Chemical waves in inhomogeneous media with circular symmetry

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\textbf{Abstract}

Wave propagation in ring shaped excitable medium having inhomogeneity with circular symmetry is studied experimentally, theoretically and with numerical simulations. Geometrical wave theory is used to determine the front shape from the propagation velocity function. An open reactor is constructed to study the propagation of chemical waves experimentally in an inhomogeneous Belousov–Zhabotinsky excitable media. The shape of the rotation invariant front is determined and a software is developed to determine the local propagation velocity. The invariant front shapes are compared with simulation results based on the geometrical wave theory.

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1. Introduction

Waves of excitation are widely studied in chemistry\textsuperscript{[1–7]} and in biology\textsuperscript{[8–10]}. They can propagate through different biological or chemical excitable media. To describe the evolution of such waves, the system can be modelled with cellular automata\textsuperscript{[11]} or by reaction–diffusion equations\textsuperscript{[12]}, but they can be also treated by the simple geometrical wave theory constructed by Wiener and Rosenblueth\textsuperscript{[13]}. They studied wave propagation in the heart and suggested that the circular movement of the waves around an obstacle in the heart is responsible for the atrial flutter. Fibrillations and flutters in the heart are still heavily researched\textsuperscript{[14,15]} and their model is generalised for wider usage\textsuperscript{[16]}.

Here we report an experimental technique to investigate wave propagation in an inhomogeneous Belousov–Zhabotinsky excitable media. The shape of the rotation invariant front is determined and a software is developed to determine the local propagation velocity. The invariant front shapes are compared with simulation results based on the geometrical wave theory.

2. Theory

To describe the time evolution of chemical wavefronts the geometrical wave theory\textsuperscript{[17]} is a useful and simple tool. In this theory the well-known concepts (fronts and rays) and the basic principles (Fermat’s principle of least propagation time, Huygens’ principle) of the geometrical optics are used. The main difference between geometrical wave theory and geometrical optics is that diffraction occurs in the former one only. The fronts in the geometrical wave theory encircle the obstacles during their evolution (perfect diffraction), but in geometrical optics the obstacles have sharp shadow zones due to the absence of diffraction\textsuperscript{[17]}.

If an initial front and the propagation velocity as a function of space are given, the evolution of the fronts can be described quantitatively with the Eikonal equation\textsuperscript{[18]}:

\begin{equation}
(\nabla S(r))^2 = \frac{1}{v(r)^2},
\end{equation}

where \( v(r) \) is the propagation velocity and \( S(r) \) is the eikonal. The fronts are the level surfaces of the eikonal, and \( S(r) = 0 \) means the initial front. This equation is equivalent to the Fermat’s principle of least propagation time\textsuperscript{[18]}.

2.1. Stationary fronts in a medium with circular symmetry

Let us consider a rotating front in a ring shaped medium with circular symmetry with boundaries \( r_1 < r_2 \), where the velocity is the function of the radius and \( v(r) > 0 \). For a constant velocity function it is proved that the shape of any initial front evolves to a stationary one, which is then preserved during rotation\textsuperscript{[19]}.

Assuming it is true for any \( v(r) \) velocity function, the shape of the stationary front can be determined. The condition for a front being stationary is:

\begin{equation}
\varphi(r) = f(r) + S_0 \theta,
\end{equation}

where \( \varphi(r) \) is the front in polar coordinates, \( f(r) \) is the shape function, \( S_0 \) denotes the angular velocity of the front, and the eikonal \( S \) is equivalent to the time. Because of the circular symmetry the polar coordinate form of the Eikonal equation is used:

\begin{equation}
\frac{(\partial S}{\partial r})^2 + \frac{1}{r^2} \left( \frac{\partial S}{\partial \varphi} \right)^2 = \frac{1}{v(r)^2}.
\end{equation}
Substituting $S$ from (2) the first derivative of the stationary front can be obtained:

$$f'(r) = \pm \frac{1}{2} \sqrt{\frac{\omega_0 - \frac{v^2}{r^2}}{r^2}}$$  \hspace{1cm} (4)$$

For stationary shape the following conditions should hold: $f'(r_1) > 0$, $f'(r_2) < 0$ and $f'$ is continuous [20], so there exists an $r_0$, where $f'(r_0) = 0$. Furthermore from (4) $\omega_0 > \max(v(r)/r)$, thus $\omega_0 = \max(v(r)/r) = v(r_0)/r_0$, assuming the $v(r)/r$ angular velocity has only one maximum. Consequently, if $r < r_0$, then $f' > 0$; and if $r > r_0$, then $f' < 0$. The circle with radius $r_0$, where the angular velocity has maximum is the so-called ‘minimal loop’ [21]. The shape of the front is the integral of $f'$:

$$f(r) = \int_{r_1}^{r} f'(\rho) d\rho + \phi_0.$$  \hspace{1cm} (5)$$

Fig. 1 shows an example where the velocity function consists of two constant segments (with velocities $v_1 \leq v_2$) and a linear segment in region $r_1 < r < r_4$. Similar velocity functions are expected from our experimental setup. The stationary fronts are calculated from (4) and (5) numerically. If $v_2/v_1 < r_4/r_1$, then the minimal loop is $r_1$ (as in the case of homogeneous medium), otherwise the minimal loop is $r_4$. So by increasing $v_2/v_1$ or decreasing $r_4/r_1$ the qualitative shape of the fronts can be changed.

3. Experimental

The reactor setup is shown in Fig. 2. The waves appeared in the membrane ring containing the catalyst and fed through the gel pieces with solutions ‘slow’ and ‘fast’ circulated in the bottom channels.

3.1. Solutions

Stock solution. 5 ml of 4 M malonic acid, 10 ml of 2 M NaBrO$_3$, 10 ml of 1.53 M NaBr and 10 ml of 5 M sulfuric acid were mixed in a 100 ml flask and the flask was closed to prevent the escape of the developing bromine. After 30 min 50 ml of 1.2 M ammonium–sulfate was added and the flask was filled up to 100 ml with distilled water.

‘Slow’ (inner) solution. 0–16 g ammonium–sulfate was added to 50 ml of the stock solution to decrease H$^+$ concentration resulting in a lower propagation velocity.

‘Fast’ (outer) solution. 0–4 ml 5 M sulfuric acid was added to 50 ml of the stock solution to increase H$^+$ concentration resulting in a higher propagation velocity.

3.2. Preparation of reinforced gel slabs

The ring and disc shaped gel slabs (Fig. 2) were made of acrylamide. To reinforce the gel slabs, Aerosil (Wacker HDK T 30) was added and polyethylene mesh (thickness: 0.6 mm, mesh size: 1 mm) was fixed into the gel. Before the gelation, mesh pieces were prepared corresponding to the required gel slabs.

To produce the gel slabs an aqueous solution containing 16 wt% acrylamide, 0.8 wt% $N,N'$-methylene-bis-acrylamide and 0.8 wt% trietanolamine was prepared (‘acrylamide solution’). 30 ml of it

![Fig. 1](image1.png)

**Fig. 1.** (a) Examples for $v(r)$ velocity functions and (b) the corresponding shapes of the fronts. The position of the minimal loop is determined by the ratio of the velocities $v(r_1)$ and $v(r_2)$.  

![Fig. 2](image2.png)

**Fig. 2.** The reactor setup. Stationary concentrations are maintained in the gels by circulating ‘fast’ and ‘slow’ solutions in the channels below. By applying different H$^+$ concentrations in the inner and outer gel, a linear H$^+$ profile is expected between them, resulting in a non-homogeneous continuous $v(r)$ velocity function. $r_2 = 23.5$ mm, $r_4 = 17$ mm, $r_3 = 7$ mm and $r_1 = 5$ or 7 mm.
was mixed with 30 cm$^3$ of Aerosil. To initiate gelation 5 drops of 20 wt% ammonium peroxodisulfate aqueous solution was added and it was poured on ring and disc shaped polyethylene meshes on a glass plate. To produce gel slab with uniform thickness another glass plate was placed on the top of the gel with 1.7 mm spacers. After the gel formation the glass plates were removed, the gelled polyethylene mesh was washed with distilled water (to remove acrylamide monomers) and the meshed regions were cut out to get the ring and the disc. It is worth to mention that the gelation time can be controlled with the amount of ammonium peroxodisulfate added and takes longer time if the solution contains Aerosil. In our case, without additional Aerosil the gelation took place within 5–10 min, while with Aerosil added, this time grew up to several hours. The gel formation can be monitored visually to check if it has finished. We did not find any effect of the gel preparation on the experiments.

3.3. Preparation of the gelled membrane

A dry polysulphone membrane disc (GelmanSciences, Tuffryn Membrane filter, diameter 47 mm, pore size 0.45 μm) was dipped into acrylamide solution for some minutes, then it was placed on the glass plate, 10–15 ml acrylamide solution with 5 drops of 20 wt% ammonium peroxodisulfate was poured on it, and an other 1 cm thick glass plate was placed on the top. After the gel formation the result is a thin gel layer on the surface of the membrane disc.

3.4. Preparation of the membrane with catalyst

A dry polysulphone membrane disc was dipped into a solution of 50 mg bathophenantroline dissolved in 5 ml glacial acetic acid for 5 min [22]. Then it was placed into 0.01 M iron(II)-ammonium–sulfate solution prepared with 0.1 M sulfuric acid for another 5 min. This procedure can be adopted to reuse membranes with catalyst.

3.5. Reactor

The gel disc soaked with the ‘slow’ solution and the gel ring soaked with the ‘fast’ solution were placed into the reactor. The corresponding solutions were circulated in the channels to maintain the concentrations in the gels stationary. We used a slightly lower hydrostatic pressure in the channels than the atmospheric pressure which fixed the gels firmly to the top of the channels. The gelled membrane soaked with ‘slow’ solution was placed on the top of the gels. After 1–2 h the membrane with catalyst was dipped in the ‘slow’ solution, wiped off and placed on the top. The rotating waves were started with a silver wire and part of them was cleared with an iron clip. Finally, the reactor was covered with a glass plate to prevent evaporation.

3.6. Determining the local propagation velocity

The wave propagation was monitored by a camera connected to a computer. Pictures were taken in every 30 s. To detect the fronts in the $n$th image, the $n$th image was subtracted from the $(n + 1)$th image and the Canny edge detection operator [23] was applied on the result of the subtraction. With edge detection the fronts from both images can be detected, but the fronts from the $(n + 1)$th image would be too noisy, so the parameters of the Canny operator were chosen such a way to detect the fronts only from the $n$th image.

Each point of a front moves with the local velocity along the ray that is perpendicular to the front, so the local velocity is approximately proportional to the distance $(\Delta s)$ of the fronts from two subsequent images $(n$ and $n + 1)$: $v = \Delta s/(t_{n+1} − t_n)$. Quadratic polynomials were fitted locally to the measured points of the fronts, so the fronts were smoothed and the direction of the local move was calculated from the derivative of the fitted polynomial.

The computed local velocities were assigned to the pixels of a velocity map using the following interpolation procedure. Velocity values calculated from two subsequent fronts were assigned to the midpoint of the ray segments perpendicular to the front. The velocity values between two subsequent midpoints were calculated using linear interpolation. If the value at a given point was computed more than once, then the average value was assigned. Velocity values of points with yet unassigned one were calculated from the averages of their neighbours.

Due to the polynomial fit the procedure is inaccurate at the end of the fronts, therefore the velocity was not computed at the boundary region of the medium.

3.7. Quantifying deformations in the fronts’ shape

While a perfect angular symmetry was assumed in the theory there were clear deviations from that in the experiments as velocity maps in Fig. 3 indicates. These small angular inhomogeneities cause deformations in the fronts’ shape. To quantify these deviations consider an arbitrary distance definition between the shapes of two fronts from the same experiment (or simulation). Each front is discretized to $N$ points: $f_n(r_i)$ denotes the $i$th point of the $n$th front (at $t_n$) in polar coordinates. The distance of two fronts is defined as the average of the distance $(d_{mn})$ of the fronts’ $i$th points.

To get the ‘distance’ of the shapes the fronts are rotated onto each other: $f^n_0$ means rotation of the front $f$ by angle $\phi$. Summarizing these considerations we get the following definition for the distance of the shape of the fronts $m$ and $n$:

$$ D_{mn} = \min_{\phi} \left\{ \frac{1}{N} \sum_{i=1}^{N} d(f_n^m(r_i), f_n^0(r_i)) \right\}. $$

For our calculations the Euclidean metric was used.

![Fig. 3](image-url) (a) and (b) are images from two different experiments, (c) and (d) are the corresponding velocity maps, respectively. The detected fronts are drawn with black line. The images (a) and (b) present the typical positions of the minimal loop: (a) the perimeter of the hole in the membrane, (b) near to the inner edge of the gel ring. According to the velocity maps the media have no perfect circular symmetry, the difference from the circular symmetry is more significant in case of map (d).
The elements of the symmetrical distance matrix $D$ are plotted to a grayscale image, where black pixels denote the zero distance of two fronts rotated onto each other and white pixels denote a distance that is larger than a given arbitrary value. Between black and white the shade is linear function of the distance. The pixelmap of the distance matrix has the following properties: (a) the main diagonal $D_{mm}$ is always black, (b) if the fronts are perfectly rotation invariant the full pixelmap is black, (c) if the fronts are not rotation invariant but their shape changes periodically then there are parallel diagonal black lines, and (d) black spots denote local stationarity in the shape.

4. Simulations

The simulations [24] were based on the geometrical wave theory. A front is represented by a set of marker points. These points move perpendicularly to the locally interpolated front according to the geometrical wave theory. The medium is represented as a velocity field, which can be given either by a formula or by a pixmap.

Each point of the medium might have three states: obstacle, resting or refractory state. The front cannot pass through points in obstacle state, they are used to model the inner hole and the outer boundary of the membrane. Resting state means the front can pass through the point and after the front has passed through, the point’s state changes to refractory. In refractory state the point behaves as if it were an obstacle, but after a certain recovery time it changes back to resting state.

The front is a set of marker points, which are called local front determinant (LFD). Each LFD moves perpendicularly to the front. To calculate the perpendicular direction at a given LFD, quadratic Lagrange polynomials are interpolated to the actual LFD and to its neighbours. The length of the movement is equal to the propagation velocity in that point of the medium. The distance of the neighbouring LFDs is kept around 1 pixel: if LFDs are too far from each other (their distance is bigger than 1.25) new ones are created between them by Lagrange interpolation, and if they are too close some of them is removed. Detailed discussion of the algorithm can be found in [24].

In our case the velocity maps (Fig. 3c and d) from the experiments are used as input velocity field. The size of the images as well as the media in the simulation is $543 \times 543$ and $561 \times 561$ pixel, respectively. The method used to calculate the propagation velocity does not give result at the boundary region of the medium, but in the first case propagation velocity around the obstacle highly influence the stationary front, thus for simulation input an additional interpolation was used. First, it was assumed that the propagation velocity at the inner boundary is equal to $r_1 \omega_b$, then linear interpolation was used in radial direction between the innermost point with measured velocity and the inner boundary (the calculation of $\omega_b$ is discussed in Section 5). For optimal results the propagation velocity is scaled to be around 1 pixel/step number. The recovery time was chosen to 20 timesteps.

We started the simulation with a straight initial front, and waited until the front reached the stationary shape (usually only one round). After the initial round the front was recorded during several rounds, and it was processed in the same way as the fronts from experiments. The fronts had 400–1000 marker points, depending on their actual shape.

5. Results and discussion

Fig. 3 presents two images from two different experiments and the corresponding velocity maps. The detected wavefronts are drawn with black line. In the first image (Fig. 3a) the minimal loop is the perimeter of the hole ($r_1 = 5 \text{ mm}$) in the membrane. Here 8 g ammonium–sulfate was added to the ‘slow’ solution and nothing to the ‘fast’ solution.

In the second image (Fig. 3b) the hole is larger ($r_1 = 7 \text{ mm}$) and 14 g ammonium–sulfate was added to the ‘slow’ solution and 3 ml 5 M sulfuric acid to the ‘fast’ solution. Due to the high acid concentration the membrane became lighter. The front shape characteristically differs from the front shape of Fig. 3a as the radius of the minimal loop is greater, about 14 mm.

The velocity map (Fig. 3c) was calculated at the end of the experiment for time period 40 min, while the change of the medium was slow. The other velocity map (Fig. 3d) was calculated also at the end of the experiment for a shorter 15 min time period. Examining the velocity maps (Fig. 3c and d) one can see that the first medium has nearly circular symmetry, but the second one has not. However, there are segments in the ring in both case where the fronts are nearly stationary which can be recognised as black spots in Fig. 4a and b. These images also present that the shape of the fronts changes nearly periodically (black lines parallel to the main diagonal). The deviation from the periodic behaviour is caused mainly by the slow changing of the media in time (due to the slow decomposition of the catalyst). The medium with high acid concentration is changing even faster, remarkably in one period, so the shapes of the fronts are less periodical (Fig. 4b).

Fig. 4c and d shows fluctuations of the fronts from simulations, where the measured velocity maps are applied. In the simulations the media are stationary in time and we get the result that the shape of the fronts is completely periodical (black lines parallel to the main diagonal fill the whole matrix).

For stationary fronts the experiments can be compared with the theory and with the simulations. Based on the distance matrices Fig. 4a and b stationary fronts are chosen and shown in their segments of the ring Fig. 5c and d. The velocity values corresponding to these segments of the rings are averaged in angular coordinate to get the velocity functions (Fig. 5a and b). The numerical fronts corresponding to the experimental ones are also shown in Fig. 5c and d. The analytical fronts are calculated from the velocity functions (Fig. 5a and b) with formulae (4) and (5). To calculate formula...
\( \Omega_0 \) is determined in the following way. If the minimal loop is at the perimeter of the medium, \( \Omega_0 \) is estimated as the angular velocity of the front, namely the angular positions of the fronts are plotted as a function of time and linear fit is applied, otherwise \( \Omega_0 \) is computed from the definition.

In the first case the agreement is very good between the fronts, in the second case there is some difference. This is probably due to the not so accurate velocity measurement, when the move of the fronts is too large between two snapshots (30 s) or from the relatively fast change of the medium in time.

6. Conclusion

A new experimental setup was presented to study chemical waves in inhomogeneous Belousov–Zhabotinsky excitable media with circular symmetry. We found that good circular symmetry conditions can be realised in case of nearly monotonous propagation velocity profile, but when the velocity function has a relatively sharp maximum it is more difficult to achieve a perfect circular symmetry. The visualised distance matrix is a very convenient and informative way to compare the front shapes during rotation. The front shapes from numerical simulations and from the theory, based on the experimental velocity function show a nearly perfect agreement for both propagation velocity profiles. The experimental and numerical or theoretical front shapes show some deviation in case of the velocity function with one maximum, most probably due to the weak circular symmetry condition. The results are proving that geometrical wave theory can be applied for chemical waves propagating not only in a (piecewise) homogeneous but also in an inhomogeneous medium.

Acknowledgement

We thank Z. Noszticzius for stimulating discussions. This work was supported by the Hungarian Academy of Sciences (OTKA K-60867).

References