Co-existence of stable states in reaction diffusion systems

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Résumé

We study the possibility of zero-velocity fronts over a finite range of control parameters.

1 Introduction

Mathematically, reaction diffusion systems are governed by partial differential equations of the type :

$$\partial_t u = f_\mu(u) + D\partial_x^2 u, \tag{1}$$

where μ is the control parameter. it is well known that steady, non propagating, fronts in reaction diffusion systems usually exist only for special sets of control parameters. When varying one control parameter, the front velocity may become zero only at isolated values (where the Maxwell condition is satisfied, for potential systems) citeArnold,Keener. The experimental observation of fronts with a zero velocity over a *finite interval* of parameters, e.g. in catalytic experiments [1] or boiling experiments [2], therefore seems paradoxical. In this work, we propose an explanation for this phenomenon: we show that fronts with an *extremely small velocity* may exist over a finite range of parameters, in a class of coupled reaction diffusion equations for two variables u_1 and u_2 with the following features :
$\mathbf{H_1}$ the two diffusion coefficients are extremely different, say $D_1 >> D_2$, and
$\mathbf{H_2}$ the variable with the small diffusion coefficient has two stable steady states over a range of control parameters.

Because of the hypothesis $\mathbf{H_1}$, the width of the region where the variable u_2 changes significantly is very narrow. Assumption $\mathbf{H_2}$ implies that the reaction term of the variable with the largest diffusion coefficient, u_1, has several branches, and in this sense, is multivalued. By *extremely small velocity*, we mean that the velocity is controlled by the smallest diffusion coefficient $v \sim \sqrt{D_2}$. This is possible when a Maxwell condition for the variable u_1 is satisfied. When this condition cannot be fulfilled, fronts propagate at a much larger velocity, $v \sim \sqrt{D_1}$.

Assumptions $\mathbf{H_1}$ and $\mathbf{H_2}$ are very plausible in the description of chemical reactions over a catalytic element, as we show with the help of an explicit, although somewhat approximate model of catalytic reaction. Our numerical study of the model confirms the analytic results. We expect that the existence of fronts with a very slow velocity should be observable in a number of systems, since the conditions $\mathbf{H_1}$ and $\mathbf{H_2}$ may be satisfied in several physical systems.

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We also investigate the structure of fast waves, when the Maxwell condition cannot be satisfied.

2 The model

In this section, we introduce the model to describe catalytic reactions over a platinum wire immersed in a gas stream at temperature T_0. The model we use has only two variables (the others may be considered adiabatically eliminated): T, the temperature, and n, interpreted as "active center" density. We will simply use the fact that (T,n) obey a set of coupled reaction diffusion equations, and that the two diffusion coefficients, D_T and D_n (respectively for temperature and for active centers), have very different orders of magnitude: $D_n << D_T$. Physically this comes from the fact that a catalytic wire has a very good thermal conductivity, whereas changes in surface conformation propagate very slowly along the wire.

The model considered explicitly in the present work is:

$$\partial_t T = D_T \partial_x^2 T + F(T,n) \qquad\qquad \partial_t n = \frac{D_n}{a}\partial_x^2 n + af(T,n) \tag{2}$$

with:

$$F(T,n) = n(1+\tanh(\gamma(T-T_*))) - \delta(T-T_0) \qquad\qquad f(T,n) = \alpha T n^2(1-n) - n + \beta T \tag{3}$$

The scaling factor a is introduced for later purpose. It will be set equal to 1 unless stated otherwise.

At a given value of T, the reaction term $f(T,n)$ is a cubic polynomial in n, which possesses either three real roots: one stable, typically close to 1, and two close to 0 (one stable and one unstable), or just one stable real root, close to 1 at large temperature, and close to 0 at small temperature. The front solutions we are looking for may exist only in an interval of temperature. They do not exist above the temperature T_u where the lower branches of n disappear, and below T_l where the higher branch disappears.

3 Slow fronts

We look for front solutions corresponding to a hot, reactive region ($n \approx 1$), propagating into a colder, inactive region ($n \approx 0$).

In all cases, when solutions exist, the jump in n occurs over a very narrow domain, much thinner than the region over which temperature jumps. This is a consequence of our hypothesis $\mathbf{H_1}$. One of the main ideas consists in looking for solutions of the n equation by simply treating T as a constant, equal to T_j. We first consider the case where the polynomial in n, $f(n,T_j)$, has three roots, n_-, n_+ and n_i, with $n_+ > n_i > n_-$; $n_+ \approx 1$ and $n_- \approx 0$. Steadily propagating front solutions can be readily found:

$$v = \Big(\frac{D_n \alpha T_j}{2}\Big)^{1/2}(n_+ + n_- - 2n_i)|_{T=T_j} \tag{4}$$

This velocity is proportional to $\sqrt{D_n}$ and hence quite small.

So far, we have not determined the temperature T_j, which remains a free parameter in Eq.4. In order to obtain a consistent solution, one has to solve simultaneously the T-equation, Eq.2, with the condition that n jumps from $n_- \approx 0$ to $n_+ \approx 1$ at $T = T_j$. for the approximation $(1+\tanh(\gamma(T-T_*)) \approx 2$ asymptotic patching leads to

$$v = \left(\frac{D_T\delta}{2}\right)^{1/2} \frac{(T_+ + T_0 - 2T_j)}{\sqrt{(T_+ - T_j)(T_j - T_0)}}\ ,\ \alpha_\pm \equiv (v/D_T)(-1/2 \pm \sqrt{1/4 + D_T\delta/v^2}) \qquad (5)$$

where $T_+ = T_0 + 2/\delta$. .

In principle, compatibility of Eq.4 and 5 fixes the value of T_j. Since according to Eq.5, the front velocity is proportional to $\sqrt{D_T}$, which is a-priori much larger than the velocity given by Eq.4, one obtains $(T_+ + T_0 - 2T_j) = \mathcal{O}(\sqrt{D_n/D_T})$. In the limit $D_n/D_T \to 0$ one has $T_j = (T_0 + T_+)/2$. This coincides with the Maxwell condition:

$$\int_{T_0}^{T_+} F(T, n(T))dT = 0. \qquad (6)$$

Quite generally one expects in the limit $D_n/D_T \to 0$ the velocity to be given from Eq.4 with T_j determined from the Maxwell condition 6 with $F = F_-$ ($F = F_+$) for $T < T_j$ ($T > T_j$).

Importantly, because the branches n_+ and n_- exist only in a finite interval of temperature, the Maxwell construction is possible only in a finite interval of values of T_0. The disappearance of the n_+ branch at $T = T_l$ and the n_- branch at $T = T_u$ implies that the Maxwell construction, Eq.6, is possible only if $T_l \leq (T_0 + T_+)/2 \leq T_u$.

The existence of slowly propagating fronts has been thoroughly checked numerically. The dependence of the velocity v on T has been shown. It is seen that the slow fronts are observed in an interval of control parameter values where the Maxwell construction is possible. In this range, slow waves are observed: the numerically observed values of the velocity are well described by Eq.4. The dependence of the velocity on $\sqrt{D_n}$ has been explicitly checked.

4 Fast fronts

Our numerical results show that steadily propagating front solutions still exist, even when the Maxwell condition Eq.6 cannot be satisfied. Numerical results show that the velocity increases sharply when $T_0 > T_u - 1/\delta$, indicating that these fronts have a much larger velocity. The aim of this section is to characterize these fast fronts. We choose to focus here on the disappearance of slow fronts above $T_0 > T_u - 1/\delta$. The fast fronts observed on the low-temperature side can be described in a similar way.

The jump in n may occur at a temperature higher than T_u which seems at first sight paradoxical, since the n_- branch disappears above T_u, hence, the solution is expected to jump to the other stable branch, $n_+ \approx 1$ above T_u. The explanation for the high values of the temperature T_j is that although the branches of solutions disappear above T_u, the function f, see Eq.2, remains small near $n \approx 0$ for $T \geq T_u$, hence, the jump in n does *not* coincide with the disappearance of the n_- branch. The temperature T_j on the other hand depends on the strength of the non-linear term, f.

To analyze the problem, we make use of the dimensionless parameter a introduced in Eq.2 to enhance the nonlinearity. In the temperature range where slow waves exist, the front velocity is independent of a. However, the width of the front in n becomes smaller when a increases. The situation changes dramatically when slow fronts no longer exist. As a increases the width of the front again becomes smaller, the jump occurs nearer to T_u, and the front velocity increases. In the limit $a \to \infty$ the velocity tends to that obtained from Eq.5 with $T_j = T_u$. It is evident, and we also checked numerically, that the diffusive term in Eq.2 becomes very small, compared to the other terms in the equation, when a increases. This suggests that the diffusive term may be dropped when considering large but finite a.

Since the jump in n occurs over a very narrow region of space, at a fixed T_j T can again be determined as above, as well as the relationship between the velocity v and T_j, Eq.5. Indeed we have checked that Eq.5 numerically works very well, and that the temperature profile is made of two exponentials, as predicted. To completely determine the solution, one has to compute the value of T_j. Thus the increase of the velocity v when a increases is related to the fact that the T_j to be inserted in Eq.5 becomes closer to T_u. The structure of the front may be completely determined in the large a limit, as we now explain.

The disappearance of the n_- branch for $T > T_u$ means that the function f can be parametrized for $T \simeq T_u$ by:

$$f(n,T) = \alpha T_u (n_+ - n)((n-n_*)^2 + \eta(T - T_u)) \tag{7}$$

where to leading order n_+, n_* and η are taken at $T = T_u$.

In addition, we use the numerically verified fact that the temperature profile is essentially linear between T_u and the region where the variable n jumps. The fact that for $a \to \infty$ one knows the temperature dependence on ξ:

$$T(\xi) \simeq T_u - \theta\xi \tag{8}$$

with $\theta = (T_u - T_0)\alpha_- = (T_u - T_+)\alpha_+$, leads, after substitution in Eq.2, and neglecting the diffusion term in the large a limit, to:

$$-v\partial_\xi n = a\alpha T_u (n_+ - n)((n - n_*)^2 - \lambda\xi) \tag{9}$$

where $\lambda = \theta\eta$.

In order to solve Eq.9, we impose as a boundary condition that $n(\xi)$ is, for large, positive values of ξ, equal to $n_-(\xi)$, the lower branch of solution. With this boundary condition, one may decompose space into (i) a regions where $n << n_+$, so the equation reduces to the Riccati equation: $-vdn/d\xi = a\alpha T_u n_+((n-n_*)^2 - \lambda\xi)$, and (ii) a region where n is large.

In region (i), the parameter a can be scaled away from the Riccati equation:

$$-\frac{d\overline{n}}{d\overline{\xi}} = (\overline{n}^2 - \overline{\xi}) \tag{10}$$

by introducing $n = n_* + e\overline{n}$, $\xi = f\overline{\xi}$; $e = (v/a)^{1/3}(\lambda/\alpha T_u n_+)^{1/3}$ and $f = (v/a)^{2/3}(1/\alpha T_u n_+)^{2/3}\lambda^{-1/3}$. The solution of this equation, with the boundary condition $\overline{n}' = 0$ at $\overline{\xi} = 0$ has a finite-time singularity, $\overline{n} \sim 1/(\overline{\xi} - \overline{\xi}_0)$ at $\overline{\xi}_0 \approx -1.99$. For other boundary condition the value of of $\overline{\xi}_0$ is changed.

In region (ii) where n is larger, the $(n_+ - n)$ term cannot be approximated by a constant any longer. Using the numerical results, we expect that the front is very steep, so ξ in the RHS of the Riccati equation may be replaced by a constant. Scaling distances in the front region by $\xi = \underline{\xi}(v/a\alpha T_u)$, one readily finds in the front region:

$$-\frac{dn}{d\underline{\xi}} = n^2(n_+ - n) \tag{11}$$

which can be integrated by quadrature. Importantly, the solution of Eq.11 and the singular solution of Eq.10 have a common domain of validity, allowing a formal matching.

The result of this analysis is that the front is located at a distance $\sim (v/a)^{2/3}$ from the location where the n_- branch disappears. Using again the fact that temperature is linear in the region considered, Eq.8, and the dependence of v on T_j, Eq.5, our analysis predicts that the front velocity behaves, for large values of a, as

$$v(a) = v(a = \infty) - const.a^{-2/3} \tag{12}$$

In addition, our analysis predicts that the front is very sharp (size of order v/a), with a very wide precursor ahead, of size $(v/a)^{2/3}$.

This is in full agreement with our numerical results. For a set of parameters, we have varied the parameter a in the range $1 \leq a \leq 128$. The width of the front defined as the difference between the points where $n = 0.2$ and $n = 0.8$ is found to scale as v/a, and the distance between the point where $T = T_u$ and the location of the jump behaves as $(v/a)^{2/3}$. Fig.5 shows the velocity v as a function of $a^{-2/3}$, demonstrating that the numerical results are consistent with the analysis presented above. In fact, the analytic estimate of the prefactor is in fair agreement with the numerical one.

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Références

[1] V. V. Barelko, I. I. Kurochka, A. G. Merzhanov and K. G. Shkadinskii, Chem. Engng. Sci. **33**, 805-811 (1978).

[2] S. A. Zhukov, V. V. Barelko and A. G. Merzhanov, Int. J. Heat Mass Transfer **24**, 47-55 (1980).

[3] V. I. Arnold, V. S. Afrajmovich, Yu. S. Ilyashenko, L. P. Shilnikov, in *Encyclopaedia of Mathematical Sciences, Volume 5 Dynamical Systems*, Springer Verlag, Berlin-Heidelberg-New-York, 1994.

[4] J. Keener and J. Sneyd *Mathematical Physiology*, Springer Verlag, New-York (1998).