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ORIGINAL RESEARCH

Gravitational Influence on an Oscillating Chemical Reaction

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Abstract Pattern formation, oscillations and wave propagation as processes in excitable media can be controlled by small external forces including gravity. The Belousov–Zhabothinsky (BZ) reaction is possibly the best studied system and exhibits temporal as well as spatial patterns. Wave propagation in BZ systems already has been shown to depend on gravity, due to interactions with diffusion and convection. In a stirred bulk BZ system stable oscillations exist in the absence of diffusion, sedimentation, buoyancy and convection with a period in the minute range. In parabolic flight missions such a system can be investigated under gravity conditions changing between 1 g, 1.8 g and μ-g just on this timescale. Here we have found that the temporal pattern formation of an oscillating BZ reaction locks to the period of the gravity changes but is also destabilized due to the partially stochastic nature of the gravity changes. This points out to a gravity dependence of chemical rate constants as given in a formal description of the BZ-system. The BZ-reaction is the perfect system for such studies and serves as a model for self-organization and pattern formation, also in biological systems. The possibility to study the lack of gravity or changes in gravity destabilizing self-organization and pattern formation is of major interest to identify the underlying mechanisms.

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Introduction

Excitable media can exhibit among others fluctuations of system parameters in time, which can be controlled by small external forces, including gravity. The Belousov–Zhabothinsky reaction (BZ) (Belousov 1959), as a stirred bulk reaction, can be set under laboratory conditions to an oscillation period of about one minute, due to the stirring without being dependent on diffusion, convection or buoyancy. In theoretical models, thus only concentrations and rate constants are given to interact with small external forces (Sagues and Epstein 2003; Walleczek 2000), again including gravity. In parabolic flight missions experiments can be done under close to laboratory conditions with gravity changes in the range of minutes between μg, 1 g, and 1.8 g. The gravity in such a mission changes on a time scale of about 50 s in a quasi stochastic/periodic way (Novespace 2007). The average period of the BZ-reaction we used under the given conditions was about 70 to 80 s, thus in the same range but always slightly longer.

According to the similar periods of gravity changes and oscillations in the BZ-reaction under these conditions additional resonance effects could be expected in an oscillating BZ-reaction during a parabolic flight mission. Consequently, after it had been shown already that waves in BZ-reactions interfere with gravity (Nagypal et al. 1986; Fujieda et al. 1997, 2002; Wiedemann et al. 2002; Hanke et al. 2009), we now did a series of such experiments.

Materials and Methods

The specific conditions of parabolic flight missions (Novespace 2007) include some rigorous safety rules which make it necessary to construct a set-up for each experiment on board strictly following these rules. The resulting mechanical design of the set-up for a fluctuating BZ-reaction is shown in Fig. 1. In part a, the complete outer safety box of the set-up can be seen. Especially in Fig. 1b, some details of the chambers and the stirring system are shown. A cylindrical chamber (length 37 mm, diameter 500 mm) made from stainless steel is closed by two windows made from polycarbonate for the optical path. The mechanical stirrer is driven by a current controlled DC-motor running at 120 rpm, and can be seen on top of the chamber. Figure 2 additionally depicts the general electrical and mechanical circuitry in a scheme of the set-up.

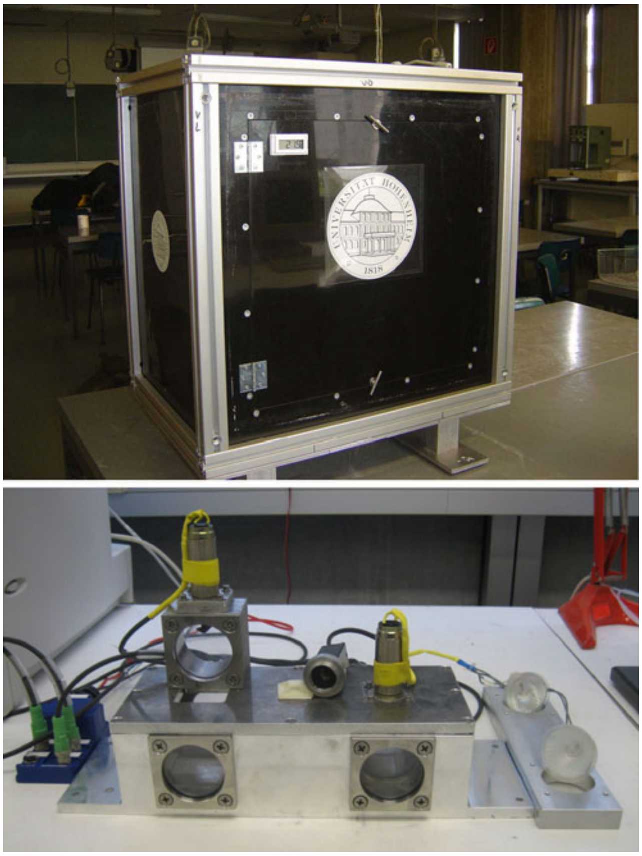

Fig. 1 In this figure some details of the mechanical construction of the set-up are shown. The *upper part* shows the outer security housing of the set-up. The *lower part* shows dismounted details the internal set-up mainly with the two BZ-chambers (one mounted in the safety-box). Additionally, the DC power distribution, the illumination pineal and a photomultiplier can be seen

For the experiments, due to safety restrictions on board the A-300 parabolic airplane, 75 ml of reaction solution composed of (starting composition: 1 M H_2SO_4, 275 mM malonic acid ($C_3H_4O_4$), 8.5 mM ammonium-cernitrate ($CeH_8N_8O_{16}$), 62 mM $BrNaO_3$, 0.4 mM Ferroin) were filled in a sealed stainless steel chamber with poly-carbonate windows in the Novespace ground laboratory. The solution was illuminated with a high-power LED at 480 nm from one side and the transmitted light was measured with a photomultiplier (Hamamatsu) at the other side. The chamber was equipped with a DC-motor driven mechanical stirring system running stable at 120 rpm. Two such chambers were placed in another sealed aluminum case (again with polycarbonate windows (see Fig. 1b) and this was placed with the complete additional technology in a third safety box (see Fig. 1a) and than in the A-300. Some more details of a similar set-up have been published previously (Hanke et al. 2009). The experiment was switched on after the airplane had reached its cruising altitude, typically about 30 to 60 min after filling the chambers.

Control experiments were run in the laboratory at constant 1 g in the same set-up using an identical temporal and stirring protocol. The mean temperature on board the A-300 was 20 ± 1°C, in the lab it was 22 ± 1°C. For the data recording, a laptop with proper hardware (AD-converter from National Instruments) and custom made software developed with LabView® (National Instruments) was used. Data evaluation, offline analysis and statistics have been done using the software LabView® and Origin®.

Results

In Fig. 3 the general situation of the experiments during parabolic flight missions is depicted. The gravity, upper trace, changes with a period in the range of 50 to 60 s, however, with a partially stochastic nature, due to the detailed flight protocol. In parallel, the oscillating BZ-reaction under the given conditions runs at a period of about 1 min as shown in the lower trace. The color change of the BZ-reaction is shown as an example in the insets.

After the control traces in the laboratory and during the parabolic flight missions had been recorded from a fluctuating BZ-reaction as described in the methods section, the data were further evaluated offline. Periods and amplitudes have been analyzed for a 90 min window after the start of the first parabola. For further analysis the periods of every experiment were plotted as a function over time and were fitted using a linear re-

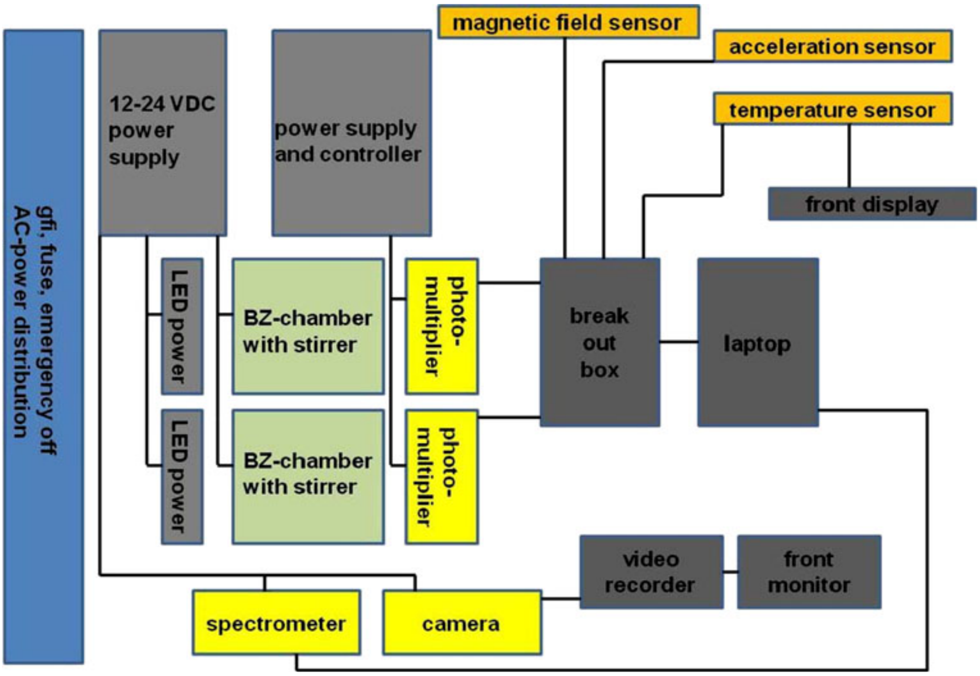

Fig. 2 In this figure a cartoon of the overall structure of the set-up is shown. (*gfi* ground failure interrupt)

gression. The obtained slopes of control and parabolic flight experiments were statistically analyzed using an unpaired *t*-test.

Under laboratory conditions at constant 1 g in a closed non-equilibrium system as used in our flight-experiments, the oscillation of the BZ-reaction is stable for about 2 h. The amplitude of the oscillation as measured by blue light transmission slightly decreases and the period becomes slightly longer. Later, due to the ongoing chemical reaction, the system runs down.

We have done two parabolic flight campaigns with three flights consisting of 31 parabola (Novespace 2007) each. Any time two chambers were used, thus overall 12 experiments have been done. For comparison, as stated above, 11 controls were done under constant 1 g in the lab.

An original recording of one flight day is shown in Fig. 4. The upper trace gives the complete gravity profile (axis perpendicular to A300 base); the trace below shows the corresponding data of light transmission of one BZ-reaction. From these original data we calculated the peak to valley amplitude and the duration of each oscillation period, which are given in the traces below. As can be already seen, the oscillation is quite stable in amplitude and period at constant 1 g before offset of the parabola. With increasing number

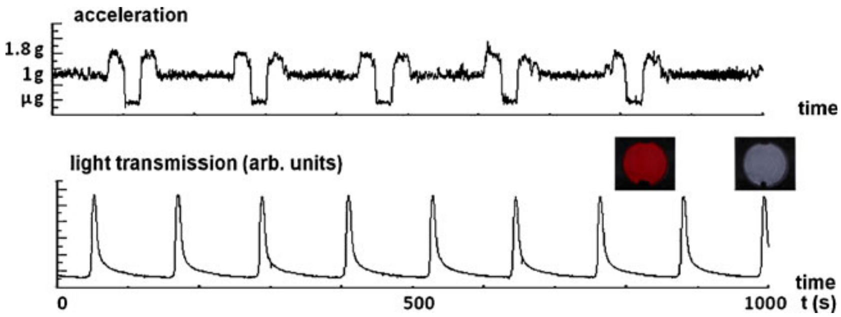

Fig. 3 In this figure the general situation of an oscillating BZ-reaction under the conditions of a parabolic flight mission is depicted. In the *upper trace*, part of the gravity profile on board the A300 Zero-g is show, below the light transmission at 480 nm through an oscillating BZ-reaction. As can be seen, the timescales of both fluctuating signals are in the same range. Both have a period in the minute range, in the given experiments. The average period of the BZ-reaction is 10–20% longer than that of the gravity changes. The *insets* show the color changes of the BZ-reaction in the experimental chamber

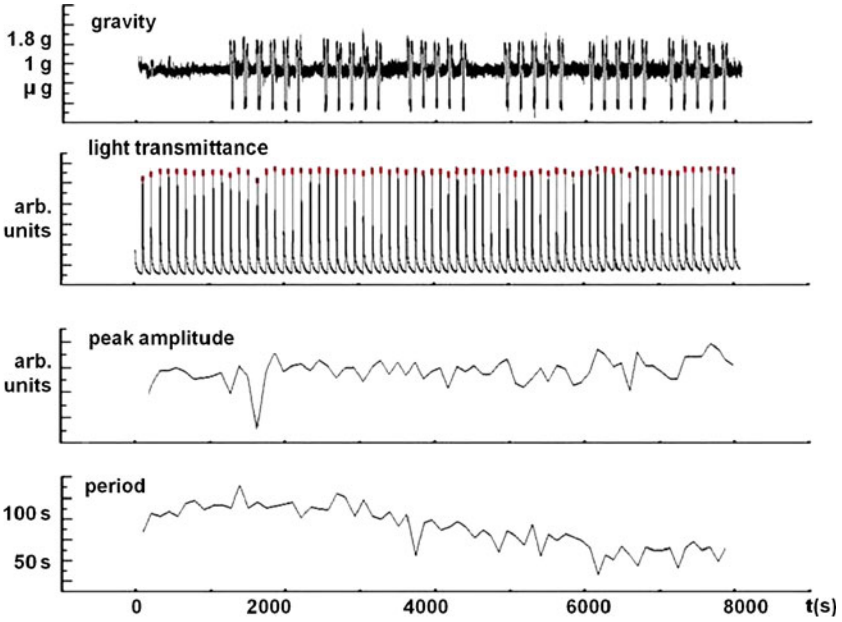

Fig. 4 Example of an oscillating BZ-experiment under the conditions of a parabolic flight mission. The full time range (about 2.5 h) is shown with the 31 parabola done. The *upper trace* depicts the complete gravity-profile, *below* is the light transmission recording of one BZ-chamber at 480 nm. The *third trace* shows the peak amplitude development of the reaction during the flight and the *lowest trace* shows the corresponding development of the fluctuation period. It can be clearly seen, after onset of the parabola, as well the peak-valley amplitude, as the period are beginning to scatter over a wider range as under constant gravity conditions. Additionally, the period becomes significantly shorter over time

of parabolas done, both, amplitude and period of the oscillation are becoming somewhat more instable as can be seen in an increasing scatter of their values. Additionally, the period obviously and in contrast to the normal behavior becomes shorter during the parabolic flight mission.

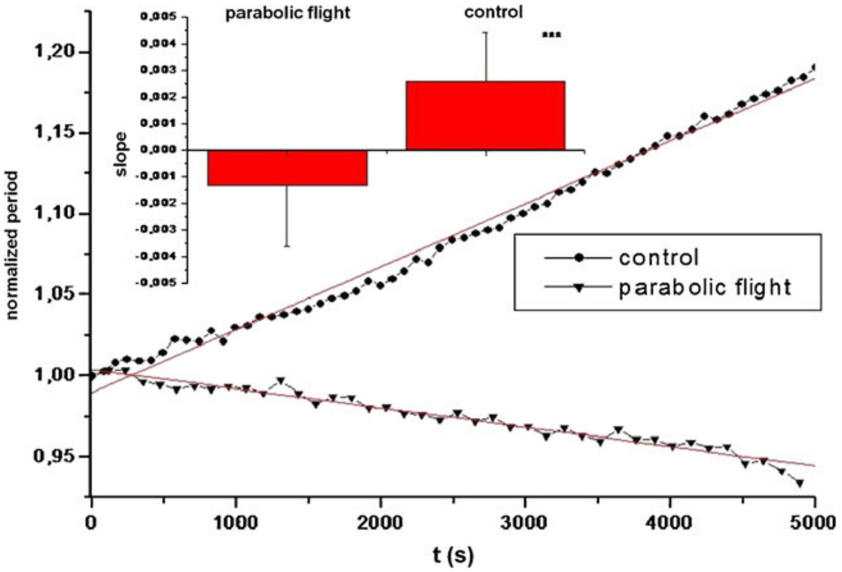

Fig. 5 The figure shows the averaged curves achieved by plotting the periods as a function of time of all control and parabolic flight experiments. For better comparison, the data is normalized to 1 at the beginning of the experiments. Under constant 1 g, the period becomes longer over time, under parabolic flight conditions; the period becomes shorter. *Inset* of the figure: the block diagram shows the mean slope of the linear fitted periods plotted over time and their standard deviation of all parabolic flight experiments compared to laboratory controls. Obviously, slope during parabolic flight differs significantly ($p = 2 \times 10^{-4}$) compared to the controls

The data-sets from the flights and the controls were evaluated as discussed above and the results of all 12 experiments together with the controls are summarized in Fig. 5. In the inset of Fig. 5, a bar graph shows the average slope of the linear fitted period. The controls and the flight data are presented as mean and standard deviation. The mean slope of the control experiments is positive and the mean slope of the parabolic flight experiments is negative. The mean of the amplitude is about identical under both situations (data not shown). In addition, as stated already, both, amplitude and period exhibited a somewhat higher, increasing scatter after the onset of the parabola.

Discussion

In previous experiments (Nagypal et al. 1986; Fujieda et al. 1997, 2002; Wiedemann et al. 2002; Hanke et al. 2009) it has been shown that wave propagation in BZ-systems is depending on gravity as well in fluid as in gel systems. This interaction can be attributed to diffusion, convection and buoyancy going on in such systems at different degrees. In bulk systems as used in the present experiments, however, all these factors do no longer play a role due to the stirring.

It should be mentioned, however, that even in well stirred chambers with proper geometry a not absolutely complete mixing might be given as a consequence of existing edges with small local gradients. Such gradients could lead, to again very small, buoyancy-driven flows, which might have consequences on the reaction. Other artifacts might be given due to changing mechanical vibration in the A300, and finally further systematic small disturbances of the system might be present (Hlavacova and Sevcik 1993; Toth et al. 2001). However, all these effects would be very small, and they could not be excluded or controlled, due to the given experimental situation in parabolic flight missions. In worst case such effects could mimic gravitational effects. Nevertheless, the principal results reported here stay and are valid. As the best was done in the presented experiments to exclude artifacts, we prefer in the following interpretation to focus on models of the BZ-reaction with only concentrations and rate contants.

Accordingly (having the just mentioned restrictions in mind), in a theoretical description, only concentrations and rate constants of chemical reactions are given (Field et al. 1972; Field and Noyes 1974; Keki et al. 1992). The reactant concentrations vary with time due to the ongoing reaction, but are not interacting with the applied forces. The rate-constants instead are fixed under constant conditions, but are depending on external and internal forces. Thus, the only interaction of the system, at least on this basic theoretical level, with gravity can be an influence of gravity on at least one of the rate constants of the chemical reactions underlying the system. In simulations of such systems it can be easily shown that changes in the rate constants result in changes in amplitude and period of the reaction changes (Quo and Wang 2008; Wang et al. 2005).

In the presented experiments, a BZ-reaction is running in a closed system at non-equilibrium conditions without convection, diffusion and buoyancy, due to the stirring of the solution. As the gravity (acceleration) during the flight changes not on a totally fixed period, it can be concluded, that this leads to the higher scatter in amplitude and period of the data throughout the flight, compared to control conditions. This effect can also be seen when comparing the data before the onset of the parabola with those during the parabola of the example presented in Fig. 4. Additionally, the gravity changes (oscillatory-stochastic) on a time scale a bit shorter than the period of the BZ-reaction used in the given experiments. This, by period coupling, can explain the shortening of the period throughout the flight (Hlavacova and Sevcik 1993).

Under the above made restrictions, our data for the first time demonstrate clearly the gravity dependence of a rate-constant in a chemical reaction. A basic mechanism of such a finding, however, is not known up to date (see above). Also, we know that a gravity dependent rate constant might be difficult to accept, however, this should not be a reason not to take it into account.

Due to the sensitivity of oscillating excitable media to small external forces, the most probably very small effect of gravity on a chemical reaction might be seen here, but not in non-oscillating chemical reactions.

Finally, the BZ-reaction can been used as a simplified but valid model for oscillating biological processes and biological rhythms, and from our results it can be concluded that these might be gravity dependent, too, just due to basic physical reasons.

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