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Complex Patterns in Reactive Microemulsions

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Complex Patterns in Reactive Microemulsions

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with thanks to
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Lingfa Yang
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Outline

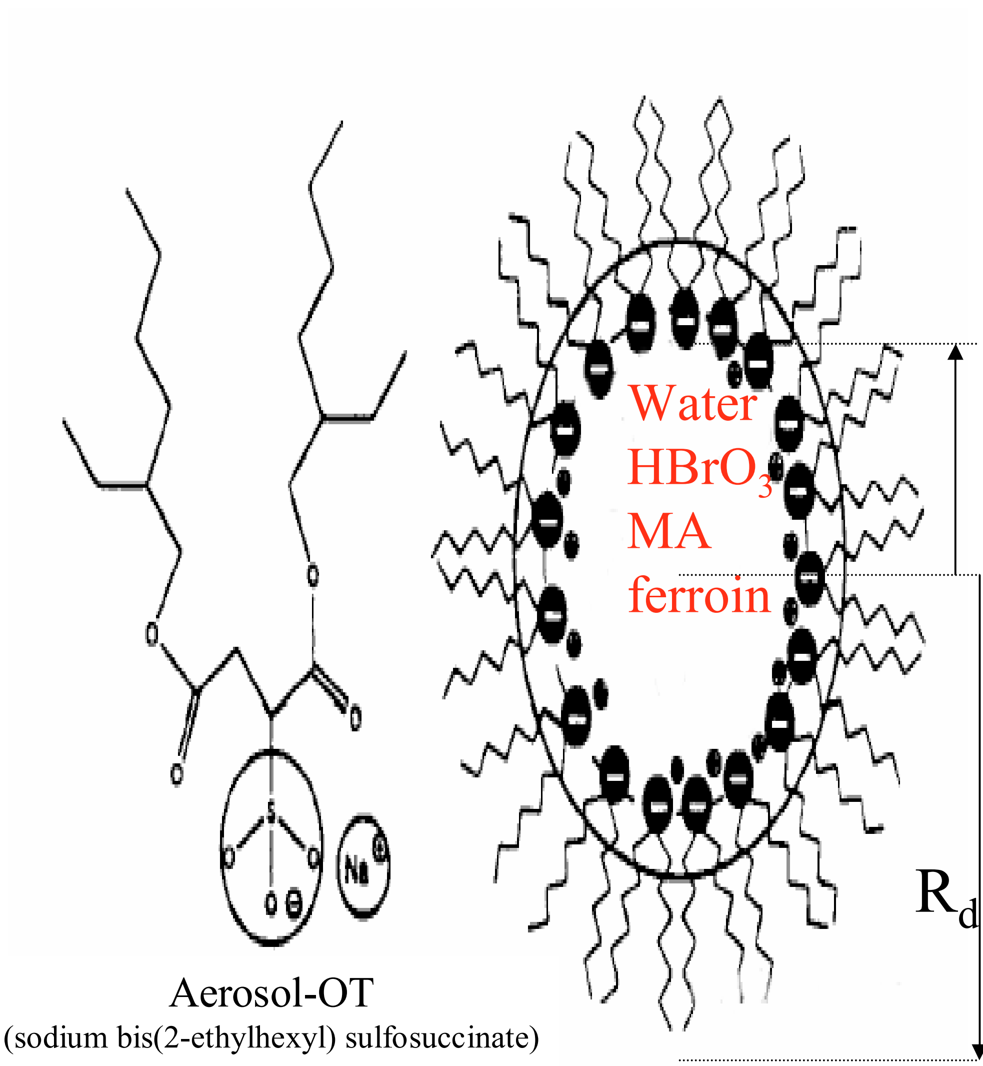
- The BZ-AOT System (Coupling of Nanodroplets)
- Properties of the BZ reaction, AOT and microemulsions
- Experimental results
- Model and simulations
- Future Work

Belousov- Zhabotinsky (BZ) Reaction

- Discovered (accidentally) and developed in the Soviet Union in the 1950'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.

Target Patterns in the BZ Reaction

AOT reverse micelles or water-in-oil microemulsion



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)

$$Oil = CH_3(CH_2)_nCH_3$$

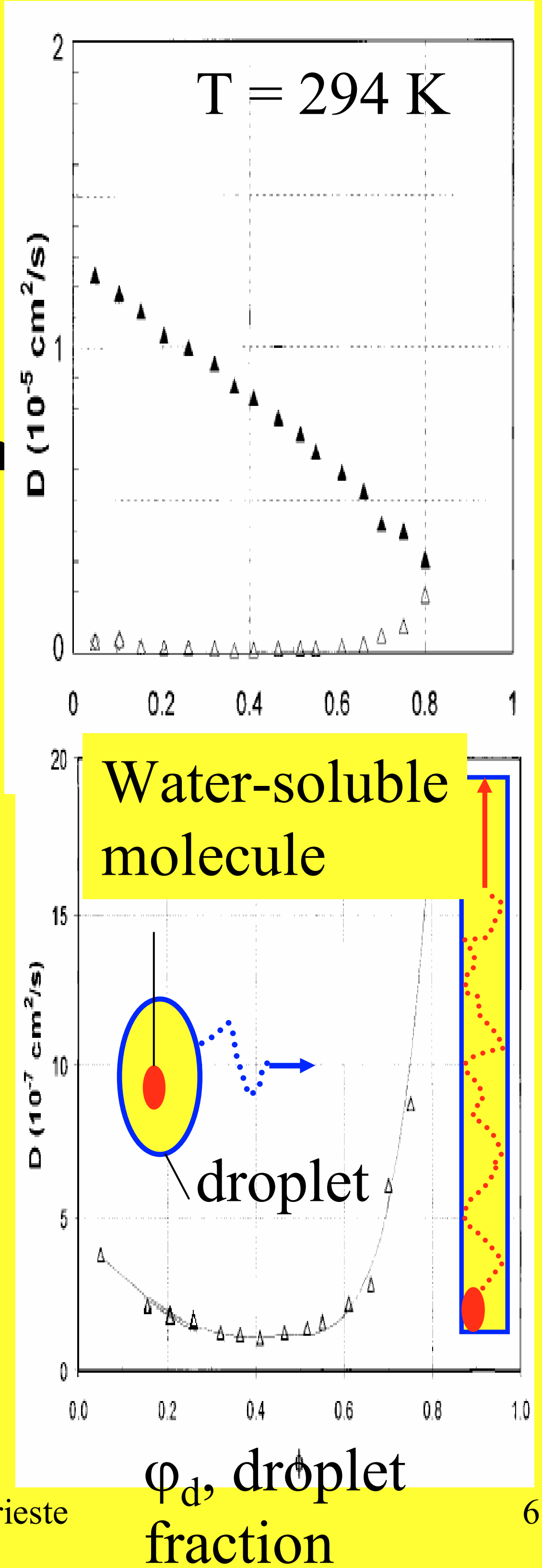
Initial reactants of the BZ reaction reside in the water core of a micelle

Diffusion Coefficients

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

$D_{oil} \cong 10^{-5}$ **cm²/s**

$D_{water} \cong 10^{-7}$ **- 10^{-6} cm**



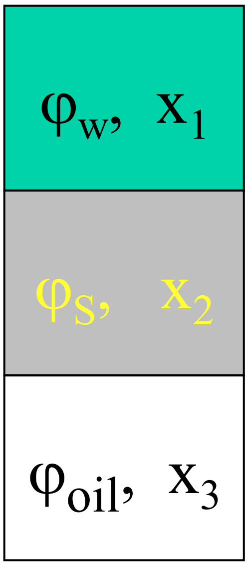
Stokes-Einstein relationship

$$D = kT/6\pi\eta R_d$$

η is the solvent viscosity
R_d is the droplet radius

Distribution of X Over Three Phases

X = Br_2 or $BrO_2^{\bullet}$ (Br_2O_4)

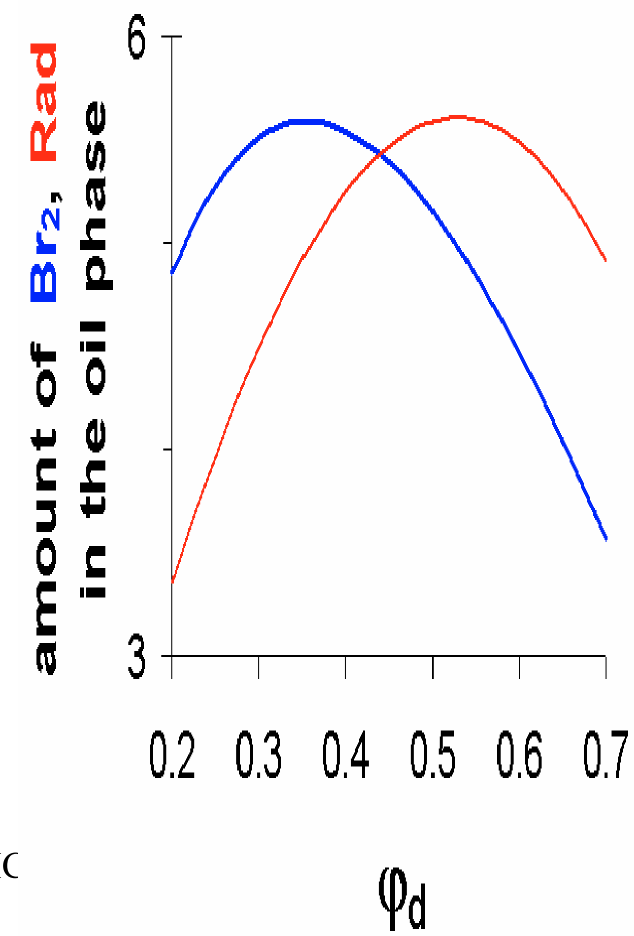


$$\varphi_w x_1 + \varphi_S x_2 + \varphi_{oil} \mathbf{x_3} = \varphi_w x_0$$

$$\varphi_w + \varphi_S + \varphi_{oil} = 1;$$

$$\varphi_w + \varphi_S \equiv \varphi_d$$

$\varphi_S = c_d \varphi_w$, where $c_d \cong 2$ for $[H_20]/[AOT] = 15$



Partition coefficients:

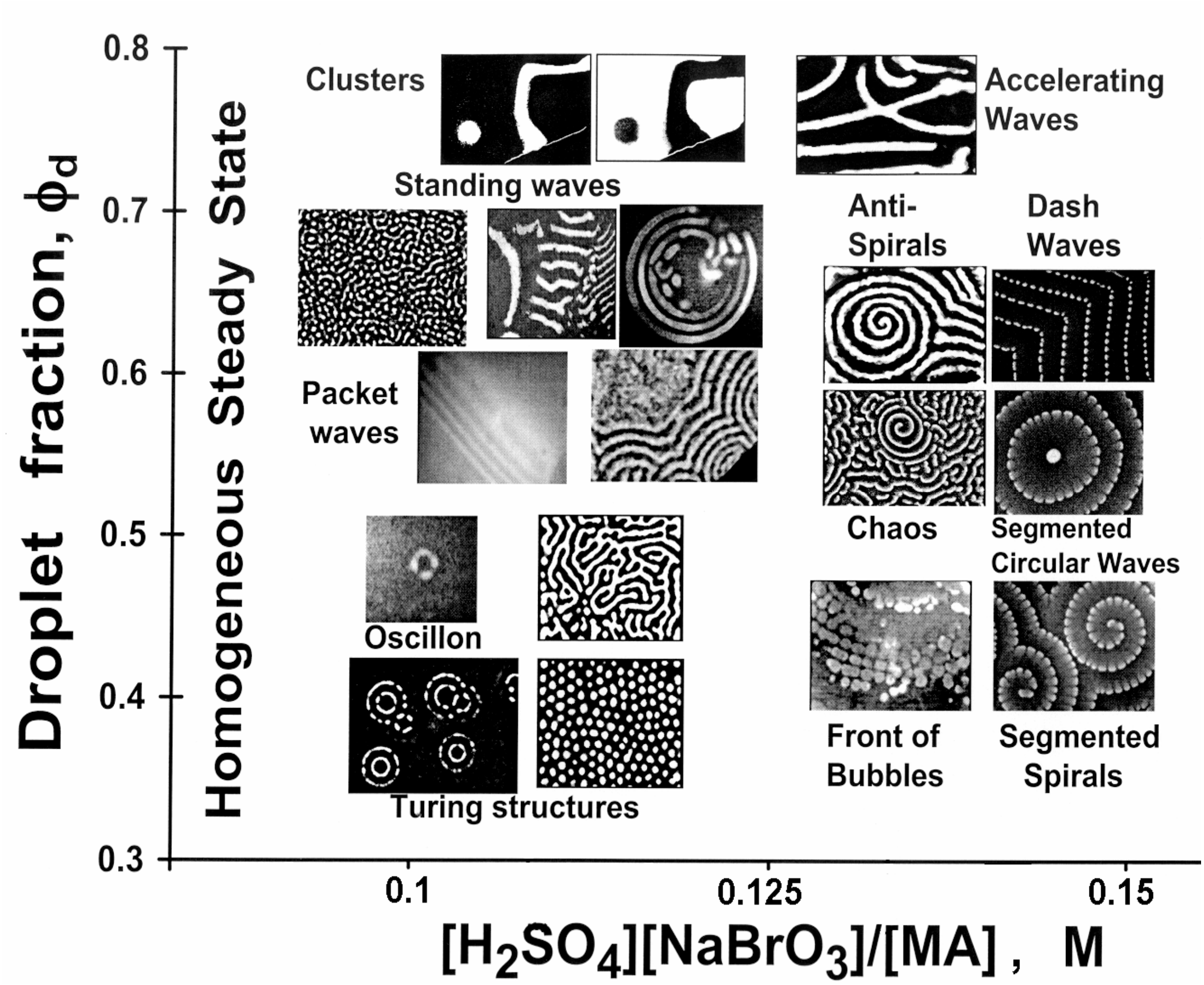
$x_1/x_2 = K_1 =$ **0.002**, **0.8**

$x_2/x_3 = K_2 =$ **5**, **0.8**

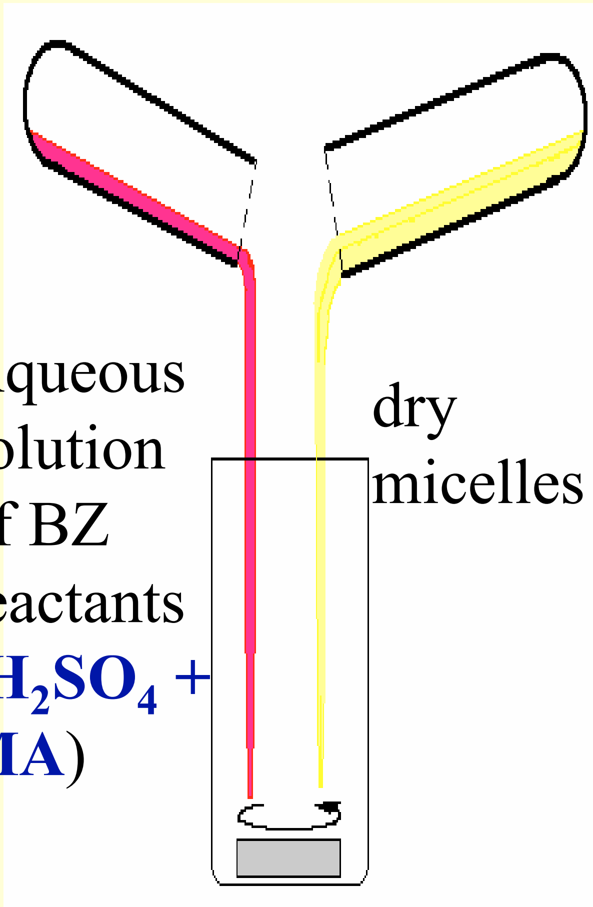
Key properties of BZ-AOT system

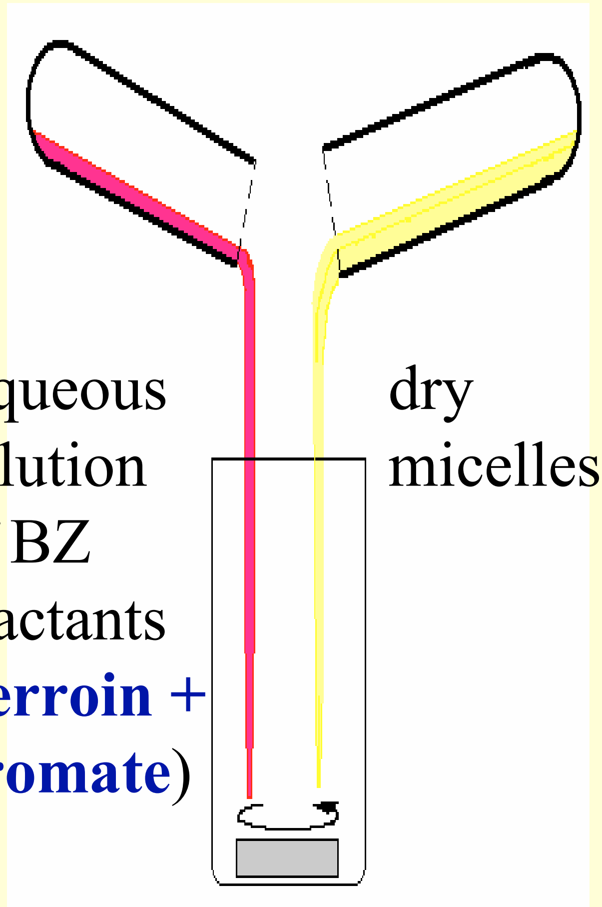
- Size and spacing of droplets can be "tuned" by varying water:AOT and water:octane ratios, respectively
- BZ chemistry occurs within water droplets
- Non-polar species (Br_2, BrO_2) can diffuse through oil phase
- Diffusion of molecules and droplets occurs at very different rates
- Dominant nonpolar species depends on droplet fraction

BZ-AOT PATTERNS

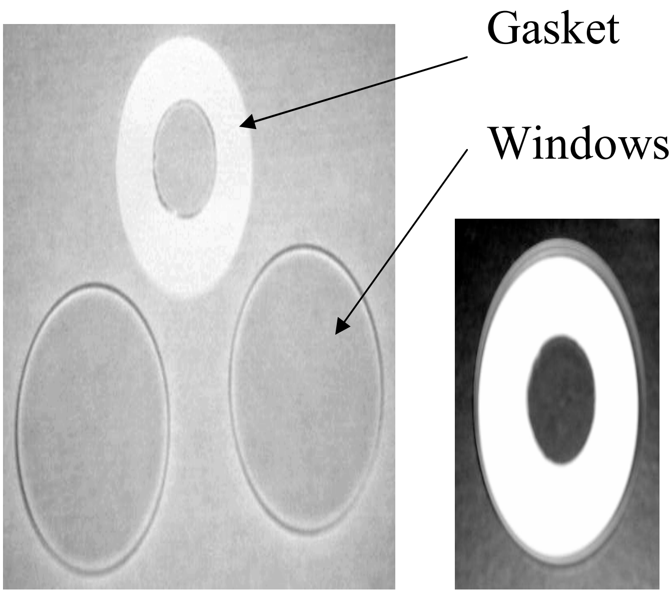


Preparation of the BZ reaction in water-in-oil microemulsions.



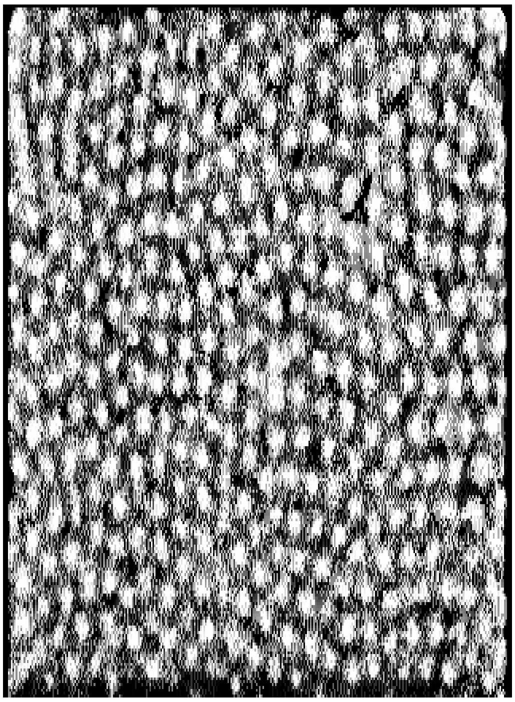


EXPERIMENTAL SETUP



A small volume of the reactive BZ-AOT mixture is sandwiched between two flat optical windows 50 mm in diameter. The gap between the windows is 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 serves as the lateral boundary of the thin layer of microemulsion and prevents oil from evaporating.

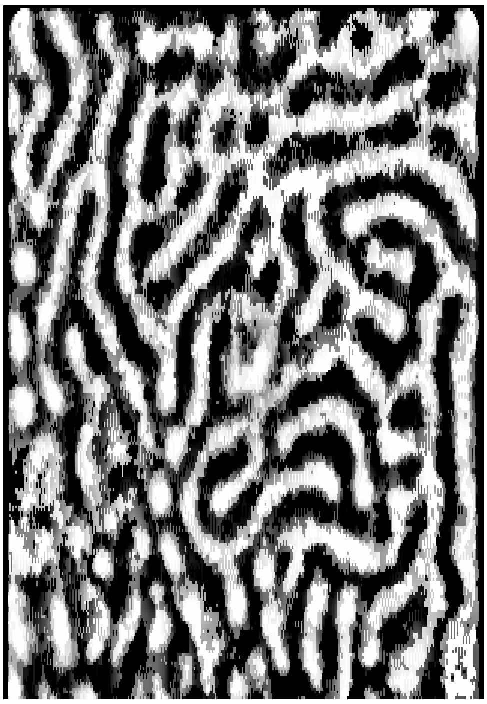
Turing structures



Spots

Spots and Stripes

Frozen waves



Labyrinth

Spirals

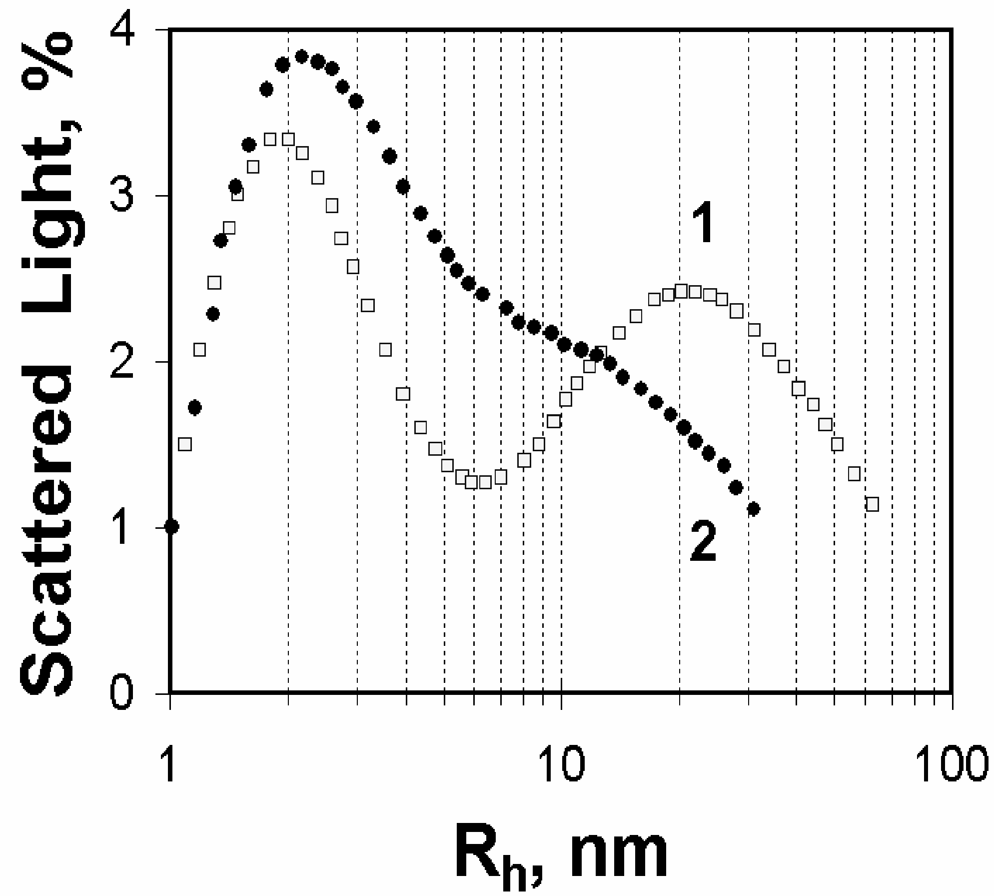
Anti-spiral

Vanag & Epstein, Science 294, 835 (2001)

Accelerating Waves

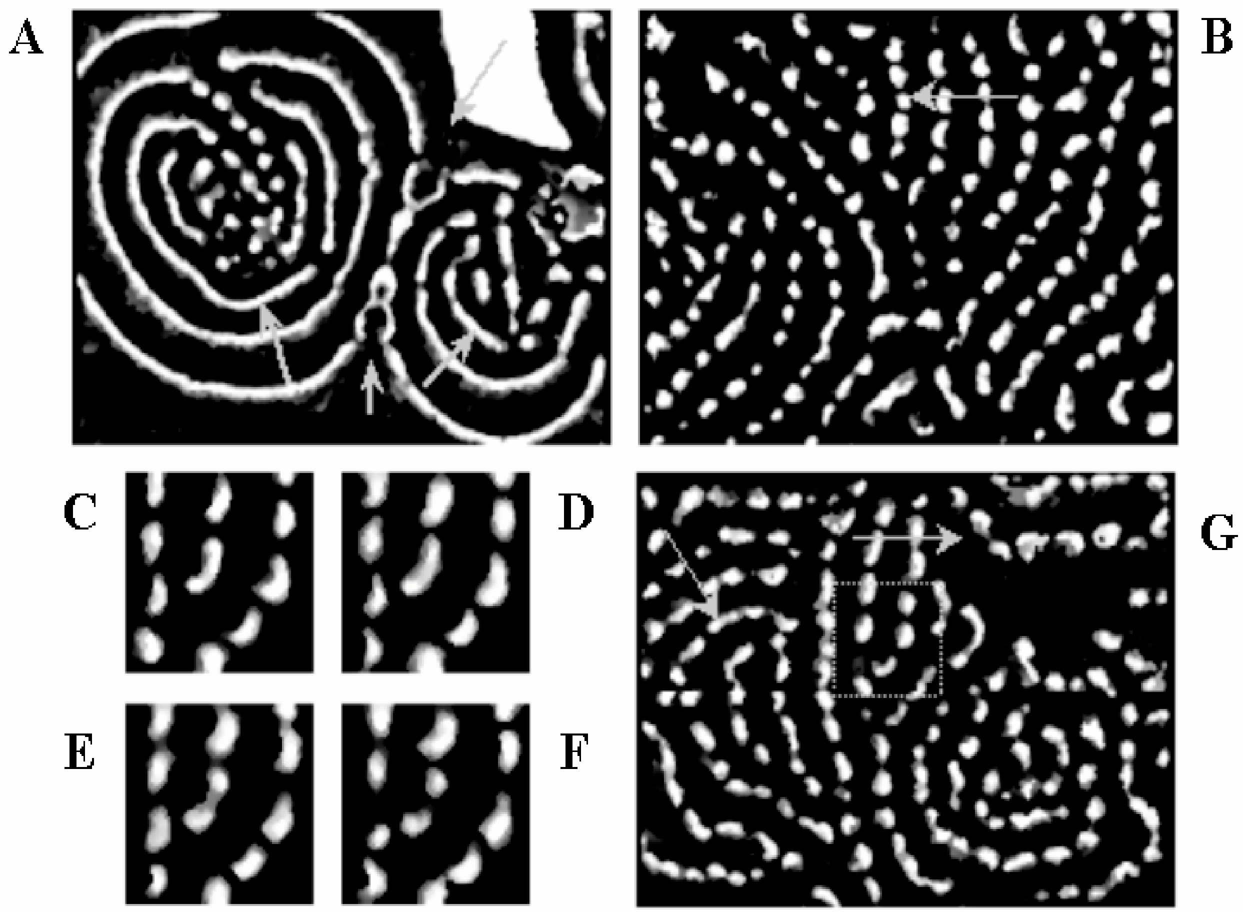
Vanag & Epstein, PRL 87, 228301 (2001)

Two Kinds of Droplets in Fresh BZ-AOT



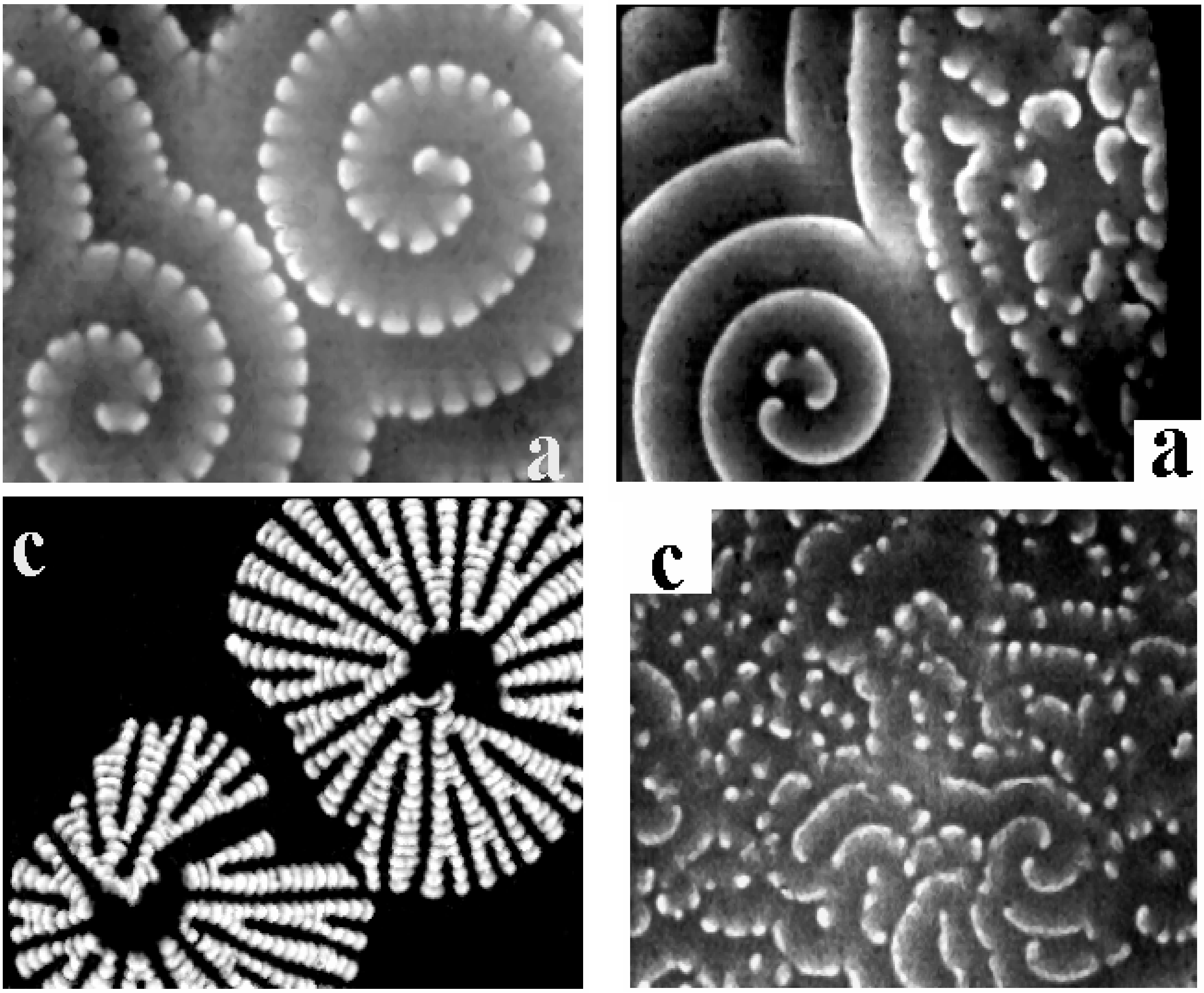
Distribution of radii of water nanodroplets. Curves 1 and 2 were obtained in light-scattering experiments for fresh and one day old microemulsions respectively, loaded with H_2SO_4 (0.4 M) and MA (0.6 M).

Dash Waves in Fresh Microemulsions



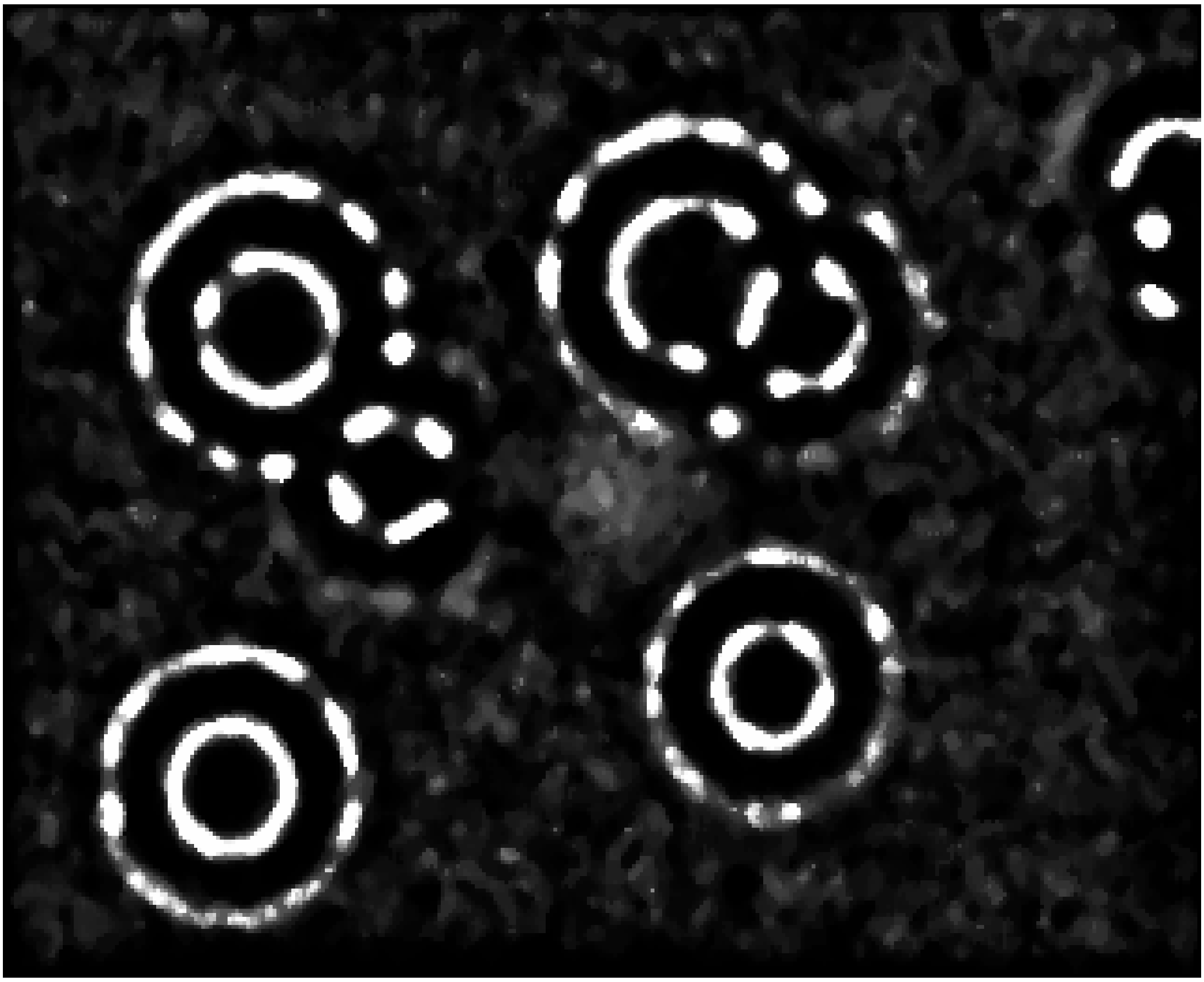
Vanag and Epstein, Phys. Rev. Lett. 90, 098301 (2003).

Segmented Spirals



Vanag & Epstein, PNAS 100, 14635 (2003)

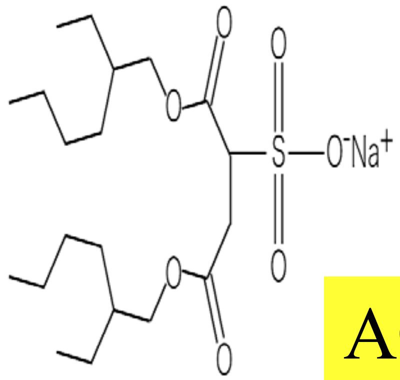
Localized Structures



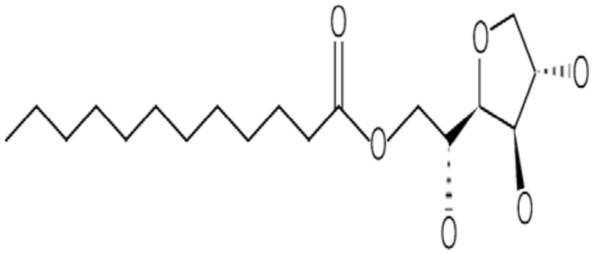
V.K. Vanag & I.R. Epstein, Phys. Rev. Lett. 92, 128301 (2004).

BZ-AOT-Span

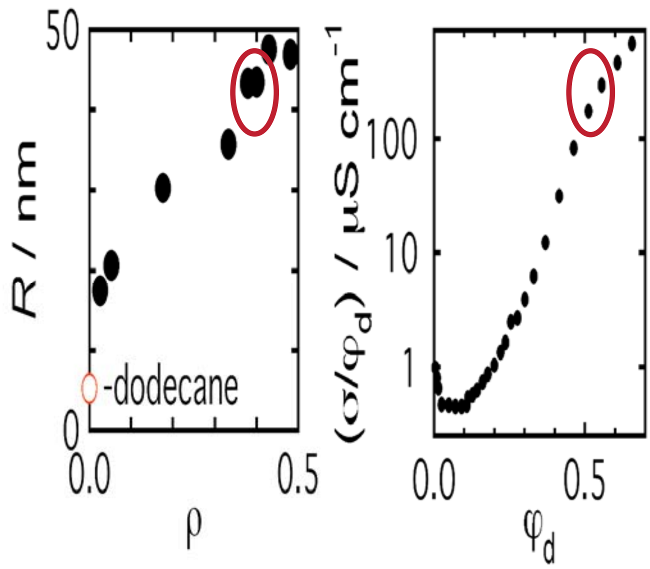
- BZ : bathoferroin-catalyzed BZ
- ME : AOT + Span-20 / hexadecane
- $\omega_2 = [H_2O]/([AOT]+[Span\text{-}20]) = \omega / (1 + \rho)$
- $\rho = [Span\text{-}20]/[AOT]$
- Droplet radius, R depends on ρ.
- Droplet fraction, φ_d is above percolation level.



AOT



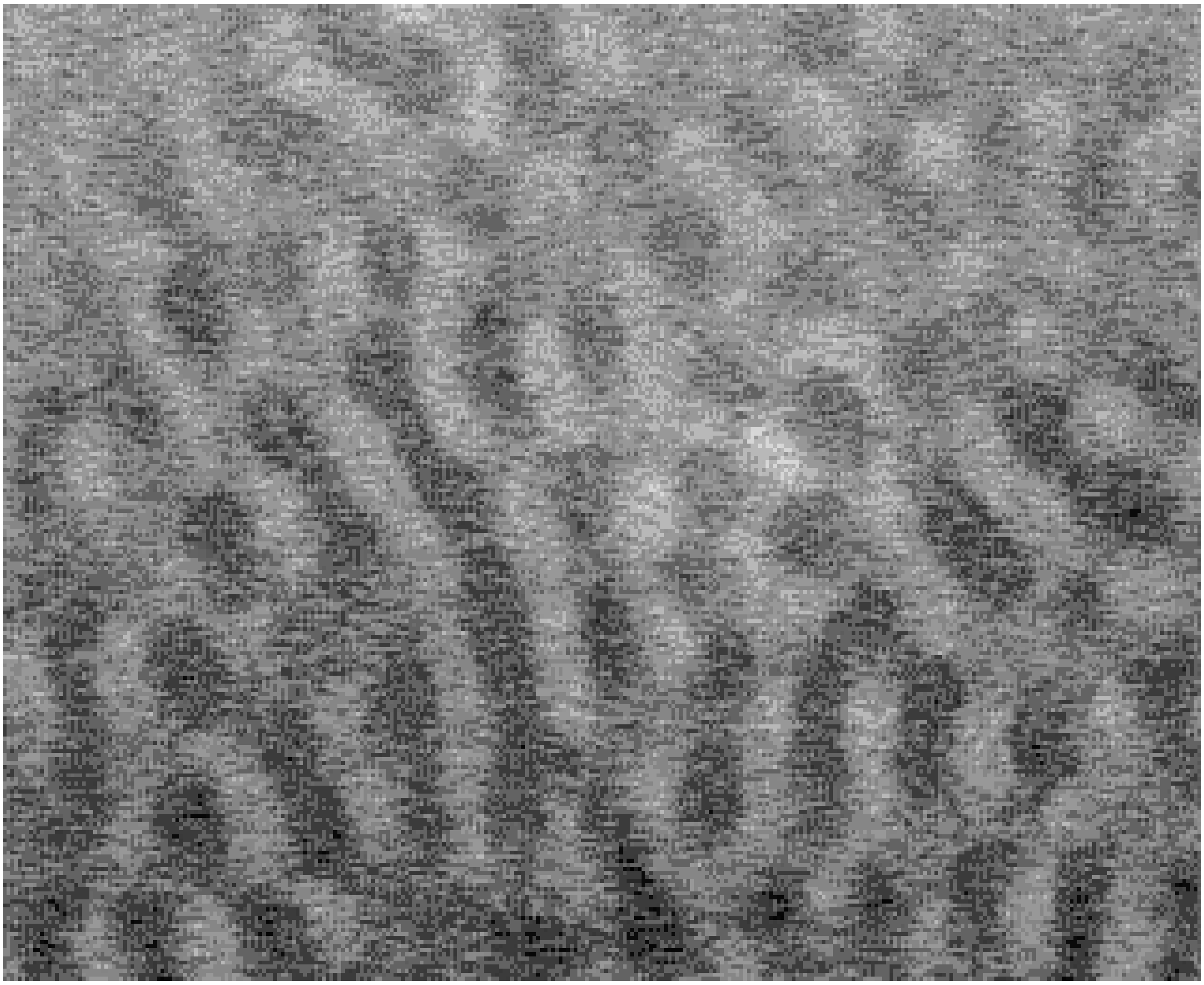
Span-20 :
Sorbitan monolaurate

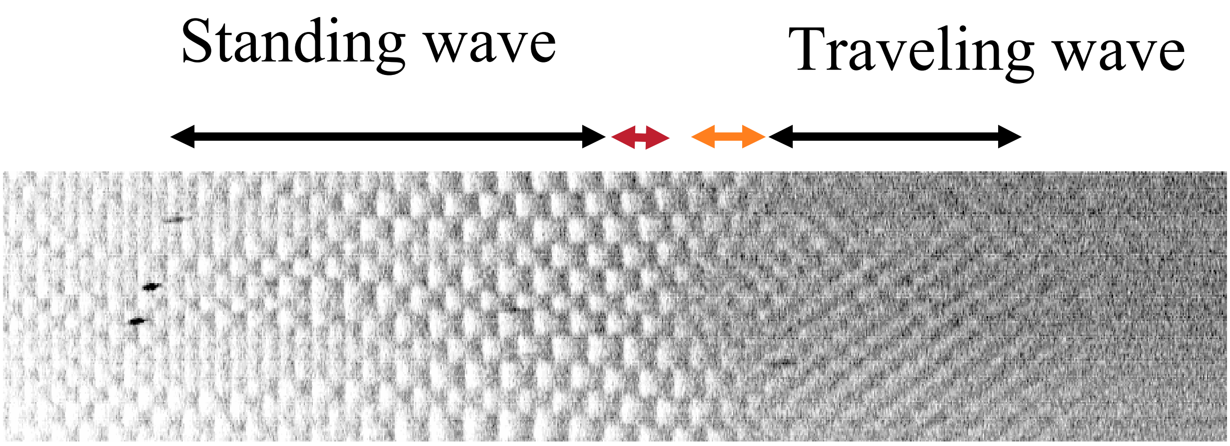


• "Wavelength-halving" transition

Wavelength halving

(1 sec = 1 min)





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:

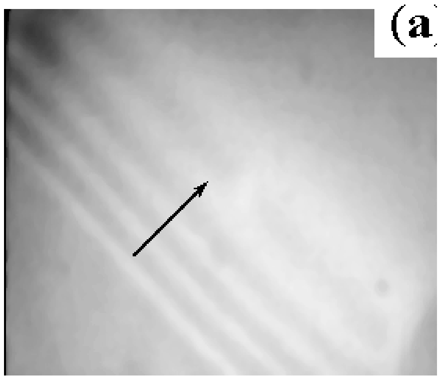
  300 at 1 M concentration

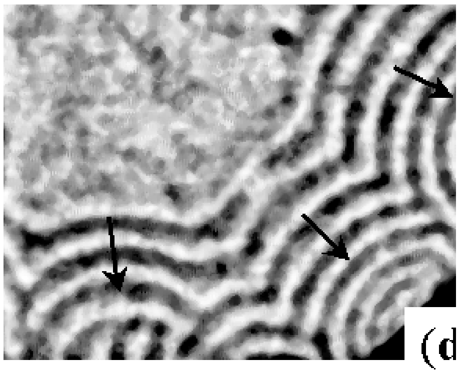
  0.3 at 1 mM concentration

“Molecular” Model

$Y \rightarrow X$	k_1	$X = HBrO_2$
$Y + X \rightarrow 0$	k_2	$Y = Br^-$
$X \rightarrow 2X + 2Z$	k_3	Z = ferriin
$2X \rightarrow 0$	k_4	
$Z \rightarrow hY$	k_5	Oregonator
$X \rightarrow S$	k_f	$S = Br_2O_4$ (or $BrO_2^\bullet$) in the oil phase
$S \rightarrow X$	k_b	$HBrO_2 + HBrO_3 \rightarrow 2\ BrO_2^\bullet + H_2O$
$Z \rightarrow W$	k_8	W is Br_2 in surfactant, AOT
$W \rightarrow U$	k_9	U is Br_2 in the oil phase
$U \rightarrow W$	k_{10}	
$W \rightarrow Z$	k_{11}	

Packet waves





$$\partial x/\partial \tau = (x - x^2 - fz(x - q)/(x + q)$$

$$- \beta x + s)/\varepsilon + D_x \Delta x$$

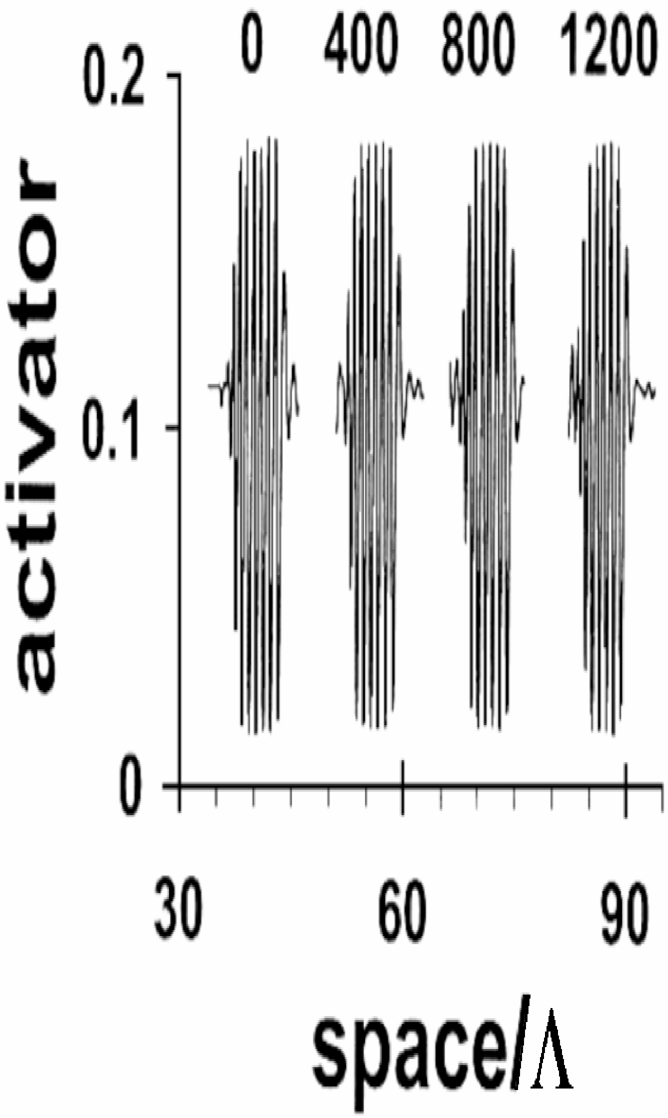
$$\partial z/\partial \tau = x - z + \gamma u - \alpha z + D_z \Delta z$$

$$\partial s/\partial \tau = (\beta x - s + \chi u)/\varepsilon_1 + D_s \Delta s$$

$$\partial u/\partial \tau = (\alpha z - \gamma u)/\varepsilon_2 + D_u \Delta u$$

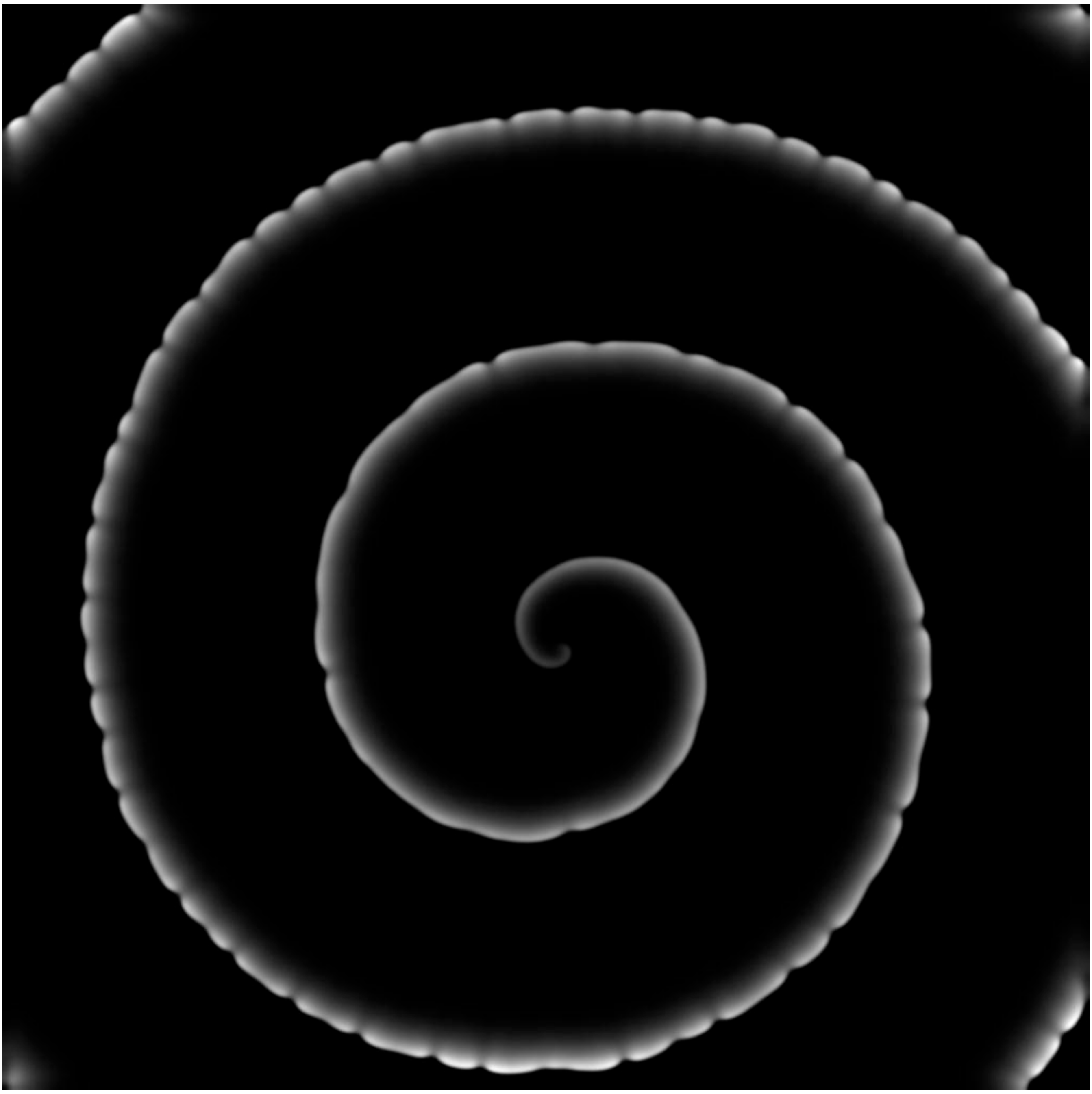
Vanag & Epstein, PRL 88, 088303 (2002)

Wave Packets. 1D Simulation



Propagation of large amplitude wave packet. Numbers above wave packets indicate time. Λ is the characteristic wavelength of wave instability.

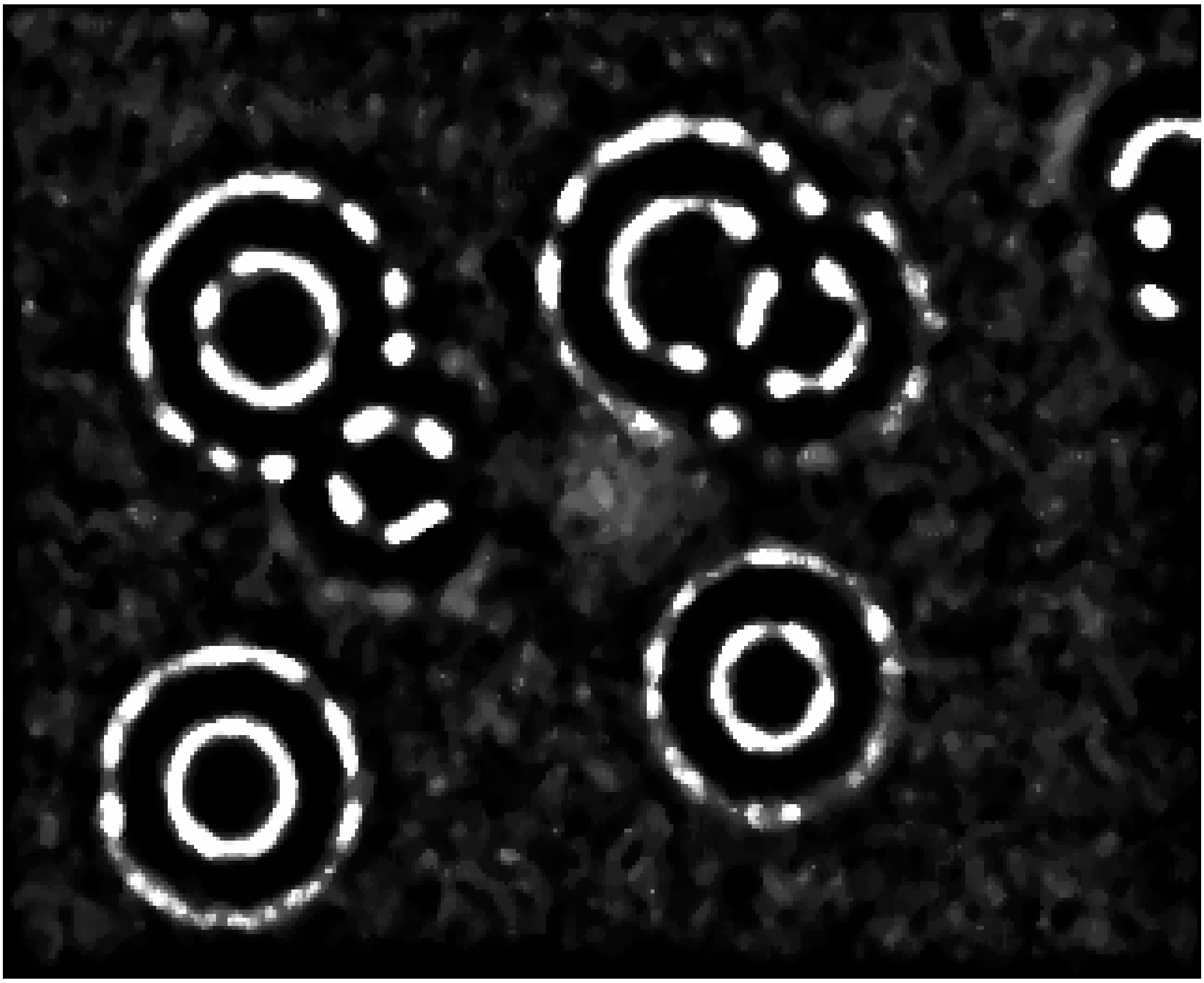
Segmented Spiral Simulation



Results of Modeling

- Simple model qualitatively reproduces most phenomena and bifurcation diagram.
- Linear stability analysis is a useful tool (within limits).
- Wave bifurcation leads to complex patterns.
- Negative $d\omega/dk$ at k_0 gives inward moving waves

Localized Structures (again)



Localized Structures May Be Useful

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A new approach to data storage using localized structures

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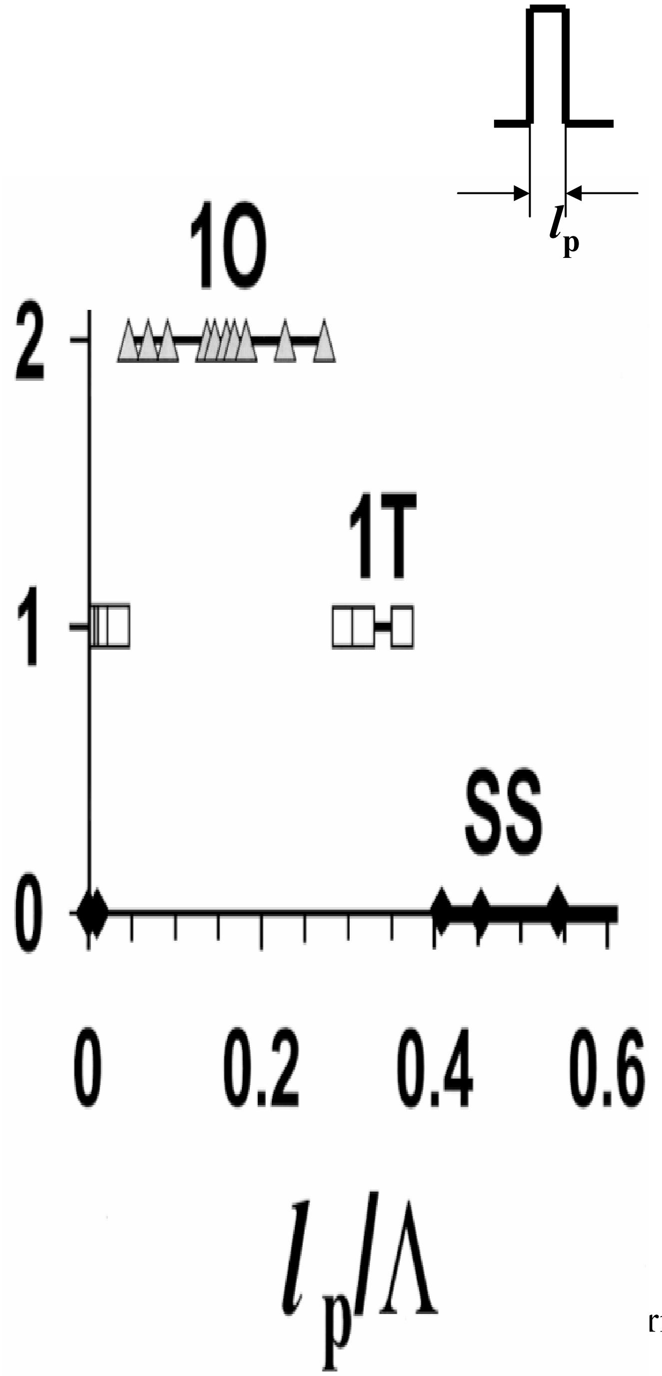
(Received 22 April 2003; accepted 1 December 2003; published online 9 February 2004)

In this paper we describe how to use the bifurcation structure of static localized solutions in one dimension to store information on a medium in such a way that no extrinsic grid is needed to locate the information. We demonstrate that these principles, deduced from the mathematics adapted to describe one-dimensional media, also allow one to store information on two-dimensional media.
 [DOI: 10.1063/1.1642311]

Localized Structures

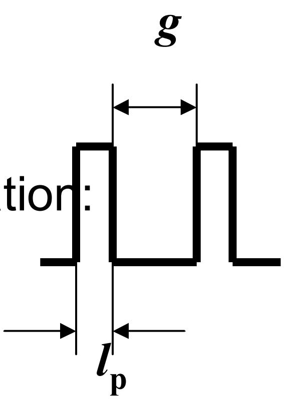
Initial perturbation determines the behavior of localized peak in the double subcritical region.

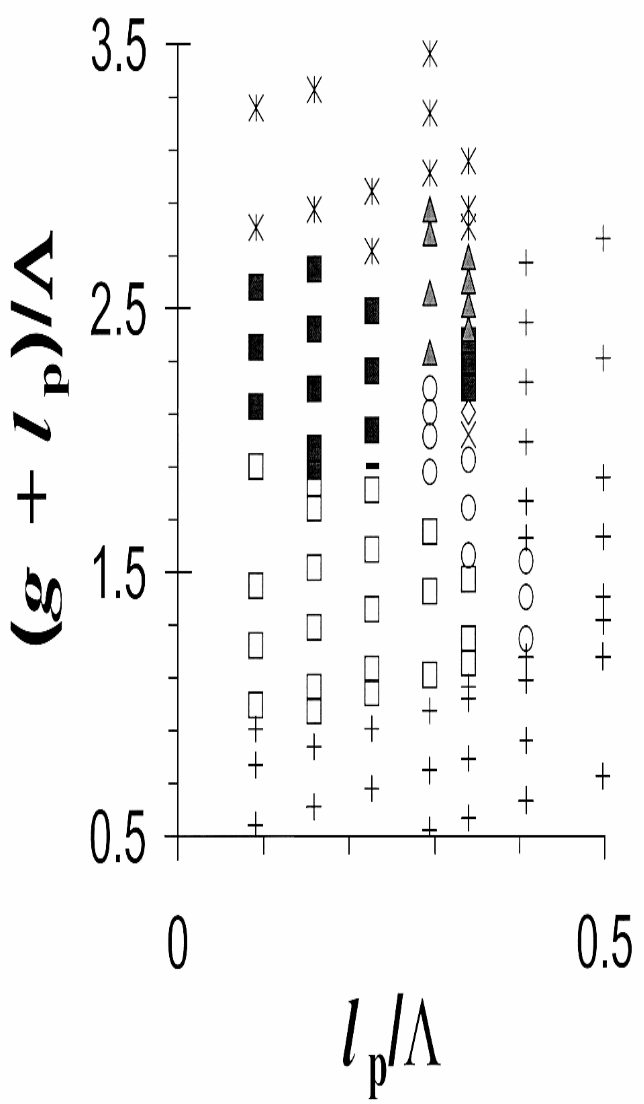


SS, steady state (assigned ordinate value 0); 1T, single stationary Turing peak (value 1); 1O, single oscillon (value 2). Λ is the characteristic wavelength of Turing instability

Interaction of Localized Peaks

Initial perturbation:





Two identical tooth-like initial perturbations are separated by a gap of length g. +, SS; □, oscillon with two synchronously oscillating peaks; ○, stationary Turing pattern with two peaks; ■, oscillon with three synchronously oscillating peaks; ▲, pattern with three peaks, the middle one oscillating and the outer ones stationary (T+O+T); ×, single oscillon; −, single stationary peak; ◊, oscillon with two peaks oscillating anti-phase; ∗, two independent Turing or oscillatory peaks.

Open questions and future work

- Smaller-scale structure
- Localized structures
- Microscale – statistical aspects
- Making materials
- Mixed surfactants
- Analogy to nonchemical systems

Conclusions

- The BZ-AOT system is a rich medium for generating novel pattern formation phenomena.
- The existence of two quite different time scales for diffusion plays a key role.
- The behavior can be modeled qualitatively with simple models for the BZ chemistry and for interfacial transfer and rapid diffusion in the oil phase.