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Experimental Study of Traveling Waves and Target Patterns in Oscillatory Reacting Media

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Recent experimental work on is presented traveling waves and target patterns developing in oscillatory Belousov–Zhabotinsky reagents. It only deals with trigger waves and relaxation oscillations. Measurements have been made on (1) the dispersion relation of waves, (2) the statistical properties of centers and targets, (3) the wavefront and speed near the core of the pattern. Several unanticipated results are reported.

KEY WORDS: Dissipative structures; nonequilibrium behavior; chemical waves; target patterns; spatial self-organization; Belousov–Zhabotinsky reaction.

1. INTRODUCTION

Physicochemical phenomena were considered for years to proceed only monotonically in space and time, and it is true that inert matter behaves in this way most of the time, more precisely, as long as conditions are such that evolution takes place near equilibrium, where the minimum entropy production theorem[1] applies. However, nonequilibrium processes are especially interesting because nonlinearities may give rise to self-organization phenomena beyond some instability threshold of the so-called thermodynamic branch. The vivid phrase *dissipative structures* was coined by the Brussels school[2] for these ordered behaviors emerging far from equilibrium. In contrast with usual equilibrium structures, such crystals, their occurrence requires a continuous flux of energy and/or matter. Such structures were already known for decades: in hydrodynamics, for example, the Bénard cells discovered at the turn of this century. Nonetheless, extensive research in this field began to be undertaken in the course of the 1960s.

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Three events, among many others, have contributed to triggering great interest in these problems:

1. It was unambiguously established that dissipative structures are not ruled out by the second law, since Boltzmann's order principle is not relevant for open systems evolving away enough from equilibrium.[2]
2. Oscillations were clearly identified in metabolic pathways of living systems.[3]
3. Kinetic models were developed, which pointed out that coherent (or cooperative) behavior is a mere outcome of nonlinear differential equation sets.[4,5]

Whereas for transport processes linear laws are valid over wide ranges of forces, this domain is, on the contrary, very small when considering a chemical reaction. This is why chemical systems form the most privileged area for observing the self-organization of matter. The explored phenomenology already includes an impressive number of items: chemical oscillations, multistability of stationary as well as oscillatory states, chemical hysteresis, spatial *stationary* structures, chemical waves, etc.[6] Even the very existence of deterministic chaos, that is, a seemingly erratic temporal evolution that has nothing to do with randomness and can be fully described in terms of strange attractors, is firmly established today in chemistry.[7]

Taking an overview of the great deal of experimental data gathered on all these phenomena during the past 20 years, it is striking to note that quantitative reliable results about spatial structures and chemical waves are yet rather few.[8] This field of research hence deserves special effort if we intend to clarify the way spatial organization sets up in a chemical system. Among the consequences, one can hope to thus reach a deeper understanding of morphogenesis, for instance. Over the past few years we have undertaken systematic measurements on chemical waves propagating in an oscillatory reacting medium. The ferroïn-catalyzed Belousov–Zhabotinsky (BZ) reaction was chosen as the chemical oscillator. It indeed exhibits different kinds of wonderful patterns: expanding concentric rings (target) and rotating single-armed or multiarmed spirals. The results reported here only deal with trigger waves, which are the most easily observable, thanks to sharp concentration profiles. These waves should not be mistaken for kinematic waves or pseudowaves (which, strictly speaking, should not be called waves) or with phase diffusion waves predicted in 1973,[9] but observed only very recently.[10] Here the propagation mechanism involves mass diffusion of certain species across their concentration gradient to trigger the reaction ahead of the front.

All experiments have been carried out in thin layer geometry (1 mm depth or less) at room temperature. Only traveling waves giving rise to target patterns like those appearing in Fig. 1 were considered. The description of the apparatus, available elsewhere, will not be given in detail, so as to focus attention on the results themselves. Section 2 reports measurements of the dispersion relation of waves; this study was performed at Stanford, in collaboration with J. Ross, in the framework of a cooperative research program sponsored by the NSF and the CNRS. In Section 3 an extensive statistical study of target patterns and their properties is presented. It was primarily designed as a first attempt to catch up on information about wave birth in an oscillatory medium. As shown in Section 4, observation under à microscope still remains the most efficient

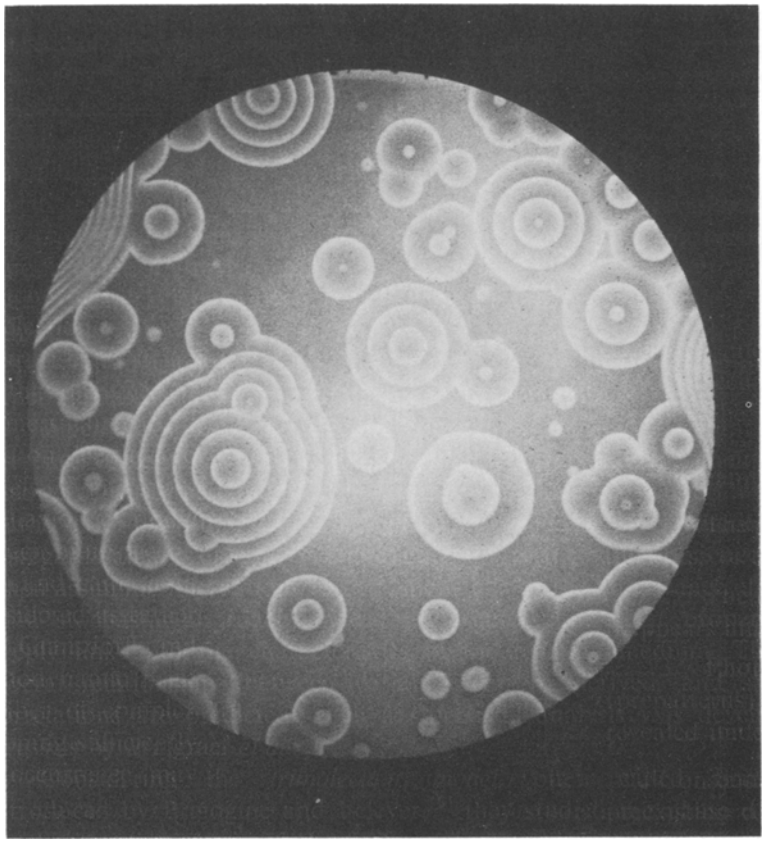

Fig. 1. Photograph of traveling waves organized in target patterns, observed in a thin layer of an oscillatory Belousov–Zhabotinsky reagent. (Picture CNRS-CRPP.)

way to watch what is happening close to the center of a target; it brings unanticipated results on the wave profile and speed near the core of the pattern.

2. MEASUREMENT OF DISPERSION RELATION

At room temperature (298 K), an oxidizing wavefront propagates through a reduced medium at a speed of typically 10^{-1} mm sec^{-1}. This wave velocity mainly depends on sulfuric acid and bromate concentrations; it is more or less insensitive to the catalyst concentration. The most frequently reported relationship has the form[11,12]

$$\text{wave velocity} \sim 0.45[H_2SO_4]^{0.5}\,[BrO_3^-]^{0.5}\ \text{mm sec}^{-1}\ \text{M}^{-1}$$

However, Kunhert and Krug[13] recently found that, under oscillatory conditions and with $Ru(bipy)_3^{2+}$ as catalyst, the dependence is different, and follows the empirical law

$$\text{wave velocity} \sim 4.8[H_2SO_4]^{1.26}\,[BrO_3^-]^{1.68}\ \text{mm sec}^{-1}\ \text{M}^{-2.94}$$

In the above-mentioned experiments, waves were periodically initiated in an excitable or, sometimes, an oscillatory medium by an external perturbation. No mention is made, however, of the influence of dispersion, which either was negligible or escaped attention. A thorough examination of the literature shows that dispersion does take place. In a one-dimensional geometry, Tatterson and Hudson[14] and later Sevcikova and Marek[15] observed a dependence of wave speed on the emission period. The first observation does not look reliable, because the velocity increases slightly with frequency. In the second, the velocity becomes smaller as the frequency grows, as one should expect. Unpublished results of Winfree going in the same direction are mentioned by Keener and Tyson.[16] Because of the need for a systematic experimental study of the dispersion relation, an experiment was recently undertaken at Stanford to collect quantitative data on this problem, taking advantage of the device originally developed by Wood and Ross.[12]

Samples of an oscillatory BZ medium were prepared at the following initial concentrations: H_2SO_4 0.2 M; $CH_2(COOH)_2$ 0.08 M; $NaBrO_3$ 0.31 M; ferroin 2×10^{-3} M. After an induction phase, the solution oscillates with a fairly constant period $T_0 = 110$ sec, during at least 15 min. A layer of 1 mm depth is poured into a Petri dish; an area of approximately 4 mm^2 is continuously irradiated with a laser beam ($\lambda = 488$ nm) whose power is adjustable. Light absorption by ferroin induces a local increase in temperature, which in turn shortens the period

of oscillation at this point. The pacemaker thus induced periodically emits a wavefront. By simply varying the light intensity of the beam, one can change the temperature shift and, consequently, the emission period. A Reticon system with 1024 photosensitive diodes is used to monitor the light transmitted by the solution (also at 488 nm), in order to accurately follow the motion of each front. Additional experimental details are given elsewhere.[17]

The main result of this experiment is displayed in Fig. 2. In this particular medium, the speed of the first oxidizing front is always close to 0.09 mm sec^{-1}. As long as the emission period remains greater than, say $\frac{1}{2}T_0$, the velocity of the second emitted front is very similar and therefore dispersion can be neglected. For shorter emission periods, the velocity clearly decreases with the number of the emitted front. As seen in Fig. 2, the velocity may even be reduced to 60 % of the *standard* value in the free medium, a very significant slowing down. Because trigger waves are reaction-diffusion phenomena, it is not very difficult to understand qualitatively the origin of such a decrease. Behind each front, the reacting solution relaxes toward its reduced stage, since the medium exhibits relaxation oscillations. However, the time necessary to reach that stage takes roughly one-half of the oscillation period T_0. If the next oxidizing wavefront is coming at shorter times, relaxation is incomplete, concentration gradients are less steep, and, consequently, the velocity is smaller. By continuity, one expects the velocity to decrease more and more as the distance between

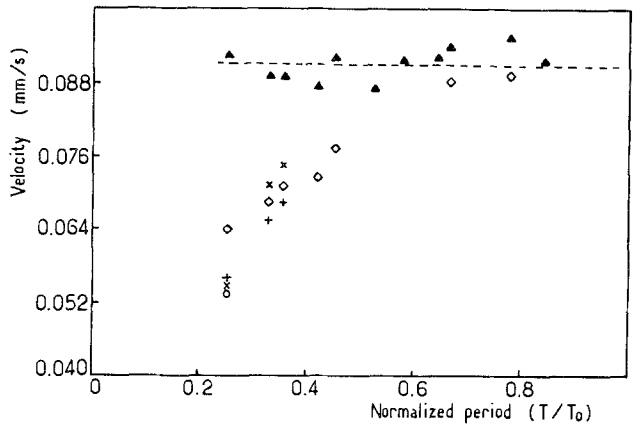

Fig. 2. Dispersion relation of trigger waves. The velocity of wavefronts depends on the period (normalized to the oscillation period T_0 of the solution) at which they are emitted, except for the first (dashed line). The successive fronts are: ▲ first; ◇ second; + third; × fourth; ○ fifth.

two fronts—that is, the emission period—diminishes. This prediction accounts for the trend of the dispersion relation in Fig. 2.[17] A quantitative explanation remains to be given, but none has been developed. The approach suggested by Keener and Tyson[16] on the basis of a two-variable model derived form the Oregonator appears to be the most promising one.

3. STATISTICAL STUDY OF TARGET PATTERNS

Target patterns such as those shown in Fig. 1 *spontaneously* appear in thin layers of excitable or oscillatory BZ reagents. If a reaction-diffusion theory provides a good framework to account for wave propagation,[18,19] the birth of the waves still remains a matter of guess—and of controversy. Puzzling questions include: (1) Does a target simply reveal a singularity of boundary conditions (e.g., dust particle in the solution, scratch at the surface of the dish) that cannot be observed otherwise? (2) Or does a symmetry-breaking actually takes place at the center? Furthermore, what king of fluctuation-nucleation mechanism would be involved, and how?

It is well known, of course, that external sources may act as pacemakers: wires, electrodes, and catalytic particles were, and still are, widely used to this end. The crucial point here deals with the very nature of the *spontaneous* centers. In short: are all these centers *heterogeneous*, or among them are at least a few *homogeneous*? No confident answer to the many questions raised by this astonishing behavior of a reacting medium can be given by metaphysical arguments about determinism and randomness. Only scientific work comparing theoretical predictions and experimental observations will enable us to settle the problem.

When *unknown* external conditions are invoked to account for the presence of centers, it is no longer possible to check experimentally the theory, because the conditions necessary to match the observations belong to the set of hypotheses. In a sense, any *heterogeneous-center* model simply disregards this problem.[19] Quite different is the situation encountered when assuming fluctuations to be responsible for the appearance of centers. In a stochastic approach, indeed, the centers and their properties are deeply linked to the characteristics of the reacting medium. Therefore, several relationships between variables can be derived, and statistical correlations are predicted. Such a stochastic analysis was developed in Brussels by Walgraef *et al.*[20]

Considering the *trimolecular model*, often called Brusselator, introduced by Prigogine and Lefever,[5] they studied the phase dynamics just beyond the subcritical Hopf bifurcation. In this oscillating regime, local fluctuations in the phase of the limit cycle may well give rise to local frequency shifts. For sufficiently large amplitudes, a pacemaker is thus

formed, wavefronts are emitted periodically, and a target builds up. The statistical distribution of these *homogeneous* centers depends on the parameters of the limit cycle (i.e., on the distance to the bifurcation point), and is also related to the wavelength of the target. In particular, the number of centers is predicted to be a monotonically decreasing function of the wavenumber. These conclusions are general and they do not depend crucially on the model itself. In fact, the two basic ingredients are the limit cycle behavior and the vicinity of a Hopf bifurcation. The last assumption, which is necessary for performing a complete analytical treatment, has an important consequence. The calculated isoconcentration lines correspond rather to phase diffusion waves, hardly observable,[10] whereas target patterns exhibited by BZ systems (see Fig. 1) are formed by trigger waves. This is not surprising at all, since visible target patterns appear in media that are either excitable or developing relaxation oscillations: in both cases very far from Hopf conditions. Despite this misfit, it seems nonetheless interesting to gather a large sample of experimental data on target patterns in order to tackle the problem of statistical properties.

To this end, an experimental apparatus especially designed to prevent as much as possible center formation by external sources has been built up. A circular reacting layer (1 mm depth, 100 mm diameter) is sandwiched between two plexiglass plates, and is illuminated from below. The layer is filmed at a speed of 25 images sec^{-1} with a tv camera and recorded on magnetic video tape. Later, certain carefully selected pictures are digitalized and analyzed with an automatic image-processing device connected to a VAX computer. An appropriate numerical treatment is performed to collect many relevant data on target patterns and their temporal evolution with a much better accuracy than that allowed by standard photographic techniques. Details on the tools and on the procedures are given in Ref. 21 and 22. From a general point of view, it is worth noting that only transients are observed. Indeed, the reacting medium cannot be renewed, because unavoidable convection would destroy the patterns: hence the need to choose initial chemical compositions exhibiting (almost) a limit cycle type behavior for a time if we intend to make a comparison with any of the available theoretical approaches. The results thus obtained with BZ systems[21] may be summarized as follows:

1. In excitable (not oscillatory) media, careful filtering of solutions completely suppresses target formation, as noticed earlier by Winfree.[23]
2. On the contrary, targets are still observed, whatever the cares taken, in certain oscillatory media, but not in all of them.

On one hand, the role of dust particles is undeniable. But on the other

hand, the influence of fluctuations is not at all ruled out, since they might be efficient in inducing a local desynchronization in an oscillating medium. Accordingly, two selected compositions having similar redox potential oscillation amplitudes but very different periods were studied in detail.[21] The statistical features and the mean properties of the observed patterns are the following (see numerical data in Table I):

1. The total number of centers, as well as the initial rate of center production, strongly diminish when the oscillation period T_s increases, as predicted by Walgraef *et al.*[20]
2. The percentage of centers grows with their emission period $T_{c,i}$, which always remains smaller than T_s. Experimental limitations rule out deciding whether this percentage diverges or, on the contrary, vanishes when $T_{c,i}$ comes close to T_s (see Fig. 3). Since almost all emission periods belong to the range $[T_s/2, T_s]$, dispersion can be further neglected, as shown in Section 2.
3. The percentage of targets is a nonmonotonic function of their wavenumber k_i; an unanticipated and yet unexplained maximum appears in the distribution (see Fig. 4).
4. Wave velocities exhibit a Gaussian-like distribution, with a standard deviation not exceeding 10% of the mean value (see Fig. 5 and Table I).
5. There is a linear relationship between the pulsation of a center $\omega_{c,i}$ and the wavenumber k_i of its target. The slope of the straight line passing

Table I. Experimental Conditions, Statistical Features, and Mean Properties of the Two Oscillating BZ Reagents Studied

Characteristic	Reagent A	Reagent B
$CH_2(COOH)_2$ (M)	0.08	0.08
$NaBrO_3$ (M)	0.31	0.31
Ferroin (M)	4×10^{-3}	4×10^{-3}
H_2SO_4 (M)	0.22	0.35
Redox amplitude (mV)	150	138
Oscillation period (sec)	139	63
Statistics: Centers	281	246
Targets	92	92
Total mean number of centers (cm^{-2})	0.13 ± 0.05	0.28 ± 0.05
Initial mean rate of center production ($cm^{-2}\,sec^{-1}$)	$8.5\ 10^{-4}$	$4.1\ 10^{-3}$
Mean wave velocity ($\mu m\ sec^{-1}$)	86 ± 9	103 ± 8
Slope (Fig. 4) ($\mu m\ sec^{-1}$)	84	102

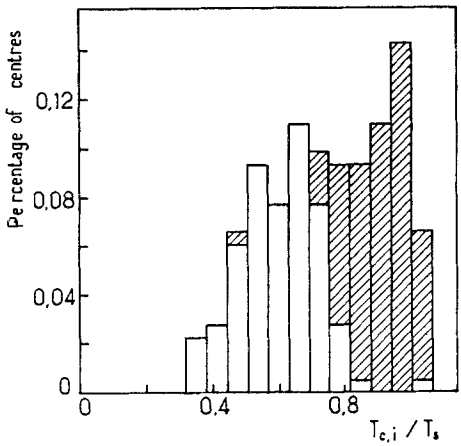

Fig. 3. Percentage of centers versus their emission period $T_{c,i}$ normalized to the oscillation period T_s of the medium. Dashed areas indicate single-ring patterns (disk); the others correspond to true targets.

through the origin (see Fig. 6) is equal to the mean value of the velocity distribution (see Table I). This is a very simple but meaningful test of the self-consistency of these measurements.

6. The loci of the centers are well scattered over all the observation cell (see Fig. 7). A few accumulation points might be due to surface defects. Nonetheless, the above-mentioned statistical features are kept the same when reanalyzing the data without taking into consideration the corresponding targets.

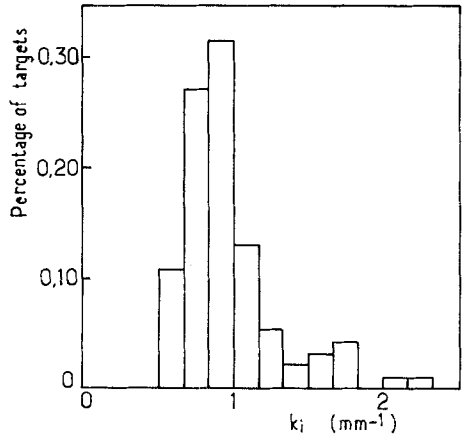

Fig. 4. Percentage of targets versus their wavenumber k_i. Of course, a disk has no wavenumber; the statistical sample is thus different from that involved in Figs. 3 and 5.

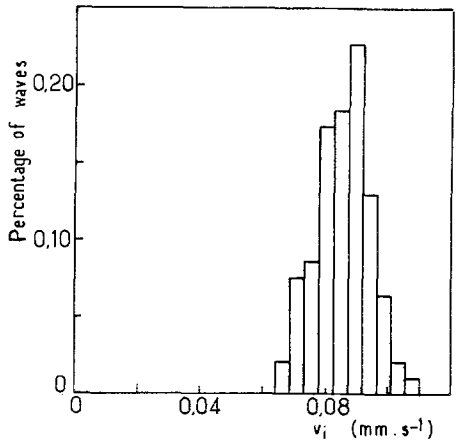

Fig. 5. Percentage of wavefronts versus their velocity v_i, showing the Gaussian-type distribution.

The uniqueness of the wave velocity thus clearly established in oscillatory solutions should not be so difficult to explain. As a matter of fact, a similar result was previously noticed in excitable media[11] and a theoretical account has been given in that case. Its main ingredient is a reduction of the modeling equations to a one-variable problem. Then, in a reference frame moving at velocity v, a planar traveling wavefront is solution of a differential equation cast in the form

$$C''_{zz} + vC'_z + f(C) = 0$$

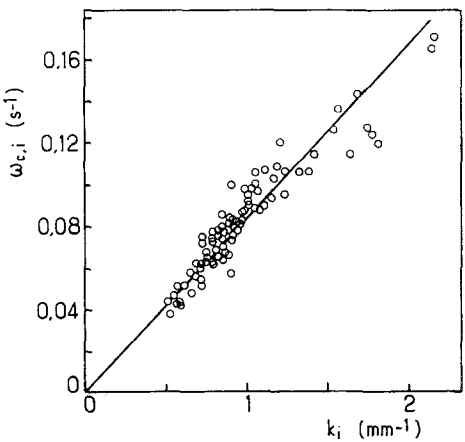

Fig. 6. Observed linear relationship between the pulsation $\omega_{c,i}$ of a center and the wavenumber k_i of the corresponding target. The slope of the straight line passing through the origin is exactly equal to the mean velocity measured in Fig. 5. See numerical values in Table I.

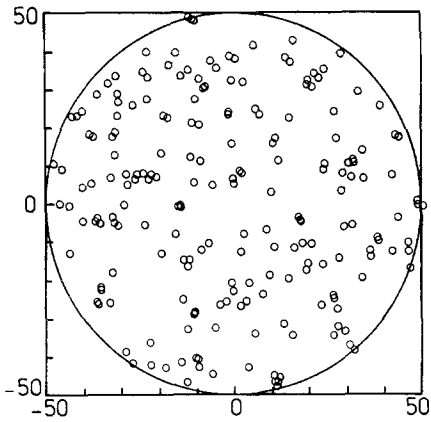

Fig. 7. Spatial distribution of center loci within the cell (100 mm in diameter). Accumulation points are rather few.

where $z = x - vt$ (x is the one-dimensional spatial coordinate); $C(z)$ is the concentration profile; and $f(C)$ is the chemical reaction term.

One must determine the solutions $C_v(z)$ of this equation, i.e., solve an eigenvalue problem, known for many years because the same equation is derived in different fields, such as biology or combustion.[18] Depending on the characteristics of the function $f(C)$, either a single eigenvalue v exists or a whole spectrum of eigenvalues with a lower boundary which is physically selected. Though a general analytical derivation has not yet been set up, one can reasonably think that the same kind of interpretation is still relevant in the presence of relaxation oscillations, provided the distance between consecutive wavefronts is sufficiently large.

Another observation whose explanation seems much less easy to work out is the wavenumber distribution (Fig. 4). Unless we ascribe its origin to *unknowable* boundary conditions, an understanding of the presence of a maximum remains to be found.

This statistical study eventually leaves unsolved the problem of the very existence of some *homogeneous* centers, whatever the new and reliable experimental data gathered. Further improvement of our knowledge requires that a stochastic description, not restricted to the vicinity of a Hopf bifurcation, be fully developed.

4. WAVE PROFILE AND SPEED NEAR THE CORE OF A TARGET

It is amazing to note how sparse the experimental data are on wavefront morphology. Wood and Ross[12] were the first to measure a wave profile (in an excitable BZ reagent), and Müller *et al.*[24] studying the

core of a spiral, were able to determine an upper limit of its diameter, namely 30 μm. In a theoretical analysis based on a simplified and suitably scaled version of the Oregonator, Keener and Tyson[16] reached the conclusion that a circular front cannot propagate outward when its initial radius is smaller than, say, 20 μm. It is therefore tempting to watch with a microscope what is happening at the center of a target and around it. Putting together an inverse microscope, a tv camera, an image-processing device, and a computer led recently to the results displayed in Figs. 8 and 9.[25] The reagent is again an oscillatory BZ solution, very similar to those previously used: H_2SO_4 0.5 M; $CH_2(COOH)_2$ 0.5 M; $NaBrO_3$ 0.31 M; ferroin 4×10^{-3} M. At room temperature the oscillation period is approximately 20 sec. An example of a three-dimensional perspective representation of light absorption in a thin layer (depth 0.7 mm) is given in Fig. 8. The oxidizing wavefronts, which correspond to the transition $Fe^{2+} \rightarrow Fe^{3+}$, move from right to left. Clearly the innermost has a smaller amplitude than the two others. The small volcanoes are nothing but CO_2 gaseous bubbles produced by the reaction. Quantitative measurements performed on a sequence of 20 images, taken at 1-sec intervals, yield the plots of Fig. 9. The variations of three important properties of a front with the distance from the center are shown. A really unanticipated result is the monotonic, quasilinear increase of the height (difference in gray levels between the bottom and the top of the front) prior to saturation at about 1.8 mm from the center (Fig. 9a). The width does not exhibit the same trend; its mean value is equal to 88 ± 16 μm (Fig. 9b). From this measurement one can figure out for the first time an order of magnitude for the ferriin concentration gradient across the front: 10^{-2} M mm^{-1} once the

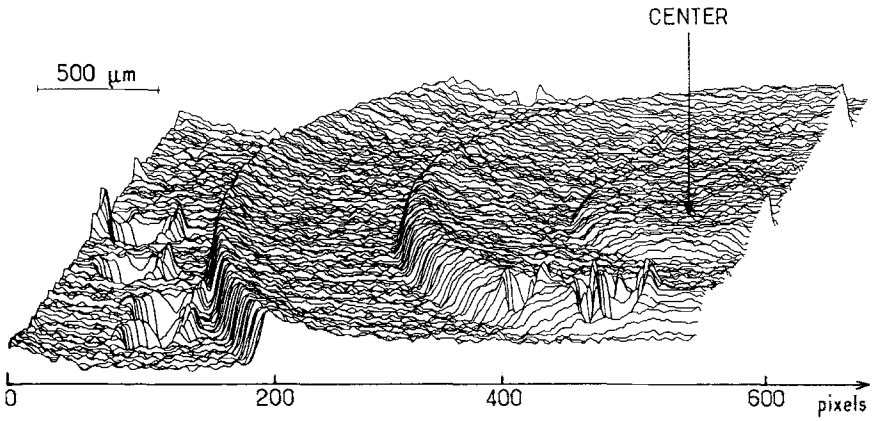

Fig. 8. Three-dimensional perspective representation of light absorption near the core of a target (compare with Fig. 1). Three rings are seen, and no heterogeneity is visible right at the center.

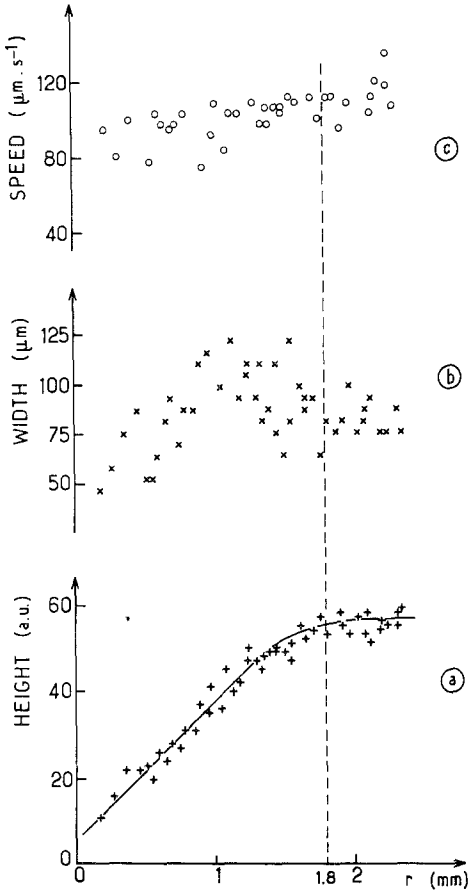

Fig. 9. Variation of the oxidizing wavefront properties as a function of the distance from the center: (a) height; (b) width; (c) speed.

full amplitude is reached. Another unexpected observation is the slight, but significant increase of the front velocity; something around 15%.

At the magnification used (5.57 μm per pixel), which is far above the limit of the device (~ 1 μm per pixel), nothing is seen right at the center. This one might well be homogeneous, although the presence of a very small heterogeneity is not precluded at all. In contrast, however, we are currently watching other targets whose center is undoubtedly heterogeneous; their behavior near the core is noticeably different.[26]

5. CONCLUDING REMARKS

A large amount of work must still be carried out before we get a satisfactory knowledge of self-organization phenomena. This article

presents a small sample of the research in progress. Looking back at the past 20 years, we can see the great strides already made. What a long journey since 1968 and the Brusselator! At the same time we realize how seminal have proved to be such concepts as nonequilibrium as a source of order, coherent behavior, dissipative structure,... .

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