# Reports

# Curvature and Propagation Velocity of Chemical Waves

## Petra Foerster, Stefan C. Müller, Benno Hess

The collision of circular chemical waves in an excitable medium, the Belousov-Zhabotinskii reaction, leads to characteristic cusplike structures. The high curvatures of these structures are especially suitable for experimentally verifying the predicted proportionality between the velocity and the shape of traveling waves. A computerized spectrophotometric video technique with microscopic resolution was used to determine the proportionality factor ( $2 \times 10^{-5}$  square centimeter per second), which in this case is the diffusion coefficient of the autocatalytic species of the reaction system. A numerical calculation of the spatiotemporal evolution of the cusp structure is in good agreement with the experimental observations.

PATIAL AND TEMPORAL ORGANIZAtion, which is characteristic of biological processes, is also found in simpler chemical and biochemical systems maintained far from thermodynamic equilibrium. The most extensively investigated chemical system that displays spatiotemporal patterns is the Belousov-Zhabotinskii (BZ) reaction (1), in which malonic acid is catalytically oxidized and brominated by acidic bromate. This reaction exhibits temporal oscillations and spatial waves (2, 3). We report here measurements of the relation between the curvature and velocity of wave fronts. This relation, together with the dispersion relation of wave propagation, forms the basis for modeling spiral-shaped waves (4, 5), which are frequently observed in the BZ reaction (6).

The oscillations of this reaction can be described by the so-called Field-Körös-Noyes mechanism (7). For theoretical calcu-



**Fig. 1.** Hyperbolic fit to the cusp structures. The pixel resolution of the experimental data is  $4.5 \,\mu$ m per pixel. The hyperbola is drawn with its asymptotes and the real axis.

lations, the reaction is often modeled by the simplified Oregonator, which includes only the five most important reaction steps derived from this mechanism and involves three independent chemical variables (8). If one intermediate ( $w = [Br^-]$ ) is in quasiequilibrium, the resulting system of rate equations for the autocatalytically produced species  $u = [HBrO_2]$  and the oxidized form of the catalyst v = [ferriin]. After these equations have been supplemented by appropriate diffusion terms, reaction-diffusion equations for the modeling of waves can be written in the following form (9):

$$\epsilon \frac{\partial u}{\partial t} = \epsilon D \nabla^2 u + u^2 - f v \frac{u - q}{u + q}$$

$$\frac{\partial v}{\partial t} = D' \nabla^2 v + u - v$$
(1)

where  $\epsilon$ , f, and q denote scaling parameters, which are introduced by the transformation to dimensionless equations, as specified in (9); D and D' are the diffusion coefficients of the respective species; and t is time.

Because  $\epsilon$  is a small positive parameter, one can treat Eqs. 1 by using singular perturbation arguments. These arguments reveal that a wave form consists of two typical regions: narrow regions in which there are sharp gradients of u (thin boundary layers) and broad regions in which u varies slowly in space. After the variables have been changed into a coordinate system in which one of the coordinate axes moves with the wave front of the boundary layer, the time derivative in the partial differential equation can be expressed in terms of the normal velocity N, and the Laplacian operator can be expressed in terms of the curvature K of the front. The quantities N and K are related to each other by an equation that describes the temporal and spatial development of a specific isoconcentration level (4, 5, 10, 11), in explicit form:

$$N = c - DK \tag{2a}$$

or, in detail:

$$\frac{\partial \gamma/\partial t}{\left[1+\left(\frac{\partial \gamma}{\partial x}\right)^2\right]^{1/2}} = c - D \frac{\partial^2 \gamma/\partial x^2}{\left[1+\left(\frac{\partial \gamma}{\partial x}\right)^2\right]^{3/2}}$$
(2b)

where c is the velocity of plane waves and D is the diffusion coefficient of the autocatalytic species.

The main statements of Eq. 2 are that for negative curvature N increases, and for positive curvature N decreases with increasing K. Furthermore, there is a minimum radius below which propagation will not take place.

In order to verify Eq. 2 experimentally, we measured the temporal evolution of cusplike structures that form after the collision of two circular waves. From these structures one can obtain areas of extremely high curvature in a reproducible fashion. Furthermore, we solved Eq. 2 numerically and compared the solutions with our experimentally determined shapes of wave cusps.

The reaction solution was prepared as described in (12). A pair of circular chemical waves was initiated by immersing two silver electrodes (diameter, 100 µm) at a distance of  $\simeq 4$  mm with a micromanipulator. We investigated the propagation of the waves and the evolution of the cusplike structures that formed after collision by applying spectrophotometric microscope video imaging techniques (13). The velocity of the waves was determined with a timer that marked every video picture (time resolution, 40 ms). A comprehensive software package (14) allowed smoothing of the image with a moving average over a  $3 \times 3$  pixel area and calculation of isoconcentration levels. Our analysis focused on the edge of the cusplike structures at the points of steepest gradients of the catalyst ferroin.

The data measured in the area of the colliding waves were fitted simply by a hyperbola (Fig. 1) given by the coordinates of the two foci and the distance between focus and vertex. We determined the best fit of a hyperbola to all data points  $(X_i, Y_i)$  by minimizing the sum of the products of weighting factors and projections onto branches of the hyperbola. The weighting factors were chosen to be inversely propor-

Max-Planck-Institut für Ernährungsphysiologie, Rheinlanddamm 201, D-4600 Dortmund 1, FRG.

tional to the number of neighbors of the data points. They were introduced because the density of the points in a contour map varies considerably owing to differences in concentration gradients at the edges of the cusps (see Fig. 2).

From the best fits the curvatures in the vertices were determined on the basis of  $K = a/b^2$ , where *a* is the real half-axis and *b* is the imaginary half-axis of the hyperbola. The propagation velocity of the cusps was calculated along the line connecting the vertex points in the successive contour maps, where it is equal to the normal velocity. The propagation velocity of plane waves was obtained from the outward motion of very large circular waves, where curvature effects can be neglected.

A typical sequence of contour maps of the cusp structures is shown in Fig. 2, A through C. In order to depict the further evolution of the cusp structures, a set of several successive contour maps was extracted from images with a lower magnification (Fig. 2D). Curvature and velocity data were calculated from such contour maps (Fig. 3). The measured value of c was 95  $\pm$  5  $\mu$ m/s (SD). For the data obtained from measure-

ments with lower spatial resolution (diamonds in Fig. 3) the slope of the regression line was determined with a least-squares fit,  $(1.996 \pm 0.07) \times 10^{-5} \text{ cm}^2/\text{s}.$ 

From the numerical solution of the partial differential equation Eq. 2b, one can determine the behavior of the curvature as a function of time. Taking into account that the rate of change of curvature becomes very fast when a front is highly bent, we found that the determination of the corresponding velocity, because of our limited temporal resolution of 25 pictures per second, becomes more faulty. Furthermore, the temporal resolution of fast processes is limited by the lag time of the camera. For these reasons we used only the data with lower spatial resolution up to a curvature of 0.6/  $\mu m$  (see Fig. 3) to estimate the slope of the regression line.

Using the experimentally determined values for *D* and *c*, we solved Eq. 2b numerically by expressing the partial derivative by difference terms. The initial geometry is that of two quarter circles, which represent the two colliding circular waves. (The radius  $R = 1900 \ \mu m$  of the colliding waves was determined from the experimental data.) Figure 4A shows the spatial change of the structure as a function of time. A direct comparison of the experimental with the numerically determined contour maps (Fig. 4B) shows a remarkably good agreement within the experimental inaccuracies, not only for the shape of the cusp but also for



Fig. 3. Relation between curvature and normal velocity determined from cusp structures with a spatial resolution of 4.5  $\mu$ m (diamonds) and 0.7  $\mu$ m (triangles) per pixel. The slope of the regression line is  $\approx$ 1996  $\mu$ m/s<sup>2</sup>; intercept, 95  $\mu$ m/s.

1900 *X* -axis/μm

3000

7000 mµ/sixe-Y

1000

0

480

405

330

180

105

30 105 180 255

(ləxid) 7 (bixel)

0

A

3800

в



**X**(pixel) **Fig. 4.** (**A**) Numerical solution of Eq. 2b at equidistant time intervals using the experimentally determined parameters for *D* and *c*. (**B**) Superposition of the numerically calculated contour maps (continuous lines) and the experimentally determined cusp structures (dots). The resolution is 4.5  $\mu$ m per pixel; the time interval between successive calculated contour maps, starting at t = 0, is 0.4 s. Experimental data were taken at t = 0.52, 1.96, and 4.2 s.

330 405 480

**Fig. 2.** (A through C) A sequence of experimentally determined cusp structures. The spatial resolution is 0.7  $\mu$ m per pixel; the time interval between (A) and (C) is  $\approx$ 0.1 s. (D) A montage of several successive contour maps. The spatial resolution is 4.5  $\mu$ m per pixel; the time interval of the whole sequence is  $\approx$ 5 s.

the temporal evolution.

Our measurements were made to verify the theoretical relation (2) between normal velocity and curvature. The experimental data yield a diffusion coefficient,  $2 \times 10^{-5}$  $cm^2/s$ , which is a good approximation of the diffusion coefficient of the autocatalytic species HBrO<sub>2</sub> and is comparable to the values given in (15, 16),  $D_{\text{KClO}_4} = 1.79 \times 10^{-5}$  $cm^2/s$  (17, 18).

#### **REFERENCES AND NOTES**

- 1. R. J. Field and M. Burger, Eds., Oscillations and Traveling Waves in Chemical Systems (Wiley-Interscience, New York, 1985).
- C. Vidal and P. Hanusse, Int. Rev. Phys. Chem. 25, 1 (1986).
- 3. J. Ross, S. C. Müller, C. Vidal, Science 240, 460 (1988)
- 4. J. P. Keener and J. J. Tyson, Physica 21D, 307 (1986).
- 5. J. P. Keener, Soc. Ind. Appl. Math. J. Appl. Math. 46, 1039 (1986).
- 6. A. T. Winfree, Science 175, 634 (1972) 7. R. J. Field, E. Körös, R. M. Noyes, J. Am. Chem.
- Soc. 94, 8649 (1972) 8. R. J. Field and R. M. Noyes, J. Chem. Phys. 60, 1877 (1974).
- 9. J. J. Tyson, in (1), pp. 93-144.
- 10. V. S. Zykov, *Biophysics* **25**, 329 (1980). 11. \_\_\_\_\_, *ibid.*, p. 906.
- 12. The mixture contains 48 mM sodium bromide, 340 mM sodium bromate, 95 mM malonic acid, and 380 mM sulfuric acid. A few minutes after these components are mixed the solution becomes colorless. Then ferroin is added (final concentration, 3.5 mM). This solution (3.6 ml) is transferred to an optically flat petri dish. The resulting thickness in the observation area of the dish is 0.5 to 0.6 mm. The measurements were performed at room temperature  $(24^\circ \pm 1^\circ \text{C})$  [S. C. Müller, Th. Plesser, B. Hess, Science 230, 661 (1985)].
- 13. The sample layer is illuminated with diffuse light filtered with an interference filter of 490-nm peak transmittance, which corresponds to the maximum absorption of the catalyst ferroin. An inverse microscope is connected to a video camera with an image raster resolution of  $512 \times 512$  picture elements. The maximum resulting resolution is 0.7 mm per picture element. Either single images with an intensity resolution of 256 gray levels at 2-s intervals or video movies with reduced spatial and intensity resolution at a frequency of 25 images per second can be recorded [S.C. Müller, Th. Plesser, B. Hess,
- Anal. Biochem. 146, 125 (1985)].
  14. S. C. Müller, Th. Plesser, B. Hess, Naturwissenschaften 73, 165 (1986).
- 15. L. Kuhnert, H.-J. Krug, L. Pohlmann, J. Phys. Chem. 89, 2022 (1985)
- 16. R. J. Field and R. M. Noyes, J. Am. Chem. Soc. 96, 2001 (1974).
- 17. R. C. Weast, Ed., Handbook of Chemistry and Physics (CRC Press, Boca Raton, FL, ed. 60, 1979), p. F-62
- 18. So far, we have confirmed the predicted relation (2) by observing areas of high negative curvature. Work s in progress to investigate propagating waves with high positive curvature to provide evidence for the predicted decrease is velocity due to the increase in curvature and to establish the existence of a minimum radius necessary for the onset of outward propagation of circular waves. With our data for D and c, this minimum radius is estimated to be 20 um.
- Fruitful discussions with J. J. Tyson and Zs. Nagy-Ungvarai are acknowledged. We thank U. Heidecke for laboratory assistance, K.-H. Müller for help with the computations, and A. Rohde for typing the manuscript. Supported by the Stiftung Volkswagenwerk, Hannover.

9 March 1988; accepted 6 June 1988

5 AUGUST 1988

## July Temperatures in Europe from Pollen Data, 6000 Years Before Present

### BRIAN HUNTLEY AND I. COLIN PRENTICE

Mean July temperatures across Europe 6000 years before present were reconstructed from palynological data by the transfer function method. Reconstructed summer temperatures were warmer than those at present over most of Europe with the greatest heating, more than 2°C, in the midcontinent and the far north. This pattern is explained by high summer insolation and a weak zonal insolation gradient 6000 years before present and the effective heating of the landmass relative to ocean and coastal areas. A strong land-sea pressure gradient may in turn have increased westerly air flow into southern Europe, which is consistent with cooler reconstructed summer temperatures in the Mediterranean region, and reduced the environmental lapse rate in the central European mountains.

APS BASED ON THE CHANGING relative abundances of taxa in fossil pollen records have shown that continental-scale vegetation patterns responded in a coherent way to long-term climatic changes during the past 10,000 to 20,000 years (1-4). In this report we use transfer functions, as developed by Webb and co-workers (5-8), to reconstruct mean July temperatures for 6000 years before present (B.P.) from European palynological data (1). Our study is part of the Cooperative Holocene Mapping Project (COH-MAP), in which paleoclimate reconstructions based on palynological and other geological evidence (4-7, 9) have been compared to atmospheric general circulation model (GCM) simulations with global boundary conditions (insolation, ice sheets, sea-surface temperatures, and CO<sub>2</sub>) appropriate to past times (10, 11).

The mean annual temperature gradient in Europe trends north-south, paralleling the gradient of annual insolation. The prevailing westerlies superimpose an east-west temperature and precipitation gradient with cool summers, warm winters, and high pre-

B. Huntley, Department of Botany, University of Dur-ham, Science Laboratories, South Road, Durham, DH1 3LE, England. I. C. Prentice, Institute of Ecological Botany, Uppsala University, Box 559, S-751 22 Uppsala, Sweden.

Fig. 1. Surface pollen samples used in the transfer function equations and calibration regions. Subregion 1 represents the gradient from Mediterranean sclerophyll vegetation through mixed-deciduous forest, bounded by the 17.5°C July isotherm. Subregion 2 represents the gradient from mixed-deciduous forest through northern/montane boreal forest and lies between the 17.5°C and 13.5°C July isotherms, excluding montane regions south of 51°N and the oceanic region west of the -4.5°C January isotherm. Subregion 3 represents the gradient from continental to oceanic boreal and mixed-deciduous forest and extends from the 13.5°C July isotherm to the Norwegian coast, including southern Norway west of 10°E but excluding northern Fennoscandia east of 18°E. Subregion 4 represents the gradient from boreal forest through subarctic Betula forest and extends east of 18°E from the 13.5°C July isotherm to the 11.5°C July isotherm, the approximate northern limit of Pinus. Subregion 5 represents the



gradient from mixed-deciduous forest south of 51°N upwards from 17.5°C through the montane forest belts. Subregion 6 represents the same July temperature range as subregion 2, west of the -4.5°C January isotherm but excluding the most oceanic area in southern Norway. Subregion 7 represents the gradient north of the 11.5°C July isotherm from sub-arctic forest to shrub-tundra on the Arctic coast.