Control of waves, patterns and turbulence in chemical systems

Alexander S. Mikhailov\textsuperscript{a},*, Kenneth Showalter\textsuperscript{b}

\textsuperscript{a}Abteilung Physikalische Chemie, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany
\textsuperscript{b}Department of Chemistry, West Virginia University, Morgantown, WV 26506-6045, USA

Accepted 23 November 2005
Available online 24 January 2006
editor: G. Comsa

Abstract

We review experimental and theoretical studies on the design and control of spatiotemporal behavior in chemical systems. A wide range of approaches have been pursued to control spatiotemporal dynamics, from periodic forcing of medium excitability to imposing static and dynamic heterogeneities and geometric constraints on the medium to global feedback with and without delays. We focus on the design and control of spatiotemporal dynamics in excitable and oscillatory media. Experimental examples are taken from the Belousov–Zhabotinsky (BZ) reaction and the oxidation reaction of CO on single crystal Pt, which have become paradigmatic chemical systems for studies of spatiotemporal dynamics. We present theoretical characterizations of spatiotemporal dynamics and control based on the complex Ginzburg–Landau equation as well as models of the BZ and CO/Pt reactions. Controlling spatiotemporal dynamics allows the realization of specific modes of behavior or may give rise to completely new types of behavior.

© 2005 Elsevier B.V. All rights reserved.

PACS: 82.40.Bj; 82.40.Ck; 82.40.Np

Keywords: Pattern formation; Diffusion; Nonequilibrium systems; Surface reactions; Belousov–Zhabotinsky reaction

Contents

1. Introduction ............................................................................................................... 80
   1.1. The Belousov–Zhabotinsky reaction ........................................................................ 80
   1.2. Catalytic CO oxidation on platinum ........................................................................ 82
2. Controlling wave behavior in excitable media .............................................................. 87
   2.1. Open reactors for studies of Belousov–Zhabotinsky excitable media ...................... 87
   2.2. Wave behavior in geometrically constrained Belousov–Zhabotinsky media ........... 88
   2.3. Finding optimal paths with propagating waves ...................................................... 93
   2.4. Wave propagation in patterned excitable media .................................................... 96
   2.5. Influence of heterogeneities on spatiotemporal behavior in the Pt–CO system ........ 98
   2.6. Control of spiral waves ........................................................................................ 99
   2.7. Initiation and control of scroll waves ..................................................................... 101
   2.8. Noise-mediated wave behavior ............................................................................. 108
   2.9. Stationary and traveling spots .............................................................................. 114
   2.10. Stabilizing unstable waves .................................................................................. 115

* Corresponding author.
E-mail address: mikhailov@fhi-berlin.mpg.de (A.S. Mikhailov).

0370-1573/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.physrep.2005.11.003
1. Introduction

Theoretical understanding of physical phenomena opens a way for purposeful manipulation and control of existing systems, as well as to the design of new, artificial systems with desired properties. In the last two decades, detailed experimental evidence of self-organization phenomena in chemical systems has been accumulated. Experiments show that simple reaction mechanisms and elementary interactions can lead to the formation of complex spatiotemporal concentration patterns that are sensitive to changes in the reaction conditions and may undergo complete rearrangement in response to small purposeful perturbations. Engineering of self-organizing chemical systems cannot be based on the same principles as traditional chemical technology. Application of rigid controls would usually destructively interfere with fine interactions between the elements of a system responsible for its self-organization. Instead, spontaneous activity of a system should be steered in a desired direction by applying weak control impulses and imposing various feedbacks. In this manner, transitions between different organization states can be initiated and new forms of collective behavior can be achieved.

The aim of this article is to review current progress in the control of wave patterns and turbulence in reaction–diffusion systems. Our attention shall be focused on systems with local excitable or oscillatory kinetics. These two classes of chemical systems possess a rich variety of wave patterns that do not depend sensitively on the choice of a particular model. The dynamics of individual elements in such media is not chaotic and turbulence (spatiotemporal chaos) can develop only as a result of interactions between the elements.

As examples, two systems—the Belousov–Zhabotinsky (BZ) reaction and the catalytic surface reaction of CO oxidation on platinum—shall be considered. Both of them have been extensively investigated, their mechanisms are well understood and satisfactory theoretical models of their kinetics are available. While belonging to different classes of chemical systems, i.e., to reactions in aqueous solutions and to heterogeneous catalysis, they show strong similarity in the kinds and properties of observed concentration patterns. General aspects of nonlinear wave propagation in reaction–diffusion systems and its control can be well illustrated using these examples. Below in this introductory section, brief descriptions of the two chosen experimental systems are given.

1.1. The Belousov–Zhabotinsky reaction

The first homogeneous oscillatory chemical reaction, the iodate-catalyzed decomposition of hydrogen peroxide, was reported by Bray in 1921 [1]. The discovery was met with scepticism by many scientists, however, because it was believed that the oscillatory behavior violated the second law of thermodynamics [2]. About 30 years later, Belousov [3]...
discovered another oscillatory reaction, the cerium-catalyzed bromate oxidation of citric acid, although the continuing scepticism prevented him from publishing his discovery for a number of years [4]. Zhabotinsky further developed the reaction by substituting the oxidation–reduction indicator ferroin for the cerium catalyst and substituting malonic acid for the citric acid substrate [5]. The result was a robust oscillatory reaction with striking color changes that is now known as the BZ reaction, which continues to be widely studied as a model system in nonlinear dynamics.

Spatiotemporal wave behavior is exhibited in unstirred BZ reaction mixtures, and the features of propagating waves in quasi-two-dimensional (2D) layers of solution were characterized in early studies by Zhabotinsky [6,7] and Winfree [8,9]. Spiral waves, which are self-sustaining wave sources that rotate around a phase singularity, were found in the BZ reaction in 1971 [10,11]. With the advent of digital imaging technology, precise measurements of the spiral structure became possible [12,13]. Fig. 1 shows an example of a BZ spiral image, where the vertical axis is proportional to the oxidized catalyst concentration in the reaction.

The simplest spiral wave behavior is rigid rotation of the spiral tip around a small circular core, where every point outside the core undergoes periodic oscillations at the period of rotation of the spiral. Winfree [8] noted in his early studies that the spiral tip may also move, and he called this motion *meander*. Quantitative studies of the spiral tip showed that the tip motion undergoes a transformation from rigid rotation to motion along epicycle-like patterns as the excitability is varied [14,15]. Theoretical studies showed that the change from rigid to compound rotation occurs at a subcritical Hopf bifurcation [16,17]. Fig. 2 shows measurements of the tip motion for three different concentrations of bromate.
Modeling studies of the BZ reaction have relied on a chemical mechanism developed in 1972 by Field, Körös, and Noyes (FKN) [18]. The essential features of the FKN mechanism were captured in a three-variable model called the Oregonator [19], which is comprised of five chemical steps:

\[
\begin{align*}
A + Y &\rightarrow X + P, \\
X + Y &\rightarrow 2P, \\
A + X &\rightarrow 2X + 2Z, \\
2X &\rightarrow A + P, \\
Z &\rightarrow fY,
\end{align*}
\]

where the variables \(X\), \(Y\), and \(Z\) represent the species \(\text{HBrO}_2\), \(\text{Br}^-\), and the oxidized catalyst. The constants \(A\) and \(P\) represent the reactant and product species, \(\text{BrO}_3^-\) and \(\text{HOBr}\). The autocatalytic generation of \(X\) occurs in step (3) after \(Y\) has been consumed to a critical concentration in steps (1) and (2). The metal ion catalyst of the reaction is oxidized in the autocatalytic process (3) to generate the oxidized catalyst \(Z\), which resets the oscillation in step (5) by regenerating \(Y\).

A two-variable version of the Oregonator [20] has been widely used to describe the spatiotemporal behavior of the BZ reaction, where diffusion terms are included for the autocatalyst species \(X\) and inhibitor species \(Z\). The profiles of these species for a rigidly rotating spiral wave are shown in Fig. 3. The Oregonator can be readily modified to describe various experimental configurations, e.g., a diffusion term is added only for the autocatalyst to describe experiments carried out with the metal ion catalyst immobilized in a gel. For the photosensitive BZ reaction, with \(\text{Ru(bpy)}_2^{2+}\) as the catalyst, a term is added for the photochemical production of the inhibiting species, \(\text{Br}^-\) [21–23].

1.2. Catalytic CO oxidation on platinum

Some chemical reactions cannot go on in the gas phase. However, when the molecules are adsorbed on a catalytic metal surface, reactions between them become possible. Such catalytic reactions are broadly used in chemical industry and in environmental technology. In industrial applications, the catalysts are usually porous materials and microparticles. For laboratory experiments, single crystals of metals with perfect surfaces are preferred. The experiments with surface chemical reactions are typically carried under very low pressures of gaseous reactants, thus preventing strong thermal effects and the development of hydrodynamical flows.

Under these conditions, a surface chemical reaction is almost an ideal system for observations of nonequilibrium, reaction-induced wave patterns. The reactants are supplied to the catalytic metal surface from the gas filling the reaction chamber. Under ultra-low pressures, the mean free paths of molecules in the gas are comparable with the linear size of the reaction chamber and mixing of reactants in the gas phase is practically instantaneous. The reaction itself takes place only within a monolayer of molecules adsorbed on the catalyst surface. The molecules diffuse over the surface and react...
when they collide, making products that go back into the gas phase. The reactants can be supplied in a well-controlled way by dosing gases into the chamber, and the products together with excess reactants are steadily pumped away.

The 2D reaction–diffusion system, formed by adsorbed reactants on the catalytic surface, may show nonequilibrium patterns characteristic for bistable, excitable or oscillatory media. These patterns have characteristic length scales of tens of micrometers and time scales of seconds. They can be observed by using special methods of optical or electron microscopy (see [163]). The photomission electron microscopy (PEEM) is based on the effect of photoelectron emission from the metal surface under ultraviolet light irradiation. The yield of photoelectrons depends sensitively on the local work function of the substrate which is changed due to the presence of adsorbates. This method produces real-time images of the lateral distribution of adsorbed species on the surface with spatial resolution of about 1 μm. Alternatively, ellipsomicroscopy for surface imaging (EMSI) can be used. This method makes use of the fact that, when polarized light is reflected from a surface, its polarization is changed depending on the presence of the adsorbates.

Nonequilibrium pattern formation has been observed in a number of different surface reactions [164]. The most extensively studied surface chemical reaction is the CO oxidation on single platinum crystals. In this reaction, CO molecules react on the catalytic surface with oxygen forming carbon dioxide (CO2) that goes back into the gas phase. This process is of high practical importance, because it is employed in car exhaust catalysts to reduce environment pollution by CO. The net reaction 2CO + O2 → 2CO2 follows the Langmuir–Hinshelwood scheme:

\[
\begin{align*}
* + \text{CO} & \rightleftharpoons \text{CO}_{\text{ad}}, \\
2* + \text{O}_2 & \rightarrow 2 \text{O}_{\text{ad}}, \\
\text{CO}_{\text{ad}} + \text{O}_{\text{ad}} & \rightarrow 2* + \text{CO}_2.
\end{align*}
\]

Here, * denotes a free adsorption site on the catalytic surface. The adsorption of oxygen is dissociative. Adsorbed CO molecules are bound much less strongly to the surface than the oxygen atoms. Therefore, they can desorb and diffuse on the surface. Such processes are negligible for O_{\text{ad}} under typical experimental temperatures (below 600 K). At temperatures above 300 K, produced CO2 immediately desorbs into the gas phase, leaving again free space for the adsorbates.

When CO oxidation takes place on perfect surfaces of single Pt crystals, its properties strongly depend on what crystallographic plane is used to run the reaction. On the Pt(1 1 1) surface, the reaction shows only bistability between the mainly oxygen covered, reactive state and the nonreactive CO covered state. This bistability is due to asymmetric inhibition of adsorption. CO molecules can still adsorb on the platinum surface covered by oxygen. In contrast to this, when the surface is completely covered by CO, adsorption of oxygen is not possible and the reaction is poisoned. A two-variable kinetic model, describing bistability and front propagation in the CO oxidation on Pt(1 1 1) was constructed by Bär et al. [175].

When CO oxidation proceeds on the Pt(1 1 0) crystallographic plane, its dynamics is much more rich. Depending on temperature and partial pressures of gaseous reactants, it can show not only bistability, but also oscillations and excitable kinetics. The dynamical behavior becomes complex, because the reaction is then accompanied by structural changes of the metal surface [164]. If platinum atoms in the top layer of metal are ordered as in the bulk of the metal, this would correspond to the 1 × 1 arrangement. This is indeed the case for the Pt(1 1 1) crystallographic plane. The atoms occupying an open Pt(1 1 0) are however undergoing spontaneous rearrangement into a 1 × 2 “missing row” geometry through a process known as surface reconstruction.

If CO molecules are adsorbed on the reconstructed Pt(1 1 0) surface and their coverage is high enough, the surface reconstruction becomes lifted and the surface atoms acquire the 1 × 1 geometry that corresponds to the bulk of the metal. This is an adsorbate-induced phase transition which takes place above a certain critical adsorbate coverage. Such structural surface phase transitions, which are usually much slower than the characteristic reaction rates, can affect the reaction. As a result of an additional inertial feedback, oscillations and excitability become possible.

A similar adsorbate-induced structural phase transition occurs when the reaction takes place on the Pt(1 0 0) plane. In this case, the reconstructed state of the open surface has the “hex” geometry. The CO oxidation reaction on this surface is also accompanied by kinetic oscillations, which are however irregular [164].

Already the first experimental PEEM observations of pattern formation in the CO oxidation reaction on Pt(1 1 0) have revealed a large variety of patterns, including rotating spiral waves, target patterns, standing waves and irregular wave regimes [165,166]. Spiral waves, observed in the excitable regime (Fig. 4), were usually pinned by material defects of
the surface and were therefore characterized by a distribution of rotation periods [167]. However, free spiral waves, that drifted over the surface as a result of intrinsic meandering or reaction parameter variations, could also be seen.

In some parameter regions inside the excitable kinetics domain, solitary traveling wave fragments were observed. Such wave fragments were not always annihilating in front collisions—reflection collisions and fusion events were also observed. These effects, as well the development of standing waves, could be related to the formation of subsurface oxygen in the CO oxidation reaction [168–170]. The adsorbed oxygen can penetrate from the surface into the next underlying layers of the metal, thus creating an oxygen depot. Later on, such subsurface oxygen can come back to the surface and participate in the oxidation reaction.

The general Langmuir–Hinshelwood scheme corresponds to the mathematical model formulated by Ziff et al. [171]. This abstract model does not, however, take into account the dissociative adsorption of oxygen on platinum and the asymmetry of inhibition, which are important for understanding of the reaction bistability. The first theoretical model taking into account surface reconstruction was proposed [172] for the CO oxidation on Pt(100). It was formulated in terms of four coupled ordinary differential equations describing the variation of the adsorbate coverages on the hex and $1 \times 1$ phases of Pt(100) and the phase transition between the two substrate phases. The phenomenological four-variable model was reformulated in terms of statistical physics of first-order phase transitions by Andrade et al. [173,174]. Stochastic lattice models of this reaction have also been constructed [176,177,178] (for a review on stochastic modeling of surface reactions, see [179]).

Oscillations and excitable behavior in the CO oxidation reaction on Pt(110) are well described by the Krischer–Eiswirth–Ertl (KEE) model [180]. This phenomenological mean-field model is formulated in terms of three variables, $u$, $v$ and $w$. The first of them, $u$, is the local CO coverage, i.e., the fraction of CO adsorption sites on the metal surface that are occupied by adsorbed CO molecules. The second variable, $v$, is the local oxygen coverage. The third variable, $w$ specifies the local fraction of the surface area occupied by the nonreconstructed $1 \times 1$ structural phase. The kinetic equations of the KEE model are

$$\frac{\partial u}{\partial t} = k_1 s_{CO} p_{CO} (1 - u^3) - k_2 u - k_3 uv + D \nabla^2 u, \quad (9)$$

$$\frac{\partial v}{\partial t} = k_4 p_{O_2} [s_{O,1\times1} w + s_{O,1\times2} (1 - w)] (1 - u - v)^2 - k_3 uv, \quad (10)$$

$$\frac{\partial w}{\partial t} = k_5 \left( \frac{1}{1 + \exp((u_0 - u)/\delta u)} - w \right). \quad (11)$$

The first term in Eq. (9) describes the process of CO adsorption. Here, $k_1$ is the adsorption rate constant, $s_{CO}$ is the sticking coefficient for CO molecules, and $p_{CO}$ is the partial pressure of CO in the gas phase. Instead of being proportional to the fraction of free CO adsorption sites, $1 - u$, the adsorption rate includes the factor $1 - u^3$. This is done to take phenomenologically into account that the formation of a physical adsorbed state of a CO molecule is preceded by the appearance of a weakly bound precursor state of this molecule at the Pt surface. The second and the third terms in this equation describe desorption of CO and its reaction with adsorbed oxygen molecules. The last term takes into account surface diffusion of adsorbed CO molecules. It was introduced into the model in a subsequent publication by Falcke et al. [181] where traveling waves in this system have been first studied.
Eq. (10) describes the kinetics of adsorbed oxygen. The first term is the adsorption rate depending on the partial pressure $p_{O_2}$ of oxygen molecules. This rate is proportional to $(1-u-v)^2$, which is the square of the fraction of available oxygen adsorption sites. Because adsorption is dissociative, each $O_2$ molecule needs two free adsorption sites on the surface. Moreover, it is taken into account here that adsorbed CO inhibits oxygen adsorption. Therefore, $O_2$ molecules can adsorb only on the sites which are both free of CO and oxygen. The last term in this equation corresponds to the chemical reaction. Under typical experimental temperatures, oxygen is strongly bound to the surface and, therefore, its desorption and surface diffusion can be neglected. The oxygen sticking coefficient depends on the structural state of the surface. It takes values $s_{O,1\times 1}$ for the nonreconstructed surface with the $1 \times 1$ geometry and $s_{O,1\times 2}$ for the reconstructed surface.

Eq. (11) is a phenomenological mean-field description of the phase transition kinetics. The surface free of CO molecules is in the reconstructed $1 \times 2$ phase, while the surface completely covered by CO is in the nonreconstructed $1 \times 1$ phase. At intermediate CO coverages, a mosaic of microscopic domains of both structural phases occupy the surface. The characteristic sizes of such domain are, however, on the nanometer scale and cannot be resolved in the above mean-field micrometer-scale description. Here, it is simply assumed that, at a fixed CO coverage $u$, the local fraction $w$ of the surface area in the nonreconstructed phase tends to approach $\bar{w}(u) = [1 + \exp((u_0 - u)/\delta u)]^{-1}$. Note that, in the original KEE model the function $\bar{w}(u)$ was chosen in the piecewise-linear form; the approximation by a continuous step function was later suggested in Ref. [168]. The variable $w$ approaches the equilibrium value $\bar{w}(u)$ at rate constant $k_5$.

The kinetics of surface reconstruction is slow. First, adsorption of CO takes place on the reconstructed surface ($w \approx 0$), but then the reconstruction becomes slowly lifted and variable $w$ increases. Because the sticking coefficient $s_{O,1\times 1}$ of CO on the nonreconstructed surface is however smaller and CO is consumed in the reaction, its coverage decreases. This leads to a reverse structural phase transition. The repetition of such cycles gives rise to kinetic oscillations. Their period is essentially determined by the rate constant $k_5$.

The KEE model can be extended to take into account surface facetting [180] and subsurface oxygen formation [168,169], which become however important only under certain conditions. For simplicity, anisotropy of diffusion is neglected here. The model parameters have been determined by using the data of various independent measurements and can be found in Ref. [180]. The phase diagram of the KEE model at temperature $T = 540$ K is shown in Fig. 5. The dash curve “h” represents the boundary of the Hopf bifurcation, the solid lines “sn” indicate the boundary of the saddle-node bifurcation and the dash-dot line marked as “sniper” corresponds to the saddle-node bifurcation on a limit cycle (saddle node with infinite period). Oscillations are found inside the dashed region in this diagram. They arise through a supercritical Hopf bifurcation and are approximately harmonical near the bifurcation boundary “h”.

When diffusion of CO molecules is taken into account, the state with uniform oscillations can become unstable with respect to phase modulation (the Benjamin–Feir instability), leading to spontaneous development of turbulence. This instability was found by direct numerical determination of the coefficients of the complex Ginzburg–Landau equation for the KEE model along the Hopf bifurcation boundary [182]. Such spontaneous development of turbulence under oscillatory conditions, starting from a uniform state, is indeed observed in the experiments.

A sequence of PEEM images showing the spontaneous development of chemical turbulence from a uniformly oxygen covered surface state is displayed in Fig. 6. A characteristic property of such turbulence is the spontaneous creation of irregular wave fronts and multiple fragments of rotating spiral waves. The spiral waves repeatedly undergo breakups, leading to the formation of new spiral fragments at different locations. Such spatiotemporal chaos is found in a wide range of temperatures for an appropriate choice of the partial pressures of gases in the chamber [183]. The statistical analysis of experimental data (including the statistics of topological defects) reveals that this chemical turbulence is similar to the amplitude turbulence in the complex Ginzburg–Landau equation [184]. Therefore, the CO oxidation reaction on Pt(1 1 0) provides a unique opportunity to experimentally investigate the generic behavior described by this equation.

In studies of the KEE model under excitable conditions, its reduced version with two equations is often used. In this model, the fast variable $v$, describing the oxygen coverage, is adiabatically eliminated [181]. The effective two-component model is further simplified by replacing a complicated nonlinear function by its piecewise-linear approximation [175]. Thus, it is transformed to a variant of the activator–inhibitor FitzHugh–Nagumo model.

Approximate analytical solutions for solitary excitation pulses and pulse trains in the KEE model have been constructed [181]. Numerical simulations have shown that rotating spiral waves in this model can spontaneously break up, leading to a state of spatiotemporal chaos [185]. An example of such instability of spiral waves is shown in Fig. 7.
Statistical properties of such chemical turbulence in excitable media have also been investigated [186]. These results are important in the context of the general theory of pattern formation and spiral wave instabilities in excitable media. Spontaneous breakup of spirals, similar to the process shown in Fig. 7, has been indeed found in the BZ reaction [187]. However, this instability of spiral waves has not been so far observed in the experiments with CO oxidation on Pt(1 1 0).
This may be due to the fact that, under excitable conditions, most of the spiral waves are pinned by material impurities and therefore are not subject to this instability, characteristic for freely rotating spirals. Moreover, the rotation frequency of pinned spirals is much higher than that of the freely rotating spirals and, in the course of time, such free spirals (and also turbulence, if it has started to develop) would be ousted by these rapid wave sources. The experiments on control of turbulence in the CO oxidation reaction, which are described later in the review, have been always performed under oscillatory conditions where turbulence spontaneously developed through an instability of the uniform state.

2. Controlling wave behavior in excitable media

We have seen how chemical waves give rise to target patterns and spiral waves in the 2D media of the BZ reaction and the surface oxidation reaction of CO on Pt. We now examine the manipulation and control of spatiotemporal behavior in 2D and 3D systems by geometrical constraints, medium inhomogeneities, and spatiotemporal perturbations. Our focus in this section is on excitable media; oscillatory media will be discussed Section 3.

2.1. Open reactors for studies of Belousov–Zhabotinsky excitable media

We begin with wave behavior affected by the geometric constraints of a system, typically imposed by particular boundary conditions. Noszticzius et al. [24] constructed an annular gel reactor in which the sulfuric acid and bromate reagents of the BZ reaction enter the outer perimeter of the gel while the ferroin and malonic acid reagents enter the inner perimeter. This study introduced the continuously fed unstirred reactor (CFUR) in which a reaction–diffusion system can be maintained in a particular nonequilibrium state by continuously supplying fresh reactants. Reaction occurs in an annular zone in the gel where the sulfuric acid and bromate reagents meet the ferroin and malonic acid reagents. Spontaneous pacemaker sites appear which generate waves that propagate in opposite directions around the circular gel. Waves propagating in only one direction were generated by annihilating waves propagating in the opposite direction with a local, temporary composition change. This procedure was used to vary the total number of unidirectional waves in the reactor and it was found that stable patterns of evenly spaced waves were exhibited when the number of waves $N$ fell within the range $6 \leq N \leq 25$. With fewer than ca. 6 waves, spontaneous pacemakers gave rise to waves that disrupted...
the rotating wave pattern; with more than ca. 25 waves, the region between each wave was too refractory to sustain any additional waves in the gel medium. Because each wave propagates into the refractory tail of the wave ahead, the wave speed also depends on the total number of waves in the reactor, with the greater the number, the lower the wave speed.

A subsequent study of rotating waves in an annular gel reactor revealed a symmetry breaking transition as the temperature was varied [25]. In this study, unwanted waves were annihilated using UV light and a particular pattern of unidirectional waves was then examined as a function of temperature. A pattern of 10 waves, originally with ten-fold symmetry, displayed two types of waves, one radially confined and the other extended, to give a pattern with five-fold symmetry, as shown in Fig. 8. The ten-fold pattern with only one wave type was displayed at temperatures below 12 °C and above 22 °C, while the five-fold pattern occurred between these temperatures. Other rotational symmetry breaking transformations were observed with patterns containing different numbers of waves, and time-dependent patterns in the corotating reference frame were also found, with some waves periodically varying in size.

2.2. Wave behavior in geometrically constrained Belousov–Zhabotinsky media

New and interesting types of spatiotemporal behavior can be observed in wave-supporting media containing obstacles or barriers with doorways. The influence of such boundary conditions on oscillatory and excitable media has been investigated in a number of theoretical and experimental studies. Babloyantz and co-workers [27,28] carried out studies of wave propagation in oscillatory media containing obstacles. Using the complex Ginzburg–Landau equation, they found that waves could propagate through narrow doorways only if the door is above a critical width and that waves propagating through two neighboring doorways with different widths may influence each other. Specifically, waves propagating through the larger door can inhibit wave propagation through the smaller door. Such doorways can also give rise to spiral wave behavior due to the influence of one wave on the other.

Pertsov and co-workers [29] studied the propagation of waves through narrow channels in an excitable medium using the FitzHugh–Nagumo equations. They also found a critical door size for wave propagation along with the development of spiral behavior from waves passing through two doors of different widths. Complex firing patterns were found for successive waves propagating through a doorway that was near the critical width. Over a small range of period of the entering waves, only one wave successfully exited the door for every two waves entering the door. On further varying the period, patterns were found of two waves exiting for every three waves entering, and then three waves exiting for every four waves entering, and so on. Other types of behavior included spiral wave formation at the edge of a boundary and wave reflection at the opening of a narrow channel that was near the critical width.

Experimental studies of wave propagation through micro-capillary tubes have provided insights into signal transmission through narrow channels of excitable media. Tóth et al. [30] studied thin layers of excitable BZ solutions separated by a barrier in which a precision-bore capillary tube was mounted to connect the solutions. A wave initiated on one side of the barrier enters and travels through the capillary tube to form a hemisphere of excited solution at the...
tube exit on the other side of the barrier. When the tube radius is greater than a critical value, the excitation serves to initiate a wave in the second compartment. The hemisphere of excited solution collapses and no wave is initiated when the tube radius is smaller than the critical value. The critical nucleation size arises because the diffusive dispersion of the autocatalyst bromous acid increases with increasing curvature of the convex wave front, and there is a critical curvature above which the diffusion of autocatalyst is insufficient to sustain wave advancement. The critical curvature can be estimated from the dependence of the normal wave velocity $N$ on the planar wave velocity $c$ and the wave front curvature $\kappa$ according to the eikonal equation. Since waves propagating out of a capillary tube form a hemisphere of excited solution, we must use an eikonal equation for 3D media:

$$N = c + D(\kappa_1 + \kappa_2),$$

where $D$ is the diffusion coefficient for the autocatalyst and $\kappa_1$ and $\kappa_2$ are the principal curvatures of the wave front [31]. A hemisphere of excitation either grows or collapses depending on the magnitude of the curvature. Thus, the critical nucleation size is given by the curvature that corresponds to the sign change in the normal propagation velocity, i.e., when $N = 0$. Assuming a perfect hemisphere ($\kappa_1 = \kappa_2 = \kappa$), the critical radius $r_c$ is then given by

$$r_c = \frac{1}{\kappa} = \frac{2D}{c}. \quad (13)$$

A wave traveling inside a capillary tube of 160 $\mu$m i.d. is shown in Fig. 9, where successive images were subtracted at 5 s intervals to generate the image. On exiting the tube, the wave forms a hemisphere of excited solution at the opening, which is large enough to initiate a propagating wave as shown in the last frame. The radius of the initial hemisphere is effectively that of the capillary tube; hence, the critical nucleation radius for this particular solution composition is less than the 80 $\mu$m inner radius of the tube, since the region of excited solution proceeds to expand.

Experiments with the same BZ solution composition and smaller capillary tubes showed that wave initiation at the tube exit does not occur below a critical tube radius. A more accurate measurement of $r_c$ was carried out by using a single capillary tube and varying the wave velocity by changing the reaction mixture composition. A systematic change in the composition until waves are no longer transmitted from one compartment to the other allows the critical radius to be determined. A number of studies have shown the concentration dependence of wave velocity in the BZ reaction to be of the form [32–34]:

$$c = A + B([\text{H}_2\text{SO}_4][\text{BrO}_3^-])^{1/2}. \quad (14)$$
Thus, a series of experiments with varying \([\text{BrO}_3^-]\) allows the critical concentration to be determined for the transmission of waves through a tube with a particular tube radius. Fig. 10 shows subtraction images of a wave traveling inside a tube with a \(\text{BrO}_3^-\) concentration slightly lower than the critical value. The wave readily enters and propagates in the solution within the tube, but on reaching the opening the excitation collapses.

The value of \(r_c\) at the critical bromate concentration allows the calculation of the diffusion coefficient from Eqs. (13) and (14). From the planar wave velocity \(c\), together with the corresponding critical radius \(r_c\), a value of \(8.86 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}\) was determined for the diffusion coefficient. Chemical wave velocities have also been used to deduce the value of \(D\). By measuring the velocity of colliding circular waves and at the collision cusp, Foerster et al. [35,36] deduced the values of \(1.996 \times 10^{-5}\) and \(1.903 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}\) in two different studies.

There are several reasons why a discrepancy might exist in the value of \(D\) determined by these different techniques. First, there is no reason to expect the eikonal equation to quantitatively predict the critical nucleation size, as this equation is based on the assumption of small curvature [31]. Second, the assumption that the tube radius is the radius of the hemisphere of excited solution is only an approximation since the ends of the glass tubes are quite irregular, as can be seen in Figs. 9 and 10. Finally, we note that measurements yielded wave velocities that were significantly higher within the tube than in the surrounding solution, indicating that the chemical environment within the tube differs from that of the bulk solution.

The transmission of successive waves through the capillary tube becomes increasingly complex as the bromate concentration is adjusted so that the tube radius corresponds closely to the critical nucleation radius. As the radius approaches \(r_c\), the normal wave velocity \(N\) approaches zero due to increasing wave front curvature. This decrease in wave velocity on exiting the tube has important consequences for the behavior of subsequent waves. As shown in Fig. 11, at a certain value of the bromate concentration, which serves as the bifurcation parameter, only one wave exits the tube for every two waves entering the tube. This behavior is related to the periodic resonances observed in the forced BZ reaction in a continuously stirred tank reactor [37–39]. The firing number \(f_n\) is defined as the number of waves exiting the tube divided by the number of waves entering the tube, which for this case is \(f_n = 1/2\).

Many studies of chemical systems forming the basis of computational devices have appeared over the years. Rössler [40] proposed logic operations based on a bistable system over 30 years ago. Various logic gates for simple computations based on coupled chemical reactors were demonstrated by Ross and co-workers [41–43]. Coupled CSTRs were also utilized by Schneider and co-workers [44,45] to develop logic gates as well as neural networks. Enzymatic reactions were considered by Okamoto and co-workers [46] as switching elements in neural networks.

Fig. 11. Chemical waves shown on each side of an impenetrable barrier, with waves electrochemically initiated on the left and waves transmitted through the capillary tube on the right. This experiment shows the results of a 1:2 resonance pattern. The dimensions of the panel are 5.0 cm × 2.7 cm. Figure from Ref. [30].

Fig. 12. Two coaxial capillary tubes of 50 μm inner radius forming an OR gate assembly for \([\text{BrO}_3^-] > [\text{BrO}_3^-]_c\). Subtraction images at 10 s intervals show a chemical wave traveling in the right tube to form an excitation in the 180 μm gap between the tube exits. Figure from Ref. [48].

It is natural to think of channels of excitable media, such as the BZ capillary tubes described above, as conduits for signal transmission [27,28,30]. The paramount example of such signal transmission is an action potential propagating down a nerve axon. In a BZ capillary tube, an input wave results in an output wave (a binary response of 1) or no output wave (a binary response of 0). However, in the case of a neuron, multiple input signals are typically required for an output response. This might be analogous to the resonance patterns for successive waves, as discussed above; however, it is more likely to occur with almost simultaneous input signals [47]. It is possible to construct configurations of chemical waves in narrow channels that give rise to behavior analogous to the “integrate and fire” behavior of neurons. In addition, these configurations can be developed into an extensive set of logic gates, where the particular geometry determines the functionality [48].

Two capillary tubes, through which BZ chemical waves can propagate, have been used to form a variety of logic gates. Fig. 12 shows two tubes, with a fixed gap width between their openings, configured to function as an AND/OR gate assembly. The binary coding of 1 or 0 is defined according to the presence or absence of wave initiation in the gap region. To design such a gate, the critical radius \(r_c\) for the particular reaction mixture and tube radius is first determined by varying the \(\text{BrO}_3^-\) concentration. Above a critical concentration, \([\text{BrO}_3^-] > [\text{BrO}_3^-]_c\), a wave traveling through the left or the right tube gives rise to an excitation, regardless if there are two waves or only one. Hence, this configuration represents an OR gate, where an input signal of (1,0), (0,1), or (1,1) gives rise to an output of 1.
Below the critical bromate concentration, $[\text{BrO}_3^-] < [\text{BrO}_3^-]_c$, no excitation occurs when there is only one input wave, as shown in Fig. 13. A small hemisphere of excitation forms and then collapses, i.e., for inputs of (1,0) or (0,1), the output is 0. However, when there are two input waves and they reach the output simultaneously, then each of their subthreshold excitations combine to give an output of 1, as shown in Fig. 14. This configuration, therefore, corresponds to an AND gate, since an input of (1,1) is required to yield an output of 1, and all other inputs yield an output of 0. The AND gate not only requires the two positive inputs (1,1), but the timing of these inputs is critically important. If the delay between the appearance of the exiting waves is too large, the excitations then do not overlap and no output wave is generated. This configuration, therefore, with two coaxial tubes through barriers that separate a central chamber from the two input chambers, can serve as an OR gate or an AND gate by simply adjusting the BrO$^-$ concentration above or below the critical concentration, $[\text{BrO}_3^-]_c$.

Other gates such as the NOT function and the XNOR gate can be constructed by adding a periodic wave source and additional channels to the AND/OR configuration [48]. Note that the timing requirement of the AND gate allows this gate to also be used as a frequency detector. Hence, one could detect an unknown frequency of a signal by scanning through a range of frequencies until an output signal was detected.

Typical logic gates are based on Boolean functions that yield binary outputs according to binary input sets. In the BZ tube logic gates, there are four possible input combinations for $I_1$ and $I_2$, and the corresponding output responses are given in Table 1. For example, if either or both inputs are true (1), then the OR gate yields an output of true (1). An AND gate yields an output of true (1) only if both inputs are true (1). If both inputs are the same, either true (1) or
Table 1
Input–output relations for logic gates (from Ref. [48])

<table>
<thead>
<tr>
<th>$I_1$</th>
<th>$I_2$</th>
<th>OR</th>
<th>AND</th>
<th>XOR</th>
<th>NOR</th>
<th>NAND</th>
<th>XNOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Fig. 15. Composite image of 50 snapshots at 50 s intervals showing a chemical wave propagating through a membrane labyrinth. The wave was initiated in the lower left-hand corner of the membrane, which has an area of $3.2 \times 3.2$ cm$^2$. Figure from Ref. [61].

false (0), the XNOR gate yields an output of true (1); for different inputs, the output is false (0). Three other gates, the NOR, NAND, and XOR gates, can be realized by combining the NOT function with the OR, AND, and XNOR gates. The NOT function yields an output of true (1) for an input of false (0) and vice versa.

Several other approaches for using chemical waves in logic operations have appeared. A geometric scheme in which circuits of wave supporting channels were printed with the BZ catalyst on a membrane gave rise to extremely complex logic functions [49]. Another scheme involving perpendicular channels of BZ media can serve as a coincidence detector, since crossings are not possible in the refractory tail of an earlier wave [50]. Another type of coincidence detector has been developed that allows the number of wave pulses from a source to be counted [51].

2.3. Finding optimal paths with propagating waves

The properties of chemical waves [2,52,53] and waves in biological systems [55–57] can be exploited to find minimum-length paths in complex labyrinths. Path finding is typically optimized by iteratively determining the shortest path between a point of origin and a target point by direct measurements among all the possibilities [59]. Babloyantz and co-workers [60] were first to point out that a propagating reaction–diffusion wave generates a map from every point in the domain to a particular target point, even when the domain includes complex arrays of obstacles.

An experimental study of path finding was carried out by monitoring BZ waves propagating through complex labyrinths [61]. A detailed record of the space–time evolution of the wave propagation was obtained using digital imaging techniques. Membranes prepared in the form of various labyrinths were saturated with BZ solution and then monitored as a single wave propagated through the medium. A typical experiment is shown in Fig. 15, where a wave is shown propagating through a BZ-membrane labyrinth in a 50-frame overlay of images. Because the wave splits at each junction, it explores the entire domain and effectively creates a map between all points that are connected to the wave initiation point, which lies at the lower-left-hand corner of the figure. When waves collide with the boundaries
or with other waves they vanish upon annihilation. The time-lapse images show the wave at an equal distance from its position in the previous image, which is given by the constant wave velocity times the time between each snapshot. The wave propagates according to Huygens’s principle, where the front advances a particular distance per unit time in a direction normal to the front.

Wave front position as a function of time allows a map to be constructed that gives the minimal distance from any point in the maze to a particular target point. The accuracy of the map is determined by the time resolution of the composite image. Fig. 16 shows a high-resolution, color-coded distance map generated from 200 images to form a composite image. The color coding indicates the elapsed time for the wave to travel from its initiation point to any particular point in the maze. The minimum distance from the target point $S$ to any point in the maze is given by the product of this time and the constant wave velocity. Hence, a single propagating wave provides a highly parallel means to efficiently determine the optimal transit time and distance to any point in the labyrinth.

The space–time information obtained in experiments like that shown in Fig. 16 allows a velocity field to be developed that gives detailed information about the optimal path. Examples of several minimum-length paths derived from the velocity field are shown in Fig. 17. These paths were computed by searching for the nearest point indexed $t-\tau$, where $t$ is the time elapsed and $\tau$ is the time increment between images in the overlaid composite. This technique provides information about nonunique optimal paths that occur on either side of path boundaries, which are created by colliding waves previously separated by barriers. Path boundaries partition different paths of equal length to the target $S$, where the routes of the paths may differ significantly. Hence, the labyrinth is divided into domains of pathways, where each path in a domain has an equal length counterpart in another domain.

A different type of boundary is created by colliding waves arising from multiple wave initiations at different locations in the maze. These collision boundaries define points of equal distance from the sources of the waves. For example, the four sources $S_1$, $S_2$, $S_3$ and $S_4$ shown in Fig. 18 create collision boundaries that separate basins associated with each of the sources. The point where three collision boundaries intersect defines a location that is equal distance to each of the sources along minimum-length pathways. The time necessary for a constant velocity wave to reach a particular point in any basin is indicated by the intensity of the color at that point. One can think of the collision boundaries as separatricies between trajectories leading to different target points. Fig. 18 shows examples of trajectories determined...
Fig. 17. (Color online.) Detailed optimal paths, shown in red, for five different locations to the target location \( S \), determined from the velocity field. Figure from Ref. [61].

Fig. 18. (Color online.) Time-indexed image generated from four different waves, which were initiated almost simultaneously at points \( S_1, S_2, S_3, \) and \( S_4 \). Each color is associated with a particular wave, where the intensity corresponds to the elapsed time from wave initiation. Seven detailed paths to the target points are shown in red. Figure from Ref. [61].

from the velocity field, where two nearby points on either side of a collision boundary give rise to completely different destinations.

The determination of optimal paths in this study neglected the effects of curvature on wave propagation, with the assumption of constant wave velocity throughout. Although wave velocity is dependent on curvature [31,62], the errors
Fig. 19. Propagating waves in a BZ system with catalyst patterns printed on a membrane that is diffusively fed with catalyst-free reaction mixture. Wave fronts are shown in white and wave backs in black. Figure from Ref. [70].

introduced by neglecting these effects were small in determining optimal paths. Curvature plays an important role in path finding as length scales in the maze become smaller, for example, in the determination of door size in barriers from the critical nucleation size [60,61].

Path optimization by reaction–diffusion waves may play an important role in biological systems, such as the slime mold Dictyostelium discoideum [63,64]. Reaction–diffusion waves of extracellular cyclic adenosine-monophosphate (cAMP) serve to organize the chemotactic cell motion of individual amoebae cells during the aggregation phase. These cells very likely migrate according to optimal paths defined by the cAMP waves.

2.4. Wave propagation in patterned excitable media

The excitable media of biological systems is inherently inhomogeneous due to its cellular nature, and this inhomogeneity may play a significant role in its dynamics. For example, the cellular anisotropy in mammalian heart tissue results in a directional velocity dependence [65–68]. In addition, it may also give rise to pinning of spiral waves [55] as well as wave propagation failure [69]. The effects of cellular inhomogeneity have been experimentally investigated using the BZ reaction, in which the ferroin catalyst of the system is printed in well-defined patterns on membranes [70].

Following Noszticzius and co-workers [71,72], the bathoferroin catalyst for the BZ reaction [73] was immobilized on polysulfone membranes. High-resolution patterns were produced by printing a bathoferroin solution onto the membranes using an ink jet printer. The printed membranes were then placed onto agarose gels saturated with catalyst-free BZ reaction mixture, which supplied the catalyst-loaded regions of the membranes with fresh reactants. The reflected light from the membrane was monitored with a video camera to record the spatiotemporal behavior.

An example of the effect of inhomogeneities on wave propagation is shown in Fig. 19, where a checkerboard array of triangular cells loaded with catalyst gives rise to global anisotropy, with hexagonal-shaped waves. Spiral waves form spontaneously in this medium, and the spiral tips were found to rotate around catalyst-free cells, much like the pinning of spiral waves at discontinuities in heart tissue [55]. Other patterns yielded different chemical wave anisotropies, such as cross-hatched linear grids giving rise to diamond-shaped waves. A catalyst pattern consisting of superimposed arrays of shifted arcs yielded waves with a five-fold symmetry, as shown in Fig. 20. The wave is pentagonal shaped, with four corners that coincide with the printed arcs, and a fifth, less prominent, corner that is directed along the unique symmetry axis of the pattern.

Simulations of the spatiotemporal behavior were carried out with a two-variable Oregonator [19,20] modified to reflect the features of the patterned medium, such that within the catalyst-loaded regions,

\[ \frac{du}{dt} = \nabla^2 u + (1/\varepsilon)[u - u^2 - f v(u - q)/(u + q)]. \]
\[
\frac{dv}{dt} = u - v, \quad (15)
\]

where the concentrations of the autocatalyst \(HBrO_2\) and the inhibitor bathoferrin are described by the variables \(u\) and \(v\), respectively. Outside the catalyst-loaded regions, the model is modified by removing all terms for the catalyst, including the equation for \(v\)

\[
\frac{du}{dt} = \nabla^2 u - (1/\varepsilon)u^2. \quad (16)
\]

This variation of the model with respect to loaded and unloaded catalyst regions allows the autocatalyst \(u\) to diffuse into the catalyst-free regions even though these regions do not support the propagation of the reaction–diffusion wave.

The experimental measurements detect the presence of the oxidized metal catalyst, bathoferrin; however, it is not possible to monitor the other species in the reaction. Numerical simulations provide insights into the dynamical behavior of the other critical species such as \(HBrO_2\). A simulation analogous to the checkerboard array of triangles in Fig. 19 is shown in Fig. 21, where a level of the autocatalyst \(u\) is indicated by the white contours. We see a similar hexagonal wave pattern as in the experimental image, where the spiral waves are pinned to particular catalyst-free cells. The simulation also reveals an elevated concentration of \(u\) in the catalyst-free cells behind the waves. The presence of catalyst-free regions gives rise to this unusual feature, not observed in homogeneous media, since there is no oxidized catalyst present to generate the autocatalyst consuming species \(Br^-\) [18]. Because these cells are surrounded by catalyst-loaded cells in the refractory state, the elevated autocatalyst concentration is unable to initiate new wave activity.

The wave patterns in Figs. 19–21 can be understood in terms of the geometry of wave propagation along paths that are impeded to varying extents with catalyst-free cells. Hence, waves traveling along paths that are unimpeded, along connected catalyst-loaded cells, generate the corners of the pattern at the farthest distances from the wave initiation. Waves traveling along the most circuitous routes make the least progress and form the sides of the polygons. The diffusion of the autocatalyst across catalyst-free cells also offers a mechanism for the transmission of wave activity and modifying the pattern. Hence, the sharpness of the geometric angles in the pattern depends on the degree of wave transmission across these obstacles.

Spiral waves are common in the inhomogeneous excitable media of biological systems, and they readily form spontaneously. This can be contrasted with behavior found in homogeneous media, where the formation of spiral waves requires special initial conditions. In the homogeneous BZ reaction, for example, spiral waves are typically generated by breaking a wave either mechanically or chemically in order to produce a wave free end [6,8,75]. Spiral waves may also be generated with special dynamical conditions, such as cross-field stimulation, where a wave travels into the back of another wave [55,76], or from wave initiation in the vulnerable zone or wave back of another wave [77]. Spiral waves form spontaneously in biological excitable media and in the inhomogeneous BZ medium without wave
Fig. 21. Simulation of propagating waves in a BZ system with a pattern of catalyst-loaded triangular cells interspersed with catalyst-free triangular cells. The concentration of $u$ is indicated by the white contour lines. Figure from [70].

breaks or special initial conditions. The spontaneous appearance of spiral waves is commonly explained in terms of heterogeneity in the refractoriness of the medium [78]; however, it is known that spiral waves may also be induced by the interaction of waves with obstacles [28,79,80]. Spiral waves are also known to form spontaneously in other cellular media, such as a BZ system comprised of a layer of catalyst-loaded beads [81] or the social amoeba Dictyostelium discoideum [82]. The anisotropy exhibited in the patterned BZ system is similar to behavior found in the reaction of $\text{NO} + \text{H}_2$ on Rh(110), in which wave deformations occur due to state-dependent diffusion anisotropy [83]. Waves in heart tissue also exhibit deformations, typically with an elliptical shape due to velocity differences depending on the propagation direction with respect to the cell axis [55].

2.5. Influence of heterogeneities on spatiotemporal behavior in the Pt–CO system

As pointed out by Li et al. [84], the influence of heterogeneities on spatiotemporal behavior ranges from various modifications of the homogeneous system behavior to completely new behavior, such as the pinning of waves at inhomogeneities [84,85]. An important example of this is the pinning of spiral waves in excitable heart tissue [55,86,87].

Early studies of the effects of heterogeneities on spatiotemporal behavior in surface reactions were carried out by Graham et al. [88]. The CO oxidation reaction on single crystal Pt(1 1 0) was studied under low pressure and isothermal conditions. Microlithography techniques were developed to precisely pattern the surface of the Pt with 80 nm layers of Ti. The domains of Ti were inert to the CO oxidation reaction occurring on the Pt surface and served as no-flux boundaries. The technique allowed a wide variety of reaction domains to be fabricated, with length scales varied to match the length scales of the propagating waves. For example, narrow circular paths of Ti-free surfaces were produced to examine waves in a quasi-1D configuration with periodic boundary conditions. A pronounced variation in wave velocity and shape was observed in these experiments depending on the position of the wave with respect to the crystallographic axis. The spatiotemporal activity was monitored using PEEM [89].

One of the new behaviors due to the medium heterogeneity was termed “grid resonance”, which occurred in a square array of Ti domains, each ca. 10 $\mu$m wide [90]. Some spiral waves became pinned to particular Ti islands, while others were “free” (not associated with a particular Ti island), as shown in Fig. 22. As the spirals rotated, the waves propagating outward became entrained to the Ti lattice. Thus, as a wave passes through a row of Ti domains it breaks into segments, reforming again as it passes beyond the row, as can be seen between the two arrows in panel (a). In this manner, the
wavelength becomes commensurate with the Ti-island lattice spacing. This behavior represents a spatial analogue of the more familiar temporal resonance observed in periodically forced systems.

It is also possible to use microlithography to fabricate active domains other than the regions on the Pt surface, which gives rise to completely new spatiotemporal behaviors [84]. For example, checkerboard domains of Rh on a Pt surface yield different levels of overall reactivity depending on the length scales. Another new behavior arises from a “leaky wall” effect, where triangular oxygen pulses travel along channels on the Pt surface surrounded by Rh [91]. Modeling studies have shown this behavior to be due to the surrounding Rh serving as a CO reservoir, and the lateral diffusion of CO into the Pt channels gives rise to the triangular-shaped pulse. Ignitions were also studied in rhombic-shaped inclusions in Rh covered Pt [84,91]. The angles of the rhombic domains were varied systematically to examine the effects of the geometry on the ignition dynamics, and it was found that the pulses initiate at the sharpest corners, and that the sharper the angle the earlier the ignition. This is due to CO laterally diffusing into the domain from the surrounding Rh regions giving rise to ignition, and the sharper the corner the greater the CO concentration.

2.6. Control of spiral waves

Periodic forcing [92–94] and positive and negative feedback [94,95] have been used to influence the dynamics of spiral waves in a number of studies. Agladze et al. [96] were the first to demonstrate that periodically forced spiral waves exhibit a lateral drift along a straight line when the forcing frequency is equal to the spiral frequency. This resonance drift was observed in a periodically forced photosensitive BZ reaction, and confirmed an earlier theoretical prediction by Davydov et al. [97]. For spiral waves rotating in opposite directions, the corresponding lateral drift occurs in opposing directions. Hence, when two counterrotating spiral waves are subjected to resonant periodic forcing, they drift toward each other and eventually collide and annihilate.

The dynamics of spiral waves in confined geometries, such as a small disk or the surface of a sphere, has been studied with global feedback [98]. A generic two-variable reaction–diffusion model [99] was used in which the extent of the wave activity served as a feedback signal to the activator dynamics. The wave activity was determined according to the integral of the inhibitor variable over the domain. The feedback can be either positive or negative, which gives rise to an increase or decrease in the excitability.

Fig. 23 shows the effect of negative feedback on the trajectory of the spiral tip, where the initial conditions correspond to the tip close to the boundary of the disk domain. The feedback strength was increased from panels (a) to (d). Panel (a) shows the trajectory of the tip following the domain boundary at low feedback strength. The drift of the tip can be halted with an increase in the feedback strength, as shown in panel (b). On further increasing the feedback strength, the
tip migrates to the center of the domain and displays a cycloid trajectory, panel (c). At the highest feedback strength employed, the cycloid behavior is suppressed and the spiral exhibits rigid rotation, as shown in panel (d).

When the sign of the feedback is switched to be positive, behavior much the opposite is observed. Thus, a spiral undergoing rigid rotation at the center of the domain becomes destabilized to drift along the boundary of the circular domain at low feedback strength. At higher feedback strength, the tip drifts to the boundary and the spiral annihilates. Other types of behavior can be observed when a delay is introduced into the feedback, such as drift around the boundary in a direction opposite to the drift of the autonomous system. Studies were also carried out of spiral wave behavior on a spherical surface when global feedback was applied. With negative feedback, counterrotating spiral waves migrate to the poles of the sphere to form a stable constant waveform. With positive feedback, the spiral waves form cycloid-like trajectories on the sphere and may undergo annihilation at higher feedback strengths.

A related experimental study of spiral waves in the light-sensitive BZ reaction has been carried out [100]. However, rather than spirals confined to a small domain, the BZ spirals were subjected to feedback based on the wave activity measured in a small circular domain. Thus, the entire medium was illuminated at an intensity \( I(t) \) proportional to the average gray level \( B \) in the circular integration area, according to the feedback law

\[
I(t) = I_0 + k_{fb} [B(t - \tau) - B_0],
\]

where \( I_0 \) is the background intensity corresponding to a spiral centrally located in the circular area with an average gray level \( B_0 \). The gain of the feedback is adjusted with the parameter \( k_{fb} \) and a delay time \( \tau \) can be added between the gray-level measurement and the illumination.

Fig. 24 shows the dependence of the spiral tip behavior on its initial position, where the gain \( k_{fb} \) is negative and there is no delay \( (\tau = 0) \). When the spiral tip is initially placed near the boundary of the circular integration region, it drifts toward the center of the area until it undergoes rigid rotation, as shown in panel (a). The intensity of the feedback illumination intensity is shown in panel (c), which exhibits oscillations in phase with the rotation of the spiral wave. After entering the circular integration region, the amplitude of the oscillations decreases as the spiral tip moves to the center, where the intensity becomes relatively constant. Completely different behavior is observed when the spiral tip is initially positioned farther away from the boundary of the circular integration region, as shown in panel (b). Now the spiral tip exhibits a drift in a circular path around the outside of the integration region.
When the gain of the feedback is positive, the spiral tip drifts to an orbit around the circular integration area, regardless whether the tip was initially at the center or outside of the area. The introduction of a delay between the measurement of wave activity and the imposed feedback gives rise to a wide variety of behavior. For example, rigid rotation of the tip at the center of the circular area is destabilized to drift out of the circular area with a small delay and positive feedback. When the delay time is increased, the drift occurs in a circular orbit much like experiments with no delay and negative feedback.

Further studies\[101\] have shown that the shape of the integration area also affects the spiral tip behavior, in addition to the domain size, feedback strength and delay. Fig. 25 shows the drift of the spiral tip for a circular domain with negative feedback and no delay (a), and for delays of ca. 1/3 (b) and 1/2 (c) the autonomous spiral period. We see that the shorter delay gives rise to a smaller circular drift of the spiral tip and the longer delay results in its migrating to the center to become stationary. Surprisingly, when there is no delay, but the domain is elliptical rather than circular, the tip also migrates to become stationary (although not at the center), shown in panel (d).

A kinematic description of the spiral wave under feedback conditions allows the construction of the velocity field for the spiral tip drift, which permits an analysis of the resonance attractors\[101,102\]. The velocity field for Fig. 25(a) reveals the center of the circular domain to be an unstable node, which is surrounded by a stable limit cycle. The drift velocity of the tip around the circular limit cycle is constant. When the circular domain is slightly distorted to an elliptical domain, the velocity field shows that the drift velocity is no longer constant. On further distortion, the stable limit cycle is destroyed in a bifurcation that creates two stable nodes and two saddles points. In a domain that is sufficiently elliptical, such as in Fig. 25(d), the spiral tip will migrate to one of the stable nodes, with which one being determined by the initial tip location.

2.7. Initiation and control of scroll waves

An experimental study carried out by Pertsov and co-workers\[103\] showed that scroll waves can be strongly influenced by excitability gradients. A temperature gradient was used to establish the local excitability, and an excitability gradient parallel to a scroll filament gives rise to “twist” in the filament, since the frequency of rotation is a function of excitability. This study also showed that when the twist reaches a critical value, or bifurcation point, the filament ruptures and new spatiotemporal behavior arises\[104\].
An excitability gradient can also be imposed on a spiral wave filament using the photosensitive BZ medium, with Ru(bpy)$_3^{2+}$ as the catalyst [105]. Illuminating a thin gel medium allows an excitability gradient to be established transverse to the filament, which also gives rise to interesting scroll wave behavior. In addition, the use of pulsed illumination over accurately timed intervals allows the generation of precisely oriented scroll rings in the medium.

The excitability dependence on illumination intensity in the photosensitive BZ reaction depends on the production of Br$^-$ ion in a photochemical cycle [23,106]. The Br$^-$ ion is an inhibitor of autocatalysis in the reaction, and, consequently, the higher the illumination intensity, the lower the excitability. The illumination should be centered around 460 nm in order to excite the Ru(bpy)$_3^{2+}$ catalyst of the reaction. When a circular wave is initiated in the thin layer of gel embedded with catalyst, an excitability gradient transverse to the wave propagation direction can be created by illuminating the layer of gel from below.

A scroll wave can be initiated from a propagating wave by perturbing the excitability in the transverse direction by suddenly increasing the illumination intensity. This causes the propagating wave to contract from the lower boundary of the medium. When the illumination intensity is then restored to its original value, the propagating wave extends only partially into the medium. The free end of the wave that is created by the perturbation evolves into a scroll wave. This technique for generating scroll waves is similar to that first used by Winfree [107,108], in which the thickness of the excitable medium is suddenly increased by adding a new layer of excitable solution or gel on top of that supporting a traveling wave. The method of increasing the medium thickness was also used in later studies by Krinsky and co-workers [109,110] and Linde and Engle [111].

A scroll ring can be conveniently created by first initiating a wave that expands as a circular ring. Once the wave has expanded to a suitable size, the medium is perturbed by illumination from below to alter the excitability. The duration of the perturbation must be sufficient to cause the wave to laterally contract. Fig. 26 shows a sequence of snapshots that captures the creation of a scroll ring from an expanding circular wave. In panel (a), the wave was initiated while a low level of illumination was applied. In panels (b) and (c), the system was perturbed by suddenly increasing the illumination intensity for a period of 8.0 s. The effect of the perturbation can be seen in panel (f), where the scroll wave appears at the surface of the gel in the wave back of the parent wave. We see that this new wave splits into two waves, as shown in panel (g), with one propagating inward and the other propagating outward. Panels (h), (k), and (n)
show a repetition of this process, with new waves successively created that split into two waves propagating inward and outward.

The evolution of the pattern of reappearing scroll waves striking the surface of the gel medium can be seen in a space–time plot, shown in Fig. 27. This figure shows the wave pattern as a function of time along the dashed line in Fig. 26(a). The minima in each curve represent the locations where the scroll wave strikes the surface. This wave splits into two waves, one propagating outward, which is the expanding circular wave, and one propagating inward, which is the contracting circular wave. An important feature in this figure is the location of the minima as a function of time, namely the position of the wave source, which expands with each successive appearance. As we will see, this represents the position of the scroll ring filament, which expands in this experiment. The perturbation method of producing scroll rings in thin slabs of gel is remarkably robust, as 20 or more scroll ring rotations can be observed.

Simulations using a three-variable Oregonator model [19] for the photosensitive BZ reaction [106,112,113] allow a detailed visualization of the experimental behavior shown in Figs. 26 and 27. The behavior clearly depends on the 3D nature of the medium and, hence, the simulation was carried out in a grid of \( N_x \times N_y \times N_z = 321 \times 321 \times 48 \) to simulate the gel slab. The Tyson–Fife [20] scaling of the three-variable “photo–Oregonator” is given by

\[
\frac{du}{dt} = \nabla^2 u + (1/\epsilon)[qw - uw + u - u^2],
\]

\[
\frac{dv}{dt} = u - v,
\]

\[
\frac{dw}{dt} = \nabla^2 w + (1/\epsilon')[\phi - qw - uw + fw].
\]

Here, \( u, v, \) and \( w \) represent the concentrations of \( \text{HBrO}_2, \text{Ru(bpy)}_3^{3+}, \) and \( \text{Br}^- \), the 3D Laplacian is \( \nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2 \), the rate of \( \text{Br}^- \) production from the illumination is \( \phi \), \( f \) is a stoichiometric factor, and \( \epsilon, \epsilon', \) and \( q \) are scaling parameters.

Although the effect of the illumination is a decrease in excitability due to the photochemical cycle producing \( \text{Br}^- \), the illumination intensity is also attenuated as the light passes through the medium. Thus, the rate of \( \text{Br}^- \) production...
is a function of distance $z$ according to a Beer–Lambert relation,

$$\phi(z) = \phi_0 e^{-\alpha z}.$$  \hspace{1cm} (19)

The molar absorption coefficient and concentration of $\text{Ru(bpy)}_2^{2+}$ is included in parameter $\alpha$ and the quantum efficiency for the photochemical generation of $\text{Br}^-$ is given by $\phi_0$.

The simulation shown in Fig. 28 illustrates the mechanism for the formation of the perturbation-induced scroll wave. The top panels show the medium from above as $x$, $y$ images, while the bottom panels show the horizontal cross-section through the center of the medium as $x$, $z$ images. Panel (a) shows a newly initiated circular wave, which, as seen in the $x$, $z$ image, has not yet reached the bottom boundary of the medium. The perturbation by high-intensity illumination occurs in panel (b), and the effect of reducing the excitability from below can be seen as free ends are formed in the wave. The original low-intensity illumination is restored in panel (c), and the free ends of the wave begin to grow and curl. This process continues, with the scroll wave striking the lower boundary of the medium in panel (f) and striking the upper boundary in panel (g). As illustrated in the upper panel (g), the wave behavior visible on the upper surface, as in the experiment, is the scroll wave striking the surface. The appearance of this circular wave splitting into inward and outward propagating waves, shown in panel (h), is simply the continuing evolution of the scroll wave, as shown in the lower panel.

In an isotropic BZ medium, scroll ring filaments are known to shrink over time to eventually collapse and disappear [103,107–109]. However, the illumination of the medium after the perturbation gives rise to an excitability gradient, which affects the evolution of the scroll ring. As can be seen in Fig. 27, the perturbation of an outwardly propagating circular wave generates a scroll ring that expands rather than contracts. The dependence of the scroll ring filament
Fig. 28. Simulations of perturbation-induced scroll waves using the Oregonator model for the photosensitive BZ reaction. The upper panels show the \(x, y\) image and the lower panels show the \(x, z\) image at each time interval. The \(z\) coordinate is expanded for clarity, with the aspect ratio \(x:y:z = 1:1:2\). Figure from Ref. [105].

Fig. 29. Scroll filament radial velocity as a function of illumination intensity. The velocity of scroll ring filaments that were generated from outward and inward propagating circular waves are shown by diamonds and squares, respectively. The velocities were normalized with respect to the maximum absolute velocity. Figure from Ref. [105].

velocity on the incident light intensity, which determines the strength of the excitability gradient, is shown by the diamonds in Fig. 29. As can be seen, the scroll ring contracts at low light intensity, in agreement with earlier observations of shrinking scroll rings in isotropic media. However, as the light intensity increases, the evolution of the scroll ring changes from contracting to expanding, with the filament velocity increasing with increasing intensity.

The perturbation of an outwardly propagating circular wave gives rise to a scroll ring having a particular rotational orientation with respect to the excitability gradient arising from the illumination of the medium, as shown in Fig. 28. Scroll waves having the opposite rotation with respect to this excitability gradient can also be generated with a modification of the perturbation technique. If the medium is subjected to a second perturbation following
the initial wave splitting, such as that shown in (f) and (g) in Fig. 26, new scroll waves are generated from these waves. One is similar to the first, in that it is the daughter of an expanding circular wave; however, the other is the daughter of a contracting circular wave and has the opposite scroll wave rotation. Hence, the effect of an excitability gradient on scroll waves with the opposite rotation can also be investigated using the same techniques. As shown in Fig. 29, these scroll rings always shrink, and the filament velocity becomes more negative with increasing illumination intensity.

Numerical studies with Eq. (18) confirm the above experimental observations. In a dark system with no excitability gradient, scroll rings collapse regardless of the direction of rotation. With an increase in the light intensity to the medium (from below), the scroll ring no longer collapses but expands, and its expansion rate increases with increasing illumination intensity. The direction of rotation with respect to the excitability gradient was changed in the simulations by simply switching the illumination to be above the medium, which was not easily accomplished in the experimental study. Measurements of the filament velocity as a function of illumination intensity showed an increasing shrinking rate with increasing illumination intensity, in agreement with the experimental results shown in Fig. 29.

The effect of the light-induced excitability gradient on the scroll wave behavior is summarized in the schematic drawings shown in Fig. 30. Drawings (a) and (b) show that scroll waves with an “outward” rotation with respect to the illumination intensity gradient contract below a critical intensity $I_{\text{crit}}$ and expand above this critical intensity. Scroll waves with an “inward” rotation with respect to the illumination intensity gradient always contract. It is important to note that the illumination gradient is negative for illumination from below, and the excitability gradient is positive.

A mechanism similar to that described above, which depends on the three-dimensionality of a medium, can also give rise to spiral wave initiation in the photosensitive BZ reaction. Rather than a global perturbation reducing the excitability, however, a local perturbation increasing the excitability is applied in the wake of a propagating circular wave. The spiral wave initiation is similar to the technique of initiating a wave in the wake back of another wave, known as the vulnerable region, to initiate a spiral wave [77,114,115]. However, rather than changing the excitability in the plane of the medium, the excitability is locally increased transverse to the direction of wave propagation.
Fig. 31. Circular and spiral waves arising from local excitability perturbation. The wave fronts and wave backs are shown by white and black, respectively. A typical primary wave (a) and the perturbation mask (black rectangle) (b). Circular wave (c), counterrotating spiral waves (d), and counterrotating spiral waves within a circular wave (e) are generated in the wave back of the primary wave. Figure from Ref. [113].

Experiments were carried out by placing a photo mask to reduce the illumination intensity at the front of a propagating wave. The wave and the imposed mask are shown in Fig. 31(a) and (b). The mask, which appears as a dark rectangle, effectively increases the excitability of the medium in this region. The effects of this type of perturbation are shown in panels (c)–(e) as a circular wave, spiral waves, or spiral waves within a circular wave, depending on the duration and light intensity of the perturbation. The secondary wave always appears at a point coinciding with the position of the parent wave when the mask was applied.

Numerical simulations using the three-variable photo-Oregonator, Eq. (18), provide insights into the mechanism of the spiral wave initiation from the local perturbation. Simulations of the perturbation and the subsequent spiral wave formation are illustrated in Fig. 32, where the upper panels show the $x, y$ image and the lower panels show the $x, z$ image along a cross-section of the medium (dashed line in panel (a)). We see the circular wave propagating in panel (a), while the lower panel shows the wave with a free end due to the illumination imposed from below. The resulting excitability gradient is sufficiently strong that the wave penetrates only slightly into the medium. The perturbation is applied in panels (b)–(d), and its effect can be seen in panels (c) and (d), with the distortion of the circular wave (upper panels) and curling of the free end of the wave (lower panels). The perturbation is turned off in panel (e), but the local scroll wave continues to exist, striking the upper surface of the medium in panel (f). When the perturbation is turned off, the higher intensity illumination causes the free end of the wave to recede. By the time the wave strikes the surface in panel (f), it is confined to a region close to the surface, and the effect is much like that of initiating a wave in the vulnerable region. As in a 2D medium, the initiated wave begins to expand; however, due to the excitability gradient in the wave back, one side of the circular wave is suppressed, giving rise to two free wave ends. The result of this perturbation in excitability in the transverse direction is therefore a pair of counterrotating spiral waves in the $x, y$ plane.

The three different perturbation-induced wave behaviors shown in panels (c)–(e) of Fig. 31 arise from differences in the illumination intensity and the duration of the perturbation. The circular secondary wave shown in panel (c) occurs with relatively low illumination intensity and short perturbation time. The secondary wave is formed according to the mechanism shown in Fig. 32; however, a weak excitability gradient in the primary wave back allows the perturbation to expand fully as a circular wave. The counterrotating spiral waves formed in panel (d) occur at a higher light intensity
Fig. 32. Simulation showing perturbation-induced spiral waves. Upper panels show \( x, y \) image and lower panels show \( x, z \) image at each time frame. White curves show highest concentration of autocatalyst and white rectangle shows the mask with zero light intensity. The \( z \)-direction in the \( x, z \) images was expanded by a factor of two. Figure from Ref. [113].

(and short perturbation time), which gives rise to a stronger excitability gradient in the wave back and to the formation of the free wave ends. The duration of the perturbation time also affects the evolution of the secondary wave. The spiral waves inside the circular wave shown in panel (e) arise from a perturbation time about twice as long as the period of the induced scroll wave (and higher illumination intensity). The circular wave forms during the first rotation of the scroll wave while the mask is in place, and the spiral waves form during the second rotation of the scroll wave with the perturbation turned off.

The mechanism of the spiral wave formation relies on the three dimensionality of the medium. This mechanism may be relevant to the spontaneous appearance of spiral wave activity in heart tissue, where fluctuations in excitability across the thickness of the tissue could give rise to a perturbation-induced spiral wave.

2.8. Noise-mediated wave behavior

Another means of affecting spatiotemporal dynamical systems is to subject them to parametric noise. This influence is related to the phenomenon of stochastic resonance [116,117], in which the detection of a subthreshold signal is made possible with imposed noise. Stochastic resonance has been demonstrated in many dynamical systems [118], including biological systems in which the detection of neuronal signals is enhanced by imposed noise [119]. Following theoretical studies of noise effects in spatiotemporal systems [120,121], studies of wave propagation in the BZ reaction with imposed noise were carried out [122].

Wave propagation was studied in weakly excitable media in which waves contract tangentially to eventually disappear. Such media are said to be subexcitable, in which sustained propagation of waves with free ends is not supported. (The properties of subexcitable media will be further discussed below.) The effect of noise on waves propagating in a subexcitable BZ medium was studied by imposing noise on the photosensitive system by the use of a video projector, in which the local illumination intensity determines the medium excitability. The gel medium was partitioned into a spatial illumination grid, where each cell of the grid was assigned an intensity chosen randomly from a Gaussian distribution to be above or below a reference intensity. The spatial grid of random intensities was updated at equal time intervals.

Fig. 33 shows the effects of imposed noise on the wave behavior of a subexcitable medium, where superimposed images in each panel represent the evolution of a single wave. The noise level ranges from zero in panel (a) to the maximum possible level in panel (d), determined by the reference illumination intensity in the experiment. Panel (a) shows wave propagation in the autonomous subexcitable BZ medium, where the wave recedes tangentially at
its free ends until it disappears [123,124]. Panel (b) shows the behavior with an imposed noise level at 30% of the maximum level, in which there is a slight enhancement of the wave propagation. A much greater enhancement of the wave propagation occurs with 60% of the maximum noise level, shown in panel (c). At this level, the medium supports apparent sustained wave propagation. At the maximum noise level, shown in panel (d), the propagation is enhanced; however, wave breaks also occur, such that the overall wave propagation is degraded. Panel (e) shows an example of the illumination grid determining the imposed noise.

The noise enhancement of wave propagation can be characterized by measuring the area of the wave segment as it passes a window in the medium. The area of each wave was measured as it passed the point where the wave disappeared in the autonomous system, shown in panel (a). A relative signal strength was defined by this area divided by the original area of the wave segment as it entered the subexcitable region. The relative signal strength as a function of the noise level is shown in Fig. 34, in which measurements were made for two cell sizes defining the noise grid, $4 \times 4$ pixels (solid curve) and $2 \times 2$ pixels (dotted curve). For the larger cell size, we see the relative signal strength increasing to a maximum and then falling off, as the signal is degraded at high noise levels due to wave fragmentation. For the smaller cell size, the relative signal strength reaches a maximum near the maximum noise level.

Fig. 33. Superimposed images of propagating waves in a subexcitable BZ medium with increasing imposed noise, (b)–(d). Wave in noise-free medium (a) and typical array of cells with random gray levels for imposing noise (e). Images of waves were collected at 20.1 s intervals and superimposed for each experiment. Dimensions of panels and superimposed noise array: 12 mm $\times$ 5.2 mm. Figure from Ref. [122].
Fig. 34. The relative signal strength as a function of noise level, where points represent averages of 12–15 measurements and bars show standard deviations. The solid (dotted) curve shows behavior for cells of $4 \times 4$ pixels or $0.33 \, \text{mm} \times 0.33 \, \text{mm}$ ($2 \times 2$ pixels or $0.16 \, \text{mm} \times 0.16 \, \text{mm}$). Figure from Ref. [122].

Fig. 35. Simulations of wave propagation with noise levels of 0 (a), 0.3 (b), 0.6 (c), and 1.0 (d) of the maximum level determined by the reference light intensity. Figure from Ref. [122].

Simulations were also carried out using the photo-Oregonator, Eq. (18), with a 2D Laplacian and the imposed noise defined in the same manner as in the experiments. The effect of the imposed noise on wave propagation is shown in Fig. 35, where the noise level is increased from zero to the maximum level. Each panel shows the evolution of a single wave as superimposed images taken at equal time intervals. As in the experiments, we see the wave disappear in the autonomous subexcitable system, shown in panel (a). With the noise level at 30% of the maximum, there is some propagation enhancement, shown in panel (b); however, with the noise level at 60%, the wave propagation is virtually sustained, as shown in panel (c). At the maximum noise level, the wave propagation is enhanced but also degraded by wave fragmentation, as shown in panel (d). Calculations showed a maximum in the relative signal strength as a function of noise level for cell sizes comparable to the wave width. Calculations were also carried out to determine the dependence on the noise time scale, and a maximum was also found in the relative signal strength as a function of noise.
refresh time. At very short refresh times, the noise time scale is fast relative to the reaction–diffusion time scale, and the chemical system simply experiences the average excitability, which is the subexcitable state. At very long refresh times, the chemical wave must propagate through an effectively static grid of excitabilities, and wave propagation may or may not be successful depending on the particular distribution. Between these time scale extremes, there is a maximum in the relative signal strength.

The noise enhancement of wave propagation, shown as the relative signal strength in Fig. 34, has features similar to those found in experiments on stochastic resonance [118]. The support of wave propagation in subexcitable chemical media suggests that noise may play a role in the wave behavior of biological systems. Noise-supported wave activity has been studied in astrocyte syncytia, which may represent a mechanism for long-range signaling in neural tissues [125].

In addition to noise-supported propagating waves, noise initiated and sustained wave behavior has been studied in subexcitable BZ media [126]. The noise level was significantly higher and noisy wave behavior was exhibited in this study, with waves continually initiated, broken, and sometimes destroyed. A statistical analysis proposed by Jung [127], based on coherent spatiotemporal structures, revealed power law relations characteristic of avalanche behavior with no inherent time or length scales [128,129].

An example of the evolution of the noise-mediated behavior is shown in Fig. 36, where panel (a) depicts the noise-free subexcitable medium and panel (f) shows a typical noise grid imposed onto the medium. As the noise is applied, a wave initiation eventually occurs, as shown in panel (b), and this event quickly gives rise to further wave activity, as new waves are initiated and existing waves are broken into wave fragments. Panels (d) and (e) show the wave activity as it approaches its asymptotic behavior, where waves are continually initiated and destroyed. The imposed noise also gives rise to annihilations and merging wave interactions, and the result is a collection of wave segments with a wide range of space and time scales.

Simulations were carried out with a Barkley model [130] modified to allow the excitability to be locally adjusted to mimic the spatiotemporal noise of the experimental system. The calculations showed that wave initiations rarely occur from a single large perturbation but, rather, arise at a cell with a favorable noise history stemming from successive perturbations that increase the medium excitability. The temporal noise history of a cell in which a wave was initiated is shown in Fig. 37, where the bars represent positive and negative perturbations and the solid curve represents the value of the activator $u$. We see that the activator varies little until there is a series of successive positive perturbations, after which the value of $u$ begins to increase at ca. 15.5. The value of $u$ is subsequently reduced, however, as the result of a negative perturbation. A wave is finally initiated at the cell following several positive perturbations, whereupon the value of $u$ reaches a maximum and then decreases as the wave propagates outward and away from the cell. The increased excitability with an accumulation of positive perturbations to give rise to wave initiations has similarities to behavior seen in self-organized criticality [128,129].
Fig. 37. Time sequence of perturbations (bars) at a particular cell and evolution of the autocatalyst concentration \( u \) (solid curve) calculated from a modified Barkley model [130]. Figure from Ref. [126].

Fig. 38. Measured values of coherent structure probability density \( p(s) \) from experiments (circles) and simulations (squares) as a function of the structure size \( s \). The solid lines are given by power laws \( p(s) = bs^a \), where the exponent \( a \) was set to 2.0. Figure from Ref. [126].

The features of noise-supported wave propagation differ somewhat from noise-induced wave initiation. Wave propagation is enhanced when there is a favorable noise history in a particular cell due to successive positive perturbations; however, the wave itself provides the autocatalyst and therefore the medium does not require perturbations as strong as in wave initiation. Noise-enhanced wave propagation has some features akin to percolation [131]; however, the wave retains the smooth features of a reaction–diffusion wave rather than the geometry of the noise grid, demonstrating the importance of self-propagation of the wave. Another important feature in noise-mediated wave propagation is that cells with strongly negative noise histories give rise to wave breaks, as the medium becomes too refractory to support propagation.

A statistical analysis of noise-mediated wave behavior can be developed by examining the coherent spatiotemporal structures [126,127]. This is carried out by stacking successive images to construct a space–time cube, and then measuring the size of the coherent structures composed of excited elements. Determining the probability of each size allows a cluster-size distribution function \( p(s) \) to be plotted as a function of size \( s \), as shown in Fig. 38, where the
circles are from the experimental measurements and the squares are from the simulations. Both the experimental and simulated data yield power laws with exponents very close to 2.0. The scatter seen at high values of $s$ arises from the limited number of large structures observable in a practical experiment or simulation. The power-law relations suggest that the coherent structures have no characteristic space or time scales, which is a result of the continually varying noise pattern. Remarkably, a similar coherent structure analysis of kainate-induced waves in networks of cultured glial cells yields a power-law relation with a similar exponent [125]. This system has dynamical similarities to the noise-mediated BZ system in that wave activity occurs only above a threshold noise level.

More recent studies of noise-supported wave behavior in the BZ reaction have demonstrated that pacemakers generating successive circular waves can be sustained with an appropriate noise level [132].

The experiment consisted of initiating a wave in a medium maintained in an excitable state by an appropriate background illumination intensity $I_0$. The wave was initiated by temporarily imposing a dark region onto the medium, where the system with $I_0 = 0$ is oscillatory. Panels (a’)-(c’) in Fig. 39 show the wave initiation in the noise-free system, in which a single circular wave propagates outward, as expected in an excitable medium. When noise is imposed onto the medium, successive waves are initiated at a pacemaker site, as shown in panels (a)-(c), even though the initial perturbation is switched off after initiation of the first wave. Hence, an oscillatory pacemaker is supported by the imposed noise.

Insights into the noise support of the pacemaker activity as well as noise support of waves in subexcitable and nonexcitable media can be found by analyzing the two-variable photo-Oregonator, with the assumption that purely white noise is imposed on the medium [132]. The noise in the model system is imposed with zero mean fluctuations of the light intensity parameter, which affects the activator variable. Because the noise is multiplicative, the nonlinear coupling gives rise to a nonzero component in addition to the zero mean fluctuations. When this nonzero component is described as the lowest order correction to the kinetics of the system, a term is added that effectively shifts the bifurcation point. Fig. 40 shows the results of this analysis along with supporting numerical simulations. Phase diagrams are plotted in terms of the photo-Oregonator parameter $f$ and the illumination intensity $\phi$. The dotted line shows the boundary between oscillatory and excitable, excitable and subexcitable, and subexcitable and nonexcitable media in the plots corresponding to the panels (a)-(c). The solid lines show how these boundaries are shifted with the assumption of white noise in the theoretical analysis. Hence, in panel (a) we see the noise-free system supports only a single wave as an excitable medium; however, the system with imposed noise supports successive waves as an oscillatory medium. In panel (b), the noise-free system is subexcitable, with wave segments contracting at their ends, while the segments grow in the system with imposed noise, showing that the system is now excitable. In panel (c), the noise-free system is nonexcitable, with the wave failing to propagate, while the circular wave propagates in the system with imposed noise, which may occur in a subexcitable medium.
2.9. Stationary and traveling spots

The experimental observation of self-replicating spots by Swinney and co-workers [133] led to a number of studies of single and interacting spots in model reaction–diffusion systems [134,135]. Krischer and Mikhailov [136] used a variation of the Rinzel–Keller model [137] with global feedback to study localized spots and their transition to translational motion. The diffusion coefficient for the inhibitor variable was chosen to be larger than that for the activator variable so that localized spots of elevated activator concentration were surrounded by a region of elevated inhibitor concentration. The global feedback was determined by the total concentrations of the activator and inhibitor in the medium, and this was used to adjust a parameter that determines the excitation threshold, yielding a negative inhibitory feedback on the growth of the activator domain. Bifurcation analysis and simulations show that, with sufficiently strong global feedback, there is a supercritical bifurcation from a stationary spot to one that is traveling. The left panels of Fig. 41 show the symmetrical distribution of the activator and inhibitor concentrations, while the right panels show how the distributions become asymmetric when the bifurcation parameter is slightly increased. The spot begins to travel when the concentrations become asymmetric, with the concentration profiles reflecting that of a traveling wave.

The traveling spots exhibit a variety of interesting behaviors when they interact with one another. For example, two spots do not annihilate when they collide, as is usually seen in colliding reaction–diffusion waves, but rather they reflect. The reflection behavior is due to the accumulation of inhibitor concentration between the spots when they are in close proximity, which serves to repel them from one another. Similar behavior is observed in the Gray–Scott model [138], where waves “bounce” off each other and no-flux boundaries [139]. The mechanism for this behavior involves the consumption of the reactant variable between the waves, which gives rise to waves repelling each other. The same mechanism is responsible for wave reflection at no-flux boundaries. Krischer and Mikhailov also found that moving spots are reflected from no-flux boundaries. Furthermore, they found that faster moving spots at conditions farther away from the bifurcation point fused on collision, and the new spot then became unstable to produce two new spots traveling apart at right angles to the collision path. In addition, it was found that spots in an oblique collision may fuse to form a stable spot, which exhibits new properties, such as traveling along no-flux boundaries. A detailed review of analytical and numerical studies, related to traveling spots, has been given by Nishiura et al. [197].
2.10. Stabilizing unstable waves

As the excitability of an active medium is decreased, a critical excitability is reached below which waves with free ends contract and disappear. An example of a wave laterally contracting until it disappears is shown in panel (a) of Fig. 33. The critical excitability depends on the size of the wave segment; for each excitability, there is a wave segment with a particular size and shape that will contract if the excitability is decreased and will grow if the excitability is increased. The wave segment size as a function of the critical excitability can be characterized by the use of feedback techniques to stabilize the unstable wave segments [140,141]. The locus of stabilized wave size as a function of excitability represents the excitability boundary for spiral wave behavior in 2D media.

Unstable wave segments are stabilized by adjusting the light intensity $\phi$ proportional to the wave area $A$ according to a negative feedback law

$$\phi = aA + b,$$

where $a$ is the feedback or gain coefficient and $b$ is the offset parameter, which determines the excitability of the medium. The area of the wave is defined by the region of the medium where the ruthenium catalyst is in the oxidized state, which is determined by counting the pixels with a gray level above some threshold value. The pixel counting algorithm is given by

$$A = \sum_{x,y} \Theta(p(x, y) - k \overline{p(x, y)}),$$

where the gray level at each pixel is $p(x, y)$, $\Theta$ is the Heaviside function, and the threshold is set at a value slightly above the average gray level $\overline{p(x, y)}$ over the image by assigning $k \gtrsim 1$. Using the average gray level of the image as the basis of the threshold allows the wave area to be accurately measured in the presence of unavoidable light intensity fluctuations.

The feedback algorithm stabilizes the unstable wave at a specific size corresponding to the particular excitability. If a fluctuation increases the wave area, the light intensity increases and the excitability decreases, causing the wave area to decrease. On the other hand, if a fluctuation decreases the wave area, the light intensity decreases and the excitability increases, which results in the wave area increasing. The control perturbations become vanishingly small as the wave assumes its stationary size and shape. Hence, the wave segment size and shape can be found for each value of the light intensity, which is determined by the offset parameter $b$. Fig. 42 shows examples of stabilized waves at four different values of $b$ in Eq. (20). We see that the area of the stabilized wave increases with increasing light intensity, corresponding to decreasing excitability.
Fig. 42. Stabilized waves in a photosensitive Belousov–Zhabotinsky medium. Panels (a)–(d) show superimposed images of waves at 40 s intervals for four different excitabilities. The scale bar in panel (d) is 1.0 mm. Figure from Ref. [141].

Simulations of the wave stabilization were carried out with a two-variable version of the photo-Oregonator, Eq. (18), together with the control algorithm, Eq. (20). The initial conditions consisted of a wave segment that, under the influence of the control, settles into its stationary size and shape, as shown in Fig. 43(a). If the control algorithm is turned off, the unstable wave will eventually decay or grow. This process can be seen in panels (b) and (c), where the rates of decay and growth were increased by short perturbations in the light intensity. The wave in panel (b) laterally contracts until it disappears, while the wave in panel (c) will grow until it either forms counterrotating spirals or becomes pinned at the boundaries of the medium. The behavior of the perturbed unstable wave demonstrates its saddle-like character.

The locus of unstable wave size as a function of light intensity can be determined by varying the offset parameter $b$ in Eq. (20). This locus for the behavior simulated with the photo-Oregonator is shown by the circles in Fig. 44. As can
be seen, the wave size increases with increasing light intensity or decreasing excitability, diverging at the value $\phi_{2D}$. The asymptote of the curve at $\phi_{2D}$ represents the excitability limit for spiral wave behavior; the sustained propagation of waves with free ends is not possible at lower excitabilities [142]. Another excitability boundary, $\phi_{1D}$, exists at a lower excitability, below which the propagation of 1D waves or unbounded planar waves in 2D media is not possible [142]. The medium is subexcitable between the excitability boundaries $\phi_{2D}$ and $\phi_{1D}$.

A simple kinematic description of the stabilized wave segments can be developed to characterize the excitability boundary for spiral wave behavior [140]. The stationary state wave is considered in a moving coordinate system, where the size and shape are constant. A contour corresponding to the concentration of the autocatalyst $u$ is shown by the dotted curve in Fig. 45. This constant form, constant velocity wave was calculated with the two-variable photo-Oregonator. The kinematic model is based on this stationary waveform, which is shown by the solid curve $s$, where only one half of the wave front is considered due to the symmetry of the wave.

The velocity $v_0$ of the wave in the positive $x$-direction is given by the normal velocity at the origin of $s$ at $y = 0$. At any point along the curve, the normal velocity forms an angle $\alpha$ with respect to the $x$-direction, where $\alpha = 0$ and $\pi/2$ at $y = 0$ and the extremum of the curve, respectively. Every point $A$ on the curve $s(t)$ becomes some point $B$ on the curve $s(t + dt)$ in the time increment $dt$ according to the normal velocity $v_\perp$. This shape stationarity can expressed as a geometric constraint,

$$v_\perp = v_0 \cos(\alpha).$$  (22)
The curvature of the wave front is small except near the free ends, and the normal velocity dependence on curvature can be approximated with the linear eikonal equation

\[ v_\perp = v_\infty - DK, \tag{23} \]

where \( v_\infty \) is the planar wave velocity, \( D \) is the diffusion coefficient associated with the diffusivity of the autocatalyst \( u \), and the curvature is \( K = \dot{z}' \). Combining the stationarity relation with the eikonal equation yields

\[ v_0 \cos(\dot{z}) = v_0 + DK_0 - D\dot{z}', \tag{24} \]

in which the curvature at the midpoint of the wave is \( K_0 \).

Eq. (24) can be solved with the assumption of small curvature to yield the approximation

\[ \dot{z} = \lambda K_0 \tan(l/\lambda), \tag{25} \]

where

\[ \lambda = \sqrt{\frac{2D}{v_0 K_0}}. \tag{26} \]

The length \( L \) of the curve can be related to the excitability by using the empirical observation from the simulated contours that the curvature at midpoint \( K_0 \) is an approximately linear function of \( \phi \),

\[ K_0 = (\phi_{2D} - \phi)/c \tag{27} \]

with an empirical constant \( c \). Combining this relation with Eq. (25) produces a relation between the length \( L \) and the light intensity \( \phi \) [140],

\[ L^2 \propto \frac{\pi^2 D}{2v_0} \frac{c}{(\phi_{2D} - \phi)}. \tag{28} \]

This semiempirical relation is in good agreement with the locus of unstable wave size determined in the numerical simulations, as shown by the solid curve in Fig. 44. Note that, except for the smallest wave segments, \( S \) and \( L \) are proportional.

We see that the size of the unstable wave diverges at the value \( \phi_{2D} \), given by the asymptote of the curve. Earlier studies of spiral waves have shown that as the excitability is decreased the period of the spiral increases. Studies of the unbounded spiral wave identified the excitability limit for spiral wave behavior as the point where the spiral opens up to become semiplanar and stationary in the moving coordinate system [142]. This point is exactly the same as the asymptote to the locus of the unstable waves, \( \phi_{2D} \). At slightly lower excitabilities, the medium is subexcitable and the unbounded spiral wave laterally contracts at its tip.

A more recent theoretical treatment [143] of stabilized wave segments has followed advances in characterizing steadily rotating spiral waves in excitable media and “critical fingers” in weakly excitable media based on wave front interaction models [144,145]. The critical finger is the unbounded spiral wave at the excitability boundary (\( \phi_{2D} \) in Fig. 44), where both the spiral core and the rotational period become infinite. The waveform of the critical finger is nearly planar with a free end, and when the excitability is reduced below the excitability boundary, the critical finger contracts at its free end [142]. A review of wave front interaction models for spiral waves and critical fingers can be found in Ref. [146]. As noted above, the excitability boundary for the unbounded spiral wave corresponds to the asymptote of the locus of unstable wave segments as a function of excitability, shown in Fig. 44.

Stabilized wave segments with a stationary waveform and constant velocity are particularly amenable to characterization with a wave front interaction model [143]. A generic two-variable, reaction–diffusion model can be used to describe these waves:

\[ \frac{\partial u}{\partial t} = D\nabla^2 u + F(u, v), \]

\[ \frac{\partial v}{\partial t} = \epsilon[G(u, v) + I(t)], \tag{29} \]
where \( u(x, y, t) \) and \( v(x, y, t) \) are the activator and inhibitor variables. For this treatment, it is useful to define the functions \( F(u, v) \) and \( G(u, v) \) for a general excitable medium [144]:

\[
F(u, v) = 3u - u^3 - v, \\
G(u, v) = u - \delta.
\] (30)

The feedback stabilizing the unstable wave segments is described by the function \( I(t) \), which represents an imposed influence on the system such as the illumination in the BZ reaction described above. The excitability boundary between excitable and subexcitable behavior, where the critical finger is exhibited, occurs at \( I(t) = I_c \). Propagating wave segments contract when \( I(t) > I_c \), where the medium is subexcitable and sustained propagation is not supported. The medium is excitable when \( I(t) < I_c \), and here wave segments of different sizes corresponding to different excitabilities can be stabilized.

The wave front interaction model not only considers the wave front, as in the treatment described above, but also the wave back, and it is the interaction of these interfaces that is key to the characterization. The width of the half-wave \( y_{\text{max}} \) is now considered rather than the arc length [140,141], and wave size is described by the location of the wave tip along the \( y \)-axis perpendicular to the direction of propagation. The stabilization feedback \( I(t) \) is proportional to \( y_{\text{max}} \), where the control law for the target width \( y_d \) is given by

\[
I(t) = k_{fb}(y_{\text{max}}(t) - y_d) + I_0.
\] (31)

Because an increase in light intensity causes a decrease in excitability, and the wave segment grows with an increase in excitability, Eq. (31) results in negative feedback to the medium excitability with wave size.

The model is developed in terms of the boundaries defined by the wave front and the wave back [143]. This represents a free-boundary problem in which the normal velocity of the boundary \( c_n \) is a function of the local curvature \( k \) and the value of the slow variable \( v \). Fig. 46 shows the half wave segment, where the normal velocity at midpoint, \( y = 0 \), corresponds to the overall wave velocity. The local curvature of the interface is defined in terms of the angle \( \Theta^+ (\Theta^-) \) between the \( x \)-axis and the outward (inward) directed normal for the wave front (back). The arc length is \( s^+ (s^-) \), which is measured from the extremum of the wave. The normal velocity for the wave front is \( c_n^+ = c(v^+) - Dk^+ \) and is \( c_n^- = -c(v^-) - Dk^- \) for the wave back, where the local curvature of the front and back is given by

\[
k^\pm = -d\Theta^\pm/\mathrm{d}s^\pm.
\] (32)
For the free boundary problem, we define the curvature at midpoint $k_m$, and note that the propagation velocity is then $c_s = c_0 - Dk_m$, where $c_0 = c(v^+) = c(v_0)$. We can then write

$$c_0 - Dk^+ = c_s \cos(\Theta^+), \quad (33)$$

$$-c(v^-) - Dk^- = c_s \cos(\Theta^-), \quad (34)$$

$$c_s \frac{dv}{dx} = -\epsilon [G(u_c(v), v) + I_s], \quad (35)$$

where $u = u_c(v)$ within the excited region, in which $u_c(v)$ is the largest root of $F(u, v) = 0$. Here, Eq. (33) describes the wave front and Eq. (34) describes the wave back, while the evolution of the slow variable $v$ between the front and the back is described by Eq. (35).

Fig. 46 shows the half-wave segment in terms of the free boundary problem, where the wave front is represented by the thick line and the wave back by the thin line. The solution of Eqs. (33)–(35) yields the critical parameter $B_k$, which depends on the control parameter $I_s$ and, hence, the excitability. For the value of $K_m$ corresponding to the particular wave shown in Fig. 46, there is a unique value of $B_k$ that satisfies the boundary condition $y^- = 0, \Theta^- = 0$. Slightly larger and smaller values of $B_k$ yield the diverging solutions shown by the dashed and dotted lines, respectively. By iteratively solving for the appropriate values of $B_k$ as a function of $K_m$ (for $K_m > 1$), a linear relation for $B_k(K_m)$ is found:

$$B_k = B_0 - \beta \frac{Dk_m}{c_0}, \quad (36)$$

where $\beta = 0.63$. The wave segment is identical to the critical finger for $K_m = 0$. Note that the value of $B_k(K_m \to 0)$ computed in the free boundary problem given by Eqs. (33)–(35) is $B_0 = 0.535$, which is same as that found for the critical finger [144,146].

The dependence of the width of the stabilized wave segment on the control parameter $I_s$ can be determined by direct numerical integration of the reaction–diffusion model Eqs. (29) and (30), which is shown in Fig. 47 by the solid line. Solution of Eqs. (33)–(35) yields the following expression for this dependence for Eqs. (29) and (30) [143]:

$$\frac{D^2}{W^2 c_0^2} = \frac{2B_0}{\beta \pi^2} \left\{ \frac{9[(\delta - I_L)^2 - 1]}{\Delta c} + \frac{1}{G_c^*} \right\} (I_c - I_L), \quad (37)$$

where $G^* = \sqrt{3} - \delta + I_L$ and $\Delta = (\delta - I_L)^3 - 3(\delta - I_L)$. Substitution of the computed wave velocity $c_0$ into Eq. (37) allows the wave width $W$ to be determined as a function of the control parameter $I_s$, which is shown in Fig. 47 by the
Fig. 48. (Color online.) Waves controlled to follow hypotrochoid target trajectories (red curves). Each panel shows a composite image of superimposed snapshots of a single propagating wave. Experimental images are shown in the left-hand panels and simulated images are shown in the right-hand panels. Figure from Ref. [147].

dashed line. We note that there is excellent agreement between the numerical results and the prediction from the wave front interaction model.

2.11. Controlling unstable waves

The stabilized particle-like waves described above can be controlled by introducing a second feedback loop in which an excitability gradient is imposed onto the wave to guide its propagation direction [147]. Many types of directional control can be imposed on a propagating wave segment, some of which are described below. The experimental setup is similar to that described above, in which the illumination determines the excitability, but now the illumination pattern is based on the feedback law

\[
\phi(x, y) = aA + b + cG(x, y),
\]

\[
A = \sum_{x, y} \Theta(p(x, y) - p_{th}).
\]

This control algorithm is essentially the same as Eqs. (20) and (21) but with the added term \(G(x, y)\), which provides the feedback control for guiding the propagation direction of a wave segment. As discussed below, different realizations of \(G(x, y)\) give rise to different implementations of spatiotemporal control. The effects of the control gradient on the stabilization feedback are minimized by centering the excitability gradient at the wave “center of mass”, where the gradient is applied perpendicular to the normal velocity. The light intensity gradient results in an excitability gradient, which causes the wave to turn to the left or right according to the gradient sign and at a rate that depends on its magnitude.

An example demonstrating the power of directional control is shown in Fig. 48. Here the control function \(G\) is dynamically varied according to the current location of the wave center of mass and the target location for the control.
In this example, the target trajectories are various hypotrochoid paths according to the geometric formulas

\[
X = (\alpha - \beta) \cos(\theta) + \gamma \cos\left(\frac{\alpha}{\beta} - 1\right)(\theta),
\]

\[
Y = (\alpha - \beta) \sin(\theta) - \gamma \sin\left(\frac{\alpha}{\beta} - 1\right)(\theta).
\]

Here, \( \theta \) is the independent variable, and \( \alpha, \beta, \) and \( \gamma \) are parameters giving the hypotrochoid trajectories shown in Fig. 48.

As the wave varies from the target trajectory, a control excitability gradient is applied that is proportional in magnitude to the distance between the current wave location and its target location. Hence, the farther the wave is from its target trajectory, the larger the gradient guiding it to its target location. Within the limitations of reaction–diffusion dynamics, virtually any target trajectory can be tracked by the stabilized waves controlled with excitability gradients.

Excitability gradient control can also be used to confine a wave to a particular region of the medium. Panels (a) and (b) of Fig. 49 show experimental and simulated waves that are confined to a particular region of the medium. No excitability gradient is applied when the wave is inside the rectangular box, and the wave therefore propagates in a straight line within the box. When the wave reaches the boundary defined by the box, a constant excitability gradient is applied perpendicular to the normal wave velocity, which causes the wave to turn in a circular path. When the wave reenters the box, the gradient is switched off again. In this manner, the wave is confined to a region that extends to twice the turning radius of the wave beyond the box boundary. It is possible to incorporate other boundary-reflection rules that result in more realistic reflection behavior.

A control algorithm can be devised for two waves interacting with each other to form a stable orbit. Panels (c) and (d) of Fig. 49 show experimental and simulated trajectories of two waves that interact according to the control law,

\[
\text{grad}(G_i) = \hat{k}_i \begin{cases} 
\left( \frac{d}{100} \cdot \theta_i + \frac{100}{d} \cdot (\theta_i - 180) \right), & \quad \theta_i \geq 0, \\
\left( \frac{d}{100} \cdot \theta_i + \frac{100}{d} \cdot (\theta_i + 180) \right), & \quad \theta_i < 0,
\end{cases}
\]

where \( i = 1, 2 \) for wave 1 and 2, \( d \) is the distance between the wave centers of mass, \( \theta_i \) is the angle between the normal wave velocity and the line connecting each wave center of mass, and \( \hat{k}_i \) is the unit vector perpendicular to the normal velocity. In both the experiments and simulations, the waves slightly repel on approaching each other and then settle.

Fig. 49. (Color online.) Experimental (a) and simulated (b) behavior shows wave constrained to rectangular region. Experimental (c) and simulated (d) waves interacting according to Eqs. (38) and (41). Fig. from Ref. [147].
into a stable orbit if the interaction strength $c$ in Eq. (38) is the same for each wave. The orbital stability is tested in the simulations by discontinuously displacing the waves and monitoring their relaxation back to the orbit, as shown in panel (d).

The excitability gradient in Eq. (38) can also be varied randomly to give rise to Brownian-like motion of a propagating wave. Experimental and simulated trajectories of three waves are shown in panels (a) and (b) of Fig. 50. The imposed noise was switched on at the same point in the experimental case, while the waves with imposed noise were started at the same point in the simulations. In both cases, the different waves explore the medium with completely different trajectories that are akin to random walks. Successive snapshots of the propagating wave for one of the trajectories in panels (a) and (b) are overlaid to show the wave behavior. Various modifications of the imposed random variations of $G$ in Eq. (38) could be made, for example, to yield a biased random walk.

It is important to stress that the wave patterns described above depend upon two feedback loops. The primary feedback loop stabilizes wave segments that otherwise would not exist. The secondary feedback loop controls the excitability gradient allowing the wave to be guided. This spatiotemporal feedback provides great flexibility in manipulating wave behavior. An interesting extension of these control methods would be a spatiotemporal version of the control methods used to probe underlying chemical mechanisms in homogeneous systems [148,149].

2.12. Controlling scroll wave turbulence

Studies of controlling scroll wave dynamics in 3D excitable media have been carried out by Alonso et al. [150,151]. Winfree [152] postulated over a decade ago that the turbulent wave behavior observed in cardiac fibrillation is due to scroll waves losing stability in the 3D medium. Specifically, scroll waves exhibit negative filament tension in weakly excitable media [153–156], and the resulting complex motions give rise to turbulent spatiotemporal dynamics. Fig. 51 shows the development of what is now known as Winfree turbulence [150], where the yellow curve shows the spiral filament and the red bands and blue background on the bottom and sides of the cubic medium indicate high and low levels of the inhibitor variable, respectively. Panel (a) shows these representations for a symmetrical scroll wave in which the filament is a uniform circle. The filament first exhibits small distortions, as can be seen in panel (b), and then grows with twists and loops in complex motions, as shown in panels (c) and (d). The expanding tangle becomes fragmented when it collides with the boundaries of the medium. The accompanying wave behavior, indicated by the red bands, becomes highly turbulent and is characterized by a broad frequency spectrum and rapid decay of the spatial autocorrelation function [150,151].

Alonso et al. [150,151] found that the turbulence could be suppressed when the excitability of the medium is varied periodically at a period less than that of the autonomous scroll wave, $T_f < T_0$. The periodic forcing was turned on in panel (e), and the subsequent panels (f)–(i) show how the filament shrinks and the wave behavior becomes regular.
Fig. 51. (Color online.) Three-dimensional spatiotemporal behavior of a scroll wave with negative filament tension (a)–(c) and turbulence suppression with periodic forcing (f)–(i). Figure from Ref. [150].

Fig. 52. (a) Time evolution of filament length for an expanding scroll ring (dark line) and under periodic forcing (gray line). (b) Evolution of filament length for a collapsing scroll ring (dark line) and under periodic forcing (gray line). (c) Boundary between expanding and collapsing scroll ring under periodic forcing for minimal forcing amplitude \( b_f \) as a function of forcing frequency \( \omega_f \). Fig. from Ref. [150].

The forcing causes closed loops of the filament to shrink and disappear, as well as the formation of new closed loops due to filament crossings, which also proceed to disappear. Typically, all wave activity eventually disappears; however, a scroll wave with a linear filament connected to opposite boundaries of the medium is occasionally displayed. The turbulence did not collapse when the forcing period was greater than the period of the scroll wave, \( T_f > T_0 \).

Further analysis of the effects of periodic forcing showed that in the parameter regime where scroll rings expand, the filament rings contract for \( T_f < T_0 \) and expand more rapidly for \( T_f > T_0 \). Fig. 52(a) shows the filament length of an autonomous scroll ring expanding (dark curve) and contracting (gray curve) when periodic forcing is imposed with
$T_f < T_0$. In the parameter regime where scroll rings collapse, forcing with $T_f < T_0$ increases the rate of collapse, while forcing with $T_f > T_0$ causes filament ring expansion, eventually leading to turbulent behavior. Fig. 52(b) shows the filament length of a scroll ring contracting (dark curve) with no forcing and expanding (gray curve) when periodic forcing is imposed with $T_f > T_0$.

A kinematic theory has been developed\cite{150,151} that predicts the effective filament tension should vanish for forcing amplitudes $b_f$ and frequencies $\omega_f$ according to

$$b_f \propto (\omega_f - \omega_0)^{1/2}, \quad (42)$$

where $\omega_0$ is the rotational frequency of the autonomous scroll wave. The scroll ring should be stabilized for these values of forcing amplitude and frequency, since it then will neither expand nor contract. The theoretical prediction was tested with numerical simulations, shown in Fig. 52(c). The open circle shows the autonomous spiral wave frequency and the filled circles show the values of forcing amplitude and frequency where the scroll ring was stabilized. As can be seen by the curve described by Eq. (42), there is good agreement between the simulations and the kinematic theory.

2.13. Pattern selection with length scale feedback

A new approach for controlling spatiotemporal behavior has been proposed that is based on feedback to the excitability of the medium in proportion to a measure of the coherent structures\cite{157}. Specifically, the feedback signal is determined from the spatial distribution of an active species, where the signal strength is proportional to the modulus of the Fourier coefficient for the distribution of that species. In this way, the feedback signal directly depends on the length scales of the instantaneous spatiotemporal patterns of the system. The feedback control method has been applied to the oxidation of CO on Pt(1 1 0). Images of the patterns were obtained using a PEEM, which allows the identification of CO and O covered areas on the Pt surface\cite{158}.

The system was studied under excitable conditions, and the CO partial pressure $p_{\text{CO}}(t)$ served as the feedback parameter according to

$$p_{\text{CO}}(t) = p_{\text{CO}}^0 + \mu |\hat{k}(t - \tau)|, \quad (43)$$

where $k$ is the modulus of the wave vector of the Fourier coefficient $\hat{k}$ from the PEEM images, $p_{\text{CO}}^0$ is the reference partial pressure, $\mu$ is an intensity coefficient, and $\tau$ is a delay time. The pattern formation occurs periodically with the growth of oxygen covered islands, where the period depends on the intensity coefficient and the delay time. The period also depends on the modulus $k$, but most interesting is the dependence of the characteristic size of the spatiotemporal structures on the value of $k$. Fig. 53(a)–(d) shows typical oscillatory oxygen coverage patterns with increasing values of $k$, where the images were taken at the maximum of the feedback signal to enable a size comparison. We see that the larger the value of $k$, the larger the coherent spatiotemporal structure. Fig. 53 also shows how the experimental (e) and simulated (f) oscillatory period increases with increasing value of $k$. These experiments and calculations demonstrate a new algorithm for controlling spatiotemporal pattern formation, where the coherent structure size is selected by the value of the feedback parameter given by the wave vector modulus $k$.

2.14. Pattern selection by controlling relative diffusivities

New modes of reaction–diffusion pattern formation have been found by Vanag and Epstein\cite{159–162} in a system comprised of the BZ reaction in a water–oil microemulsion. The surfactant aerosol OT (AOT) gives rise to a microemulsion of nanometer-sized water droplets dispersed in octane. The water soluble species of the BZ reaction are localized in the aqueous droplets, which have a characteristic diffusion rate in the octane medium, while the octane soluble species may diffuse between droplets. Thus, the AOT-BZ system provides a means to generate widely different diffusivities of the reacting species, which gives rise to new and interesting spatiotemporal patterns.

Different regimes of pattern formation can be explored by varying the radius of the aqueous droplets, the concentrations of the BZ reactants, or the volume fraction of the dispersed phase, which includes the droplets and the surfactant. In a narrow region of constraint space, a hybrid between traveling waves and Turing patterns called “dash waves” has been found\cite{162}. Fig. 54 shows an example of these waves, where the closed system evolves in time from exhibiting phase waves, panel (a), to the excitable medium with traveling dash waves, panels (b)–(g). Most of the dash waves
Fig. 53. (a–d) Images showing oxygen coverage taken at maximum of feedback signal for increasing values of the wave vector modulus $k$. Dependence of period on value of $k$ in experiments (e) and in simulations (f). Figure from Ref. [157].

Fig. 54. Evolution of spatiotemporal behavior in the AOT-BZ system exhibiting dash waves. Panels (b)–(g) show behavior at 1800, 935, 940, 945, 950, and 1000 s following the image shown in panel (a). Panels (c)–(f) show the time evolution of a small region in panel (g). The gray levels indicate the concentration of ferroin, where black (white) corresponds to high (low) levels. Dimensions of panels (a), (b) and (g): 2.54 × 1.88 mm$^2$; dimensions of panels (c)–(f): 0.53 × 0.53 mm$^2$. Figure from Ref. [162].

travel in a direction parallel to their neighboring waves; however, some waves at apparent defects or turning points split to become two waves. An example of a splitting wave is shown in panels (c)–(f).

A key experimental observation provided an essential insight into the spatiotemporal behavior. Light scattering measurements showed that the system exhibits two maxima in the droplet size distribution, one at about 2 nm and the other near 20 nm. An Oregonator-based model was then developed that described the chemistry and transport in a system with two different droplet sizes. This model proved to be bistable, with three homogeneous steady states. One
state is stable and excitable, one is always an unstable saddle, and one is unstable to homogeneous perturbation but exhibits a Turing-like instability. Because it is unlike the classical Turing instability, where $\text{Re}(\lambda) < 0$ at $k = 0$, it is called a pseudo-Turing instability (PT). When the parameters are chosen such that the PT instability occurs, spatiotemporal behavior is exhibited that includes waves much like the dash waves observed in the experiments. The dash waves arise from the presence of the two states, where a perturbation causes the system to change from the excitable state with traveling waves to the state with the PT instability. Although this state is unstable, the system does not relax uniformly to the excitable state. Instead, the relaxation is nonuniform and dash waves are formed with a characteristic wavelength dependent only on the system parameters and not on the medium size.

The existence of the 1D Turing instability incorporated into the traveling wave was confirmed with numerical simulations. Fig. 55 shows the behavior calculated from the Oregonator model described above, panel (a), and from a reduced two-variable Oregonator model with a feed term to induce the required bistability, panel (b). A Gray–Scott model [138] was also examined in which the parameters were tuned to generate bistability, with one of the states exhibiting the PT instability. Dash waves were also found in this study, shown in panel (c).

3. Control of waves in oscillatory media

Application of periodic forcing and global feedbacks to oscillatory media allows to create new kinds of wave patterns and to control them by variation of the forcing or feedback parameters. In this Chapter, we shall consider only such media where, without forcing or feedback, uniform oscillations are stable and chemical turbulence is absent. This is characteristic for the experiments with the oscillatory BZ reaction where turbulence does not spontaneously develop. For surface chemical reactions, both stable uniform oscillations and the state of spatiotemporal turbulence can be experimentally realized, depending on the choice of an experimental system and reaction parameters. Our survey begins with the effects of periodic forcing, followed by the discussion of additional phenomena observed when global feedbacks are present. As the principal theoretical model, the complex Ginzburg–Landau equation shall be mainly used here. In the experiments with the photosensitive BZ reaction, periodic forcing or global feedback are implemented by varying the illumination intensity. For surface chemical reactions, the rates of supply of gaseous reactants can be controlled, thus affecting the reaction course on the entire catalytic surface.

3.1. Uniform periodic forcing

When periodic forcing acts on any dynamical system, its effects strongly depend on the relationship between the forcing frequency $\Omega_t$ and the natural oscillation frequency $\Omega_0$ of the system. When conditions $n\Omega_t = m\Omega_0$ with integers $n, m = 1, 2, 3, \ldots$ are realized, the system becomes particularly sensitive to external forcing and resonances.
are expected. Such resonances are conventionally classified through their respective frequency ratios $m : n$. The strongest $1:1$ resonance takes place when the forcing frequency coincides with the frequency of natural oscillations ($n = m = 1$). Higher resonances with $n > 1$ or $m > 1$ are usually divided into superharmonic ($m > n$) and subharmonic ($m < n$).

Another important parameter, specifying external forcing, is its intensity $B$. Sufficiently strong periodic forcing can entrain a dynamical system even if its frequency does not exactly match a resonant condition. In the entrained state, the system oscillates not at its natural frequency, but at the resonant frequency imposed by the external forcing. For any fixed intensity $B$, the entrainment with respect to a particular $m : n$ resonance is only possible if the detuning $\nu$, defined as $\nu = \Omega t - (m/n)\Omega_0$, is not too large. This means that, for a particular resonance and a given forcing intensity, an entrainment window $\nu_-(B) < \nu < \nu_+(B)$ can be identified.

The entrainment windows grow with the forcing intensity and, in the parameter plane $(\nu, B)$, they form characteristic structures known as Arnold tongues. Generally, the tongues corresponding to higher resonances are more narrow. At high forcing intensities different tongues overlap, giving rise to complex dynamical behavior.

Investigations of resonances in dynamical systems is a classical problem in the theory of nonlinear ordinary differential equations. Their results are applicable to dynamical systems of any origin, including chemical reactions in well-stirred tanks where spatial variation is insignificant. Because of the obvious generality of such mathematical results, their special discussion for chemical systems is superficial. The situation is however different for oscillatory reaction–diffusion systems, described by partial differential equations for chemical concentrations. Action of uniform periodic forcing on such chemical systems leads to new interesting phenomena which we are going to review.

Suppose that a reaction–diffusion system is described by a set of kinetic equations for reactant concentrations $c = \{c_1, c_2, \ldots, c_N\}$

$$
\dot{c} = f(c, p) + \tilde{D} \nabla^2 c,
$$

(44)

where $\tilde{D}$ is the diffusion matrix and $p$ is some global reaction parameter (not varying across the reaction volume). The system exhibits stable periodic oscillations with frequency $\Omega_0$. Uniform external forcing is introduced by periodically varying the global reaction parameter

$$
p(t) = p_0 + B \sin(\Omega_0 t),
$$

(45)

at frequency $\Omega_0$ with amplitude $B$.

When only uniform spatial states of the chemical system are considered, the diffusion term in Eq. (44) plays no role and general results of nonlinear dynamics are valid. System (44) with forcing (44) will have a set of resonances and the respective pattern of Arnold tongues. Our aim is to consider spatial concentration patterns in the forced system, where diffusion of reactants is important. We shall assume that forcing is so weak that Arnold tongues do not overlap and different resonances are independent. Suppose that we are near a particular $m : n$ resonance with $\Omega_0 = (m/n)\Omega_0$.

Because we are more interested in studying the universal behavior than in the discussion of special properties of particular chemical systems, we shall restrict our analysis to systems near the soft onset of self-oscillations described by a supercritical Hopf bifurcation. Such systems are approximately described by the complex Ginzburg–Landau equation for the complex oscillation amplitude $A(\mathbf{r}, t)$. In dimensionless variables, this equation reads

$$
\dot{A} = (1 + i\omega_0)A - (1 + i\beta)|A|^2A + (1 + i\epsilon)\nabla^2A.
$$

(46)

The system performs harmonic uniform oscillations with frequency $\Omega_0 = \omega_0 + \beta$ and amplitude $R = |A| = 1$. The oscillations are stable if the Benjamin–Feir condition $1 + \epsilon\beta > 0$ is satisfied, as we shall assume below.

Eq. (46) corresponds to the unforced system ($B = 0$). If forcing is present but weak, there should be additional terms on right-hand side of this equation, proportional to various powers of the forcing intensity $B$. Thus, we have an equation of the form

$$
\dot{A} = (1 + i\omega_0)A - (1 + i\beta)|A|^2A + (1 + i\epsilon)\nabla^2A + Bg(A, A^*)\sin(\Omega_0 t) + B^2h(A, A^*)\sin^2(\Omega_0 t) + \cdots,
$$

(47)

where $g(A, A^*), h(A, A^*), \ldots$ are some functions of the complex oscillation amplitude and its complex conjugate $A^*$, depending on a particular considered system (44). Note that these functions can also be decomposed in
powers of amplitudes,
\[ g(A, A^*) = g_0 + g_{11}A + g_{12}A^* + g_{21}A^2 + g_{22}|A|^2 + g_{23}A^{*2} + \cdots, \]
(48)
\[ h(A, A^*) = h_0 + h_{11}A + h_{12}A^* + h_{21}A^2 + h_{22}|A|^2 + h_{23}A^{*2} + \cdots. \]
(49)

Let us compare the role of different forcing terms in the equation obtained after such decompositions. A term proportional to \( A^j(A^*)^k \exp(i\Omega t) \) oscillates approximately as \( \exp[i(j - k)\Omega_0 t + i\Omega t] \) and thus as \( \exp[i(j - k + lm/n)\Omega_0 t] \) near the considered resonance \( \Omega_\ell = (m/n)\Omega_0 \). Because the complex amplitude \( A \) oscillates as \( \exp(i\Omega_0 t) \), only the resonant terms with \( j - k + lm/n = 1 \) will have the same oscillation frequency as the amplitude \( A \). The other terms are nonresonant and their effect is negligible (note that nonresonant terms are not also included into the complex Ginzburg–Landau equation). Furthermore, it would suffice to keep only the resonant term \( l = n \) and \( j = 0 \) with the lowest order in \( A \) and \( B \) here. Retaining this dominant resonant term, we arrive at the equation
\[ \dot{A} = (1 + i\omega_0)A - (1 + i\beta)|A|^2 A + (1 + i\epsilon)\nabla^2 A + \zeta B^n(A^*)^{m-1} \exp[i\Omega t], \]
where \( \zeta \) is a numerical coefficient.

Examining this equation, it can be noticed that the \( mn \) resonances with \( n > 1 \) are formally equivalent here to the \( m:1 \) resonance with respect to external forcing at frequency \( n\Omega \) with intensity \( B^n \). Hence, they should not be specially considered. Moreover, the numerical coefficient \( \zeta \) can be incorporated into the parameter \( B \) defining the forcing intensity. With these arguments, we arrive at the canonical form of the complex Ginzburg–Landau equation with external forcing in the vicinity of a \( m:1 \) resonance
\[ \dot{A} = (1 + i\omega_0)A - (1 + i\beta)|A|^2 A + (1 + i\epsilon)\nabla^2 A + B(A^*)^{m-1} \exp[i\Omega t]. \]
(51)

It is convenient to use slowly varying oscillation amplitudes, defined by \( \eta(t) = A(t) \exp[-i(n/m)\Omega t] \), and write this equation as
\[ \dot{\eta} = (1 + iv)\eta - (1 + i\beta)|\eta|^2 \eta + (1 + i\epsilon)\nabla^2 \eta + B(\eta^*)^{m-1}, \]
(52)
where \( v = \omega_0 - (n/m)\Omega \) is the detuning parameter. After this transformation the explicit time dependence disappears from the forcing term and the considered systems becomes effectively autonomous. Eq. (52), which was originally proposed by Coullet and Emilsson [188], is the starting point in the theoretical analysis of effects of external forcing in distributed oscillatory media. Below, we shall separately consider the phenomena characteristic for \( 1:1, 2:1 \) and higher resonances.

### 3.2. The 1:1 resonance—traveling kinks

When the forcing frequency is close to the frequency of uniform oscillations, the conditions of the 1:1 resonance are fulfilled. In the framework of the complex Ginzburg–Landau equation, the behavior of a system is then described by
\[ \dot{\eta} = (1 + iv)\eta - (1 + i\beta)|\eta|^2 \eta + (1 + i\epsilon)\nabla^2 \eta + B. \]
(53)

If forcing is absent, an individual element of the system oscillates at a frequency \( \Omega_0 = v - \beta \). When the intensity \( B \) of external forcing is gradually increased, the oscillation frequency \( \Omega \) decreases. At a certain critical intensity \( B = B_c \), the oscillation frequency vanishes, signaling the onset of entrainment. To the linear order in \( v - \beta \), the critical forcing intensity needed for the entrainment is given by
\[ B_c(v) = \frac{|v - \beta|}{\sqrt{1 + \beta^2}}. \]
(54)

The entrainment is found inside the Arnold tongue determined by the condition \( B > B_c(v) \). In terms of the amplitudes \( A(t) = \eta(t) \exp[i\Omega_\ell t] \), the entrained region inside the tongue corresponds to oscillations with the forcing frequency \( \Omega_\ell \).

From a general mathematical viewpoint, the entrainment transition at \( B = B_c \) in Eq. (53) represents a special case of the bifurcation, known as the saddle-node bifurcation on a limit cycle.
For Eq. (53), the limit cycle for small forcing intensities $B$ is close to a circle of radius $\rho = |\eta| = 1$. Since this orbit remains attractive during the bifurcation, a reduced description involving only the phase $\phi$ of motion along this cycle is possible (this phase is defined by $\eta = \rho e^{i\phi}$). For an individual element of the system, the approximate phase dynamics equation is

$$
\dot{\phi} = v - \beta - B\sqrt{1 + \beta^2 \sin(\phi + \delta)},
$$

(55)

where $\delta = \arctan \beta$. The stable and unstable fixed points above the bifurcation (i.e., for $B > B_c$) are given by the phases $\phi_0 = -\delta + \arcsin(B_c/B)$ and $\tilde{\phi}_0 = -\delta + \pi - \arcsin(B_c/B)$, respectively. At $B = B_c$ the two fixed points merge and no stationary solutions of the phase equation are possible below the bifurcation. The excitation threshold for such elements is given by $\Delta \phi = \tilde{\phi}_0 - \phi_0 = \pi - 2 \arcsin(B_c/B)$. It vanishes at the bifurcation point $B = B_c$ and thus the elements are highly excitable in the vicinity of the bifurcation. A response of an element to a superthreshold perturbation represents a single phase rotation.

For periodically forced oscillators near the 1:1 resonance, the analogies with excitable systems were pointed out [188] suggesting to view Eq. (53) as a prototype model for pattern formation in excitable media. As we shall show below, spatiotemporal patterns formed by arrays of forced oscillators indeed bear strong similarities with the excitation waves. However, there are also significant differences with the behavior typical for the classical activator–inhibitor excitable media which have been considered in the previous section.

The principal kind of 1D patterns, induced by periodic forcing near the 1:1 resonance, are traveling kinks. In a kink, the phase rotates by $2\pi$ within a narrow region, where some decrease of the modulus of the oscillation amplitude is observed (Fig. 56).

Because the states with the phase differing by $2\pi$ are physically identical, the kinks represent localized perturbations similar to traveling pulses in excitable media. The kinks in externally forced oscillatory media were first described and investigated by Coullet and Emilsson [188,189]. In several publications [190–192], kinks caused by global coupling were considered (they were called “phase flips” there). Because for localized patterns, such as kink, global coupling is effectively equivalent to uniform periodic forcing, the results of such investigations are presented here, and not in the next section dealing with global feedback. A detailed analysis of kink properties has been performed by Chaté et al. [193] and Argentina et al. [194].

For sufficiently weak forcing, motion of kinks can be described within the phase dynamics approximation.

$$
\dot{\phi} = v - \beta - B\sqrt{1 + \beta^2 \sin(\phi + \delta)} + (\beta - \varepsilon)(\nabla \phi)^2 + (1 + \varepsilon \beta)\nabla^2 \phi.
$$

(56)

A kink corresponds to a special solution of this equation having the form of a traveling front with a constant profile, $\phi(x, t) = \Phi(\xi)$ where $\xi = x - Vt$. This solution should satisfy boundary conditions $\Phi(\xi) \rightarrow \phi_0$ for $\xi \rightarrow \infty$ and $\Phi(\xi) \rightarrow \tilde{\phi}_0 + 2\pi$ for $\xi \rightarrow -\infty$. The propagation velocity $V$ can be either positive or negative. If $V > 0$, the phase increases by $2\pi$ after passage of a kink. When $V < 0$, the kink propagation is accompanied by a decrease of the oscillation phase by $2\pi$.

Fig. 56. Profiles of amplitude (a) and phase (b) in a traveling kink; $\varepsilon = 0.5$, $\beta = 0.14$, $\varepsilon = 0.065$. From [192].
To show the existence of such solutions and analyze their properties [191,192], it is convenient to perform the Cole–Hopf transformation of variables in Eq. (56). The new local variable \( u \) is defined by

\[
\phi + \delta = \frac{1 + \epsilon \beta}{\beta - \epsilon} \ln u.
\]  

(57)

The evolution equation for this new variable is easily obtained:

\[
\dot{u} = Q(u) + (1 + \epsilon \beta) \nabla^2 u,
\]  

(58)

where the nonlinear function \( Q(u) \) is given by

\[
Q(u) = \frac{\beta - \epsilon}{1 + \epsilon \beta} \left[ v - \beta - B \sqrt{1 + \beta^2} \sin \left( \frac{1 + \epsilon \beta}{\beta - \epsilon} \ln u \right) \right] u.
\]  

(59)

The roots \( Q(u) = 0 \) yield uniform steady states of system (58) and are given by

\[
u_{0,n} = \exp \left[ \frac{\beta - \epsilon}{1 + \epsilon \beta} \left( \phi_0 + \delta + 2\pi n \right) \right]
\]  

(60)

and

\[
\tilde{u}_{0,n} = \exp \left[ \frac{\beta - \epsilon}{1 + \epsilon \beta} \left( \tilde{\phi}_0 + \delta + 2\pi n \right) \right],
\]  

(61)

where \( n = 0, 1, 2, \ldots \). Because \( Q'(\nu_{0,n}) < 0 \) and \( Q'(\tilde{\nu}_{0,n}) > 0 \), the first sequence of roots corresponds to stable steady states, whereas the states corresponding to the second sequence are unstable. The states with different \( n \) are obtained by a phase rotation of \( 2\pi n \) and, therefore, are physically identical.

Thus, the system is described in the phase approximation by a reaction–diffusion (58) for a single-component bistable medium. The kinks represent traveling front solutions switching the medium from one stationary state to another. Eq. (58) is variational and can be also written as

\[
\dot{u} = -\frac{\delta F[u]}{\delta u(x,t)},
\]  

(62)

where the functional \( F[u] \) is given by

\[
F = \int \left[ U(u) + \frac{1}{2}(1 + \epsilon \beta)(\nabla u)^2 \right] dx
\]  

(63)

and the potential \( U(u) \) is

\[
U(u) = \int_0^u Q(u') \, du'.
\]  

(64)

Using the variational representation, the existence and stability of traveling kink solutions within the phase dynamics approximation can be analytically demonstrated. An important role is played by the quantity

\[
W = U(\nu_{0,1}) - U(\nu_{0,0}) = \int_{\nu_{0,0}}^{\nu_{0,1}} Q(u) \, du.
\]  

(65)

Generally, the sign of \( W \) determines the sign of the propagation velocity, i.e., \( \text{sign} V = \text{sign} [(\beta - \epsilon) W] \). If \( W = 0 \), the velocity \( V \) vanishes and standing kinks should be observed [191,215]. By computing the integral (65), we find that such standing kinks exist along the line \( B = B_{st}(v) \) where \[195\]

\[
B_{st}(v) = (v - \beta) \sqrt{4(\epsilon - \beta)^2 + (1 + \epsilon \beta)^2} \cdot \frac{2(\epsilon - \beta) \sqrt{1 + \beta^2}}{2(\epsilon - \beta) \sqrt{1 + \beta^2}}.
\]  

(66)

When \( \beta > \epsilon \), kinks with the reversed propagation velocity \( V < 0 \) are found below this line, i.e., for \( B < B_{st}(v) \).
In the limit of $\beta \ll 1$, $\varepsilon \ll 1$ and $v \ll 1$, an approximate analytical expression for the kink propagation velocity has been constructed [188]. It reads

$$V \approx \frac{\pi}{4\sqrt{B}} \left[ 2(\varepsilon - \beta)B - (v - \beta) \right]. \quad (67)$$

Note that the kinks move slowly under such conditions. According to this estimate, the velocity vanishes and standing kinks are observed when $B \approx (1/2)(v - \beta)/(\varepsilon - \beta)$, in agreement with Eq. (66). The velocity is also zero in the special case $\beta = \varepsilon = v = 0$.

The existence of standing patterns and the reversal of the propagation velocity are characteristic for fronts in single-component bistable media [196]. Traveling pulses in two-component activator–inhibitor systems, in contrast to this, cannot stop their motion or reverse its direction. We see that though kinks can be interpreted as solitary excitation pulses, they differ significantly from the usual traveling pulses in excitable media with respect to this property.

The phase dynamics approximation is applicable only for the description of patterns with sufficiently slow spatial variation. For the considered kinks, the applicability condition is $B \ll 1$. Because the kinks are found only inside the Arnold tongue (54), this condition further implies that $|v - \beta| \ll 1$. It can be shown that the characteristic width $\delta x$ of a kink scales as $\delta x \sim B^{-1/2}$. Thus, the kinks become more narrow for higher forcing intensities $B$. The amplitude variation in a pattern described by the phase dynamics approximation is

$$\rho \approx 1 + \frac{1}{2} B \cos \phi - \frac{1}{2} (\nabla \phi)^2 - \frac{\varepsilon}{2} \nabla^2 \phi. \quad (68)$$

Therefore, as the kink becomes more narrow for the higher forcing, it starts to show substantial variation not only in its phase, but also in its amplitude.

If forcing is not weak, the properties of kinks can be only numerically investigated. The main result of such investigations [193] is that the kink solutions disappear for sufficiently strong forcing. The disappearance of kinks corresponds to a saddle-node bifurcation. On the bifurcation line, stable traveling kinks merge with unstable localized traveling solutions and both cancel each other.

The destruction of a stable traveling kink under an increase of forcing takes place through the formation of an amplitude defect [192,193]. Fig. 57 shows subsequent stages of the destruction process [192].

The initial kink slightly accelerates, the amplitude depression in its center increases and the phase profile gets steeper ($T = 112.5$). Within a very short time, the amplitude at a certain point inside the kink drops down to zero and a jump develops in the phase profile ($T = 113.07$). If the oscillation amplitude vanishes at a certain point, the oscillation phase is not defined there. The phase distributions in the regions lying on the left- and the right-hand sides of this point become effectively disconnected and the phase can now be shifted by $2\pi$ on one of the sides, so that the phase levels at both ends of the medium far from the kink become equal. Later on, the remaining local pattern smears out ($T = 113.22$ and 114.5) and uniform oscillations are eventually established.

The increase of the forcing intensity $B$ can be interpreted as leading to a decrease in the effective excitability of the medium. Thus, the kinks disappear when the medium gets less excitable. This behavior is also characteristic for traveling pulses in excitable activator–inhibitor systems [196]. With respect to this property, the kinks are indeed similar to the excitation pulses.

Close to the boundary of the Arnold tongue for relatively strong forcing, replication of kinks through a backfiring process is found [193,194]. The initial kink disappears through the occurrence of a defect, but the residual perturbation grows and gives rise to two new kinks. The process then repeats itself and a cascade of reproducing kinks is formed (Fig. 58).

Generally, it is known that multidimensional systems in the vicinity of a homoclinic loop are highly sensitive to perturbations and dynamical chaos easily develops in such systems. The reproduction cascade of kinks should often be irregular and represents a form of spatiotemporal chaos. This chaos coexists with the regime of stable uniform oscillations in the medium and is known as intermittent turbulence.

Backfiring is also characteristic for traveling pulses in classical excitable media, described by activator–inhibitor models. Reproduction of pulses in these media is related to the presence of unstable saddle solutions, or scattors [197]. Chaotic regimes develop through an interplay between scattors and the appearance of homo- and heteroclinic loops.
We see that application of resonant 1:1 forcing to a medium with stable uniform oscillations permits to create in this medium a new kind of patterns—traveling kinks with interesting spatiotemporal dynamics. Using such resonant forcing, one can however also effectively control pattern formation in heterogeneous oscillatory media.

If a medium includes a modified small region where the local oscillation frequency is higher than that of the uniform oscillations, this region can act as a pacemaker which emits waves forming a target pattern [198,199]. Even slight heterogeneities, such as dust or gas bubbles in the BZ reaction or material surface defects in catalysis, suffice to develop pacemakers. Since such heterogeneities are present in large numbers in real systems, oscillatory media become naturally populated by pacemakers and, instead of uniform oscillations, multiple target patterns are observed.

This is changed when resonant 1:1 forcing is applied. Now, only relatively strong local heterogeneities can emit waves and develop target patterns, whereas the activity of all weaker pacemakers gets suppressed. The critical size of a heterogeneity is determined by the forcing intensity. Thus, by applying strong enough forcing, all pacemakers can be damped out and uniform oscillations stabilized even in heterogeneous media.

Properties of pacemakers under periodic forcing have been theoretically investigated [199,191] using the complex Ginzburg–Landau equation with global feedback which reduces in the considered case to Eq. (53). Suppose that the local oscillation frequency is increased by $\delta \omega$ inside a surface region which is so broad that oscillations inside it are already approximately uniform and diffusion effects can be neglected. Even if external forcing is so strong that it entrains oscillations in the medium outside of this region, it may fail to do this within it. This occurs when the elements of the medium are out of the Arnold tongue inside this region, i.e., if the local detuning $\nu + \delta \omega$ exceeds a certain threshold. More rapid oscillations in the central modified regions produce then waves propagating out of it. Hence, the region becomes a pacemaker and a target pattern is formed.
This behavior has indeed been seen in the experiments with a chemical reaction of catalytic reduction of NO with CO on a Pt(100) [190]. In this case, the role of forcing was effectively played by periodic variation of partial pressure of gaseous reactants in the chamber. Such variation resulted from the periodic consumption of supplied reactants by the oscillatory reaction and was not therefore external (but rather represented a form of a global feedback). Nonetheless, insofar as uniform oscillations are maintained, its role was the same as those of external forcing. Decreasing temperature and thus making the forcing effectively weaker, a sudden breakdown of uniform oscillations was observed in the NO+CO reaction. The destruction of the spatially homogeneous state took place as some macroscopic surface defects became supercritical and started to emit waves.

Under periodic forcing, the waves emitted by a pacemaker represent traveling kinks. Since the central region of a pacemaker oscillates at a frequency higher than the frequency of uniform oscillations, each outwards propagating kink should increase the phase by a full $2\pi$ rotation. But we have seen above that, for some parameter values, the propagation direction of a kink can be reversed. The kinks with the reversed propagation rather move in such a way that the phase decreases by $2\pi$ after their passage. Obviously, such kinks cannot propagate away from the pacemaker.

Properties of pacemakers under periodic forcing were studied by numerical simulations [191,195]. If the velocity $V$ of kinks is positive, they autonomously propagate from their origin to the periphery of the medium, with a speed that is independent of the generation frequency. This yields a sparse pattern of kinks, running away from a pacemaker. The situation is different if the kink propagation is reversed ($V < 0$). In this case, the supercritical inhomogeneity forming the core of the pacemaker generates $2\pi$ phase slips which, instead of propagating away as single kinks, form a cluster surrounding the core. Since further phase slips are continuously produced and added to this cluster, it slowly grows with time. As a result, a pattern, that can be viewed as an aggregation of kinks, becomes formed. Suppose that a pacemaker has operated for some time, and then its activity was stopped by removing the central heterogeneity and making the medium again uniform (Fig. 59). After the pacemaker termination, new kinks cease to be created in the central region. When $V > 0$, the previously created kinks run away from the center [Fig. 59(a)]. In contrast to this, if $V < 0$ they begin to move back to the central region, undergoing repeated pair annihilations there [Fig. 59(b)]. One can roughly say that, once new kinks are not further created, the “pressure” maintaining the kink aggregation is released and the pattern collapses via subsequent central annihilations.
The pacemakers generate periodic kink trains in the forced oscillatory media. Generally, the velocity of motion of a train is different from that of a solitary kink. It depends on the spatial period $\lambda$ of a train. For large separations $\lambda$ between the kinks the velocity becomes constant and equal to that of a solitary kink [191]. When separation between the kinks is decreased, the velocity of the train grows. It is interesting to compare the dependence $V(\lambda)$ for kink trains with the respective dependence for the waves propagating in the same oscillatory medium in absence of forcing. When $B = 0$, the oscillatory medium described by the complex Ginzburg–Landau equation (53) has wave solutions with wavenumbers $k$ and the frequency $\omega(k) = \Omega_0 + (\beta - \varepsilon)k^2$, where $\Omega_0$ is the frequency of uniform oscillations. The phase velocity of such waves is $V(k) = \omega(k)/k = \Omega_0/k + (\beta - \varepsilon)k$. Expressing it as a function of the wavelength $\lambda = 2\pi/k$, we obtain the dependence of the velocity of waves on their wavelength in the complex Ginzburg–Landau equation,

$$V(\lambda) = \frac{\Omega_0}{2\pi} + 2\pi(\beta - \varepsilon) \frac{1}{\lambda}. \tag{69}$$

Comparing it with the respective dependence for kinks trains in the same medium, one finds that the kink trains with short spatial periods move essentially at the same velocity as the waves in the unforced system [191]. Apparently, diffusion plays a dominant role in such patterns characterized by strong spatial gradients. Dense kink trains are essentially the same as traveling periodic waves in the unforced system.

According to Eq. (66), the critical forcing intensity for propagation reversal of single kinks depends on the parameters $\beta$ and $\varepsilon$ of the oscillatory media. If such parameters are varied across the medium, kink propagation may be reversed in some parts of it and normal in the rest of the medium. This allows to design kink traps in such oscillatory systems [195].
In 2D media, kinks correspond to extended traveling patterns where the oscillation phase changes by $2\pi$ at a certain line. When this line is straight, the pattern is effectively described by the 1D solution. Generally, the kink line is however curved. Because the states of the medium are physically identical on both sides of such a pattern, it can be viewed as an analog of traveling waves in 2D excitable media. The difference with respect to traveling excitation waves is that kink patterns may be stationary and can reverse their propagation direction. Kink traps in 2D media can be constructed [195].

Note that kink waves can also be considered as "strings": All variation of state variables is compressed in such patterns into a narrow string of a certain shape. When a string is broken, two opposite topological charges (amplitude defects) appear at the open ends.

Spontaneous break-up of kink waves in forced oscillatory media occurs when forcing intensity $B$ is increased [192]. This process is illustrated in Fig. 60. The upper row shows spatial distributions of the modulus $\rho$ of the complex oscillation amplitude at three subsequent time moments $T$. The bottom row displays lines $\text{Re} \eta = 0$ and $\text{Im} \eta = 0$ at the same time moments. The initial string is curved, with the highest curvature reached in the middle of the pattern. It can be seen that the string becomes first more narrow there and, at time $T = 230$, the oscillation amplitude drops to zero in the center. The string breaks into two parts, with amplitude defects with $\rho = 0$ (corresponding to intersections of the curves $\text{Re} \eta = 0$ and $\text{Im} \eta = 0$) developing at both open ends. Subsequently, the string fragments shrink towards the medium boundaries and disappear, so that oscillations become uniform.

Kink waves can also form rotating spirals which can be obtained by applying periodic forcing to a medium where a rotating spiral wave is already present. Such spiral patterns become, however, destroyed when forcing becomes strong [192]. Fig. 61 shows destruction of a spiral wave by an increased forcing.

The simulation is performed using no-flux boundary conditions. Panels (a) and (b) show in gray scale spatial distributions of the modulus $\rho$ of the complex oscillation amplitude and the phase $\phi$, respectively, at different time moments. The snapshots at $T = 0$ display a spiral wave in absence of forcing. The modulus $\rho$ is significantly decreased only inside a small region (and reaches zero in its center). Outside of the central region, the variable $\rho$ is practically constant. When forcing is introduced ($T = 73$), the spiral is already visible not only in the phase distribution, but also in the distribution of $\rho$. Inside a narrow curled dark string, repeating the shape of the phase front, the variable $\rho$ is slightly decreased. This indicates that a kink wave has been formed. After a while, this dark stripe becomes detached from the boundary of the medium and starts to shrink towards the rotation center ($T = 88$). Examining the phase distribution at this moment, we notice that oscillations in the region surrounding the shrinking spiral are uniform. This means that there is an amplitude defect sitting at the open end of the spiral-shaped string and similar to another amplitude defect located in the center. As the string contracts, the outer defect moves closer to the center ($T = 90, 92$) and eventually annihilates with the central defect ($T = 94$). At this moment the phase singularity in the medium disappears and uniform oscillations are soon established.
3.3. The 2:1 resonance—Bloch and Ising walls

This resonance is found when the forcing frequency is twice higher than the frequency of uniform oscillations, i.e., $\Omega_t \approx 2\Omega_0$. For systems near a supercritical Hopf bifurcation, the effects of this forcing are described by the amplitude equation

$$\dot{\eta} = (1 + iv)\eta - (1 + i\beta)|\eta|^2\eta + (1 + i\epsilon)\nabla^2\eta + B\eta^*, \quad (70)$$

where $\eta$ is the slow complex oscillation amplitude, $\eta(x, t) = A(x, t) \exp(-i\Omega t/2)$ and $v$ is the detuning parameter, $v = \omega_0 - \Omega t/2$.

Individual oscillators are entrained by such forcing within an Arnold tongue. For weak forcing, the oscillator phases obey approximately the equation

$$\dot{\phi} = v - \beta - B\sqrt{1 + \beta^2} \sin[2(\phi + \delta)], \quad (71)$$

where $\delta = (1/2) \arctan \beta$. Thus, the entrainment condition, determining the boundaries of the Arnold tongue, is again given for weak forcing by Eq. (54), where $v = \omega_0 - \Omega t/2$. There are four fixed points of this equation, yielding the entrained states,

$$\phi_0 = -\delta + \arcsin(B_c/B), \quad \phi_1 = -\delta + \pi + \arcsin(B_c/B),$$

$$\tilde{\phi}_0 = -\delta + \pi/2 - \arcsin(B_c/B), \quad \tilde{\phi}_1 = -\delta + 3\pi/2 - \arcsin(B_c/B). \quad (72)$$

Only the states $\phi_0$ and $\phi_1$ are stable. On the Arnold tongue boundary, these stable entrained solutions disappear in a saddle-node bifurcation, by merging with the unstable states $\tilde{\phi}_0$ and $\tilde{\phi}_1$, respectively.

The existence of two stable entrained states, differing by the phase shift of $\pi$, is a property of the 2:1 resonance distinguishing it from the 1:1 resonance which we have already discussed. Its primary consequence is that, instead of the kinks representing $2\pi$-fronts, such systems possess traveling $\pi$-fronts which represent waves of transition between two different entrained states $\phi_0$ and $\phi_1$.

These traveling $\pi$-fronts are also known as nonequilibrium Bloch walls; similar patterns exist in equilibrium anisotropic ferromagnetics and ferroelectrics where, however, their velocity is zero [200].
In the phase dynamics approximation, propagation of Bloch walls is described by the equation

$$\dot{\phi} = v - \beta - B \sqrt{1 + \beta^2} \sin[2(\phi + \delta)] + (\beta - \varepsilon)(\nabla \phi)^2 + (1 + \varepsilon \beta) \nabla^2 \phi. \quad (74)$$

Through the Cole–Hopf transformation (57) it is again reduced to Eq. (58) describing front propagation in a one-component reaction–diffusion system [195]. The function $Q(u)$ in this equation is now given by

$$Q(u) = \frac{\beta - \varepsilon}{1 + \varepsilon \beta} \left[ v - \beta - B \sqrt{1 + \beta^2} \sin \left( \frac{2(1 + \varepsilon \beta)}{\beta - \varepsilon} \ln u \right) \right] u. \quad (75)$$

The uniform steady states are given by the roots of $Q(u) = 0$, or explicitly by

$$u_{0,n} = \exp \left[ \frac{\beta - \varepsilon}{1 + \varepsilon \beta} (\phi_0 + \delta + \pi n) \right], \quad \tilde{u}_{0,n} = \exp \left[ \frac{\beta - \varepsilon}{1 + \varepsilon \beta} (\tilde{\phi}_0 + \delta + \pi n) \right] \quad (76)$$

with $n = 0, 1, 2, \ldots$. The sign of the propagation velocity $V$ of the Bloch walls is determined by the integral (65). Standing Bloch walls are found when the condition $W = 0$ holds. By calculating the integral, we find that this condition is satisfied along a line inside the Arnold tongue, defined by $B = B_{st}(v)$ where, for the considered 2:1 resonance, we have [195]

$$B_{st}(v) = (v - \beta) \frac{\sqrt{4(\varepsilon - \beta)^2 + 4(1 + \varepsilon \beta)^2}}{2(\varepsilon - \beta) \sqrt{1 + \beta^2}}. \quad (77)$$

The solutions based on the phase dynamics approximation are valid only for sufficiently weak forcing, $B \ll 1$. Generally, only numerical integration can be used to obtain wall solutions. There is however a special case when exact analytical solutions are available for any forcing amplitude.

When $\varepsilon = \beta = v = 0$, Eq. (70) becomes variational and also describes pattern formation in equilibrium anisotropic ferromagnets and antiferromagnets (the anisotropic X–Y model). It has been shown [201] that the equation possesses then two different solutions representing $\pi$-fronts. The Bloch walls are described by

$$\text{Re} \eta = \sqrt{1 + B} \tanh \left( \sqrt{2Bx} \right), \quad \text{Im} \eta = \pm \frac{\sqrt{1 - 3B}}{\cosh \left( \sqrt{2Bx} \right)}, \quad B < 1/3. \quad (78)$$

The Ising walls are given by

$$\text{Re} \eta = \sqrt{1 + B} \tanh \left( \sqrt{(1 + B)/2x} \right), \quad \text{Im} \eta = 0. \quad (79)$$

In a Bloch wall, the phase $\phi$ undergoes a gradual (left or right) rotation by $\pi$ as the wall is transversed. The modulus of the complex amplitude $\rho = \sqrt{(\text{Re} \eta)^2 + (\text{Im} \eta)^2}$ does not vanish at any point in such a pattern. The Bloch walls exist only for sufficiently weak forcing, $B < 1/3$. In contrast to this, the solution describing Ising walls is possible for all forcing intensities. In the center of an Ising wall, $\rho = 0$ and the phase $\phi$ abruptly changes by $\pi$ when crossing this point. Both kinds of solutions are stationary ($V = 0$) in the considered special case $\varepsilon = \beta = v = 0$.

Additional investigations reveal [200] that Ising walls are unstable for $B < 1/3$, i.e., when Bloch wall solutions are possible. Thus, as the forcing intensity $B$ is increased, Bloch walls should eventually become replaced by Ising walls.

Fig. 62 illustrates this transition. When forcing is relatively weak ($B = 0.1$), the Bloch wall is broad and the amplitude $\rho$ is only slightly decreased in its center. Increasing the forcing intensity to $B = 0.3$ and 0.33 leads to narrowing of the wall and to a strong decrease in the oscillation amplitude $\rho$ in its center. At the critical forcing intensity $B = 1/3$, the amplitude $\rho$ drops to zero in the center and an amplitude defect is therefore formed. The phase $\phi$ abruptly jumps by $\pi$ in this point and remains constant to the left and the right sides of it. As seen from Eqs. (78) and (79), the Bloch wall transforms thus into the Ising wall solution at $B = 1/3$. For stronger forcing, only the Ising wall solution is available.

It is instructive to compare this behavior with the properties of kinks under the 1:1 resonance which we have earlier considered. As seen in Fig. 57, the kinks also become more narrow under an increase of the forcing intensity and develop an amplitude defect ($\rho = 0$) when some critical forcing is reached. However, the kink solutions disappear at
Fig. 62. Transition from a Bloch to the Ising wall as the forcing intensity $B$ is increased.

this critical point, by merging in a saddle-node bifurcation with the solutions describing unstable pulses. For the 2:1 resonance, two stable Bloch solutions (with left and right rotations inside the wall) are replaced at $B = 1/3$ by a stable Ising solution which continues to exist above the bifurcation point. The new solution is qualitatively different in that it possesses a persistent amplitude defect.

As shown by Coullet et al. [202], a similar nonequilibrium Ising–Bloch bifurcation is also found for nonvariational systems where the coefficients $\varepsilon$, $\beta$ and $\nu$ in Eq. (70) are not zero. By using singular perturbation approach, they have constructed an approximate analytical solution for Bloch walls when $\varepsilon \ll 1$, $\beta \ll 1$ and $\nu \ll 1$. Their main conclusion was that, in a nonvariational system, the Bloch walls are traveling and the direction of their motion is determined by sense of rotation of phase $\phi$ inside a wall, i.e., by the wall chirality. The propagation velocity is approximately given in this limit by

$$V = \frac{3\pi \sqrt{1 + B}}{2\sqrt{2B(3 - B)}} [(\varepsilon - \beta)B - (\nu - \beta)] \sqrt{1 - 3B}.$$  (80)

Such traveling Bloch solutions exist only for $B < 1/3$. Their velocity gradually decreases as the forcing intensity $B$ is increased, and it vanishes at the critical point $B = 1/3$. Above the critical point, they are replaced by stationary Ising wall solutions. Note that the propagation direction of a Bloch wall with a given chirality becomes reversed and standing Bloch walls therefore exist at $B = (\nu - \beta)/(\varepsilon - \beta)$, in agreement with the result (77) for the considered limit.

The nonequilibrium Ising–Bloch bifurcation was also demonstrated [202] by numerical integrations in the parameter regions where the coefficients $\varepsilon$, $\beta$ and $\nu$ are not very small. For instance, when $\nu = 0.1$, $\varepsilon = -0.1$ and $\beta = -0.15$ this bifurcation was found at the forcing intensity $B = 0.44$.

Interactions between $\pi$-fronts have been considered in the variational limit $\varepsilon = \beta = \nu = 0$ [203]. Ising walls always attract each other and annihilate under collision. However, the interaction force falls down exponentially with separation between the Ising walls, and the interactions are practically absent when distance between such walls is much larger than their width. Bloch walls with opposite chiralities also always attract each another and annihilate. The situation is more complicated for Bloch walls with the same chirality. It was found [203] that such walls repel each another
if spacing between them is sufficiently large, $L > L_{\text{min}}$, and attract each another for smaller separations. The critical distance $L_{\text{min}}$ approaches logarithmically zero near the nonequilibrium Ising–Bloch bifurcation

$$L_{\text{min}} = \sqrt{\frac{3}{2}} \ln(1 - 3B)^{-1}.$$  

(81)

Trains of propagating Bloch walls are also possible. Such trains are, for example, emitted by pacemakers representing small regions where the oscillation frequency is locally modified. Similar to solitary Bloch walls, such trains can undergo propagation reversal when the forcing intensity is varied [195]. When the frequency of a pacemaker is higher than half of the forcing frequency, it generates Bloch walls with the right chirality, increasing the oscillation phase. If the natural propagation velocity of single Bloch walls with such chirality is however reversed, they cannot run away from a pacemaker and a cluster of Bloch walls sticking to the pacemaker is formed. The cluster slowly grows as further Bloch walls are created by a pacemaker. If action of the pacemaker is terminated, the already created Bloch walls begin to propagate back towards the center. This phenomenon closely resembles what we saw in Fig. 59 for the 1:1 resonance. By introducing appropriate heterogeneities, it is also possible to construct traps for traveling Bloch walls [195]. The trains with the spatial period less than $L_{\text{min}}$ are unstable due to attractive interactions between the walls.

In two-dimensions, traveling Bloch walls can form rotating spirals [188]. To obtain them, one can start with a rotating spiral wave and then introduce resonant 2:1 forcing. In contrast to the spiral waves in absence of forcing, such Bloch spirals are formed by two regions with almost constant phases locked to external forcing. The phase difference between the regions is $\pi$ and they are separated by two spiral-shaped Bloch fronts, so that the spiral appears having two arms. The two arms join in the central point, where the oscillation amplitude is zero and the phase is not defined. Thus, the central point represents an amplitude defect (corresponding to Neel points in solid-state physics). When the forcing intensity is increased, the Bloch fronts slow down and the rotation frequency decreases. Above the critical point of the nonequilibrium Ising–Bloch bifurcation, Bloch fronts become transformed into immobile Ising fronts and the pattern freezes (some slow motion of Ising front due to curvature effects is possible).

Another 2D effect is that, near the nonequilibrium Ising–Bloch bifurcation, planar Bloch walls can become unstable with respect to transverse modulation. As a result, small perturbations grow and, eventually, a state of Bloch-front turbulence with the persistent creation and destruction of vortex pairs is established [204].

If forcing is nonuniform and the local forcing intensity $B(\mathbf{r})$ exceeds in some spatial domains the threshold of the Ising–Bloch bifurcation, a propagating Bloch front that encounters an Ising domain undergoes a change in its chirality and is reflected from the domain [205]. Fig. 63 shows a planar Bloch front, traveling to the right and encountering a small Ising disc. The front wraps around the disc and reconnects on the other side of it. As a result, two structures appear: the original front which passes through undisturbed and an expanding circular wavefront which is formed from the reflected wave. When many Ising heterogeneities are present in a medium, complex wave dynamics may be observed.

### 3.4. Higher resonances

The phenomena found for higher $m:1$ resonances with $m \geq 3$ are in many respects similar [188] to what we have seen above for the 2:1 resonance. The patterns are described by Eq. (52). Inside the Arnold tongue (54), the system has $m$ stable uniform locked states. Furthermore, interfaces separating spatial regions occupied by different locked states represent $2\pi/m$-fronts.
In the case \( m = 3 \), such fronts are traveling at any forcing intensity [188]. In two dimensions, rotating three-phase spirals are always found under 3:1 forcing [188]. In 2D systems with inhomogeneous, spatially random 3:1 forcing, front roughening and spontaneous nucleation of target patterns are observed [206]. Systematic numerical investigations of patterns in 2D systems in the vicinity of the first three resonances have been performed [208].

Let us consider further a system described by Eq. (52) near a 4:1 resonance. Generally, this system possesses four locked uniform states \( \eta_1, \eta_2, \eta_3 \) and \( \eta_4 \). There are four possible \( \pi/2 \)-fronts connecting neighboring locked states, which correspond to the transitions indicated by dotted lines in this figure. Additionally, two \( \pi \)-fronts connecting opposite phase states are possible. A \( \pi \)-front separates spatial regions with the phase difference of \( \pi \).

Suppose that we have two subsequent \( \pi/2 \)-fronts separated by distance \( 2\gamma \). If this distance is very large, the fronts are independent and do not feel each another. For smaller separations, some interactions between the fronts should however be present. Using the perturbation theory, Elphick et al. [209,210] have shown for an almost variational system with \( \varepsilon \ll 1 \), \( \beta \ll 1 \) and \( \nu \ll 1 \) that the distance between the fronts changes with time according to the equation

\[
\frac{d\gamma}{dt} = -\left( B - \frac{1}{3} \right) g(\gamma),
\]

where the function \( g(\gamma) \) is defined as

\[
g(\gamma) = \frac{27}{16} \int_{-\infty}^{\infty} \frac{\tanh^2(z+2\gamma) \tanh z}{\sinh^2 z} \, dz.
\]

Because \( g(0) = 0 \), the state with \( \gamma = 0 \) represents a fixed point of this equation. It can be checked that \( g'(0) > 0 \). Therefore, for \( B < 1/3 \) this fixed point is unstable and the fronts repel each another. On the other hand, for \( B > 1/3 \) attractive interaction between the \( \pi/2 \)-fronts should take place. But the bound state of two state \( \pi/2 \)-fronts with \( \gamma = 0 \) is simply a \( \pi \)-front. Thus, we see that when the forcing amplitude exceeds a threshold \( B = 1/3 \), pairs of \( \pi/2 \)-fronts become unstable with respect to attraction between them and merge into a single \( \pi \)-front.

It can be analytically shown in the weakly nonvariational case [209] that, while \( \pi/2 \)-fronts are always traveling, the \( \pi \)-fronts are immobile. Moreover, they are characterized by the presence of an amplitude defect (\( \eta = 0 \)) in their center.

Fig. 64 shows an example [211] of the described phase-front instability obtained by numerical integration of the amplitude (52) for the 4:1 resonance with the parameters \( \beta = \varepsilon = 0 \), \( \nu = 0.02 \) and \( B = 0.3 \). In the left panel, the space–time diagram of the process is displayed. In the dark domain between the pair of traveling \( \pi/2 \)-fronts, oscillations are shifted by \( \pi/2 \) with respect to the black and light gray domains. On the right side in this figure, snapshots at times \( t = 0 \), 100 and 300 are displayed, showing the instability in the complex \( \eta \) plane.

In 2D systems, this instability leads to a transformation of rotating four-phase spiral waves into an immobile \( \pi \)-front. This transformation is illustrated in Fig. 65. The initial spiral wave [Fig. 65(a)] was obtained by solving Eq. (52) for a lower forcing intensity. The following three frames [Fig. 65(b–d)] are snapshots showing the evolution of this spiral into a standing two-phase pattern. The evolution begins at the spiral core where attractive interactions between pairs of \( \pi/2 \) fronts are the strongest. The coalescence of \( \pi/2 \)-fronts leaves behind a stationary \( \pi \)-front which grows in length until no \( \pi/2 \)-fronts are left. The frames on the right-hand side in the figure show the corresponding evolution in the complex \( \eta \) plane. Here, each pixel corresponds to a grid point in the 2D medium and displays the instantaneous state of the oscillator occupying this grid point.

In numerical simulations, similar phase-front instabilities and transformations of rotating four-phase spiral waves were also observed for the forced FitzHugh–Nagumo and Brusselator models [211]. Numerically, such instabilities have been further demonstrated for the higher 6:1 and 8:1 resonances [211]. This suggests that they may be characteristic for forced oscillatory media near to all \( 2n:1 \) resonances with \( n > 1 \).

### 3.5. Periodic forcing of the oscillatory Belousov–Zhabotinsky reaction

Experiments studying effects of periodic forcing in the vicinity of various resonances have been performed for the oscillatory BZ reaction [211–213]. In the experiments, the reaction occurred in a 0.4 mm-thick porous membrane disk of diameter 22 mm that was placed between two reservoirs continuously refreshed with the BZ reagents. The light-sensitive modification of the BZ reaction was used. Forcing has been implemented by applying a sequence of
light pulses, switching the illumination on and off at regular time intervals (hence, forcing was not harmonical in these experiments).

Fig. 66 shows an example [212] of a pattern observed under the conditions of the 2:1 resonance, when forcing was applied only to the lower part of the medium. In the upper part, a spiral wave continues its rigid rotation. The forcing destroys this wave and transforms it into a labyrinthine pattern of standing waves, seen in the lower part of Fig. 66. Comparing this labyrinthine pattern with theoretical predictions for the 2:1 resonance, one can conclude that it represents an array of immobile Ising walls.

When the frequency of forcing was varied, a sequence of resonance patterns, each persisting for a range of forcing frequencies, was found [212]. Fig. 67 shows patterns observed in the frequency-locked near 1:1, 3:2, 2:1 and 3:1 resonances. In the 1:1 regime, uniform locked oscillations occurred. Under the conditions of the 3:2 resonance, bubble-shaped structures developed. The bubbles appeared and disappeared in a seemingly random fashion, but the temporal spectrum at any spatial point had well-defined peaks at multiples of $\Omega_t/3$.

In the 2:1 regime, two kinds of patterns were seen in this experiment. For smaller frequency ratios ($\Omega_t/\Omega_0 < 1.9\pm0.1$), the pattern consisted of a stable stationary front (an Ising wall) separating two oscillating uniform domains. The shape of the domains did not change, it was determined by the concentration profiles in the beginning of the experiment. Some localized spots with the opposite phase were also seen inside the uniform domains. For higher-frequency ratios near the 2:1 resonance, frozen labyrinthine patterns were found. Once this pattern has grown to fill the entire forced region of the reactor, the nodal lines between the domains became stationary. The pattern in the 3:1 resonance regime had three types of domains oscillating with phases different by $2\pi/3$. After three periods of forcing, the original pattern was recovered, except for a very slow drift of the domain boundaries.
Fig. 65. Evolution of a rotating four-phase spiral wave into a standing two-phase pattern. The frames below show spatial distributions of the phase $\phi$ at subsequent time moments; the frames above show the complex $\eta$ plane. Parameters: $\beta = \epsilon = 0$, $\nu = 0.1$ and $B = 0.6$. From [211].

A systematic investigation was further performed for the case of the 2:1 forcing [213]. The top row in Fig. 68 shows reactor images ($9 \times 9$ mm$^2$) of different observed patterns.

To analyze resonant patterns, the complex Fourier amplitude $a$ of the temporal subharmonic response of the pattern was determined at each image pixel by employing a finite-width frequency filter. At each spatial point, the temporal data series was Fourier transformed. The resulting spectrum was then convolved with the spectrum of coefficients from a sinc function of width $\Omega f / 2$, thus removing higher harmonics. A Fourier transform was then applied to return to the time domain. The complex Fourier amplitude $a$ can be viewed as an experimental analog of the complex oscillation amplitude $\eta$ in the theoretical studies based on the complex Ginzburg–Landau equation.

The middle row in Fig. 68 shows phase portraits of the patterns displayed in the top row. The construction and the meaning of such phase portraits is clarified in Fig. 69. As examples, an unforced rotating spiral wave [Fig. 69(a)] and a subharmonic standing wave pattern [Fig. 69(b)] are chosen here. The points labeled $A$, $B$, $C$ and $D$ in each real space image span the dynamic range of the patterns. The plot below each real space image is a corresponding phase portrait. The point labeled $A$ in the complex plane is the complex Fourier amplitude coefficient $a$ of the $\Omega f / 2$ mode for a pixel labeled $A$ in the real space image, and similarly for other points $B$ to $E$. Through the distribution and connectivity of the Fourier coefficients, the phase portrait shows the distribution of oscillation phases and magnitudes along the dashed...
line in the real space images. The phase portrait of the unforced spiral pattern in Fig. 69(a) is a circle, indicating that the phase angles of the discretized oscillations in one wavelength of the unforced traveling spiral wave are distributed monotonically from 0 to $2\pi$ and have a uniform magnitude. In contrast, for the standing wave pattern displayed in Fig. 69(b), the phase portrait shows that the oscillations remain shifted by phase $\pi$ on either side of the zero amplitude oscillation node, and the magnitude of oscillations decreases monotonically as the node is approached. Thus, this pattern can be classified as formed by an Ising wall. Additionally, the bottom row in Fig. 68 shows histograms of phase angles in each phase portrait.

In absence of forcing, all phases are equally represented in the rotating spiral wave pattern and the histogram of phase angles is flat [68(a)]. Under weak forcing, a pattern consisting of many spiral waves is observed [Fig. 68(b)]. For this pattern, two slight maxima in the histogram of phase angles are already visible. The patterns in Fig. 68(c–e) correspond to moderate forcing intensities and can be viewed as mixtures of rotating and standing waves. Two standing wave patterns in Fig. 68(f, g) are formed by immobile Ising walls.
To assist in the interpretation of experimentally observed patterns and to demonstrate generality of the experimental results, numerical simulations of pattern formation in the Brusselator model with periodic 2:1 forcing have also been performed [213]. While it does not correspond to any realistic system, the Brusselator model is known to exhibit the behavior which is typical for many realistic systems. In the simulations, a model described by equations

\[
\frac{\partial u}{\partial t} = A - (B + 1)u + [1 + \gamma \sin(\Omega t)]u^2v + D_u \nabla^2 u \\
\frac{\partial v}{\partial t} = Bu - u^2v + D_v \nabla^2 v
\]

was used. The forcing intensity is controlled by the parameter \(\gamma\). Under entrainment, two-phase spirals [Fig. 70(b)], labyrinths [70(c)], and Ising front patterns [Fig. 70(d)] are found in this model, whereas rotating spirals develop in the nonlocked regime [Fig. 70(a)]. The phase portrait in Fig. 70(b) shows no zero crossings at the phase fronts (no nodes), indicating that this pattern is formed by a traveling Bloch wave. The phase of oscillations varies continuously as one
passes from one-phase-synchronous domain to another. In contrast, the phase portraits of the standing wave patterns in Figs. 70(c, d) show that the phase angle remains fixed and the oscillation magnitude monotonously decreases to zero as the node of a phase front is approached; the phase angle abruptly changes sign from $-\pi$ to $+\pi$ at the node. These properties are characteristic for the patterns formed by Ising walls.

In the recent experiments [204], transverse instability of Bloch fronts in the 2:1 forced BZ reaction has been observed. First, a state with a standing plane Ising front separating two regions with antiphase oscillations has been prepared. Then the forcing amplitude has been decreased, until the front transformed into a Bloch wall and started to travel. Near this transition, complex behavior shown in Fig. 71 has been observed. Small front perturbations start to grow and nucleation of spiral vortex pairs takes place. Eventually the system is found in the state of Bloch-front turbulence, characterized by irregular dynamics of antiphase domains (Fig. 71a–c). This instability leads to the generation of vortices, in the centers of which lie amplitude defects where the local oscillation amplitude vanishes. Initially, the defects are distributed near the front line (Fig. 71(c)), but later they fill the entire medium (Fig. 71(f)).

Experiments with the 4:1 forcing have also been performed [211]. In these experiments, rotating four-phase spirals were found as the asymptotic states of the system in frequency-locked regimes. An example of such a pattern is shown in Fig. 72(a). The image is a plot of the phase angle $\text{Arg}(a)$ where $a(x, y)$ is the complex Fourier amplitude associated with the $\Omega f/4$ mode for each pixel $(x, y)$ in the pattern. The four domains (white, light gray, dark gray, and black) correspond to the four phases separated by $0$, $\pi/2$, $\pi$, and $3\pi/2$ with respect to the forcing. Fig. 72(b) gives the phase portrait of this pattern. The four corners of the diamond shape are the four stable phase states. The edges of the diamond shape in Fig. 72(b) are formed from pixels at phase fronts separating adjacent domains.

Another series of experiments with periodic optical forcing of the oscillatory BZ reaction was performed by Vanag et al. [217]. In these experiments, a one-sided CFUR was used. Moreover, the forcing signal represented a sequence of pulses and both the duration of a single pulse and the distance between the pulses were varied. A number of different cluster patterns was observed. Not only two-phase, but also three- and three–four-phase clusters were found. Moreover, irregular and localized clusters were reported. On the other hand, labyrinthine two-phase patterns could not be seen. Generally, the observed phenomena resembled the experimental data for the same reaction under global feedback, which will be described in detail in the next section.

External periodic forcing in the surface reaction of CO oxidation on Pt was investigated shortly after self-sustained oscillations had been discovered in this reaction [214,180]. In these investigations, the oxygen partial pressure was modulated with a harmonic signal of varying period and amplitude. The reaction state of the surface was monitored with a Kelvin probe, yielding information on the work function averaged over the entire surface. The response of the reaction to external forcing was interpreted in these studies within the framework of the general theory of frequency locking and resonant entrainment in oscillatory systems. However, information about spatial patterns formed on the reacting surface under forcing was not available.

---

Fig. 70. Patterns in the Brusselator model (top), their phase portraits (middle) and histograms of phase angles (bottom). From [213].
Fig. 71. Transverse instability of Bloch fronts and transition to Bloch-front turbulence in the forced Belousov–Zhabotinsky reaction. Frames (a)–(c) show the oscillation phase for three subsequent time moments. Frames (d)–(f) show the front line and the vortices (as solid circles) at corresponding times. From [204].

In subsequent experiments, effects of periodic forcing and global feedback on pattern formation in this chemical reaction have been investigated by using spatially resolving microscopy methods. Most of these studies were performed under the conditions when, in absence of forcing, the system was in the state of spatiotemporal chaos (chemical turbulence) and therefore they will be discussed in the next section. Periodic forcing of the CO oxidation reaction in the state with regular patterns of standing waves has, however, been also undertaken. The experiments show entrainment of such patterns by external forcing in an interval of frequencies [169].

The emergence of standing waves in the experiments was explained by intrinsic periodic forcing, present in this system. The reacting surface was not uniform and part of it was occupied by regions with uniform oscillations. These regions were periodically consuming reactants from the gas inside the pumped chamber, thus leading to oscillations in
the partial pressure of gaseous reactants. This periodic variation was acting on other regions on the surface and inducing the formation of standing waves there. The surface elements in such other regions were apparently in an excitable state, but close to a transition to oscillations in absence of forcing. An important role in the development of standing waves was also played by the presence of an additional reaction species, subsurface oxygen, that was responsible for reflecting collisions of traveling excitation pulses.

3.6. Global delayed feedback

Similar to periodic uniform forcing, global delayed feedback is realized by variation of one of the global reaction parameters. However, this variation is not externally prescribed. Instead, it is controlled by a signal collectively generated by all oscillators. Therefore, it depends on the patterns developing in the oscillatory system and the patterns can thus act back on themselves. Introduction of such global feedback loops can lead to changes in the properties of existing wave patterns and the emergence of new kinds of patterns in active media.

Suppose that a chemical system is described by a set of reaction–diffusion equations

\[ \dot{c} = \mathbf{f}(c, p) + \hat{D} \nabla^2 c \]

for a set of chemical concentrations \( c = \{c_1, c_2, \ldots, c_N\} \) and its local kinetics is controlled by a global parameter \( p \). To introduce global delayed feedback, we should make this global control parameter dependent on some integral properties of concentration distributions. The simplest way of doing this is to assume that this parameter depends on the spatial average of one of the oscillating concentration variables taken at a delayed time moment. Hence, we choose

\[ p(t) = p_0 + \mu_0 [\overline{c_i}(t - \tau) - c_{i,0}] \]

with

\[ \overline{c_i}(t) = \frac{1}{S} \int_{S} c_i(r, t) \, dr, \]

where the averaging of the concentration of the selected species \( i \) is performed over the entire reaction area \( S \), the coefficient \( \mu \) specifies the feedback strength and \( \tau \) is the delay time. Because we want that the feedback signal depends on the variation of the spatial average \( \overline{c_i} \) and does not shift the base level \( p_0 \) of the control parameter \( p \), we have subtracted from \( \overline{c_i}(t - \tau) \) in Eq. (87) some constant reference concentration \( c_{i,0} \) of species \( i \).

If the feedback signal is weak, kinetic equations (86) can be linearized with respect to the variations of the control parameter and we obtain

\[ \dot{c} = \mathbf{f}(c, p_0) + \hat{D} \nabla^2 c + \mu_0 g(c)[\overline{c_i}(t - \tau) - c_{i,0}], \]

where \( g(c) = \partial \mathbf{f}(c, p) / \partial p \) at \( p = p_0 \).

Suppose furthermore that the considered chemical system is near a supercritical Hopf bifurcation, so that its concentrations \( c \) perform small-amplitude oscillations near an unstable steady state \( c_0 \), i.e., \( c = c_0 + \delta c \). In this case, the concentration of species \( i \) in this unstable steady state can be conveniently chosen as the reference state and thus we have

\[ \dot{c} = \mathbf{f}(c, p_0) + \hat{D} \nabla^2 c + \mu_0 g(c)\delta c_i(t - \tau). \]

Considering the feedback term in Eq. (89), we notice that since the feedback is weak and already proportional to the concentration variation, we can replace \( g(c) \) by \( g(c_0) \) there.

Introducing complex oscillation amplitudes \( A \), we write

\[ \delta c(r, t) = \mathbf{h} A(r, t) + \mathbf{h}^* A^*(r, t). \]

In absence of feedback oscillation amplitudes \( A \) should obey the complex Ginzburg–Landau equation. The additional feedback term in Eq. (90) is linear in perturbations \( \delta c \) and, if we follow the same derivation as that leading to the complex Ginzburg–Landau equation, we would find that it leads to an additional term which is linear in the average oscillation amplitude. The resulting equation should therefore have the form [215]

\[ \dot{A} = (1 + i\omega_0)A - (1 + i\beta)\dot{A}^2 A + (1 + i\epsilon)\nabla^2 A + \mu e^{i\omega_0} A(t - \tau), \]
where $\overline{A}$ is the average oscillation amplitude,

$$\overline{A}(t) = \frac{1}{S} \int_{(S)} A(\mathbf{r}, t) \, d\mathbf{r}. \quad (93)$$

The coefficient $\mu$ is proportional to the parameter $\mu_0$ in the expression (87) determining the control signal. Moreover, a phase shift $\chi_0$ is present in the feedback term. It depends on the vector $\mathbf{g}(\mathbf{c}_0)$ which specifies how the feedback signal affects evolution of different concentrations [cf. Eq. (90)]; it is also influenced by the choice of the species $i$ used for generation of the control signal (87) and by the coefficient $\mathbf{h}$ in Eq. (91) that expresses concentration variations in terms of the complex oscillation amplitudes $A$. This phase shift is strongly sensitive to the details of a particular system (86) and no simple expression for this parameter can be constructed.

Time in Eq. (92) is measured in units of the amplitude relaxation time which is inversely proportional to the distance from the critical point of the Hopf bifurcation (the critical slowing down). The oscillation period remains however finite at this bifurcation and, therefore, it becomes very small when measured in these units. Thus, frequency $\omega_0$ in Eq. (92) is large. Moreover, the delay time $\tau$ would also typically be small near the bifurcation when it is measured in such units. This means that the situation with $\omega \gg 1$ and $\tau \ll 1$ is realistic. Note that, however, we would typically have $\omega \tau \sim 1$ because this parameter combination does not depend on time rescaling.

Introducing slowly varying oscillation amplitudes $\eta(\mathbf{r}, t) = A(\mathbf{r}, t)e^{i\chi(t)}$, we expect that their characteristic time scale shall be of order unity. Indeed, by expressing $A$ in terms of $\eta$ in Eq. (92), we find

$$\dot{\eta} = \eta - (1 + i\beta)|\eta|^2 \eta + (1 + i\epsilon)\nabla^2 \eta + \mu e^{i(\chi_0 + \omega_0 \tau)} \eta(t - \tau). \quad (94)$$

If the parameters $\beta$ and $\beta$ are of order unity and $\mu \ll 1$, all terms in this equation are of order unity and this is the time scale of the slow amplitude $\eta$.

This implies that the slow amplitudes cannot significantly change within a short delay time $\tau \ll 1$. Hence, we can neglect the delay in the term $\eta(t - \tau)$ and obtain the following equation:

$$\dot{\eta} = \eta - (1 + i\beta)|\eta|^2 \eta + (1 + i\epsilon)\nabla^2 \eta + \mu e^{i\chi}(t), \quad (95)$$

where

$$\chi = \chi_0 + \omega_0 \tau. \quad (96)$$

This equation has first been proposed as a model for oscillatory systems with global coupling [190] and later formulated as the general amplitude equation for reaction–diffusion systems with global delayed feedbacks in the vicinity of a supercritical Hopf bifurcation [215].

Eq. (95) does not include any delay. Nonetheless, the delay time $\tau$ plays an important role here, because it determines the effective phase shift $\chi = \chi_0 \pm \omega_0 \tau$ in this equation. In contrast to $\chi_0$, the delay time $\tau$ is one of the parameters that can be easily controlled in an experiment. The variation of $\tau$ provides a simple way for changing the phase shift of the global feedback, and thus the feedback effects.

First, we consider uniform oscillations in system (95). Substituting $\eta(t) = \rho_0 e^{i\Omega t}$, we find that $\Omega = -\beta + \mu(\sin \chi - \beta \cos \chi)$ and $\rho_0 = (1 + \mu \cos \chi)^{1/2}$. Thus, global feedback shifts the oscillation frequency and modifies the oscillation amplitude. Note that, if the system is in the synchronized state of uniform oscillations, its individual element effectively experience external periodic forcing described by

$$\dot{\eta} = \eta - (1 + i\beta)|\eta|^2 \eta + (1 + i\epsilon)\nabla^2 \eta + \mu \rho_0 e^{i(\chi + \Omega \tau)}. \quad (97)$$

This is equivalent to Eq. (53) near a 1:1 resonance with the forcing amplitude $B = \mu \rho_0 = \mu(1 + \mu \cos \chi)^{1/2}$ and detuning $\nu = -\Omega = -\beta - \mu(\sin \chi - \beta \cos \chi)$.

To describe evolution of patterns with weak phase gradients, the phase dynamics approximation has been developed [191]. When $\mu \ll 1$, the local oscillation phase $\psi$, defined as $\eta = \rho \exp[i(\Omega t + \psi)]$ approximately obeys the equation

$$\dot{\psi} = g(\psi - \Psi) + (\beta - \epsilon)(\nabla \psi)^2 + (1 + i\beta)\nabla^2 \psi \quad (98)$$

with

$$g(\psi - \Psi) = \rho \sqrt{1 + \beta^2} \{ R \sin(\psi - \Psi + \chi + \delta) + \sin(\chi - \delta) \} \quad (99)$$
and $\delta = \arctan \beta$. Here, $R$ and $\Psi$ are the magnitude and the phase of the spatial average $\overline{\eta}(t) = R(t) \exp[i(\Omega t + \Psi(t))]$ or, explicitly,

$$R(t) \exp[i\Psi(t)] = \frac{1}{S} \int_{(S)} \exp[i\psi(r, t)] \, dr.$$  \hspace{1cm} (99)

Thus, the local evolution of phases in the phase dynamics (97) depends on the spatial integral (99) of the phase distribution in the entire medium. This distinguishes Eq. (97) from the analogous phase dynamics Eq. (56) for external forcing near the 1:1 resonance.

In the synchronous state, all oscillation phases are equal, $\psi(r, t) = \Psi = \text{const}$. Since $g(0) = 0$, such uniform state is always a solution of Eq. (97). To investigate stability of the synchronous state [191], suppose that the local oscillation phase is slightly shifted ($\psi = \Psi + \delta\psi$) in some spatial region with respect to the global oscillation phase $\Psi$, fixed by uniform oscillations in the rest of the medium. We assume that this region is small in comparison to the total size of the medium, but still so large that all spatial derivatives in (97) can be neglected. Evolution of such phase perturbations is described by the linearized equation

$$\frac{d\delta\psi}{dr} = g'(0)\delta\psi,$$  \hspace{1cm} (100)

where

$$g'(0) = \left. \frac{\partial g}{\partial \psi} \right|_{\psi=\Psi} = \mu\sqrt{1 + \beta^2} R \cos(\chi - \delta).$$  \hspace{1cm} (101)

When $\cos(\chi - \delta) > 0$, we have $g'(0) > 0$ and therefore small phase perturbations grow with time, indicating absolute instability of the synchronous uniform state inside the interval $\pi/2 + \delta > \chi > -\pi/2 + \delta$ of phase shifts $\chi$.

To investigate the nonlinear stage of development of such instability, numerical integration of Eq. (95) inside an interval of length $L$ with no-flux boundary conditions has been performed [191]. It was found that the above instability results in desynchronization of oscillations proceeding through the formation of a standing periodic pattern of phase domains. The initial spatial period of this pattern is relatively short. Later the pattern undergoes restructuring and a smaller number of larger domains appears. This slow restructuring is repeated until the entire medium is occupied by a single half-period pattern where the opposite ends of the medium oscillate out of phase. This nonlinear evolution is accompanied by a progressive decrease of the global oscillation amplitude $R$. The time dependence of $R$ demonstrates several plateaus corresponding to a succession of the transient patterns with growing spatial periods. The final pattern corresponds to a single wall occupying the entire system. The residual amplitude corresponding to this final state can be roughly estimated as $R \sim (1 + \epsilon\beta)/(\mu L^2)$; it becomes vanishingly small for the systems of large length $L$. Thus, when the condition $\cos(\chi - \delta) > 0$ is satisfied, global coupling induces its own breakdown through spontaneous emergence of large-scale phase domains. Note that diffusive coupling plays no role in such an instability and it is essentially the same as the desynchronization instability in a population of globally coupled phase oscillators [198].

When the opposite condition $\cos(\chi - \delta) < 0$ holds, uniform oscillations are stable. In this case, the system can form propagating kinks which represent traveling $2\pi$-fronts [191,192]. These patterns are the same as for the external 1:1 forcing. Indeed, in such a pattern the whole medium, except the narrow front region, is found in the state of synchronous uniform oscillations. If the size of the medium is large, the contribution from the front region into the spatial average $\overline{\eta}$, determining the force that acts on the oscillators, can be neglected. Thus, the forcing is practically the same as for the uniform oscillations [cf. Eq. (96)]. For weak feedbacks ($\mu \ll 1$) the effective forcing amplitude is $B = \mu$ and the effective detuning is $v = \beta - \mu(\sin \chi - \beta \cos \chi) = \beta - \mu\sqrt{1 + \beta^2} \sin(\chi - \delta)$.

Because of this close analogy, we have already presented examples of traveling kinks in a globally coupled system above, when discussing patterns induced by external forcing near the 1:1 resonance. Substituting into (66) the above expressions for the effective detuning and forcing amplitude, we find that the reversal of the propagation direction of kinks occurs when $W = 0$ where

$$W = \sin(\chi - \delta) + \frac{2(\epsilon - \beta)}{1 + \beta \epsilon} \cos(\chi - \delta).$$  \hspace{1cm} (102)

At $W = 0$, standing kinks in the globally coupled system are found.
Fig. 73. Desynchronization diagram ($\beta = 1$). Global feedback leads to desynchronization of uniform oscillations inside the gray region; oscillation death is taking place inside the dark region.

For stronger feedbacks, the phase dynamics approximation cannot be used to describe phase kinks because spatial gradients become high in the front region. When a critical feedback strength is reached, kinks disappear through the formation of amplitude defects. Fig. 57, which we have earlier presented, has actually been obtained for a system with global coupling with the parameters $\varepsilon = 5$, $\beta = 0.5$, $\chi = 0$ and $\mu = 0.175$. The destruction of kink waves (strings) in two dimensions occurs through their breakup accompanied by the appearance of point amplitude defects. This process has previously been shown in Fig. 60 for $\varepsilon = 5$, $\beta = 0.5$, $\chi = 0$ and $\mu = 0.18$.

In our previous discussion of external forcing near a 1:1 resonance, we have noticed that sufficiently strong forcing prevents development of pacemakers at medium heterogeneities. The same is true for systems with global feedbacks. When the feedback is strong enough and the condition $\cos(\chi - \delta) < 0$ is satisfied, the system exhibits uniform oscillations even if its parameters show some local variation.

An interesting behavior is found in such systems when feedback intensity is gradually decreased [190,191]. Below some critical feedback intensity, the strongest heterogeneity present in the medium is no longer suppressed and begins to act as a pacemaker, sending waves (outwards propagating kinks). Inside the spatial region, filled with the waves, the phase is periodically varying. Therefore, this region gives vanishing contribution into the spatial average $\bar{\eta}$ and the magnitude $R = \vert \bar{\eta} \vert$ decreases. Now, only the rest of the medium, still filled with uniform oscillations, is generating the force which acts back on the oscillators. As the waves spread, the feedback signal gets weaker and finally disappears when the waves are covering the whole medium. Thus, strong heterogeneities lead to breakdown of global coupling in oscillatory media. This phenomenon has indeed been observed in the experiments with surface chemical reactions [190]. Note that, when global coupling is effective, the frequency of uniform oscillations is shifted by $\Delta \Omega = \mu(\sin \chi - \beta \cos \chi)$ with respect to the frequency of individual oscillators in the noncoupled system. When global coupling breaks down and synchronization disappears, the local oscillation frequency should therefore change by such amount. This effect has also been experimentally observed.

Above, we have discussed stability of uniform oscillations within the phase dynamics approximation which is valid only for weak feedbacks ($\mu \ll 1$). However, this stability analysis can also be easily performed in the framework of the full model (95). Uniform oscillations are unstable and desynchronization occurs within the region $0 < \mu < \mu_u$, where

$$\mu_u = -\frac{2(\cos \chi + \beta \sin \chi)}{1 + 2\cos^2 \chi + \beta \sin(2\chi)}.$$ (103)

Such desynchronization region for $\beta = 1$ is shown as the gray domain in Fig. 73. At $\mu = 0$, the boundaries of such region are given by $\cos \chi + \beta \sin \chi = 0$, or equivalently, by $\cos(\chi - \delta) = 0$, in agreement with the previous phase dynamics approximation analysis.
There is yet another effect that can lead to desynchronization in the globally coupled system. As we have already seen, the amplitude of synchronous uniform oscillations is \( \rho_0 = (1 + \mu \cos \chi)^{1/2} \). When the condition

\[ \mu > -\frac{1}{\cos \chi} \]

is satisfied, uniform oscillations become impossible in the system and the uniform steady state \( \eta = 0 \) becomes stable in the class of uniform solutions. For a single oscillator, that would have corresponded to oscillation death. For an oscillator array, this implies only the absence of uniform oscillating states. It can be easily shown that, when the condition (104) is satisfied, the stationary uniform state \( \eta = 0 \) is still unstable with respect to the growth of nonuniform modes with wavevectors \( k \neq 0 \). In Fig. 73, the instability related to the death of uniform oscillations takes place inside the black domain.

Thus, the synchronization region (white in Fig. 73) becomes more broad for stronger feedbacks, but then another desynchronization mechanism, based on the oscillation death, comes into play.

Although Eq. (95) remains well-defined even for relatively strong feedbacks, we should remember that it provides a general approximation for various reaction–diffusion models in the vicinity of a Hopf bifurcation only for weak feedbacks with \( \mu \ll 1 \). This means that the behavior of a system, described by this equation for \( \mu \sim 1 \), is not universal and may represent a special property of this particular model. In the next section, we consider effects of global delayed feedbacks in a model of CO oxidation on platinum and show that new kinds of patterns and spatiotemporal regimes, which are not even qualitatively described by Eq. (95), become possible at sufficiently strong feedbacks in such realistic reaction model.

3.7. Global feedback control of patterns in the CO oxidation reaction

In this section, we present results of numerical simulations for a realistic model of an extensively catalytic reaction, CO oxidation on a Pt(110) surface, together with some available experimental data. This reaction and its mathematical modeling have already been discussed by us in Section 1.2. Its simplified mathematical model (9)–(11) includes three variables: the surface coverages \( u \) and \( v \) of adsorbed CO and oxygen and a variable \( w \) specifying the structural state of the platinum surface. A global feedback loop can be introduced in this reaction by means of continuous computer-controlled variation of the partial pressure \( p_{CO} \) of CO in the chamber. The external pressure variations globally affect the dynamics on the entire catalytic surface. A spatially resolving technique, such as photoemission electron microscopy, is used to monitor the coverage patterns forming in the active surface area. For the generation of the control signal the spatial average of the measured PEEM intensity is simultaneously computed. The continuous signal, that is the difference between the average and a reference intensity multiplied by a factor determining the feedback intensity, is applied back to the reaction with a certain artificially introduced delay.

The PEEM images are sensitive to local surface coverages of both reacting components, CO and oxygen. The dependence of the image intensity on such variables is generally nonlinear and its exact form is not known. To approximately model feedback experiments, we assume that the feedback signal is generated by using spatial average of only one adsorbed species, the CO.

Thus, the feedback is introduced into the model by assuming that the CO partial pressure in Eq. (9) depends as

\[ p_{CO}(t) = p_{CO}^0 - \mu[u(t - \tau) - u_{ref}] \]

on the spatial average

\[ \bar{u}(t) = \frac{1}{S} \int_{(S)} u(r, t) \, dr \]

of the CO coverage \( u \). The parameter \( \mu \) specifies the feedback intensity, \( \tau \) is the delay, and \( p_{CO}^0 \) is the CO partial pressure for vanishing feedback, \( \mu = 0 \). Hence, the CO partial pressure in Eq. (9) is adjusted according to the difference between the integral delayed CO coverage \( \bar{u}(t - \tau) \) and its reference value \( u_{ref} \). The reference value is chosen as the CO coverage in the unstable steady state in absence of feedback.
The numerical study of the feedback effects has been performed [216] for a model corresponding to the temperature \( T = 545 \text{ K} \) with the parameter values \( k_1 = 3.14 \times 10^5 \text{ s}^{-1} \text{ mbar}^{-1}, \ k_2 = 10.21 \text{ s}^{-1}, \ k_3 = 283.8 \text{ s}^{-1}, \ k_4 = 5.86 \times 10^5 \text{ s}^{-1} \text{ mbar}^{-1}, \ k_5 = 1.61, \ s_{\text{CO}} = 1, \ s_{\text{O}_1} = 0.6, \ s_{\text{O}_1} = 0.4, \ u_0 = 0.35, \ \delta t = 0.05, \ D = 40 \mu \text{m}^2 \text{ s}^{-1}, \ \rho_{\text{O}_2} = 9.00 \times 10^{-5} \text{ mbar}, \) and \( \rho_{\text{CO}}^0 = 4.15 \times 10^{-5} \text{ mbar}. \) Unless stated otherwise, the system size is 0.8 mm for 1D and 0.8 \times 0.8 \text{ mm}^2 for 2D simulations. Long integration times \( t > 5000 \text{ s} \) ensured that transients had decayed at the end of each calculation. The model parameters were chosen in such a way that the system performed unharmonic limit-cycle oscillations that were stable in absence of feedback. The feedback intensity and the delay time were varied in the simulations, while all other parameters were kept fixed.

Our analysis of the effects of global feedback has been based on the complex Ginzburg–Landau equation, valid in the vicinity of a Hopf bifurcations where oscillations are almost harmonical. The oscillations observed in real experimental situations are usually unharmonic, so that the system is not close to a Hopf bifurcation. Nonetheless, the normal form theory is often applied to interpret the experimental data even in such cases. Indeed, the predictions of the CGLE may remain qualitatively correct in a larger neighborhood of the bifurcation.

It is therefore convenient to have the amplitude and the phase variable also defined for unharmonic oscillations, in such a way that they correspond to the amplitude and the phase of quasi-harmonic oscillations in the normal form theory. It should be noted that the local phases of general unharmonic oscillations were first introduced by Kuramoto [198] in his analysis of phase dynamics. However, only small amplitude deviations from the nonperturbed limit cycle were then considered.

In the analysis of periodic forcing for the Belousov–Zhabotinsky reaction (see Section 3.5), such transformation of variables was undertaken by employing a frequency demodulation technique to filter relevant information from numerical and experimental data [213]. This technique used a finite width frequency filter to extract the behavior of a certain mode in the patterns. The complex Fourier coefficients of this mode were computed from the time series at various locations in the patterns to provide a local phase and amplitude characterization of the dynamics. This technique is efficient when the majority of the dynamical power is concentrated in a single mode, but it is also limited to this case. The time-resolved description of oscillatory behavior requires extensive data processing and is only achievable for sufficiently slow pattern evolutions.

The variable transformation used in Ref. [216] follows a different idea. It is an empirical method to transform a pair of model variables into an amplitude and a phase after computational modeling.

When a system has periodic oscillatory dynamics in absence of spatial coupling, visualization of two variables is sufficient to capture the relevant dynamical features. In the projection plane of these two variables, the limit cycle yields a closed trajectory. The projection variables can be chosen in such a way that this trajectory has no self-intersection. It should be further assumed that, when spatial coupling is eventually introduced, the local oscillations in the medium are not greatly different from those that correspond to the uniform limit cycle, except for relatively small localized areas where strong deviations from the uniform attractor may still occur. The projected uniform limit cycle can therefore be used as a reference for the characterization of dynamics in a spatiotemporal pattern.

The employed variable transformation is illustrated in Fig. 74. Suppose that \( u \) and \( w \) are the projection variables and the reference limit cycle projection is the closed orbit shown in the figure. For any state \( P \) with coordinates \((u, w)\) in the projection plane, a pair of new variables \( R \) and \( \phi \) can be defined, interpreted as an amplitude and a phase corresponding to this local state of the system. To do this, one first chooses some point \( O \) inside the reference orbit and takes it as the coordinate origin in the projection plane. Hence, any point \( P \) is characterized by a radius vector of length \( \rho = \overrightarrow{OP} \). Furtheron, one notices the point \( Q \) where this radius (or it extension) intersects with the chosen orbit. The length \( \rho_{\text{ref}} = \overrightarrow{OQ} \) determines the reference radius for the point \( P \). Next some “initial” point \( Q_0 \) on the orbit is marked and the time \( T \) needed to reach point \( Q \) along the reference cycle is determined. The amplitude and the phase are then defined as \( \rho = \rho_{\text{ref}} \) and \( \phi = \frac{2\pi T}{T_{\text{ref}}} \), where \( T_{\text{ref}} \) is the period of the reference limit cycle.

Note that according to this definition, the amplitude is \( R = 1 \) as long as the system stays on the reference limit cycle. Moreover, for the motion corresponding to the reference limit cycle, the phase increases at a constant velocity with time and changes by \( 2\pi \) after each cycle period. When local oscillations are nearly harmonical and the reference orbit is a circle with point \( O \) in its center, the above definition yields the usual phase and amplitude variables. The coordinate origin \( O \) is best chosen as the unstable uniform steady state of the system to guarantee that a local suppression of oscillations indeed corresponds to a vanishing amplitude \( R \).

This empirical amplitude-phase description has been applied [216] to qualitatively interpret spatiotemporal patterns obtained in numerical simulations of the CO oxidation reaction with artificial global feedback. To obtain the reference
orbit, the projection of uniform oscillations in the model on the plane with the variables $u$ and $w$, representing CO coverage and the fraction of the nonreconstructed surface area, was used.

The results of numerical investigations of 1D systems are summarized in Fig. 75. This diagram shows the types of stable regimes reached after transients in the considered system. The delay time is measured in multiples of the natural oscillation period in absence of feedback, $T_0 = 3.33$ s (note that when feedbacks are operating the actual period of uniform oscillations is feedback dependent and will to some extent differ from $T_0$). The feedback intensity in Fig. 75 is normalized to the equilibrium CO partial pressure $p_{\text{CO}}^0$ in the reaction chamber in absence of feedback. Note that the ratio $\mu/p_{\text{CO}}^0$ yields an estimate of the relative variation of partial pressure caused by such a feedback.

Depending on the delay and intensity, the feedback can maintain uniform oscillations or induce various spatiotemporal patterns. Examining Fig. 75, it can be seen that as the delay is increased, the diagram is approximately repeated at integer multiples of $T_0$. However, the stability regions of the patterns other than uniform oscillations shrink at larger delays. Uniform oscillations are found in a large region of the parameter plane. The uniform oscillations have strong hysteresis (bold lines show the boundaries where uniform oscillations set on when increasing the feedback intensity, whereas dashed lines indicate the boundaries where such oscillations break down as the feedback intensity is decreased). In the hysteresis regions the final pattern depends on the initial conditions because the uniform attractor coexists here with the attractor of another pattern.
Fig. 76. Feedback-induced patterns: (a) a kink, (b) asynchronous oscillations, and (c) a cluster pattern. For each pattern the values of the parameters $\tau/T_0$ and $\mu/\mu_{CO}$ are, respectively, (a) 0.165, 0.012, (b) 0.781, 0.012, and (c) 0.045, 0.289. From [216].

For comparison, the dotted line in Fig. 75 shows the boundary where in absence of diffusion the unstable steady state of the system becomes stabilized by the applied feedback (the stabilization takes place at small delays $\tau/T_0 < 0.06$ and large feedback intensities $\mu/\mu_{CO} > 0.11$). In the pattern forming system that includes diffusion the spatially uniform suppression of oscillations on the entire surface is however not observed. Instead, at small delays the system evades the suppression of oscillations through the formation of clusters.

Fig. 76 displays three typical examples of different nonuniform feedback-induced patterns. In the pattern shown in Fig. 76(a) the medium is in the uniform state almost anywhere except for a narrow interval with strong spatial variation. This pattern corresponds to a kink (called “phase flips” in Ref. [192]) traveling across the medium. In contrast to this, the pattern in Fig. 76(b) is characterized by a gradual spatial variation extending over the whole medium. Such patterns are found when desynchronization through the feedback is taking place. In Fig. 76(c) the pattern consists of large regions with almost uniform distributions separated by narrow by narrow interfaces. Such cluster patterns are also discussed below.

As we have already noted, we consider now only the case when uniform oscillations are stable with respect to spontaneous phase modulation in absence of feedback. Depending on the choice of the initial and the boundary conditions, traveling waves (and spiral waves in the 2D system) can still be observed in this case. Sufficiently strong global delayed feedbacks suppress all such structures, so that only uniform oscillations are found inside the blank region in Fig. 65. After a transient, any initial condition eventually leads to uniform oscillations here. The time needed to reach uniform oscillations greatly increases near the instability boundaries of uniform oscillations.

At small feedback intensities corresponding to the dashed areas in Fig. 75, either uniform oscillations or patterns of propagating phase kinks are found in the simulations, depending on the initial conditions. To produce a kink, a simulation is started with a constant phase gradient of $2\pi$ across the system. The feedback tends to establish uniform oscillations, but, if it is relatively weak, it cannot achieve this in the whole medium. Thus, a narrow region with strong concentration gradients is formed, see Fig. 76(a). This region travels through the medium.

To analyze the properties of such traveling patterns, the variable transformation technique, described above, has been used. After transformation to local phase and amplitude variables, the pattern of a phase kink takes the form displayed in Fig. 77(a). The oscillation phase $\phi$ undergoes a full rotation of $2\pi$ inside the nonuniform region whereas the amplitude $R$ displays only small modulations. The states of the medium on the left and right side of the kink differ by a phase shift of $2\pi$ only and hence are physically indistinguishable.

A phase portrait of the same structure is shown in Fig. 77(b). Here, the amplitudes and phases of all points along the kink are displayed in polar coordinates. The phase $\phi$ of a point is represented by the polar angle and the amplitude $R$ is the distance to the coordinate origin. The points accumulate in the state corresponding to the uniformly oscillating regions. The previous analysis of kinks in the periodically forced complex Ginzburg–Landau equation (see Section 3.2) has revealed that, depending on the system parameters, a kink can stop and reverse its direction of motion. This effect has also been found in the model of the CO oxidation reaction [216]. The kinks become unstable when the feedback intensity exceeds a certain delay-dependent threshold (See Fig. 75). They disappear through the formation of an amplitude defect, similar to the process described above for the kinks in the forced complex Ginzburg–Landau equation.

Patterns with smooth spatial gradients of chemical variables can be induced by the feedback in the desynchronization region displayed in Fig. 75. Below the dashed lines in this region, asynchronous patterns develop starting from any
Fig. 77. (a) Spatial dependence of the amplitude $R$ (solid line) and the phase $\phi$ (dashed line) in a kink. The phase portrait (b) shows the same data in polar coordinates. The same parameters as in Fig. 76(a). From [216].

Fig. 78. Spatial dependence (a) of the phase (dashed line) and the amplitude (solid line) and the phase portrait (b) of a pattern of asynchronous oscillations. The same parameters as in Fig. 76(b). From [216].

initial condition. The duration of the desynchronization process diverges for feedbacks of vanishing intensity. Applying the transformation to local phase and amplitude variables, asymptotic asynchronous patterns established in this regime can be analyzed. Spatial profiles of $R$ and $\phi$ in such a pattern are shown in Fig. 78(a). Note that only the local oscillation phase $\phi$ is varying in this pattern, whereas the amplitude $R$ is almost constant. This means that all local oscillations correspond to the same limit cycle. The phase profile shows smooth variation. When the size of the medium was varied, the pattern adjusted to the size of the medium, therefore lacking an intrinsic wavelength. In the phase portrait representation of such a pattern all points are distributed on the unit circle, see Fig. 78(b). However, not all possible phases are occupied, and the density of points increases towards the ends of the structure that correspond to the extrema of the phase profile. As time goes on, the structure rotates in the plane with constant velocity.

Under periodic boundary conditions, the total phase gradient along the pattern adjusts to an integer multiple of $2\pi$ given by the winding number of the initial phase distribution. For a nonzero winding number, the asymptotic spatial profile of the phase $\phi$ is linear, so that the temporal shift between oscillations at different sites is proportional to their spatial distance. No-flux boundary conditions do not conserve the winding number. In the latter case the final total phase gradient does not exceed $2\pi$.

An important consequence of the spatial desynchronization of oscillations is the accompanying breakdown of the global oscillations that generate the feedback signal. The amplitude of the feedback signal decreases as the desynchronization gradually develops in the system. Thus, the global feedback effectively induces its own breakdown. It should be noted that the feedback oscillations do not, however, completely vanish in the asymptotic state. A small remaining feedback signal that compensates the synchronizing tendency of diffusion is needed to maintain the desynchronized state. Similar desynchronization phenomena have been discussed above for the CGLE with global feedback.

The third principal mechanism of feedback-induced pattern formation involves clustering of oscillations. The cluster regimes include a variety of qualitatively different patterns. Their common feature is the presence of a small number
of synchronized domains, occupied by one of two possible oscillatory states. No intrinsic spatial wavelength of the domains is observed. Different cluster solutions can be divided into amplitude clusters, phase clusters, and cluster turbulence.

In amplitude clusters, not only the oscillation phases $\phi$, but also the oscillation amplitudes $R$ are different in the regions occupied by the two different states, as shown in Fig. 79(a). Thus, uniform oscillations within two different clusters correspond to different coexisting limit cycles of equal period. The phase shift between the oscillations in the two cluster states (about 0.88 in the example shown) is constant, but depends on the feedback parameters. At the interface between two stationary cluster domains, the phase $\phi$ is monotonously increased and the amplitude $R$ undergoes small variations. The total size ratio of the domains that belong to each state is independent of the initial domain sizes and has a characteristic value that changes with the feedback parameters. The difference in the contributions to global oscillations coming from the two clusters results in period-doubled oscillations of the control signal, see Fig. 79(b).

Phase clusters are characterized by equal oscillation amplitudes and a constant phase shift between the cluster states. The oscillations in both cluster states correspond now to the same limit cycle, but are of opposite phase. The phase fronts that separate different cluster domains exhibit rich behavior, as demonstrated below. At high feedback intensities, stationary phase clusters prevail, see Fig. 80(a). The asymptotic spatial formation of the domains in such a pattern depends on the initial conditions. However, the total fraction of the medium occupied by the domains of each cluster is balanced. When a simulation is started with a different initial size ratio, the fronts between the cluster domains slowly drift and finally come to rest in the state of phase balance. As a consequence, the average that generates the feedback signal is periodic and resonantly oscillates with a frequency twice larger than that of the periodic local oscillations inside the cluster domains.

Stationary phase clusters can undergo a transition to traveling clusters, when the feedback intensity is increased [216]. Periodic boundary conditions are necessary for the observation of such propagating patterns, because they preserve the
size ratio between the clusters. This transition is related to nonequilibrium supercritical Ising–Bloch bifurcation that leads to fronts traveling with constant velocity.

It is interesting to compare the phase and amplitude properties of oscillations in stationary and traveling phase-cluster patterns. The phase portraits of such patterns are shown in Fig. 81. In the stationary cluster pattern displayed in Fig. 81(a), the two cluster states correspond to the ends of the S-shaped structure where the points accumulate. The other points in this structure correspond to the front that separates the clusters. Note that the S-shaped structure goes through the origin of the plane, i.e., there is a point inside the front where the oscillation amplitude \( R \) vanishes. At this point the phase \( \phi \) undergoes a jump by \( \pi \). At the transition to traveling Bloch fronts, the phase portrait is qualitatively changed and the S-shaped curve splits into two different branches that connect the two cluster states. Farther away from the transition point, the fronts between the cluster states are mapped almost to a circle, as shown in Fig. 81(b). The phase \( \phi \) undergoes a continuous rotation with a total of \( \pi \) when traversing such a Bloch front, whereas \( R \) shows only small modulations.

Furthermore, a transition to oscillating phase clusters has also been observed in numerical simulations. The origin of this transition is an instability of the phase balance that gives rise to periodic oscillations of the cluster size ratio. As a consequence, cluster fronts periodically change their spatial position. This transition corresponds to a subcritical Hopf bifurcation. At larger distances from the bifurcation point, the front oscillations become strongly unharmonic and zigzag shaped.

Starting from strongly unharmonic front oscillations, a suitable change of feedback parameters leads to turbulent phase front behavior. An example of such irregular front behavior is shown in Fig. 82, where a front separating two \( \pi \)-shifted clusters branches out in a cascade of reproductions. The distribution of the oscillation amplitude is displayed in Fig. 82(a), and frame (b) shows the phase distribution in a rotating coordinate frame. The corresponding chaotic global oscillations are shown in frame (c). Such cluster turbulence does not spontaneously develop from a completely uniform oscillating state, i.e., a sufficiently strong local perturbation is needed to initiate the cascade. The fronts not only reproduce, but also can die out. Once initiated, the cluster turbulence can thus either spread over the whole medium, or die after some time. The velocities of traveling fronts in this turbulent regime are almost constant. A front travels for some time, until an amplitude defect with vanishing amplitude \( R \) develops inside it.

Feedback-induced pattern formation has also been numerically explored in two-space dimensions [216]. The simulations show the formation of spiral waves formed by propagating Bloch fronts. In the parameter region, corresponding to oscillating fronts in the 1D system, a different kind of patterns was observed in 2D simulations. The area occupied by each of the clusters in Fig. 83 is almost balanced and no significant oscillations of the fronts take place. The global oscillations are almost periodic here. The front separating the two clusters is broken into parts (see the bottom row in Fig. 83). As time goes on, the amplitudes in different front parts periodically drop down at opposite oscillation phases. On a large time scale of several hundred oscillation periods, weak drift of the clusters and slow gradual variation of their shapes are observed. The splitting of the front into different parts is a 2D phenomenon that is typically observed starting from nonuniform initial conditions.

When cluster fronts show irregular motion in one space dimension, the respective 2D clusters also exhibit complex turbulent evolution. As an example, two subsequent snapshots of a turbulent cluster pattern are shown in Fig. 84.
Fig. 82. Spatiotemporal plots showing evolution of local oscillation amplitude $R$ (a) and phase $\phi$ (b) in the reproduction cascade leading to a turbulent cluster pattern. The corresponding chaotic feedback signal is shown in frame (c). Parameters: $\tau/T_0 = 0.126$ and $\mu/\rho^0_{\text{CO}} = 0.193$. From [216].

Fig. 83. Snapshots of the oscillation phase (top) and amplitude (bottom) distributions in a cluster pattern with time-dependent front profile. The snapshots (a) and (b) are separated by half the oscillation period. Parameters: $\tau/T_0 = 0.067$ and $\mu/\rho^0_{\text{CO}} = 0.072$. From [216].

Fig. 84. Turbulent cluster patterns. The two consecutive snapshots (a,b) of the oscillation phase (top) and amplitude (bottom) distributions separated by two oscillation periods. Parameters: $\tau/T_0 = 0.067$ and $\mu/p_{CO}^0 = 0.024$. From [216].

(top and bottom rows again correspond to the phase and amplitude distributions). Each cluster consists of different patches that continuously vary their shape while the separating fronts propagate through the medium. The front propagation occurs at an almost constant velocity in the planar front parts. Turbulence is maintained in this system through repeated popping up of bubble-like domains with the opposite phase in the region occupied by any of the two-phase clusters. These bubbles or spots grow for a few oscillation cycles and eventually merge with the larger cluster patches. On the other hand, cluster patches can also shrink and disappear. New cluster spots usually originate at the locations that were previously visited by the fronts, where amplitude and phase heterogeneities were left. Uniform oscillations are stable in this parameter region and to initiate a turbulent cascade, sufficiently strong local perturbations must be applied to the uniform state.

In contrast to the complex Ginzburg–Landau equation, oscillations in the CO oxidation reaction are not harmonical. This difference is important to understand the results of numerical simulations of this model. When clusters with opposite oscillation phases occupy equal surface areas and the phase balance condition is satisfied, the global feedback signal would vanish for harmonic oscillations. In the case of nonharmonic oscillations, the same condition leads however to the generation of the feedback signal with the twice shorter period. Therefore, the system is effectively under periodic 2:1 forcing. This explains why cluster boundaries can behave as Ising or Bloch walls here. In the regimes without phase balance, the generated feedback signal can be more complicated and even chaotic, leading to complex cluster behavior.

3.8. Global feedback control of patterns in the oscillatory Belousov–Zhabotinsky reaction

Experiments with global feedback applied to the photosensitive Ru(bpy)$_3$-catalyzed Belousov–Zhabotinsky reaction have been performed [218,219]. The reaction was taking place inside a thin layer of silica gel. The photochemical negative global feedback was introduced through illumination. By measuring the gel adsorption at a certain wavelength, the average concentration $Z_{av}$ of Ru(bpy)$_3$ in the working area of the silica gel was continuously monitored. The illumination intensity $I$ was set as

$$I = I_{\text{max}} \sin^2 \left[ g \left( Z_{av} - Z_r \right) \right],$$

(107)
where the target $Z_t$ was chosen close to the steady-state value. The coefficient $g$ was thus determining the feedback intensity. The reaction parameters were chosen in such a way that, without the feedback, periodic bulk oscillations took place. By varying the parameters, a transition to the uniform steady state corresponding to a Hopf bifurcation could be induced.

Far from the Hopf bifurcation boundary (i.e., in the parameter regions where oscillations were strongly unharmonical), four different types of clusters were observed at sufficiently high feedback intensities. They are standing two-phase clusters, three-phase clusters, irregular clusters, and localized irregular clusters (see Fig. 85).

Oscillations inside the two-phase clusters (Fig. 85a) are shifted by half a period and the boundaries separating different phase regions are stationary. Three-phase clusters occur in a narrow range of feedback intensities $g$ between standing and irregular clusters. The domains in these patterns slowly move and change their form. The phase shift between clusters was different from $2\pi/3$. Moreover, the local amplitude of oscillations in the gray domains (Fig. 85b) was significantly smaller than in the white domains. Such patterns resemble two-phase standing clusters where the white domains are split into white and gray subdomains.

Local oscillations in the irregular clusters (Fig. 85c) are aperiodic, but the average concentration and, therefore, the feedback signal oscillate approximately periodically. By comparing consecutive snapshots separated by the global oscillation period, it was found that these domains do not overlap and thus the oscillations are antiphase [219]. The overlapping area of white domains in frames separated by two oscillation periods $T_0$ is small, indicating the absence of temporal periodicity. The irregular cluster patterns are not stationary and the entire area is eventually covered by white domains, typically over several tens of periods.

Domains of antiphase oscillations in localized clusters (Fig. 85d) occupy only part of the area, and no visible oscillations are taking place in the remaining dark area. With increasing feedback intensity, the portion of the medium occupied by localized clusters shrinks. Eventually, clusters disappear and small-amplitude bulk oscillations are established in the medium.

Close to the Hopf bifurcation, only standing two-phase and localized clusters could be observed, depending on the feedback intensity. Additionally, small bright spots appearing at the same location in each period of global oscillation and separated by the nonoscillatory dark region have been sometimes found in this case [219].

Numerical simulations using the Oregonator model of the Belousov–Zhabotinsky reaction with a global linear feedback term have been performed [218,220]. Generally, they reproduce all basic kinds of cluster patterns seen in the experiments. Two-phase clusters possess no intrinsic wavelength and domains with different phases are separated by nodal lines. After a transient accompanied by the disappearance of smaller domains, the pattern formed by two-phase
clusters becomes stationary. Another property of this pattern is that it is characterized by phase balance. In contrast to this, the patterns formed by three-phase clusters are never stationary, i.e., the boundaries between the phase domains always move. Sometimes, three domains with phases shifted by $2\pi/3$ meet at a singular point. Around this point, the borders rotate periodically, creating a cluster spiral wave. The condition of phase balance holds also in this case: the sum of the areas belonging to each of the three phases converges to one-third of the total area. Under phase balance, the oscillations of the global control signal are periodic with the frequency three times larger than the frequency of the local concentration oscillations. In irregular clusters (see Fig. 86), local oscillations in domains of different clusters are not periodic, even during a short interval of time, although global oscillations are nearly periodic.

Fig. 87 shows localized clusters seen in numerical simulations. The irregular localized clusters (Fig. 87a, b) occupy only part of the space, and small-amplitude bulk oscillations occur in the rest of the system. When the feedback intensity is increased, the area occupied by such bulk oscillations grows. Then, the pattern of regular localized patterns
emerges (Fig. 87c,d). The clusters in this pattern have stationary nodal lines. At still higher feedback intensities, uniform small-amplitude bulk oscillations occupy the whole medium.

Additional analysis has shown that the emergence of localized cluster patterns, i.e., of spatial domains with large oscillation amplitude on the background of small-amplitude oscillations, is related to the canard phenomenon [221]. The canard phenomenon is a sudden explosion of a limit cycle born at a supercritical Hopf bifurcation, as the control parameter passes a certain critical value.

4. Control of chemical turbulence

In oscillatory media considered in the previous section, uniform oscillations and waves were intrinsically stable. Therefore, external forcing and global feedback could be used in such systems only to modify the properties of waves and/or create new wave patterns. If the medium intrinsically finds itself in the state of turbulence (spatiotemporal chaos), the primary question is whether and under what conditions this turbulence can be suppressed. Furthermore, periodic forcing and global feedback can be used then to bring a system to the edge of chaos—a state where it becomes highly labile and where a variety of new, easily controllable patterns is possible.

In this review article, we focus our attention on global control techniques which do not require access to and manipulation of individual reaction elements. Such global methods work best when the dynamics of individual elements is regular (e.g., periodic or excitable) and spatiotemporal chaos is a consequence of interactions between them due to diffusion of reactants. General aspects of control of turbulence in oscillatory media shall be discussed in the framework of the complex Ginzburg–Landau equation. As the respective experimental system, catalytic CO oxidation on Pt will be considered. For excitable media, control of the Winfree turbulence of scroll waves by means of periodic external forcing has already been discussed in Section 2.12.

4.1. Uniform periodic forcing of turbulence in oscillatory media

The starting point for our analysis is the complex Ginzburg–Landau equation with uniform external periodic forcing near an $m:1$ resonance

$$\dot{\eta} = (1 + iv)\eta - (1 + i\beta)|\eta|^2\eta + (1 + i\varepsilon)\nabla^2\eta + B(\eta^{m-1}).$$

(108)

In absence of forcing ($B = 0$), uniform oscillations in this system are linearly unstable and turbulence spontaneously develops if the Benjamin–Feir condition $1 + \varepsilon\beta < 0$ is satisfied, as we always assume in this section. Effects of periodic forcing in this system were first studied by Coulet and Emilson [188].

If forcing suppresses turbulence and the frequency-locked state is established, the phase and the amplitude of oscillations become constant for the whole medium. If the viscosity of a transition to this synchronous uniform state the system can form nearly synchronous patterns where the phase is slowly spatially modulated and the oscillation amplitude is almost constant. Such patterns can be described in the phase approximation which is valid under weak forcing ($B \ll 1$) in the neighborhood of the Benjamin–Feir instability (when $|1 + \varepsilon\beta| \lesssim B^{1/2}$) and for sufficiently small detuning (when $|\nu - \beta| \lesssim B^{3/2}$). By writing $\eta = (1 + \delta\varphi)\exp[i(\psi + \varphi_0)]$, the following reduced equation for the local oscillation phase $\psi$ can be derived [188]

$$\dot{\psi} = -mB\sqrt{1 + \beta^2}\psi + (1 + \varepsilon\beta)\nabla^2\psi - (\varepsilon - \beta)(\nabla\psi)^2 - \frac{1}{2}\varepsilon^2(1 + \beta^2)\nabla^4\psi,$$

(109)

where

$$\varphi_0 = \frac{\nu - \beta}{mB\sqrt{1 + \beta^2}} - \frac{1}{m}\arctan \beta.$$

(110)

After rescaling the variables in this equation as

$$x = \left[\frac{1}{2}\varepsilon^2(1 + \beta^2)\right]^{1/4}x', \quad \psi = -\left[\frac{\varepsilon^2(1 + \beta^2)}{2(\varepsilon - \beta)^2}\right]^{1/2}\psi',$$

(111)
it takes the standard form of the damped Kuramoto–Sivashinsky equation

\[
\dot{\psi}' = [\sigma - (\nabla^2 + k_0^2)^2] \psi' + (\nabla \psi')^2
\] (112)

with

\[
\sigma = \frac{(1 + \epsilon \beta)^2}{2\epsilon^2(1 + \beta^2)} - mB
\] (113)

and

\[
k_0^2 = -\frac{1 + \epsilon \beta}{\sqrt{2\epsilon^2(1 + \beta^2)}}.
\] (114)

According to Eq. (112), the uniform frequency-locked state (\(\psi' = 0\)) is stable, if \(\sigma < 0\) which implies that forcing is sufficiently strong, \(B > B_c\) where

\[
B_c = \frac{(1 + \epsilon \beta)^2}{2m\epsilon^2(1 + \beta^2)}.
\] (115)

Below this threshold, the uniform state is linearly unstable with respect to the growth of periodic spatial phase modulation with the wavenumber \(k_0\). The weakly nonlinear analysis of this instability shows [188] that in one dimension it corresponds to a supercritical bifurcation and leads to the development of a periodic stationary pattern of the local oscillation phase \(\psi\). In two dimensions, a weakly subcritical transition to a stationary pattern of hexagons takes instead place (see Fig. 88).

Such patterns with weak spatial modulation of the oscillation phase and almost constant oscillation amplitude exist near any \(m:1\) resonance. When \(m = 2\), one further kind of patterns becomes possible. If we write \(\eta = U + iV\) and consider the limit of strong forcing when \(B \sim \nu \sim \epsilon\) are large compared to other parameters, it can be shown [188] that Eq. (108) reduces to an equation that involves only the real part \(U\) of \(\eta\),

\[
\dot{U} = \left( B - \frac{\nu^2}{B} \right) U - U^3 + \left( 1 - \frac{\epsilon \nu}{B} \right) \nabla^2 U - \frac{\epsilon^2}{B} \nabla^4 U.
\] (116)

Under such conditions, the frequency-locked state with \(U = \pm \sqrt{B - \nu^2/B}\) undergoes a finite wavelength instability when the forcing amplitude is decreased below the threshold \(B_2\) determined by the following:

\[
(B - \epsilon \nu)^2 = 8\epsilon^2(B^2 - \nu^2).
\] (117)
The corresponding critical wavenumber $k_2$ is given by

$$k_2^2 = \frac{1}{2\varepsilon^2} (\varepsilon \nu - B).$$  \hspace{1cm} (118)

The weakly nonlinear analysis of this instability reveals [188] that it leads subcritically to patterns of modulated phases (stripes) and bubbles (hexagonal). Note that, in contrast to the other hexagonal or stripe patterns which are possible for any resonance order $m$, the oscillation amplitude $\eta$ vanishes along nodal lines in such Ising-like patterns.

Numerical simulations with 2:1 forcing yielded [188] the following scenario in two-space dimensions: starting from a uniform frequency-locked state at high forcing amplitude with a small local perturbation and decreasing the forcing intensity $B$, nucleation of a localized bubble pattern has been seen (Fig. 89a). As the forcing is reduced, this hexagonal pattern spreads and eventually covers the whole medium. Further decreasing $B$, leads to a hexagonal-stripe transition in which hexagons merge to form stripes (see Fig. 89b). Depending on the parameters, labyrinthine patterns shown in Fig. 89c were also observed. By lowering the forcing intensity even more, the destruction of stripe pattern through nucleation and growth of domains filled with defect turbulence takes place. An example of such a process is shown in Fig. 89d.

If forcing is so strong that turbulence is suppressed and uniform oscillations are stabilized, phase fronts become possible. Such fronts are connecting different locked states of the medium. Under 1:1 forcing they represent kinks ($2\pi$-fronts), for 2:1 forcing they are Bloch walls (traveling $\pi$-fronts) or Ising walls (standing $\pi$-fronts), and for 3:1 forcing only traveling $2\pi/3$-fronts are possible.

When 1:1 forcing is applied, traveling kinks are stable for strong forcing. When forcing is made weaker, periodic spatial phase modulation can develop in the originally uniform regions separated by a traveling kink. First, this modulation is regular, so that a kink (in one dimension) propagates on the background of a periodically modulated oscillatory pattern [193]. At still weaker forcing, phase modulation becomes irregular and the state of phase turbulence is reached. This is accompanied by a backfiring transition, which gives rise to cascades of replicating kinks.
For the 2:1 forcing, the transition from a stationary Ising wall to turbulence under the decrease of forcing intensity is complex [188,222,223]. In 1D systems, the first bifurcation is a Hopf bifurcation leading to an oscillating wall. The position and the profile of such a wall are periodically changing with time, but its average velocity is zero. As the forcing intensity is decreased, a symmetry-breaking bifurcation is observed which transforms an oscillating wall into an oscillating front traveling in a certain direction. At still lower forcing, a cascade of subcritical period-doubling bifurcations takes place that leads the system to a chaotic regime. In two and three dimensions, oscillating walls soon experience an instability leading to irregular modulation (rougkening) of the interface [223]. When forcing is lowered, the modulation amplitude grows and, eventually, the front undergoes fragmentation. An example of the evolution of an interface, leading to fragmentation and spatiotemporal chaos, is shown in Fig. 90.

Domains formed by pairs of $\pi$-fronts were considered under the 2:1 forcing [224]. At sufficiently strong forcing, the fronts were immobile and represented Ising walls. Hence, a domain bounded by two subsequent flat $\pi$-fronts was motionless. As forcing was decreased, the two fronts began to move. Initially, their motion was irregular. However, for weaker forcing a stable bound state of a pair of the fronts was formed. The resulting pattern looked like an isolated domain with oscillations shifted by half the period which was propagating on the background of a uniform state. Near the boundary where uniform oscillations were getting unstable with respect to the phase modulation and the development of a cellular structure, traveling “cellular trains” were observed. They represented flat domains, filled with one phase-modulated state and propagating at a constant velocity through the medium filled with the opposite phase-modulated state.

Dynamics of $2\pi/3$-fronts in 2D media under 3:1 forcing has been investigated [225]. At high forcing intensities, such fronts are always traveling. They are characterized in this case by a steep but smooth variation of the phase variable inside the front. When forcing intensity is decreased, complex dynamics sets in inside the interfacial zone. Two examples of such complex interfaces for different forcing intensities are shown in Fig. 91. We see that, inside this zone, irregular phase variations are observed. Moreover, the interface is not planar. Although complex dynamics is already present inside the interface and its shape changes irregularly with time, its average width remains saturated at some finite value on the long time scale for relatively large forcing intensities.

Starting from a certain critical forcing intensity, the behavior of interfaces is however qualitatively different. Now, a finite interfacial zone can no longer be maintained and the front “explodes”. The dynamics of the front in this regime is shown in Fig. 92. There are two counter-propagating fronts where the turbulent phase consumes each of the two locked phases, so that asymptotically the turbulent phase fills the entire medium. The statistical analysis of fronts, separating locked phases from the expanding turbulent phase, has shown that they follow the same scaling law as the irregular
Fig. 91. Traveling $2\pi/3$-interfaces under 3:1 forcing for (a) $B = 0.475$ and (b) $B = 0.462$. The medium size is twice larger in frame (b). Other parameters are $\varepsilon = -1.3$, $\beta = 1.5$, $\nu = 1.55$. From [225].

Fig. 92. Evolution of an exploding interface under 3:1 forcing. Two subsequent snapshots at $t = 1000$ (left frame) and $t = 3000$ (right frame) are shown; $B = 0.454$, other parameters are the same as in Fig. 91. The arrows indicate the directions in which the two fronts propagate. From [225].

Fronts in the stochastic Kardar–Parisi–Zhang equation [225]. Front explosions have also been theoretically investigated in the realistic model of CO oxidation on Pt, when periodic forcing is applied through periodic variation of the partial CO pressure in the reaction chamber [207].

4.2. Global feedback control of turbulence in oscillatory media

General aspects of control of turbulence in oscillatory media near a supercritical Hopf bifurcation can be considered using the complex Ginzburg–Landau equation with an additional feedback term (95)

$$
\dot{\eta} = \eta - (1 + i\beta)|\eta|^2\eta + (1 + i\varepsilon)\nabla^2\eta + \mu e^{i/2} \bar{\eta}(t),
$$

(119)

where

$$
\bar{\eta}(t) = \frac{1}{S} \int_{(S)} \eta(r, t) \, dr
$$

is the global average of the complex oscillation amplitude $\eta(r, t)$. This equation was originally proposed in Ref. [190] (see also [191,226,215,192]) and we have discussed its derivation in Section 3.6. We have also considered in this section the properties of patterns induced by the feedback, under the conditions that uniform oscillations are stable in its absence. Below we choose the case where uniform oscillations are modulationally unstable in absence of feedback and turbulence spontaneously develops. This situation is realized when $1 + \varepsilon \beta < 0$ and thus the Benjamin–Feir instability of uniform oscillations is present.

If the system performs uniform oscillations, the additional forcing term in this equation is periodic with the same frequency as the frequency of these oscillations. Therefore, the feedback terms acts in this case as the periodic 1:1 forcing. But if the feedback is not able to enforce uniform oscillations, the feedback signal depends on the properties of patterns present in the medium, so that $\bar{\eta}(t)$ may have more complex temporal behavior, include other harmonics and also be chaotic.

Eq. (119) admits a simple solution corresponding to bulk oscillations, $\eta(t) = \rho_0 e^{-i\Omega_0 t}$ with $\rho_0 = (1 + \mu \cos \chi)^{1/2}$ and $\Omega_0 = \beta + \mu(\beta \cos \chi - \sin \chi)$. As the feedback intensity $\mu$ is decreased, the effective forcing, which amplitude is
Fig. 93. Synchronization diagram for $\varepsilon = 2$ and $\beta = -1.4$. Bulk oscillations are linearly stable above the curve DABCE. From [192].

proportional to $\mu$, becomes weaker and patterns characterized by spatial modulation of the oscillation phase can develop. To study the behavior of the globally coupled system near this first desynchronization transition [226,228,215,227], one can write $\eta(r, t)$ as a superposition of active modes. In one dimension, we have

$$\eta(x, t) = e^{-i\Omega t}[H + A_+ e^{i\chi x} + A_- e^{-i\chi x}],$$

where the complex amplitudes obey the following:

$$\dot{H} = (1 + i\Omega) H + \mu e^{i\chi} H - (1 + i\beta)|H|^2 H - 2(1 + i\beta)(|A_+|^2 + |A_-|^2) H - 2(1 + i\beta)A_+ A_- H^*,$$

$$\dot{A}_\pm = (1 + i\Omega)A_\pm - (1 + i\varepsilon)\kappa^2 A_\pm - (1 + i\beta)|A_\pm|^2 A_\mp - 2(1 + i\beta)(|A_\mp|^2 + |H|^2)A_\pm - (1 + i\beta)H^2 A_\mp^*.$$  

The destabilization of uniform oscillations ($H_0 = \rho_0, A_+ = A_- = 0$), is the consequence of self-induced parametric forcing described by the last term in the second equation. The linear stability analysis [192,227] allows to determine the threshold $\mu_c$ and the critical wave number $\kappa_c$ of this instability (as the wave number of the modulation mode that first begins to grow). They can be found by solution of two equations:

$$\mu_c = -\frac{1 + \varepsilon\beta + (1 + \varepsilon^2)\kappa_c^2}{(2 + \varepsilon\beta) \cos \chi + \varepsilon \sin \chi}$$

and

$$(1 + \varepsilon^2)\kappa_c^4 = Q(\mu_c),$$

where

$$Q(\mu) = 2\mu(\cos \chi + \beta \sin \chi) + \mu^2 + 2\mu^2(\cos \chi)^2 + \mu^2 \beta \sin(2\chi).$$

Fig. 93 shows the stability diagram of bulk oscillations obtained by numerical solution of these equations. When the curve AB is crossed while decreasing the feedback intensity $\mu$, spatial modulation of the oscillation phase with the wavelength $\lambda = 2\pi/\kappa_c$ develops. Along the curve BC, bulk oscillations become unstable with respect to the long-wavelength spatial modulation with $\kappa_c \to 0$ (in a finite system of length $L$ with periodic boundary conditions, the critical wave number $\kappa_c = 2\pi/L$ on this line). Numerical simulations show [192] that, when such instability occurs, the medium breaks into large phase domains (clusters) whose sizes are about the dimension of the medium. The line BC is determined by Eq. (126) with $\kappa_c = 0$. Note that, as one moves along the curve AB, the critical wave number $\kappa_c$ gradually decreases and then vanishes at the point B. The boundaries AD and CE are given by the condition $\mu = -1/\cos \chi$. On these lines, the amplitude $\rho_0 = (1 + \mu \cos \chi)^{1/2}$ of bulk synchronized oscillations should vanish. However, oscillations
Fig. 94. Suppression of defect turbulence through development of a hexagonal cellular structure under gradual increase of the feedback intensity \((\varepsilon = 2, \beta = -1.4, \chi = -0.2\pi)\). The lower panel shows three snapshots at subsequent time moments, the upper panel shows temporal evolution along the central vertical cross-section. From [192].

in the system cannot disappear (indeed, the steady state \(\eta = 0\) is always unstable). When such boundaries are crossed, long-wavelength periodic modulation of the uniform oscillatory state also develops. Note that suppression of turbulence and stabilization of bulk oscillations is possible only inside a window of phase shifts \(\chi\). Outside of this window, the turbulent state persists at any feedback intensity.

Slightly below the boundary AB, the state of the 1D system is a superposition of a uniform oscillation and a standing wave,

\[
\eta(x, t) = e^{-i\Omega_s t}[\rho_s + 2\theta_s e^{i\varphi_s} \cos(\kappa_c x)].
\]  

(129)

The real amplitudes \(\rho_s\) and \(\theta_s\), the frequency \(\Omega_s\) and temporal phase shift \(\varphi_s\) can be calculated [227] from Eqs. (122) and (124) by substituting \(H = \rho_s, A_+ = A_- = \theta_s e^{i\varphi_s}\) and \(\Omega = \Omega_s\). The bifurcation is supercritical and the amplitude \(\theta_s\) of standing waves is proportional to the distance \(\mu_s - \mu\) from the bifurcation boundary BC.

In two dimensions, such standing waves correspond to oscillating stripes. Additionally, resonant patterns of hexagonal symmetry dominated by a triplet interaction of modes forming an equilateral triangle \((\kappa_1 + \kappa_2 + \kappa_3 = 0)\) should then be considered. The evolution equations for the complex amplitudes of three interacting modes include quadratic terms proportional to the amplitude of the uniform mode [227]. In analogy with the standard hexagons-stripes competition for stationary patterns, such terms destabilize oscillating stripes in favor of a mixed mode corresponding to a superposition of a uniform oscillation and standing waves of hexagonal symmetry. Because the quadratic terms are destabilizing, the instability leading to these cellular hexagonal structures is subcritical. This picture is however modified when \(\chi < -\pi/2\).

In this parameter region, hexagonal cellular patterns are destabilized in favor of oscillating stripes [227]. If \(\mu\) is further decreased, the mixed-mode states undergo subharmonic instabilities. The subharmonic modes should be added to the set of active modes describing the system. In one dimension, the growth of subharmonic modes gives rise to breathing standing waves. In two dimensions, this transition leads to breathing cellular patterns in which the size of the cells varies periodically in time. Such subharmonic instabilities, leading to breathing cells, were indeed seen in numerical simulations [192].

Fig. 94 shows transition from defect-mediated turbulence though a hexagonal cellular pattern to uniform oscillations for \(\chi = -0.2\pi\), under gradual increase of the feedback intensity [192]. The bottom row displays three snapshots at subsequent time moments; the upper panel is the spatiotemporal diagram showing evolution of the pattern along the central vertical cross-section. The modulus \(\rho\) of the complex oscillation amplitude is displayed in gray color, with dark regions corresponding to the smaller values of the variable \(\rho\). Initially the system is in the state of amplitude turbulence,
characterized by the presence of many amplitude defects. These defects occupy irregular cells that are formed by the shocks, i.e., the lines with an increased oscillation amplitude seen as bright membranes in the figure. As the feedback intensity is increased, amplitude defects disappear from some of the cells (see the first snapshot) and the area covered by such “empty” cells grows. Thus, an intermittent state of localized amplitude turbulence on the background of a cellular structure develops. For higher feedback intensities, amplitude defects disappear and a regular cellular structure with a number of topological defects (one pentagonal defect is seen in the middle snapshot) is established. As the feedback intensity grows, the amplitude of amplitude modulation in the cellular structure gets smaller and it finally gives way to the uniform oscillations.

Fig. 95 shows two examples of intermittent regimes in a 1D system [191]. Here, the feedback intensity is maintained constant. Each burst represents a cascade of backfiring kinks. Pairs of amplitude defects, seen as bright spots in this figure, are repeatedly generated inside such cascades. The cascades are spontaneously nucleated on the background of the “laminar” state filled with standing waves. A cascade can die out after a number of reproduction events. For the parameters chosen in Fig. 95a, the cascades are rare and the “laminar” state occupies a large part of the medium. In Fig. 95b, turbulent bursts occupy most of the medium and “laminar” areas with standing waves are relatively rare. If the phase shift of the feedback signal is increased, the transition to uniform oscillations from amplitude turbulence is different. An example of such transition for is shown in Fig. 96. Starting from the state of amplitude turbulence, some empty cells are again formed when the feedback in introduced (first snapshot). As the feedback in increased, empty cells forming the “laminar” background, disappear now giving rise to the areas filled with uniform oscillations, before the “active” cells populated by amplitude defects have vanished. As a result, a regime of localized turbulence is established. When the neighboring empty cells disappear, the shock membrane separating an active cell from the surrounding area with uniform oscillations becomes roughly circular, so that the cell starts to look like an isolated bubble. Apparently, this membrane tends to minimize its length, thus possessing some kind of elasticity. The bubbles can form clusters, but individual bubbles (see the middle snapshot) are also observed. Inside active cells, expanding amplitude defects with a roughly circular shape (string loops) are seen. As the string loops expand and approach the cell boundary, they can break, giving rise to new string loops. In the spatiotemporal diagram along the vertical cross-section (top panel), such string loops look like pairs of kinks. The intermittent turbulence, localized inside a cluster of active cells, is maintained as long as the reproduction cascade continues. If break-up has not occurred inside a cell, this cell dies out and gives way to uniform oscillations.

This transition to uniform oscillations through localized turbulence is also seen, when the real part of the complex oscillation amplitude \( \eta(\mathbf{r}, t) \) is displayed (Fig. 97). The initial amplitude turbulence is formed by a population of rotating spiral waves. As the feedback intensity is gradually increased, this population responds by confining the activity of individual spirals inside islands surrounded by the areas with approximately uniform oscillations. For stronger feedbacks, the islands get smaller and acquire roughly circular shapes. At this stage, the pattern looks like a population of expanding and disappearing bubbles on the background of uniform oscillations.

When the feedback phase shift of is increased approaching \( \pi = 0.275\pi \) (point B in the synchronization diagram, Fig. 93), the cells get larger. In the interval \( 0.275 < \chi/\pi < 0.599 \) (corresponding to the segment BC in Fig. 93), regular cellular arrays are replaced by large phase domains (clusters). Fig. 98 shows how such clusters gradually develop, starting from the state of defect turbulence and gradually increasing the feedback intensity. This figure displays spatial
Fig. 96. Suppression of defect turbulence via the development of localized turbulent spots; \( \varepsilon = 2, \beta = -1.4, \chi = 0 \). The feedback intensity \( \mu \) is gradually increased with time. From [192].

Fig. 97. Suppression of spiral wave turbulence by the growing global feedback. Six subsequent snapshots, displaying the real part of the complex oscillation amplitude, are shown from the top left to the bottom right; \( \varepsilon = 1.3, \beta = -0.8, \chi = 0 \). From [192].

distributions of the modulus \( \rho \) of the local oscillation amplitude \( \eta \). We see that, inside the clusters, not only the phase, but also the amplitude of oscillations is changed. Such clusters, resulting from the long-wavelength instability of the uniform mode, were first considered by Falcke et al. [229]. It can be shown (see [230]) that the conditions for this instability are the same as those determining clustering in populations of globally coupled oscillators [231]. For still higher feedbacks, the clusters shrink and give way to uniform oscillations.

Fig. 99 presents a summary of typical patterns found in numerical simulations of the complex Ginzburg–Landau equation with global feedback. For each pattern, the distributions of phase \( \varphi \) and amplitude \( \rho \) are shown. Additionally, the bottom row displays phase portraits of these patterns, constructed by plotting the states of all elements in the polar coordinates \( (\rho, \varphi) \).
Fig. 98. Suppression of defect turbulence through development of phase clusters under gradual increase of the feedback intensity ($\varepsilon = 2$, $\beta = -1.4$, $\chi = 0.3\pi$). The lower panel shows three snapshots at subsequent time moments, the upper panel shows temporal evolution along the central vertical cross-section. From [192].

Fig. 99. Different two-dimensional patterns in the CGLE with global feedback ($\varepsilon = 2$, $\beta = 1.4$). For each pattern, the distributions of phase (top row), amplitude modulus (middle) and the phase portraits (bottom row) are shown. (a) Amplitude turbulence on background of an irregular cellular structure ($\mu = 0.18$, $\chi = -0.2$), (b) a cellular structure ($\mu = 0.26$, $\chi = -0.2$), (c) localized turbulence ($\mu = 0.55$, $\chi = 0$), and (d) amplitude clusters ($\mu = 4$, $\chi = 0.4$). From [232].
According to Eq. (132), the feedback signal (i.e., the last term) should vanish if the delay time
should be of order $O(1/\sqrt{L})$ under such conditions. On the other hand, when the feedback
applied and entrains the turbulence, the global average $\overline{\eta}(t)$ does not vanish and would oscillate with approximately
constant amplitude.

The behavior of the global average $\overline{\eta}(t)$ under gradual increase of the feedback strength $\mu$ was investigated [233]. It was found that a critical value $\mu_c$ of the feedback strength exists. For $\mu < \mu_c$, the global average $\overline{\eta}$ (and, thus, the global control signal) are vanishingly small in the limit of a large system. When the critical value $\mu = \mu_c$ is exceeded, the global average starts to oscillate with an amplitude $R = |\overline{\eta}(t)|$ which tends to a constant in the limit of $L \to \infty$. The approximate analytical theory developed by these authors predicts that the turbulence entrainment transition is described by the noisy Stuart–Landau equation for the global average $\overline{\eta}(t)$, which has the form

$$
\frac{d\overline{\eta}}{dt} = a[(\mu - \mu_c) + i\Omega]\overline{\eta} - (b + ic)|\overline{\eta}|^2\overline{\eta} + \zeta(t),
$$

where $\zeta(t)$ is the white Gaussian noise. In the limit $L \to \infty$, this equation predicts that $\langle R(t) \rangle = 0$ for $\mu < \mu_c$ and $\langle R(t) \rangle \propto \sqrt{\mu - \mu_c}$ for $\mu > \mu_c$. This asymptotic behavior was indeed approximately found in numerical simulations for large systems. Furthermore, the finite-size scaling implied by Eq. (131) was also numerically verified for the considered control problem.

Model (119), that was considered above in this section, was obtained by a reduction of the global feedback system (92) valid for relatively short delay times $\tau \ll 1$. Since time is measured by us in units of the relaxation time for the oscillation amplitudes, which diverges near a supercritical Hopf bifurcation, this assumption always holds sufficiently close to the Hopf bifurcation point. Nonetheless, it may be also interesting to consider the global control problem without assuming that the delay time is short.

The global control implemented in the reduced model (119) and the original (92) is invasive. This means that when turbulence is suppressed and uniform oscillations are stabilized, the control signal does not vanish and, effectively, the system is then under the action of a uniform periodic driving force. It is known that for chaotic dynamical systems, described by a small number of variables, stabilization of unstable periodic orbits can be achieved in a noninvasive way by using the “time-delay autosynchronization” proposed by Pyragas [234]. Applications of this method to stabilize traveling waves in the CGLE using a local feedback scheme (where the control signal was separately generated for each point of the medium) have been studied [235,236].

Beta and Mikhailov [237] have studied a modification of the global feedback control, described by equation

$$
\dot{A} = (1 + i\omega)A - (1 + i\beta)|A|^2A + (1 + i\epsilon)\nabla^2A + \mu e^{i\zeta} [\overline{A}(t - \tau) - \overline{A}(t)],
$$

where

$$
\overline{A}(t) = \frac{1}{S} \int_{(S)} A(r, t) \, dr.
$$

According to Eq. (132), the feedback signal (i.e., the last term) should vanish if the delay time $\tau$ is equal to the period $T_0$ of uniform oscillations or, generally, whenever $\Omega_0\tau = 2\pi n$ with $n = 1, 2, 3, \ldots$, where $\Omega_0 = 2\pi/T_0$. Thus, one might expect that stabilization of uniform oscillations with a vanishingly weak control signal can be achieved by using this modified method.

Investigations of Eq. (132) have shown, however, that this is not possible. Fig. 100a gives the analytically constructed synchronization diagram for this model in the parameter plane ($\mu, \tau$). Here, the parameters are chosen in such a way.
Fig. 100. (a) Synchronization diagram. Uniform oscillations are stable inside the shaded region. (b, c) Dependences of the critical wavenumber $\kappa_c$ and the critical frequency $\Omega_c$ on the delay time $\tau$. The parameters are $\varepsilon = 2$, $\beta = -1.4$, $\omega = 2\pi - \beta$, $\gamma = \pi/2$. From [237].

that the period of (unstable) uniform oscillations in absence of feedback is $T_0 = 1$. The solid curve in this figure shows the stability boundary of uniform oscillations in the presence of feedback, obtained by the linear stability analysis. Fig. 100c shows the actual frequency $\Omega_c$ of stabilized uniform oscillations along this boundary. We see that the solutions with $\Omega_c = \Omega_0 = 2\pi$ are not possible. Instead, the frequency undergoes jumps at $\tau = n$ with $n = 1, 2, 3, \ldots$. Thus, noninvasive global control is impossible for the considered system.

4.3. Numerical investigations on control of turbulence in the CO oxidation reaction

First theoretical studies of feedback effects for the oscillatory reaction of CO oxidation on Pt(110) were motivated by the discovery of standing wave patterns in this surface chemical reaction [166]. Levine and Zou [238,239] have suggested that such waves emerge as a result of resonant forcing provided by the same reaction, because of the global coupling through the gas phase. Indeed, the gaseous reactants (CO and oxygen) are consumed during the reaction which leads to a decrease of their partial pressures in the reaction chamber. Therefore, the oscillatory reaction is always accompanied by some periodic variation of partial pressures of reactants (with the magnitude of a few percent). Because these partial pressures are important global control parameters of the reaction, their variation leads to periodic self-forcing of the system. These authors derived the amplitude equations, describing interactions between a uniform oscillation mode and two wave modes with the opposite wave numbers, similar to Eqs. (122) and (124) for the CGLE with global coupling. Numerically, they have shown that the system can indeed develop standing waves with large wavelengths. However, global coupling was taken into account phenomenologically in these publications. The partial pressures of CO and oxygen had contributions proportional to the average surface coverages for these two chemical species and it was assumed that the partial pressure of CO increases with an increase of its surface coverage, which is not realistic. Later, Falcke and Engel [182] have derived the equations accurately describing global coupling through the gas phase in the experiments with CO oxidation. Numerical simulations of the CO oxidation model (9)–(11) with such global coupling terms have been performed [240,229,230]. Under the conditions, when uniform oscillations were
unstable without global coupling, they have shown the development of large clusters, with the sizes comparable with the size of the system. Such cluster regimes were similar to those shown in Fig. 98 for the complex Ginzburg–Landau equation. Standing waves with a short intrinsic wavelength, independent from the system size, could be observed only near a transition from the cluster states to turbulence and were rather irregular [230]. Standing waves with a large wavelength comparable with the size of the system and resembling those reported in [238,239] were also found. All these patterns were, however, still qualitatively different from the standing waves seen in the experiments (see discussion [229]). In the subsequent detailed theoretical and experimental study [169] of standing waves in the CO oxidation reaction, it was demonstrated that heterogeneity of the catalytic surface and the effects of subsurface oxygen formation, not taken into account in the simple model (9)–(11), should play an important role in the development of standing waves.

Battogtokh and Mikhailov [215] proposed that artificial global delayed feedbacks can be used to control turbulence in reaction–diffusion systems and demonstrated this using, as an example, the complex Ginzburg–Landau equation. Their proposal was implemented in the experiments with the CO oxidation reaction that will be described in the next section. Below, we review the results of theoretical investigations [241,242] of this control problem. While providing interpretation to the experimental data, these studies also show new effects, related to the nonharmonicity of oscillations and absent for the complex Ginzburg–Landau equation.

Simulations were performed for the model (9)–(11) with the global delayed feedback introduced through the dependence (105) of the partial pressure of CO on the average CO coverage. To analyze numerical data, the empirical transformation to phase and amplitude variables (see Fig. 74) was used. The model parameters were chosen in such a way that, in absence of feedback, an isolated system element performed nonharmonic stable oscillations of period $T_0 = 2.73 \text{s}$, but the system with diffusion showed spatiotemporal chaos characteristic for amplitude turbulence. The synchronization diagram, based on the simulations of the 1D system, is displayed in Fig. 101.

Fig. 101a shows that, if the feedback intensity is sufficiently large, global delayed feedback allows to suppress amplitude turbulence and induces uniform oscillations in a wide range of delays (light gray-shaded regions). The minimal value of $\mu$ needed to stabilize uniform oscillations, i.e., the efficiency of the feedback, strongly depends on the choice of $\tau$. When the feedback intensity is fixed at an intermediate level, several synchronization windows alternate with turbulent zones upon variation of the delay. Note that in certain small intervals of the delay (e.g., in the approximate range $0.03 < \tau/T_0 < 0.10$), turbulence can be suppressed at relatively low values of the feedback intensity, but the feedback fails to stabilize uniform oscillations at higher values of $\mu$. At very small delays, $\tau/T_0 < 0.03$, the suppression of turbulence is impossible for realistic values of $\mu$.

Even if global delayed feedback is too weak to completely suppress turbulence, it still can alter the properties of the turbulent state. An interesting dynamical regime is observed close to the synchronization border (the boundary between the white and the gray-shaded regions in Fig. 101a). Here, a large part of the system is sometimes already in the state of uniform oscillations, but a few localized amplitude defects persist. Individual defects either die out in the further evolution of the system, or they initiate a cascade of defect reproduction. This is the state of intermittent turbulence.
At feedback parameters corresponding to the dark gray regions in Fig. 101, the turbulent state is suppressed via the formation of cluster patterns. Cluster patterns consist of large, homogeneously oscillating domains that are separated by narrow domain interfaces. As is shown later, two different types of stable clusters are observed: phase clusters with antiphase oscillations and amplitude clusters with coexistent limit cycles.

A different synchronization diagram is obtained when a uniform state with small superimposed random perturbations is taken as initial condition in the simulations, see Fig. 101b. Examining this diagram, it is found that the stability region of uniform oscillations extends far beyond the former synchronization boundary (dashed line in Fig. 101b). Thus, for a broad range of delays, the uniform state shows strong hysteresis when the feedback intensity is decreased from large values. Turbulence spontaneously develops from almost uniform initial conditions only at feedback parameters outside the shaded regions. However, in the intermediate parameter range inside the shaded regions but below or to the left of the dashed line, a sufficiently strong local perturbation of the uniform state is able to initiate a defect cascade, yielding either intermittent or fully developed turbulence. Further types of patterns exist in the hatched region in Fig. 101b. In this region, uniform oscillations are unstable, and wave patterns characterized by an intrinsic wavelength develop from small random perturbations. The parameter region where wave patterns develop in the 1D system approximately coincides with the parameter range for which cellular structures are found in the 2D system.

Intermittent turbulence is characterized by the occurrence of turbulent bursts on a laminar background. In this regime, a certain degree of long-range order is retained. An example of such behavior is displayed in Fig. 102. The chosen parameter values are close to the synchronization border in Fig. 101a. The resulting state is characterized by repeated cascades of amplitude defects on the background of uniform oscillations. The defects reproduce until nearly the entire system is covered with turbulence. Then, they simultaneously annihilate in some parts of the medium. Sometimes only a few defects survive and initiate another reproduction cascade. In this way, the system behavior alternates between strongly turbulent states with only short-range spatial correlations and nearly uniform states with large-scale spatial correlations. Note that the global oscillations used to generate the feedback signal in the state of intermittent turbulence are chaotic.

In two-space dimensions, intermittent turbulence is characterized by irregular cascades of nearly circular structures on the background of uniform oscillations. Fig. 103 displays three subsequent snapshots of the spatial distributions of CO coverage, phase, and amplitude in such a pattern. Additionally, phase portraits are shown in the bottom row of Fig. 103, obtained by plotting the amplitudes and phases for all pixels of a pattern in polar coordinates. The phase of a point in the phase portrait is represented by the polar angle and the amplitude by the distance to the coordinate origin. At constant feedback parameters, the pattern evolution is as follows: at a given instant, individual bubbles and ring-shaped structures are present on an almost uniform background, see Fig. 103a. The ring-shaped structures represent a later stage in the evolution of bubbles. They are similar to the strings observed during fully developed turbulence, but their shape typically is more circular. Inside the localized bubbles and along the border of the ring-shaped objects, the oscillation amplitude is strongly decreased. The phase varies strongly in space perpendicular to such objects. A distinct structure
Fig. 103. Snapshots of CO coverage (top row), phase (second row), amplitude (third row), and phase portraits (bottom row) for intermittent turbulence into space dimensions. The time interval between the subsequent images shown in each row approximately corresponds to two periods of the oscillating background. The system size is $0.6 \times 0.6 \text{ mm}^2$. From [242].

is then found in the phase portrait shown in the bottom of Fig. 103a, where the uniform background corresponds to the sharp end of the tail. As time goes on, the localized bubbles grow in size and transform into expanding rings, see Fig. 103b. New turbulent bubbles are then created inside such structures. During this process, the structure in the phase portrait slowly scatters. When the expanding rings gain direct contact, they merge, such that a few oscillation periods later, only small laminar regions are left in the system, as displayed in Fig. 103c. In this state, extended line defects with almost vanishing amplitude separate the remaining uniform regions from parts of the medium now covered by turbulence. Another such evolution cycle is again initiated some time later, after large parts of the turbulent regions have again spontaneously synchronized and only a few localized defects have survived.

Inside the cluster regions in Fig. 101, two different types of stable clusters have been observed. Their common feature is the presence of a small number of synchronized domains belonging to one of the two different oscillatory states. No intrinsic spatial wavelength is present in such patterns. Usually, two-phase clusters characterized by the phase balance are found. The space–time diagram of a state with such clusters in a 1D system is shown in the left panel in Fig. 104. Examining this diagram, it can be noticed that local oscillations inside the phase domains are period-doubled and characterized by alternating magnitudes of subsequent oscillation maxima (see also the curves below the space–time diagram). The period doubling is, however, absent inside a narrow interface separating different phase domains. Inside this interface, local oscillations have the same period as that of the oscillations of the average coverage, shown by the solid line in the figure. The interfaces are stationary for such clustered states. A different cluster type exists at $\tau/T_0 \approx 0.15$ and at high feedback intensities, $\mu/p_0 > 0.17$. The space–time diagram of such amplitude clusters, which are due to the coexistence of two limit cycles, is shown in the left panel in Fig. 104. Inside the small domain, oscillations are simple periodic and have a large amplitude, while the other domains of the pattern show period-two oscillations with much smaller amplitude. The domain interfaces are stationary and phase balance is absent in such a pattern.
Close to the upper boundary of the hatched region in Fig. 101b, standing waves were found in numerical simulations of the 1D system. Such structures are stable with respect to small perturbations, but transform into intermittent or developed turbulence when a sufficiently strong local perturbation is applied. Such patterns consist of periodic modulations of both the spatial distributions of the oscillation phase and the amplitude (Fig. 105a). A local increase of $R$ corresponds to a decrease of $\phi$. The modulations are stationary, so that all system elements show periodic oscillations, as seen in the space–time diagram (Fig. 105b). The phase and amplitude variations are small for feedback parameters close to the border to uniform oscillations, and continuously grow as the feedback intensity is decreased at a constant delay. At a given set of feedback parameters, the wavelength of the modulations is a characteristic property of the pattern, i.e., it is almost independent of the system size. When the feedback intensity is decreased, standing waves become unstable. Neighboring phase minima start to oscillate weakly around their mean position, and a pattern of breathing waves becomes formed. Under further decrease of the feedback intensity, the regularity of this pattern breaks down and it is transformed to phase turbulence.

In roughly the same region of the feedback parameters where wave patterns and phase turbulence are found in one-space dimension, oscillatory cellular structures develop in 2D systems. Like wave patterns, such structures represent small-amplitude modulations of uniform oscillations and are replaced by intermittent or amplitude turbulence upon a sufficiently large local perturbation. Close to the border to uniform oscillations, the cell arrays are regular and show a hexagonal symmetry. Decreasing the feedback intensity, first a transition to an array of breathing cells and then to phase turbulence are observed.

Fig. 106 presents a summary of different 2D structures and their amplitude and phase properties. The images in the top, second, and third rows display spatial distributions of CO coverage, phase, and amplitude, respectively. Additionally, the bottom row shows the phase portrait of each pattern. The unperturbed turbulent state (Fig. 106a) is
characterized by strong amplitude and phase fluctuations. This state is similar to fully developed amplitude turbulence in the unforced CGLE. The patterns shown in Figs. 106(b)–(e) represent typical 2D patterns induced by the feedback. Intermittent turbulence (Fig. 106b) is observed close to the synchronization border under increasing feedback intensity. This regime is characterized by irregular cascades of bubbles developing into ring-shaped structures on the background of uniform oscillations. The amplitude is strongly decreased inside such localized objects. Stationary two-phase clusters (Fig. 106c) were observed under further increase of the feedback intensity in narrow intervals of the delay time. Because the local oscillations inside the cluster domains exhibit period-two local oscillations, oscillations within different cluster domains at a given time differ not only in phase, but also in amplitude; nonetheless, they correspond to the same limit cycle. In addition to phase clusters, amplitude clusters with coexistent limit cycles are also observed, but not shown in the figure. Hexagonal cell arrays (Fig. 106d) arising from a finite wavelength instability are found in a range of feedback parameters where standing waves develop in one-space dimension. Secondary instabilities lead to breathing cellular structures (not shown in the figure), and to phase turbulence (Fig. 106e). As seen in the corresponding phase portraits, both the phase and the amplitude are modulated in cellular structures, though the amplitude variations are weak.

4.4. Experiments on feedback control and periodic forcing of turbulence in the CO oxidation reaction

In this section, results of systematic experimental investigations [241,183,244,243] on control of spatiotemporal chaos in the oscillatory surface reaction of CO oxidation on Pr(110) are presented. For the visualization of spatiotemporal adsorbate patterns on the catalytic surface, PEEM was used in these experiments. This method produces real-time images of the lateral distribution of adsorbed species on the surface. More precisely, the distribution of photoelectron emission from the surface under ultraviolet light irradiation is displayed. The yield of photoelectrons depends sensitively on the local work function \( w \) of the substrate, which is changed due to the presence of adsorbates. Compared to the
free Pt(110) surface, a monolayer of oxygen coverage increases the work function by $\Delta w \approx 0.8$ eV, thereby strongly decreasing the brightness of PEEM images. Full CO coverage also increases the work function but produces a smaller effect ($\Delta w \approx 0.3$ eV). Using PEEM, a surface area of approximately 500 mm in diameter was monitored. The spatial resolution of the images was about 1 µm. A frame rate of 25 camera images per second guaranteed a sufficiently good temporal resolution of the PEEM recordings. Image processing including background subtraction, contrast-brightness adjustments, and image averaging was performed to improve the signal-to-noise ratio of the images.

As a consequence of mass balance, global gas-phase coupling is generally present in surface chemical reactions. To minimize the effects of such internal coupling, specially prefabricated single crystals have been used. About 80% of the Pt(110) single-crystal surface (10 mm in diameter) has been covered by microlithographic deposition with Ti. The Ti layer was then oxidized in the reaction chamber, thereby producing a TiO$_2$ layer which is catalytically inactive for the considered reaction. Only the free Pt areas remained active. In this way, isolated surface reactors of various sizes could be created. For the experiments, reactive areas of about 1 mm$^2$ have been chosen.

Global delayed feedback was introduced through the gas phase by making the instantaneous dosing rate of CO gas dependent on real-time properties of the developing patterns. While monitoring the patterns on the surface, the PEEM intensity was simultaneously averaged over the entire observation window by means of an electronic integrating device. The level of intensity was scaled such that a CO (oxygen) saturated surface corresponded to a value of 1 (0). From the resulting global signal $I(t)$, a reference value $I_{\text{ref}}$ was then subtracted using a preset potentiometer. The reference value has been determined in the beginning of each series of experiments, before global delayed feedback was applied. It was chosen as the time average of the global PEEM intensity $I(t)$ in the initially developing state of spiral-wave turbulence. In the following step, the signal was delayed by a certain time $\tau_d$ using a computer. Afterwards, the delayed signal was electronically amplified by a factor determining the feedback intensity. A high-frequency filter was used to reduce electric noise and to invert the signal. Finally, the control signal was applied back to the system by controlling the automated inlet system for CO gas. The variation of the CO partial pressure $p_{CO}$ in the reaction chamber followed the temporal modulations of the dosing rate with an additional delay $\tau_0 \approx 0.4$ s due to the finite response time of the inlet system and the residence time of gases in the pumped chamber. Thus, a global delayed feedback could be artificially introduced, such that

$$p_{CO}(t) = p_0 - \mu [I(t) - I_{\text{ref}}],$$

where $p_{CO}$ is the CO partial pressure in the reaction chamber, $I(t)$ denotes the integral PEEM intensity at time $t$, $\tau = \tau_0 + \tau_d$ is the effective time delay, the parameter $\mu$ specifies the feedback intensity, and $p_0$ and $I_{\text{ref}}$ are the CO partial pressure and the mean base level of the integral PEEM intensity in absence of feedback, respectively.

In the beginning of each series of experiments, the parameters of temperature and partial pressures have been chosen in such a way that the reaction was oscillatory and, furthermore, a complex state of chemical turbulence characterized by only short-scale spatial correlations developed in absence of feedback. A sequence of PEEM images showing the spontaneous development of chemical turbulence from a uniformly oxygen covered surface state has already been displayed earlier in Fig. 6. A characteristic property of such turbulence is the spontaneous creation of irregular wave fronts and multiple fragments of rotating spiral waves. The spiral waves repeatedly undergo breakups, leading to the formation of new spiral fragments at different locations.

Starting from the regime of spiral-wave turbulence, global delayed feedback was switched on. In the experiments with a systematic variation of the feedback parameters, it was observed that turbulence could be suppressed and replaced by stable uniform oscillations for any delay time (delays up to $\tau = 10$ s have been probed) provided that the feedback intensity $\mu$ was sufficiently high (up to the value, corresponding to the CO partial pressure variations of about 20% in the state of synchronous oscillations). Usually, the synchronization threshold was significantly lower (about 5% variations in $p_{CO}$). The period of uniform oscillations was affected by the feedback and varied approximately between 3 and 10 s, with a tendency to increase for longer delays and decrease for stronger feedbacks.

For lower feedback intensities, the feedback does not transform spiral-wave turbulence into stable uniform oscillations but leads to the formation of novel spatiotemporal patterns. In the initial state of spiral-wave turbulence in absence of feedback, the integral PEEM intensity is almost constant except for small random fluctuations. As the feedback intensity is increased starting from zero, global oscillations set in, and turbulent spiral waves are first replaced by intermittent turbulence. This state is characterized by turbulent cascades of localized objects on a uniformly oscillating background. Intermittent turbulence is found for any choice of the time delay when the feedback intensity is increased from low values. Strong hysteresis is present at the transition from intermittent turbulence to uniform oscillations, that is,
Fig. 107. Intermittent turbulence in CO oxidation reaction. (a) Six subsequent PEEM images of size $360 \times 360 \text{m}^2$ during a single cycle of local oscillations; the time interval is 0.7 s. (b) Eighteen images shown at subsequent evolution cycles (from left top to right bottom); the time interval is 3.5 s. (c) Space–time diagram of the evolution along the line AB in the first image in (a), together with the corresponding temporal variations of the partial CO pressure (solid line) and of the inversed integral PEEM intensity (gray line). From [183].

At a fixed time delay, uniform oscillation disappears at significantly lower values upon a decrease of the feedback intensity than they appear from intermittent turbulence upon an increase of $\mu$.

By fixing the feedback intensity below the transition to uniform oscillations, two different types of localized turbulent objects representing intermittent turbulence have been identified, namely, bubble-shaped structures and spiral-wave fragments. An example of the first type of intermittent turbulence is displayed in Fig. 107. The PEEM images in Fig. 107a are snapshots taken within one cycle of the pattern evolution. Starting from a dark, uniform state, bright spots develop at different locations. When the growing spots reach a certain size, darker regions develop in the middle of these objects, transforming them into ring-shaped structures. Because the wave back of the expanding rings propagates faster than the wave front, after some time the whole pattern fades away and is replaced by the uniform dark state. Then the entire cycle repeats.

The temporal evolution of the pattern is further analyzed in Fig. 107c, showing the space–time diagram along the line AB indicated in the first image in Fig. 107a. Expanding bubbles are represented by triangular structures in the cross-section. Examining this diagram, it is found that the bubbles can die and reproduce. When the bubbles have reproduced
until many of them are found, massive annihilation occurs and only a few of them survive. Thus, an irregular behavior of repeated reproduction cascades is observed. In a sequence of PEEM images taken at subsequent evolution cycles of the pattern, this behavior is reflected by a repeated alternation between system states with large and small fractions of the surface occupied by turbulent objects, see Fig. 107b. In the example shown, the number and size of the turbulent bubbles typically vary on the time scale of about six evolution cycles. During intermittent turbulence, the variations of the CO partial pressure are aperiodic but rigidly correlated with the evolution cycles of the pattern, see the curves below the space–time diagram in Fig. 107 showing the temporal variations of CO pressure (black line) and inverted integral PEEM intensity (gray line).

In addition to the turbulent bubble structures, a similar state of intermittent turbulence characterized by localized fragments of spiral waves has also been observed. This state predominantly occurred at higher values of temperature, where chemical turbulence in absence of feedback was more strongly developed and displayed a higher density of small spiral fragments. The localized spirals during intermittent turbulence undergo similar evolution cycles as the bubble structures. They also reproduce until they occupy almost the entire monitored surface area, and then annihilate such that only few of them survive. Typical PEEM images of spiral wave fragments on the background of uniform oscillations are displayed in Fig. 108.

By increasing the feedback intensity from the state of intermittent turbulence, additional spatiotemporal patterns (standing waves, cellular structures, and clusters) were observed below the transition to uniform oscillations for delays in the interval $0.5 \, s < \tau < 1.0 \, s$. Oscillatory standing waves were characterized by the repeated development of bright stripes from the dark uniform state (see Fig. 109). They formed a spatially periodic array and, depending on the chosen parameters, had a wavelength of roughly 20–50 $\mu$m. The stripes are only visible during relatively short intervals of each oscillation cycle. The space–time diagram in the middle row of Fig. 109 shows that the locations of stripes at subsequent oscillation cycles are shifted, so that a new stripe develops in the middle between two stripes seen in the previous cycle. Thus, the initial pattern is repeated after two periods of local oscillations. The periodic emergence of the spatial structure is rigidly correlated with the variations of CO partial pressure in the chamber.

Another type of pattern seen near the transition from turbulence to uniform oscillations is represented by oscillatory arrays of cells. Four snapshots of such a pattern, sampled within a single oscillation period, are displayed in the top row of Fig. 110. The cellular structure is visible only during short time intervals within each period. The appearance of cells at the transition from a predominantly oxygen covered to a mainly CO covered surface state is displayed in the second frame, and its recurrence during the transition back to an oxygen covered state is shown in the fourth frame in the top row of Fig. 110. The space–time diagram in the lower part of Fig. 110 shows the development of the cellular structure from standing waves upon a sudden decrease of the feedback intensity at time $t = 14 \, s$. The standing waves...
that were initially present are not seen in the space–time diagram because the cross-section is chosen parallel to the orientation of the stripes. Like standing waves, cellular structures usually occupied the entire imaged surface area. The local oscillations in this pattern were in harmonic resonance with the almost periodic variations of the global control signal. The observed arrays of cells were irregular. The irregularity could be explained as an indication of phase turbulence. Alternatively, such irregularity could also, at least partly, be caused by the presence of small structural surface defects.
When phase clusters develop, the catalytic surface splits into large regions belonging to either one of two different oscillatory states where frequencies are equal but phases are shifted by half a period. Usually, each of the two antiphase states occupies multiple spatial domains on the surface. An intrinsic spatial wavelength is missing in such a pattern. In the top and the second row of Fig. 111, snapshots of such a pattern are shown at time intervals of one oscillation period between subsequent frames within each row. Snapshots lying one upon the other are separated by half an oscillation period. Compared to the images shown in the top row, predominantly CO covered and oxygen covered regions have approximately interchanged in the second row. After a full period, the spatial distribution of the different domains is almost repeated. The temporal evolution of the pattern along a cross-section is shown in the space–time diagram in the middle of Fig. 111. It is seen that the shape of cluster domains undergoes small periodic variations. This breathing mode is rigidly correlated with the period of local oscillations in the pattern. On long time scales, the average locations of the interfaces between the antiphase domains are almost stationary or undergo only a weak drift. Finally, the curves at the bottom of Fig. 111 display the temporal variations of the PEEM intensity at two sample points located within the opposite phase domains. The positions of the sample points are indicated by arrows on the left of the space–time diagram. Each maximum of PEEM intensity in the two curves is followed by a second, smaller peak, which indicates period-two oscillations. The local oscillation period is about twice the period of uniform oscillations occurring at a slightly increased feedback intensity. By analyzing the time series of local oscillations at sample points located within the small domain interfaces, it is found that the difference between subsequent oscillation maxima is strongly decreased there. The difference nearly vanishes in the center of an interface so that oscillations are almost simple periodic and have an intermediate amplitude.

To analyze the observed patterns, a variant of the analytic signal approach [245,246] was applied. This method has allowed us to transform sequences of (typically 250) experimental PEEM images into time-dependent spatial
Fig. 112. (Color online.) PEEM images (top), distributions of phase (second row), amplitude (third row), and phase portraits (bottom) for several typical patterns observed in the CO oxidation experiments: (a) turbulence in absence of feedback, (b) intermittency with cascades of bubble-shaped structures, (c) intermittency with spiral fragments, (d) clusters, (e) cellular structures, and (f) standing waves. In PEEM images, blue color denotes surface areas predominantly covered by oxygen, and red regions are mainly CO covered. For phases and amplitudes, the yellow color stands for high, green for intermediate, and blue for low values. From [183].

Distributions of phase and amplitude variables. For the local PEEM intensity $I(x, t)$ at an observation point $x$, its Hilbert transform

$$
\tilde{I}(x, t) = \pi^{-1} \int_{-\infty}^{\infty} (t - t')^{-1} I(x, t') \, dt'
$$

was computed (this could be easily realized by determining the Fourier transform of $I$, shifting each complex Fourier coefficient by a phase of $\pi/2$, and performing the reverse Fourier transform). This was repeatedly done for all pixels $x$ in an $100 \times 100$ array covering the respective pattern. Using $I(x, t)$ and its Hilbert transform $\tilde{I}(x, t)$, a complex variable

$$
\zeta(x, t) = I(x, t) + i\tilde{I}(x, t),
$$

known as the analytic signal [245], was defined.

Afterwards, the time-dependent spatial distributions of phase $\phi(x, t)$ and amplitude $R(x, t)$ were determined from the analytic signal in the following way. The phase was directly computed as $\phi = \arg(z)$, thus representing the polar angle in the plane spanned by the variables $I$ and $\tilde{I}$. The amplitude was defined as $R = \rho/\rho_{\text{ref}}(\phi)$, where $\rho = |\zeta|$ is the standard definition of the amplitude modulus within the analytic signal approach. The normalization to $\rho_{\text{ref}}(\phi)$ was introduced to approximately compensate for deviations from harmonicity in the observed oscillations. To obtain $\rho_{\text{ref}}(\phi)$, the statistical distribution of $\zeta(x, t)$ for all $100 \times 100$ pixels and at all 250 time moments was plotted into the complex plane. The reference amplitude $\rho_{\text{ref}}(\phi)$ was then determined as the statistical average of $\rho = |\zeta|$ inside each of 200 equidistant narrow intervals of the polar angle $\phi$ (see Ref. [183]).

By applying this transformation separately to each of the different types of patterns, time-dependent spatial distributions of phase $\phi$ and amplitude $R$ in each pattern were constructed. In Fig. 112, snapshots of PEEM images (top row) for various observed patterns, and the corresponding snapshots of the phase (second row) and amplitude distributions (third row) are shown. Additionally, the bottom row of Fig. 112 shows a phase portrait of each pattern, obtained by displaying the amplitudes and phases for all resolving pixels in polar coordinates. The phase $\phi$ of a point is represented by the polar angle and the amplitude $R$ is the distance to the coordinate origin.
In the spiral-wave turbulence (Fig. 112a), fluctuations of amplitude and phase are strong, as indicated by the broadband structure in the phase portrait. For the intermittent turbulence (Figs. 112b, c), the amplitude and the phase are almost constant in the main part of the medium where uniform oscillations take place. The amplitude is significantly decreased in the bubble-shaped objects (Fig. 112b) and small localized spirals (Fig. 112c), so that they represent extended amplitude defects. Perpendicular to such objects, the oscillation phase varies rapidly in space. The phase portraits of intermittent turbulence show a spot corresponding to the uniform state of the medium and a tail corresponding to the amplitude defects. When cluster patterns (Fig. 112d) develop, the medium breaks into two-phase states seen as spots in the corresponding phase portrait. The amplitudes of the two oscillatory states differ, because local oscillations exhibit period-two behavior. The “bridge” in the phase portrait, connecting the two spots, corresponds to the interfaces between the cluster domains; note that the phase varies smoothly and the amplitude is not significantly reduced at the interface for such cluster patterns. In cellular structures (Fig. 112e), small phase modulations are observed, while the amplitude remains approximately constant. In standing waves (Fig. 112f), both the phase and the amplitude are periodically modulated.

A different feedback scheme, known as time-delay autosynchronization [234], has also been tested in the experiments [243]. To implement this scheme, the feedback signal was computed by taking the difference between the instantaneous integral image intensity $I(t)$ and the integral intensity $I(t - \tau)$ delayed by some time $\tau$. This feedback signal, multiplied by an additional intensity factor $\mu$, was used as the input signal for the electronically operated dosing system for the CO gas. The CO partial pressure in the reaction chamber was thus modulated as $p_{CO}(t) = p_{CO}^0 + \mu[I(t - \tau) - I(t)]$.

If uniform oscillations are stabilized and the oscillation period coincides with the delay time $\tau$, the feedback signal should vanish in this method. In the experiments [243], this was not observed. Instead, the behavior shown in Fig. 113 was found. When the delay time $\tau$ was varied, a jump occurred at $\tau = T$. The magnitude $M$ of the time-averaged control signal, defined as $M = \langle |I(t - \tau) - I(t)| \rangle$, decreased near $\tau = T$, but did not vanish there. Hence, the noninvasive global feedback stabilization of uniform oscillations was impossible in the experimental system. This result was also reproduced in numerical simulations [243] and explained by the intrinsic instability of the uniform state under a vanishing feedback intensity. The spatiotemporal patterns, observed in the experiments with time-delay autosynchronization, were similar to those described above in this section.

Action of periodic forcing on turbulence in the CO oxidation reaction was experimentally studied [244]. Spatially uniform periodic forcing was implemented via the gas phase by using a frequency generator to control the dosing rate of CO gas. In this way, the CO partial pressure in the reaction chamber could be periodically modulated with a nearly harmonic signal of amplitude $\gamma$ and frequency $\nu_f$, while its temporal average $p_0$ was kept constant. The effects of forcing were investigated in a frequency interval of $0.20 \text{Hz} \leq \nu_f \leq 0.67 \text{Hz}$. In the experiments, relatively large relative variation of CO partial pressure (about 10–20%) was usually needed to suppress turbulence and observe frequency-locked patterns. In this range of the forcing amplitude, the 1:1 entrainment was mostly observed. The behavior characteristic for the 2:1 resonance was however already found for $\nu_f \geq 0.5 \text{Hz}$. 

![Image](image.png)

Fig. 113. Period $T$ of uniform oscillations (black squares) and feedback magnitude $M$ (open circles) in dependence on the delay time $\tau$. From [243].
In a wide range of forcing parameters, upon stepwise increase of the forcing amplitude, a transition from developed turbulence to intermittent regimes was observed. Such intermittent regimes were characterized by repeated emergence and disappearance of localized bubble-like structures on the background of locked uniform oscillations. They were similar to the intermittent turbulence seen in the experiments with global delayed feedbacks [241,183,243].

Oscillatory cellular structures were often observed in the forcing experiments. Such arrays of cells were arising for the 1:1 resonance as small modulations of frequency-locked uniform oscillations, when the forcing amplitude was decreased. At higher forcing amplitudes, the cells are small and visible only during a short time interval of each oscillation cycle. With a decrease of the forcing amplitude, the cells get larger and they are seen within a longer time during each oscillation cycle. Starting from resonant uniform oscillations, the formation of cellular structures was also observed under an increase of the forcing frequency.

The four PEEM images in Fig. 114 are taken within a single forcing cycle. In the first frame, the cells emerge as small CO covered islands whereas the main part of the surface is predominantly covered by oxygen. The bright regions then extend (second frame), until they fill almost the entire imaged surface area (third frame). The cell array is again seen for a short instant during the transition back to the mainly oxygen covered state (fourth frame). From one forcing cycle to another, however, the cell positions change significantly, so that the cells form a complex, irregular pattern in the space–time diagram taken along a cross-section through the 2D images.

At higher forcing frequencies, \( \Omega_f \geq 0.5 \text{ Hz} \), additional resonant patterns arise due to 2:1 subharmonic entrainment of local oscillations. At the low-frequency edge of this resonance, irregular oscillatory stripes prevail. The sequence of PEEM images displayed in Fig. 115 illustrates the growth mechanism of such a structure. The pattern originates from small-amplitude uniform oscillations taking place around a mainly CO covered state. The predominantly oxygen covered state is only reached at certain locations on the surface where fragments of stripes first appear. During the further evolution, starting from such locations the structure grows stripe by stripe, until it occupies the entire imaged surface area. As time goes on, the number of dislocations in the pattern, i.e., the regions where individual stripes merge to form a fork-like structure, slowly decrease and a more regular, quasi-stationary configuration is established; see the
Fig. 115. (Color online.) Irregular oscillatory stripes under periodic forcing. Six snapshots of PEEM images showing the development of the pattern and the fully developed stripe structure (last snapshot). The forcing amplitude is $\gamma = 20.2\%$ and the frequency is $\nu_f = 0.50$ Hz. From [244].

Fig. 116. (Color online.) Irregular oscillatory stripes. Three subsequent PEEM images at a time interval of half the forcing period (top) and space–time digram of the evolution along the line AB (middle). Two curves at the bottom show temporal variation of the local PEEM intensity at two different points indicated by arrows. From [232].

sixth frame in Fig. 115. Due to diffusion anisotropy of the Pt(110) single crystal surface, the stripes are then mainly oriented along the surface direction of fast CO diffusion.

Fig. 116 displays a space–time diagram of the fully developed stripe pattern taken along a cross-section perpendicular to the orientation of stripes. The dark stripes are seen in this diagram only during relatively short intervals of each oscillation cycle. After each forcing period, the locations of the stripes are shifted, and new stripes have appeared in
Fig. 117. Phase clusters under periodic forcing. (a) Three snapshots of PEEM images, separated by time intervals of one forcing period between subsequent images. (b) Space–time diagram taken along the line AB and the corresponding temporal variation of the CO partial pressure. (c) Phase pattern (top left), amplitude pattern (top right), phase portrait (bottom left), and phase histogram (bottom right) for the phase clusters demodulated at the frequency $\nu_1/2$. The forcing parameters are $\gamma = 16.4\%$ and $\nu_1 = 0.67$ Hz. From [244].

the middle between those seen at the previous cycle. Thus, the initial pattern is repeated every two forcing cycles. Local oscillations within the central regions of alternating stripes hence have the same shape and frequency ($\nu = \nu_1/2$), but are shifted in time by one forcing period. Examining the phase and amplitude properties of the oscillatory stripes, strong similarity to the labyrinthine patterns near the 2:1 resonance in the forced complex Ginzburg–Landau equation [188] and in the periodically forced Belousov–Zhabotinsky reaction [247] was found. The more ordered geometry of the stripes was probably explained by the diffusion anisotropy of the metal surface, favoring a particular stripe orientation.

At still higher forcing frequencies than needed for the observation of oscillatory stripes, cluster patterns are induced by the periodic forcing. After the formation of phase clusters, the surface splits into relatively large domains belonging to one of two different dynamical states (see Fig. 117a). After each period of the driving force, predominantly oxygen and CO covered regions interchange with respect to the previous PEEM image, so that the pattern almost exactly repeats after two forcing cycles. Thus, the local oscillations within the different domains are also entrained at half the frequency of the driving force and oscillate in anti-phase, as for the oscillatory stripes. However, an intrinsic wavelength is absent in the case of phase clusters. The oscillation amplitude is strongly reduced in the interfaces separating different phase domains. The temporal evolution of phase clusters is illustrated in Fig. 117b. Examining the space–time diagram, one finds that the interfaces between domains of opposite phase are stationary and that the spatial distribution of domains is stable over several forcing periods.

The results of a demodulation at the subharmonic mode with frequency $\nu_1/2$ are displayed in Fig. 104c. From left to right and top to bottom, the frames show the resulting phase pattern, amplitude pattern, phase portrait, and histogram of phases. Note that the oscillation amplitude is strongly reduced in the domain interfaces (black lines in the top right frame in Fig. 104c), and that it is the same within the domains of opposite phase. The phase portrait shows two spots of accumulating points, corresponding to the pixels located within the anti-phase domains; the scattering of points is due to experimental noise. The points that connect these spots correspond to pixels located within the phase fronts. As seen in the phase histogram, the two-phase states are not evenly weighted. The size ratio between the two peaks was different each time phase clusters were observed. Thus, the boundaries between such phase clusters represent immobile $\pi$-fronts (Ising walls).

Both cluster patterns and oscillatory stripes transformed into resonant uniform oscillations upon a sufficiently strong increase of the forcing amplitude.
5. Conclusions

We have presented an overview of experimental and theoretical studies of control of spatiotemporal dynamics in chemical systems. Many different approaches for controlling such behavior have been pursued. Some, such as those based on feedback techniques, take advantage of the inherent sensitivity to perturbations displayed by nonlinear dynamical systems, and very small perturbations are typically sufficient to significantly alter the behavior or stabilize a particular desired state. Global feedback, for example, gives rise to a rich variety of spatiotemporal dynamics, including behavior not observed in autonomous systems. Local feedback, such as variations of excitability gradients, allows directional control of propagating waves to yield virtually any desired pattern. Periodic forcing provides another means of manipulating spatiotemporal dynamics as well as producing completely new types of dynamical behavior. Spatiotemporal turbulence, for example, can be suppressed under some conditions, while it can be promoted under other conditions. Other methods of influencing spatiotemporal behavior include imposing medium heterogeneities or dynamical noise. Surprisingly, the application of noise may give rise to coherent structures that would not exist in comparable noise-free media. Medium heterogeneities also result in behavior, such as pinned spiral waves, that otherwise would not exist. The interaction of a spatiotemporal dynamics with particular geometric boundaries may generate new types of behavior, such as resonance patterns, as well as allow deliberately designed logic gates based on the characteristics of reaction–diffusion waves. Dynamical behavior arising from differences in diffusivities has long been known, e.g., Turing patterns; however, many other types of pattern formation are possible when diffusivities are manipulated over wide ranges, such as in a microemulsion BZ system.

We have described the control of excitable and oscillatory spatiotemporal dynamics using the BZ and Pt–CO systems as prototypical examples. These systems offer extraordinarily rich spatiotemporal dynamics, and they are particularly amenable to a wide variety of techniques for controlling their dynamics. While we have drawn heavily on studies from our own laboratories to illustrate control methods and techniques, there are many other studies of these and other systems that offer similar insights. In particular, we note that major progress has been made in manipulating and controlling physiological systems. Controlling the dynamics of biological systems, such as preparations of heart tissue, is actively pursued both experimentally and theoretically, as applications are anticipated that will be beneficial to human health. Control of spatiotemporal behavior also has important applications in other areas, such as in population dynamics and the emerging area of dynamical networks.

Controlling spatiotemporal dynamics provides an avenue for exploring new dynamical behavior as well as generating particular desired behaviors. In explorations of spatiotemporal dynamics, control methods offer flexibility that is not easily attained in autonomous systems. Chemical systems are particularly well defined for studies of controlling spatiotemporal dynamics, and they offer a means for characterizing behavior that is relevant to more complex biological systems.

Acknowledgments

We are grateful to G. Ertl for stimulating discussions and wish to thank our friends and collaborators H.H. Rotermund, M. Bertram and V. Zykov for their valuable contributions. During the work on this review, one of us (K.S.) was financially supported by the Alexander von Humbold Foundation (Germany) through a Humboldt research award. A.S. M. acknowledges financial support from the German Science Agency (DFG) in the framework of the Cooperative Research Programme “Complex Nonlinear Processes” and from the European Science Foundation through the Marie Curie Research and Training Network “Universal Principles of Pattern Formation”. K.S. acknowledges financial support from the US National Science Foundation (CHE-0415392) and the W.M. Keck Foundation.

References