Refraction and Reflection of Chemical Waves

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When a chemical wave encounters a boundary between two media with different wave speeds, refraction and reflection can occur. We demonstrate experimentally that the refraction of chemical waves obeys Snell's law. Reflection of chemical waves has been observed for the first time. The waves do not show specular reflection, but rather exhibit a single reflection angle, equal to the critical angle.

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The study of reaction-diffusion wave propagation and pattern formation in two- and three-dimensional systems has advanced rapidly in the past 25 years since the introduction of homogeneous, isothermal chemical excitable media [1]. While the most basic properties of these waves in spatially uniform systems have been established, wave propagation in nonuniform media is also of considerable interest because natural reaction-diffusion media such as biological excitable tissues and ecological systems are strongly nonuniform. In uniform systems only symmetry-breaking initial conditions give rise to new patterns [2]. Nonuniformities and gradients of concentrations and of other local parameters bring with them an initial asymmetry that provides new routes for pattern formation and makes possible the emergence of new types of wave patterns [3].

The simplest phenomena connected with wave propagation in nonuniform media are wave transformations during passage across a boundary between two different uniform media. Among these phenomena, refraction and reflection are ubiquitous in conservative media [4]. Refraction, obeying Snell's law, was recently demonstrated experimentally for diffuse photon density waves in turbid media by O'Leary *et al.* [5].

Refraction and reflection have not, however, been thoroughly studied in excitable reaction-diffusion systems. Delayed reflection in a one-dimensional nerve fiber has been investigated both theoretically and experimentally [6]. Such reflection can take place only if the duration of the excited state in the target medium is longer than the refractory period in the primary medium. Refraction was studied theoretically by Mornev [7] in a two-dimensional reaction-diffusion system consisting of two regions with different diffusion coefficients and identical local chemical kinetics. His predictions are supported by recent experiments by Agladze and De Kepper [8], though the jump in wave velocity produced by the difference in diffusion coefficients was small, and the authors were unable to make quantitative measurements.

To create large differences in wave speeds across a boundary, we have employed an important advantage of chemical reaction-diffusion systems: the possibility they offer of varying significantly the wave speed by controlling the local chemical parameters that determine reaction rates. We report here a study of refraction and reflection of chemical waves in the Belousov-Zhabotinsky (BZ) reaction-diffusion medium [1,9] using the oxygen inhibition of excitability in the BZ reaction [10] to create a sharp boundary between two regions with different wave velocities.

The reaction employed is the ferroin-catalyzed BZ reaction at 25 ± 1 °C. The medium consists of rectangular pieces of polyacrylamide or silica gel of various thicknesses, saturated with the above solution. A jump in the oxygen concentration is created either by using gel specimens with stepwise changes in thickness or by covering part of the gel slab with a flat glass plate. In some experiments, the difference in wave speed between polyacrylamide gel and aqueous solution was also employed.

Initial incident waves are triggered by touching a gel specimen with a piece of silver wire. The wave propagation is recorded with a video camera and then processed with an image analysis system. Gray levels in Figs. 1 and 2 correspond to the light absorbance determined by the concentration of ferroin ($\varepsilon_{510} = 11\,000 M^{-1}$ cm^{-1}). Darker regions correspond to higher concentrations of ferroin; light wave fronts correspond to low ferroin concentrations. The recorded shape of the wave differs significantly in the two adjacent parts of the medium in Figs. 1 and 2. This is a result of two nonlinear effects. The first one is intrinsic: Because of the strong nonlinearity of the system's chemical kinetics, the oxygen inhibition affects not only the speed of the waves but also their shape. The second effect stems from the Lambert-Beer law and the approximately twofold difference in the thicknesses of the two media. As a result, the lighter leading part of the wave with low ferroin concentration appears elongated in the thinner medium.

In Fig. 1 we show refraction of a chemical wave at the boundary between two regions of different wave speeds. A simple analysis (see below) shows that refraction must obey Snell's law [4]. This prediction is confirmed by direct measurements. The incident wave is a large-radius circular wave whose center lies on the boundary. Because of this geometry, the angle of incidence is 90° ± 3°, while the angle of refraction is 27° ± 3°. Snell's law gives $v_r/v_i = 0.45 \pm 0.05$, where v_i is the speed of the incident wave and v_r is the speed of the refracted wave. Direct

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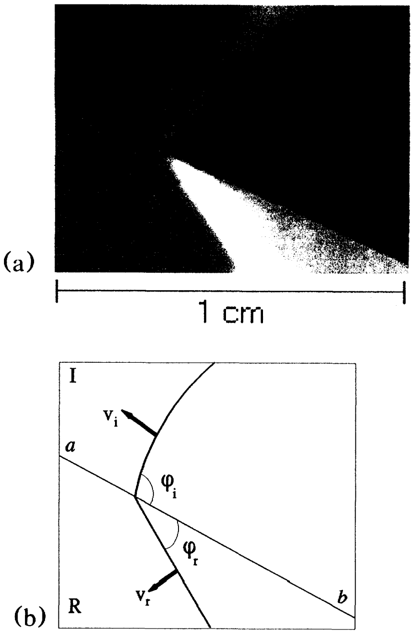

FIG. 1. Refraction of a chemical wave. (a) Silica gel layer open to air with stepwise thickness; (b) schematic of (a). *ab*: boundary between regions I (2.15 mm) and R (1 mm). v_i and v_r: wave vectors of the incident and refracted waves; φ_i and φ_r: angles of incidence and refraction. Initial reagent concentrations (M): $[NaBrO_3]=0.3$, $[CH_2(COOH)_2]=0.03$, $[Fe(phen)_3]=0.002$, and $[H_2SO_4]=0.05$.

measurement of the speeds yields $v_r/v_i=0.43\pm0.002$. As in conservative media, refraction obeying Snell's law takes place when the incident wave comes from the medium with higher speed at any angle, and when it comes from the medium with lower speed if the angle of incidence is less than the critical angle.

Reflection of chemical waves has not been observed previously in reaction-diffusion systems. In Fig. 2 we illustrate reflection of chemical waves at a boundary created by differential oxygen inhibition. This reflection is instantaneous and independent of the specific local kinetics, in contrast to the delayed reflection observed earlier in nerve fibers [6]. Reflection takes place only if the incident wave comes from the medium with lower wave speed and the angle of incidence is larger than a critical value. Our experiments employ very different angles of incidence, yet in all cases the angle of reflection is close to the critical angle, $\sin^{-1}(v_i/v_s)$, where v_s is the wave speed in the reflective medium. For instance, (a) polyacrylamide gel, thickness 0.6 mm, boundary between a region open to air and a region covered by glass plate; angle of incidence $59.0°\pm3°$, angle of reflection $32.5°\pm1°$, $v_i/v_s=0.4\pm0.012$; (b) boundary between polyacrylamide gel and aqueous solution (thickness 0.6 mm); angle of incidence $90.0°\pm3°$, angle of reflection $32.4°\pm2.1°$, $v_i/v_s=0.5\pm0.03$.

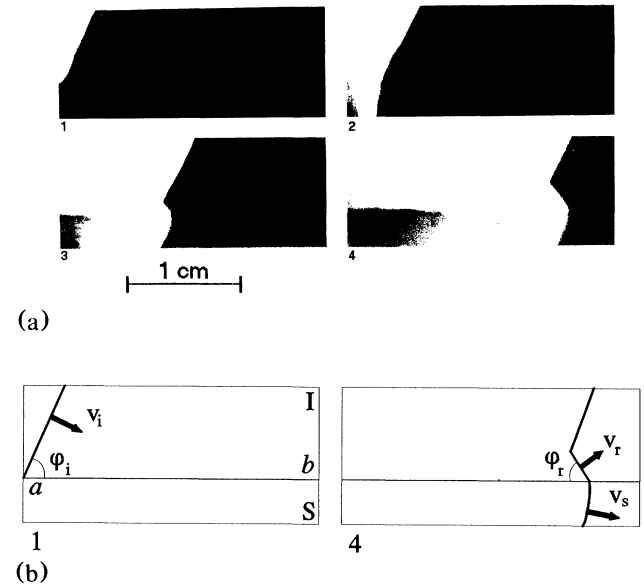

FIG. 2. Reflection of chemical waves. (a) Polyacrylamide gel layer open to air with stepwise thickness; interval between frames (sec) 1 and 2, 75; 2 and 3, 130; 3 and 4, 200. (b) Schematic of frames 1 and 4. *ab*: boundary between regions I (0.45 mm) and R (0.75 mm); v_i, v_s, and v_r: wave vectors of the incident, secondary circular, and reflected waves; φ_i and φ_r: angles of incidence and reflection. $\varphi_i=67.4°\pm3°$, $\varphi_r=54.0°\pm2°$, and $v_i/v_s=0.76\pm0.03$. Initial reagent concentrations (M): $[NaBrO_3]=0.3$, $[CH_2(COOH)_2]=0.03$, $[Fe(phen)_3]=0.002$, and $[H_2SO_4]=0.1$.

A simple kinematic analysis of a chemical wave front encountering a boundary between two regions i and r with different wave speeds v_i and v_r utilizes Huygens' principle to determine consecutive positions of the front and a condition for its continuity. If the pattern remains stationary in time in a coordinate system that moves with the wave along the boundary, and if the wave front is continuous across the boundary, then, owing to the continuity of the component of the wave vector parallel to the boundary, the refraction of chemical waves must be governed by Snell's law [4]:

$$\frac{\sin\varphi_i}{\sin\varphi_r}=\frac{v_i}{v_r}\,.$$

Here φ_i and φ_r are angles of incidence and refraction, and v_i and v_r are the incident and refracted wave speeds. Also, as a generic feature of the wave propagation, refraction of plane waves is impossible when the angle of incidence of a wave from the lower speed region exceeds the critical angle φ_{cr} given by the familiar expression,

$$\varphi_{cr}=\sin^{-1}(v_i/v_r),\quad v_i<v_r\,.$$

However, the behavior of waves in strongly dissipative

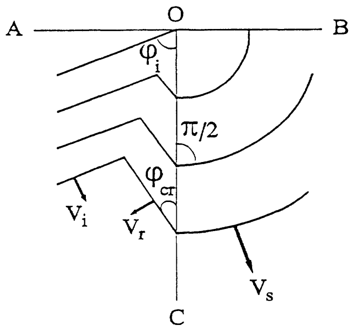

FIG. 3. Kinematic model of chemical wave reflection. $v_i = v_r$, the speed of incident and reflected waves; v_s, the speed of circular wave initiated in the higher speed region by incident wave; φ_i, the angle of incidence; and φ_{cr}, the angle of reflection, always equal to the critical angle, $\varphi_i > \varphi_{cr}$.

excitable media differs strikingly in other respects from that of waves in conservative or weakly dissipative media. When the incident wave comes from the medium with higher speed, only Snell's law refraction takes place, without reflection. Reflection of chemical waves with continuity of the parallel component of the wave vector can occur only if the incident wave originates in the medium with lower speed and if the angle of incidence exceeds the critical angle. In this case, no wave propagation takes place in the medium with higher speed in optics or acoustics, while in reaction-diffusion systems the wave propagates in the high-speed medium but with distortion of the wave front. In contrast to optical reflection, where the angle of incidence equals the angle of reflection, for chemical waves the angle of reflection always equals the critical angle.

A simple kinematic model of chemical wave reflection is as follows. When a plane wave is incident on the boundary from the low-speed region (v_i) at an angle larger than the critical one, it initiates in the high-speed region (v_s) a circular wave whose wave vector at the boundary lies parallel to that interface (Fig. 3). This circular wave then initiates in the low-speed medium a plane wave (the reflected wave) which, according to Snell's law, must propagate at the critical angle, $\sin^{-1}(v_i/v_s)$.

Our experimental data confirm that reflection of chemical waves differs strikingly from that of waves in conservative media, while refraction shows notable similarities that arise from the most general properties of wave propagation.

Reflection of concentration waves should take place in all nonuniform reaction-diffusion and related systems. This phenomenon appears to be of importance in sustaining the repeated propagation of concentration waves in confined excitable media such as the heart and other systems of interest in biology and medicine [1,11,12]. Two sources of sustained wave generation are well known: local pacemakers and circulation of waves along closed pathways, including the formation of spiral waves [1]. Reflection provides a new route to sustained propagation of concentration waves in confined systems. This mechanism can support such wave activity under conditions when pacemakers are absent and spiral wave formation is impossible due to wave-front curvature effects [13]. Reflection mechanisms may be especially important for ecological systems, where river valleys and seashores can form pathways for propagation of population waves [12,14] with an enhanced speed in comparison with adjacent areas. Such high-speed, finite-length pathways can play the role of mirrors that support sustained wave motion within an area, even in the absence of wave circulation along closed pathways.

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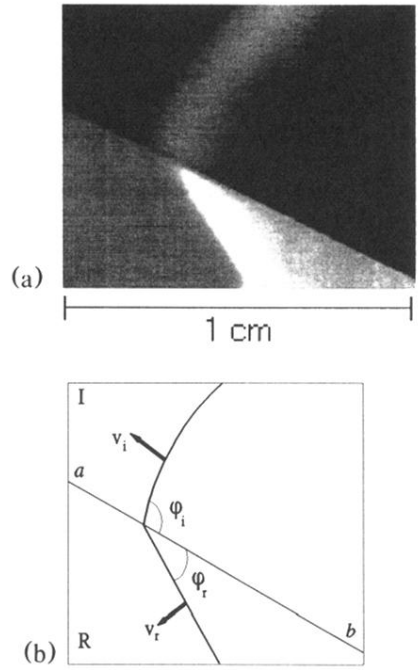

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