The effect of reaction vessel parameters on convection in autocatalytic fronts

Thesis of the PhD dissertation

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2009

1 Introduction

Convection is one of the most common driving forces in the world, since it often occurs in our surrounding, like tectonic motions, ocean or atmospheric flows, or the transport of pollution in the oceans or in the ground. Fluid motion can be influenced by the change in density, viscosity, and surface tension. From these three factors I have been interested in the simplest one: I have studied the convective instability arising from density change experimentally in a simple autocatalytic chemical reaction.

The study of pattern formation by convection in autocatalytic reactions has gained considerable interest and importance in the last three decades. In the beginning the velocities of chemical waves were investigated experimentally, then cellular pattern formation was studied in thin tubes and capillaries. The evolution of computer technics has led to the improvement of existing theoretical models. In numerical simulations Anne De Wit's work was remarkable who investigated the convective instability in autocatalytic reactions using a realistic reaction scheme. The experimental confirmation of theoretical models was, however, missing. Our goal was to study the density fingering experimentally and to obtain quantities comparable with the theoretical descriptions.

The convective instability was investigated in the autocatalytic reaction between chlorite and tetrathionate ions, where hydrogen ion is the autocatalyst. The reactive interface develops through the reaction which keeps a constant density change between the two sides of the interface where the density of the products is greater than that of the reactants resulting in density fingering in this system. The isothermal density change due to the change in chemical composition is hence positive. The reaction is highly exothermic therefore the density change generated by the heat evolution near the front is negative. The two effects are opposite, therefore both simple and multicomponent convection can appear depending on the experimental conditions. In simple convection the upward propagating fronts remain planar and the downward traveling fronts become unstable and cellular structures develop. In the case of multicomponent convection, however the density change due to the exothermicity of the reaction influences the pattern formation in both directions.

The ultimate goal of our group is to investigate and understand convection in porous media for which we used the "from simple to complex" approach. In this PhD dissertation I studied density fingering in regular reaction vessels with constant gapwidth as a continuation of earlier works. I then introduced periodic spatial heterogeneities in the inner side of the walls as the first approximation towards porous media. I systematically varied the parameters of the reaction vessel like thickness, spatial periodicity or depth of the grooves and investigated how the pattern formation was altered.

2 Experimental

The pattern formation was studied in narrow and wide, so called Hele-Shaw cells which are built up of two parallel Plexiglas walls and a thin spacer. At first I carried out the experiments using regular reaction vessels, and investigated how thermal effects alter the pattern formation. To eliminate the thermal density change, the system was cooled down to 3 °C with two cooling jackets which were fixed on the outside of the Hele-Shaw cell. The length of the cell was doubled and its width was varied between 1–4 cm in order to generate stable single-cell structures. As a first step towards investigating porous medium, we introduced spatial periodic heterogeneities in the inner side of the walls. The modulation were introduced not only in parallel to the direction of front propagation (see in Fig.1(a)), but also perpendicular to that, in the form of round depressions, as shown in Fig.1(b). Planar fronts were then initiated electrochemically by applying 2–5 V potential difference between two thin parallel Pt-wires. The traveling fronts were monitored by a monochrome CCD camera connected to a standard imaging system.

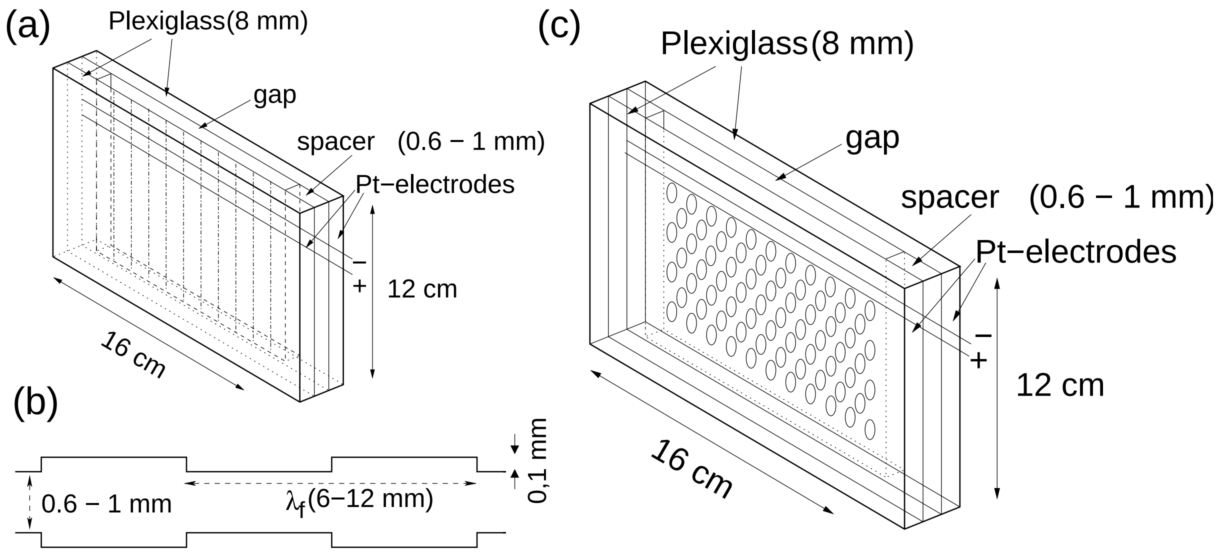

Figure 1: Scheme of the Hele-Shaw reaction vessel with modulation parallel to the direction of front propagation (a), and the top view of a cell segment (b). Scheme of the bimodulated Hele-Shaw cell (c).

3 Methods of evaluation

Both the initial and the long time behavior have been studied experimentally and the evolving structures have been characterized. To quantitatively describe the initial front evolution, we used dispersion curves where the growth rates were plotted as a function of the corresponding wave number. The front profiles were determined from consecutive images of the traveling front. We then calculated the Fourier-modes of the profiles with fast Fourier transformation and from the temporal change of the Fourier-amplitudes the appropriate growth rate was determined. The dispersion curve was characterized by two parameters: the wave number and the growth rate of the most unstable mode corresponding to the fastest growing mode. For the characterization of the long time behavior we used the mixing length and the temporal average profile. The former was defined as the standard deviation of the mean front which is a better definition since it considers all points of the front. The latter was constructed by averaging the front profiles obtained by subtracting the average front position from each point. In the spatially modulated vessels we found periodical evolution of the fingers. For characterization of this periodical formation the spatial autocorrelation function was used.

4 New scientific results

I. *Thermal effects stabilize the low wave number modes during the evolution of the initial patterns.* [1]

   In 1 mm thick reaction vessels, where the three-dimensional flow is negligible, we find that at room temperature the upward propagating front (in Fig.2 dashed-dotted line) is slightly unstable at low wavenumbers and the downward propagating front (dotted line) has values close to zero in the same interval. When the system has been cooled down to 3 °C (solid and dashed line), where the thermal density change is eliminated, the stabilization at low wavenumbers is not observed. This stabilization is hence due to the thermal effect only.

II. *At the long time evolution the thermal effects are dominant in stabilizing the patterns with constant shape and velocity.* [1]

   On investigating the long time evolution of the patterns, we have observed the generation of stable single cells in 4 cm wide vessel only by applying greater reactant concentration and increasing the thickness of the container, in which case considerable temperature gradient builds up due to the exothermicity of the reaction. However the third dimensional effect may come into play as the container thickness is significantly greater. When the experiments are carried out at 3 °C a different structure developed, fingers exhibited continuous splitting. Thus, the thermal effects lead to the stabilization of the stable single-cell pattern.

III. *The geometric parameter of the stable single cell is proportional to the width of the container, and independent of the orientation of the vessel in the* θ *= 0-60° range.* [3]

   Stable single fingers with constant velocity and shape evolve up to 2.5 cm width in a thin layer of hydrodynamically unstable reactive solutions. When the temporal average front profiles scale with the width of the container, the lines fall on the same curve in the central region, away from the boundaries, which confirms that the geometric parameter of the

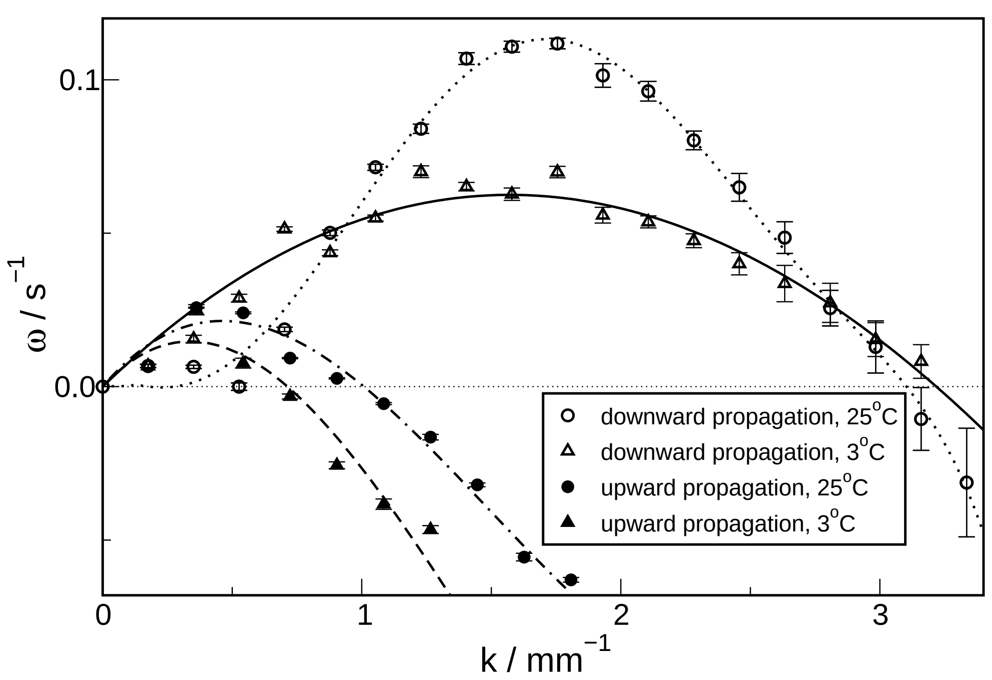

Figure 2: Dispersion curves for upward and downward propagating fronts at 3 °C and at 25 °C with 1 mm gapwidth and $[K_2S_4O_6]_0$ = 6,25 mM, $[NaClO_2]_0$ = 25 mM és $[NaOH]_0$ = 20 mM.

front is proportional to the width of the container as predicted theoretically. The stable single finger is found to be independent of the orientation of the vessel for θ = 0-60° range of tilt angles with respect to the vertical.

IV. *In Hele-Shaw cells with parallel periodic grooves three types of cellular structures controlled by the spatial modulation have been observed depending on the parameters of the reaction vessel and on the chemical composition.* [2]

The systematic variation of the parameters of the reaction vessel like thickness, spatial periodicity of the grooves and the concentration of sodium hydroxide yields three different types of patterns, as shown in Fig.3(a-c). In the first case (see in Fig.3(a)) the leading segments of the cells are in the thinner regions and the cusps are in the thicker ones. In the middle image (Fig.3(b)) the cells split further and the cusps appear in each segment. The increase in the wavelength of the spatial modulation yields an interesting pattern, as shown in Fig.3(c), where there is no cell formation in the thinner regimes and a pair of cells is observed in the thicker ones. In all cases the cellular structures are periodic. To determine the appropriate periodicities, spatial autocorrelation functions have been used. The measured wavelength corresponds to the wavelength of the introduced heterogeneity. Consequently the pattern formation is driven by the vertical grooves in the cell.

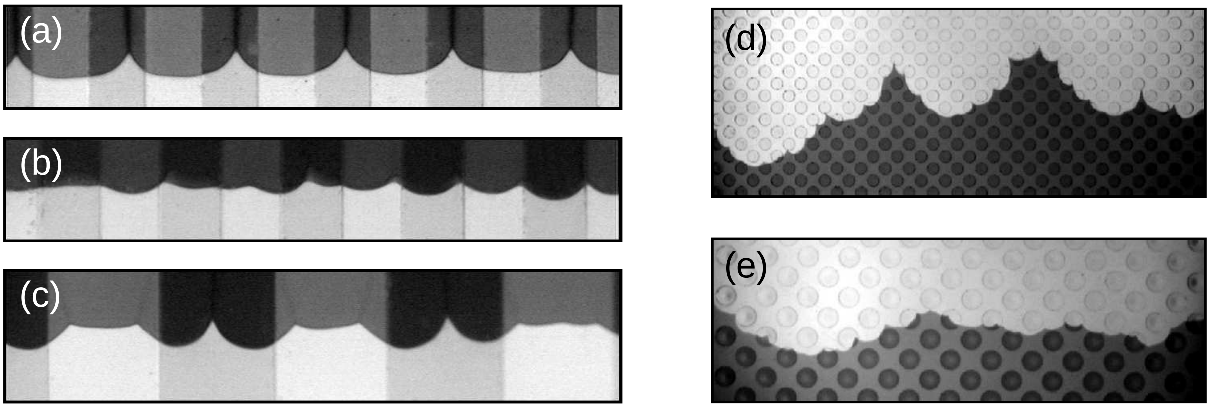

Figure 3: Images of fronts propagating downward in heterogeneous Hele-Shaw cells with periodicity of λ = 6 mm (a,b), λ = 12 mm (c), and in bimodulated cells with periodicity of λ = 6 mm (d), λ = 12 mm (e).

V. *Resonance amplification is exhibited in the cell with vertical grooves under appropriate conditions.* [2]

   If the wavelength of the spatial heterogeneity introduced perpendicular to the front propagation is approximately equal to that of the fastest growing mode in the regular reaction vessel, resonance amplification, the result of which is shown in the Fig.3(a), can be exhibited. The wavelength determined by the autocorrelation function is similar to the wavelength of the grooves, thus the inhomogeneity drives the pattern formation.

VI. *The bimodulation of the cell does not affect the initial pattern formation, however the long time evolution is driven by it, resulting in an enhanced tip splitting in the structure.* [4]

   The initial evolution of the cellular structure using bimodulated cells is similar to the formation under regular conditions while the modulation drives the pattern formation for cells with vertical periodic grooves. During the long time behavior the cells start splitting which will be dominant, as shown in Fig.3(d,e) for the spatially bimodulated case. This results in higher cell number for the spatially bimodulated case compared to the regular and the horizontally modulated conditions where the cell number settles to a lower value.

5 Publications related to the dissertation

1. T. Tóth, D. Horváth, Á. Tóth: Thermal effects in the density fingering of the chlorite - tetrathionate reaction, Chem. Phys. Lett. **442**, 289 (2007). (IF=2.207)
2. T. Tóth, D. Horváth, Á. Tóth: Density fingering in spatially modulated Hele-Shaw cells, J. Chem. Phys. **127**, 234506 (2007). (IF=3.044)
3. T. Tóth, D. Horváth, Á. Tóth: Scaling law of stable single cells in density fingering of chemical fronts J. Chem. Phys. **128**, 144509 (2008). (IF=3.044)
4. T. Tóth, D. Horváth, Á. Tóth: Density fingering in spatially bimodulated Hele-Shaw cells. (submitted for publication Chem. Phys. Lett.)

6 Publications not related to the dissertation

1. G. Schuszter, T. Tóth, D. Horváth, Á. Tóth: Convective instability in horizontally propagating chemical fronts, Phys. Rev. E **79**, 016216 (2009). (IF=2.483)
2. L. Rongy, G. Schuszter, Z. Sinkó, T. Tóth, D. Horváth, Á. Tóth, A. De Wit: Influence of thermal effects on buoyancy-driven convection around autocatalytic chemical fronts propagating horizontally, Chaos **19**, 023110 (2009). (IF=2.188)

7 Lectures and poster presentations related to the dissertation

1. T. Tóth, D. Horváth, **Á. Tóth**: Thermal effects in the chlorite - tetrathionate reaction, Workshop of the ESA Topical Team - "Chemo-hydrodynamic instabilities at interfaces", Toulouse, France, 2007. (lecture)
2. **T. Tóth**, D. Horváth, Á. Tóth: Thermal effects in the density fingering of the chlorite - tetrathionate reaction, International Congress of Young Chemists 2007, Jurata, Poland, 2007. (poster)
3. **T. Tóth**, D. Horváth, Á. Tóth: A hőmérséklet hatása a konvektív instabilitásra a klorit-tetrationát rendszerben, XXX. Kémiai Előadói Napok, Szeged, 2007. (lecture in Hungarian)
4. **T. Tóth**, D. Horváth, Á. Tóth: Scaling law of stable single cells in density fingering, Workshop of the ESA Topical Team - "Chemo-hydrodynamic instabilities and patterns at interfaces between reactive solutions", Paris, France, 2008. (lecture)

5. **T. Tóth**, G. Schuszter, Z. Sinkó, D. Horváth, Á. Tóth: Scaling law of stable single cells in density fingering of chemical fronts, 2008 Gordon Research Conference on Oscillations and Dynamic Instabilities in Chemical Systems, Waterville, ME, USA, 2008. (poster)

6. **T. Tóth**, D. Horváth, Á. Tóth: Időben állandó mintázatokra érvényes skálázási törvény kísérleti meghatározása, XXXI. Kémiai Előadói Napok, Szeged, 2008. (lecture in Hungarian)

7. **T. Tóth**: A reakcióedény paramétereinek hatása a közegmozgásra autokatalitikus frontokban, Reakciókinetikai és Fotokémiai Munkabizottság, Balatonalmádi, 2009. (lecture in Hungarian)