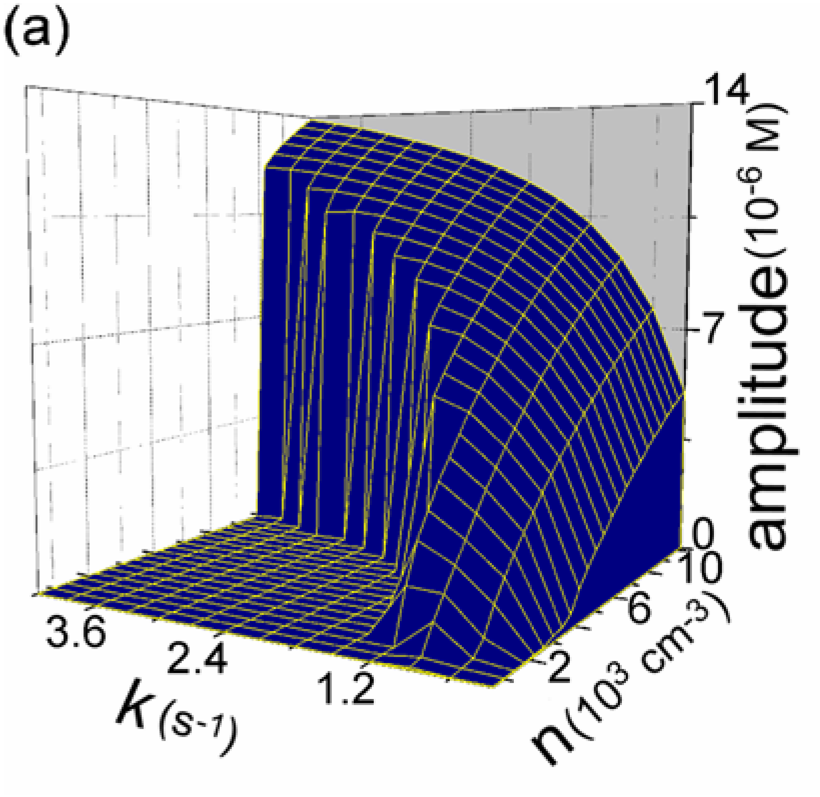
$$\frac{dY_s}{dt} = \frac{<V_i>}{V_s} \sum_i^N k(Y_i - Y_s) - k_2 h_0 X_s Y_s - k_3 h_0 A Y_s + k_9 B$$

parameters	A	BrO_3-
	B	MA + BrMA
	C	Total catalyst
	h_0	Acid
	$k_1 - k_9$	Rate constants
Fitted parameters	q_i	Stoichiometric factor
	k	Mass exchange rate constant
	$<V_i>/V_s$	Dilution factor

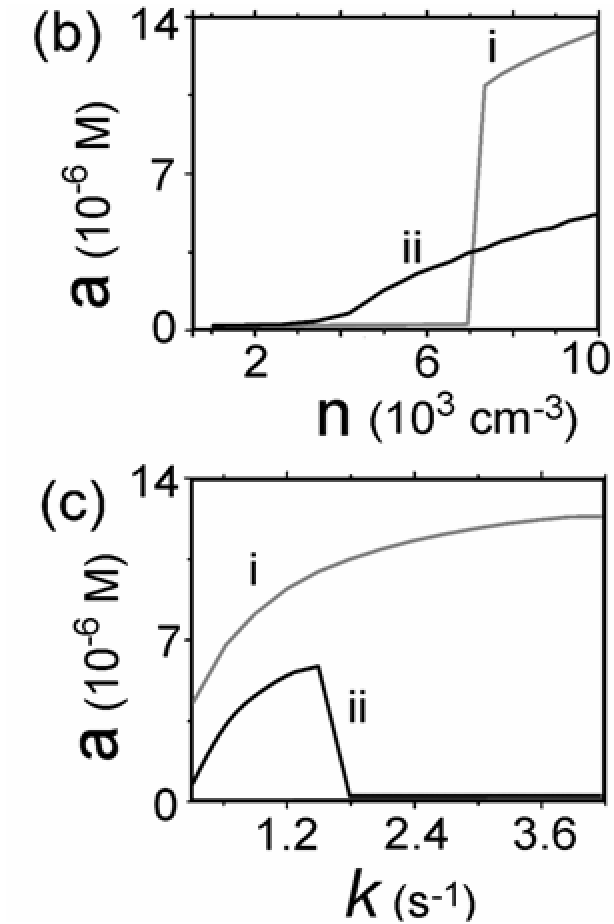
ZBKE Model: Zhabotinsky, Buchholtz, Kiyatkin, Epstein, J. Phys. Chem. 97, 7578 (1993).

Global Signal: Amplitude of Variable X_S

b(i) $k = 3\ s^{-1}$, b(ii) $k = 0.3\ s^{-1}$

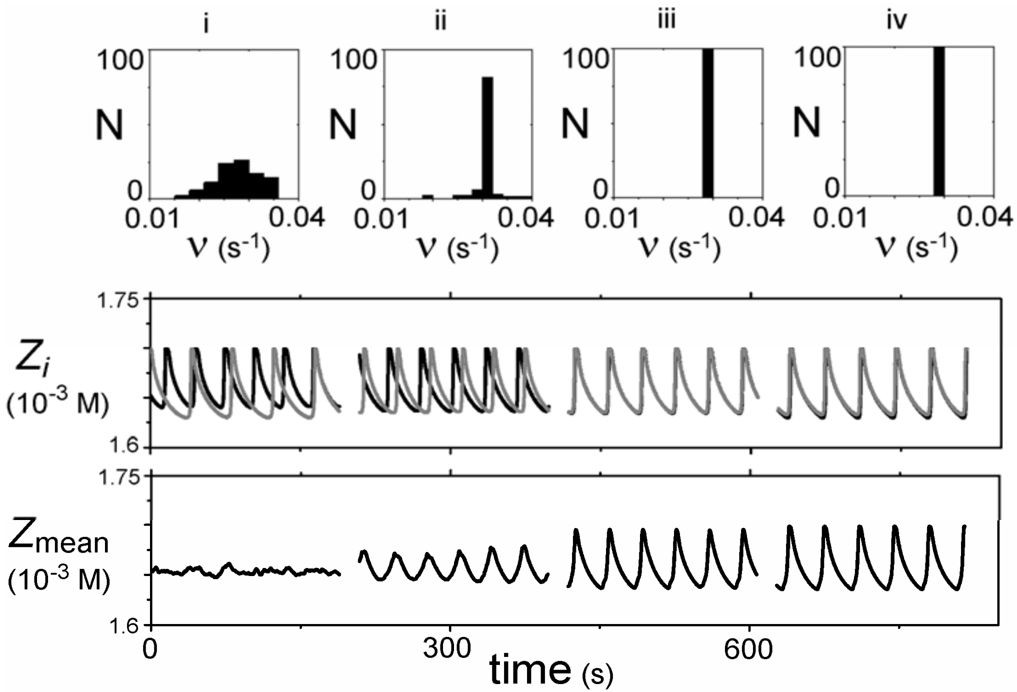


Amplitude of $HBrO_2$ in solution.

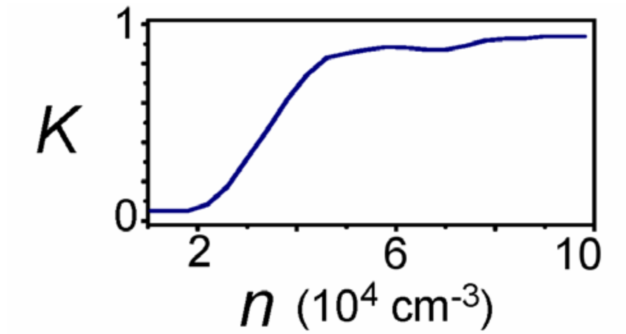


c(i) $n = 8200\ cm^{-3}$, c(ii) $n = 4200\ cm^{-3}$

Synchronization at Low Exchange ($k = 0.3\ s^{-1}$)



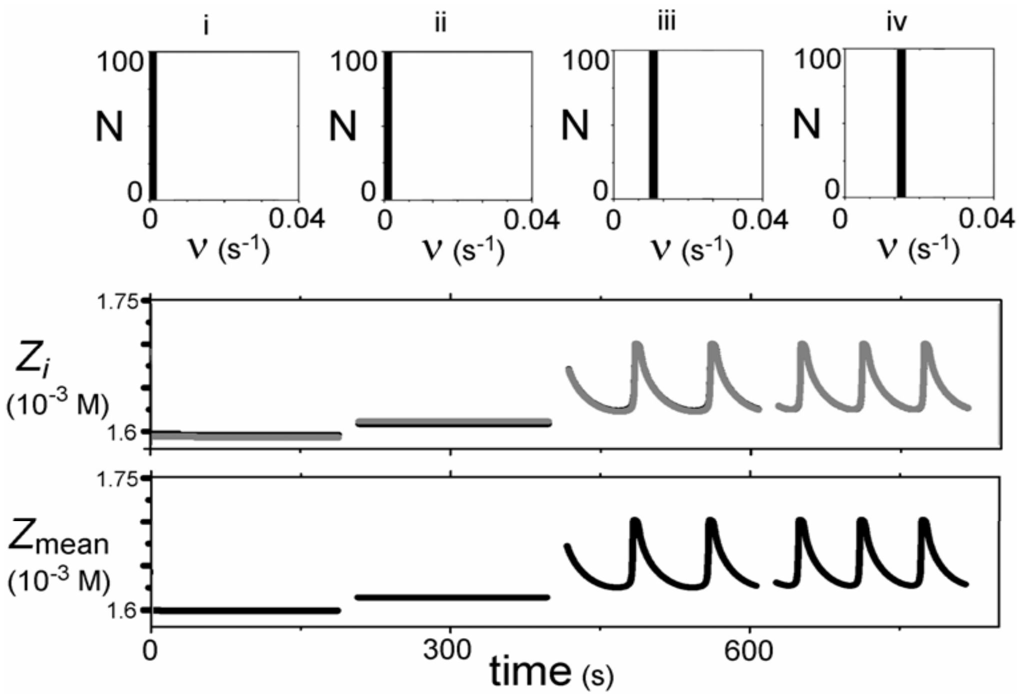
(i) n = 1000 cm^{-3}
(ii) n = 3400 cm^{-3}
(iii) n = 6200 cm^{-3}
(iv) n = 10000 cm^{-3}



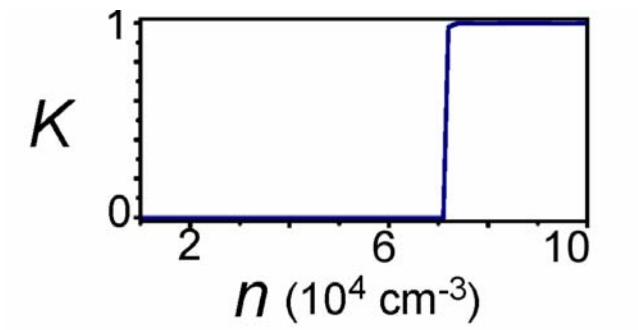
$$K = \left\langle \left| N^{-1}\sum_{j}^{N} e^{i\theta_j} - \left\langle N^{-1}\sum_{j}^{N} e^{i\theta_j} \right\rangle \right| \right\rangle$$

The coherence measure K is 0 when all particles oscillate out of phase with each other (or when the particles are not oscillating) and 1 when all particles oscillate in perfect synchrony. S. Shinomoto and Y. Kuramoto, Prog. Theo. Phys. 75, 1105 (1986).

Synchronization at High Exchange (k = 3.0 s^{-1})



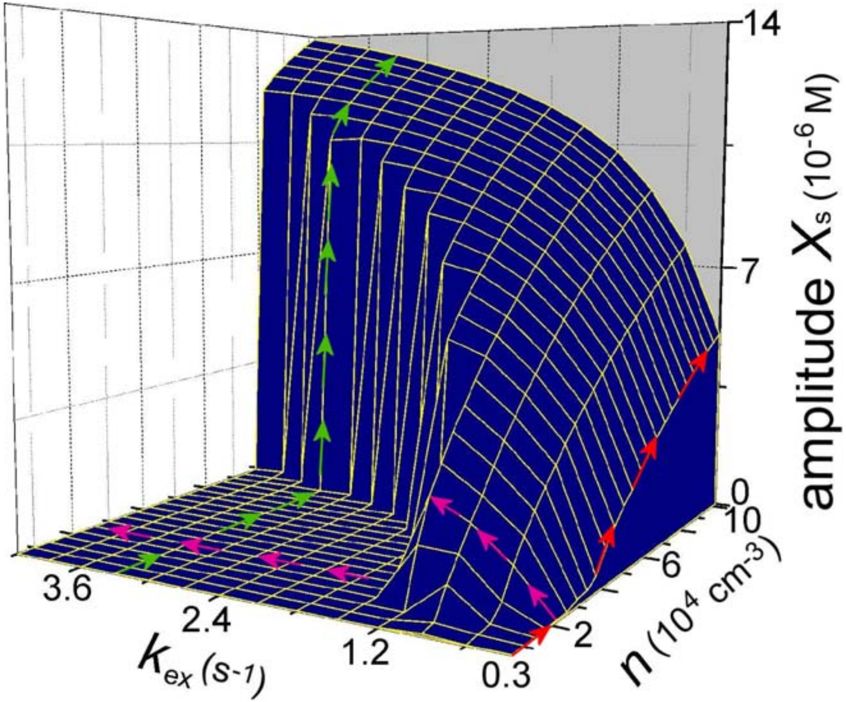
(i) n = 1000 cm^{-3}
(ii) n = 3400 cm^{-3}
(iii) n = 7400 cm^{-3}
(iv) n = 10000 cm^{-3}

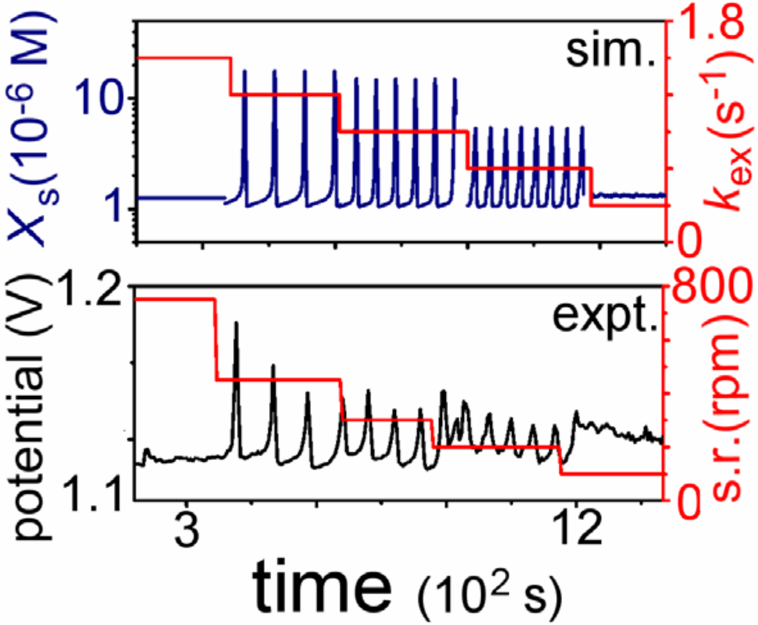


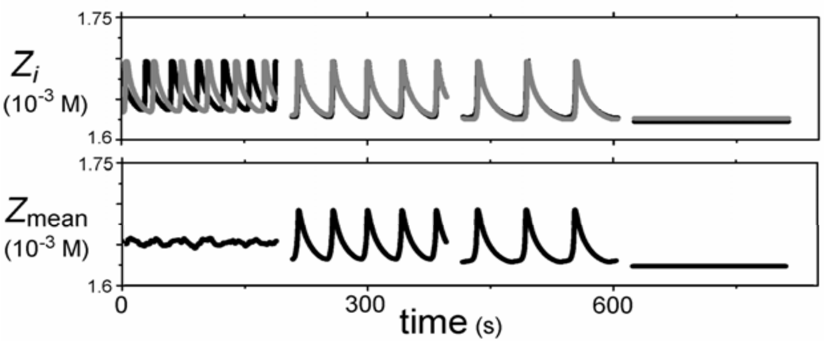
$$K = \langle | N^{-1}\sum_{j}^{N} e^{i\theta_j} - \langle N^{-1}\sum_{j}^{N} e^{i\theta_j} \rangle | \rangle$$

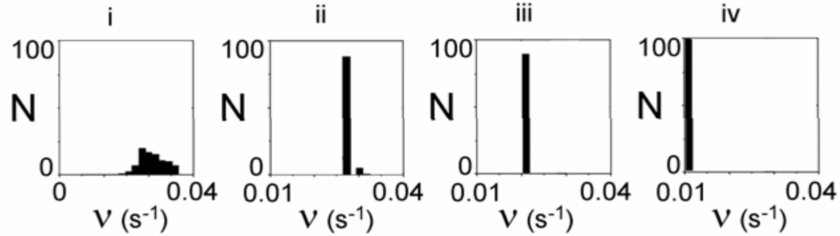
The coherence measure K is 0 when all particles oscillate out of phase with each other (or when the particles are not oscillating) and 1 when all particles oscillate in perfect synchrony. S. Shinomoto and Y. Kuramoto, Prog. Theo. Phys. 75, 1105 (1986).

Transitions at Low Particle Density (n = 1800 cm^{-2})



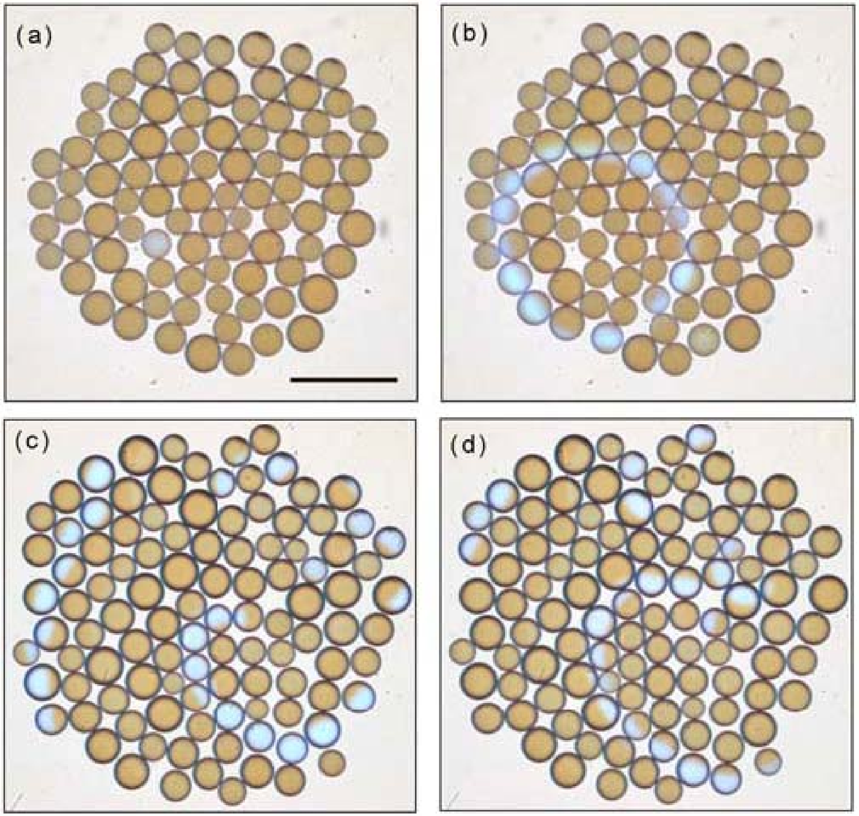






$\boldsymbol{k}_{\mathbf{ex}}$ = 0.3 s^{-1} (i), 0.9 s^{-1} (i), 1.2 s^{-1} (i), 1.5 s^{-1} (i).

Spatiotemporal Behavior



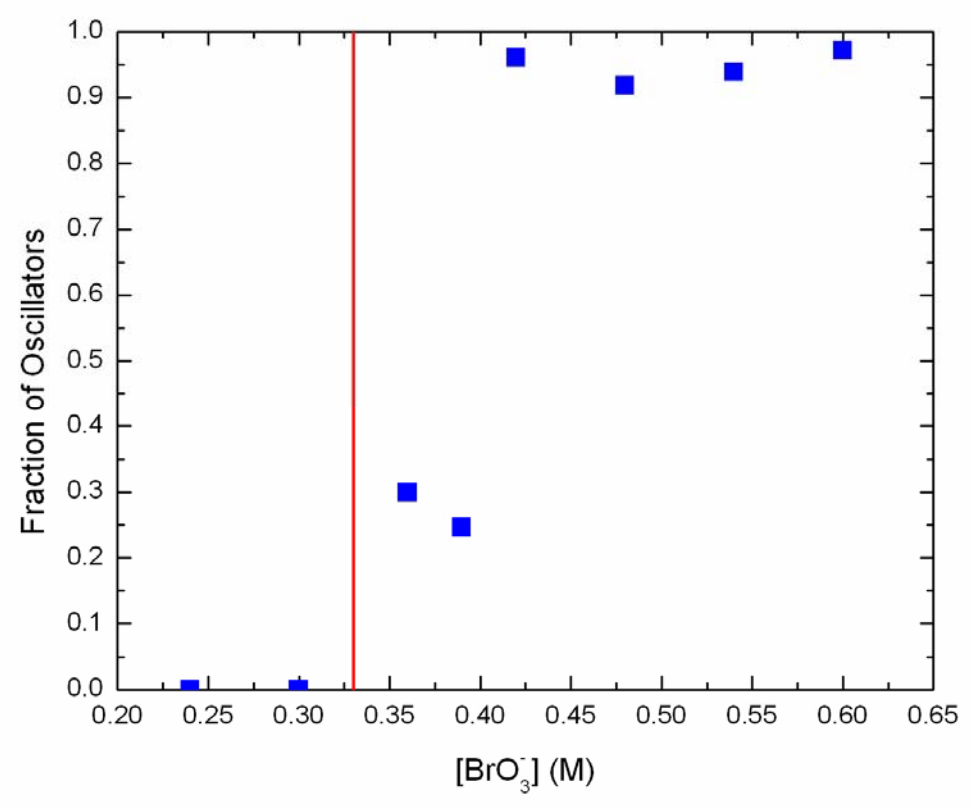
Images separated by 12 s of a target wave in a group of 89 catalyst-loaded particles.

Images separated by 8 s of spiral wave behavior in a group of 106 catalyst-loaded particles.

. Scale bar length is 1.0 mm.

M. R. Tinsley, A. F. Taylor, Z. Huang, and K. Showalter, Phys. Rev. Lett. 102, 158301 (2009).

Isolated Particle Behavior



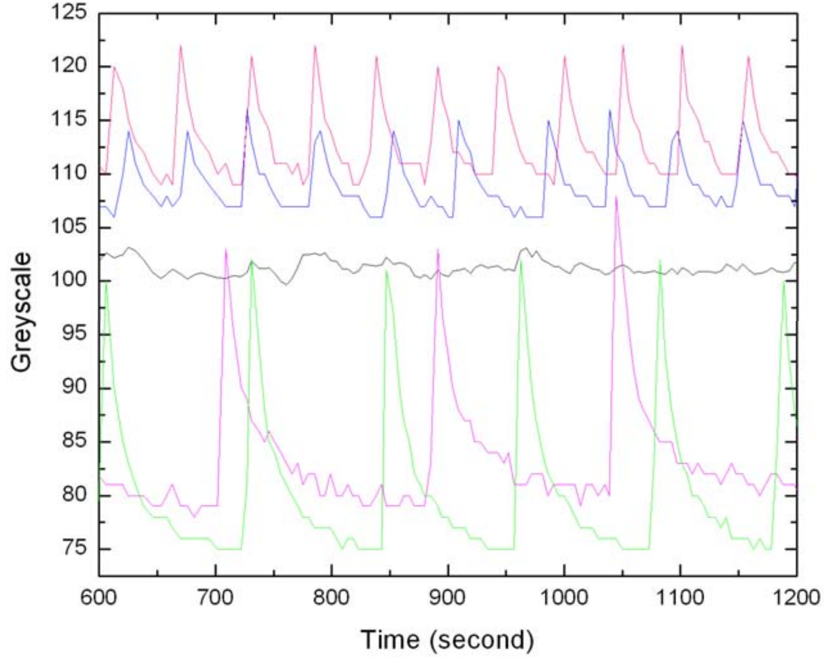
Particles are positioned > 5 mm from nearest neighbor particles.

Reaction mixture composition:
[NaBr] = 0.10 M, [MA] = 0.20 M, [H_2SO_4] = 0.30 M

Catalyst particle loading:
ferroin = 1.7 $\times 10^{-5}$ mol g^{-1}

Number of particles in each experiment: between 50 and 150.

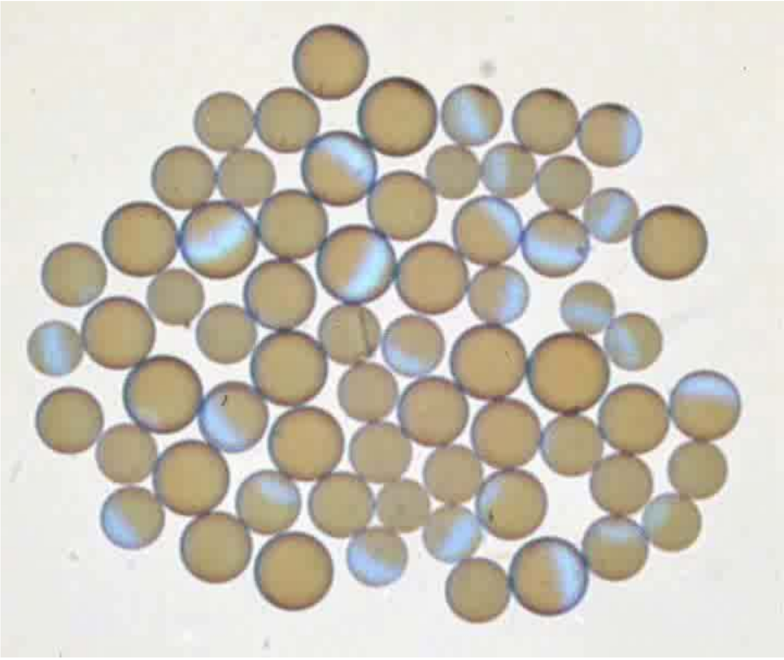
Isolated Oscillatory Particles



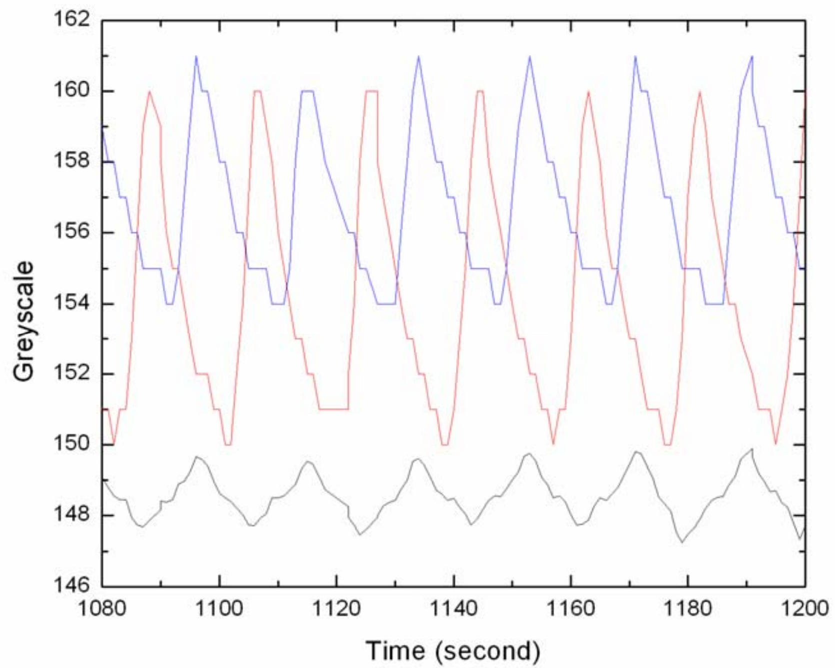
Click Image to Play Movie

Reaction mixture composition:
$[NaBrO_3]$ = 0.51 M, [NaBr] = 0.10 M, [MA] = 0.20 M, $[H_2SO_4]$ = 0.30 M.
Catalyst particle loading: ferroin = 1.7×10^{-5} mol g^{-1}
Time scale: video 5 fps, original 1 fps

Group of Oscillatory Particles

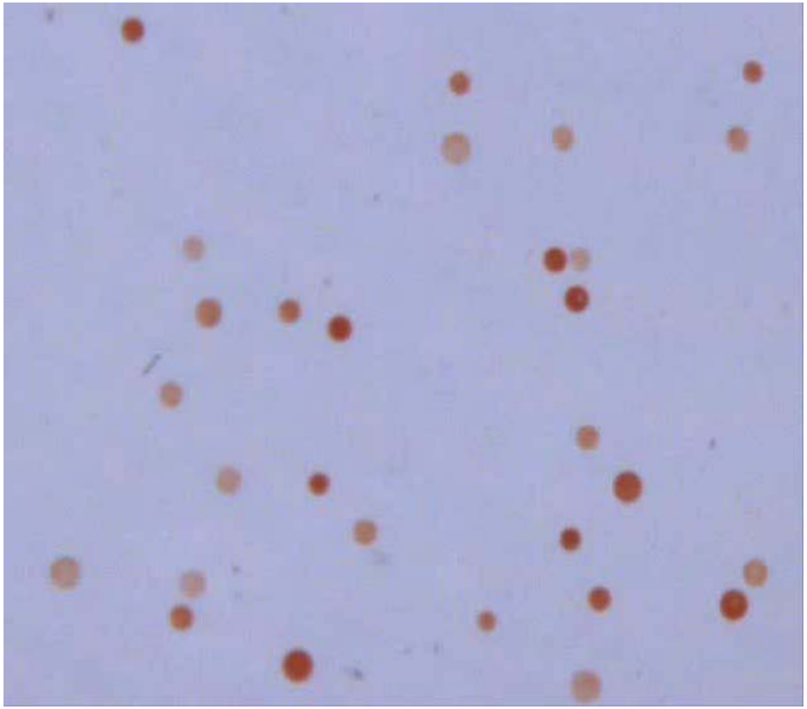


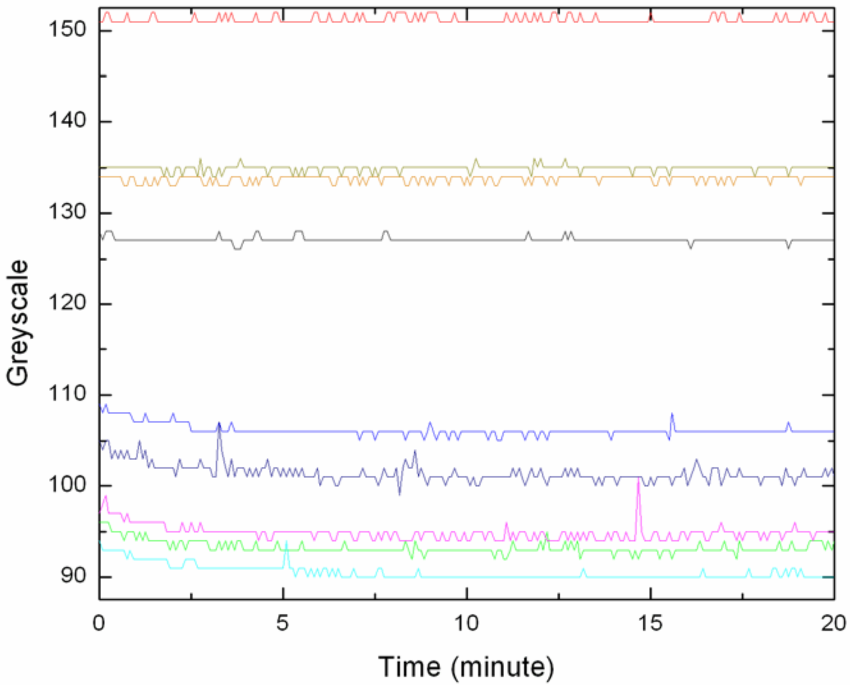
Click Image to Play Movie



Reaction mixture composition:
$[NaBrO_3]$ = 0.54 M, [NaBr] = 0.10 M, [MA] = 0.20 M, $[H_2SO_4]$ = 0.30 M
Catalyst particle loading: ferroin = 1.7×10^{-5} mol g^{-1}
Time scale: video 5 fps, original 1 fps
Group size: 66 beads

Scattered Excitable Steady State Particles





Click Image to Play Movie

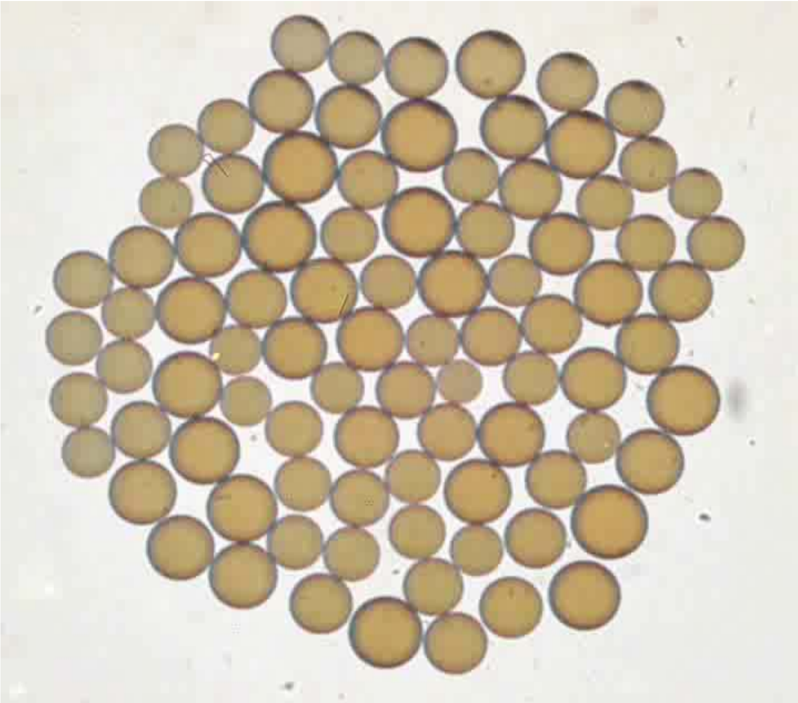
Reaction mixture composition:

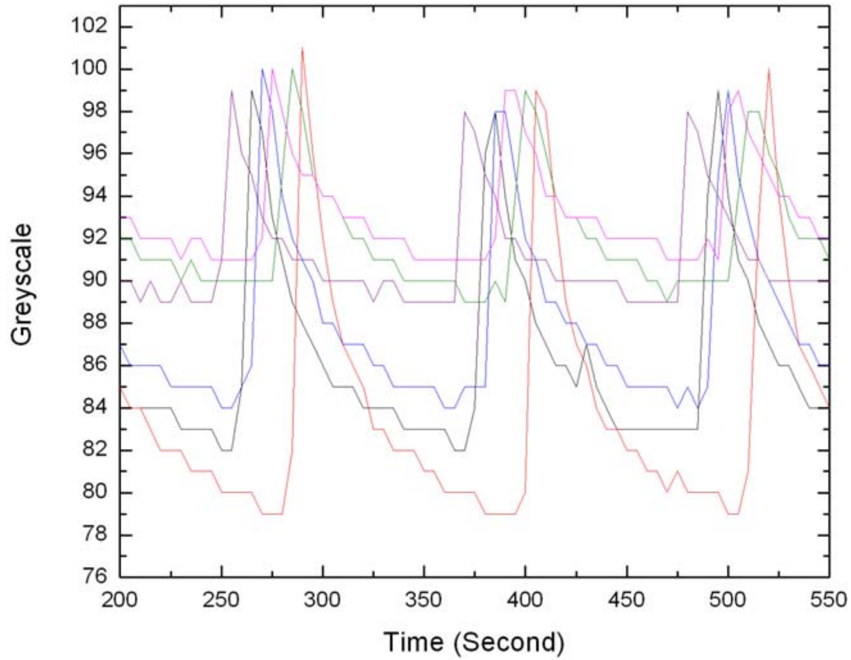
$[NaBrO_3]$ = 0.30 M, [NaBr] = 0.10 M, [MA] = 0.20 M, $[H_2SO_4]$ = 0.30 M

Catalyst particle loading: ferroin = 1.7 $\times 10^{-5}$ mol g^{-1} (per gram resin)

Time scale: video 5 fps, original 1 fps

Group of Excitable Particles – Pacemaker





Click Image to Play Movie

Reaction mixture composition:

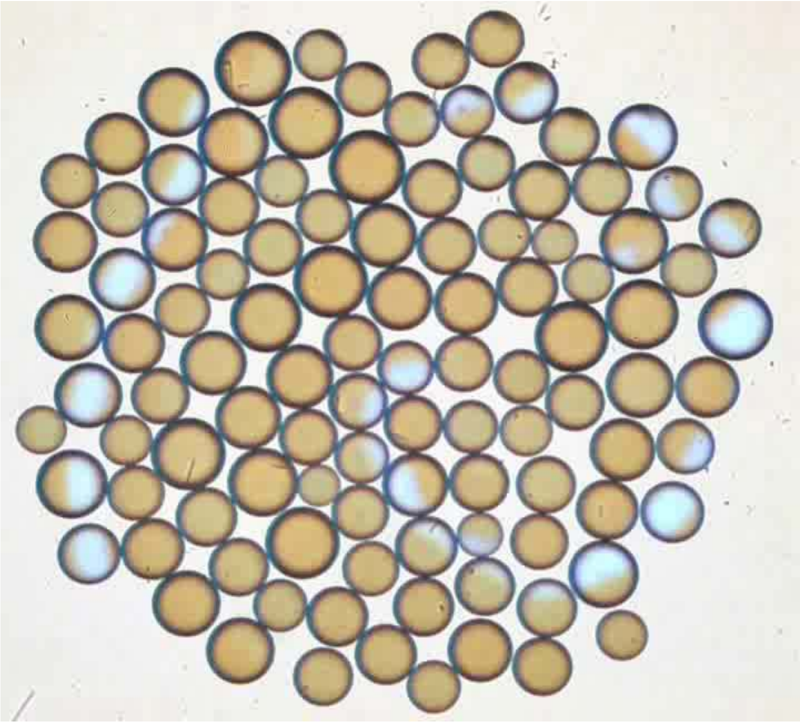
$[NaBrO_3]$ = 0.30 M, [NaBr] = 0.10 M, [MA] = 0.20 M, $[H_2SO_4]$ = 0.30 M

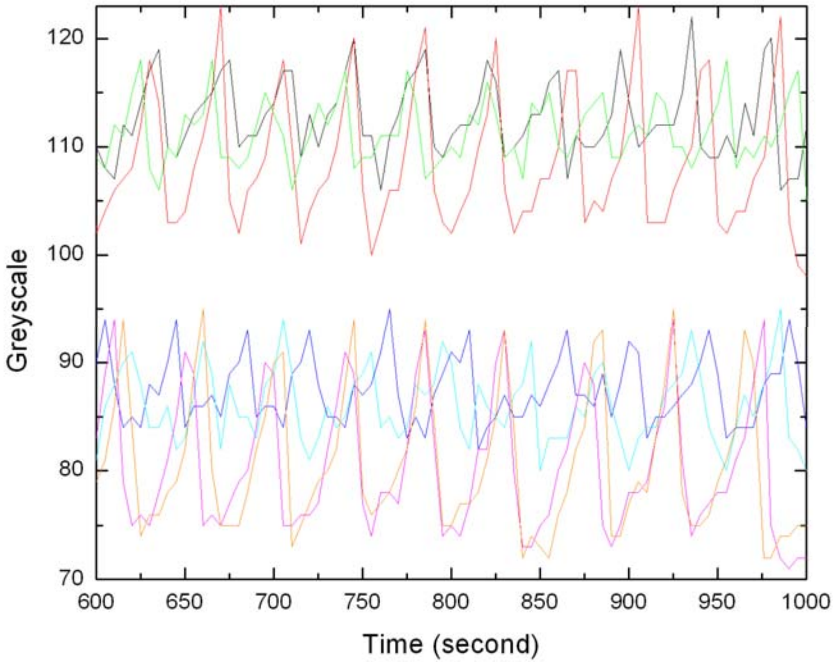
Catalyst particle loading: ferroin = 1.7×10^{-5} mol g^{-1}

Time scale: video 5 fps, original 1 fps

Group size: 89 beads

Group of Excitable Particles – Spirals

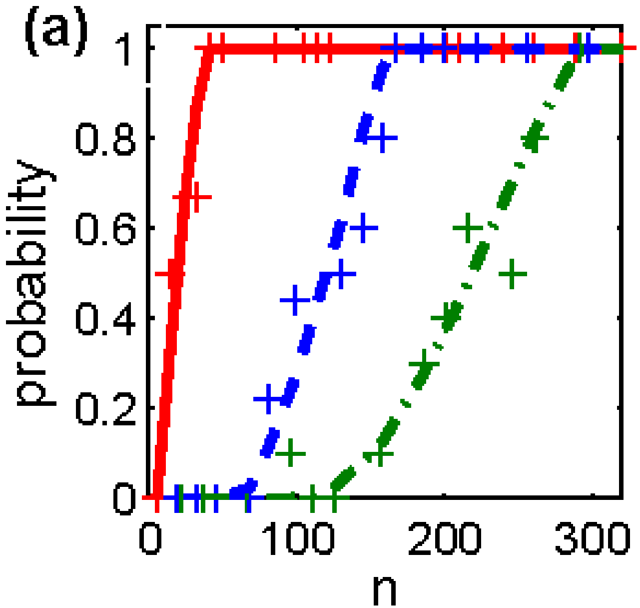




Click Image to Play Movie

Reaction mixture composition:
$[NaBrO_3]$ = 0.30 M, [NaBr] = 0.10 M, [MA] = 0.20 M, $[H_2SO_4]$ = 0.30 M
Catalyst particle loading: ferroin = 1.7×10^{-5} mol g^{-1} (per gram resin)
Time scale: video 5 fps, original 1 fps

Wave Probability Dependence on Group Size

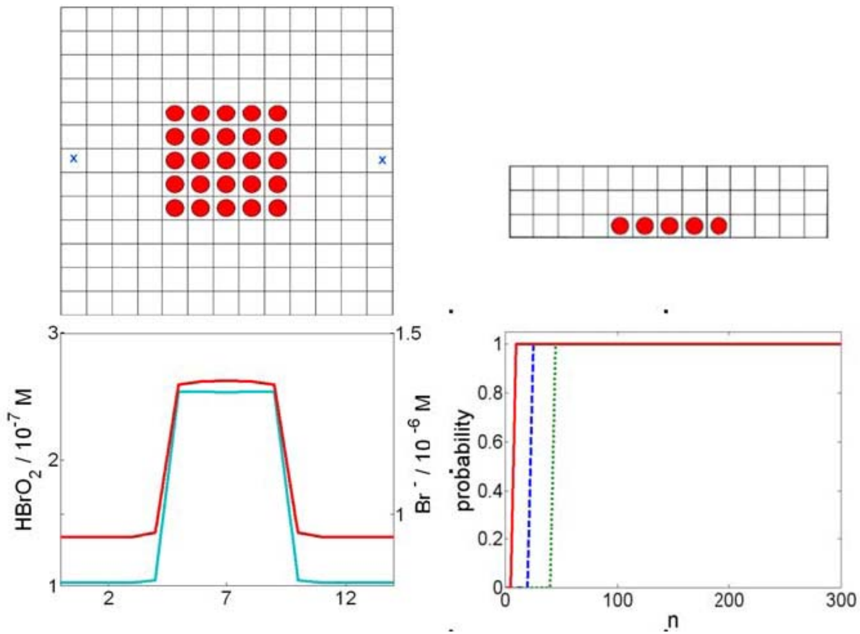


Probability of wave activity in a group as a function of the number of particles n for $[NaBrO_3]$ = 0.30 M (red), 0.27 M (blue), and 0.24 M (green).

Each point corresponds to ~8 experiments (over 300 to construct the figure).

Not a single oscillatory particle was found in follow-up procedure. Hence, group wave activity arises as the result of collective dynamics.

Excitable Particle Model



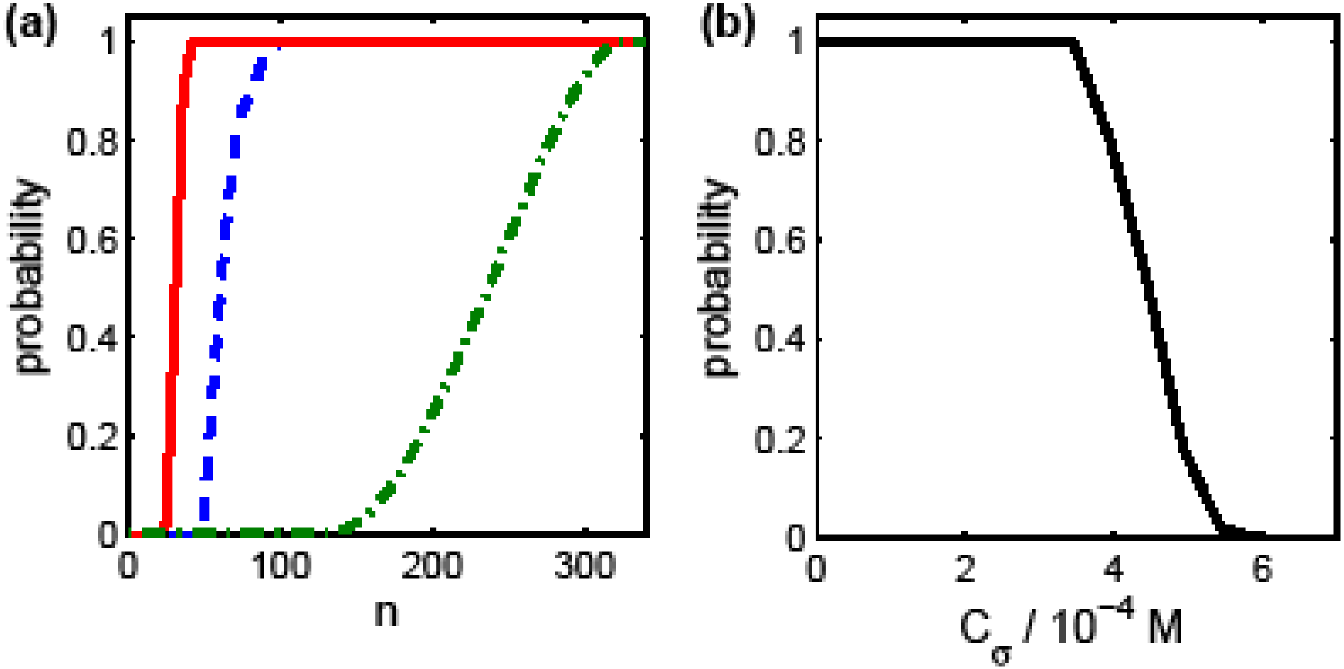
Schematic 2D representation of a 3D cell model (13×13×4) with a 5×5×1 group of catalyst particle cells, n = 25.

Particles are indicated by a cell containing a red dot and the surrounding solution is indicated by empty cells.

Steady state concentrations of activator X (blue) and inhibitor Y (red)

Probability of spatiotemporal wave activity in 3D cell model for identical particles as a function of group size n for A = 0.2430 M (red solid), 0.2425 M (blue dashed), and 0.2420 M (green dotted).

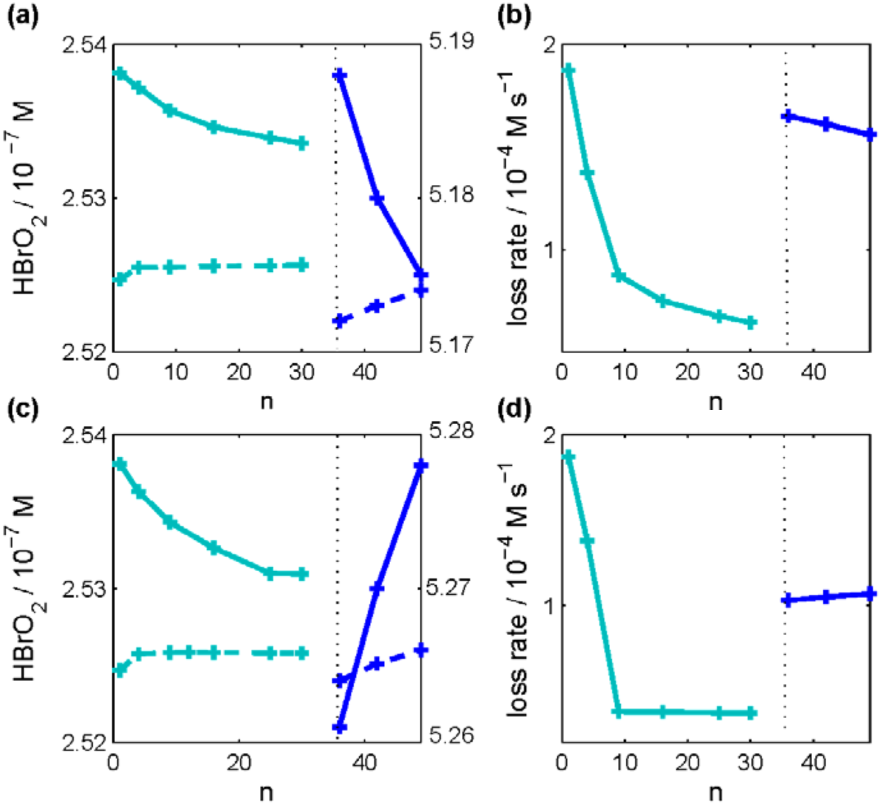
Effects of Heterogeneity



Probability of wave activity with increasing group size n. Points determined from a Gaussian distribution of particle cell catalyst concentrations: $C_{mean} = 0.0053$ M, $C_\sigma = 0.0006$ M. Curves: A = 0.2430 M (red), 0.2425 M (blue), and 0.2420 M (green).

Probability of wave activity with increasing C_σ, where $C_{mean} = 0.0053$ M, A = 0.2420, and n = 49. Wave activity occurs when $C_\sigma \leq 3.7 \times 10^{-4}$ M, whereas no activity is found for $C_\sigma \geq 6.0 \times 10^{-4}$ M. Oscillator death?

Collective Behavior: Dynamical Quorum Sensing



(a) Average $[HBrO_2]$ on group particles (solid line) and in the solution cells directly above the particle cells (dashed line).

(b) Average loss rate of $HBrO_2$ to the surrounding solution.

(c) $[HBrO_2]$ on the central particle (solid line) and in the solution cell directly above the particle cell (dashed line).

(d) Loss rate of HBrO2 from the central particle.

The vertical dashed line in each plot represents the value of n_{crit}, above which spatiotemporal wave activity occurs.

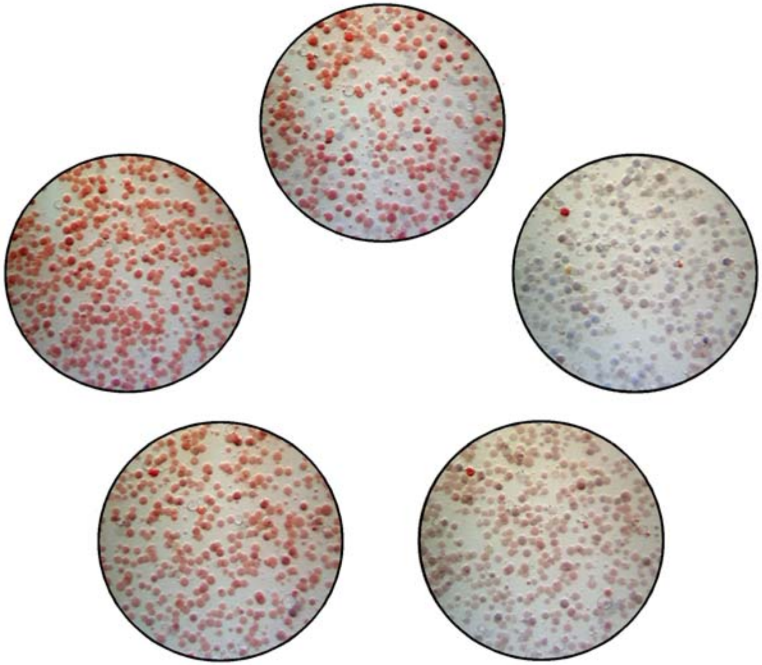
Synchronization and Spatiotemporal Dynamics in Chemical Systems

Oscillatory Reactions and
Propagating Chemical Waves

Waves on Spheres and
Heterogeneous Media

Globally Coupled System:
Kuramoto Synchronization
Dynamical Quorum Sensing

Spatially Distributed System:
Oscillatory Particle Synchronization
Excitable Particle Dynamical Quorum Sensing



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http://heracles.chem.wvu.edu