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WAVE BIFURCATION IN MODELS FOR HETEROGENEOUS CATALYSIS

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Abstract. Heterogeneous Catalysis means that the reacting species and the catalyst do not have the same phase. A mathematical model for such a reaction has to take into account as well the complex kinetic processes and the spatial coupling. Depending on how strong the reactants are bound to the surface of the catalyst, the diffusion coefficients may vary by orders. Diffusion does not only smoothen the concentration gradients which are given by the initial data or result from the reaction kinetic processes. It is also able to induce instabilities which give rise to stable inhomogeneous steady or time-periodic solutions.

The conditions for such a bifurcation are rather restrictive but can be checked by only considering the kinetic part. Numerical simulations can be carried out more precisely in the neighborhood of the critical parameters.

1. Diffusion-Induced Instabilities

Diffusion-induced instability or **Turing instability** means that for a reaction-diffusion system of at least two scalar equations there is a spatially constant steady solution which is asymptotically stable in the sense of linearized stability in the space of constant functions. Nevertheless, it is unstable to spatially inhomogeneous perturbations.

Consider a parameter dependent system of N equations on a bounded domain with appropriate boundary conditions

$$u_t = D\Delta u + f(u, \Lambda)$$

with $D = \operatorname{diag}(d_1, \dots, d_N)$, $d_i \geq 0$. With regard to the phenomena of spatio-temporal oscillations, it is quite natural to ask if there are bifurcations from a stable zero solution to periodical solutions in space and time.

A wave bifurcation is a supercritical Hopf bifurcation from a stable steady constant solution to a stable periodic and nonconstant solution. The bifurcating solution in the case of Neumann boundary conditions then is a standing wave

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solution. The constant solution is an equilibrium point of the kinetic system $u_t = f(u, \Lambda)$. The aim is to destabilize this solution by diffusion coefficients, as in the case of the classical **Turing Instability**, where a single eigenvalue becomes positive and the bifurcating solution is a nonconstant steady state. If the real part of a single pair of complex eigenvalues of the linearization of the whole system at this point crosses the imaginary axis and the bifurcation is supercritical, there exists a nonconstant time-periodic solution.

To bifurcate from a constant to a spatio-temporal pattern one has to avoid the principal eigenvalue of $-\Delta$, which is zero, because it belongs to the eigenfunction that is the constant solution $\mathbb{1}$. This eigenvalue leads to the so called **space independent** Hopf bifurcation and one has to deal with oscillations of constant solutions.

2. Routh-Hurwitz Theory

For an $N \times N$ matrix A the characteristic polynomial is the sum of the symmetric functions σ_i with alternating signs.

$$\chi_A(\lambda) = \lambda^N - \sigma_1 \lambda^{N-1} + \cdots + (-1)^i \sigma_i \lambda^{N-i} + \cdots + (-1)^N \sigma_N \lambda^0 = 0\,.$$

The matrix H called **Hurwitz matrix** is filled according to the Hurwitz scheme with the coefficients of the characteristic polynomial. It is a square matrix of order N.

Their principale minors Δ_i, $i = 1, \ldots, N$ are the so called **Hurwitz determinants**.

The number of eigenvalues with positive real part of a linearization is the number of roots in the right half plane of its characteristic polynomial. This number can be computed with the help of the Routh-Hurwitz Theorem.

Theorem 2.1 (Routh-Hurwitz). *The number k of roots of a normed real polynomial of order N which lie in the right half plane is given by the formula*

$$k = V\left(1, \Delta_1, \frac{\Delta_2}{\Delta_1}, \frac{\Delta_3}{\Delta_2}, \cdots, \frac{\Delta_N}{\Delta_{N-1}}\right)$$

with Δ_i, $i = 1, \ldots, N$ the successive principal minors of a square matrix H of order N, and V the number of changes of sign of adjacent members of a finite sequence (Gantmacher [**4**, p. 230]*).*

If and only if all the Hurwitz determinants are positive, the number k is zero (this is the so called **Routh-Hurwitz Criterion**).

The idea behind the wave bifurcation uses Orlando's formula (see [**4**]).

$$\Delta_{N-1} = (-1)^{\frac{N(N-1)}{2}} \prod_{i<k}^{1\ldots N} (\lambda_i + \lambda_k)$$

from which follows that $\Delta_{N-1} = 0$ if and only if the sum of at least one pair of roots of the polynomial is zero. In particular this is true for a conjugate pair of pure imaginary roots. Together with the Routh-Hurwitz Theorem the case of a single pair of pure imaginary roots and all other roots with negative real part can be characterized by:

(a) $\Delta_i > 0 \quad \text{for} \quad i = 1, \ldots, N-2$
(b) $\Delta_{N-1} = 0$
(c) $(-1)^N \det A > 0$

The last inequality is needed to keep away from zero as a (multiple) root.

2.1 Application to Reaction-Diffusion Systems

The following notations are used: Let the tilde $\sim$ always denote the PDE system and let the index m indicate the respect to the appropriate mode via the eigenvalue ${\mu_m}^2$ of the negative Laplace operator with Neumann boundary conditions. If Ω is the unit interval, $-\Delta\xi_m = {\mu_m}^2\xi_m$ results in $\xi_m = \cos(\pi m x)$ the eigenfunction for the eigenvalue ${\mu_m}^2 = (\pi m)^2, m \in \mathbb{N}_0$. Claiming that all eigenfunctions of $\tilde{A}$ have the form $(c_1, c_2, c_3)^t\xi_m$ with coefficients $c_i \in \mathbb{R}$, they form three-dimensional functional subspaces of the solution space. The diffusion coefficients appear in the Jacobian as $d_{im} := d_i{\mu_m}^2$, $i = 1, \ldots, N$.

$$\tilde{A}(\mu_m) = A - D(\mu_m) = (a_{ij})_{i,j \in \{1,\ldots,N\}} - \text{diag}\,(d_{1m}, \ldots, d_{Nm})$$

The trace of a submatrix of A consisting of the i_1 and i_2 column and row will be denoted as $\text{tr}\,(A_{i_1 i_2})$. The minors with the same columns as rows will be abbreviated with $|A_{i_1 i_2}|$.

For reaction-diffusion systems, the number of eigenvalues in the right half plane is the sum

$$\tilde{k} := \sum_{m=0}^{\infty} k_m,$$

where the nonnegative integer k_m belongs to the m^{th} spatial mode. Therefore one has to compute the Hurwitz determinants of all $\tilde{A}(\mu_m)$. The sum $\tilde{k}$ is zero if and only if the sign conditions are fulfilled for all m, that is $\tilde{\Delta}_i(\mu_m) > 0$, $i = 1, \ldots, N$ for all m, or, in short, $\tilde{\Delta}_i > 0$. If no special mode is explicitly indicated, this notation refers to all modes.

2.1.1 Planar Systems

The Hurwitz determinants for $N = 2$ give simple conditions for stable nodes.

$$H = \begin{pmatrix} -\text{tr}\,A & 0 \\ 1 & \det A \end{pmatrix}, \qquad \begin{array}{ll} \Delta_1 = -\text{tr}\,A & > 0 \\ \Delta_2 = -\text{tr}\,A \,\det A & > 0 \end{array}$$

Two variables reaction-diffusion systems with **activator-inhibitor** kinetic are widely studied (see for example [**3**]). The variable with positive diagonal entry in the Jacobian is called the activator, the variable with negative entry is the inhibitor.

Then an appropriate diffusion coefficient d_1 can make the term $a_{11}d_2 + a_{22}d_1$ positive, although the trace $a_{11}+a_{22}$ is negative, and thereby change the sign of the determinant in the presence of spatial inhomogeneities. This is often abbreviated in the rule:

$$\frac{d_1}{d_2} > \frac{-a_{11}}{a_{22}} > 1 \qquad \Rightarrow \qquad \text{The inhibitor has to diffuse faster.}$$

For a wave bifurcation, when $\tilde{k}$ increases by 2 and $\tilde{k}_m$ is even, the $(-1)^N \det \tilde{A}(\mu_m)$ is positive. In two variables systems, the Hopf bifurcation can only be realized when the trace becomes positive. But in the regular as well as in the singular perturbation, that is $d_1 \to \infty$ or $d_2^{-1} \to \infty$, the trace is always diminished by a diffusion operator, so that $\operatorname{tr} A$ has to be nonnegative, contradicting the requirement of a stable equilibrium. The number of equations has to be increased to get a diffusion-induced supercritical Hopf bifurcation.

It is not possible to get a wave bifurcation for a two variables system (see Turing [**8**], and therein the cases e) and f): **e)** Oscillatory case with a finite wave-length and **f)** Oscillatory case with extreme short wave-length, [...] possibilities [that] can only occur with three or more morphogens. [...] no attempt was made to develop formulae for these.).

2.1.2 Systems of Three Equations

The eigenvalues of a system of three equations are the roots of

$$\chi_A(\lambda) = \lambda^3 - \operatorname{tr} A\ \lambda^2 + \sum_{1\le i<j\le 3} |A_{ij}|\ \lambda - \det A = 0$$

and for $N = 3$ the Hurwitz matrix is

$$H = \begin{pmatrix} -\operatorname{tr} A & -\det A & 0 \\ 1 & \sum |A_{ij}| & 0 \\ 0 & -\operatorname{tr} A & -\det A \end{pmatrix} = \begin{pmatrix} -\sigma_1 & -\sigma_3 & 0 \\ 1 & \sigma_2 & 0 \\ 0 & -\sigma_1 & -\sigma_3 \end{pmatrix}$$

with successive Hurwitz determinants to be computed using the coefficients $(-1)^i \sigma_i$, $i = 1, 2, 3$ of the symmetric functions.

$$\begin{aligned} \Delta_1 &= -\operatorname{tr} A &&= -\sigma_1 \\ \Delta_2 &= -\operatorname{tr} A(\textstyle\sum |A_{ij}|) + \det A &&= -\sigma_1\sigma_2 + \sigma_3 \\ \Delta_3 &= -\Delta_2\ \det A &&= -(-\sigma_1\sigma_2 + \sigma_3)\sigma_3 \end{aligned}$$

All three eigenvalues have negative real parts if $\Delta_i > 0$ for $i = 1, 2, 3$ (Routh-Hurwitz Criterion). This is equivalent to simultaneously satisfying $-\sigma_1 > 0$, $-\sigma_1\sigma_2 + \sigma_3 > 0$ and $-\sigma_3 > 0$.

The conditions $-\sigma_1 > 0$ and $-\sigma_3 > 0$ are as easy to check as in the case of planar systems. The second Hurwitz determinant is critical at the surface $\sigma_1\sigma_2 = \sigma_3$ which is a hyperbolic paraboloid. For a kinetic system of three equations the number k computes as follows:

$$k = V\left(1, \Delta_1, \frac{\Delta_2}{\Delta_1}, \frac{\Delta_3}{\Delta_2}\right) = V(1, \Delta_1, \Delta_3) + V(1, \Delta_2)$$
$$= V(1, \Delta_1) + V(\Delta_1, \Delta_3) + V(1, \Delta_2)$$

To illustrate the formal computations of k, the following figures give an impression where the regions of stable nodes are ($k = 0$, shaded areas) and which lines or surfaces separate the regions for the various numbers of k in two and three variables systems. In contrast to Figure 1 the three variables system in Figure 2 shows the possibility of a linearization A having a negative trace and a determinant indicating an even number k, without necessarily being in the area of stable nodes.

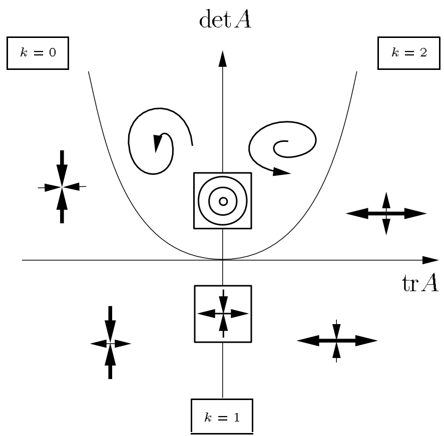

Figure 1. For a two variables system a sign change of the trace results in an increase of k by 2.

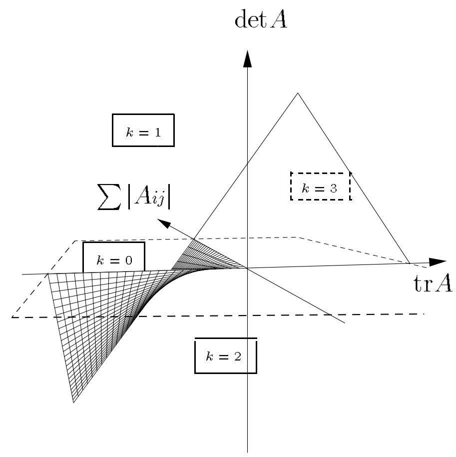

Figure 2. For a three variables system the surface $\sigma_1\sigma_2 = \sigma_3$, $\sigma_2 > 0$, has to be crossed to increase k by 2.

Crossing the surface $\sigma_1\sigma_2 = \sigma_3$ has no effect on k for $\sigma_2 < 0$. Here only the sign of $\sigma_3 = \det A$ decides if k is one or two.

Qualitatively, the pictures do not change when considering $\tilde{A}(\mu_m)$ and $\tilde{k}_m$ instead of A and k, respectively.

If a single diffusion coefficient is able to induce a destabilization of the stable zero solution, then k is zero and at least one $\tilde{k}_m$ has become nonzero on varying this coefficient.

On condition that $-\operatorname{tr} A > 0$, $(V(1, \Delta_1) = 0)$ it yields $-\operatorname{tr} \tilde{A} > -\operatorname{tr} A > 0$, since diffusion only decreases the trace. Therefore $-\operatorname{tr} \tilde{A} = \tilde{\Delta}_1$ is always positive. Since

$V(\tilde{\Delta}_1, \tilde{\Delta}_3) = 0$ is equivalent to $(-\mathrm{tr}\,\tilde{A})(-\det \tilde{A})\tilde{\Delta}_2 > 0$, the expressions $-\det \tilde{A}$ and $\tilde{\Delta}_2$ have to be of the same sign in order not to change the sum $\tilde{k}$.

What can be observed by now is that a change in sign of $\det \tilde{A}(\mu_m)$ for a single m gives exactly one positive real eigenvalue as well as in the two-dimensional case. In general a Turing bifurcation from a stable constant solution to a stable steady but nonconstant solution can be decided by the sign of the determinant.

Consider the case when $\tilde{k}$ increases by 2 in the system of three equations. This is equivalent to the question: Can diffusion change the sign of the second Hurwitz determinant without changing the sign of the first and third?

That means that $-\mathrm{tr}\,\tilde{A} > 0$ and $-\det \tilde{A} > 0$ for all m whereas

$$\tilde{\Delta}_2(\mu_m) = -\mathrm{tr}\,\tilde{A}(\mu_m) \sum_{1\le i<j\le 3} |\tilde{A}(\mu_m)_{ij}| \; + \; \det \tilde{A}(\mu_m)$$

changes sign for a single m, but $\tilde{\Delta}_2 > 0$ for all $j \neq m$. If this is the case, generically two complex conjugate roots cross the imaginary axis and the equilibrium is no longer asymptotically stable. A critical diffusion coefficient d_i^* leads to $\tilde{\Delta}_2(\mu_m, d_i^*) = 0$.

Remark 2.1. The case of negative $\mathrm{tr}\, A$ and thereby negative $\mathrm{tr}\,\tilde{A}$ is assumed. Generically either $\det \tilde{A}(\mu_m)$ or $\tilde{\Delta}_2(\mu_m)$ changes sign first.

In the case of a first change of sign of $\det \tilde{A}(\mu_m)$, this is the usual Turing bifurcation to a steady state solution. If afterwards $\tilde{\Delta}_2$ changes sign, this can only happen for $\sum |\tilde{A}(\mu_m)_{ij}| < 0$ where it has no effect on $\tilde{k}_m$. If the sign of $\det \tilde{A}(\mu_m)$ changes back in this area, two positive (real) eigenvalues exist, which of course can meet and become a complex conjugate pair. But such oscillating solutions do not necessarily give rise to a time-periodic solution.

In case of $\tilde{\Delta}_2(\mu_m)$ changing sign first while $\mathrm{tr}\,\tilde{A}$ and $\det \tilde{A}$ are negative, the number $\tilde{k}$ of eigenvalues in the right half plane increases by two so that there is a pair of pure imaginary eigenvalues.

With Orlando's formula it is clear that the eigenvalue condition for the Hopf bifurcation in a three variables system depends on the second Hurwitz determinant.

The terms of the second Hurwitz determinant $\tilde{\Delta}_2(\mu_m, d_1, d_2, d_3)$ which are not in Δ_2 can cause a change in sign.

$$\begin{aligned}
&\tilde{\Delta}_2(\mu_m, d_1, d_2, d_3)\\
&\quad= \left[2d_1d_2d_3 + (d_1)^2(d_2+d_3) + (d_2)^2(d_1+d_3) + (d_3)^2(d_1+d_2)\right] \left({\mu_m}^2\right)^3\\
&\quad - \left[\mathrm{tr}\,(A_{23})(d_1)^2 + \mathrm{tr}\,(A_{13})(d_2)^2 + \mathrm{tr}\,(A_{12})(d_3)^2\right.\\
&\quad + \left. 2\mathrm{tr}\,A(d_1d_2 + d_1d_3 + d_2d_3)\right] \left({\mu_m}^2\right)^2 \qquad (1)\\
&\quad + \left[(|A_{12}| + |A_{13}| + \mathrm{tr}\,(A_{23})\mathrm{tr}\,A)d_1 + (|A_{12}| + |A_{23}| + \mathrm{tr}\,(A_{13})\mathrm{tr}\,A)d_2\right.\\
&\quad + \left.(|A_{13}| + |A_{23}| + \mathrm{tr}\,(A_{12})\mathrm{tr}\,A)d_3\right] {\mu_m}^2\\
&\quad + \Delta_2
\end{aligned}$$

3. Wave Bifurcation in Case of $d_1 \neq 0$

The wave bifurcation cannot occur for systems with less than three equations. However, even in the case of three equations, a rule like that in the case of two equations and **activator-inhibitor kinetic** cannot be read off the Hurwitz determinant $\tilde{\Delta}_{N-1} = \tilde{\Delta}_2$ immediately. In order to derive conditions on the kinetic system that allow a wave bifurcation, consider some positive d_1 and a singular limit with $d_2 \to 0$ and $d_3 \to 0$. The formal limit

$$\lim_{\substack{d_2\to 0\\ d_3\to 0}} \tilde{\Delta}_2(\mu_m, d_1, d_2, d_3) = \tilde{\Delta}_2(\mu_m, d_1, 0, 0)$$

$$= -\mathrm{tr}\,(A_{23})(d_1{\mu_m}^2)^2 + (|A_{12}| + |A_{13}| + \mathrm{tr}\,(A_{23})\mathrm{tr}\,A)\, d_1{\mu_m}^2 + \Delta_2 \tag{2}$$

results in a parabola $\tilde{\Delta}_2(\mu_m, d_1, 0, 0) =: \tilde{\Delta}_2(d_1{\mu_m}^2)$ in d_1. The following conditions for a change in sign of $\tilde{\Delta}_2(d_1{\mu_m}^2)$ by the diffusion coefficient d_1 and the m^{th} spatial mode imply wave bifurcation.

Conditions for Wave Bifurcation:

(C1) $-\mathrm{tr}\,A > 0$
(C2) $\Delta_2 = -\mathrm{tr}\,A(\sum |A_{ij}|) + \det A > 0$
(C3) $-\det A > 0$
(C4) $-\mathrm{tr}\,(A_{23}) > 0$
(C5) $-(|A_{12}| + |A_{13}| + \mathrm{tr}\,(A_{23})\mathrm{tr}\,A) > 0$
(C6) $(|A_{12}| + |A_{13}| + \mathrm{tr}\,(A_{23})\mathrm{tr}\,A)^2 + 4\mathrm{tr}\,(A_{23})\Delta_2 > 0$

Remark 3.1. The conditions (C1)–(C3) guarantee a stable constant equilibrium of the kinetic system. The normed parabola to be discussed is

$$\frac{1}{-\mathrm{tr}\,(A_{23})}\tilde{\Delta}_2(d_1{\mu_m}^2) = (d_1{\mu_m}^2)^2 - \frac{(|A_{12}| + |A_{13}| + \mathrm{tr}\,(A_{23})\mathrm{tr}\,A)}{\mathrm{tr}\,(A_{23})} d_1{\mu_m}^2 - \frac{\Delta_2}{\mathrm{tr}\,(A_{23})}.$$

This is the normed second Hurwitz determinant depending on the diffusion coefficient d_1 and the m^{th} spatial mode. (C4) is needed for the right opening of the parabola, (C5) is needed for positive real parts of the roots and (C6) is sufficient for the existence of two real roots $\nu^{\pm} > 0$. Now the second Hurwitz determinant becomes negative for $d_1{\mu_m}^2$ in the open interval (ν^-, ν^+) and this results in complex eigenvalues for the Jacobian $\tilde{A}(\mu_m)$. Note that all these conditions only concern the kinetic system.

Theorem 3.1. *Consider system* (3) *of a parabolic and two ordinary differential equations that has an asymptotically stable constant equilibrium E^* (i.e.* (C1)–(C3) *are satisfied).*

$$\begin{aligned} u_{1_t} &= B(u_1, d_1) + g_1(u_1, u_2, u_3) \\ u_{2_t} &= \qquad\qquad\quad\; g_2(u_1, u_2, u_3) \quad \text{in } \Omega \times (0, T^+) \\ u_{3_t} &= \qquad\qquad\quad\; g_3(u_1, u_2, u_3) \end{aligned} \tag{3}$$

and appropriate boundary conditions such that the spectrum of $-B(\,\cdot\,, d_1)$ *is non-negative, real and discrete.*

The linearized kinetic system at the constant solution fulfills (C4)–(C6). *Now*

$$\tilde{\Delta}_2(d_1^*{\mu_m}^2) = 0 \quad \text{for } m$$
$$\tilde{\Delta}_2(d_1^*{\mu_l}^2) > 0 \quad \text{for } l \neq m$$

for a single $m \in \mathbb{N}$, *where* ${\mu_m}^2$ *denotes the* m^{th} *eigenvalue of* $-B$. *Then*

(i) $\{\pm i\omega\}$ *are simple eigenvalues of* $\tilde{A}$, *where* $\omega > 0$,
(ii) *there are no eigenvalues of the form* $ik\omega$ *for* $k \in \mathbb{Z} \setminus \{\pm 1\}$ *and*
(iii) $\partial_{d_1} \mathrm{Re}\rho(d_1^*) \neq 0$, *where* $\rho(d_1)$ *is the unique continuation of the eigenvalue of* $\tilde{A}$ *for* d_1 *in a neighborhood of the critical* d_1^* *satisfying* $\rho(d_1^*) = i\omega$.

Then the system (3) *has a unique one-parameter family of noncritical nonconstant periodic orbits in an appropriate neighborhood; precisely for* $u := (u_1, u_2, u_3)$, *the minimal period* T *and the bifurcation parameter* d_1 *it yields*

$$(u(\cdot), T(\cdot), d_1(\cdot)) \ \in \ C^\infty((-\varepsilon, \varepsilon), V \times \mathbb{R} \times \mathbb{R})$$

satisfying

$$(u(0), T(0), d_1(0)) = \left(E^*, \frac{2\pi}{\omega}, d_1^*\right)$$

such that

$$\gamma(s) := \gamma(u(s))$$

is a noncritical nonconstant periodic orbit of system (3) *of period* $T(s)$ *passing through* $u(s) \in V$ *for* $0 < s < \varepsilon$.

Remark 3.2. Via cyclic changes of the indices $i = 1, 2, 3$ in (C4)–(C6), Theorem 3.1 can be formulated for a spatial operator in the second or third equation.

Sketch of the Proof (of Theorem 3.1*).* The local existence of a bifurcating periodic solution follows from Crandall, Rabinowitz [**1**] in the case that (i)–(iii) can be satisfied.

These three conditions are a consequence of the conditions imposed on the kinetic equations, i.e. (C1)–(C6), and those are obtained from conditions (a), (b) and (c).

It remains to prove that $-\det \tilde{A}(\mu_m, d_1, 0, 0) > 0$ (see Figure 2), which guarantees an even number of eigenvalues with positive real part. Consider the following limit:

$$\lim_{\substack{d_2 \to 0 \\ d_3 \to 0}} \left(-\det \tilde{A}(\mu_m, d_1, d_2, d_3)\right) =: -\det \tilde{A}(d_1 {\mu_m}^2) = |A_{23}| d_1 {\mu_m}^2 - \det A \tag{4}$$

If $|A_{23}|$ is positive, then $-\det \tilde{A}(d_1{\mu_m}^2) > -\det A > 0$ for all d_1 and all m, so that there is no change in sign of the determinant. The above conditions already imply that $|A_{23}|$ is positive, and this is proved in the following lemma.

Lemma 3.1. *Let A be such that* (C1)–(C5) *are fulfilled. Then* $|A_{23}|$ *is positive.*

Proof.

$$\begin{aligned}(C5) &\Rightarrow |A_{12}| + |A_{13}| + \mathrm{tr}\,(A_{23})\mathrm{tr}\,A < 0\\ &\Leftrightarrow |A_{12}| + |A_{13}| < -\mathrm{tr}\,(A_{23})\mathrm{tr}\,A \overset{(C1)(C4)}{<} 0\\ &\Rightarrow |A_{12}| + |A_{13}| < 0\end{aligned}$$

Assume $|A_{23}| \leq 0$, then

$$0 < \mathrm{tr}\,A\Big(|A_{12}| + |A_{13}| + |A_{23}|\Big) \overset{(C2)}{<} \det A \overset{(C3)}{<} 0$$

which is a contradiction. □

The following figure illustrates the picking of a single mode that becomes unstable.

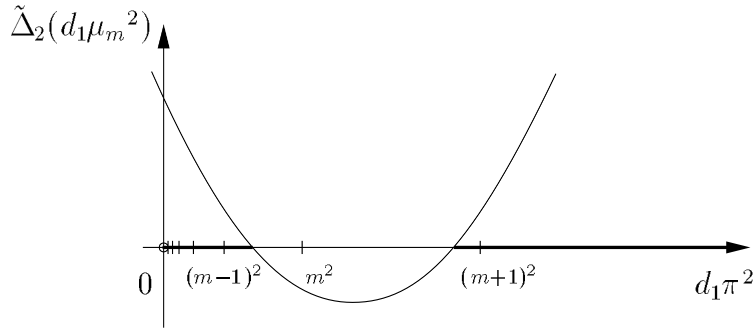

Figure 3. The parabola $\tilde{\Delta}_2(d_1\mu_m{}^2)$ selects a single mode of oscillating solutions when the kinetic system is regularly perturbed with a diffusion operator in a single equation (here for the Laplace operator on a one-dimensional domain).

For the wave bifurcation $|A_{23}|$ has to be positive. But since equation (2) might have no positive roots this is not sufficient. A simple computation shows that existence of positive roots can only be achieved if (C5) and (C6) are satisfied.

Nevertheless the positivity of $|A_{23}|$ can be used as a first check whether wave bifurcation is possible or not. A submatrix with only positive Hurwitz determinants (for a 2×2 matrix that means negative trace and positive determinant) will be called **stabilizing**. There are two different cases that can be distinguished for system (3) at an asymptotically stable constant solution:

Remark 3.3. If the constant steady solution satisfies (C1)–(C3) and $|A_{23}| < 0$ then there is a critical diffusion coefficent d_1^* for an appropriate mode m which causes a bifurcation to a Turing type stationary solution. The submatrix is **not stabilizing** in this case.

A Turing type stationary solution can also be caused by a simultaneous change of sign of $\det \tilde{A}(\mu_m)$ and $\tilde{\Delta}_2(\mu_m)$. For negative $\mathrm{tr}\,\tilde{A}$ this implies $\sum|\tilde{A}_{ij}| = 0$. In the limit of $d_2 = d_3 = 0$ the terms to become zero are $-\det \tilde{A}(d_1{\mu_m}^2) = -\det A + d_1{\mu_m}^2|A_{23}|$ and $\sum|\tilde{A}(d_1{\mu_m}^2)_{ij}| = \sum|A_{ij}| - d_1{\mu_m}^2\mathrm{tr}\,(A_{23})$. This means $|A_{23}| < 0$ and $\mathrm{tr}\,(A_{23}) > 0$. Again the submatrix is **not stabilizing**.

If the constant steady solution satisfies (C1)–(C6), there are critical diffusion coefficents d_1^* causing a Hopf bifurcation. Conditions (C4) and (C5) imply $\mathrm{tr}\,(A_{23}) < 0$ and $|A_{23}| > 0$. This submatrix is **stabilizing**.

The results of the computations on the stability at the equilibrium point can now be summarized.

Remark 3.4. In a stable constant solution the sum $\sum|A_{ij}|$ is positive. For wave bifurcation at least one $|A_{jk}|$ has to be negative to satisfy (C5). The spatial operator occurs in the j^{th} or k^{th} equation. The submatrix in which no spatial operator occurs is **stabilizing**.

3.1 Estimation of Mode Selection

Further investigations of the wave bifurcation concern the biggest mode M that can be isolated. For one-dimensional domains Ω and the Laplace operator, this wavenumber is estimated by $\nu^{\pm}$, the roots of $\tilde{\Delta}_2(d_1{\mu_m}^2)$ (see Figure 3). For all integers m less than M, a bifurcation to a wave solution with the appropriate wavenumber can be arranged either for shrinking or growing d_1. But for wavenumbers greater than M, at least two modes are within the unstable area. This does not mean that there is no such solution, but it strongly depends on the initial data which solution will survive.

Lemma 3.2. *The biggest wavenumber M for which only a single mode is destabilized in a one space dimensional system can be estimated by* $\mu^- := \dfrac{2\nu^-}{\nu^+ - \nu^-}$ *with*

$$\mu^- - 1 < M < \mu^- + \frac{1}{2}$$

where $\nu^{\pm}$ are the roots of the parabola $\tilde{\Delta}_2(d_1{\mu_m}^2)$ of Theorem 3.1.

Proof. For the proof see [**6**]. □

3.2 Considerations on Stability

Once the maximal M is found, the critical $d_{1_{M_r}}$ for which there is bifurcation to the standing wave solution for shrinking $d_1 < d_{1_{M_r}}$ can be calculated easily. In the same way a critical $d_{1_{M_l}}$ is calculated for $M - 1$, and there is a bifurcation to a time-periodic solution for growing $d_1 > d_{1_{M_l}}$. The two possibilities correspond to the situations of either touching the square number with the right wing or with the left wing of the parabola. This yields the following sequence

$$\cdots\ d_{1_{M_l}} < d_{1_{M_r}} < d_{1_{(M-1)_l}} < d_{1_{(M-1)_r}}\ \cdots$$

and there is no mode destabilized within the open interval $(d_{1_{M_r}}, d_{1_{(M-1)_l}})$. So the mode destabilization is well separated up to the mode with the maximal number which can be estimated with Lemma 3.2.

In contrast to the transcritical bifurcation the stability in case of a Hopf bifurcation has to be computed from third derivatives of the vector field.

Note that ω as well as the root z_3 do not depend on μ_m and that therefore only the basis of the kernel N changes.

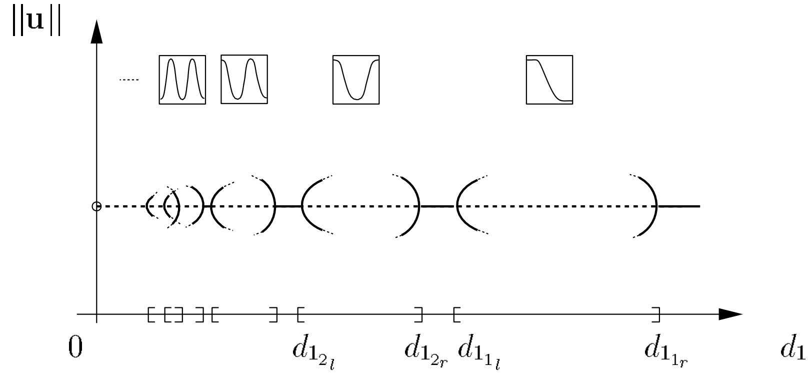

Figure 4. The branches of periodic solutions are sketched as maximal amplitude of the solution in an appropriate norm versus the diffusion coeffcient d_1 as bifurcation parameter. The mode destabilization is well separated up to the mode with the maximal number that can be estimated with Lemma 3.2.

4. Application to Autocatalytic Surface Reactions

The following system of three equations has a background as an autocatalytic reaction-diffusion system. It is derived with the help of stoichiometric network analysis (see Eiswirth [**2**]). It may be interpreted to describe a surface reaction enhanced by a reconstruction process of the surface.

In this network it is essential to have three equations. Figure 5 sketches a process in which a species w depends quadratically on itself and on an additional species v. While consuming two parts of w, there are four parts produced by the loop indicated by the parameter p_4.

This network gives rise to the following differential equations with kinetic parameters p_1 to p_4, assuming a diffusion matrix with diagonal entries d_1 to d_3. The

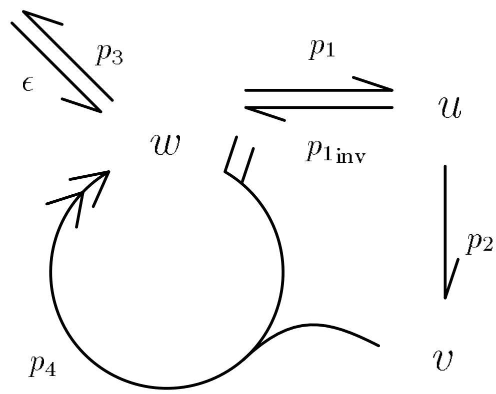

Figure 5. This stoichiometric network sketches an autocatalytic process. Reaction kinetic parameters are written to the corresponding arrows which indicate the stoichiometry by the numbers of flags and feathers.

integer multiples come from the stoichiometry of the chemical network, so that all parameters can first be set identical one.

No flux boundary conditions on the cylinder $\partial\Omega \times (0, T]$ are considered.

$$\begin{aligned} \dot{u} &= d_1 \Delta u - p_{1_{\text{inv}}} u - 2p_2 u + 3p_1 w \\ \dot{v} &= d_2 \Delta v + p_2 u - p_4 v w^2 \\ \dot{w} &= d_3 \Delta w + p_{1_{\text{inv}}} u - 3p_1 w - p_3 w + 2p_4 v w^2 + \epsilon \end{aligned} \quad \text{in } \Omega \times (0, T] \tag{5}$$

Solving the system for constant equilibria yields a single solution that requires

$$u = \frac{3\epsilon p_1}{(p_{1_{\text{inv}}} + 2p_2)p_3}, \ v = \frac{3p_1 p_2 p_3}{(p_{1_{\text{inv}}} + 2p_2)\epsilon p_4}, \ w = \frac{\epsilon}{p_3}.$$

Setting the parameters identical one yields an asymptotically stable equilibrium $E^* = (u^*, v^*, w^*)^t = (1, 1, 1)^t$. This equilibrium does not change when the paramters p_3 and ϵ are varied simultaneously such that $\epsilon/p_3 \equiv 1$.

The linearization at this point is

$$\begin{aligned} A|_{E^*} &= \begin{pmatrix} -(p_{1_{\text{inv}}} + 2p_2) & 0 & 3p_1 \\ p_2 & -p_4(w^*)^2 & -2p_4 v^* w^* \\ p_{1_{\text{inv}}} & 2p_4(w^*)^2 & -3p_1 - p_3 + 4p_4 v^* w^* \end{pmatrix} \\ &= \begin{pmatrix} -3 & 0 & 3 \\ 1 & -1 & -2 \\ 1 & 2 & 1 - p_3 \end{pmatrix} \end{aligned}$$

with the following set of eigenvalues

$$\left\{-3,\ -\frac{1}{2}\left(p_3-\sqrt{{p_3}^2-4p_3}\right),\ -\frac{1}{2}\left(p_3+\sqrt{{p_3}^2-4p_3}\right)\right\}$$

indicating an asymptotically stable oscillatory fixed point.

Now the paramters p_3 and ϵ are varied simultaneously for small values of p_3.

A nonzero diffusion term in the v-equation can be ruled out as a source for the instability by a first check whether the submatrix is **stabilizing**: $|A_{13}| = -3(2-p_3)$ is negative for $p_3 < 2$.

Diffusion in the w-equation fails in principle for condition (C5), that is $-(|A_{23}|+|A_{13}| + \mathrm{tr}\,(A_{12})\mathrm{tr}\,A) = 8(1-p_3) - 17$ which is negative.

For a nonzero diffusion coefficient d_1 the condition (C5) is $-(|A_{12}| + |A_{13}| + \mathrm{tr}\,(A_{23})\mathrm{tr}\,A) = -{p_3}^2 - 6p_3 + 3$ which is positive for positive $p_3 < -3 + 2\sqrt{3}$.

To fulfill condition (C6) the parameter p_3 has to solve ${p_3}^4 - 4{p_3}^3 - 6{p_3}^2 - 36p_3 + 9 > 0$ and this expression is positive for $p_3 < 0.23904883974$. Note that the system gets singular for $p_3 \to 0$. For values of p_3 inbetween zero and its upper limit critical diffusion coefficients ${d_1}^*$ can be determined for each wavenumber up to the maximal wavenumber to be estimated with Lemma 3.2. The closer p_3 gets to its upper limit, the bigger is this maximal number.

The conditions (C1)–(C6) are fulfilled for $d_1 \neq 0$ and $d_2 = d_3 = 0$. If the mobility of a single variable is considered as a source of a standing wave solution, only the u-species is able to destabilize the stable constant solution.

Existence of the solution is guaranteed via the asymptotic stability of E^*. This yields a neighborhood of the fixed point that is positively invariant such that the reaction diffusion system (also in case of zero diffusion coefficients) has a solution for all time if the initial data is within this neighborhood (see Smoller [**7**], Invariant regions).

The numerical result of Figure 6 can be predicted.

Numerical parameters

A sustained oscillation in space and time for the above model of an autocatalytic reaction can also be verified numerically. The discretized system of ordinary differential equations is solved with the LSODE package (see Hindmarsh [**5**]), using numerical estimates of the Jacobian matrix, and a relative error tolerance of 10^{-8} and an absolute error tolerances of 10^{-12}. The maximal stepsize in time was allowed to be 0.01, and the appropriate space discretization for a diffusion coefficient $d_1 = 0.003$ then is 182 gridpoints on a unit interval. Time discretization is done implicitly.

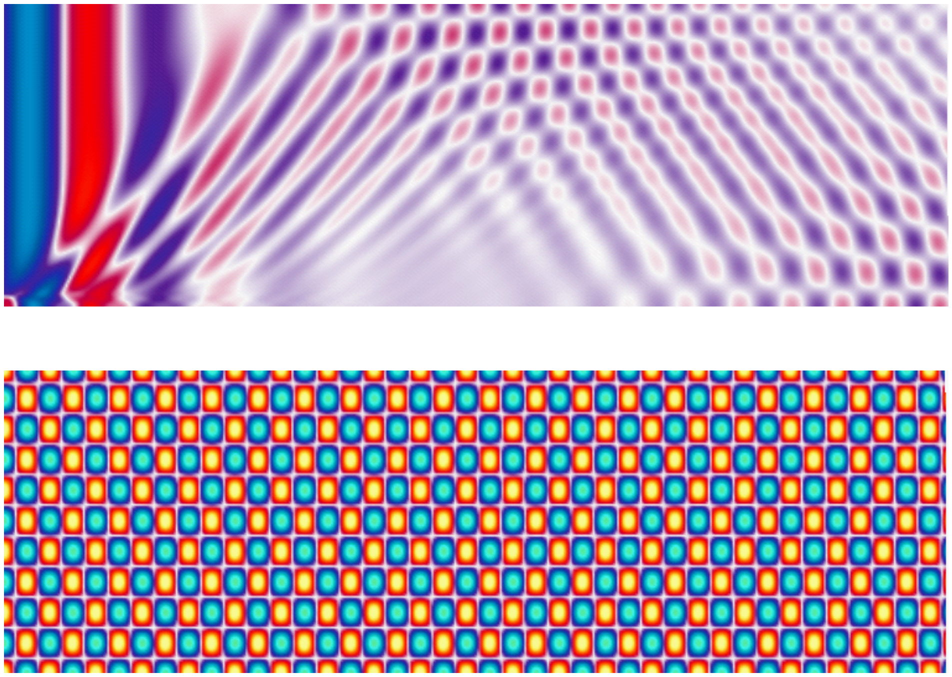

Figure 6. The horizontal axis shows the temporal evolution of (vertical) one-dimensional spatially nonuniform initial data (above, time steps 1-100) to a standing wave pattern (below, time steps 4900-5000). The color ranges from light blue (minimum) to light yellow (maximum) and indicates the w-equation.

4.1 An Example from the Literature

Zhabotinsky et al. [**9**] also numerically show the phenomenon of wave bifurcation in a three variables system modelling cubic autocatalysis. Their kinetic system is coupled with the same simple diffusion terms and looks as follows:

$$\begin{aligned} \dot{u} &= d_1 \Delta u + m\left(-uv^2 + w^2 - \frac{au}{g+u}\right) \\ \dot{v} &= d_2 \Delta v + n(uv^2 - v + b) \qquad \text{in } \Omega \times (0,T] \\ \dot{w} &= d_3 \Delta w + u - w \end{aligned} \tag{6}$$

with Neumann boundary conditions at the cylinder wall. The authors use the same solver with the same tolerances and discretization schemes.

They perform the simulations with zero diffusion coefficients in the first and second equation. Other parameters are $m = 28$, $a = 0.9$, $n = 15.5$, $b = 0.2$, $d_3 = 1$ and a length of the interval Ω of $L = 20$ units. The initial conditions are chosen to be the stationary constant solution of approximately $(u, v, w) =$

$(1.1308, 0.5787, 1.1308)$ where only a single one of the 300 gridpoints on the boundary of the domain is perturbed slightly. The standing wave result with a wavenumber of twelve can be reproduced easily. For further numerical experiments, they vary the length of the domain and the kinetic parameter m.

The same set of parameters as above but different initial data, as for instance a bigger part of the interval on which the stationary solution is perturbed or initial data which are perturbed randomly on every gridpoint in a neighborhood of the stationary solution, lead to a standing wave with a wavenumber of eleven. Since $d_3 = 1$ and a length of Ω of $L = 20$ is equivalent to a diffusion coefficient $d_3 = 0.0025$ and $L = 1$, this result can be interpreted with the help of Figure 7. The roots $\nu^{\pm}$ of the parabola of Theorem 3.1 provide a left and right critical diffusion coefficient for each mode. For the above system, the stationary solution is destabilized for perturbations of wavenumber eight up to fifteen.

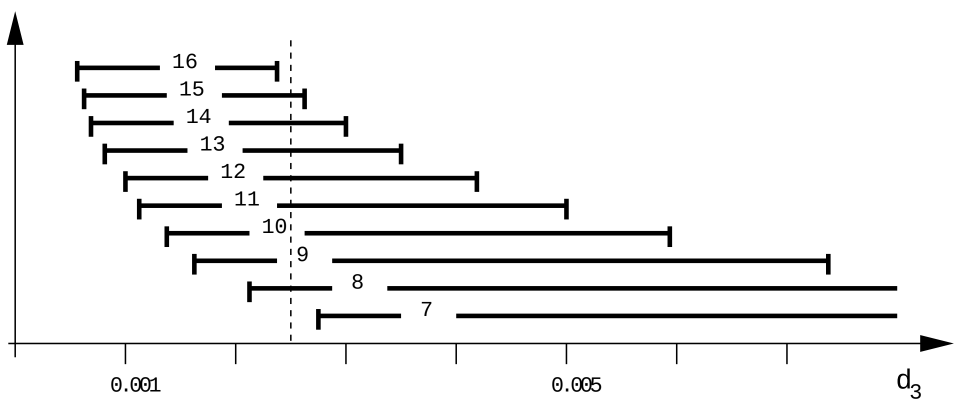

Figure 7. For system (6) with parameters $m = 28$, $a = 0.9$, $n = 15.5$, $b = 0.2$ the roots of approximately $\nu^- = 1.3389$ and $\nu^+ = 5.8545$ give the above intervals of diffusion coefficients which destablize the constant solution with respect to the mode with the indicated wavenumber. The dashed line marks the diffusion coefficient $d_3 = 0.0025$. The modes which are destablized range from wavenumber eight to fifteen.

Increasing m slightly to a value of $m = 28.56$ makes the roots $\nu^{\pm}$ move closer to each other so that the picking of a mode is more selective. The biggest wavenumber to be estimated with Lemma 3.2 is fourteen and for $d_3 = 0.0025$ only the standing wave of wavenumber twelve is destabilized. For even bigger $m = 28.566616$, the wave bifurcation is not possible any more. Decreasing m to a value less than $m = 26.75$ yields in a destabilization of even the zero mode, i.e. the constant solution itself is not stable any more.

Discussion

The parameter m serves as the one to be varied for the different numerical tests in the paper of Zhabotinsky et al. [**9**]. With the help of the conditions for wave bifurcation of Section 3 an interval of $m \in (26.75, 28.567)$ can be given for which standing wave solutions can be expected.

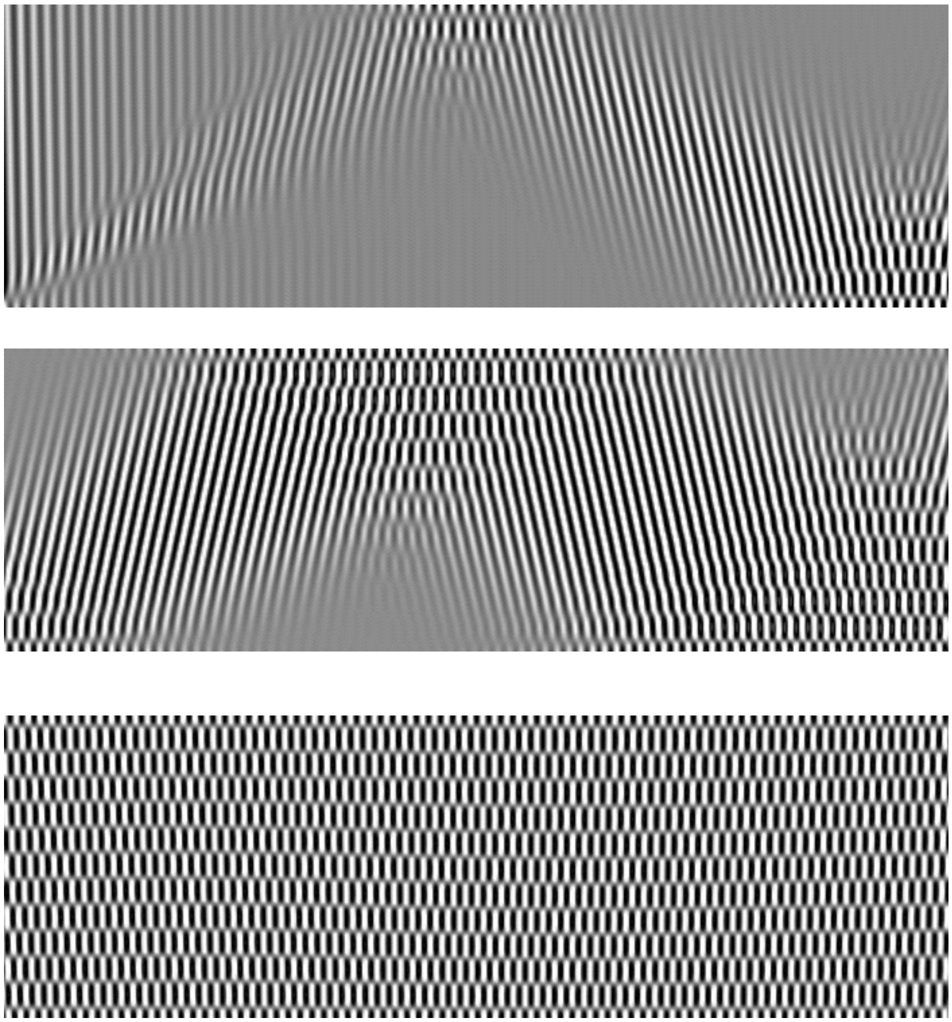

Figure 8. The horizontal axis shows the temporal evolution of (vertical) one-dimensional spatially nonuniform initial data (above, time steps 1-100, and 101-200) to a standing wave pattern (below, time steps 401-500).

The bigger m is, the more selective is the parabola, and the more sensitive the system reacts on a change in the diffusion coefficient (or, equivalently, on the length of the domain). Changes in the initial data are not recognized by the final waveform as long as the wavenumber is below the estimated maximal number.

Since standing wave patterns evolve much quicker from randomly chosen initial data than from an initial perturbation at a single gridpoint, it is worthwhile to determine the kinetic parameters such that only the diffusion coefficients and not the initial data influences the final pattern.

For m nearer to the lower end of the interval the solutions depend even more on the initial data.

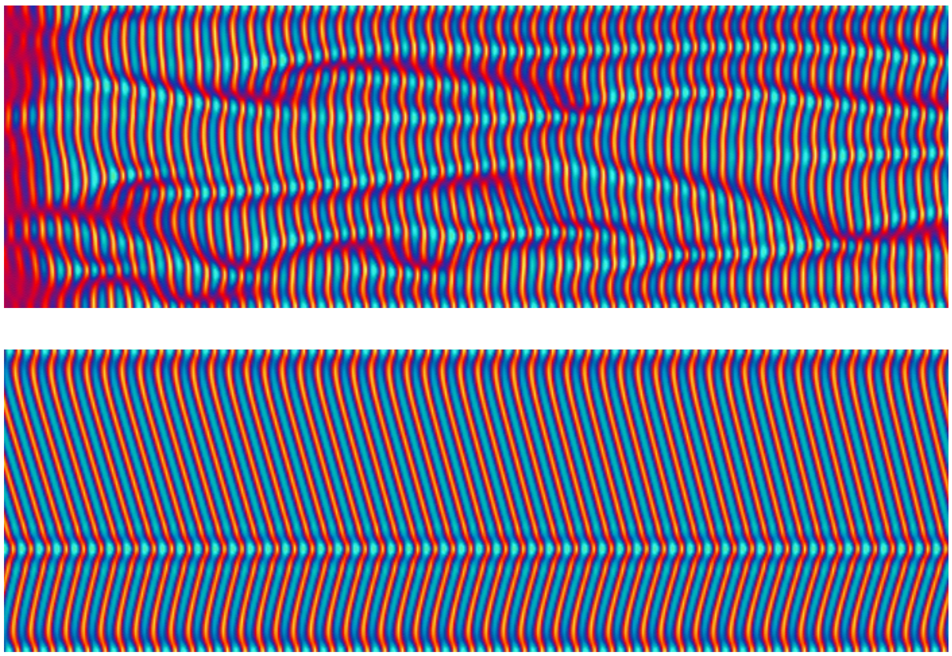

Figure 9. The initial data are chosen at random around the critical equilibrium. For a parameter $m = 18$ the so called **Standing Travelling Waves** evolve. These were considered to yield a target pattern in the two-dimensional case.

If m gets even smaller the space-independent Hopf bifurcation occurs as well. Naturally, a straightforward integration of the initial value problem gives rise to quite different solutions, as the **Standing Traveling Waves** of Figure 9. A single wave source pushes through in the one-dimensional domain, independently of (randomly chosen) initial data. In the above paper this was considered to be a source of a target pattern in a two-dimensional setting. But this could not be verified in the numerical experiments.

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