

Chemical wave refraction phenomena

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Motivated by recent work of Steinbock, Tóth, and Showalter [Science **267**, 868 (1995)] examining chemical wave propagation within membrane labyrinths soaked with Belousov-Zhabotinsky reagent, we have investigated refraction phenomena using similar tools, with an eye to verify the general applicability of Snell's law for such nonlinear waves, as well as to unearth the physicochemical origin of the drastically reduced trigger wave velocities we find within quasi-two-dimensional porous media. Altered reaction-diffusion kinetics appear to play no role. Rather, our results indicate *intramembrane* wave-front curvature, induced perhaps by differential wetting properties, to be the mechanism responsible for these refraction effects.
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Since their discovery by Zaikin and Zhabotinsky [1] several years ago, chemical wave phenomena, manifest within the Belousov-Zhabotinsky (BZ) reagent mixture [2], wherein malonic acid is catalytically oxidized and brominated, have become the paradigm in our understanding of reaction-diffusion systems and the complex spatiotemporal self-organization it engenders [3]. Thanks primarily to Winfree's geometrical motivations [4], research early on concentrated primarily on the dynamics of spiral waves with much effort devoted to determining their dispersion relation [5], in addition to rather extraordinary experimental work noting, for example, the structure of the core [6], tip meandering [7], and existence of multiarmed spirals [8]. Subsequent studies also concerned themselves with the dynamics of more complicated topological structures such as scrolls and vortex rings [9], as well as issues of torsion and curvature [10].

The reaction kinetics underlying the propagation of BZ chemical waves were first put forth by Field and Noyes [11], their essential features captured by the simplified Oregonator model [12], which focuses attention upon the central chemical species via three coupled partial differential equations (PDE's) dictating the spatiotemporal evolution of the Br, HBrO_2 , and transition-metal (canonically Ce^{4+}) ion concentrations. Among the *numerically* achieved and experimentally confirmed predictions of the Oregonator are (i) a very sharp wave front, complemented by a diffuse trailing edge, as evidenced by the cerium ion concentration; (ii) a bromous acid profile that jumps abruptly by a factor of 10^5 across the leading edge of the wave; and finally, (iii) the existence of a critical bromide ion concentration below which an oxidation pulse is triggered. Interestingly, if one is concerned with the strictly kinematical aspects of the BZ chemical wave, such as propagation speed and potential refraction effects, it is possible to strip the Oregonator down to a single nonlinear PDE (close kin to the Fisher equation [13], governing dynamics of gene propagation in host media), which dictates the reaction and diffusion of bromous acid, then achieving highly non-trivial *analytical* results. In particular, it is known that, at this level of approximation, the velocity of planar wave front

$c = \sqrt{Dk[\text{BrO}_3^-][\text{H}^+]}$, a result that has been carefully corroborated in various BZ reagent recipes, including ferroin [12,14], rubidium [15], and cerium [16] catalyzed versions. Here, D is the diffusion coefficient of the autocatalytic species HBrO_2 , k the dominant rate constant, and $[]$ refers to molar concentrations.

When one considers chemical wave propagation in two and three dimensions and allows for the possibility of curved fronts, interesting new physical phenomena arise. As stressed initially by Tyson and Keener [10] the local normal velocity of a nonplanar wave front is *curvature*-dependent and is given, at least for small deviations, by the eikonal expression

$$v = c - D\kappa,$$

where κ is the sum of principal curvatures of the front. With typical BZ planar wave speeds corresponding to roughly $c \approx 6.0$ mm/min and the oft-quoted room-temperature value $D = 2.0 \times 10^{-5}$ cm²/sec, it is apparent that the correction $D\kappa$ is only manifest in situations of highly curved fronts, with $\kappa > 1/50 \mu\text{m}$. Consequently, the implications for an ever-expanding BZ circular wave appear utterly negligible, for once the radius of the wave exceeds several hundred micrometers (indeed, the silver wires usually employed [17] to initiate BZ trigger waves are already of this size or larger . . .), the propagation is essentially that of a plane wave. Nevertheless, the eikonal equation indicates a critical radius of curvature $r_c = D/c$, below which the BZ trigger wave will not propagate. Interestingly, in an experiment using silver-coated glass capillaries, Foerster, Müller, and Hess [18] observed precisely this effect, finding $r_c \approx 20 \mu\text{m}$ and extracting the diffusion constant $D = 1.9 \times 10^{-5}$ cm²/sec. Indeed, this same group had elegantly verified the eikonal relation previously for situations of extreme *negative* curvature [19], studying enhanced speeds of cusped wave fronts formed at the intersection of two colliding circular waves; extrapolation of their data to positive κ indicated a critical radius of curvature $\approx 70 \mu\text{m}$. Later efforts by Nagy-Ungvarai *et al.* [20] revealed values of $r_c \approx 14\text{--}55 \mu\text{m}$ over a broad range of reagent concentrations. In related work, Tóth and co-workers [21] examined BZ circular waves emanating from narrow micropipette tubing. By varying their recipe,

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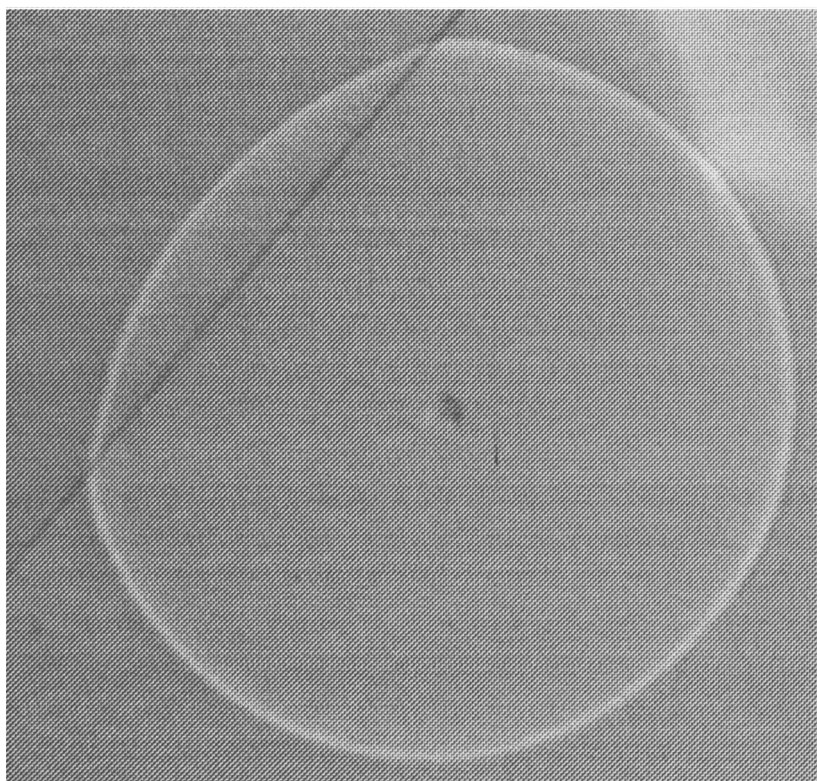


FIG. 1. A circular BZ trigger wave is *slowed* as it propagates into a thinner membrane. The geometry of the refracted wave front is consistent with that dictated by Snell's law, assuming a relative index of refraction $n = 1.45 \pm 0.05$. Independent measurements of chemical wave speeds in the two different media, obtained simply by tracking the radius of the expanding circle as a function of time, indicate a velocity ratio, 1.44 ± 0.06 , in fine agreement with this value. At moment captured, incident trigger wave radius is 21 mm.

they managed to orchestrate a vanishing propagation speed consistent with that dictated by the eikonal relation.

In this Brief Report we discuss experimental investigations of severely reduced BZ trigger wave speeds in quasi-two-dimensional media, using membranes sufficiently thin in the third dimension that curvature effects return to play an important role. As an added benefit, by using membranes of various thicknesses, we were able to provide an explicit test of Snell's law of refraction within the BZ context [22], orchestrating chemical wave propagation between discrete media with different indices of refraction. In this regard, our work is complementary to efforts of Zhabotinsky *et al.* [23], who, relying upon the transverse O_2 gradient [24] present within a BZ silica gel medium to alter propagation speeds, provided preliminary confirmation of Snell's law and observed, for the first time, reflection of nonlinear chemical waves. Very recently, Oosawa *et al.* [25] have managed an independent examination of Snell's law, employing ferroin-loaded cation-exchange resin beads. Both these refraction experiments, however, use overtly *chemical* mechanisms to instigate differential trigger wave speeds, their samples being too thick to exhibit the curvature effects (i.e., the *physical* mechanism) we discuss here. In turn, as we relate later, a careful examination of the dependence of BZ wave speed upon reagent concentrations provides strong evidence against the possibility of altered reaction-diffusion kinetics in our own thin membrane experiments. Preliminary findings were presented previously [26].

In Fig. 1, we show a snapshot of a circular trigger wave [27], which, having been initiated previously in a double-layer membrane (thickness $304 \mu\text{m}$), has propagated across the interface into a single layer ($152 \mu\text{m}$), where it travels more slowly, the refracted wave front being noticeably flat-

tened. Visual inspection suggests the refracted wave front to be the segment of a circular arc, but this is precluded by Snell's law. An elementary derivation indicates that, with $n = v_2/v_1 > 1$ denoting the ratio of velocities in the two different media, the refracted wave front is given parametrically by the mildly cumbersome equations

$$x = [d(n^2 - 1) \tan \alpha + R \sin \alpha] / n^2, \quad (1)$$

$$y = [(R - d \sec \alpha) \sqrt{n^2 - \sin^2 \alpha}] / n^2, \quad (2)$$

where R is the time-dependent radius of the incident wave. Here, x and y refer, respectively, to the coordinates along and transverse to the interface separating the two media, the origin coinciding with the point at which the incident wave front first crosses the boundary, having been initiated a perpendicular distance d away. The parameter $0 < \alpha < \cos^{-1}(d/R)$. Examination of the entire wave front is particularly advantageous because its time evolution incorporates results for all angles of incidence. This is in contrast to previous work [23,25], which examined only isolated cases. With the above curve for our refracted wave front, a best fit to the data yields the velocity ratio $n = 1.45 \pm 0.05$. We obtain the same result when propagation proceeds in reverse, from single layer to bilayer, leading to a distended rather than flattened wave front. In this scenario, however, reflected waves are also generated when the incident angle becomes sufficiently large [23]. Interestingly, an entirely separate, but again intrinsically geometric technique produced a similar value. By initiating a circular trigger wave at the edge of the sample along (but ever so slightly to the faster, double-layer side of) the interface, it is possible to observe the situation recorded in Fig. 2, which reveals a refracted, essentially

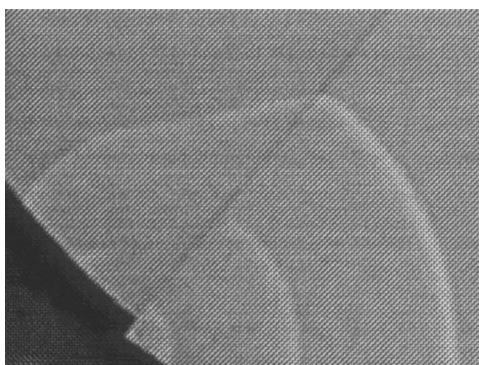


FIG. 2. By initiating a trigger wave at the diameter end point of the membrane sandwich, being sure to touch silver wire on double-layer side of interface, we generate a wave front effectively incident at 90° . The refracted wave front in the single layer is observed canted at the maximal angle $\theta = \sin^{-1}(1/n)$, as predicted by Snell's law. Our measured value $\theta = 43 \pm 1^\circ$ yields a velocity ratio $n = v_2/v_1 = 1.47 \pm 0.02$, in good agreement with previous, alternative determinations.

planar wave front on the other side of the interface, in the single layer. With the incident angle equal to 90° , Snell's law of refraction dictates the *maximal* deflection $\theta = \sin^{-1}(1/n)$, all angles measured with respect to the interface rather than to the normal vector since the discussion is most naturally phrased in terms of wave fronts, not rays. Measuring the angle from our computer-enhanced images, we find $\theta = 43 \pm 1^\circ$, yielding $n = 1.47 \pm 0.02$, consistent with our previous determination. Finally, we made independent and direct determinations of the BZ chemical wave speeds by tracing radius vs time plots for isolated circular trigger waves. Using this method, we found $v_2 = 70.0 \pm 2.0 \mu\text{m/s}$ and $v_1 = 48.7 \pm 1.9 \mu\text{m/s}$ for the bilayer and single-layer speeds, respectively, which gives $n = v_2/v_1 = 1.44 \pm 0.06$. Taken as a whole, these and similar findings at different temperatures and concentrations provide strong support for the notion that BZ chemical waves obey Snell's law of refraction, regardless of the physiochemical mechanism responsible for reduced wave speeds.

In an attempt to unearth the mechanism responsible for the diminished BZ propagation velocity in the thinner layer, we observe that the difference of our BZ trigger wave speeds in the single and double membranes is $v_2 - v_1 \approx 21 \mu\text{m/s}$. Interestingly, if one makes the admittedly crude assumption that the curvature of the BZ wave front *within* the cross section of the membrane is that of a simple semicircle, which implies $\kappa = 1/76 \mu\text{m}$ for the single layer, and uses the time-honored [18–20] value $D = 2000 \mu\text{m}^2/\text{s}$, the eikonal relation indicates a curvature correction $v_2 - v_1 = D\kappa/2 \approx 13^+ \mu\text{m/s}$, a rough estimate that is a bit low, though not far from the mark. Nevertheless, for reasons delineated below, we strongly suspect wave-front curvature to be the source of these refraction phenomena and have little reason to believe, for example, that physiochemical effects may have altered the value of the diffusion constant D within the membrane. Indeed, to this end, we made a systematic investigation of trigger wave propagation in single-layer membranes as a function of reagent concentrations. As mentioned earlier, the

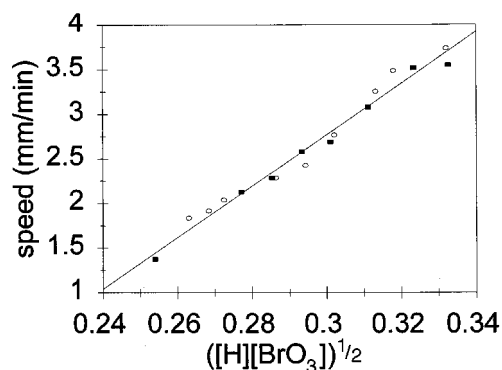


FIG. 3. Speed v_1 of a circular BZ trigger wave for varied concentrations of bromate or sulfuric acid; the square-root dependence following from the minimal Oregonator model [12,3]. The bromate series (■) has a standard recipe $[\text{H}_2\text{SO}_4] = 0.4M$ with $[\text{NaBrO}_3] = 0.168 - 0.288M$, while the acid series (○) has $[\text{NaBrO}_3] = 0.2M$ and $[\text{H}_2\text{SO}_4] = 0.346 - 0.551M$. All other species' concentrations are fixed by the standard recipe [27]. All experiments are performed in a single-layer membrane of thickness $152 \mu\text{m}$. A least-squares fit to all data yields a slope, $28.8 \pm 1.1 \text{ mm/min mol}$, consistent with all previous work [12,14,15] done at $T = 25^\circ\text{C}$. The intercept, $-5.87 \pm 0.11 \text{ mm/min}$, however, is entirely *anomalous*, being much larger than past determinations made in thick liquid layers of BZ reagent and arises, we believe, from wave-front curvature within the cross section of the membrane. It is this curvature effect that is the physical basis for the reduced wave speed and refraction phenomena discussed above.

minimal Oregonator predicts [11,12] and experiment [12,14,15] confirms a chemical wave speed proportional to $\sqrt{Dk[\text{BrO}_3^-][\text{H}^+]}$. In particular, Field and Noyes [12] find a slope $+27.9 \text{ mm/min mol}$, while Showalter [14] obtains $+27.33 \text{ mm/min mol}$, both for ferroin-based recipes similar to our own, but in thick (1–2-mm) *liquid* layers of BZ reagent. Interestingly, both groups note a small, but nonzero intercept, equal to -0.8 and -0.999 mm/min , respectively. Kuhnert and Krug [15], substituting Ru for Fe as catalyst, measure a similar slope, $+27.5 \text{ mm/min mol}$, and intercept, -1.2 mm/min . This small negative, nonvanishing vertical intercept, not easily accommodated within the minimal Oregonator, has been attributed by Kuhnert, Krug, and Pohlmann [28] to a retardation effect associated with Br^- concentration ahead of the reaction front, their model calculations leading to an estimate, -0.83 mm/min , surprisingly close to the observed value. Our own data for trigger wave speeds in a $152\text{-}\mu\text{m}$ -thick membrane, shown in Fig. 3, reveal a much more dramatic effect. A least-squares fit to the bromate series yields a slope of $+28.4 \pm 1.2 \text{ mm/min mol}$; the slightly more sensitive H^+ series gives $+29.3 \pm 1.9 \text{ mm/min mol}$. In any case, the data are well approximated by a straight line and the slope extracted from the combined data sets, $+28.8 \pm 1.1 \text{ mm/min mol}$, is in good agreement with the previous studies done in free-standing liquid layers [12,14,15], suggesting that both D and k are unchanged, reaction and diffusion phenomena not significantly affected by the presence of the porous membrane. Even so, our line is shifted significantly downward. More specifically, the combined data sets produce a vertical intercept of $-5.87 \pm 0.11 \text{ mm/min}$. Subtracting off the bromide effect, we see trigger

wave speeds that are lower in the single-layer membrane by some 5 mm/min or 82 $\mu\text{m/s}$. Clearly, we cannot account for such a large number via crude calculation, as above. More work is necessary by other experimental teams. Nonetheless, we believe curvature will be key to any future explanation, for as we increase the membrane vertical dimension by using multilayers, we observe still larger trigger wave speeds; e.g., for the triple layer, of nominal thickness 456 μm , we find $v_3 \approx 85 \mu\text{m/s}$. The behavior, while monotonic, is certainly nontrivial, indicating that the nature of the true intramembrane curvature is probably thickness dependent. As a closing comment, we hazard a guess that differential wetting

properties (distinct chemical mixtures behind and beyond the front—both in contact with inert silicon oil) may be responsible for a meniscus-shaped wave front within the membrane cross section.

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