Anomalous Dispersion and Pulse Interaction in an Excitable Surface Reaction

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Experiments on the catalytic reduction of NO with CO on a Pt(100) surface reveal attractive interaction between pulses leading to the eventual merging of two pulses to a single one. The results can be reproduced with a realistic reaction-diffusion model which yields a negative slope in the dispersion relation over a large range of the interpulse distance. [S0031-9007(99)08476-8]

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Pulse interactions in excitable media are often discussed within the context of a refractory zone behind a traveling pulse (see, e.g., [1]). It is usually found that the velocity of a pulse decreases the closer it follows another pulse. Thus, the velocity of wave trains usually increases monotonously with their wavelength (distance of pulses). However, for excitable media near a Hopf bifurcation of the rest state, some authors obtained oscillatory dispersion curves giving rise to alternating attractive and repulsive pulse interaction [2]. This can lead to coexisting free spirals of different wavelengths [3]. A general kinematical description for ensembles of pulses has first been given by Rinzel and Maginu [4]. They point out the decisive role of the sign of the slope of the dispersion curve. The refractoriness concept corresponds to a positive slope of the dispersion relation that stabilizes periodic wave trains. Most experiments in chemical reactions and other reaction-diffusion media behave accordingly [1,5]. To our knowledge, only an isolated observation during the early stages of the aggregation cycle of the slime mold *Dictyostelium Discoideum* shows attractive pulse interaction [6] still awaiting a theoretical explanation. In a separate experiment, an inversion of the slope of the dispersion curve has been found, if the slime molds were exposed to caffeine [6].

Here, we present an experimental example of attraction between traveling pulses in a chemical surface reaction, the isothermal NO reduction with CO on Pt(100). The findings are reproduced in a chemically realistic reaction-diffusion model of the NO-CO reaction and can be explained within a kinematic framework. The computations show both the attractive interaction and the negative slope of the dispersion curve for a wide range of interpulse separations. The inverted slope in the dispersion curve can be rationalized from the specific form of the nullclines given by the reaction-diffusion model for NO and CO as well as from simple chemical arguments.

Chemical wave patterns occur in the NO + CO reaction on the unreconstructed Pt(100) surface in a temperature range from ca. 350 to 500 K (at 10^{-6} mbar) [7–9]. They are not associated with overall oscillations in the reaction rate and comprise traveling pulses, spiral waves, and target patterns. A convenient way to study the behavior of pulses is the use of microstructured surfaces which can be prepared by photolithographic techniques [10]. By depositing thin layers of Ti (ca. 500 Å) with a mask onto a Pt(100) surface, one can create reactive Pt(100) domains of varying size and geometry which are surrounded by an inert Ti/TiO_2 layer.

The reaction is studied under isothermal conditions at low pressure (10^{-6} mbar) operating the UHV chamber as a gradient-free flow reactor. As a spatially resolving method, we employ photoemission electron microscopy (PEEM), which images the local work function differences in real time with a resolution of ca. 1 μm [11]. Pulses, which represent reactive low coverage areas propagating on an unreactive high coverage background, are thus images as traveling white spots. In the following, we study the behavior of pulses on a Pt ring (cf. [12]) of 110 μm outer diameter and 10 μm width, which can be regarded as quasi-one-dimensional.

Figure 1(a) displays the propagation of pulses on the ring in a space-time representation in which the spatial coordinate is given by the angular position of the pulse. Because of a preferential orientation of steps on the surface, it is no longer isotropic, and the pulses move about twice as fast parallel than perpendicular to the step edges. Initially, several of these pulses are present, but

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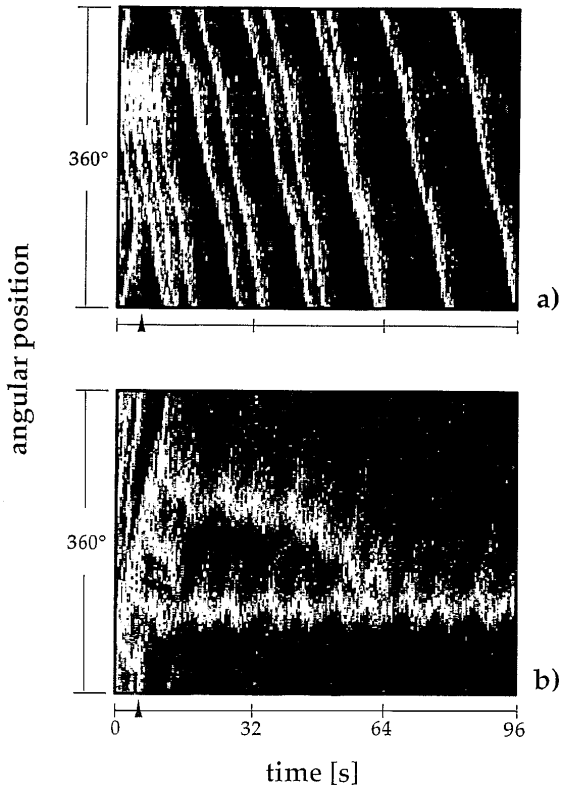

FIG. 1. Space-time plots of pulses on a ring as observed with PEEM. At the marked point in time, T was lowered from 427 to 426 K, after which only two pulses remain, which subsequently merge; (b) shows the same event as (a), but in a moving coordinate frame (in which the leading pulse appears nonpropagating).

a temperature decrease from 427 to 426 K causes most of them to die out and only two survive. In order to better follow the interaction of the two pulses, we switch to a rotating coordinate system shown in Fig. 1(b). The oscillations which occur superimposed on the trajectories of the pulses result from the above-mentioned anisotropy of the surface and exhibit a period corresponding to the time it takes a pulse to advance by 180°. After the temperature decrease, the two pulses are about 150° apart. The second pulse accelerates as it approaches the first one and merges with the first pulse, whose velocity is not noticeably influenced by this event. The process seen here is just the opposite of the typical behavior of pulses because, instead of slowing down with decreasing distance, we observe an acceleration.

The mechanism of the reaction NO + CO $\rightarrow \frac{1}{2}\,N_2 + CO_2$ is known to proceed via adsorption of NO and CO, subsequent dissociation of NO, and reaction of O with CO, while the nitrogen (which recombines) and CO_2 formed desorb immediately. Instability occurs as a consequence of the vacant site requirements of NO dissociation. This leads to the following model, in which u, v, and w represent CO, NO, and O coverage, respectively [13,14].

$$\partial_t u = k_1 p_{\mathrm{CO}}(1 - u - v) - k_2(u, v)u - k_3 uw + D\nabla^2 u\,, \tag{1}$$

$$\partial_t v = k_1 p_{\mathrm{NO}}(1 - u - v) - k_4(u, v)v - k_5 v f(u + v, w) + D\nabla^2 v\,, \tag{2}$$

$$\partial_t w = k_5 v f(u + v, w) = k_3 uw\,. \tag{3}$$

$k_2(u, v)$ and $k_4(u, v)$ take the coverage dependence of desorption into account, while $f(u + v, w)$ contains the fact that the combined coverages have to fall below a critical value to allow noticeable dissociation of NO (see [14] for details). We use the same rate constants and coverage dependencies as in Refs. [13,14], which were obtained in independent experiments and kinetic measurements, such that the model does not contain any arbitrary parameters. Diffusion and desorption of oxygen can be neglected. The model exhibits pulse solutions over a wide range of parameters (at $T = 424$ K for about 5.5×10^{-7} mbar $< p_{\mathrm{CO}} < 7 \times 10^{-7}$ mbar and 8.5×10^{-7} mbar $< p_{\mathrm{NO}} < 10^{-6}$ mbar). The nullclines in the u, v plane and a pulse profile are shown in Fig. 2. Note that the nullclines for NO and CO do not have the shape of a standard activator-inhibitor system, but nevertheless represent an excitable medium. Spatiotemporal simulations were carried out with $D = 1\ \mathrm{s}^{-1}$ and dimensionless space units. For a realistic value of D (about $10^{-7}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$), one spatial unit corresponds to 3 μm.

In order to compute the dispersion relation, a wave train with wavelength L was mimicked by putting a single pulse on a ring of length L (i.e., a spatially one-dimensional simulation with periodic boundary conditions). The length was decreased stepwise and the propagation velocity determined at each point [Fig. 3(a)]. The velocity changes only slowly for large L, but increases sharply as soon as the ring becomes so small that the pulse starts to feel its own refractory zone. Only for very small L, just before the pulse dies, the velocity decreases again. Figure 3(b) shows the computed pulse velocity c as a function of p_{CO}. Anomalous dispersion results over the whole existence range of pulses except for the small region to the left where c increases with p_{CO}. Qualitatively, the same behavior resulted for all NO pressures in the range given above.

Anisotropy can be introduced by replacing the diffusion terms in Eqs. (1) and (2) by angle-dependent diffusion operators [15]. In polar coordinate, the problem again becomes one-dimensional since the radius is fixed. In order to mimic the anisotropy obtained in the experiment, we performed simulations with $D_x = 1$ and $D_y = 0.25$.

Simulations results for the interaction of two pulses on a ring for the isotropic and anisotropic case are reproduced in Figs. 4(a) and 4(b) respectively, 4(c) and 4(d). The distance between the pulses in Figs. 4(a) and 4(b) at first decreases slowly, but the acceleration of the second pulse increases as it approaches the first one until they merge. The picture for the anisotropic case is qualitatively the

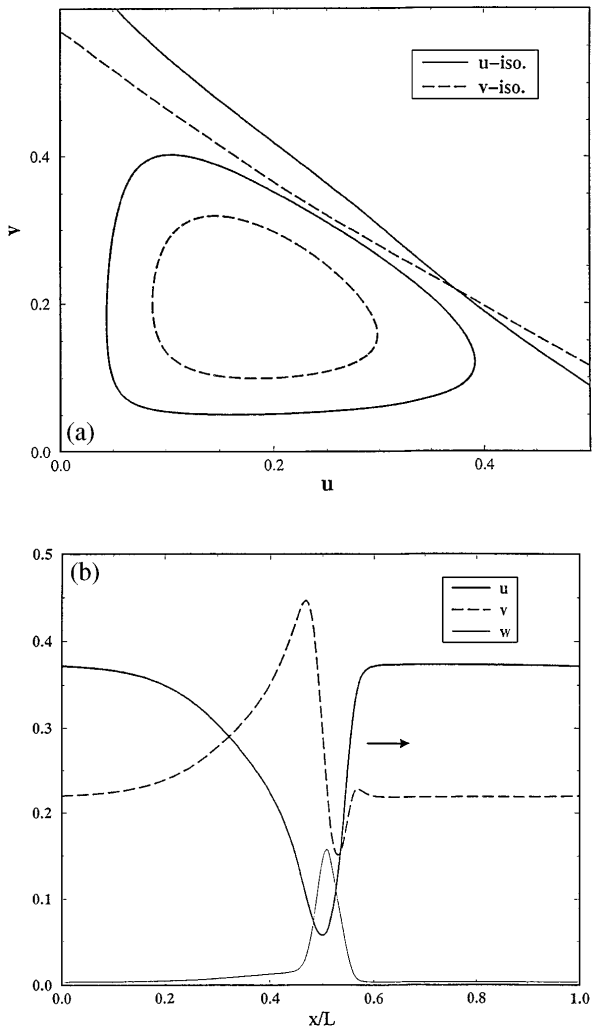

FIG. 2. (a) Nullclines of the model of Eqs. (1)–(3) of the CO/NO reaction; (b) shape of a traveling pulse ($p_{NO} = 9 \times 10^{-7}$ mbar, $p_{CO} = 6 \times 10^{-7}$ mbar, $T = 424$ K).

same, but due to the decrease of the diffusion constant in the y direction the process takes considerably longer. Note that anisotropy is not needed to explain the merging of pulses, but was introduced here only to accurately reproduce the experimental situation.

The dispersion relation, the resulting acceleration of the second pulse, and the merging of the pulses can be rationalized through the pulse profile of Fig. 2(b). The excited state is essentially indicated by a high O coverage. The excitable rest state consists of a mixture of adsorbed CO and NO with CO present in some excess. One would expect that the excitation is easiest (and, hence, the pulse fastest) for the stoichiometric ratio of CO to NO, i.e., 1:1. When approaching the pulse from behind, this ratio decreases very slowly at first, then more pronouncedly [Fig. 2(b)], and reaches unity right behind the pulse. Thus a second pulse is expected to accelerate up to about this point. At the same time it becomes deformed, in particular, the O profile gets flatter and smeared out.

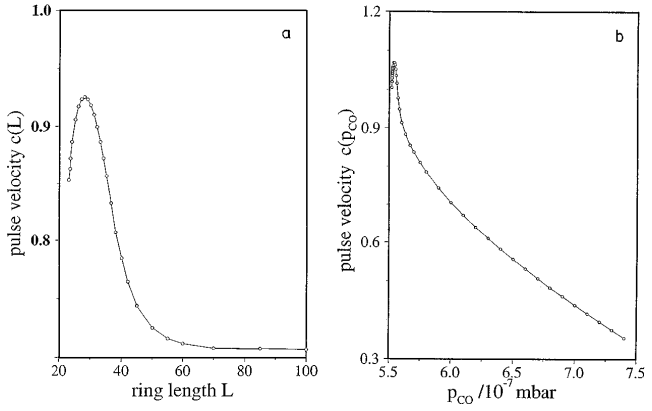

FIG. 3. (a) Dispersion relation $c(L)$ of pulses in the excitable regime of models (1)–(3) obtained with a single pulse on a ring of length L (same parameters as Fig. 2, spatial unit corresponds to about 3 μm). (b) Pulse velocity c as a function of p_{CO}. Anomalous dispersion as in (a) is obtained over the whole range where c decreases with increasing p_{CO}.

Then the pulses are so close that the (already reduced) CO coverage between the oxygen maxima cannot be maintained, so that the O profile (anticorrelated with CO due to the fast reaction) merges to a curve with a single maximum, resulting in a single pulse which quickly shrinks to its asymptotic shape.

We apply kinematic theory [4] to the situation of two pulses on a ring with positions p_1 and p_2: $\dot{p}_1 = c(d_1)$ and $\dot{p}_2 = c(L - d_1)$, where L is the circumference of the ring, $c(d)$ is the dispersion relation, and $d_1 = p_2 - p_1$ is the distance between pulse 2 and pulse 1 with $p_2 > p_1$. A traveling wave solution is given for $d = L/2$.

When we switch to the frame moving with speed $c(L/2)$, the equations read $\dot{p}_1 = c(d_1) - c(L/2)$, and $\dot{p}_2 = c(L - d_1) - c(L/2)$, and there is a family of steady state solutions with $d_1 = L/2$. Linearizing the new dynamical system in the moving frame, we obtain $\dot{p}_1 = c'(L/2)\,(p_2 - p_1 - L/2)$, and $\dot{p}_2 = c'(L/2)\,(L/2 - p_1 - p_2)$ [with $c'(d)$ being the derivative of $c(d)$ with respect to d]. The eigenvalues are simply 0 and $-2c'(L/2)$ with the corresponding eigenvectors (1,1) and $(1, -1)$ in the $p_1 - p_2$ space. While the first eigenvalue indicates translational invariance of the two-pulse traveling wave solution, the second one represents the interaction of the two pulses. This treatment can be easily extended to the collective behavior of n pulses on a ring [16], but the essential results are already contained in the two-pulse case. The stability problem in the kinematical description is thus determined by the slope of the dispersion curve for the wavelength of a given pulse train. Anomalous dispersion (i.e., negative slope) leads to a positive eigenvalue due to pulse interaction, i.e., the distance will decrease in agreement with experiment and simulations, while the final fate of the pulses cannot be predicted from this simple argument.

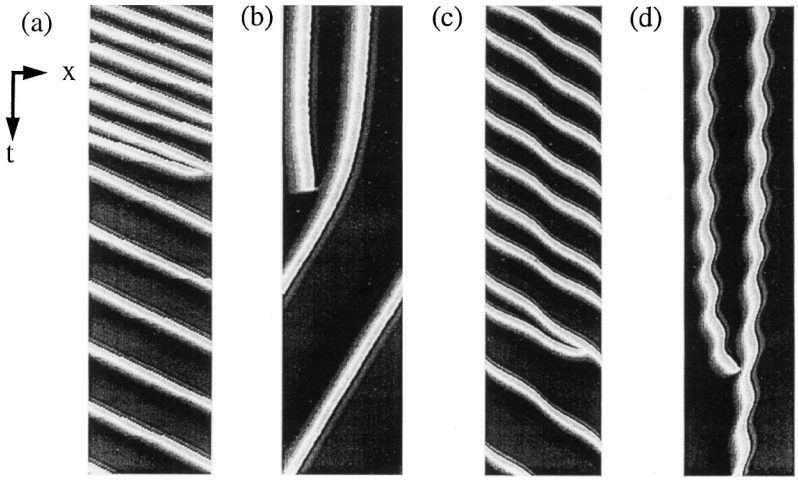

FIG. 4. Computer simulation of merging pulses in the CO/NO reaction (same parameters as Fig. 2); (a), (b): isotropic case; (c), (d): anisotropic case; (b) and (d) correspond to (a) and (c) in a moving coordinate frame (length of system $L = 80$, $D_{CO} = D_{NO} = 1$, integration time in all cases is 823 s). For the anisotropic cases $D_x = 1$, while $D_y = 0.25$; moving frames with $c = 0.98967\ s^{-1}$ (b) and $0.587\ s^{-1}$ (d).

In summary, we have provided experimental evidence and model calculations for anomalous dispersion which extends to very large interpulse distances, and thus added a third possibility to the observed cases of normal and oscillatory dispersion in excitable media. In the system presented here, the destabilizing interaction of the pulse pair led to annihilation of one of the pulses. In principal, other outcomes such as mutual annihilation (cf. [6]) or formation of a bound pair are possible and should be obtainable for similar experimental as well as model systems.

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