Compartmentalized Reaction-Diffusion Systems

F. Chavez
R. Kapral

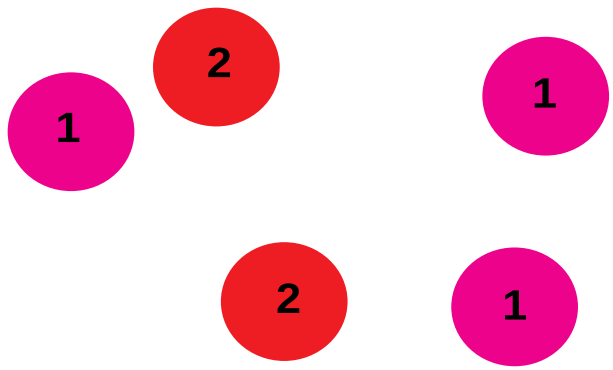
F. Chavez and R. Kapral, Phys. Rev. E, 63, 016211 (2000)
F. Chavez and R. Kapral, Phys. Rev. E, 65, 056203 (2002)

reactions often take place in

- open systems; complex reaction dynamics with feedback
- heterogeneous media with compartmentalization of species

what effects do these features have on pattern formation?

reactive compartments, each supporting one step of an autocatalytic mechanism, coupled by diffusion



example: bistable system – Schlögl model

$$\text{compartment 1}: \quad A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X,$$

$$\text{compartment 2}: \quad B + 2X \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 3X,$$

neither step is bistable but the combined effect of both steps leads to bistability general analysis: system with m chemically reactive species; overall reaction mechanism consists of n elementary steps

$$\sum_{k=1}^{m} \nu_k^{\alpha} X_k \underset{k_{-\alpha}}{\overset{k_{\alpha}}{\rightleftharpoons}} \sum_{k=1}^{m} \bar{\nu}_k^{\alpha} X_k, \qquad (\alpha = 1, \ldots, n)$$

X_k, $(k = 1, \ldots, m)$ are m chemical species
ν_k^{α} and $\bar{\nu}_k^{\alpha}$ are stoichiometric coefficients for reaction step α

reaction-diffusion equations

$$\frac{\partial \mathrm{c}(\mathrm{r}, t)}{\partial t} = \mathrm{D} \nabla^2 \mathrm{c}(\mathrm{r}, t) + R(\mathrm{c}(\mathrm{r}, t)),$$

compartmentalized reaction rates on N domains

$$\mathcal{R}_k(\mathrm{c}(\mathrm{r}, t)) = \sum_{i=1}^{N} R_k^{\{\alpha_i\}}(\mathrm{c}(\mathrm{r}, t)) \Theta_i(\mathrm{r}).$$

formal solution

$$c_k(\mathrm{r}, t) = \int_0^t \int G(\mathrm{r}, t; \mathrm{r}_0, t_0)\mathcal{R}_k(\mathrm{c}(\mathrm{r}_0, t_0))d^s\mathrm{r}_0 dt_0 + c_k^0 + \mathcal{I}_k^\phi + D_k\mathcal{I}_k^B$$

first term accounts for the reaction rates; c_k^0 is the solution of the associated homogeneous problem ; last two terms account for the initial and boundary conditions

$G(\mathrm{r}, t; \mathrm{r}_0, t_0)$ – time-dependent Green function

tough to solve; focus on volume average over domain j

$$c_{k,j}(t) = \frac{1}{V_j}\int c_k(\mathrm{r}, t)\Theta_j(\mathrm{r})d^s\mathrm{r}$$

average over a domain and use a multipole expansion of the domain contributions

$$R_k^{\{\alpha_i\}}(c(\mathrm{r},t))\Theta_i(\mathrm{r}) \approx \left[\int d^s\mathrm{r}\ R_k^{\{\alpha_i\}}(\mathrm{c}(\mathrm{r},t))\Theta_i(\mathrm{r})\right]\delta(\mathrm{r}-\mathrm{r_i}), \quad (\mathrm{r} \in \Omega_j)$$

to obtain

$$c_{k,j}(t) = \sum_i^N \int_0^t \omega_{k,ji}(t,t_0) R_k^{\{\alpha_i\}}(\mathrm{c}_i(t_0))dt_0 + c_k^0 + I_{k,j}^{\phi} + D_k I_{k,j}^{B}$$

integrals describe the effect of the reactions within domain i on the mean concentration in domain j

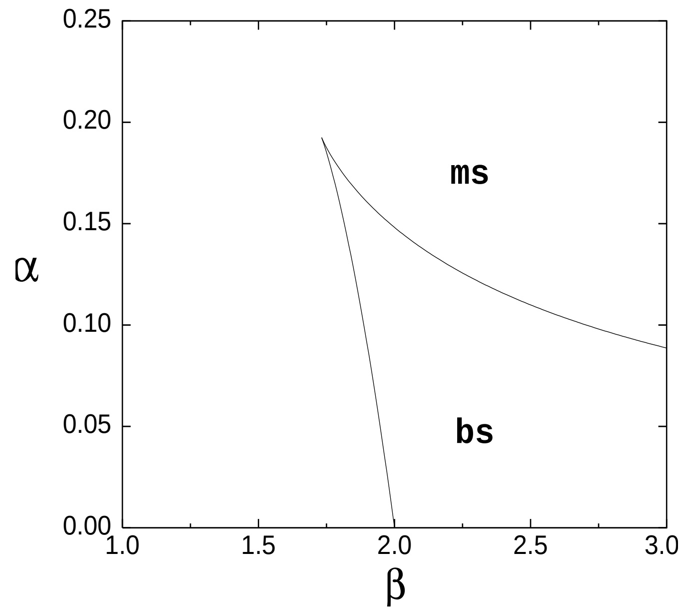
$$\omega_{k,ji}(t,t_0) = \frac{1}{V_j}\iint_{\Omega_j} G(\mathrm{r},t;\mathrm{r}_0,t_0)d^s\mathrm{r}_0\ d^s\mathrm{r}\ \delta_{ji} + \int_{\Omega_j} G(\mathrm{r},t;\mathrm{r}_i,t_0)d^s\mathrm{r}\ (1-\delta_{ji})$$

Schlögl model steady state bifurcation diagram – no compartments

$$\frac{dc}{dt} = k_{-2}c^3 - k_2bc^2 + k_{-1}c - k_1a = 0$$

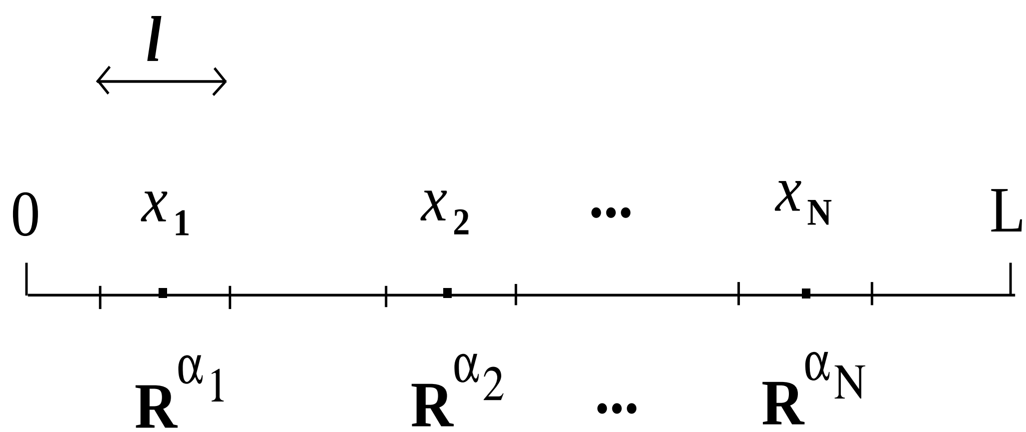
or in scaled variables $\alpha x^3 - x^2 + \beta x - 1 = 0$ where

$$\alpha = \frac{k_{-2}}{k_1a}\left(\frac{k_1a}{k_2b}\right)^{3/2}, \qquad \beta = \frac{k_{-1}}{k_1a}\left(\frac{k_1a}{k_2b}\right)^{1/2}.$$



geometric effects on reaction dynamics

one-dimensional medium consisting of N reactive domains of length l centered at positions x_i



stable states − time-independent RD equation in 1d

$$D\frac{\partial^2 c(x)}{\partial x^2} = -\mathcal{R}(c(x))$$

type-1 domains (step 1): $c_1 = k_1 a/k_{-1}$
type-2 domains (step 2): $c_2 = k_2 b/k_{-2}$

general equations can be solved analytically for the two-domain and periodic regular array Schlögl model

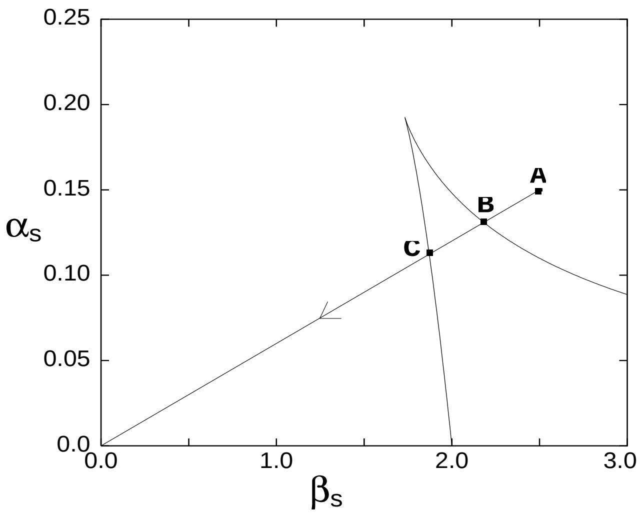
steady states are the solutions of $\alpha_s x^3 - x^2 + \beta_s x - 1 = 0$ where

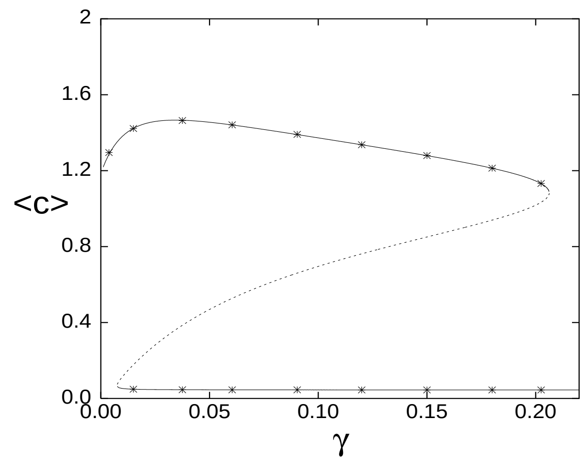
$$\alpha_s = \alpha\sqrt{\frac{\gamma}{\gamma + k_{-1}}}. \quad \beta_s = \beta\sqrt{\frac{\gamma}{\gamma + k_{-1}}}$$

$$\gamma = \begin{cases} \frac{6D}{3dl - 2l^2}, & \text{fixed-concentration BC} \\ \frac{24dD}{l(24d^2 + l^2 - 8dl)}, & \text{zero-flux BC.} \end{cases}$$

l is domain length and d is the distance between the domain centers

induce bistability by variations of D or l − regular arrangement of N domains





$$\alpha_s = \alpha_s(k_i, a, b, \gamma) \quad \beta_s = \beta_s(k_i, a, b, \gamma).$$

$$\gamma = 24dD/l(24d^2 + l^2 - 8dl)$$

random distribution of two types of domain – mean field approximation

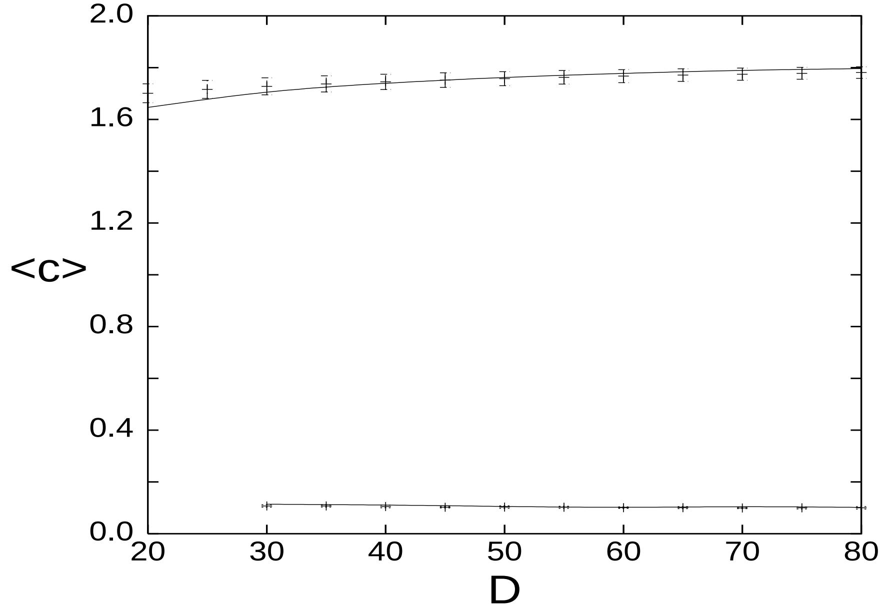
sum over all like domains to obtain coupled equations for their mean concentrations

$$\begin{aligned} c_1 &= W_{11}R^1(c_1) + W_{12}R^2(c_2) + c_0, \\ c_2 &= W_{22}R^2(c_2) + W_{21}R^1(c_1) + c_0 \end{aligned}$$

where

$$\begin{aligned} W_{11} &= \frac{2}{N}\sum_{i,j} w_{ji}\delta_{\alpha_i,1}\delta_{\alpha_j,1} \\ W_{22} &= \frac{2}{N}\sum_{i,j} w_{ji}\delta_{\alpha_i,2}\delta_{\alpha_j,2} \\ W_{12} = W_{21} &= \frac{1}{N}\sum_{i,j} w_{ji}(1-\delta_{\alpha_i,\alpha_j}) \end{aligned}$$

random distribution of domains – system parameters: $L = 1000$, $N = 50$, $l = 10$, 10 realizations



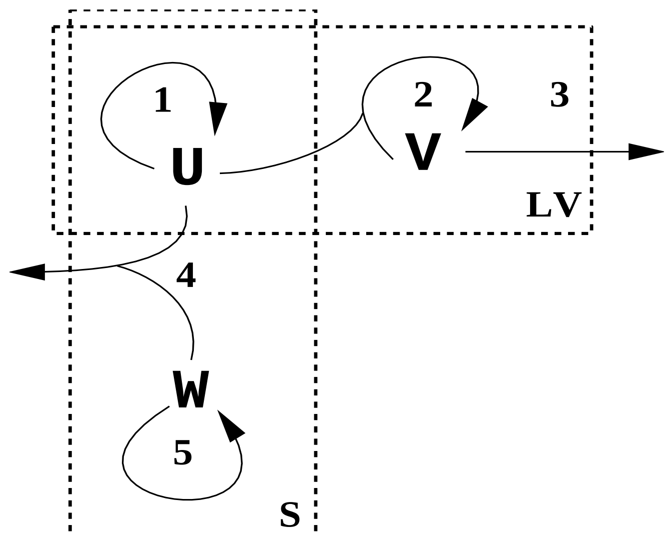
solid line – mean field model solution of the compartmentalized RD equations

Oscillatory and Chaotic Dynamics in Compartmentalized Geometries

Compartmentalized Willamowski-Rössler model

$$(1)\quad A_1 + U \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2U\ , \qquad (2)\quad U + V \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2V\ , \qquad (3)\quad A_5 + V \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} A_2\ ,$$

$$(4)\quad U + W \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} A_3\ , \qquad (5)\quad A_4 + W \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} 2W$$



Lotka-Volterra (LV) and switch (S) steps in separate compartments

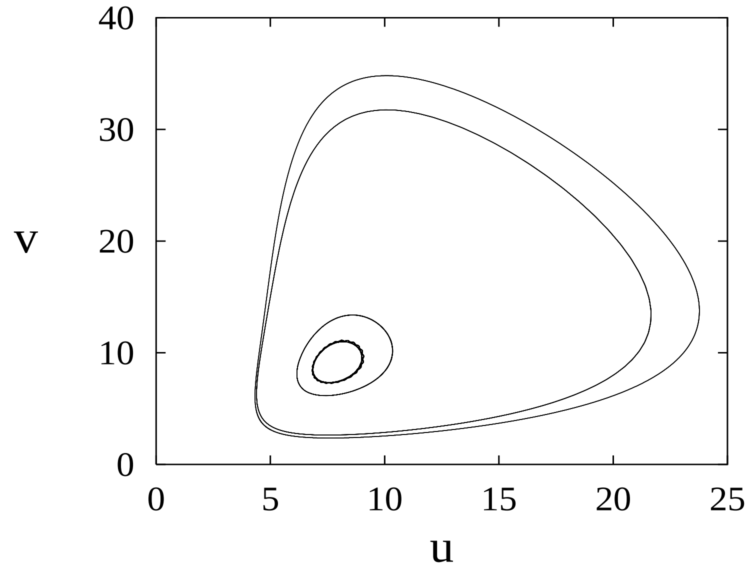
• LV domains – single stable focus; S domains – two stable nodes separated by an unstable node

1d medium of length L with alternating LV and S domains; domain length $l = L/2$, center-to-center inter-domain distance $d = L/2$; $D_u = D_v = D_w = D$; periodic BC

scaled time and length units, $t \to t/\tau$ and $x \to x/\sqrt{D\tau}$; then with $\tau = 1$, $\mathbf{D} = \mathbf{I}$

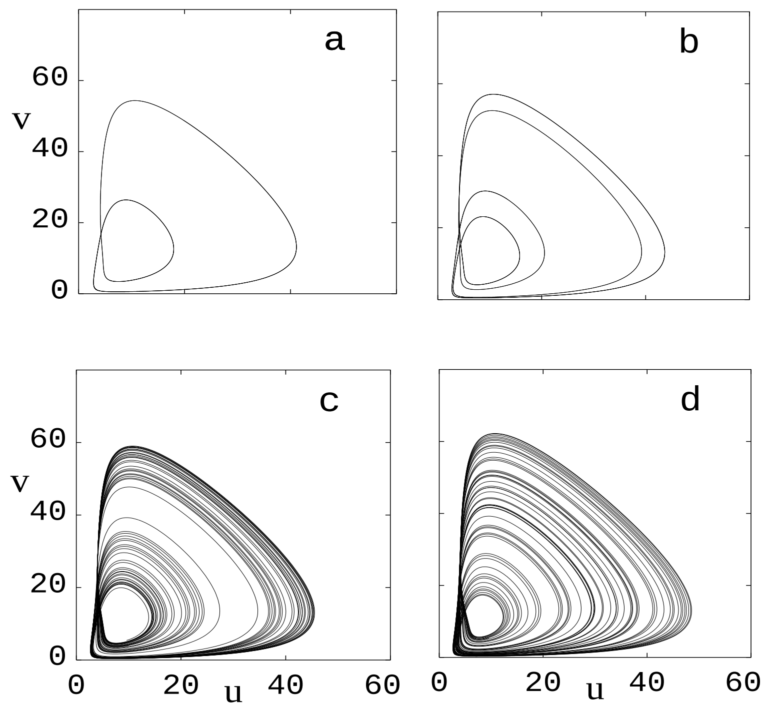
diffusion length $\ell_D = \sqrt{Dt_c} \to \sqrt{t_c/\tau}$, where t_c is characteristic time scale taken to be the period of one oscillation which lies in the range $1.5 \geq t_c/\tau \geq 5$ and thus $1.2 \geq \ell_D \geq 2.2$

globally averaged concentration fields projected onto the uv-plane for $k_{-2} = 0.11$ and different values of L



- well-mixed WR system has a period-1 limit cycle
- large L, system evolves to a stable fixed point determined by the stationary states of the independent LV and S domains
- limit cycle develops at $L = 0.777$, as L decreases size of limit cycle grows until it resembles that of the well-mixed WR system

$k_{-2} = 0.072$: well-mixed WR system has a chaotic attractor – system size L again plays role of bifurcation parameter



development of a chaotic attractor in the compartmentalized WR system; (a)-(d): $L = 0.283, 0.258, 0.2309$ and 0.179

boundary conditions have important effects – integral representation

$$c_{k,j}(t) = I^{\phi}_{k,j} + D_k I^{B}_{k,j} + \sum_{i=1}^{N} \int_0^t \omega_{k,ji}(t,t_0) R_k^{\{\alpha_i\}}(\mathrm{c}_i(t_0))dt_0$$

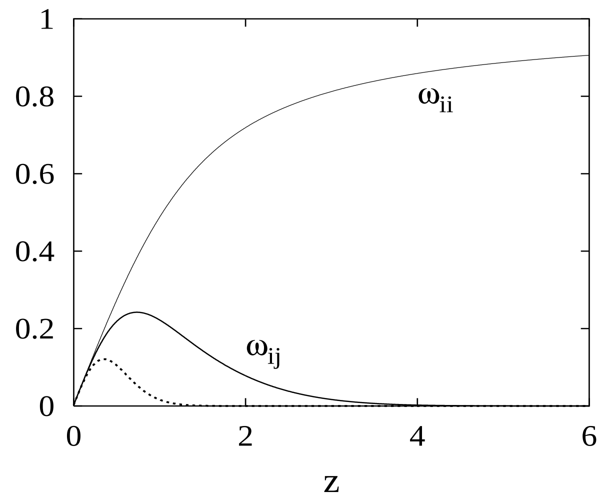
infinite system with zero concentrations at $x = \pm\infty$ – Green function is given by

$$G(x,x_0;t,t_0) = \frac{e^{-\frac{(x-x_0)^2}{4(t-t_0)}}}{2\sqrt{\pi(t-t_0)}}$$

prefactors are

$$\begin{aligned} \omega_{ii}(t,t_0) &= \frac{2}{l}\sqrt{\frac{t-t_0}{\pi}}\left[e^{-l^2/4(t-t_0)} - 1\right] + \mathrm{erf}\left(l/2\sqrt{t-t_0}\right) \ , \\ \omega_{ij}(t,t_0) &= \frac{1}{2}\left[\mathrm{erf}\left(\frac{2d_{ij}+l}{4\sqrt{t-t_0}}\right) - \mathrm{erf}\left(\frac{2d_{ij}-l}{4\sqrt{t-t_0}}\ ,\right)\right] \end{aligned}$$

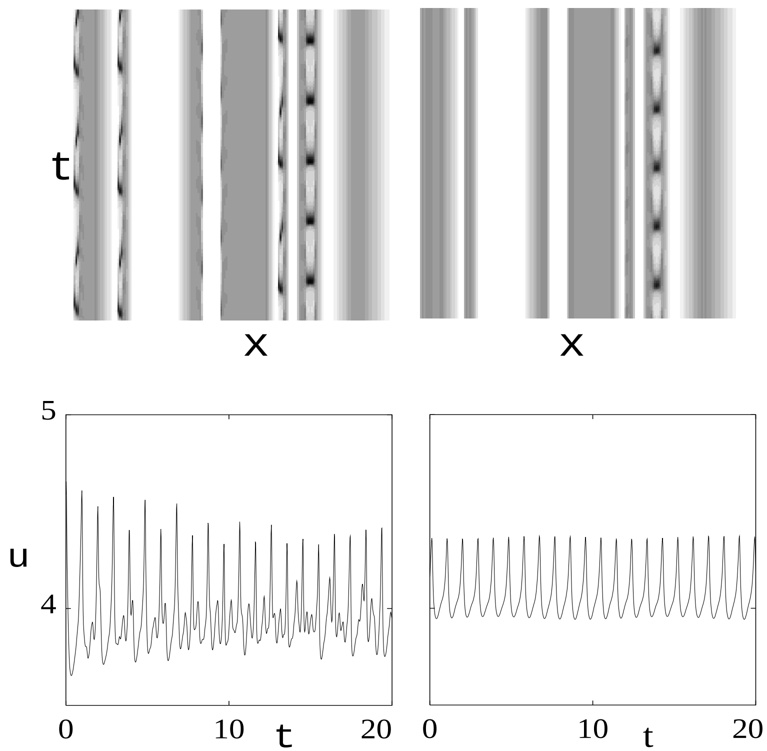
prefactors ω_{ii} and ω_{ij} as a function of z; off-diagonal term: (dotted line) $a = 2$, (solid line) $a = 1$



$z = l/\sqrt{4(t - t_0)}$; a_{ij} is the distance between domains in units of the domain length ℓ, $d_{ij} = a_{ij} l$

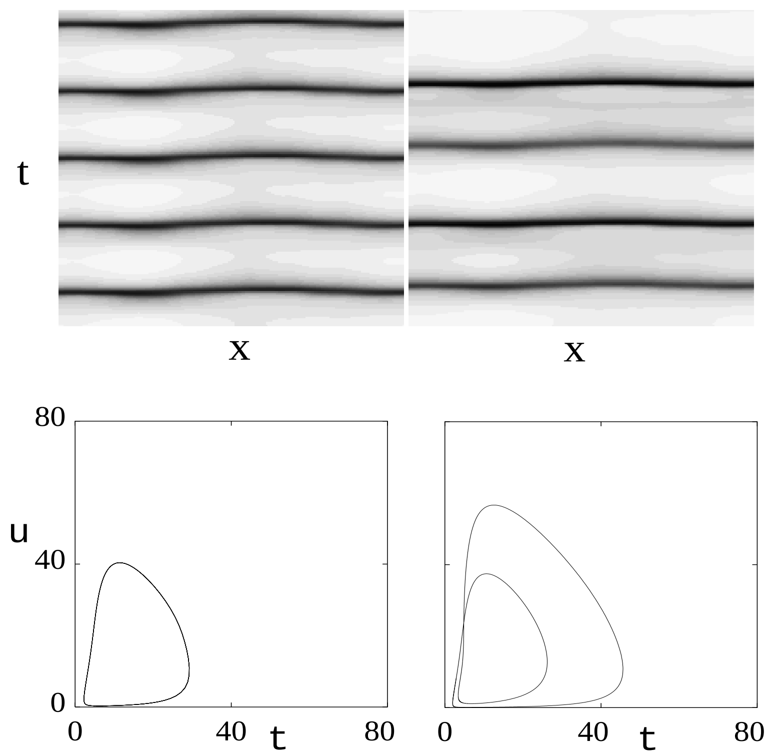
• self contributions from reactive domains are always much larger than the contributions from the neighboring domain when $t_0 \rightarrow t$, except for very small l; all prefactors tend to zero and boundaries dominate

• strong boundary effects preclude the appearance of oscillations when the reactive domains are strongly coupled random distributions: N domains randomly chosen to be of types LV and S; if domains overlapped, overlapping regions assumed to support full WR mechanism; $k_{-2} = 0.072$ in the chaotic regime



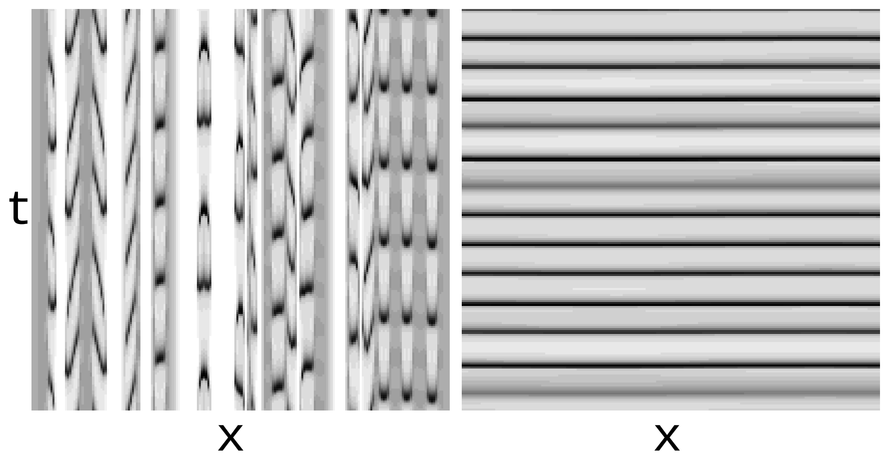
space-time plots for $N = 26$ and $L = 200$ (left) and $L = 115.47$ (right); bottom – globally averaged u fields versus t – low $< \rho_C >= 0.053$

Further decrease of L leads to a region of global oscillations when $L \approx \ell_D$



space-time plots for $N = 26$ for small L: $L = 2.82$ (left) and $L = 2.39$ (right); (bottom) phase plane plots of the globally averaged u and v

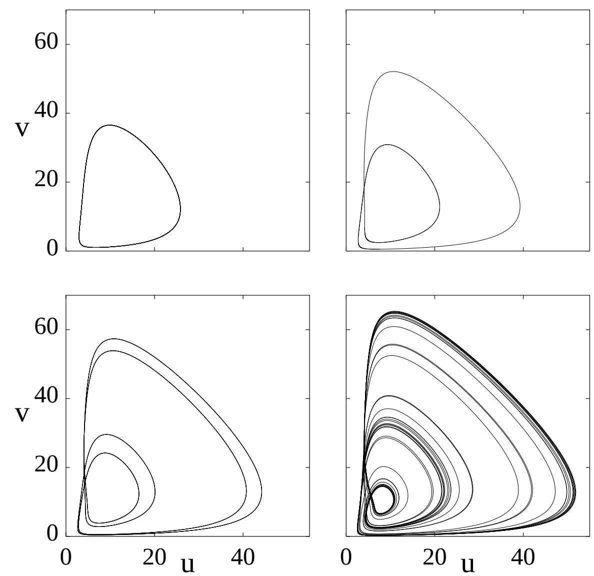
higher average density of overlapping domains $< \rho_C >= 0.43$; the medium contains larger clusters of C domains and clusters close to each other tend to synchronize



space-time plots for $N = 80$: $L = 200$ (left) and $L = 0.70$ (right)

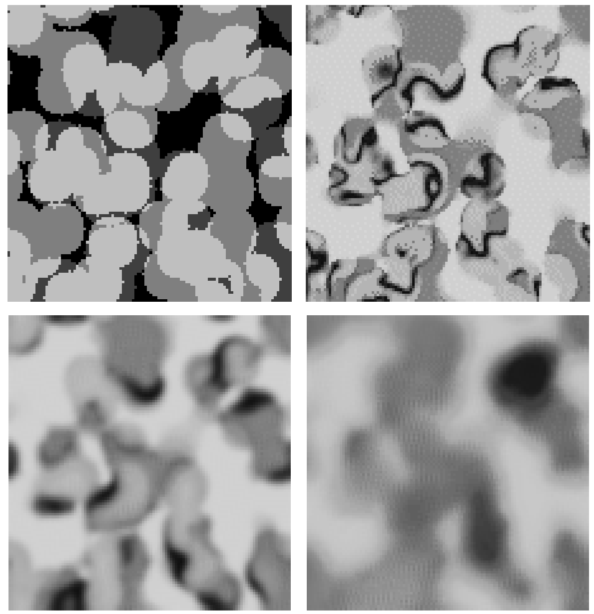
global attractors for one realization for different L

globally averaged dynamics shows a partial period doubling cascade and a chaotic attractor corresponding to the dynamics in the right panel of previous figure



phase plane plots of the globally averaged u and v fields for $N = 80$ and $L = 2.0$ (upper left) , 1.41 (upper right), 1.15 (lower left) and 0.70 (lower right).

two-dimensional media



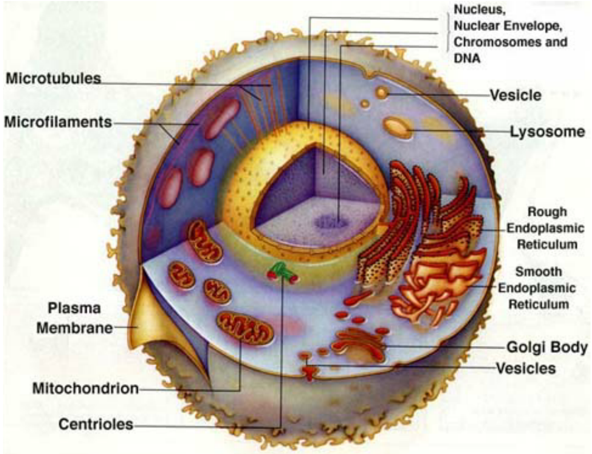
top left: One realization of the random configuration of LV, S and C domains. The domain type is color coded by shades of gray; the darkest shades correspond to inactive areas of the medium and the lightest to C-type overlapping domains. The other panels are instantaneous configurations of the u field for $L = 112$ (top right), 35.42 (bottom left) and $L = 11.20$ (bottom right)

magnitude of u is proportional to the intensity of gray shade

comments

- compartmentalization can influence nature of chemical dynamics and patterns
- applications to chemical patterns on catalytic surface; inhomogeneous reactor beds; reations in heterogeneous media
- extensions – derivation of effective reaction-diffusion equations for heterogeneous media

biological systems



features of biochemical reactions in cells

- open systems; complex reaction dynamics with feedback
- heterogeneous media with compartmentalization of species
- some species present in very small numbers, sometimes one or a few molecules
- transport by simple diffusion, protein or other motors, etc.