PHYSICAL REVIEW E **70**, 046302 (2004)

Coarsening in the buoyancy-driven instability of a reaction-diffusion front

Martin Böckmann* and Stefan C. Müller†
Institut für Experimentelle Physik, Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, D-39106 Magdeburg, Germany

(Received 16 July 2003; revised manuscript received 26 April 2004; published 7 October 2004)

When propagating in a vertical direction an autocatalytic reaction front associated with a change in density can become buoyantly unstable, leading to the formation of a fingerlike pattern. Later on these fingers start to interact. Their temporal evolution is studied experimentally by tracking the horizontal and vertical locations of the extrema of the front pattern. A proceeding development towards larger spatial scales is found. This is reflected in the differences in the vertical speed of neighboring fingers: continually some fingers start to decelerate and vanish finally in the neighboring ones which show a simultaneous acceleration. In addition, weak lateral movements of fingers towards gaps are observed, but there is no evidence for a correlation with the extinction of fingers.

DOI: 10.1103/PhysRevE.70.046302 PACS number(s): 47.20.Bp, 47.54.+r, 47.70.Fw

I. INTRODUCTION

Placing a fluid of a higher density on top of a less dense one can lead to a buoyancy-driven convection, known as the Rayleigh-Taylor instability [1]. If the two fluids are miscible and not separated by an interfacial tension, diffusion tends to stabilize an initially straight boundary against deformations caused by buoyant flow [2]. Inside the narrow gap of a Hele-Shaw cell, where the flow is dominated by viscous forces, and thus described by Darcy's law or a gap-averaged Navier-Stokes equation [3,4], the interplay of buoyancy and diffusion causes fingerlike extensions of one fluid into the other [5]. The initial phase displays a preference for the growth of a finite, most unstable wavelength of the interface deformation [6,7]. As time proceeds, these fingers show rich dynamics of growing, merging, and splitting.

Like simple miscible fluids, the two states of an autocatalytic reaction front can undergo a buoyant instability, provided that the reaction is associated with an appropriate density change [8]. The sharp reaction front then takes the role of the fluid boundary. If the density is lowered by the front reaction, fronts ascending against gravity bear a stratification of low density fluid inside the front below heavier, unreacted fluid and may be buoyantly unstable, whereas descending fronts represent the reverse, stable stratification. As compared with miscible fluids, there are, however, some important differences: First, the reaction maintains a constant extension of the front. Therefore the density transition zone is not widening with time. Second, most planar autocatalytic fronts move through the medium with a constant speed due to the interplay of reaction and diffusion. Third, this speed depends on the local front curvature, providing a very robust stabilization of a straight front. Due to this, any persistent deformation of the front must be maintained by a hydrodynamic flow [9]. Additionally, any convection at the front enhances mixing of the components and increases the propagation speed [10–12].

A suitable system for such investigations is the reaction of iodate and arsenous acid with monostable kinetics under batch conditions [13]. When arsenous acid is in excess, the density is lower in the reacted phase as compared to the unreacted phase [14]. Consequently, descending fronts are stable and remain flat, whereas ascending fronts are buoyantly unstable. In Hele-Shaw cells with gap widths below 1 mm, ascending fronts develop into a series of fingerlike structures [15,16]. The onset of this instability is governed by a mode of maximum growth rate at wave numbers between 1 mm^{-1} and 2.5 mm^{-1}, depending on the permeability of the cell, whereas modes beyond 4 mm^{-1} are stabilized. These growth rates have been compared with several linear stability analyses assuming Darcy flow [11,16,17] or a more general gap-averaged Navier-Stokes equation [18].

Corresponding observations have been made in experiments on the monostable reaction of chlorite and tetrathionate which shows also exothermic fronts and monostable kinetics [19,20]. Since here the net density change at the front is positive, descending fronts are unstable. Model calculations of a bistable front [21] show that after the onset of the instability fingers become elongated and finally shed disconnected droplets of one state from their tips into the other state. This droplet formation seems to depend on the bistability of the kinetics. Experiments in that direction require an open spatial reactor and thus are a challenging work for the future.

In all systems mentioned above, the pattern is reported to undergo a continuous reduction in the number of fingers with the further evolution of the instability, reminiscent of the coarsening in viscous [22] or density fingering [5]. However, for autocatalytic fronts, this process has not been described in detail yet. To follow the mechanism of finger erasure in the intermediate state of the pattern formation in the iodate-arsenous acid reaction, we analyze the horizontal and vertical movement of the maxima of fingers and the ravines between them. If the finger number is reduced by the vanishing of a finger, a horizontal movement of the adjacent ones may occur to close the gap. Tracing the vertical speed of the fingers

---

*Present address: Abt. Exp. Audiologie und Med. Physik, Otto-von-Guericke-Universität Magdeburg, Leipziger Strasse 44, D-39120 Magdeburg, Germany.

†Electronic address: stefan.mueller@physik.uni-magdeburg.de

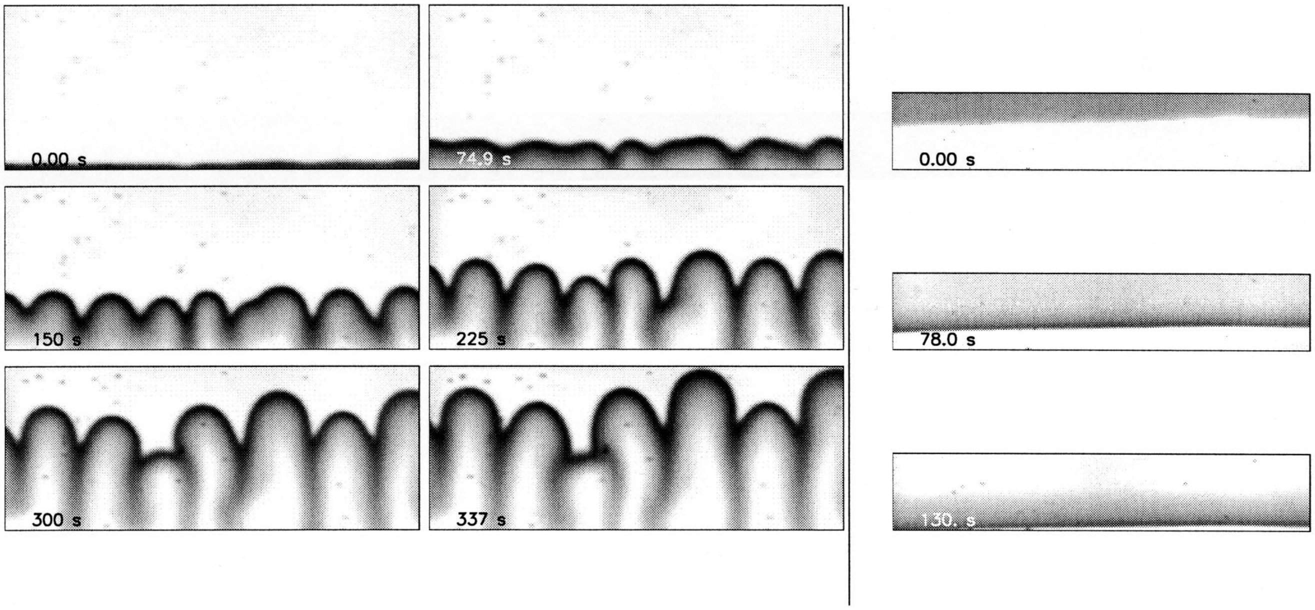

FIG. 1. Left and center column, development of finger formation of an ascending front in a Hele-Shaw cell. Gap width 0 . 9 mm, time is indicated with respect to front formation. Right column, undisturbed planar shape of the descending front of the same experiment. Numbers denote the time after front formation. Window width, 34 mm.

will demonstrate if the erasure of a finger is associated with its deceleration or an acceleration of its neighbors.

II. EXPERIMENTAL PROCEDURE

Details on the experimental setup have been reported previously [16]. The oxidation of arsenous acid by iodate produces monostable fronts propagating with a well-defined profile and speed [13]. The reaction solution is prepared with initial concentrations of $[\mathrm{NaAsO_2}]=16.5$ mM, $[\mathrm{H_2SO_4}]=14.0$ mM, and $[\mathrm{NaIO_3}]=4.8$ mM. A starch concentration of 0.04 % serves to visualize the location of the front as a dark stripe of 0.8 mm width. The density of the initial solution and the isothermal density decrease at the front were determined in a vibrating tube densitometer as $\rho_0=1.0020$ kg/l and $\Delta\rho=1.4\times10^{-4}\rho_0$, respectively.

The Hele-Shaw cell consists of two glass plates separated by a U-shaped spacer made of chemically inert PTFE (Teflon) that closes the cell at the bottom and the sides and defines the gap separation that was chosen for this investigation to be $a=0.9$ mm. For smaller gap widths, all of the effects described below have also been found qualitatively, but turn out to be too small for a detailed evaluation. In gaps wider than 1.0 mm the deformation can no more be regarded as two-dimensional. In order to start a planar, ascending front one of the glass plates has several horizontal strips (width 5 mm) of a conducting indium-tin-oxide coating. When applying a voltage of 3 V across two of them a propagating front forms at the negative electrode after about 3 minutes.

Images are stored on a time-lapse videotape recorder and digitized from high-quality still frames at time intervals of 3.1 s. After a background substraction, the front position is traced in every frame. This is achieved by determining the range of grey levels in every vertical line. The front position is taken as the highest pixel where the grey level falls below 75% of the range of grey levels covered along this line. This procedure proved quite robust but is restricted to a front line unique with respect to the horizontal coordinate. A lateral overgrowth of fingers, which can occur in the late stage of the experiment, cannot be handled by this analysis.

III. RESULTS

A. Formation of fingers

Directly after the formation of a horizontally extended front its lower edge assumes a straight shape that propagates downward at a constant speed of $c_0=23.6(\pm0.1)$ μm/s (Fig. 1, right column). The upper edge, in contrast, undergoes an immediate undulation and ascends at a significantly higher speed. This early phase is characterized by the growth of a preferred wave number [16] and lasts about 40 s in this gap width, increasing strongly in narrower gaps. Soon the undulation develops into segments of rounded upward dents separated by sharp cusps that have been named fingers (Fig. 1, left and center column) [15]. Note that for a time beyond 300 s some fingers show an overhang that limits the correct determination of the front height.

We focus on the phase subsequent to the linear growth. Other than the elongating fingers in the Rayleigh-Taylor instability [5], here the front deformations spread laterally at the expense of their neighbors: As some fingers stay behind adjacent ones, they decelerate and become stunted, giving room to the more advanced competitors ($t=225$ s). Finally, they vanish by being outrun ($t\geqslant300$ s). This process continues progressively: After having swallowed up another finger, the surviving one can get into disadvantage of a third neighbor and vanish itself. In cells of 0.9 mm gap width the disappearance of a finger is observed every 60 s on the average. A tip splitting of advanced fingers like in the Saffman-Taylor fingering in the presence of weak surface tension was never observed. We note, however, that in significantly longer cells highly developed fingers with a large width tend to undulate. This effect obviously corresponds due to the basic instability of a flat front and will be addressed more thoroughly in future work [23].

B. Horizontal movement

Once a finger has been extinguished, the local wavelength, as represented by the vertex distances of the adjacent fingers, has increased by about a factor of 2 as compared with the situation before the disappearance. In order to reinstall a uniform wavelength distribution, a movement of the surviving fingers towards the gap may be expected. To examine any such process, we track the positions of the vertices during the erasure of a finger. To this end, the horizontal positions of the front line maxima (representing the vertices) as well as the minima (corresponding to the cusps between two fingers) are detected at every instant. In a space-time plot of these positions, the disappearance of a finger is reflected in the collision and subsequent annihilation of a finger vertex and one of its adjacent ravines. In a symmetric situation, both ravines annihilate with the vertex, and a single ravine occurs at the former position of the vertex.

Figure 2 displays time traces obtained from two experiments. In both cases, the convergence of ravines towards vanishing fingers is obvious. Every ending trace of a vertex meets the location of one [cf. vertex at $x=13$ mm in Fig. 2(a)] or both [cf. vertex at $x=29$ mm in Fig. 2(b)] adjacent ravines. However, only little movement of the vertices themselves is found. A significant lateral movement of a finger is in most cases connected with its own forthcoming erasure. An example is given by the vertex located initially at $x=6$ mm in Fig. 2(b), but also by the slowly moving finger located initially at $x=16.2$ mm. This can be seen from Fig. 3(d): Here the evolution of the front line is plotted in steps of 23.4 ms; the open downward triangles correspond to this finger that obviously is being outrun by its neighbors. The mean time span from one erasure event to another is of the order of one minute. On the other hand, there are also fingers extinguished earlier that do not move. A horizontal shift of a finger that does not decay during the experiment was never observed.

C. Vertical movement

If a finger vanishes by being overgrown by an adjacent one, it has to assume a lower speed than the survivor. However, there is no direct evidence whether this occurs by its deceleration or an acceleration of the other finger. Therefore, we determine the velocity at the vertex of vanishing fingers and their surviving neighbors. As long as the lateral movement can be considered as small, it is sufficient to determine the speed from the height at a fixed horizontal position. The derivative of the front location is calculated after averaging over nine time instants.

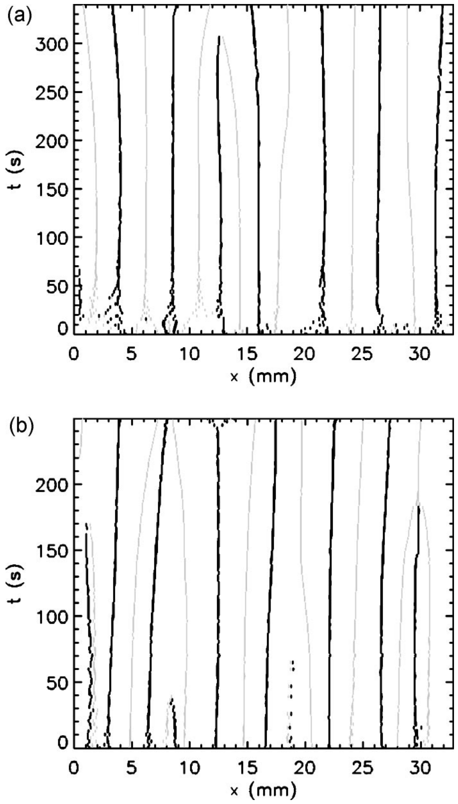

FIG. 2. Time trace of the lateral location of fingers during the erasure of a finger for two experiments (a), (b). (a) corresponds to the experiment displayed in Fig. 1. Black, vertex location. Grey, location of ravine between fingers. Fingers vanish at the end points of black lines.

The vertex speed of several neighboring fingers is displayed in Figs. 3(a)–3(c). During the initial 10 to 20 s the front is still developing; since the front position cannot be detected accurately in this interval, the corresponding values of the speed are omitted. Generally, a significant slowing down of fingers is observed before they are swallowed up, as indicated by the triangles pointing downward. Simultaneously with the slowing down, one or both adjacent, surviving fingers (marked by upward triangles) will speed up. In fact, this acceleration tends even to appear somewhat earlier than the vanishing finger's deceleration. The temporal correlation suggests that the finger selection is connected with a local interaction of adjacent fingers. In a cell of 0.9 mm gap width, the deceleration can result in a stopping or even repulsion of the finger [Fig. 3(a)], indicated by the transition to negative values of the speed. However, a completely stagnating or receding finger is an extreme case which has been found in only few experiments. We note that in Hele-Shaw cells with gap widths smaller than 0.6 mm the vanishing fingers decelerate at a much smaller rate and were never found to stop.

In some cases, the two surviving neighbors move in a very synchronous way [Fig. 3(b)]. In Fig. 3(c), two fingers vanish successively between two other survivors. The stronger one of them grows initially as fast as one of the surviving ones, whereas the other one is not even allowed to develop. As soon as the first finger has vanished ($t\approx 100$ s), the stron-

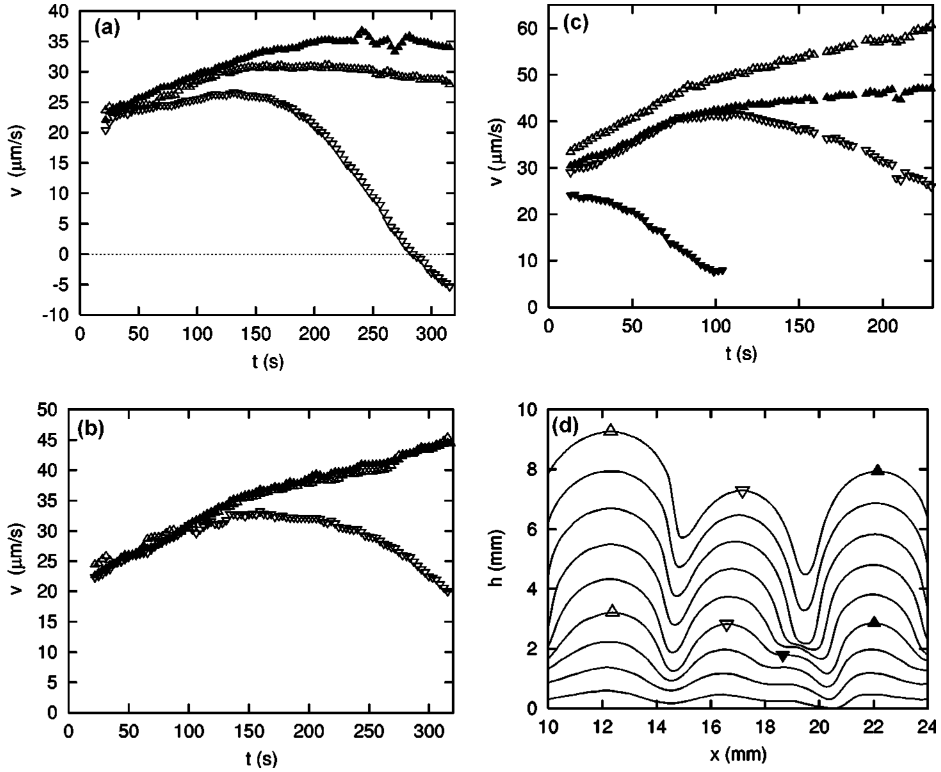

FIG. 3. Evolution of the vertex speed of vanishing fingers (downward triangles) and their surviving neighbors (upward triangles). Open symbols indicate the finger left to, solid symbols the finger right to the vanishing one. (a), (b) correspond to the experiment in Fig. 1 and Fig. 2(a) (vanishing fingers starting at $x=13$ mm and $x=26.5$ mm, respectively); (c) corresponds to the experiment in Fig. 2(b) (vanishing fingers starting at $x=16.5$ mm and $x=18.5$ mm). (d) Successive front lines of the four fingers traced in (c) and Fig. 2(b) for the space interval 10 mm $\leqslant x \leqslant 24$ mm, from $t=0$ s to 187.2 s in time steps of 23.4 s.

ger one starts itself to slow down. The spatial arrangement of these fingers at successive time steps is shown in Fig. 3(d). The striking coincidence of the vanishing of one finger and the start of the decay of the adjacent ones corroborates the presence of a local interaction of the fingers.

IV. DISCUSSION

In some of the reported experiments a finger was found to stop completely or recede [cf. Fig. 3(a)]. To achieve such a stagnancy, an opposing flow with a velocity of the order of the planar propagation speed, c_0, is expected because the fluid motion adds as a vector to the front propagation. However, it was demonstrated experimentally in thin tubes [10,14] and in models [11] that any shear flow at the front causes an additional increase of the propagation speed due to enhanced mixing by Taylor dispersion. Thus, a stagnating front is probably accompanied by an opposing flow with a velocity somewhat larger than c_0. For a better understanding of this flow it would certainly be desirable to measure the flow field around the individual fingers and in the whole cell. Currently, the main effect appears to be local: the neighboring fingers speed up when (or better, slightly before) a vanishing finger starts to decelerate.

The lateral movement of the fingers occurs generally on a slow time scale compared with the average time of finger erasure events. A clear movement could only be observed for fingers that are already weakening. On the other hand, some fingers show no shifting during their decay. More data is necessary to understand how much this is predetermined by a symmetric situation of the surviving adjacent fingers. Currently, no rule for predicting the lateral movement of a finger can be given.

We have started from the hypothesis that a *surviving* finger could move towards a gap left by a vanished finger, in order to level the local distance of finger vertices and reinstall a wavelength of deformation which is homogeneously distributed along the front line. This kind of behavior is definitely not confirmed by our experiments. Obviously, since a lot of fluid is to be moved, the lateral movement of a finger is energetically costly, and therefore too slow to occur on surviving fingers as compared with their own lifetime. During the observation time which was limited by the evaluation process, no substantial movement could be detected. It appears, however, that an approximately equal spacing of the fingers is rather reinstalled by a preference for the erasure of every second finger along the front line.

The development of the most prominent fingers on very long time scales is still under investigation. In the experiments presented only a reduction and no multiplication of fingers was found. However, some preliminary experiments in cells with a height of more than 30 cm have shown an intermediate undulation that appears to be a secondary instability [23]. To clarify if nevertheless a final single finger remains, in analogy with some scenarios in viscous fingering with high surface tension, detailed measurements in still higher cells must be performed.

V. CONCLUSION

In this work, we have characterized the later stage of the buoyancy-driven instability of an autocatalytic reaction front. After the initial formation of fingers, there occurs a selection mechanism due to which some of the fingers are swallowed up by adjacent ones, thus onwards reducing the mean wave number. We found that the erasure of a finger is associated with its deceleration as well as an acceleration of its neighbors which is in the same order of magnitude. The selection appears mainly as a localized process. After the disappearance of a finger, the surviving neighbors may be expected to move towards the gap to adjust the wave number. However, in the time evolution of the lateral finger locations this process is found to be hardly significant. A shift of the lateral location of a vertex is only found on fingers that themselves are already weakening towards vanishing.

ACKNOWLEDGMENTS

The authors thank M. Schröter, A. De Wit, J. Martin, N. Rakotomalala, and D. Salin for valuable discussions. O. Inomoto has made useful suggestions for future work. This study was supported by the German Research Foundation (DFG) and the German Aerospace Center (DLR).

---

[1] D. H. Sharp, Physica D **12**, 3 (1984).
[2] G. K. Batchelor and J. M. Nitsche, J. Fluid Mech. **227**, 357 (1990).
[3] J. Huang and B. F. Edwards, Phys. Rev. E **54**, 2620 (1996).
[4] P. Gondret and M. Rabaud, Phys. Fluids **9**, 3267 (1997).
[5] R. A. Wooding, J. Fluid Mech. **39**, 477 (1969).
[6] J. Fernandez, P. Kurowski, P. Petitjeans, and E. Meiburg, J. Fluid Mech. **451**, 239 (2002).
[7] J. Martin, N. Rakotomalala, and D. Salin, Phys. Fluids **14**, 902 (2002).
[8] J. A. Pojman and I. R. Epstein, J. Phys. Chem. **94**, 4966 (1990).
[9] B. F. Edwards, J. W. Wilder, and K. Showalter, Phys. Rev. A **43**, 749 (1991).
[10] I. Nagypál, G. Bazsa, and I. R. Epstein, J. Am. Chem. Soc. **108**, 3635 (1986).
[11] D. Vasquez, J. Wilder, and B. Edwards, J. Chem. Phys. **104**, 9926 (1996).
[12] B. F. Edwards, Phys. Rev. Lett. **89**, 104501 (2002).
[13] J. H. Merkin and H. Ševčíková, Phys. Chem. Chem. Phys. **1**, 91 (1999).
[14] J. A. Pojman, I. R. Epstein, T. McManus, and K. Showalter, J. Phys. Chem. **95**, 1299 (1991).
[15] M. R. Carey, S. W. Morris, and P. Kolodner, Phys. Rev. E **53**, 6012 (1996).
[16] M. Böckmann and S. C. Müller, Phys. Rev. Lett. **85**, 2506 (2000).
[17] A. De Wit, Phys. Rev. Lett. **87**, 054502 (2001).
[18] J. Martin, Rakotomalala, D. Salin, and M. Böckmann, Phys. Rev. E **65**, 051605 (2002).
[19] D. Horváth, T. Bánsági, and A. Tóth, J. Chem. Phys. **117**, 4399 (2003).
[20] T. Bánsági, D. Horváth, A. Tóth, J. Yang, S. Kalliadasis, and A. De Wit, Phys. Rev. E **68**, 055301 (2003).
[21] A. De Wit, P. De Kepper, K. Benyaich, G. Dewel, and P. Borckmans, Chem. Eng. Sci. **58**, 4823 (2003).
[22] G. M. Homsy, Annu. Rev. Fluid Mech. **19**, 271 (1987).
[23] O. Inomoto (private communication).