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LETTERS

Anomalous Dispersion of Chemical Waves in a Homogeneously Catalyzed Reaction System

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We present experimental results that demonstrate anomalous dispersion in a Belousov−Zhabotinsky system. The reaction is carried out at high concentrations of sulfuric acid and involves 1,4-cyclohexanedione as its organic substrate. The unusual dispersion behavior of this excitable medium induces an attractive interaction between pulses that results in fusion or closed stacking of waves. Experimental results from quasi-one-dimensional as well as two-dimensional media are presented. In two-dimensional reaction systems, a complex dependence of the propagation velocity on the relative direction between fronts is found and the formation of spiral defects is observed.

Propagating waves of excitation have been observed in a variety of chemical and biological reaction−diffusion systems such as the Belousov−Zhabotinsky (BZ) reaction,[1] the oxidation of CO on Pt surfaces,[2] aggregating slime molds,[3] yeast extracts,[4] and cardiac tissue.[5] Excitation waves have typically constant profiles and propagation velocities. The propagation velocity of wave trains, however, shows a pronounced dependence on the distance between the pulses (i.e., the wavelength of the wave train). The dispersion relation that describes this dependence between propagation velocity and wavelength has been studied for numerous excitable systems. Most excitable systems show normal dispersion meaning that the velocity of a wave decreases with decreasing distances to the leading pulse.[6] For high wavelengths the velocity saturates, since the inhibitory influence of the leading pulse diminishes. Furthermore, it is known that below a critical distance waves cannot coexist, since the medium is fully refractory.

The underlying chemical processes that give rise to the dispersion relation are closely related to the nonlinear kinetic coupling of activator and inhibitor species.[7] The excitation pulse arises from the autocatalytic production of the activator, which is self-limited by an increase of the inhibitor concentration. In the wake of a normal-dispersion pulse, the excitability of the system is continuously recovered due to a simple, often first-order, decay of the inhibitor.[8] The propagation velocity of a subsequent pulse is determined by the local concentration of inhibitor left behind by the leading wave.

The normal dispersion of excitation waves has been often considered a universal feature of excitable media. For example, Flesselles et al. analyzed data on the dispersion of chemical waves in the BZ reaction as taken from several earlier publications[9,10] and found that the propagation velocities vary as the hyperbolic tangent of the normalized periods.[11] However, theoretical studies by Elphick et al. stressed the possibility of anomalous dispersion. The hallmark of anomalous dispersion is the decrease of velocities with increasing distance between subsequent waves (i.e., $dc/d\lambda < 0$).[12]

This study focuses on wave propagation in a modified Belousov−Zhabotinsky (BZ) system. While the classical BZ reaction involves the ferroin-catalyzed oxidation of malonic acid by bromate in an acidified aqueous solution, our experiments were carried out using 1,4-cyclohexanedione as the organic substrate. This compound has recently gained considerable interest since its use in the BZ reaction prevents the formation of undesired CO_2 bubbles.[13]

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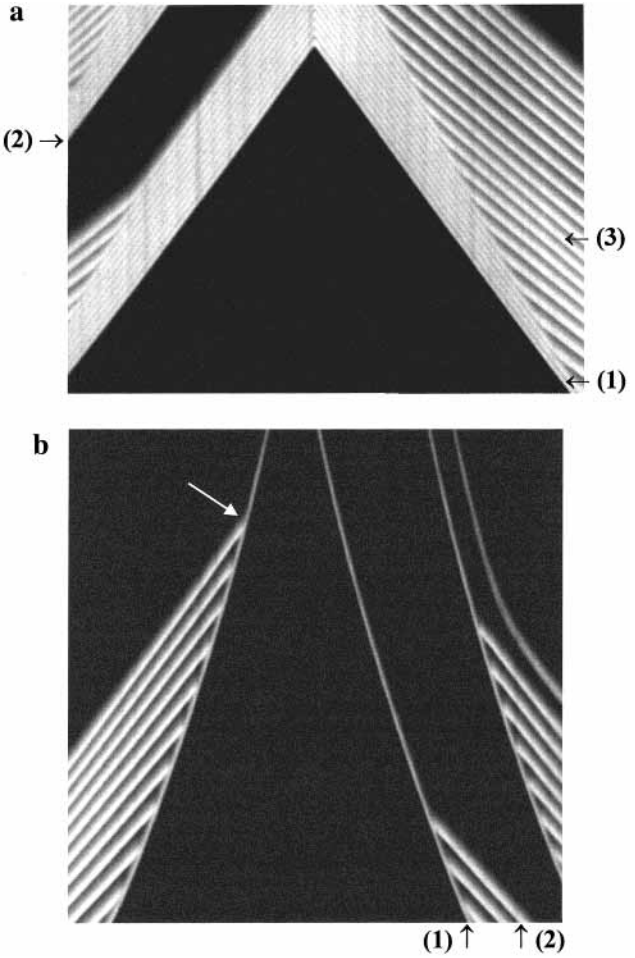

Figure 1. Time−space plots of one-dimensional systems with anomalous dispersion. The pulse interaction that gives rise to stacking (a) and merging (b) of waves is observed. Initial concentrations: $[H_2SO_4] = 2.0$ M, [ferroin] = 0.5 mM, [1,4-CHD] = 0.1 M, and $[NaBrO_3] = 0.06$ M (a) and 0.05 M (b). Time increases in the upward direction and spans an interval of 460 s in (a) and 600 s in (b). The horizontal axes (space) correspond to 29 mm.

All reagents are of the highest grade commercially available and used without further purification. For experiments on wave propagation in quasi-one-dimensional systems, thin capillary tubes (inner radius: 0.5 mm) were filled with the reaction solution. Two-dimensional media were created by constraining the reaction system between two plexiglass plates (height: 0.40 mm). Both approaches minimize perturbations that arise from ambient molecular oxygen.

Parts a and b of Figure 1 show time−space plots obtained from a typical capillary experiment. Time−space plots are produced by piling up spatial absorption profiles at constant sampling rate (here: $\Delta t = 2$ s). The vertical and horizontal axes correspond to time and space, respectively. Dark and bright regions indicate reduced and oxidized states, respectively. The plots show bright bands that correspond to different propagating oxidation pulses. Their propagation velocities equal the inverse slope of the bands.

Figure 1a illustrates an experiment in which several waves nucleated spontaneously at the open ends of the capillary tube. Waves emanating from the left- and right-hand side collide and mutually annihilate in the central region of the system. The first front, which propagates into the apparently fully excitable system, is marked as (1). Its propagation velocity is $c_1 = 2.2$ mm/min and does not change significantly in time. The same velocity was found for the wave labeled as (2). This pulse has a relatively large distance of $\lambda_2 = 5.9$ mm from its predecessor. The velocity c_1 is therefore the saturation limit of c for large wavelengths λ. In an excitable medium with normal dispersion, this velocity would also denote the upper velocity limit for trigger waves.

Under the given experimental conditions, however, subsequent waves can propagate faster. For example, we found that the tenth wave (labeled (3)), which enters the observation field from the right-hand side, travels with an initial velocity of $c_3 = 3.5$ mm/min and is, thus, 1.6 times faster than wave (1). The distance to the preceding wave is approximately $\lambda_3 = 1.2$ mm. Nearly identical values were found for all waves in the upper right-hand side and some smaller regions in the left portion of the plot. The velocity and the wavelength of these wave trains decrease significantly if they approach the wake, i.e., back, of a leading slow pulse. For the given set of initial concentrations, this “traffic jam” mechanism gives rise to closely stacked wave packages. In Figure 1a these stacked waves appear as broad bright regions with thin dark (i.e., reduced) stripes separating the individual pulses. The stacked waves have a constant propagation velocity that equals the velocity of the leading slow wave (i.e., 2.2 mm/min) and a wavelength of 0.37 mm.

The velocity data obtained from Figure 1a exemplify the existence of an anomalous dispersion relation in the medium. Starting at a very small distance, the velocity increases rapidly from c_1 to a maximal value c_2. At larger distances, however, it decreases to the low value c_1. For our knowledge, this finding is the first example of negative slopes and a local maximum in the dispersion relation of a homogeneously catalyzed reaction−diffusion system.

The occurrence of anomalous dispersion in this modified BZ system is not limited to a particular set of initial concentrations. Figure 1b shows a time−space plot obtained from an experiment at lower bromate concentration. Under these conditions, waves propagate with a constant velocity of about 0.96 mm/min, if the distance to their predecessor is larger than 1.5 mm. An example for these slow waves is the front labeled as (1) in Figure 1b. For smaller distances, however, greater velocities of approximately 2.2 mm/min were observed A typical example for these fast moving fronts is labeled as (2). On the basis of these findings, it is concluded that the slope $dc/d\lambda$ of the dispersion relation is negative.

A striking difference between the wave dynamics shown in Figure 1a,b is the asymptotic behavior of closely separated pulses. In both cases, the negative slope of the dispersion relation causes the distance between a leading (slow) wave and its immediate (fast) successor to decrease continuously. Consequently, the pulses can come into direct front-to-back contact. At high concentrations of bromate (Figure 1a), this collision is prevented by a sudden decrease in propagation velocity that occurs at very small distances and gives rise to closely stacked wave pulses. In Figure 1b, however, fast pulses merge with the leading wave and no stacking is found (e.g., see white arrow in Figure 1b). The absence of wave stacking suggests that anomalous dispersion extends over the entire range of pulse distances.

Careful inspection of numerous time−space plots revealed no evidence for dark (reduced) gaps in the merging bands created by front-to-back collisions (e.g., Figure 1b). However, this finding does not rule out the possibility of a thin repulsion zone in the wake of the pulses, since the existence of an inhibitor barrier appears to be a necessity for establishing the directionality of wave propagation.

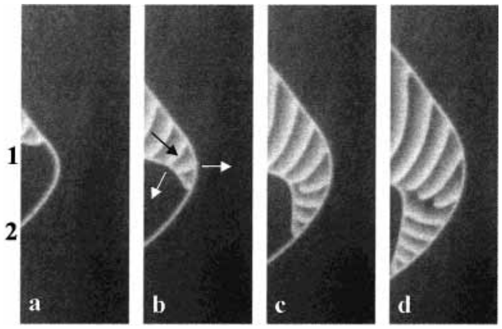

Figure 2. Consecutive snapshots of a two-dimensional system with anomalous dispersion. The initial concentrations are identical to those of Figure 1b with the exception of $[H_2SO_4] = 1.5$ M. Time between snapshots is 120 s. Field of view: (7.7×20.8) mm^2. The white and black arrows indicate the propagation direction for slow and fast waves, respectively.

Anomalous dispersion as well as pulse interaction that gives rise to stacking and fusion of waves are also found in quasi-two-dimensional systems. Figure 2 shows four consecutive snapshots of a wave pattern evolving in a thin layer of the reaction solution. The velocity of the ⊃-shaped wave (labeled 2) that propagates into a fully reduced (dark) medium is 0.4 mm/min. A similar velocity is found for the wave labeled as 1 in Figure 2a. All other waves (compare black arrow in Figure 2b) travel approximately 5.5 times faster and, thus, indicate the presence of anomalous dispersion. Furthermore, the branching structure of the depicted wave pattern is one possible manifestation of *merging* waves in two dimensions and, therefore, related to the dynamics shown in Figure 1b.

The behavior of two-dimensional patterns is of high complexity since pulses can approach the back of a slowly traveling wave at different relative angles, as exemplified by the pattern shown in Figure 2. The initially nearly horizontal, slowly moving wave (labeled 1 in Figure 2a) is propagating into a medium that had been earlier excited by the ⊃-shaped front (labeled 2). The right portion of the horizontal wave is in close vicinity to its predecessor, while the left portion is further away. In accordance with the anomalous dispersion relation of the system, we observe that the right portion propagates faster than the left side (Figure 2b−d). Consequently, the initially planar wave deforms into a hook-shaped curve and the two slow moving waves begin to form a cone-shaped envelope for the fast waves. The black arrow in Figure 2b indicates the propagation direction of these fast waves.

The waves in the interior of the cone are closely spaced (1.1−1.8 mm). Initially, these fronts extend from the left to the right side of the cone, thus being in contact with the two slowly propagating envelope waves 1 and 2 (Figure 2a,b). Parts c and d of Figure 2, however, show the formation of spiral defects along the evolving kink of the cone. A similar route to the formation of spirals has been recently reported by Agladze et al., who studied the nucleation of spirals from high-frequency wave trains at a corner of a physical boundary.[14] The phenomenon shown in Figure 2, however, occurs due to the anomalous dispersion of the unconstrained homogeneous system, since the highly curved cusp of the right envelope wave would not form in a medium with normal dispersion. Anomalous dispersion should furthermore allow the coexistence of spiral waves with pronounced differences in rotation period and wavelength (i.e., pitch).

This study documents the existence of anomalous dispersion in the Belousov−Zhabotinsky reaction. Two different modes of pulse interaction have been described that either lead to front-to-back merging of pulses or their closed stacking. Major challenges for future studies include the detailed investigation of wave interaction in two dimensions and the elucidation of the reaction mechanism that causes anomalous dispersion. The experimental evidence at hand suggests the involvement of an additional feedback loop that could account for the observed pulse dynamics. A similar approach has been proposed by Christoph et al. in order to explain anomalous dispersion in the catalytic reduction of NO with CO on Pt(100).[15] They found that the gradient of the stoichiometric ratio between absorbed CO and NO changes its sign in the wake of a pulse, thus creating a thin repulsive and a larger attractive region. It seems likely that the attractive interaction observed in our experiments is closely related to the introduction of 1,4-cyclohexanedione, since anomalous dispersion is not known for the BZ reaction with malonic acid.

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