Pattern formation in reaction-diffusion and reaction-diffusion-convection systems

Thesis of PhD dissertation

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1. Introduction

Transport of chemical species by either *diffusion* or *convection* (quite often by their combination as well), plays key role in the formation and dynamics of chemical patterns (fronts, waves, spots, etc.) in unstirred reacting systems. In this thesis, the results of my PhD research are summarised by these two keywords.

In our experiments with *reaction-diffusion* systems, we studied the dynamics of circular waves and wave train travelling on membrane surface or in thin layer of solution:

- We have proved that the dispersion relation (velocity *vs.* period) of spiral waves in BZ media is valid for circular waves as well. The effect of temperature has been also studied by solution phase experiments. Based on the results of numerical modelling, we have derived a generalised formula for the dispersion relation.
- A new method for initiation of chemical waves in the bathoferroin-catalysed BZ system has been found. It is based on the following observation: on illumination with a He–Ne laser a photoreduction process takes place that changes the concentration ratio of the oxidised and reduced forms of the catalyst immobilised on a polysulfone membrane. Since it locally changes the excitability of the media, the illuminated area may act (after illumination is turned off) as an excitation center for a new chemical wave.

Concerning *reaction-diffusion-convection* systems, we studied (also using the BZ system) two phenomena both experimentally and numerically:

- The first phenomenon is "chemical instability" induced by differential flow of activator and inhibitor species (DIFICI). The simplest experimental arrangement involves immobilisation of the catalyst, while the other reactants of the BZ media are flown. Dynamics of propagating waves formed under such conditions have been studied both experimentally and numerically.
- The other phenomenon is the "flow-distributed oscillations" (FDO), when – unlike the previous case – all species flow with the same velocity. To observe pattern formation, the same reacting system should exhibit oscillations in a well-stirred batch reactor. In this case, the instability is induced also by the flow of reactants, however, waves with different (sometimes very complex) dynamics are formed.

2. Results

2.1. Reaction-diffusion systems

2.2.1. Universal dispersion relation

I. *We proved that the universal dispersion relation of spiral waves is valid for circular waves as well* [5].

By studying the velocity of spiral waves (c) as a function of rotation period (T), Flesselles, Belmonte, and Gáspár showed that all experimental data – including those measured in ferroin-catalysed BZ systems – known from literature fit well on the theoretical curve calculated by the dispersion relation derived by them. The dimensionless equation of the universal dispersion relation is the following:

$$M = \beta x \tanh^2 x, \tag{1}$$

where $M = p^2/DT$ is the so called spiral-diffusion number (p is the wavelength, D is the characteristic diffusion coefficient of the medium), $\beta = c_\infty^2 T_s/D$ is a dimensionless constant characterising the medium (c_∞ is the propagation velocity of a single wave, T_s is the period of spontaneously formed spiral wave), and $x = T/T_s$ is the dimensionless period. Based on experiments in open membrane and batch reactors, we have proved that the above relation is valid for circular waves as well. All dimensionless data originating from measurements at different concentrations of bromate ion and sulphuric acid fit well on the dispersion curve defined by equation (1).

We also studied the "temperature-dependence" of the dispersion relation. Experiments at three different temperature values (20, 25 and 30 °C) indicate that temperature has no effect on the validity of the relation.

II. *Our finding that the dimensionless dispersion relation is valid for different excitable media indicates the universality of the law* [5].

Analysing dispersion data of corrosion waves on an iron wire immersed in nitric acid and of spreading depression waves in chicken retina, we found that the dimensionless dispersion relation (1) can be applied to characterise the dynamics of different type of excitable media, which indicates the universality of the law.

III. *Based on the results of numerical modelling we derived a generalised dispersion relation and proved that the universal law is a limit case of it* [5].

Numerical modelling has been carried out by the so-called Barkley model; a simple scheme for excitable systems in general. Five dispersion curves have been calculated by varying those model parameters that modify the excitability of the system. However, the calculated dispersion data did not fit to the universal curve corresponding to equation (1), which indicated that the simplifications applied to derive the simple relation are not valid to the general case. The following generalised dispersion relation has been derived:

$$m = \frac{M(x)}{M(1)} = x \frac{\tanh^2(1)\{1-[1-4\gamma\tanh^2 x]^{1/2}\}^2}{\tanh^2 x\,\{1-[1-4\gamma\tanh^2(1)]^{1/2}\}^2}\,, \qquad (2)$$

where m is the reduced spiral-diffusion number, and γ is a fitting parameter. Its value has been found to vary from system to system, that is, the dispersion relation cannot be characterised with a unique curve but only with a series of curves defined by equation (2). We have proved that if $\gamma \to 0$, the generalised dispersion relation (2) reduces to the simple relation equation (1).

2.1.2. A new method for initiation of chemical waves

IV. *We demonstrated that chemical waves can be initiated in the bathoferroin-catalysed BZ reaction by using a red laser* [1].

Polysulfone membrane loaded with bathoferroin catalyst was illuminated with red light from a He–Ne laser (20 mW, λ = 632.8 nm) for a few seconds. Depending on the experimental conditions, the laser light – focused on a small area of the membrane – initiated a circular wave or a pair of counter-rotating spirals.

On membranes loaded with small amount of bathoferroin, circular waves are formed due to illumination. Similar response can be observed when illumination is applied to a small region far behind an oxidation front. However, when the illumination is applied much closer to the front, a pair of counter-rotating spirals develops.

On membranes loaded with much larger amount of bathoferroin, no excitation center could be generated even by illumination far away from the front. Illumination close enough to the front resulted in a pair of counter-rotating spirals in this case as well.

V. *Formation of an excitation center at the area of illumination has been explained by the occurrence of a local photoreduction process* [1].

Since a reduction process at the illuminated area always precedes the appearance of the oxidation wave, we have extended the Oregonator model for the BZ system with the following photochemical reaction:

$$M_{ox} + h\nu \rightarrow M_{red}, \tag{3}$$

in which process the concentration of the oxidised form of the catalyst decreases. By studying the dynamics of the following two-variable system of dimensionless differential equations:

$$\begin{aligned} \varepsilon \frac{dx}{dt} &= x(1-x) - fz\frac{(x-q)}{(x+q)}, \\ \frac{dz}{dt} &= x - (1+\kappa(\phi))z, \end{aligned} \tag{4}$$

derived from the model, we showed that illumination greatly affects the excitation threshold. In equation (4), κ (its value depends on light intensity φ) is the dimensionless rate constant of reaction (3), x and z are the dimensionless concentrations of $HBrO_2$ and M_{ox}, respectively, while ε, f, and q are model dependent parameters. Analysing the model, we concluded that the simultaneously occurring local reduction of the catalyst and decrease in the concentration of Br^- – an inhibitor species – play the key roles in the formation of an excitation center.

2.2. Reaction-diffusion-convection systems

2.2.1. Differential flow induced chemical instability (DIFICI)

VI. *We found that the wave velocity and the wavelength are linearly dependent on the concentration of bromate ion* [2].

In DIFICI experiments with BZ media of three different concentrations of bromate ion, the moving waves have been studied at different flow velocities (c_f). Linear relationship has been found between the wave velocity (c_w) and the actual flow velocity of the medium. On the other hand, the value of c_w is only slightly affected by changing the concentration of bromate ion.

Wavelength (λ) has been found to increase with increasing flow velocity, while it decreases with increasing concentration of bromate ion. The gradient (m) of λ *vs.* c_f plots is proportional to the concentration of bromate ion as follows: $m \sim [BrO_3^-]_o^{-2.4(\pm 0.1)}$.

VII. *Stability analysis of an extended Oregonator model proved that appearance of moving waves is related to the convective instability of the system* [2].

The two-variable system of dimensionless differential equations derived from the Oregonator model has been extended with diffusion and convection terms representing, respectively, the diffusion and flow of $HBrO_2$ as follows:

$$\varepsilon\frac{\partial u}{\partial t}=\frac{\partial^2 u}{\partial x^2}-\phi\frac{\partial u}{\partial x}+u(1-u)-\frac{fw(u-q)}{(u+q)},$$
$$\frac{\partial w}{\partial t}=u-w. \qquad (5)$$

where $0 < x < \infty$ and $t > 0$ are the dimensionless space and time variables, u and w are the dimensionless concentrations of $HBrO_2$ and M_{ox}, respectively, and ϕ is the dimensionless flow velocity. Results of numerical modelling (Figure 1.) indicated unambiguously that the formation of DIFICI waves is related to the convective instability of the system: the waves appearing on the effect of an initial perturbation will travel trough the tubular reactor in the direction of the flow. Finally, the system will return to its original resting state. The results of modelling are in good qualitative agreement with the experimental observations.

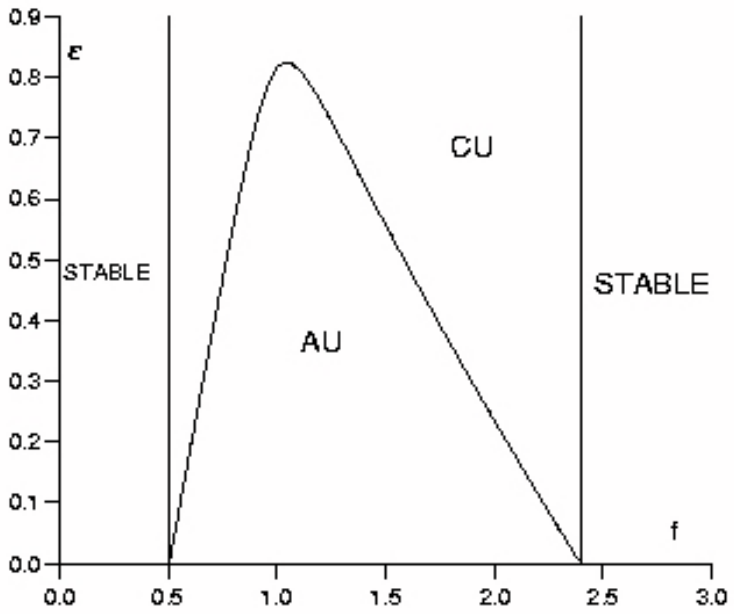


Figure 1. Results of stability analysis based on equations (5): convective instability (CU) is possible only in a limited region of ε–f parameter plane. The width of this region increases by increasing the value of ε (which means lowering the acidity of the medium). In the region of absolute instability (AU), the model results in oscillations in closed systems and gives a continuous propagating wave train in the flow system. Outside these two regions the system is stable (STABLE) [2].

2.2.2. Flow distributed oscillation (FDO)

VIII. *By stability analysis of a reaction-diffusion-convection model of the BZ reaction, analytical formulas have been derived for the critical conditions for the formation of FDO patterns* [3].

The two-variable system of dimensionless differential equations derived from the Oregonator model has been extended with diffusion and convection terms representing, respectively, the diffusion and flow (ϕ_P) of both $HBrO_2$ (u) and M_{ox} (v) as follows:

$$\begin{aligned}\frac{\partial u}{\partial t} &= \frac{\partial^2 u}{\partial x^2} - \phi_P \frac{\partial u}{\partial x} + \frac{1}{\varepsilon}\left\{u(1-u) - f\frac{v(u-q)}{u+q}\right\},\\ \frac{\partial v}{\partial t} &= \frac{\partial^2 v}{\partial x^2} - \phi_P \frac{\partial v}{\partial x} + u - v.\end{aligned} \tag{6}$$

By stability analysis of the model, we have determined the different regions of convective and absolute instability, stationary patterns and transient waves in the $\phi_P - \varepsilon$ parameter plane (Figure 2.).

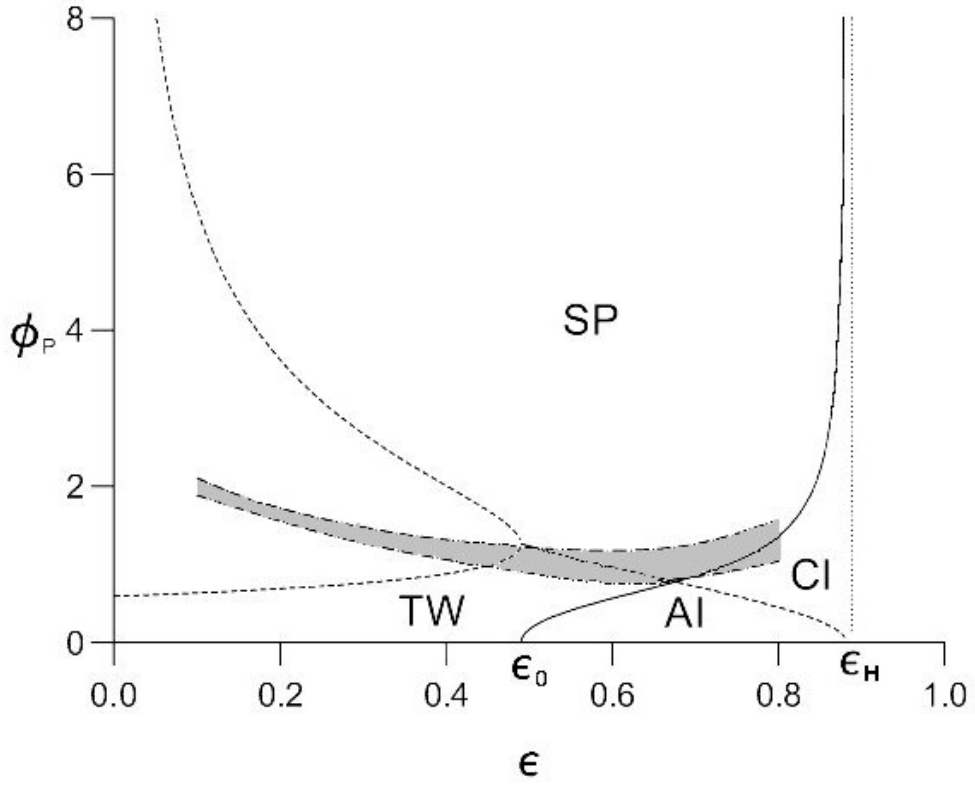


Figure 2. Results of stability analysis based on equation (6): regions of absolute instability (AI), convective instability (CI), stationary patterns (SP) and transient waves (TW) in the $\phi_P - \varepsilon$ parameter plane. Shaded area indicates region for complex dynamical behaviour.

The critical flow velocity for the transition between regions of AI and CI is given by:

$$\phi_{AC} = \frac{\sqrt{2(\alpha - \varepsilon)}}{\varepsilon}, \tag{7}$$

while the critical flow velocity for the transition between regions of SP and TW is as follows:

$$\phi_{P,cr} = \sqrt{\frac{4\varepsilon\beta - (\alpha + \varepsilon)^2}{2(\alpha - \varepsilon)\varepsilon}}. \tag{8}$$

In equations (7) and (8), α and β are model dependent dimensionless parameters.

IX. *Existence of stationary and travelling wavefronts has been experimentally verified in BZ systems, in which the activator and inhibitor species flow with the same velocity* [4].

The experimental apparatus comprised a continuously-fed well-stirred reactor (CSTR), of which the residence time was always such that the system was operated in a stable steady state. The outflow from the CSTR formed the inflow to a packed-bed reactor: a vertically-mounted cylindrical glass tube packed with spherical glass beads. Patterns with different dynamics are formed in this tube, if the BZ system of the same composition shows oscillations in a well-stirred batch reactor.

X. *We predicted numerically* [3] *then verified experimentally* [4] *that the wavelength of stationary patterns increases linearly with the flow velocity, and it shows an inverse square root dependence on the concentrations of BrO_3^- and H^+.*

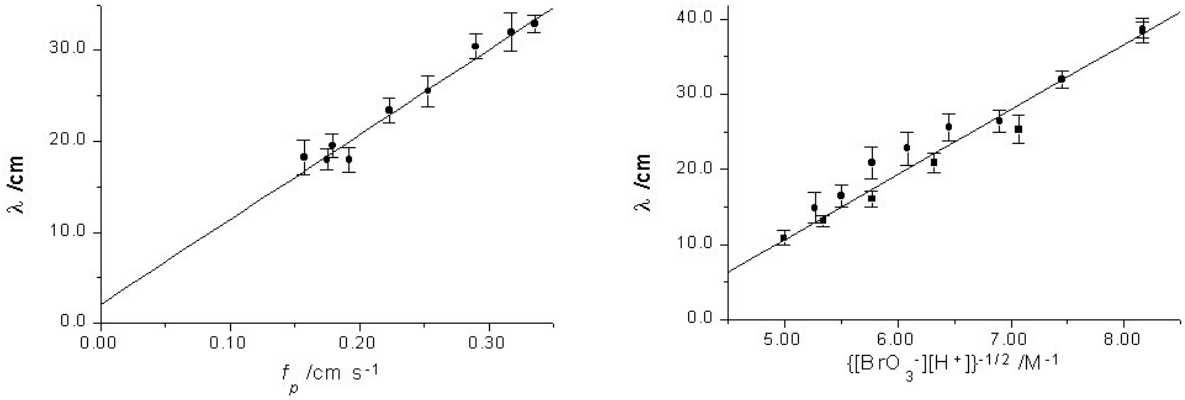


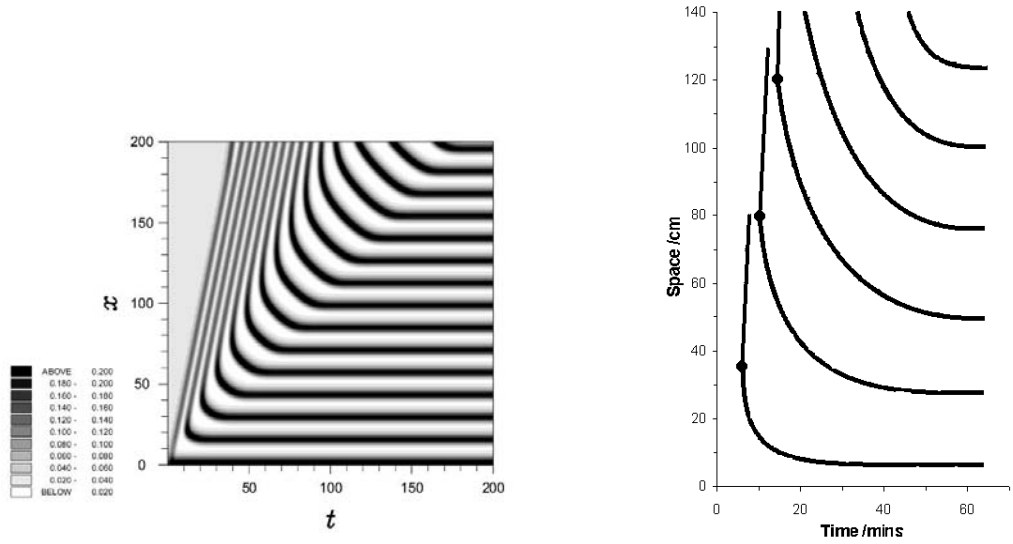
Figure 3.

(a) Dependence of wavelength λ of FDO-patterns on flow velocity f_p. $[BrO_3^-]_o$ = 0.20 mol dm^{-3}, $[H^+]_o$ = 0.15 mol dm^{-3}.

b) Dependence of wavelength λ of FDO–patterns at flow velocity f_p = 0.17 cm s^{-1} on the inflow concentrations of BrO_3^- (■) at $[H^+]_o$ = 0.15 mol dm^{-3} and $[BrO_3^-]_o$ = 0.10 – 0.24 mol dm^{-3}; and on the inflow concentration of H^+ (●) at $[BrO_3^-]_o$ = 0.20 mol dm^{-3} and $[H^+]_o$ = 0.075 – 0.20 mol dm^{-3}.

XI. *We have predicted numerically then verified experimentally that the stationary FDO patterns develop through a wave-splitting mechanism* [4].

At given region of the parameter plane (Figure 2), it has been found that a point source of excitation (a pacemaker) appears at some distance along the tube, which then grows into an oxidation band that later splits into two waves. One of the waves travels in the direction of the flow, while the other one travels against of it. This wave slows down, and, eventually, it stops creating a new band of the FDO-pattern.



(a) (b)

Figure 4. Numerical (a) and experimental (b) space–time plots showing development of stationary FDO patterns through a wave-splitting mechanism [4]. Location of pacemaker centers in figure (b) is indicated with solid circle.

We have proved that when a stationary pattern (established by a wave-splitting procedure) is disturbed by change in the flow velocity, the system adjusts itself to the new condition but without a wave-splitting procedure.

XII. *Complex dynamics have been observed in numerical modelling and experiments as well at parameter values close to the bifurcation curves* [4].

Transient dynamics of the development of FDO patterns have been investigated at ε and ϕ_P values close to the bifurcation curves separating regions of different patterns; specifically, close to the curves representing the transition between transient waves (TW) and stationary patterns (SP) and between convective instability (CI) and stationary patterns (Figure 2). Complex dynamics have been observed: some of the subsequent lower waves collapse failing to establish a new band of the stationary pattern.

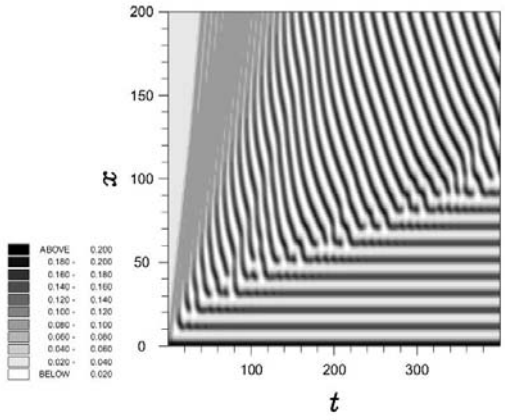


Figure 5. Ultimately, the simulation yields a regular stationary pattern while several transient waves die [4].

Similar complex behaviour has been observed in the experiments at low values of flow velocity.

3. Publications

[1] **R. Tóth**, V. Gáspár, A. Belmonte, M. C. O'Connell, A. Taylor, S. K. Scott: Wave initiation in the ferroin-catalysed Belousov-Zhabotinsky reaction with visible light, *Phys. Chem. Chem. Phys*., **2000**, 2, 413-416.

[2] **R. Tóth**, A. Papp, V. Gáspár, J. H. Merkin, S. K. Scott, A. F. Taylor: Flow-driven instabilities in the Belousov-Zhabotinsky reaction: Modelling and experiments, *Phys. Chem. Chem. Phys*., **2001**, 3, 957-964.

[3] J. R. Bamforth, J. H. Merkin, S. K. Scott, **R. Tóth**, V. Gáspár: Flow-distributed oscillation patterns in the Oregonator model, *Phys. Chem. Chem. Phys*., **2001**, 3, 1435-1438.

[4] J. R. Bamforth, **R. Tóth**, V. Gáspár, S. K. Scott: Scaling and dynamics of „flow distributed oscillation patterns" in the Belousov-Zhabotinsky reaction, *Phys. Chem. Chem. Phys*., **2002,** 4, 1299-1306.

[5] **R. Tóth**, V. Gáspár, S. C. Müller, S. K. Scott: Dispersion relation of excitable waves in chemical and biological media, (manuscript).

4. Presentations and posters

1. J.-M. Flesselles, A. Belmonte, **R. Tóth**, V. Gáspár: On the dispersion relation for waves in the Belousov-Zhabotinsky reaction, CHISA'98, 13th International Congress of Chemical and Process Engineering, Praha, Czech Republic, 1998 (lecture).

2. V. Gáspár, **R. Tóth**, A. Belmonte, J-M. Flesselles: Universal Dispersion Relation of Chemical Waves in Excitable Media, 218th ACS National Meeting, New Orleans, LA, USA, 1999 (lecture).

3. **Tóth, R**.; Gáspár, V.: Kémiai hullámok gerjesztése a ferroin-katalizálta BZ-reakcióban látható fény segítségével, Reakciókinetikai és Fotokémiai Munkabizottság, Balatonalmádi, 1999 (lecture).

4. **R. Tóth**, V. Gáspár, A. Belmonte, M. C. O'Connell, A. Taylor, S. K. Scott: Wave initiation in the ferroin-catalysed BZ reaction with visible light, Gordon Research Conference on 'Oscillations and Dynamic Instabilities in Chemical Systems', Bristol, RI, USA, 2000 (poster).

5. **R. Tóth**, A. Papp, V. Gáspár, J. R. Bamforth, A.Taylor, J. H. Merkin, S. K. Scott: Flow driven and flow-distributed oscillations in the Belousov-Zhabotinsky reaction, European Science Foundation, Project REACTOR Workshop, Palermo, Italy, 2001 (poster).

6. J. R. Bamforth, S. K. Scott, **R. Tóth**, V. Gáspár: Dynamic evolution of flow distributed oscillations: the movie, European Science Foundation, Project REACTOR Workshop, Leeds, UK, 2001 (poster).

7. J. R. Bamforth, S. K. Scott, **R. Tóth**, V. Gáspár: Developments of FDO Patterns in the BZ Reaction, European Science Foundation (ESF) REACTOR Program, Workshop 2, Leeds, UK, 2001 (lecture).

8. J. R. Bamforth, S. K. Scott, **R. Tóth**, V. Gáspár: Dynamic evolution of flow distributed oscillations: the movie, Faraday Discussion 120, Nonlinear Chemical Kinetics: Complex Dynamics and Spatiotemporal Patterns, Manchester, UK, 2001 (poster).