Compensation of curvature effects by illumination

On-Uma Kheowan a,*, Vasily A. Davydov b, Niklas Manz c,1, Stefan C. Müller d,*

a Department of Chemistry, Mahidol University, Rama 6 road, Bangkok 10400, Thailand
b Department of Physics, MIREA, Vernadskogo 78, 117454 Moscow, Russia
c Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306-4390, USA
d Institut für Experimentelle Physik, Otto-von-Guericke-Universität Magdeburg, Universitätsp­latz 2, D-39106 Magdeburg, Germany

Received 24 November 2005; received in revised form 2 March 2007; accepted 9 March 2007
Available online 14 March 2007

Abstract

Front deformation of initially planar excitation waves can be observed in nonplanar media or in spatially heterogeneously illuminated systems. The deformation of propagating reaction–diffusion waves in either of these systems has been investigated earlier separately. Here we present a combination of both heterogeneous systems, which can lead to a compensation of wave deformations. Our theoretical analysis of the evolution of propagating excitation waves, based on the framework of a kinematical theory, shows that the curvature effect can be compensated by illumination. Supporting experiments were performed with the light-sensitive Belousov–Zhabotinsky system.

© 2007 Elsevier B.V. All rights reserved.
PACS: 05.45.-a; 05.70.Ln; 82.40.Ck

Keywords: Belousov–Zhabotinsky reaction; Curved surfaces; Excitation waves; Light-sensitive system; Nonlinear dynamics; Reaction–diffusion waves

1. Introduction

Propagating excitation waves are observed in a variety of biological, chemical, and physical systems [1–3]. Among these systems, the Belousov–Zhabotinsky (BZ) reaction [4–6] is the most suitable laboratory system to study the dynamics of the excitation waves. The BZ reaction has been investigated with a large variety of system parameters in planar [4,5] and nonplanar [7–9] geometries. A photosensitive modification of this reaction that uses the catalytic complex ruthenium–bipyridyl Ru(bpy)2 [10,11] provides a powerful tool to control the excitation waves in excitable media with spatially homogeneous [12–19] and inhomogeneous [20–22] illuminations. It was reported that the propagation velocity of a wave propagating in a planar system illuminated in a spatially modulated fashion becomes nonuniform, which leads to a deformation of wave front [20,21].

Similar phenomena was also observed with a wave propagation on a nonuniformly curved surface [23]. The kinematic theory [24–26], which is used to develop analytical functions to describe the motion of fronts in such nonuniformly modulated systems, suggests that it is possible to compensate the front deformation observed on a curved surface by an inhomogeneous illumination.

In this Letter we present a theoretical idea how to compensate the deformation of a propagating wave in a nonplanar medium (a spherical cap and a periodically curved surface) with a heterogeneous illumination (light mask). Our considerations are based on the kinematical theory for specific conditions of each system. The experimental observations were performed with the light-sensitive BZ system.

2. Theoretical consideration

Propagating fronts in excitable media can be described by a set of nonlinear, reaction–diffusion equations [27]. On
curved surfaces a commonly used two-variable model for two-
dimensional media of the following form is applied:
\[
\begin{align*}
\frac{\partial u}{\partial t} &= F_1(u, v) + D_u \frac{1}{\sqrt{g}} \frac{\partial}{\partial x^i} \left( g^{ik} \sqrt{g} \frac{\partial u}{\partial x^k} \right), \\
\frac{\partial v}{\partial t} &= \epsilon F_2(u, v) + D_v \frac{1}{\sqrt{g}} \frac{\partial}{\partial x^i} \left( g^{ik} \sqrt{g} \frac{\partial v}{\partial x^k} \right),
\end{align*}
\]
(1)
where \( u \) and \( v \) are referred to as the activator and inhibitor
species, respectively, with \( D_u \) and \( D_v \) as their diffusion coeffi-
cients, \( x^i \) the coordinates on the surface, and \( g \) the determin-
ant of the metric tensor \( g^{ik} \). The functions \( F_1 \) and \( F_2 \) specify
the local kinetics in the excitable system and the form rate coefficient \( \epsilon \) determines the time scale for the recovery process.

Wave propagation in a combined system of a nonplanar medium with heterogeneous illumination can be described with
equations containing the specific conditions of each system. An
analytical study of excitation waves with the described Eq. (1) is
usually not possible. To describe wave propagation in heteroge-
neous media such as curved surfaces [9,28,29] or spatially mod-
ulated, light-sensitive systems [20,21] one can use the “kine-
matic approach”. In the framework of the kinematic theory the
evolution of an endless front is completely determined by spec-
fying the line of the front. The shape and evolution of the wave
front can be described by its natural equation \( K = K(\ell, t) \),
where \( K \) is the geodetic curvature, \( \ell \) the arc length, and \( t \) is
the time. Each section of the front moves in the normal direc-
tion with the velocity \( V(K) \). The evolution of a wave front on a
curved surface can be described by the main kinematic integro-
differential equation [24]
\[
\frac{\partial K}{\partial t} \left( \int_0^\ell K V \, d\xi \right) + \frac{\partial K}{\partial \ell} + \frac{\partial^2 V}{\partial \ell^2} + K^2 V = -\Gamma V,
\]
(2)
where \( \Gamma \) denotes the local Gaussian curvature of the surface.
In a planar system the right-hand side of Eq. (2) is equal to 0.
For sufficiently small \( K \) the dependence of \( V \) on \( K \) is linear
(eikonal equation [30]):
\[
V = V_0 - D_u K,
\]
where \( V_0 \) denotes the velocity of a planar front with zero geo-
detic curvature.

If a photosensitive BZ reaction on a curved surface is hetero-
geneously illuminated, the velocity of a planar front will depend
on its coordinate vector \( r \). This dependence can be written as follows:
\[
V(r) = V_0 - D_u K - V_1(r),
\]
(3)
where \( V_0 \) is the velocity of a planar front in an unlit media and
\( V_1 \) is the velocity change due to external illumination. The
negative sign in front of \( V_1 \) indicates that the illumination slows
down the propagation velocity.

If the front deformations are sufficiently small (\( K \ll
V_0/D_u \)), then the main kinematic equation (2) can be linearized,
by keeping only linear terms in \( K \), and written as [9]
\[
\frac{\partial K}{\partial t} - D_u \frac{\partial^2 K}{\partial \ell^2} = -\Gamma V_0 + \frac{\partial^2 V_1}{\partial \ell^2}.
\]
(4)
One can see that the effects of curved surface and external
illumination are additive and will compensate each other if
\( \Gamma V_0 = \partial^2 V_1/\partial \ell^2 \). Although the idea of such a compensation
seems to be simple, the corresponding effects are not trivial.
We will show calculations of illumination masks for different
nonplanar systems.

First we consider a surface with cylindrical symmetry. In
this case the Gaussian curvature depends only on radius \( r \):
\( \Gamma = \Gamma(r) \), \( r = \sqrt{x^2 + y^2} \). The problem is to find the velocity
change \( V_1(r) \) with a cylindrical symmetry which will compen-
sate the propagation of the plane front.

For smoothly curved surfaces the deformation of a straight
(infinity) front propagating along the \( y \)-axis will be small and
the arc length \( \ell \) will be approximately equal to \( x \). In this case
one can write the following equation:
\[
\frac{\partial^2 V_1}{\partial \ell^2} = \frac{\partial^2 V_1}{\partial x^2} = \frac{d^2 V_1}{dr^2} \left( \frac{\partial r}{\partial x} \right)^2 + \frac{dV_1}{dr} \frac{\partial^2 r}{\partial x^2}.
\]
\[
= \frac{1}{r^2} \left( \frac{d^2 V_1}{dr^2} x^2 + \frac{1}{r} \frac{dV_1}{dr} y^2 \right).
\]
The derivative \( \partial^2 V_1/\partial x^2 \) must have a cylindrical symmetry.
This requirement can only be realized if
\[
\frac{\partial^2 V_1}{\partial \ell^2} = \frac{1}{r} \frac{\partial V_1}{\partial r},
\]
(5)
is valid. The differential equation (5) has the following solution:
\[ V_1 = B r^2 + C, \] where \( B \) and \( C \) are arbitrary constants. The
surface which corresponds to this velocity is a sphere with the
constant Gaussian curvature \( \Gamma = 2B/V_0 \).

We have obtained an important and unexpected result. The
only cylindrically symmetrical surface which can be compen-
sated by cylindrically symmetrical illumination (for planar ex-
citation fronts propagating along any direction) is a sphere or a
spherical meniscus on a plane. Therefore, the velocity change
\( V_1 \) can be expressed as
\[ V_1 = \frac{V_0 \Gamma}{2} \left( r^2 - R^2 \right), \]
(6)
where \( R \) is the radius of the sphere. From Eq. (3) and the
Gaussian curvature of a spherical surface \( \Gamma = R^{-2} \), we obtain
\[ V = V_0 - D_u K + V_{cp}, \]
where
\[ V_{cp} = \frac{V_0}{2} \left( 1 - \frac{r^2}{R^2} \right). \]
(7)
is the compensating velocity due to an external illumination for
the deformation of a planar front propagating across a spherical
cap.

For all other surfaces one can compensate the curvature ef-
fect for a propagating planar front only along one direction.
The corresponding illumination will not be compensative for all
other directions. Thus the compensative velocity for the front
propagating along the \( y \)-axis on a parabolic meniscus \( z = Ar^2 \) is
as follows:
\[ V_{cp} = 2A^2 V_0 (R^2 - r^2)(3 - 4A^2(r^2 + R^2) - 16A^2 y^2), \]
where \( R \) is the meniscus radius. This velocity however will not be compensative for fronts propagating along other directions.

As a next example we consider a smooth periodically curved surface

\[
z = A \sin(bx) \sin(by),
\]

with \( b = 2\pi/\lambda \) as the wave number and \( \lambda \) as the wavelength of the surface modulation. The parameter \( A \) defines the amplitude of the surface. Such a surface was already used to investigate the dynamic of excitation fronts propagating on a modulated curved surface [9].

This surface has the following Gaussian curvature:

\[
\Gamma(x, y) = -\frac{A^2 b^4}{2}(\cos(2bx) + \cos(2by)).
\]

This example has not a radial symmetrically deformation as the first example. Therefore the angle between the propagating front and the axes has to be considered. We consider two particular cases: The “diagonal case” with wave propagation in a 45° angle to the axes and the “horizontal case” with wave propagation parallel to the \( y \)-axis.

If the planar front propagates along the \( y \)-axis (horizontal case) the curvature effects can be compensated by the following velocity:

\[
V_{cp} = -\frac{A^2 b^2 V_0}{8}[\cos(2bx) - 2b^2 \cos(2by)(x - C_1)^2 + C_2],
\]

where \( C_1 \) and \( C_2 \) are arbitrary parameters. This velocity however will not compensate the curvature effects for planar fronts propagating along any other directions. Thus, the plane front will move along the diagonal direction without deformations if one uses the following compensating velocity:

\[
V_{cp} = -\frac{A^2 b^2 V_0}{2}(\cos(2bx) + \cos(2by)).
\]

The examples considered above show that the curvature effects can be compensated, in principle, by the corresponding velocity due to illumination. However, in general, compensating illuminations for fronts propagating along fixed direction will not suppress the deformations of the front moving along other directions. The only exclusion is the spherical meniscus.

3. Experimental results and discussion

In our experiments, we investigate the propagating front in the photosensitive BZ reaction. The catalytic complex ruthenium-bipyridyl Ru(bpy)_2^3+ used in this reaction provides a suitable tool to examine the responses of the propagation velocity to the external illumination experimentally [19]. The relationship between the propagation velocity \( V \) and the illumination intensity \( I \) can be expressed by a linear approximation: \( V = a - bI \), where \( a \) and \( b \) are positive constants. In our experiments, the constants \( a \) and \( b \) are \( 68 \pm 4 \) \( \mu \)m s\(^{-1}\) and \( 39\pm 5 \) m\(^2\) W\(^{-1}\) \( \mu \)m s\(^{-1}\), respectively, where the dimensions of \( V \) and \( I \) are \( \mu \)m s\(^{-1}\) and W m\(^{-2}\), respectively. The negative slope indicates that the illumination inhibits the propagation of wave front, which can be explained by the production of inhibitor species (bromine) by an impact of light [31].

The calculation in the first part of the previous section shows that the deformation of a planar front propagating on a spherical cap can be compensated by the compensating velocity \( V_{cp} \) yielding Eq. (7). By substituting the linear approximation \( V = a - bI \), we obtain

\[
I_{cp} = \frac{a}{b} - \frac{1}{2b}(a - bI_0)(1 - \frac{r^2}{R^2}),
\]

where \( I_{cp} \) and \( I_0 \) are the compensating intensity and background intensity, respectively. The term \( a/b \) is the suppression intensity resulting in zero velocity. Therefore, we can neglect it from the compensating intensity \( I_{cp} \). Then the total illumination for our experiments can be expressed as

\[
I = I_0 + I_{cp} = I_0 - \frac{1}{2b}(a - bI_0)(1 - \frac{r^2}{R^2}).
\]

We consider the case of a spherical cap with the base’s radius \( r^* \) at the constant height \( z = h \), where \( 0 < h \leq R \). The intensity along the radial direction of the compensating illumination corresponds to an integration of the parabola area with \( I < I_0 \) in Fig. 1. The illumination intensity is proportional to the gray level printed on a compensating mask, where the percent transmittance \( T\% \) is a linear approximation of the gray level \( G \); \( T\% = 6.71 + 0.28G \). The light mask is printed on a transparency using a monochrome laser printer with a resolution of 600 dpi.

In our experiments, the Ru(bpy)_2^3+ catalyst is immobilized in a silica gel matrix (thickness of 0.4 mm, area of 7.9 cm × 7.9 cm) with a concentration of 4.2 mM. The gel is prepared by using a pair of complementary acrylic glass molds that, once put together, create a thin hollow space with a spherical cap shape (see Fig. 2 and Ref. [32]). The liquid gel solution is filled into the mold shortly before the gelation. After jelling, the upper part of the mold is remove to put the reaction solution onto the
The reactants and their concentrations (disregarding bromination of malonic acid) are: NaBrO₃ (0.20 M), malonic acid (0.17 M), H₂SO₄ (0.31 M), and NaBr (0.09 M). The experiments are carried out at an ambient temperature of \((21 \pm 1)°C\). A planar excitation wave is created near the boundary of the square medium by placing a straight silver wire onto the gel in the reaction solution. After the first wave appeared, the silver wire is removed from the gel immediately in order to allow only one wave to propagate in the medium. The reaction layer is uniformly illuminated from below with a light box. The light mask is placed directly under the acrylic glass mold, as shown in Fig. 2. The oxidation waves are monitored in transmitted light by a monochrome charge-coupled-device (CCD) camera. The video signal is digitized by an image-aquisition card and stored on a personal computer.

The deformation of an initially planar front propagating across the spherical cap layer of the BZ reaction is shown in Fig. 3(a)–(e), where the parameters of the spherical cap are \(R = 5.26 \text{ mm}\) and \(h = 2.00 \text{ mm}\) and the background illumination intensity is 0.577 W/m². In the bottom part of Fig. 3(a), the initiated flat front moves upwards to the cap (shaded circle). The deviation starts slowly when the front begins to travel across the cap [Fig. 3(b)] and appears clearer after it moves over the maximum [Fig. 3(b)–(c)]. Finally, the front deforms into a shape of an upside-down cusp [Fig. 3(e)]. This deformation is as a result of the combination between the curvature effect and the difference of propagating distances. It is obviously that a path over the hemisphere is longer than a path on a flat surface. The expected deformation of an initially planar front due to the distance differences is shown above Fig. 3(e) (dotted line). In contrast to the experimental wave with a cusp, the calculation appears as a smooth curve over the cap with sharp edges at the points \(r = r^*\).

The deformation is compensated by a light mask calculated from Eq. (12) and the result of the compensation is shown in Fig. 3(f)–(j). Due to the dark light mask (gray circle) the observation is limited during the front propagation across the spherical cap [Fig. 3(g)–(i)]. However, after the front passed the spherical cap the nearly flat front is visible. This proves that the light mask successfully compensates the curvature effect. Nevertheless, there are two small wriggles of the front corresponding to the abrupt change of the curvature of the spherical cap at \(r = r^*\).

With a similar experimental setup, the compensation of the curvature effect of a modulated surface Eq. (8) by a light mask is shown in Fig. 4, where the wave is parallel to the \(x\)-axis. An initially planar front propagates in horizontal direction from bottom to top across the surface. Without the mask, the part of this wave which propagates over the nodes is always leading, whereas the front always lags behind at the location of the extrema (black dot in Fig. 4(a)) as reported previously [9]. The deformation of the planar front is reduced, when the light mask is applied as shown in Fig. 4(b). The wave front is not completely flat, but it is obviously smoother. We assume that this disagreement is caused by two factors: (i) The propagation velocity of a planar front is not a perfect linear function of the illumination intensity for the range of the used light intensity. (ii) There is a delay response by the propagation velocity of the wave front to a change of the illumination intensity.

![Fig. 2. Schematic diagram of the experimental setup.](image)

![Fig. 3. Compensation of the curvature effect of an initially planar front propagating on a spherical cap surface by a light mask (f)–(j), compared with the experiment without the light mask (a)–(e). The spherical cap has a radius of 5.26 mm and a height of 2.00 mm. The intensity of the background illumination is 0.577 W/m². The calculated deformation of a planar front due to the different path length is shown as a dotted line in (e). Time between snapshots: 50 s. Scale bar: 1 cm.](image)

![Fig. 4. Compensation of the curvature effect of an initially planar front propagating on a modulated surface by a light mask (b), compared with the experiment without a light mask (a). The modulated surface is described by Eq. (8), where \(A = 1.00 \text{ mm}\) and \(b = 4\). The light mask is calculated from Eq. (9) with \(C_1 = C_2 = 0\). The intensity of the background illumination is 0.577 W/m². Scale bar: 1 cm.](image)
4. Conclusions

In conclusion, we have presented a theoretical and experimental analysis regarding the compensation of the curvature effects of deformed reaction–diffusion waves by illumination. Our theoretical analysis is based on the framework of the kinematical theory. We have derived illumination masks for two different curved surfaces to compensate the front deformation of propagating waves caused by the nonplanar surface of the system.

For the first surface, with a cylindrical symmetry, we obtained an interesting and unexpected result that a sphere or a spherical meniscus on a plane is the only cylindrically symmetrical surface that can be compensated by a cylindrically symmetrical illumination mask. The obtained illumination mask was applied to the experiment with the photosensitive BZ reaction on a spherical cap surface. Our experimental result demonstrates that the light mask can reduce the front deformation caused by the curvature effect.

For the second surface, which is a periodically modulated, we obtained two analytical solutions for the illumination masks. These masks are applicable if the waves propagate parallel, or in a 45° angle, to the axis. We tested the first case experimentally and obtained a qualitative improvement of the deformation due to the curvature effect of the surface.

These results show the general ability of illumination masks to compensate wave front deformation of propagating light-sensitive reaction–diffusion waves caused by nonplanar media. We will conduct further investigations to obtain quantitative parameter values for the compensating illumination functions of different nonplanar systems. We expect that our findings can be applied to other nonlinear systems with front deformations caused by different heterogeneities [33].

Acknowledgements

O.K. thanks the Postgraduate Education and Research Program in Chemistry funded by the Royal Thai Government. N.M. thanks the German Academy of Natural Scientists Leopoldina (Grant No. BMBF-LPD 9901/8-85) for financial support. V.A.D. was partly supported by the US CRDF-RF Ministry of Education, Grant No. VZ-010-0.

References