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ICTP-INFM SUMMER SCHOOL ON "TRANSPORT, REACTION AND PROPAGATION IN FLUIDS"

followed by

CONFERENCE ON "KOLMOGOROV'S LEGACY IN PHYSICS: ONE CENTURY OF CHAOS, TURBULENCE AND COMPLEXITY"

(8 - 17 September 2003)

"Propagating chemical fronts"

presented by:

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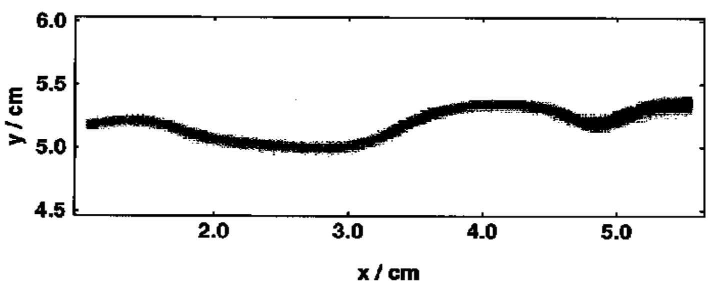
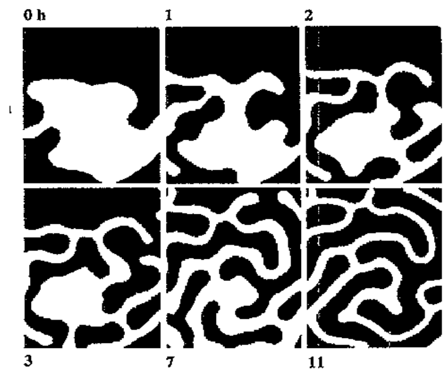
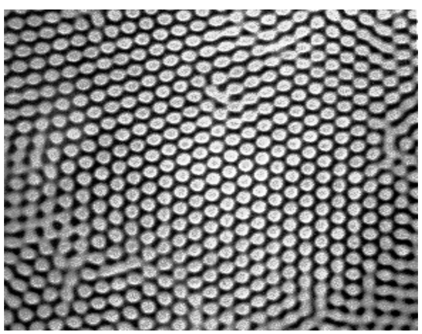
reaction-diffusion systems and chemical patterns



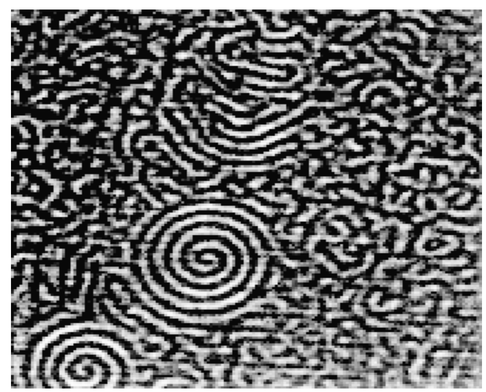
chaotic chemical fronts



labyrinthine patterns



Turing patterns



spiral waves and chemical turbulence

Transverse Front Instabilities in Chemical Systems

- origin of transverse instabilities
- Kuramoto-Sivashinsky equation
- cubic autocatalysis
- experimental observations

in reaction-diffusion media mechanism of front instabilities relies on the fact that species may diffuse at different rates

cubic autocatalytic reaction

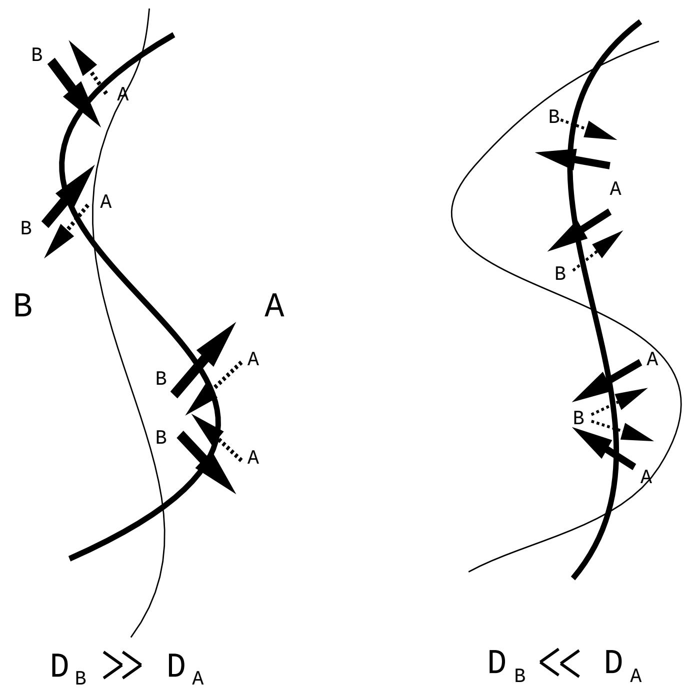
$$A + 2B \xrightarrow{k} 3B$$

where the autocatalyst B consumes the fuel A

two-dimensional system infinitely extended along x and of width L along y; initially, let the domain $x < 0$ of the system contain B and the domain $x \geq 0$ contain A, with a sharp planar interface separating them at $x = 0$

the autocatalyst will consume the fuel and the front will move to the right (increasing x) with velocity v; does the front remain planar or develop structure along y?

physical argument:



for some ratio of diffusion coefficients $d = D_A/D_B > 1$ the planar front will lose its stability

reaction-diffusion equation

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

reduce the RD equation to an equation for the dynamics of the front

to study the instability we need the solution to the planar front problem

planar travelling fronts – constant speed v along x; connects two different concentration regions at $x = \pm\infty$

$\mathrm{c}_0(u)$ – concentration field, $u = x - vt$ the moving frame coordinate

RD equation

$$\left(\mathrm{D}\frac{d^2}{du^2} + v\frac{d}{du}\right)\mathrm{c}_0(u) + \mathrm{R}(\mathrm{c}_0(u)) = 0$$

solved for front speed v and the front profile

stability of 1d front – linearize 1d RD equation about $\mathbf{c}_0(u)$

$$\mathbf{c}(x,t) = \mathbf{c}_0(u) + \delta\mathbf{c}(u,t)$$

substitution into RD equation yields

$$\begin{aligned} \frac{\partial \delta\mathbf{c}(u,t)}{\partial t} &= \left(\mathrm{D}\frac{d^2}{du^2} + v\frac{d}{du} + \frac{\delta \mathrm{R}}{\delta \mathbf{c}_0}\right)\delta\mathbf{c}(u,t) \\ &\equiv \Omega_R(u)\delta\mathbf{c}(u,t) \end{aligned}$$

defines the linear operator Ω_R

some notation – let $\langle u|c\rangle = c(u)$ and $\langle u|\hat{\Omega}_R|u'\rangle = \Omega_R(u)\delta(u-u')$

eigenvalue problem for $\hat{\Omega}_R$ is

$$\hat{\Omega}_R|\zeta_i\rangle = \lambda_i|\zeta_i\rangle$$

$\zeta_0(u) = dc_0/du$ is an eigenfunction of $\hat{\Omega}_R$ with eigenvalue $\lambda_0 = 0$ – broken translational invariance along u

$\hat{\Omega}_R$ is not self-adjoint so consider adjoint eigenvalue problem

$$\langle\zeta_i|\hat{\Omega}_R^\dagger = \lambda_i\langle\zeta_i|$$

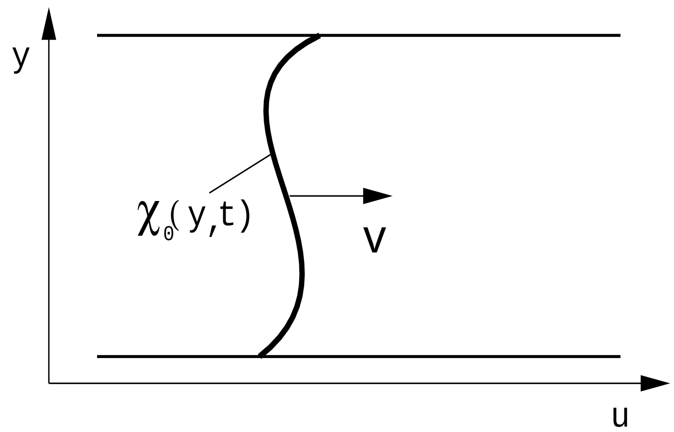
adjoint operator is

$$\Omega_R^\dagger(u) = D\frac{d^2}{du^2} - v\frac{d}{du} + \frac{\delta R}{\delta c_0}$$

eigenfunctions satisfy the orthonormality condition $\langle\zeta_i|\zeta_j\rangle = \delta_{ij}$ – assume eigenvalue problem is solved and determine the interfacial dynamics in 2d

Kuramoto-Sivashinsky equation

suppose a propagating front exists in a 2d system; interfacial profile $\chi_0(y,t)$



if transverse variations in front are not too large, solution to RD equation has the form

$$\mathbf{c}(\mathbf{r},t) = \mathbf{c}_0(u + \chi_0(y,t)) + \delta\mathbf{c}(u,y,t)$$

concentration field corresponding to 1d front solution evaluated at $u + \chi_0(y,t)$; accounts for displacement of front position from u arising from transverse variations in front position goal is to obtain equation of motion for the front profile, $\chi_0(y,t)$

linearizing about $\mathbf{c}_0$

$$\frac{\partial \delta \mathbf{c}(u,y,t)}{\partial t} + \frac{\partial \chi_0(y,t)}{\partial t}\zeta_0(u) = \left\{\Omega_R(u) + \mathrm{D}\frac{\partial^2}{\partial y^2}\right\}\delta \mathbf{c}(u,y,t)$$
$$+\mathrm{D}\left\{\frac{\partial^2 \chi_0(y,t)}{\partial y^2}\zeta_0(u) + \left(\frac{\partial \chi_0(y,t)}{\partial y}\right)^2 \zeta_0'(u)\right\}$$

where $\zeta_0'(u) = d\zeta_0(u)/du$

eigenfunctions of $\hat{\Omega}_R$ form a complete set in the u space; expand deviation in these eigenfunctions

$$\delta \mathbf{c}(x,y,t) = \sum_{i>0} \chi_i(y,t)\zeta_i(u)$$

expansion coefficients are $\chi_i(y,t)$

substitute expansion of $\delta c(u,y,t)$ in terms of eigenfunctions of 1d problem and project onto the interfacial mode $|\zeta_0\rangle$

eigenvalue problem for $\hat{\Omega}_R$ is not self-adjoint and left and right eigenfunctions corresponding to the zero eigenvalue needed

projecting onto $|\zeta_0\rangle$

$$\frac{\partial \chi_0(y,t)}{\partial t} = \sum_{i=0}^{\infty} \langle \zeta_0 | \mathrm{D} | \zeta_i \rangle \frac{\partial^2 \chi_i}{\partial y^2} + \langle \zeta_0 | \mathrm{D} | \zeta_0' \rangle \left(\frac{\partial \chi_0(y,t)}{\partial y} \right)^2$$

equation expresses $\dot{\chi}_0(y,t)$ in terms of $\chi_0(y,t)$ and all other $\chi_i(y,t)$, $(i > 0)$

to obtain a closed solution construct evolution equations for the $\chi_i(y,t)$ – project onto $|\zeta_i\rangle$ $(i \neq 0)$

$$\frac{\partial \chi_i(y,t)}{\partial t} = \sum_{j=0}^{\infty} \mathcal{W}_{ij}\chi_j + \langle \zeta_i|\mathrm{D}|\zeta_0'\rangle \left(\frac{\partial \chi_0(y,t)}{\partial y}\right)^2$$

matrix operator $\mathcal{W}$ has elements

$$\mathcal{W}_{ij} = \lambda_i \delta_{ij} + \langle \zeta_i|\mathrm{D}|\zeta_j\rangle \frac{\partial^2}{\partial y^2}$$

equation for χ_i, $(i > 0)$ may be solved formally treating χ_0 as an independent function to obtain a closed equation for $\chi_0(y,t)$; full solution does not admit a simple analysis

approximate solution for weakly curved interfaces

neglect spatial gradients along y in $\mathcal{W}$ and higher than second order derivative terms which are quadratic in χ_0 to get

$$\frac{\partial \chi_0(y,t)}{\partial t} = \langle \zeta_0 | \mathrm{D} | \zeta_0 \rangle \frac{\partial^2 \chi_0}{\partial y^2} + \langle \zeta_0 | \mathrm{D} | \zeta_0' \rangle \left(\frac{\partial \chi_0(y,t)}{\partial y} \right)^2 - \\ - \left[\sum_{i>0} \frac{\langle \zeta_0 | \mathrm{D} | \zeta_i \rangle \langle \zeta_i | \mathrm{D} | \zeta_0 \rangle}{\lambda_i} \right] \frac{\partial^4 \chi_0}{\partial y^4}$$

to simplify equation introduce the definitions:

$$\begin{aligned} \nu &= \langle \zeta_0 | \mathrm{D} | \zeta_0 \rangle \\ \kappa &= \sum_{i>0} \frac{\langle \zeta_0 | \mathrm{D} | \zeta_i \rangle \langle \zeta_i | \mathrm{D} | \zeta_0 \rangle}{\lambda_i} \end{aligned}$$

coefficients must be evaluated for problem of interest but, typically, sign of ν depends on diffusion coefficient ratio d while κ is positive

coefficient of nonlinear term in $\chi_0(y,t)$ may be evaluated explicitly – since $\langle \zeta_0 | \hat{\Omega}_R | \zeta_0 \rangle = 0$

$$\langle \zeta_0 | \mathrm{D} | \zeta_0' \rangle = -v/2$$

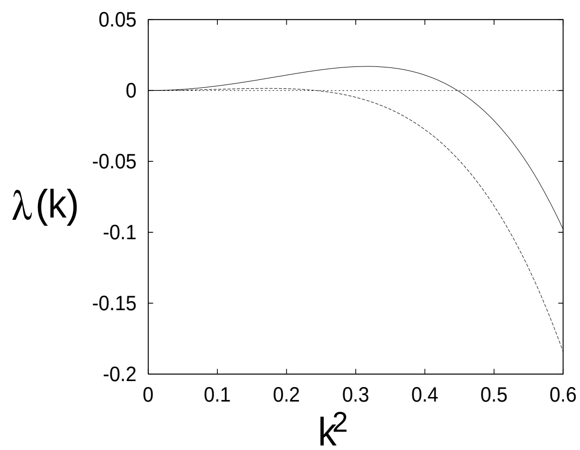
substituting these results we obtain the Kuramoto-Sivashinsky (KS) equation

$$\frac{\partial \chi_0(y,t)}{\partial t} = \nu \frac{\partial^2 \chi_0}{\partial y^2} - \frac{v}{2}\left(\frac{\partial \chi_0}{\partial y}\right)^2 - \kappa \frac{\partial^4 \chi_0}{\partial y^4}$$

that describes the evolution of the front profile

linear stability analysis and front dynamics – linearize and Fourier transform in y

$$\frac{\partial \chi_0(k,t)}{\partial t} = -(\nu k^2 + \kappa k^4)\chi_0(k,t) \equiv \lambda(k)\chi_0(k,t)$$

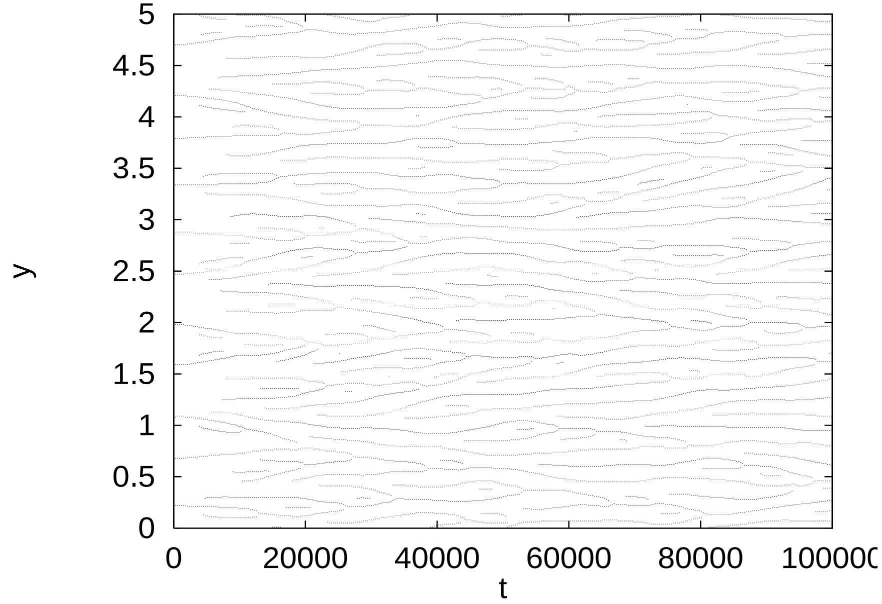


decay rate $\lambda(k) = -\nu k^2 - \kappa k^4$ for parameters above instability threshold; assumed $\nu < 0$ (diffusion destabilizing) and $\kappa > 0$ (fourth-order derivative term stabilizing at high wavenumbers)

• plot characteristic of a phase instability: a band of unstable wavenumbers extends from zero to some maximum value

• maximum in the dispersion relation lies at $k_m = (-\nu/2\kappa)^{1/2}$ and maximum unstable wavenumber is $k_{max} = (-\nu/\kappa)^{1/2}$ – long wavelength instability with dissipation at short wave lengths; characteristic dissipation length $\ell_c \approx 2\pi/k_m$

results of direct simulation of KS equation (in scaled units where $-\nu = \kappa = v/2 = 1$) – minima in field plotted

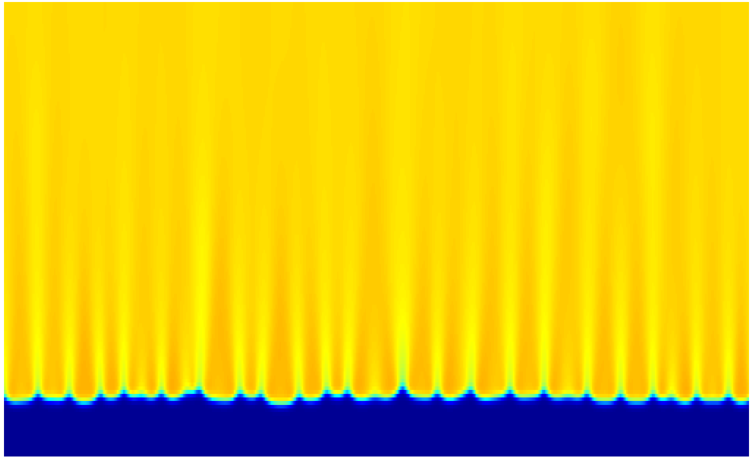


front dynamics exhibits spatio-temporal chaos an example: cubic autocatalysis – RD equation

$$\frac{\partial c_A(\mathrm{r},t)}{\partial t} = -k c_A(\mathrm{r},t) c_B(\mathrm{r},t)^2 + D_A \nabla^2 c_A(\mathrm{r},t)$$
$$\frac{\partial c_B(\mathrm{r},t)}{\partial t} = k c_A(\mathrm{r},t) c_B(\mathrm{r},t)^2 + D_B \nabla^2 c_B(\mathrm{r},t)$$

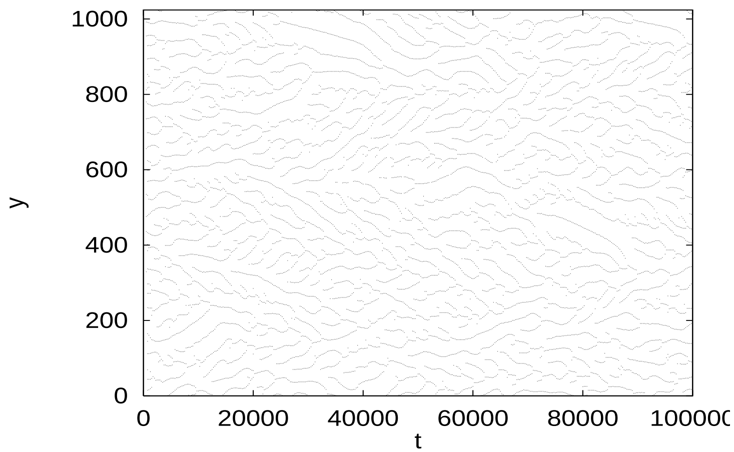
- small values of d – simulations show front is planar

- for sufficiently large d planar front unstable front has a complex cellular structure for $d = 5$



movie: www.chem.utoronto.ca/~rkapral

front dynamics of cubic autocatalysis in terms of space-time representation



space-time dynamics has same appearance as that for KS equation simulations

• to determine value of d at instability, extract front equation from full RD equation

• possible numerically for arbitrary diffusion coefficients

• analytical estimate of KS parameters using perturbation theory about equal diffusion case

planar front profiles for cubic autocatalysis

$$\left(d\frac{d^2}{du^2} + v\frac{d}{du}\right) c_A(u) - c_A(u)c_B^2(u) = 0 \; ,$$
$$\left(\frac{d^2}{du^2} + v\frac{d}{du}\right) c_B(u) + c_A(u)c_B^2(u) = 0$$

scaled time $t \longrightarrow kt$ and space $\mathbf{r} \longrightarrow (D_B/k)^{-1/2}\mathbf{r}$

boundary conditions are $c_A(\infty) = c_B(-\infty) = 1$ and $c_A(-\infty) = c_B(\infty) = 0$

equal diffusion – additional conservation law $c_A(u) + c_B(u) = 1$; pair of equations reduces to

$$\left(\frac{d^2}{du^2} + v\frac{d}{du}\right) c_A(u) - c_A(u)(1 - c_A(u))^2 = 0$$

with solution $c_A(u) = (1 + \exp(-vu))^{-1}$ and front speed $v = 1/\sqrt{2}$

• eigenvalues and right and left eigenvectors can be computed for $d = 1$ and KS parameters evaluated using perturbation theory: instability occurs when ν passes through zero at $d = d_c = 5/2$ – larger than $d = 1$ so perturbation theory doubtful

• direct numerical solution gives $d_c = 2.300$

experimental observation of a front instability – iodate-arsenous acid reaction

reaction rates for $IO_3^- = A$ and $I^- = B$ species are

$$R_A(c_A, c_B) = -R_B(c_A, c_B) = -(k_a + k_b c_B) c_B c_A c_{H^+}^2$$

RD equations are

$$\begin{aligned} \frac{\partial c_A(\mathrm{r}, t)}{\partial t} &= R_A(c_B, c_A) + D_A \nabla^2 c_A \ , \\ \frac{\partial c_B(\mathrm{r}, t)}{\partial t} &= R_B(c_B, c_A) + D_B \nabla^2 c_B \end{aligned}$$

in experiments reaction is carried out in thin (α-cyclodextrin=C) gel film; gel suppress convective effects and complexes with the autocatalyst $I^- = B$

$$B + C \rightleftharpoons C \cdot B$$

with equilibrium constant $K_C = c_{C \cdot B}/(c_C c_B)$

– species B exists in two forms: free B and complex $C \cdot B$; total concentration of B in both forms is $c_B^T = c_B + c_{C \cdot B} = c_B(1 + K_C c_C) \equiv c_B \sigma$

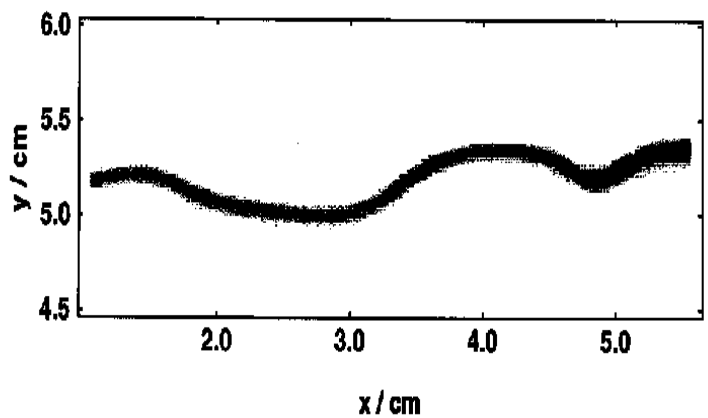
– assuming $C \cdot B$ does not diffuse, RD equation for total concentration of B is

$$\frac{\partial c_B(\mathrm{r}, t)}{\partial t} = \sigma^{-1}(R_B(c_A, c_B) + \sigma^{-1} D_B \nabla^2 c_B$$

by varying concentration of gel one may change the diffusion coefficient of the autocatalyst (and its reaction rate) and trigger a front instability planar front will be stable or unstable to transverse perturbations depending on the relative values of the diffusion coefficients of the iodine and iodate species

rapid diffusion of the autocatalyst iodine (B) causes the decay of perturbations, stabilizing a planar front while the diffusion of iodate (A) tends to be destabilizing

experiments confirm this scenario (Horvath and Showalter, 1995); low values of gel concentration – planar fronts; for gel concentrations beyond certain value front developed a transverse structure



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