Pattern Formation in Reaction-Diffusion Systems in Microemulsions

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Patterns in BZ-AOT Microemulsions

- Introduction and Motivation
- Properties of AOT and microemulsions
- The BZ-AOT system
- Experimental results
- Localized patterns - mechanism and simulations

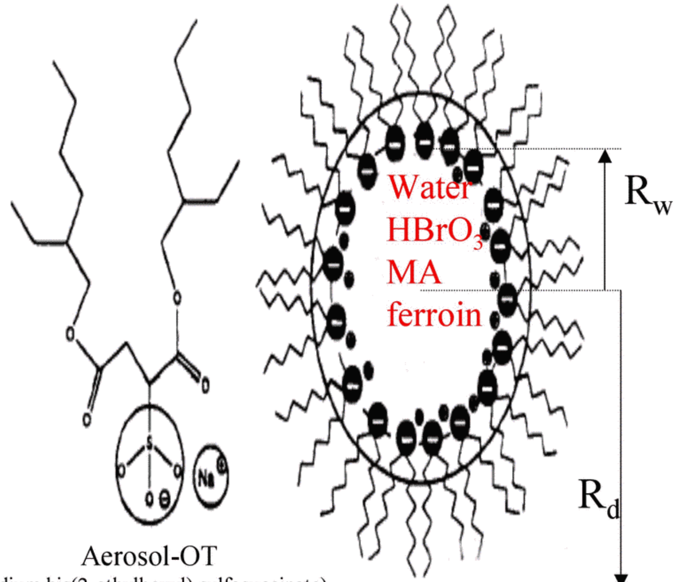
BZ-AOT References

- V.K. Vanag and IRE, “Inwardly Rotating Spiral Waves in a Reaction-Diffusion System,” Science 294, 835 (2001).
- VKV & IRE, "Pattern Formation in a Tunable Reaction-Diffusion Medium: The BZ Reaction in an Aerosol OT Microemulsion," PRL 87, 228301 (2001).
- VKV & IRE, “Packet Waves in a Reaction-Diffusion System,” PRL 88, 088303 (2002).
- VKV & IRE, “Dash-waves in a Reaction Diffusion System,” PRL 90, 098301 (2003).

Belousov- Zhabotinsky Reaction

- Discovered (accidentally) and developed in the Soviet Union in the 50’s and 60‘s
- Bromate + metal ion (e.g., Ce^{3+}) + organic (e.g., malonic acid) in 1M H_2SO_4
- Prototype system for nonlinear chemical dynamics – gives temporal oscillation, spatial pattern formation
- Zhabotinsky at Brandeis since 1990

AOT reverse micelles or water-in-oil microemulsion



Aerosol-OT
(sodium bis(2-ethylhexyl) sulfosuccinate)

MA = malonic acid

R_w = radius of water core

R_d = radius of a droplet,

$$\omega = \frac{[H_2O]}{[AOT]}$$

$R_w = 0.17\omega$

R_d = 3 - 4 nm

ϕ_d = volume fraction of dispersed phase (water plus surfactant)

Oil = $CH_3(CH_2)_nCH_3$

Initial reactants of the BZ reaction reside in the water core of a micelle

Diffusion coefficients

L. J. Schwartz at al., Langmuir 15, 5461 (1999)

Motions of Water, Decane, and AOT

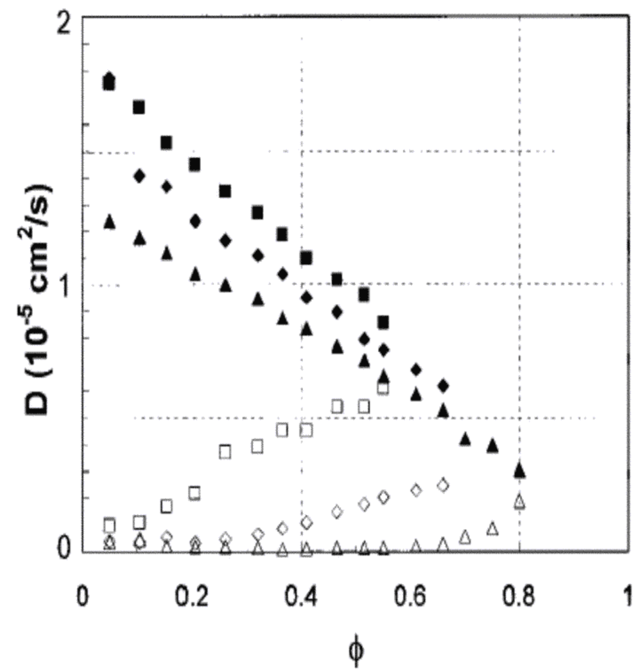
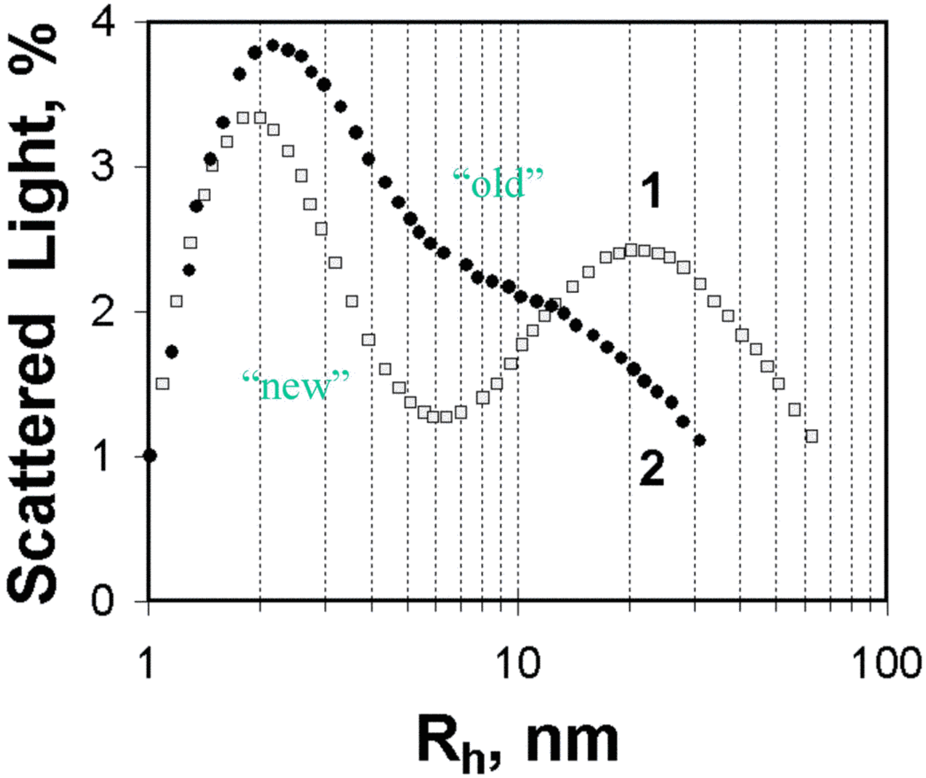
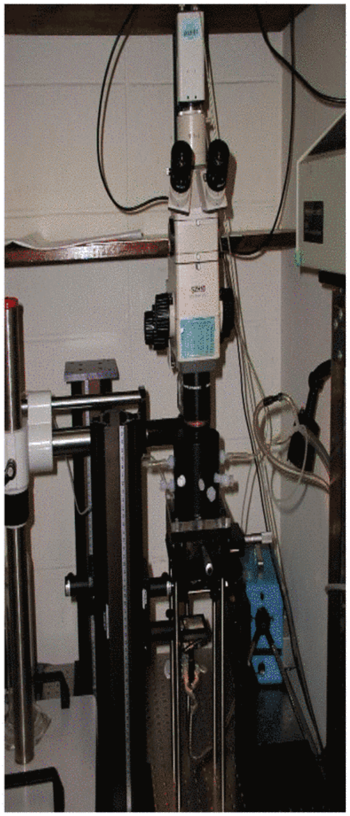


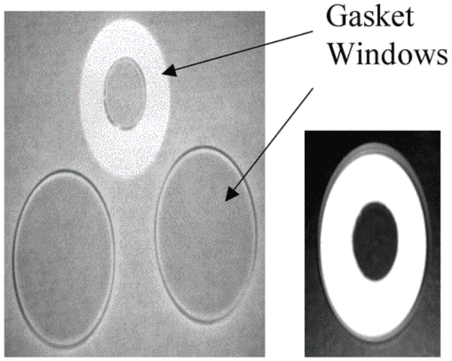
Figure 7. *D* for decane and water in the water-AOT-microemulsions as a function of ϕ. Decane: 294 (▲), 303 (◆), and 313 (■) K. Water: 294 (△), 303 (◇), and 313 (□) K.

Droplet Size Distribution



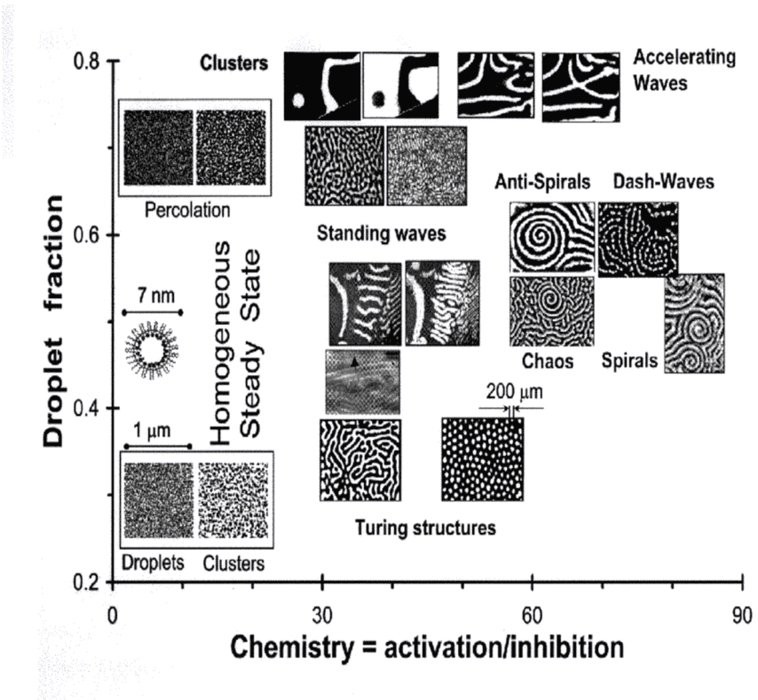
Experimental Setup





A small volume of the reactive BZ-AOT mixture was sandwiched between two flat optical windows 50 mm in diameter. The gap between the windows was determined by the thickness h (= 0.1 mm) of an annular Teflon gasket with inner and outer diameters of 20 mm and 47 mm, respectively. The gasket served as the lateral boundary of the thin layer of microemulsion and prevented oil from evaporating.

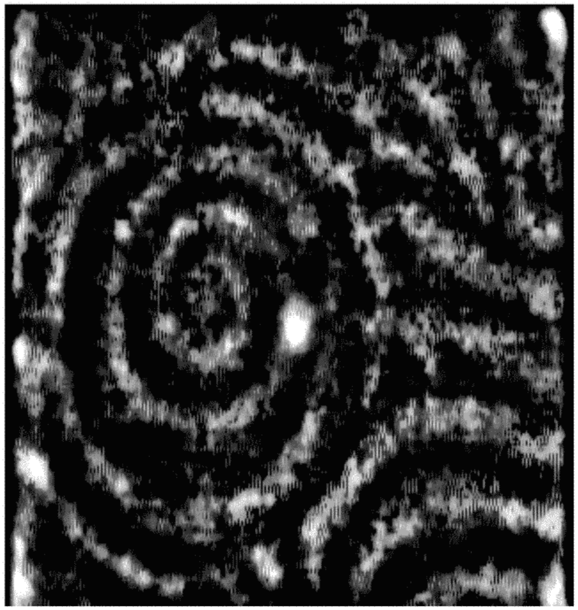
BZ-AOT PATTERNS



Vanag and Epstein, Phys. Rev. Lett. 87, 228301 (2001).

Spirals

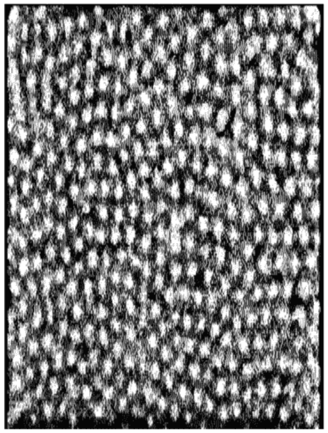
1-arm anti-spiral



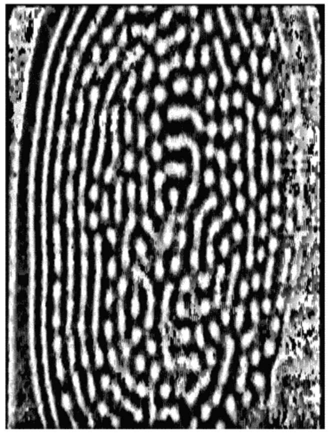
Vanag and Epstein, Science 294, 835 (2001).

Inwardly moving circles

Turing structures

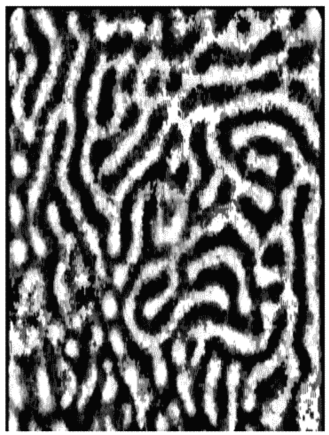


Spots



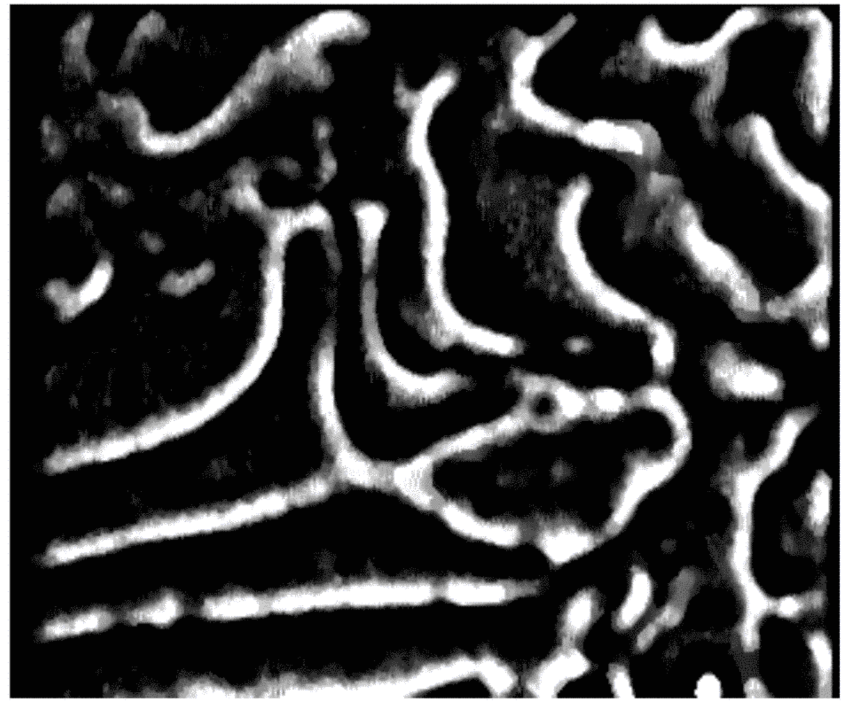
Spots and Stripes

Frozen waves



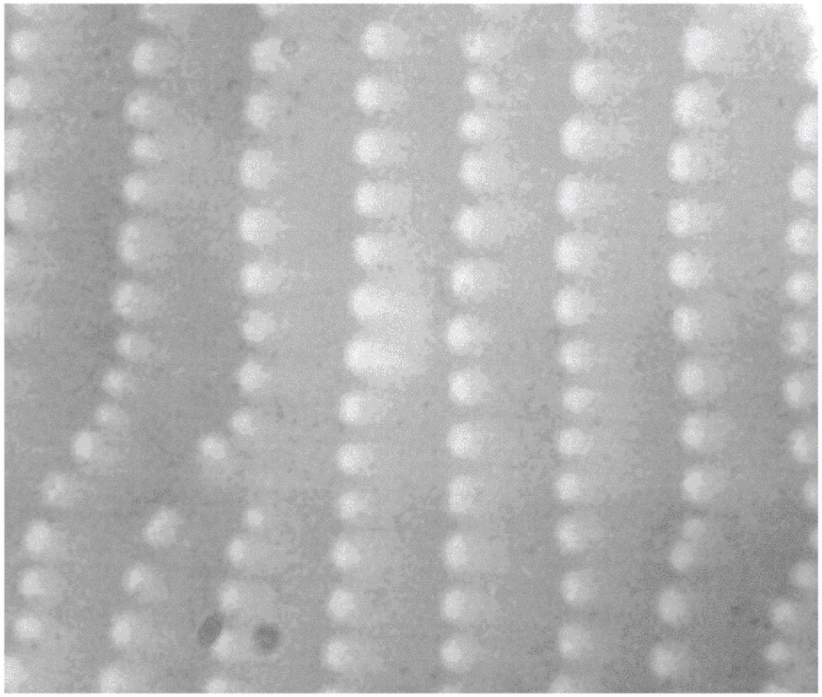
Labyrinth

Accelerating Waves



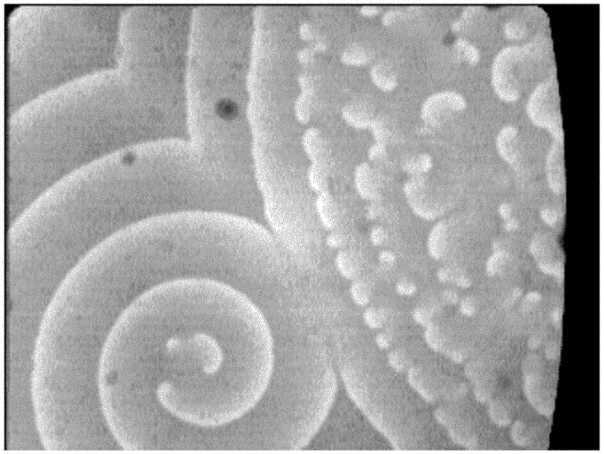
Chaotic and Plane Waves

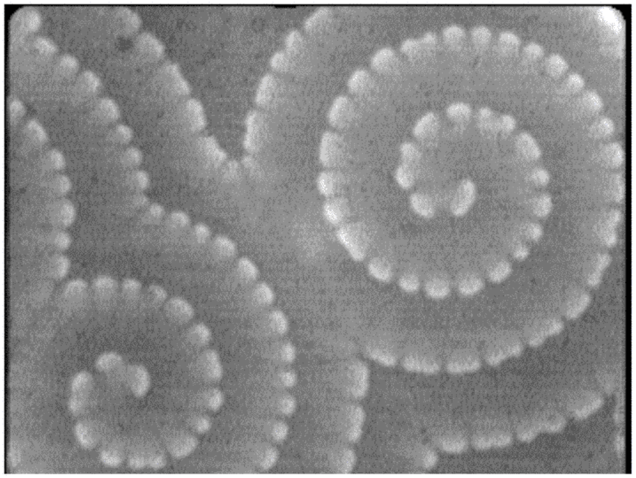
Dash-Wave



Vanag and Epstein, Phys. Rev. Lett. 90, 098301 (2003).

Segmented Spirals





Some crude estimates

- Droplet diameter = 10 nm
- $V = (4/3)\pi(d/2)^3 = 5 \times 10^{-25}\ M^3$
  $= 5 \times 10^{-22}$ L
- 1 zeptoliter = 10^{-21} L
- 1 M = 6×10^{23} molecules/L
- In each droplet, average number of molecules is:
  300 at 1 M concentration
  0.3 at 1 mM concentration

A Model for BZ-AOT

Oregonator

$A + Y \rightarrow X$	k_1
$X + Y \rightarrow 0$	k_2
$A + X \rightarrow 2X + 2Z$	k_3
$2X \rightarrow 0$	k_4
$B + Z \rightarrow hY$	k_5

Interfacial Transfer

$X \rightarrow S$	k_f
$S \rightarrow X$	k_b

and/or

$Y \rightarrow T$	$k_{f'}$
$T \rightarrow Y$	$k_{b'}$

where $A = HBrO_3$, $X = HBrO_2$, $Y = Br^-$, Z = ferriin, $B = MA^+$, BrMA, and $S = BrO_2^{\bullet}$ in the oil phase.

Key properties of BZ-AOT system

- Size and spacing of droplets can be "tuned" by varying water:AOT and water:octane ratios, respectively
- BZ chemistry occurs within water droplets
- Non-polar species (Br_2, BrO_2) can diffuse through oil phase
- Diffusion of molecules and droplets occurs at very different rates
- Initial bimodal distribution of droplet sizes slowly transforms to unimodal

Localized Patterns - Mechanisms

- Bistability (subcritical bifurcation) - need way to stabilize zero-velocity front
- Periodic forcing
- Global negative feedback
- Coupled layers

Global Feedback

- A control parameter (e.g., illumination intensity, rate constant) in a spatially extended system depends on values of a quantity (e.g., concentration, temperature, electrical potential) over the entire system (e.g., integral or average) .

Global Feedback/Coupling References

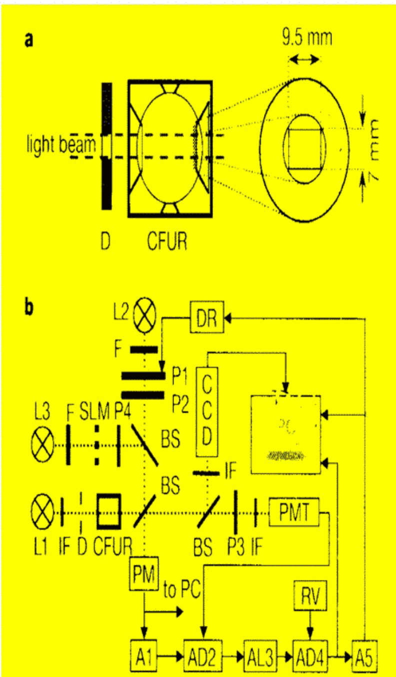
- V.K. Vanag, L. Yang, M. Dolnik, A.M. Zhabotinsky and I.R. Epstein, "Oscillatory Cluster Patterns in a Homogeneous Chemical System with Global Feedback," Nature 406, 389-391 (2000).
- V.K. Vanag, A.M. Zhabotinsky and I.R. Epstein, "Pattern Formation in the Belousov-Zhabotinsky Reaction with Photochemical Global Feedback," J. Phys. Chem. A 104, 11566-11577 (2000).
- L. Yang, M. Dolnik, A.M. Zhabotinsky and I.R. Epstein, "Oscillatory Clusters in a Model of the Photosensitive Belousov-Zhabotinsky Reaction-Diffusion System with Global Feedback," Phys. Rev. E 62, 6414-6420 (2000).
- V. K. Vanag, A. M. Zhabotinsky and I.R. Epstein, "Oscillatory Clusters in the Periodically Illuminated, Spatially Extended Belousov-Zhabotinsky Reaction," Phys. Rev. Lett. 86, 552-555 (2001).
- H.G. Rotstein, N. Kopell, A. Zhabotinsky and I.R. Epstein, "A Canard Mechanism for Localization in Systems of Globally Coupled Oscillators" SIAM J. App. Math. (2003, in press).

Clusters and Localization

Oscillatory clusters consist of sets of domains (clusters) in which the elements in a domain oscillate with the same amplitude and phase. In the simplest case, a system consists of two clusters that oscillate in antiphase; each cluster can occupy multiple fixed, but not necessarily connected, spatial domains. Clusters may be differentiated from standing waves, which they resemble, in that clusters lack a characteristic wavelength. *Standing clusters* have fixed spatial domains and oscillate periodically in time. *Irregular clusters* show no periodicity either in space or in time.

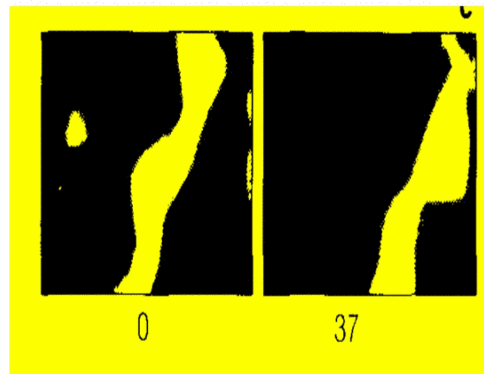
Localized clusters **display periodic oscillations in one part of the medium, while the remainder appears uniform (may oscillate at low amplitude).**

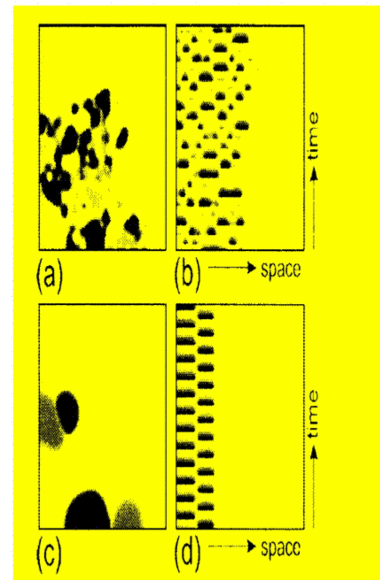
Global Feedback - Experimental Setup



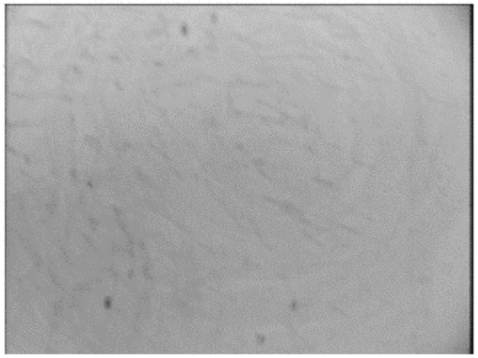
- $I = I_{max}\sin^2[g(Z_{av}-Z)]$
- $Z = [Ru(bpy)_3^{3+}]$
- L2 = 450 W Xe arc lamp
- I_{max} = 4.3 mW cm^{-2}
- L1 = analyzer (45 W)
- L3 sets initial pattern (150 W)

Global Feedback Experimental Results





Global Feedback Experimental Results



Global Feedback Modeling - Discrete Version

$$d[X_i]/dt = k_1[A][Y_i] - k_2[X_i][Y_i] + k_3[A][X_i] - 2k_4[X_i][X_i]$$

$$d[Y_i]/dt = -k_1[A][Y_i] - k_2[X_i][Y_i] + f k_5[B][Z_i] + g Z_{av}$$

$$d[Z_i]/dt = 2k_3[A][X_i] - k_5[B][Z_i]$$

where $Z_{av} = \sum[Z_i]/N$,

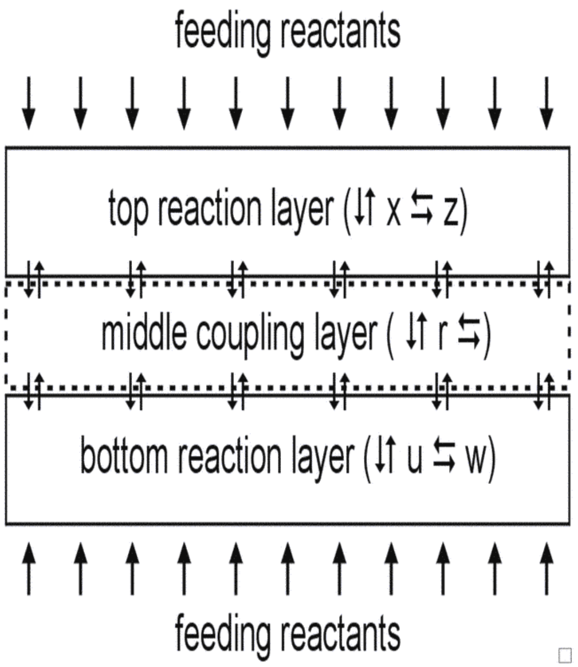
g = *feedback strength*

Coupled Layers

L. Yang and IRE, "Oscillatory Turing Patterns in Reaction-Diffusion Systems with Two Coupled Layers," PRL 90, 178303 (2003).

- Two reactive layers coupled by a nonreactive "interlayer".
- In each reactive layer, kinetics (activator-inhibitor) and diffusion are the same.
- Coupling through interlayer occurs either via activator or inhibitor, but not both, therefore no reaction in that layer.
- Constraints (e.g., feed concentrations, illumination) may differ for reactive layers.

Coupled Layers "Experimental" Setup



Coupled Layers – Model

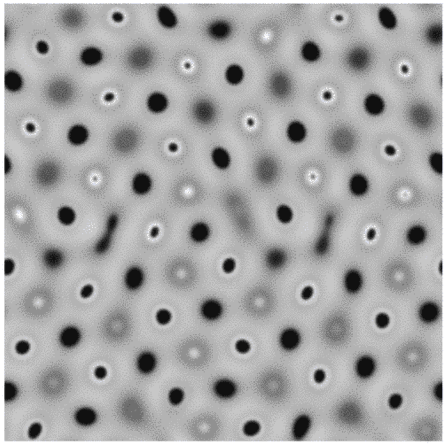
$\partial x/\partial t = D_x\nabla^2 x + F(x,z) - (1/\delta)(x-r)$
$\partial z/\partial t = D_z\nabla^2 z + G(x,z)$
$\partial r/\partial t = D_r\nabla^2 r + (1/\delta)(x-r) - (1/\delta')(u-r)$
$\partial u/\partial t = D_u\nabla^2 u + F(u,w) - (1/\delta')(u-r)$
$\partial w/\partial t = D_w\nabla^2 w + G(u,w)$

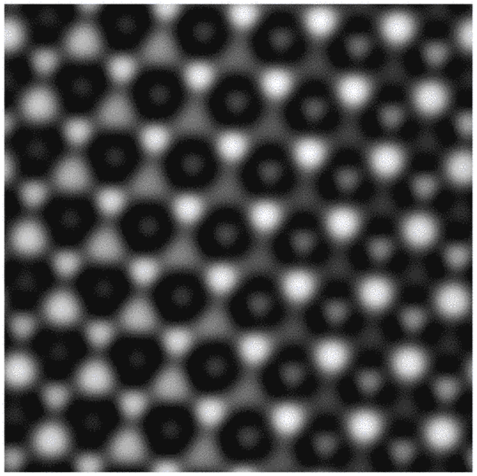
δ and δ' describe inter-layer diffusion (coupling)

Oregonator:
$F(x,z) =$
$(1/\varepsilon)[x - x^2 - fz(x-q)/(x+q)]$
$G(x,z) = x - z$

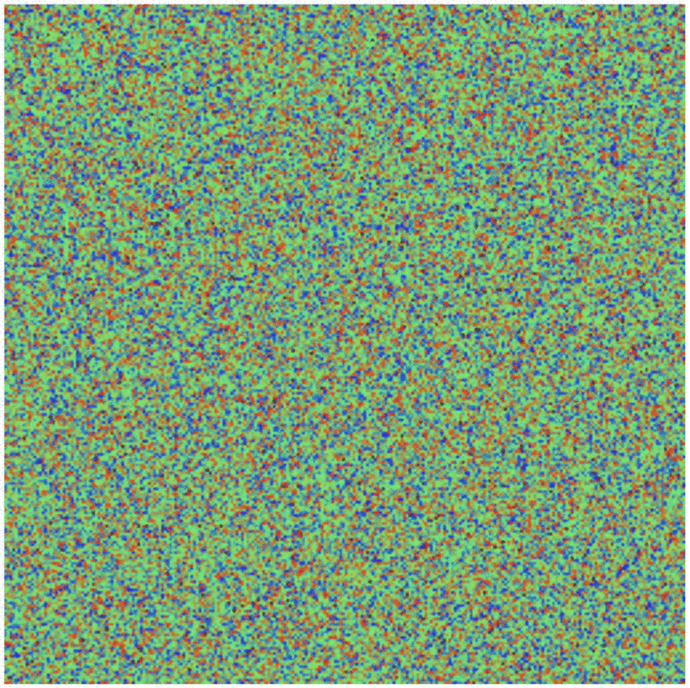
Brusselator:
$F(x,z) = a - (1+b)x + x^2y$
$G(x,z) = bx - x^2y$

Twinkling eye

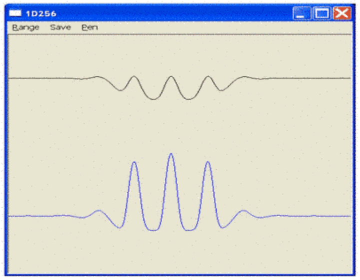




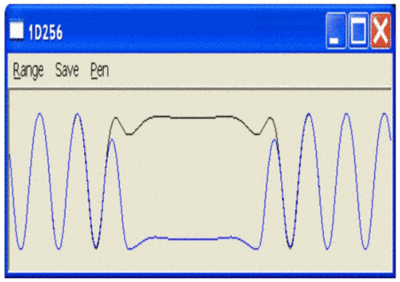
Coupled Layers: Simulation of 1-D Localized Structure



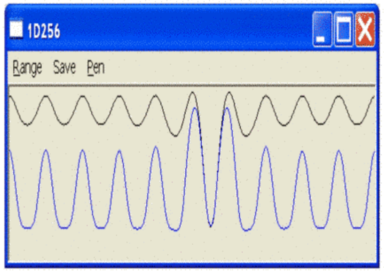
Stationary Localized Structures in Coupled Layers (1D)



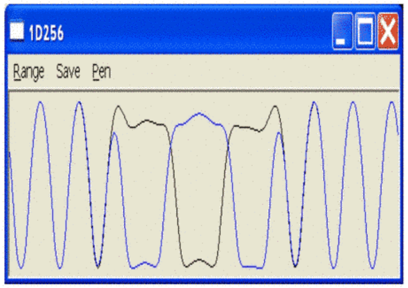
a-Tu on a-SS



a-SS on s-Tu



s-Tu on a-Tu

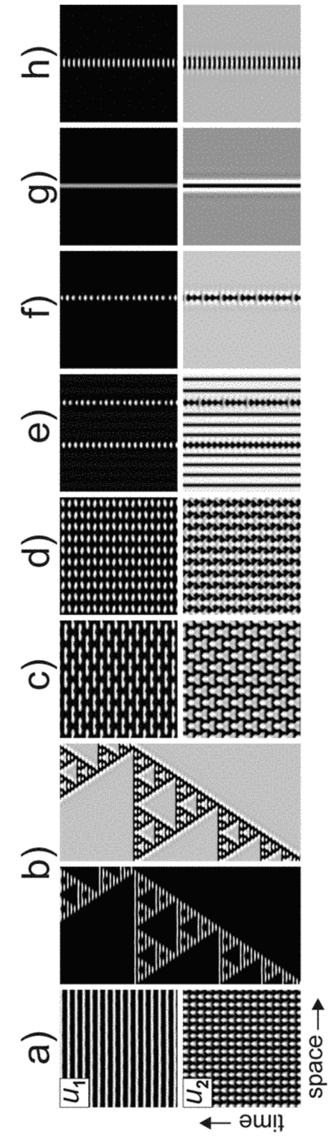


anti-Tu on s-Tu

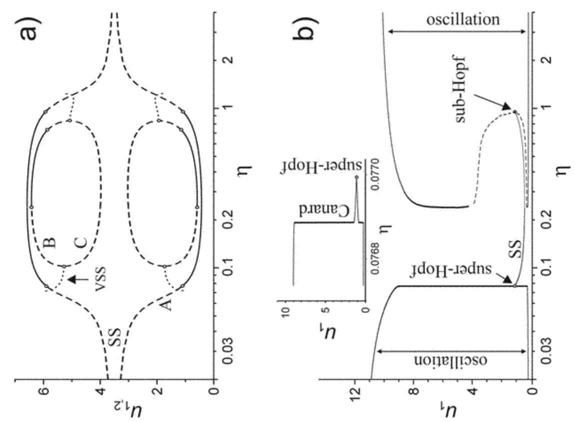
Localized Structures

- Global coupling, e.g., in photosensitive systems, leads to localized clusters, probably via a canard mechanism
- Coupling between "layers" can also generate structures of interest.
- Microemulsions provide a convenient experimental system that exhibits rich pattern formation and may be thought of as either globally coupled or "multi-layered".

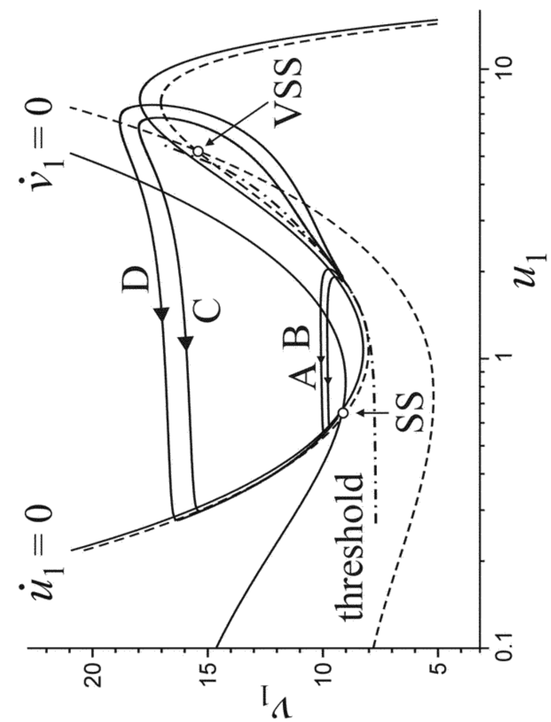
Breathing and oscillatory Turing structures and their localization in a model system with two coupled layers



Bifurcation



Excitability



Equations

$$\frac{\partial u_1}{\partial t} = F_1(u_1, v_1) + \nabla^2 u_1 + \eta(u_2 - u_1) \quad (1)$$

$$\frac{\partial v_1}{\partial t} = \sigma_1 \left\{ G_1(u_1, v_1) + d_1 \left[\nabla^2 v_1 + \eta(v_2 - v_1) \right] \right\} \quad (2)$$

$$\frac{\partial u_2}{\partial t} = F_2(u_2, v_2) + \nabla^2 u_2 + \eta(u_1 - u_2) \quad (3)$$

$$\frac{\partial v_2}{\partial t} = \sigma_2 \left\{ G_2(u_2, v_2) + d_2 \left[\nabla^2 v_2 + \eta(v_1 - v_2) \right] \right\} \quad (4)$$

where the kinetic terms are

$$F(u, v) = a - u - 4\frac{uv}{1 + u^2} \quad (5)$$

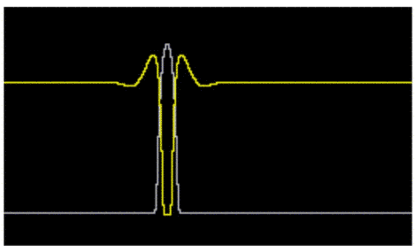
$$G(u, v) = b\left(u - \frac{uv}{1 + u^2}\right) \quad (6)$$

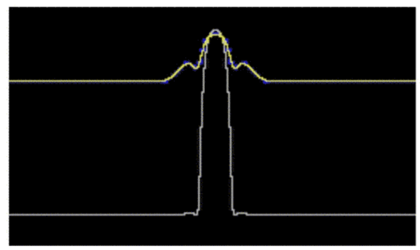
Spatio-temporal Sierpinski gasket

- 1D simulation, horizontal for space; vertical for concentration
- Pulse duplication & collective oscillation death
- Reflect at 0-flux BCs, or total death

Localized breathing structure (in-phase)
Localized oscillatory structure (anti-phase)

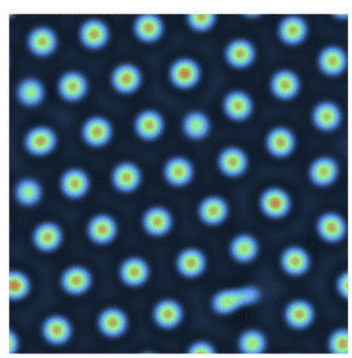
- 1D simulation, horizontal for space; vertical for concentration
- Background is stable steady state





Breathing Turing structure

- 2D simulation, size 64x64
- Concentration by color (high by red)
- Spot Turing as hexagonal lattice is modulated by bulk oscillation



Localized breathing Turing structure

- 2D simulation, size 64x64
- Concentration by color (high by red)
- The background is spotlike Turing as reverse hexagonal lattice
- Dislocated short stripes are under oscillation