The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
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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

1668/12

Interacting Populations of Chemical Oscillators

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Dynamical Order and Complexity in Populations of Electrochemical Oscillators

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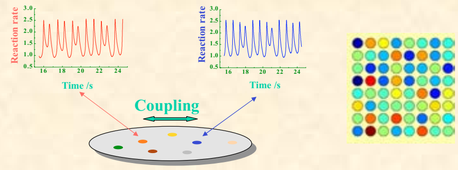
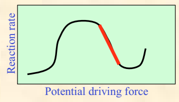
Department of Chemical Engineering
University of Virginia, Charlottesville, USA



Dynamics of Metal Electrodissolution

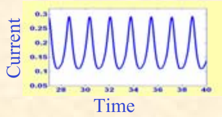
Oscillations

Fast positive feedback loop through the potential (negative differential resistance)



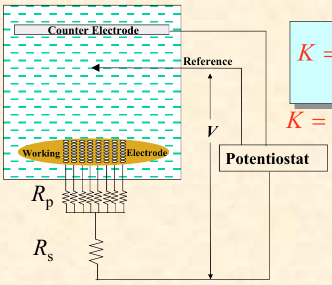
Passivation
Adsorption of an inhibitor

Slow negative feedback loop through surface concentration(s) of chemical species due to mass transport



Population of Electrochemical Oscillators:

Coupling weak via electrolyte: added globally



Global coupling strength

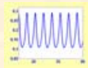
$$K = \frac{R_s}{R_p / N} \qquad \varepsilon = \frac{R_s}{R_{tot}}$$

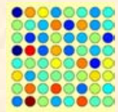
$$K = [-1 \ldots \infty] \qquad \varepsilon = [-\infty \ldots 1]$$

Total resistance

$$R_{tot} = R_s + \frac{R_p}{N}$$

Populations of Oscillators: Emerging Coherence and Clustering





Emergence of Order through Global Coupling

Kiss, Zhai, Hudson, *Science* **296**, 1676 (2002)
Zhai, Kiss, Hudson, *Ind. Eng. Chem. Res. 43 (2)*, 315-326 (2004).
Mikhailov, Zanette, Zhai, and Hudson, *Proc. Natl. Acad. Sci. USA 101 (30)*, 10890-10894 (2004).

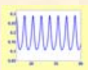
Cluster Formation and Itinerancy

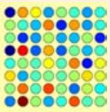
Wang, Kiss, Hudson, *Chaos* **10**, 248 (2000)
Kiss, Hudson, *Chaos* **13**, 999 (2003)

Predicting Entrainment with Experiment-based Phase Models

Kiss, Zhai, Hudson, *Phys. Rev. Lett. 94*, 248301 (2005).

Populations of Oscillators: Engineering of Chemical Complexity





Review article

Kiss, István Z and John L. Hudson, *AIChEJ 49*, 2234-2241 (2003).

Desynchronization

Zhai, Kiss, Tass, Hudson *Phys. Rev.E. 71* 065202(R) (2005).

Forcing

Wang, Kiss, Hudson, *Phys. Rev. Lett.* **86**, 4954 (2001);
Wang, Green, Hudson, *J. Phys. Chem* **105**, 7366 (2001)

Feedback

Wang, Kiss, Hudson, *Phys. Rev. Lett.* **86**, 4954 (2001)
Wang, Kiss, Hudson, *Ind. Eng. Chem. Res.* **41**, 330 (2002)

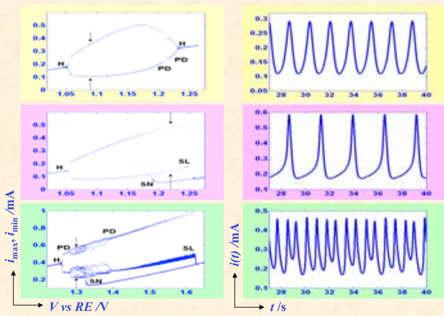
Nickel Electrodissolution in Sulfuric Acid: Dynamics of One Oscillator

Type/conditions | Bifurcation diagram | Current time series

Smooth
R = 452 Ω
c = 3 M

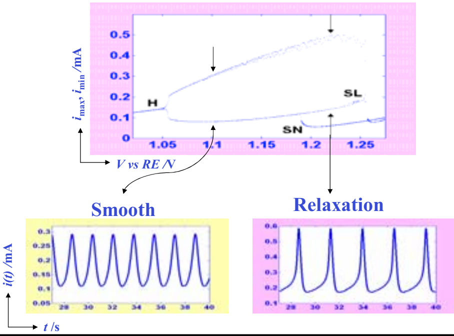
Relaxation
R = 652 Ω
c = 3 M

Chaotic
R = 906 Ω
c = 4.5 M

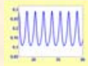


Nickel Electrodissolution in Sulfuric Acid: Dynamics of One Oscillator

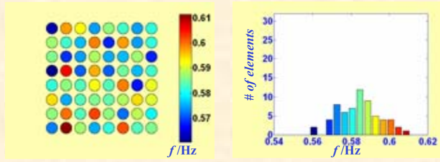
(R = 652 Ω, c = 3 M)



Population of Smooth Oscillators (no added coupling)

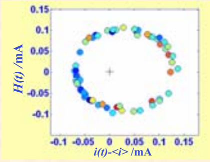


Frequency distribution

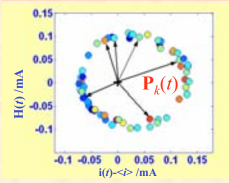


Snapshot of phase space reconstructed using Hilbert transform.

$$H(t) = 1/\pi \int_{-\infty}^{\infty} \frac{i(\tau) - \langle i \rangle}{t - \tau} d\tau$$



Order Parameter: $r(t)$

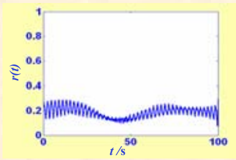


$$Z(t) = \frac{\sum_{k=1}^{64} P_k(t)}{\sum_{k=1}^{64} |P_k(t)|}$$

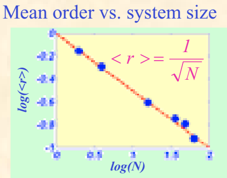
$P_k(t) = [i(t) - \langle i \rangle] + j\,H(t)$ are vectors of points in phase portrait at time t.

Magnitude of order: $r(t) = |Z(t)|$

Order vs. time

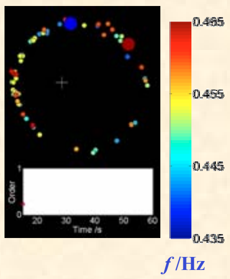


Mean order vs. system size

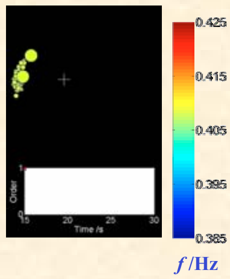


Smooth oscillators

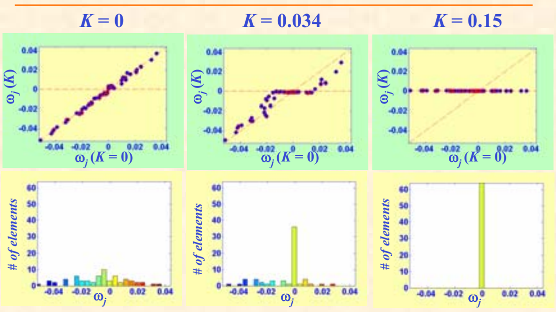
No added coupling $K = 0$



Added coupling $K = 0.15$



Smooth Oscillators: Effect of global coupling on frequencies



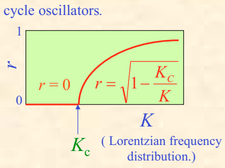
$\omega_j = f_j / \langle f \rangle - 1$ (dimensionless frequency)

Smooth Oscillators: The effect of global coupling on order

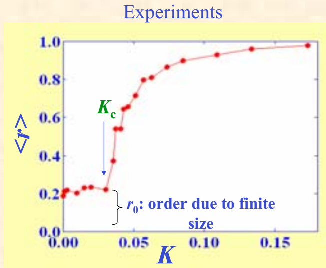
Theory

A.T. Winfree, (1967)
Onset of mutual synchronization at threshold (K_c).

Y. Kuramoto (1975)
Analytical solution of $\langle r \rangle$ vs. K for an infinite number of smooth limit-cycle oscillators.

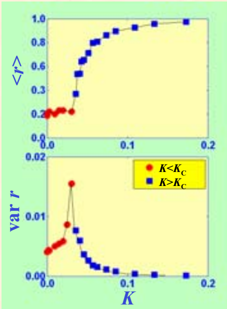


Experiments

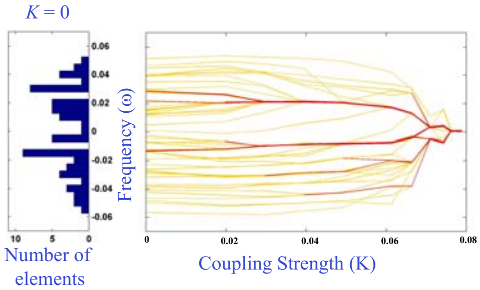


Kiss, Zhai, Hudson, *Science* **296**, 1676 (2002)

Smooth Oscillators: The Effect of Global Coupling on Variance of Order Parameter

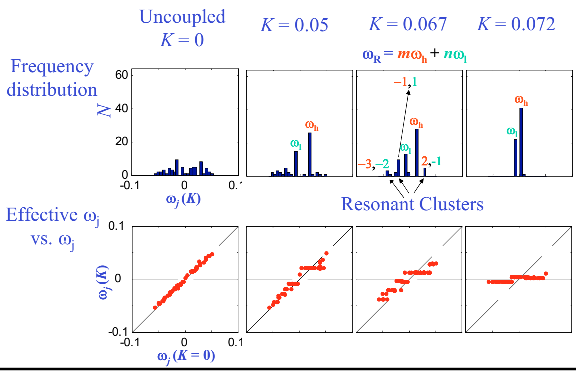


Multimodal Population of Smooth Oscillators Frequency Distribution



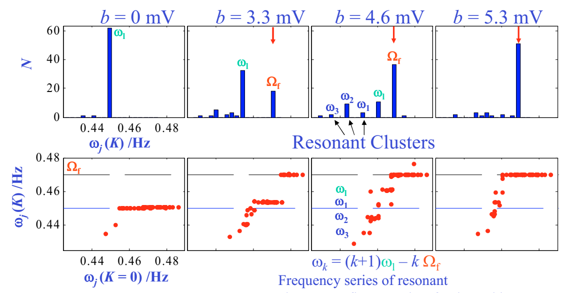
Mikhailov, Zanette, Zhai,. Kiss, Hudson, *PNAS 101 (30)*, 10890-10894 (2004).

Multimodal Population of Smooth Oscillators Resonant clustering



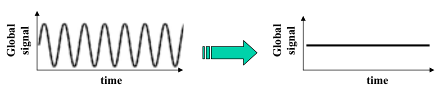
Resonant Clustering in External Forcing of a Coupled Unimodal Population ($K = 0.044$)

External forcing: $V(t) = V_0 + b\sin(2\pi\Omega_f t)$

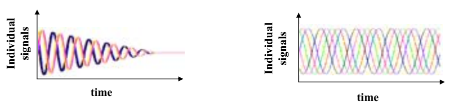


Frequency series of resonant clusters confirms results of Sakaguchi Prog. Theor. Phys. 79, p 39 (1988)

Suppression of collective oscillations

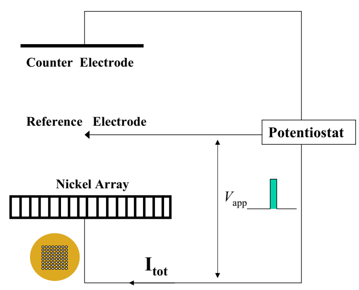


Two possible routes:

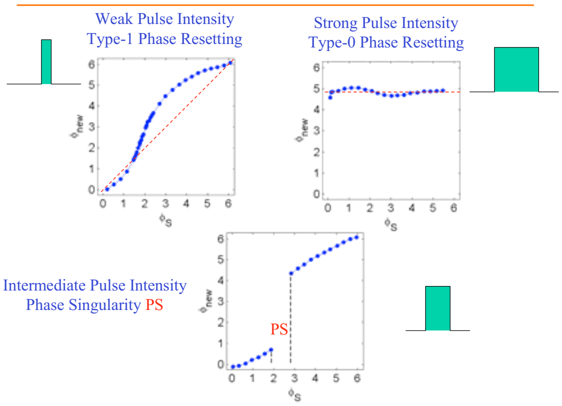


Oscillator quenching **Desynchronization**

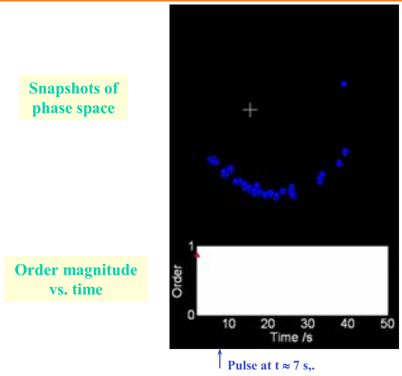
External Pulse Stimulation



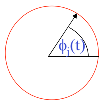
Effect of pulse on collective signal in a synchronized population



Single pulse administered at phase singularity (ϕ_P =0.35)



Coupled Oscillators: Phase Models



$$\frac{d\phi_j}{dt} = \omega_j + \sum_{k=1}^{N} H(\phi_k, \phi_j)$$

ϕ_j: phase of oscillator j, $j = 1\ldots N$
ω_j: inherent frequency
$H(\phi_k, \phi_j)$: interaction function

Assumption:

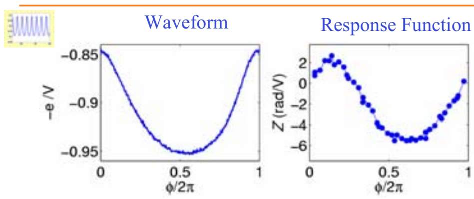
$$H(\phi_k, \phi_j) = H(\phi_k - \phi_j) = H(\Delta\phi_{k,j})$$

Example:

$$H(\Delta\phi_{k,j}) = sin(\Delta\phi_{k,j})$$ Kuramoto, 1975

- Once $H(\Delta\phi)$ is known, many of the synchronization properties can be predicted.
- What is $H(\Delta\phi)$ in experimental systems and does it predict synchronization correctly?

Experimental Determination of Response Function $Z(\phi)$



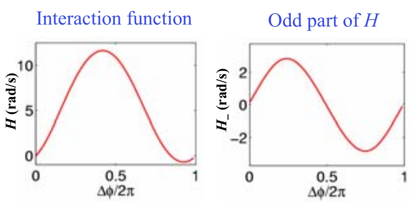
$$Z(\phi) = \Delta\Phi(\phi) \,/\, \Delta X$$

where
$\Delta\Phi(\phi)$: the phase advance due to a perturbation at phase ϕ
ΔX: perturbation (electrode potential in this example)
ϕ: phase, $\phi = 2\pi t/T$, t: time from maximum, T: period of the oscillation

Experimental Determination of Interaction Function $H(\Delta\phi)$

$$H(\Delta\phi) = \frac{1}{2\pi}\int_{\phi=0}^{2\pi} Z(\phi)K[X(\phi+\Delta\phi) - X(\phi)]d\phi$$

where
$\Delta\phi$: phase difference, K: intensity of diffusive coupling
Kuramoto, 1984

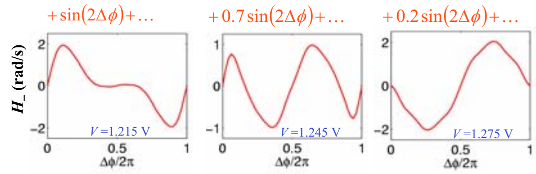


Relaxation Oscillators: Extent of Relaxation Character

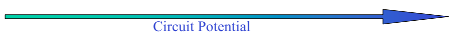
$H_-(\Delta\phi) = \sin(\Delta\phi) + \sin(2\Delta\phi) + \ldots$

$H_-(\Delta\phi) = -0.5\sin(\Delta\phi) + 0.7\sin(2\Delta\phi) + \ldots$

$H_-(\Delta\phi) = -2\sin(\Delta\phi) + 0.2\sin(2\Delta\phi) + \ldots$



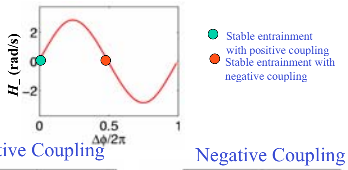
Mild	Moderate	Strong
Sine wave with higher harmonics	Dominant two-peak	-Sine with higher harmonics



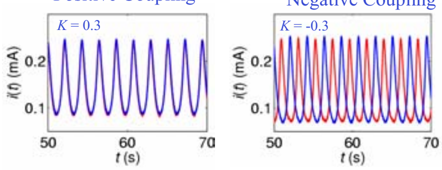
Stable Mutual Entrainment of Two Oscillators with Positive and Negative Coupling

'Smooth'

Prediction



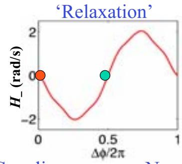
Experiment



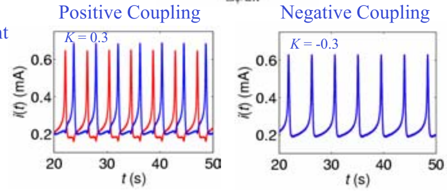
Stable Mutual Entrainment of Two Oscillators with Positive and Negative Coupling

'Relaxation'

Prediction



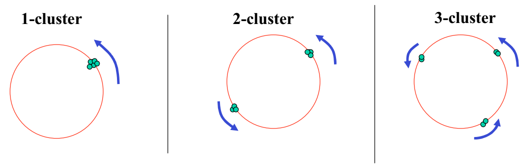
Experiment



Populations: cluster states in phase models

$$d\phi_j / dt = 1/N \sum_{k=1}^{N} H\left(\Delta\phi_{k,j}\right)$$

Possible solutions: cluster states



Any M-cluster state is possible (M<N) but only some are stable.
Stability analysis of *M*-cluster state:

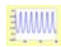
For $p = 0,\ldots,$ M-1: $\lambda_p = \frac{1}{M}\sum_{k=0}^{M-1} F'\left(\frac{2\pi k}{M}\right)\left[1-\exp(-2\pi i k p / M)\right]$

and λ_M with multiplicity *N* - *M*: $\lambda_M = \frac{1}{M}\sum_{k=0}^{M-1} F'\left(\frac{2\pi k}{M}\right)$

$F(x) = H(-x)$

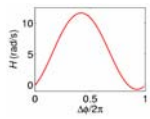
Okuda (1993)

Experiment-based phase model for smooth oscillators

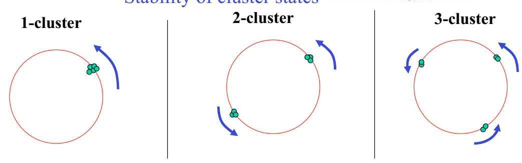


$$d\phi_j / dt = 1/N \sum_{k=1}^{N} H\left(\Delta\phi_{k,j}\right)$$

Experimental interaction function



Stability of cluster states

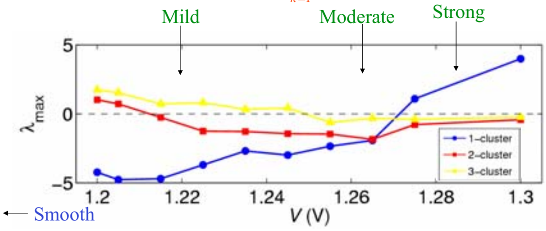


Stable **Unstable** **Unstable**

Only cluster-1 state is stable

Populations of relaxation oscillators

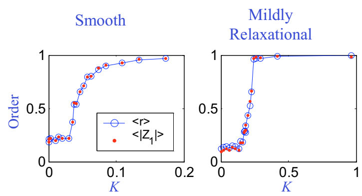
$$d\phi_j / dt = 1/N \sum_{k=1}^{N} H\left(\Delta\phi_{k,j}\right)$$



← Smooth

Comparison of different types of oscillators

Order parameter vs. coupling strength

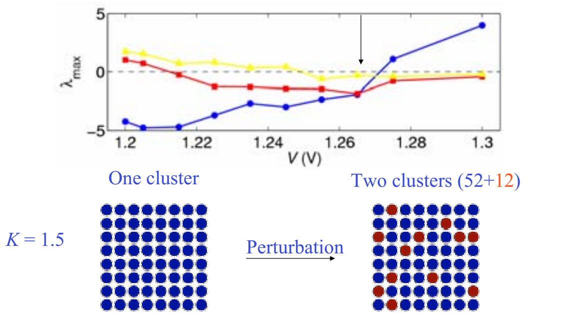


$r \propto (K - K_c)^{0.56}$ $r \propto (K - K_c)^{0.89}$

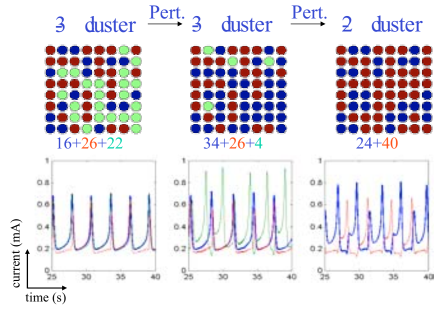
Kuramoto (1975): $r \propto (K - K_c)^{0.5}$

Daido (1996): $r \propto (K - K_c)^{1}$

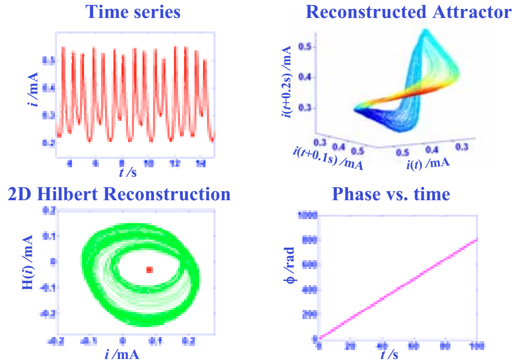
Coexistence of one duster and two duster states in moderately relaxational oscillators



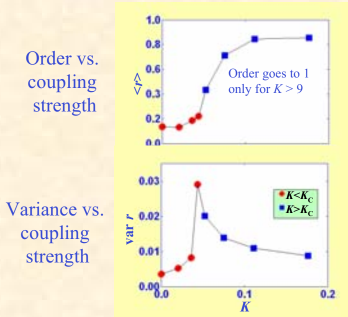
Stable 2 dusters and 3 dusters in strongly relaxational oscillators



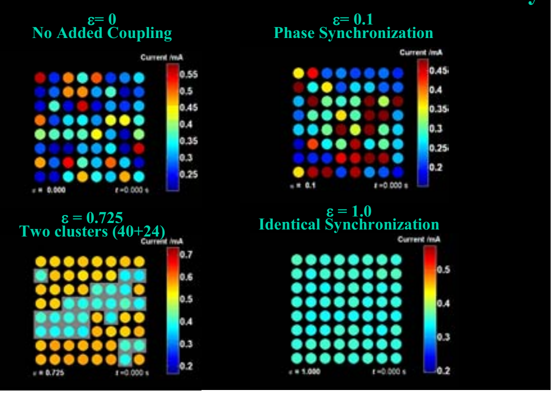
Single Chaotic Oscillator



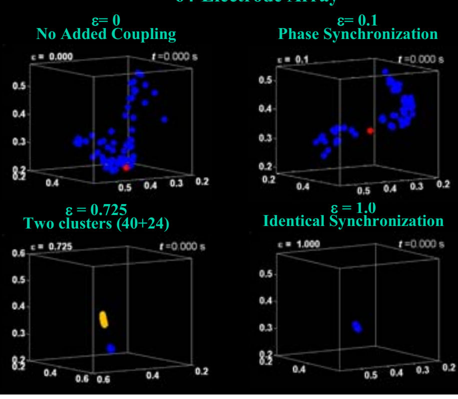
Emerging Order in a Population of Chaotic Oscillators



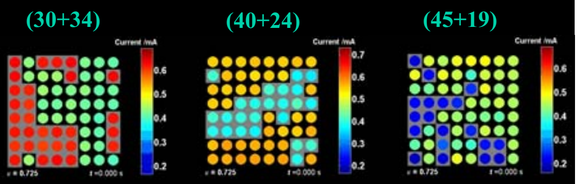
Current Distribution on the 64-Electrode Array



State Space Representation 64-Electrode Array

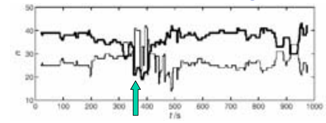


Current Distribution on the 64-Electrode Array
ε = 0.725

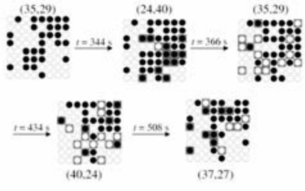


Chaotic Itinerancy (ε = 0.73)

Number of elements in the two largest clusters



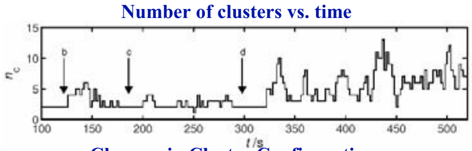
Changes in Cluster Configurations



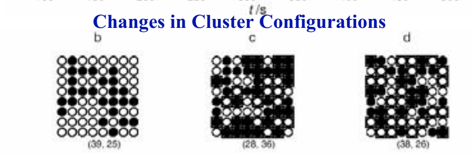
Series of transitions of groups.
The system has a 'memory'.
Elements are loyal to their sub-clusters, and the sub-clusters to the clusters.

Chaotic Itinerancy (ε = 0.4)

Number of clusters vs. time

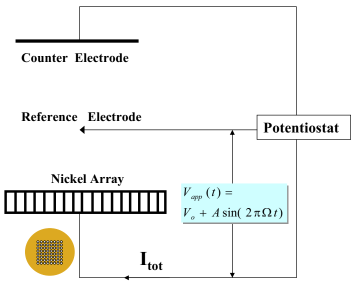


Changes in Cluster Configurations

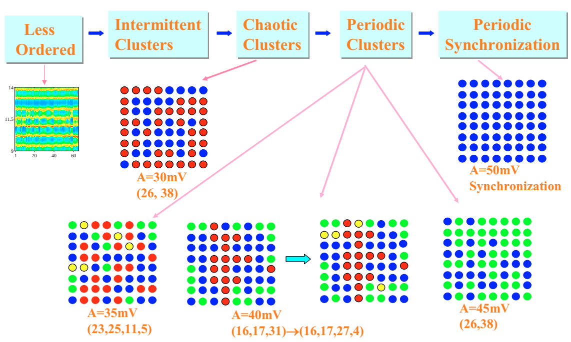


Substantial rearrangements, no loyalty.

External Forcing

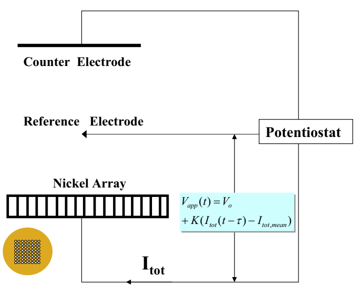


External Periodic Forcing
64-electrode array, Ω=1.3Hz, ε=0.56



Wang, Kiss, Hudson, *Phys. Rev. Lett.* **86**, 4954 (2001); Wang, Green, Hudson, *J. Phys. Chem* **105**, 7366 (2001)

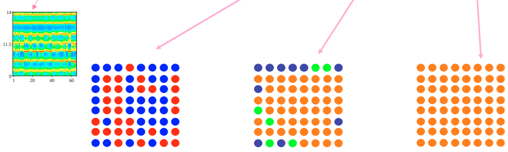
Feedback



Feedback

64-electrode array, τ=0, ε=0.56

Less Ordered → Intermittent Clusters → Chaotic Clusters → Periodic Clusters → Periodic Synchronization



K=2.2 mV/mA
Two Clusters
(29,35)

K=3.2 mV/mA
Three Clusters
(6,10,48)

K=3.8 mV/mA
Synchronization

Wang, Kiss, Hudson, *Phys. Rev. Lett.* **86**, 4954 (2001)
Wang, Kiss, Hudson, *Ind. Eng. Chem. Res.* **41**, 330 (2002)

Conclusions

- Laboratory experiments with populations of periodic and chaotic chemical oscillators show phase transitions to coherent states, resonant clustering, and stable and itinerant dynamical differentiation.
- Phase models obtained from experiments are useful tools for predicting behavior of sets of oscillators. Interaction functions bridge local dynamics to emergent collective behavior.
- Collective properties of populations can be tuned through global interactions, external forcing, and feedback.

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