Turbulent decomposition of chemical waves by spontaneously induced hydrodynamic oscillation

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The dynamic evolution of a chemical reaction–diffusion pattern and its interaction with hydrodynamic flow is investigated by two-dimensional velocimetry and spectrophotometry based on microscope video imaging techniques. Oscillatory deformation and turbulent decomposition of chemical wave fronts are observed which are induced by a pronounced oscillatory flow excited spontaneously in a Belousov–Zhabotinsky solution layer with a free surface.

I. INTRODUCTION

Structure formation in reactive media due to the coupling of chemical reaction with transport processes has received considerable attention ever since the phenomenon of chemical wave propagation was discovered in the Belousov–Zhabotinsky (BZ) reaction.[1] The occurrence of traveling chemical waves in thin layers of this reaction, such as target patterns or rotating spirals, has been treated theoretically by modeling the coupling of nonlinear chemical reaction kinetics with molecular diffusion.[2,3] Recently, there is increased interest in the phenomenon of Turing patterns, which were found in several reaction–diffusion systems.[4,5] In these and other studies, the use of gel reactors for improved control of system parameters has become common.[6,7]

On the other hand, in liquid systems without using a gel matrix, "hybrid" structures are frequently observed that stem from complex interaction of chemical reaction, diffusion and hydrodynamic flow.[8–10] A typical example is the deformation and irregular decomposition of chemical waves propagating in a liquid layer with an open liquid/gas interface.[11–13] Because of the free boundary at the open layer, the origin of these structures has been discussed in terms of convective flow caused by temperature gradients and/or inhomogeneities in surface tension due to evaporative cooling or inhomogeneities in chemical composition.[10,12] A mechanism related to density changes due to the reaction in a propagating front has been suggested in experiments performed in thin glass tubes where a large open surface is absent.[14]

In previous studies the authors observed that a wave train emerging from a rotating spiral wave gives rise to periodically changing deformations of chemical wave profiles associated with oscillatory hydrodynamic flow.[15] These oscillations were found to occur both in open and closed (covered) containers with a free liquid/gas interface.[16] The flow was most pronounced near the free surface of the BZ reagent and its maximum velocity was usually of the order of the propagation velocity of the waves (≈ 50 μm/s or less).

In this letter, we report experiments performed in a covered dish containing a BZ solution layer with a free surface. We show that pronounced oscillatory deformations and subsequent turbulent behavior of chemical waves occur even in this system. These effects are induced by an extremely developed oscillatory flow attaining much higher velocity (more than 100 μm/s) than that of wave propagation.

II. EXPERIMENTS

Experiments were carried out in a quiescent, excitable BZ solution catalyzed by ferroin in a batch reactor (petri dish, diam 7 cm) at room temperature (25 °C$\pm$1 °C) prepared as specified in Ref. 15: the initial concentrations after mixing the reagents were 48 mM NaBr, 340 mM $NaBrO_3$, 95 mM $CH_2(COOH)_2$, 378 mM H_2SO_4, and 3.5 mM ferroin. A volume of the mixture resulting in a 0.85 mm layer was poured into the dish and spiral waves were produced according to the procedure given in Ref. 17 at a location about 1 or 2 cm away from its center (Fig. 1). By carefully cleaning the dish only very few CO_2 bubbles formed and no other waves were initiated at the dish boundaries. A glass cover was placed on the dish, leaving an air gap of 11 mm above the layer, thus efficiently suppressing evaporative cooling of the upper solution interface.

The correlation between chemical wave dynamics and hydrodynamic flow was investigated by two-dimensional velocimetry[15,18–20] and spectrophotometry,[13,17] based on the combination of an inverted microscope with video imaging techniques. For the flow measurements, polystyrene particles (diam 0.48 μm) serving as scattering centers were mixed into the BZ solution and illuminated by He–Ne laser light (632.8 nm) from a slightly tilted angle. The measuring position was changed vertically by adjusting the focus of the microscope observation plane. Temporal traces of the velocity were measured locally near the center of the dish (see Fig. 1) by analyzing the motion of the suspended particles in a video movie taken at high magnification (image area 0.3×0.3 mm^2, i.e., raster resolution 0.6 μm per pixel). Additional illumination with a homogeneous light beam (490 nm) allowed to detect hydrodynamic flow and chemical wave propagation simultaneously. More global

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FIG. 1. Spiral pattern in an excitable BZ-reaction layer in a petri dish (diam, 7 cm; layer depth, 0.85 mm). Preparation as specified in the experimental section. The pattern was observed 5 min after triggering the pair of spiral centers, using a band pass filter at 490 nm. Temperature: 25 °C.

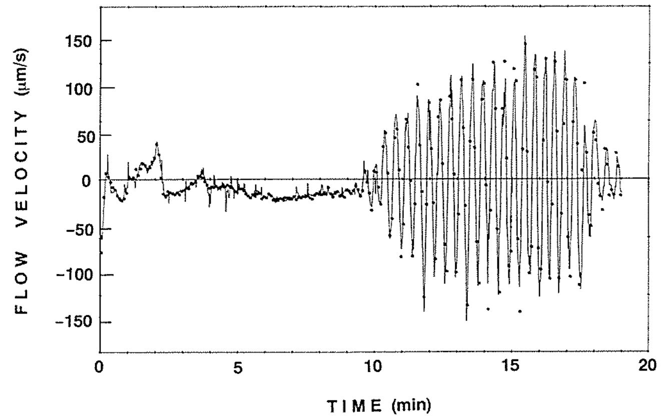

FIG. 2. Time trace of extremely pronounced flow oscillation in a covered BZ-solution layer (preparation as in Fig. 1) with a free liquid/gas interface. Temperature: 26 °C. Solid circles are obtained manually by tracing the moving particles in the video movie (Ref. 16). The solid line shows a result obtained by automatic analysis through dynamic image processing [2D velocimetry (Ref. 20)], confirming the reliability of the velocimetry method.

characteristics of the pattern dynamics were observed at lower magnification in a 7.2×7.2 mm^2 area. For this purpose the layer was illuminated only with the monochromatic light beam without polystyrene particles and laser illumination.

III. RESULTS

A. Pronounced flow oscillations

As reported previously, an oscillatory hydrodynamic flow is induced spontaneously in a shallow layer of BZ solution in which spiral waves rotate. Usually, the maximum amplitude of the flow oscillation is less than 50 μm/s and its period is twice that of chemical wave trains (about 20 s) indicating a strong tendency for a period 2 entrainment.[15] However, in our investigations we also observed unusually high flow velocities accompanied by strong wave deformation and decomposition. These occurred about 5 times within 30–40 experiments performed under apparently identical conditions (same chemistry as in Ref. 15), that is with a probability of 10%–15%.

A time trace of extremely pronounced flow velocities measured close to the liquid/gas interface of the BZ solution is shown in Fig. 2. Ten minutes after triggering the spiral waves in this system, the hydrodynamic flow starts quite suddenly to change its direction in an oscillatory manner. The oscillation amplitude attains a maximum of 150 μm/s, thus exceeding by far the propagation speed of the chemical waves (about 50 μm/s at this time stage). The period of the flow oscillation (22.5 s) is about 1.3 times that of chemical wave trains (17.7 s). These results are quite different from those usually observed,[15] where the period of flow oscillation is twice that of the wave trains, their maximum amplitude 40–50 μm/s, the oscillations continue for only 4–6 min and stop at about 18 min after triggering the spiral waves. In these experiments, one recognizes on the whole four distinctively different phases of hydrodynamic motion in the reactive layer (Fig. 2):

(1) 0–4 min: initiation phase with alternating flow induced by a few discrete waves in a chemically well reduced medium (as described in Ref. 16); (2) 4–10 min: unidirectional, mean flow phase with a velocity up to 20 μm/s; (3) 10–18 min: sharp transition to flow oscillations with large amplitude, correlated with periodic passage of wave trains (oscillatory phase); and (4) from 18 min on: terminating phase with rapidly decreasing amplitude of the flow oscillations.

B. Pattern dynamics

The corresponding dynamic evolution of a chemical wave pattern is shown in Figs. 3 and 5. There is no remarkable change of the regular symmetric pattern in the initial time period of 10 min [Fig. 3(a)], except for a gradual increase of the wavelength of the chemical waves. About 10 min after triggering the spiral waves, deformations of the moving wave fronts appear [Figs. 3(b) and 3(c)], by which they lose their symmetry with respect to the center of the spiral pair. These asymmetric deformations turn out to switch periodically from the left- to the right-hand side of the symmetry axis of the spiral pair and vice versa. For supporting this observation, Fig. 4 shows intensity profiles of the wave fronts extracted along the cut labeled *X-X'* in Fig. 3(b). The dashed vertical line represents the location of the symmetry axis. Profile 4(a) corresponds to the state of stationary spiral rotation depicted in Fig. 3(a). The profiles with respect to the spiral centers are symmetric. Later, in the oscillatory phase [profiles 4(b) and 4(c), extracted from the patterns of Fig. 3(b) and 3(c), respectively] the profiles are not spatially symmetric any more. Their shape to the left and right of the dashed line indicates the periodically changing nature of the wave fronts. The observation of periodic motion of accidentally

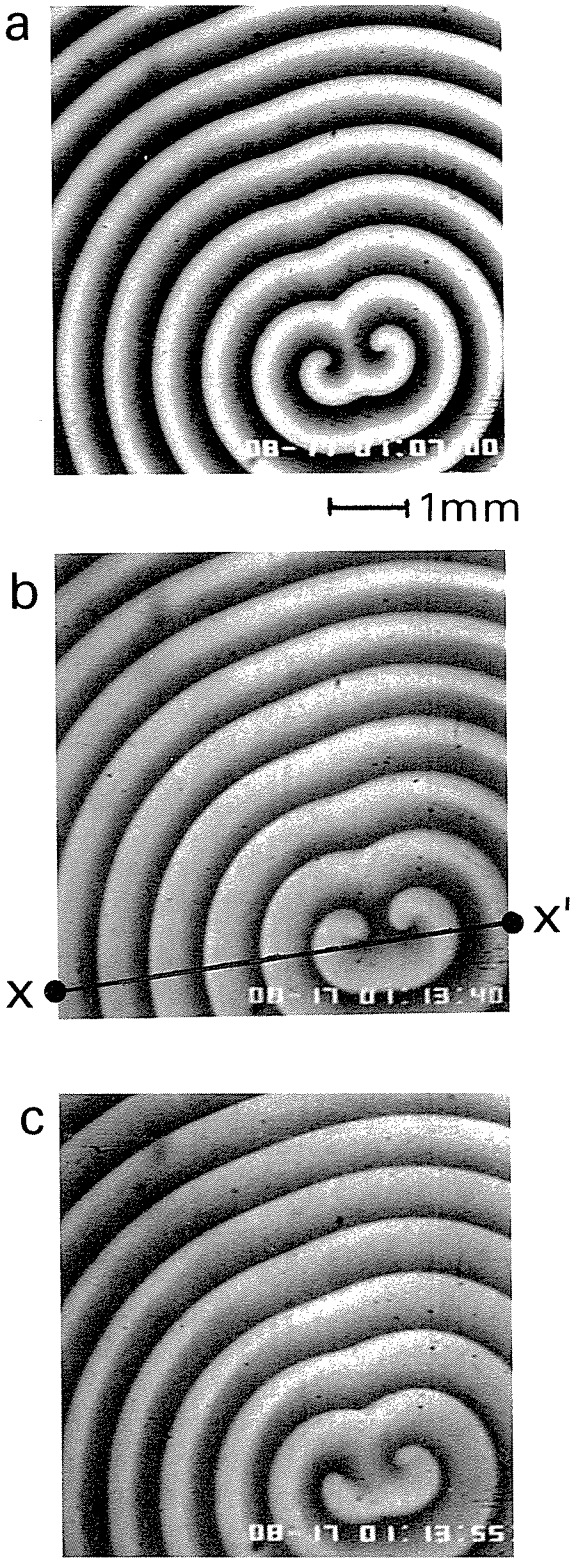

FIG. 3. Oscillatory deformation of spiral wave fronts observed in the same BZ-solution layer as in Fig. 2 (26 °C). Times after start of experiment: (a) 7 min (unidirectional flow phase), (b) 13 min 40 s, and (c) 13 min 55 s (oscillatory phase).

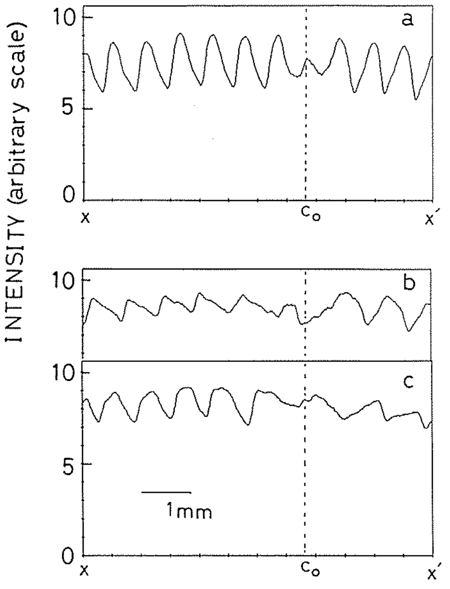

FIG. 4. Intersecting image-intensity profile of wave fronts along the line *X-X'* in Fig. 3(b). (a) profile of stationary spiral rotation corresponding to Fig. 3(a) (unidirectional flow phase), (b) and (c) profiles of oscillatory phase corresponding to Figs. 3(b) and 3(c), respectively.

present dust particles (size about 50 μm) on the surface of the layer confirms that the profile deformation is closely correlated with the oscillatory hydrodynamic flow detected near the surface. This corroborates that the dynamic deformation is caused by the oscillatory flow (compare Ref. 16).

When the flow amplitude exceeds by far the propagation speed of the chemical waves (more than 100 μm/s, after typically 13 min), the rhythmic deformation turns into a more irregular dynamic behavior which corresponds to the oscillatory and terminating phase of the hydrodynamic oscillation (Fig. 2). This is shown by a sequence of 4 pictures in Fig. 5. In the case illustrated, the oscillatory phase continues for 10 min, the terminating phase starts after 23 min. The intact train of waves (picture a) is disrupted along some direction (pictures b and c) leaving many open wave ends which curl up to form a rather complex mixture of wave fronts and wave ends at later stages of the experiment (picture d). After 23 min, the oscillatory flow stops and the open ends of the disrupted wave fronts have developed to additional spiral structures (the terminating phase).

One has to take into account that the experiments were performed in a batch reactor and that during the time interval of the experiment the initial reactants were used up to some extent. The system is not in a stationary state but the state of the system changes gradually with time. Since this change is very slow compared with the time scale of wave propagation, the states of observation are considered as quasistationary.

IV. DISCUSSION

This work shows that oscillatory deformation and turbulent behavior of chemical waves in the BZ solution layer

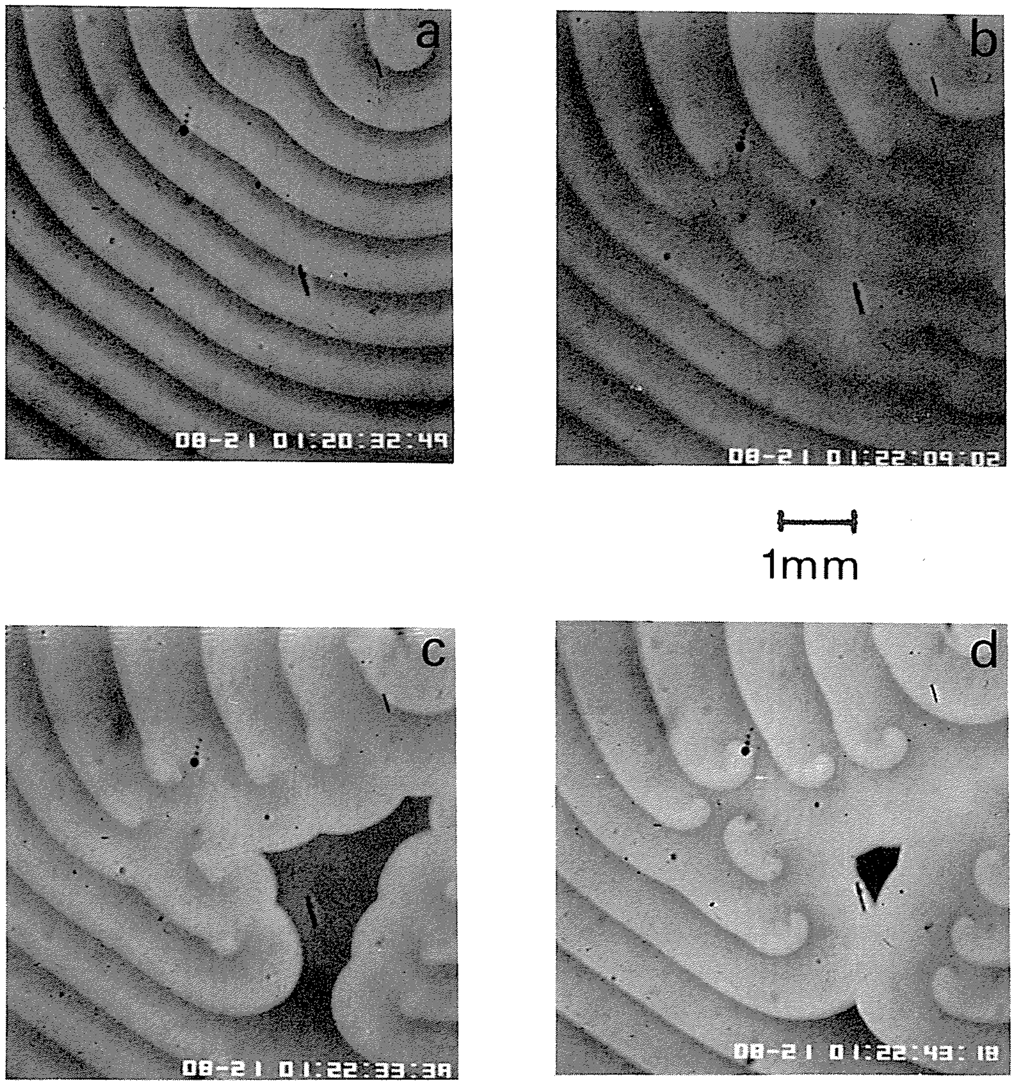

FIG. 5. Turbulent decomposition of chemical spiral pattern observed in the covered solution layer (same preparation as in Fig. 1) with a free surface, correlated with very pronounced flow oscillations. Times after start of experiment: (a) 20 min 32 s (oscillatory phase), (b) 22 min 10 s (end of oscillatory phase), (c) 22 min 33 s, and (d) 22 min 43 s (terminating phase). Because of a slightly lower temperature than in Fig. 3, the oscillatory phase started later (13 min after triggering spirals) and continued more than 10 min.

are closely connected with simultaneously detected pronounced flow oscillations. Since a protective cover was placed on the sample dish in all experiments, this behavior is not likely to be driven by external thermal disturbances, e.g., evaporative cooling (Marangoni instability[21,22]). Evaporation is strongly reduced under these conditions, i.e., evaporation rate has been found to be at least 20 times less than in an open layer without a cover. In spite of performing the experiments under apparently identical conditions, the pronounced oscillatory flow is observed only occasionally (probability of 10%–15%). In the experiments, several chemical and physical parameters (e.g., temperature and concentration of the mixture) are well controlled. However, it is more difficult to maintain an always equally clean condition of the dish and to fix the geometrical location of the center of spiral waves. This location is chosen at a distance 2 cm away from the dish boundary (see Fig. 1), but fluctuates by ±0.5 cm in every new experiment. In fact, recent experiments confirm that the evolution of the flow amplitude is very sensitive to the location of the spiral centers.

The main problem is to elucidate the internal mechanism establishing the oscillatory flow and the following enhancement of flow oscillations. In a previous report,[16] the authors proposed some phenomenological explanations for the flow oscillation in terms of chemical entrainment and curvature-driven hydrodynamic instabilities. Furthermore, two possible mechanisms should be considered for the hydrodynamic instability associated with chemical waves. As suggested by Pojman and Epstein,[14] a density gradient caused by the chemical reaction in a horizontal container causes an antisymmetric fluid flow without any threshold. The other possibility arises from concentration gradients in the chemical wave fronts. These could produce an unbalance in surface tension resulting in a motion on the surface and a flow in the bulk of the fluid due to the viscosity of the medium (Marangoni convection).[23,24] Since the derivative of the surface tension with respect to chemical composition is not known for the BZ solution, an evaluation of the critical Marangoni number cannot be provided yet. Considering the fact that the hydrodynamic effects cannot be observed in a thin layer (1 mm depth) without any air/liquid boundary, the surface-tension driven convection must be a key mechanism for the reported hydrodynamic instability.

Preliminary experiments indicate that the off-center location of the center of spiral waves plays an important role to establish the pronounced flow oscillation. The off-center spiral structure means nonsymmetric geometry of the system creating chemical gradients in the layer. These findings call for further experiments and for theoretical approaches which model the interaction of reaction–diffusion patterns with hydrodynamics.

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