Anomalous kinetics of reaction–diffusion fronts

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Abstract

We review our recent studies on the $A + B \rightarrow C$ reaction–diffusion system with initially separated components and describe the novel kinetic properties of the reaction front. When the reaction is slow, the two species will mix before reacting. This leads to a series of cross-overs in the kinetic properties from a rich initial behaviour to an asymptotic time behaviour. We focus on the non-universal and non-monotonic motion of the reaction front centre and discuss the possibilities of one or two switches in the direction of motion of the front, as well as other types of motion. The anomalous kinetics depend on the system parameters, namely the diffusion coefficients and the initial densities of the two species.

§ 1. Introduction

The kinetics of the $A + B \rightarrow C$ reaction–diffusion process are very sensitive to initial conditions. Systems with initially uniformly mixed reactants have been widely studied theoretically, but such a condition is difficult to achieve in a real chemical system. On the other hand, systems with initially separated components are more readily amenable to experimental studies. The initial separation of reactants leads to the formation of a dynamic reaction front, which is a spatially localized region with non-zero reactant production. The presence of such a reaction interface is a characteristic of many processes in nature and has recently attracted much research interest.

The following set of mean-field type reaction–diffusion equations for the local concentrations $\rho_a$ and $\rho_b$ has been assumed to describe the initially separated $A + B \rightarrow C$ reaction–diffusion system (Gállfi and Rácz 1988):

\begin{align}
\dot{\rho}_a &= D_a \nabla^2 \rho_a - k \rho_a \rho_b, \\
\dot{\rho}_b &= D_b \nabla^2 \rho_b - k \rho_a \rho_b,
\end{align}

where $D_a$ and $D_b$ are the diffusion constants, and $k$ is the microscopic reaction constant. The equations are subject to the initial separation condition along the $x$ axis:

$$\rho_a(x,0) = a_0 H(x), \quad \rho_b(x,0) = b_0 \left[1 - H(x)\right],$$

where $a_0$ and $b_0$ are the initial densities and $H(x)$ is the Heaviside step function. This means that initially the $A$ are uniformly distributed on the right side ($x > 0$), and the $B$ on the left ($x < 0$). This mean-field description has been argued by Cornell et al. (1991) to be valid above an upper critical dimension $d_{\text{up}} = 2$.

The local production rate of $C$, defined as the reaction term in equation (1) and given by

$$R(x,t) = k \rho_a(x,t) \rho_b(x,t),$$

is the basis for defining the kinetic characterizations of the system. The global reaction rate \( R(t) \) is the spatial integration over \( R(x, t) \); the centre \( x_f(t) \) of the reaction front is defined as the position where \( R(x, t) \) has a maximum, the width \( w(t) \) of the front is defined through its second moment, and the height of the front is simply the local rate at \( x_f \), denoted by \( R(x_f, t) \).

§ 2. Methods and Results

Two main analytical methods have been used to study the model system. The first is a scaling theory by Gállfi and Rácz (1988), which is valid in the asymptotic time limit. They assume a scaling form for \( R(x, t) \), from which they obtain the asymptotic behaviour of the above-mentioned quantities. The second analytical approach is a perturbation theory by Taitelbaum et al. (1991), which is valid for relatively short times, when very little reaction takes place before the species become effectively mixed. The perturbation expansion is based on a description of the initial behaviour using a small dimensionless reaction constant, given by

\[
\epsilon = \frac{k}{(a_0 b_0 D_a D_b)^{1/2}}.
\]  

(3)

The combination of the results from these two theoretical methods is reflected in a series of cross-overs from an initial to an asymptotic time behaviour of the kinetic properties of the reaction front. These cross-overs depend on the microscopic reaction constant, as well as on the ratios of diffusion coefficients and initial densities of the two species. For example, the global reaction rate \( R(t) \) changes dramatically from an initial \( t^{1/2} \) increase to a final \( t^{-1/2} \) decrease, at time proportional to \( k^{-1} \) (Taitelbaum et al. 1991). In practice, when \( k \) is very small, these cross-overs take place on a real time scale of hours, thus providing a useful means to extract microscopic parameters from macroscopic experiments.

In table 1 we summarize the cross-over behaviour of the kinetic characteristics of the reaction front. These results have been confirmed by various numerical methods (Jiang and Ebner 1990, Koo et al. 1990, Koo and Kopelman 1991, Taitelbaum et al. 1991).


<table>
<thead>
<tr>
<th>Quantity</th>
<th>Notation</th>
<th>Short-time behaviour</th>
<th>Long-time behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global rate</td>
<td>( R(t) )</td>
<td>( t^{1/2} )</td>
<td>( t^{-1/2} )</td>
</tr>
<tr>
<td>Centre of front</td>
<td>( x_f(t) )</td>
<td>Non-universal</td>
<td>( t^{1/2} )</td>
</tr>
<tr>
<td>Width of front</td>
<td>( w(t) )</td>
<td>( t^{1/2} )</td>
<td>( t^{-1/6} )</td>
</tr>
<tr>
<td>Local rate at ( x_f )</td>
<td>( R(x_f, t) )</td>
<td>Constant</td>
<td>( t^{-2/3} )</td>
</tr>
</tbody>
</table>

Table 1 A summary of the cross-over behaviour of the reaction front properties in the initially separated \( A + B \rightarrow C \) reaction–diffusion system.
§ 3. Experiments

The experimental studies of this system have been performed at the University of Michigan by the group of Professor R. Kopelman. The experiments are based on optical absorbance measurements of the reactants and the product and have been performed in a glass reactor 52 cm long made of a rectangular capillary with 4 mm × 2 mm cross-section (figure 1). Using syringes, the reactants were poured slowly into each end arm of the reactor. They met at the centre, forming a vertical boundary at $t = 0$. Light sources of appropriate wavelengths have been used for the optical excitation (with low-pass filters for noise reduction), and a photomultiplier tube (PMT) as a detector. A slit unit, composed of two slits with adjustable widths, allowed light to pass to and from the reactor. The slit widths were 0.05 mm on the light source side and 0.09 mm on the detector side to ensure a 0.1 mm mechanical resolution. The light source, the solenoid with the filters, the slit unit and the detector were all fixed on a stepping motor, which moved the system along the reaction front domain, the length of which was less than 5 cm after 24 h. The glass reactor itself was separately fixed over the slit unit. A typical snapshot of one scan, which yields the absorbance profile of the product, is shown in figure 2. Further details about the experimental technique have been described by Koo and Kopelman (1991).

In order to test the asymptotic predictions, Koo and Kopelman (1991) have chosen the inorganic bimolecular reaction $\text{Cu}^{2+} + \text{‘tetra’} \rightarrow 1:1$ complex (in a gel solution), where ‘tetra’ is the molecule disodium ethyl bis(5-tetrazolylazo)acetate trihydrate. This reaction is instantaneous, which means that $k$ is large, and the reaction passes immediately to the asymptotic diffusion-limited regime. With these

![Figure 1](image-url)  
**Figure 1.** The glass reactor. A view of the experimental system used by Koo and Kopelman (1991). The top of the figure is a side view of the glass reactor and the bottom is a top view of the experimental set-up.
materials, the asymptotic results for the global reaction rate $R(t)$, the width $w(t)$, and the reaction front centre $x_f(t)$ have been confirmed.

However, in order to test the cross-over predictions, one has to use reactants which react slowly. For this purpose, Taitelbaum et al. (1992) and Koo et al. (1993) chose the reaction $\text{Cr}^{3+} + \text{XO} \rightarrow 1:1$ complex in gel, where XO is the dye xylenol orange. In this slow reaction the colour changes from orange (of the XO) to purple (of the product). In figure 3 we show the behaviour of the global production rate $R(t)$

![Absorbance profile of a product: a typical snapshot.](image1)

**Figure 2.** Absorbance profile of a product: a typical snapshot. (From Taitelbaum (1994).)

![Experimental results of the global reaction rate $R(t)$ as a function of time for the reaction $\text{Cr}^{3+} + \text{XO} \rightarrow 1:1$ complex.](image2)

**Figure 3.** Experimental results of the global reaction rate $R(t)$ as a function of time for the reaction $\text{Cr}^{3+} + \text{XO} \rightarrow 1:1$ complex. (From Taitelbaum (1994).)
which crosses over from an initial increase proportional to $t^{1/2}$ to a final decrease proportional to $r^{-1/2}$, as has been predicted by Taitelbaum et al. (1991). The cross-over point enables estimation of the microscopic reaction constant.

The experimental results have confirmed the general cross-over predictions and provided more data which can be explained on the grounds of more complicated reaction schemes (Taitelbaum et al. 1996a, b).

§ 4. KINETICS OF THE REACTION FRONT CENTRE

The centre $x_t$ of the reaction front, which is defined as the position where the local production rate $R(x, t)$ of $C$, is a maximum, has been found to exhibit very interesting and non-trivial behaviour. The general expression for $x_t$ in the early time region has been found by Taitelbaum et al. (1992) to be given by

$$x_t \approx \frac{\pi^{-1/2}(D^{-1/2} - D^{1/2})t^{-1/2} + \epsilon M(D_x r)t^{1/2}}{\pi^{-1}t^{-1} + \epsilon N(D_r)},$$

where

$$D = \left(\frac{D_a}{D_b}\right)^{1/2}, \quad r = \left(\frac{a_0}{b_0}\right)^{1/2},$$

and $M$ and $N$ are time-independent constants, which depend in a non-trivial manner on $D$ and $r$. A detailed examination of equation (4) results in four different universality classes in the early-time regime as a function of $D$ and $r$ (Taitelbaum et al. 1992), as is summarized in table 2.

4.1. Non-monotonic motion

The most interesting behaviour of $x_t(t)$ as a function of time is that it can have an extremum point with the physical implication of a non-monotonic motion along the separation axis. The time $t^*$ for which $x_t(t)$ has such an extremum point depends in a complicated manner on $D$ and $r$, through the cumbersome expressions for $M$ and $N$. The condition for a positive $t^*$, and thus for a physical meaning of switching directions, is found to be \{2 + $3^{1/2}$ > $D > 1$, $r < 1$\}, or basically \{D > 1, r < 1\}, provided that the value of $D$ is relatively close to unity, as discussed by Taitelbaum et al. (1992). Similarly, the other possible condition is \{1 > $D > 2 - 3^{1/2}$, $r > 1$\}, or basically \{D < 1, r > 1\}. The non-monotonic motion is understood as follows. Suppose, for example, that $D_a > D_b$ and $a_0 < b_0$. At very early times diffusion effects are dominant, and the direction of motion is determined by the penetration of the A species to the left B side of the system. Later, the reaction

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Table 2  A summary of the various time dependences of $x_t$, the centre of the reaction front, as a function of the system parameters $D$ and $r.$

<table>
<thead>
<tr>
<th>${D, r}$</th>
<th>Short times</th>
<th>Intermediate times</th>
<th>Long times</th>
</tr>
</thead>
<tbody>
<tr>
<td>{1, 1}</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>{1, r \neq 1}</td>
<td>0</td>
<td>$r^{3/2}$</td>
<td>$r^{1/2}$</td>
</tr>
<tr>
<td>$D \neq 1, r = 1$</td>
<td>$t^{1/2}$</td>
<td>$t^{1/2}$</td>
<td>$t^{1/2}$</td>
</tr>
<tr>
<td>$2 + 3^{1/2} &gt; D &gt; 1, r &lt; 1$ or $1 &gt; D &gt; 2 - 3^{1/2}, r &gt; 1$</td>
<td>$t^{1/2}$</td>
<td>$r^{3/2}$ (non monotonic)</td>
<td>$t^{1/2}$</td>
</tr>
<tr>
<td>$D &gt; 1, r &gt; 1$ or {D &lt; 1, r &lt; 1}</td>
<td>$t^{1/2}$</td>
<td>$r^{3/2}$</td>
<td>$t^{1/2}$</td>
</tr>
</tbody>
</table>
comes into play, and the species with higher concentration, B, will govern the direction of motion, which will be towards the right A side. Note that this result involves both two lowest orders in $\varepsilon$, so one expects the transition of the front from one direction to the other to occur at a rate proportional to $t^{3/2}$.

In figure 4 we show the experimental evidence for the non-monotonic motion of the reaction front centre (Taitelbaum et al. 1992). The system parameters are $5 \times 10^{-5}$ M XO (diffusion constant $3.5 \times 10^{-10}$ m$^2$/s$^{-1}$), and $7.5 \times 10^{-4}$ M Cr$^{3+}$ (diffusion constant, $2.7 \times 10^{-10}$ m$^2$/s$^{-1}$), so that $D = 1.14$ and $r = 0.26$ in accord with the requirements for an extremum position. In addition, one can clearly see that the change in direction occurs at a rate much higher than the asymptotic $t^{1/2}$. This formal short-time limit behaviour takes place at time $t = 223$ min, which is definitely quite long. This is because of the very small reaction constant $k$ in this particular system, so that the corresponding small parameter $\varepsilon$ defined in equation (3) is extremely small, and the short-time limit is extended over an easily measurable time interval.

4.2. More complicated types of motion

The switch in the direction of motion occurs in the early-time regime. The next question is what happens when the system enters its asymptotic time phase? How does the front location attains its $t^{1/2}$ asymptotic behaviour? What happens at the cross-over time?

Intuitively, the $t^{1/2}$ asymptotic time behaviour of $x_t$ follows from the diffusive nature of the reaction-diffusion system. Gálf and Rác (1988) pointed out that in the symmetric system, that is when $a_0 = b_0$ (assuming that $D_a = D_b$), the front does not
move at all and $x_f = 0$ for all time $t$. Jiang and Ebner (1990) showed later that the more general condition for the centre of the front to be stationary is

$$a_0 D_a^{1/2} = b_0 D_b^{1/2}. \quad (6)$$

This is based on the observation that in the long-time limit the reaction zone is fed by the diffusive fluxes of A and B, which at time $t$ are given by $a_0(D_a/t)^{1/2}$ and $b_0(D_b/t)^{1/2}$ respectively. Equality of these fluxes would result in a stationary front, while unequal fluxes will cause a motion of the front. Jiang and Ebner support their findings by numerical calculations. The validity of (6) has been recently confirmed analytically by Koza (1996).

In the case of non-monotonic motion of the front in the early-time regime, that is $\{D > 1, r < 1\}$ (or vice versa), these parameters can fulfil also the relation $r^2 D = 1$. Then owing to equation (6), one can expect the front to become asymptotically stationary. So is it possible that the front would start to move, change its direction and finally stop? If not, will it continue in the same direction?

We propose that three different parameters govern the direction of motion as time evolves. Based on the above discussion of the non-monotonic case, it is reasonable to assume that at the very earliest times the direction depends on $D$ only, whereas later, still within the short-time regime, it is $r$ that determines the direction. In the asymptotic time regime we suggest that the dominant parameter is the combination $r^2 D$, following from equation (6). In each time region, if the relevant parameter of this region ($D$, $r$ or $r^2 D$) is greater than unity, the front will move from the A side to the B side. If it is less than unity, the motion will be in the opposite direction, from the B side to the A side, and if it is equal to unity, the front will be stationary or temporarily stationary. Thus, various combinations of these parameters are expected to yield rich kinetic behaviour of the reaction front, in particular unusual non-monotonic properties.

We have performed numerical calculations based on the standard finite-difference method, to confirm our claim. In these computations we have used a new method to calculate the location of $x_f$ (Koza and Taitelbaum 1996). The calculations have been performed for a wide range of the system parameters.

In figure 5 we show our results for a system whose parameters are chosen so that $\{D < 1, r > 1\}$ for various possibilities of $r^2 D$. The specific values are $k = 0.01$, initial densities $a_0 = 0.2$ and $b_0 = 0.1$ ($r = 1.414$), diffusion coefficients $D_a = 0.1$ and various $D_b = 0.38, 0.4$ and 0.42, so that $D = 0.513, 0.5$ and 0.488 and $r^2 D = 1.026, 1$ and 0.976 respectively. Since $D < 1$ and $r > 1$, the directions of the front motion will be $B \rightarrow A$ and then $A \rightarrow B$ in the short-time regime. After the asymptotic time region sets in, we have all three possibilities: continuation in the $A \rightarrow B$ direction (for $r^2 D > 1$), approaching a stationary position (for $r^2 D = 1$), and the most surprising phenomenon, namely a second switch to $B \rightarrow A$ (for $r^2 D < 1$), which is reflected by a second extremum point in the curve for $x_f(t)$. All these three asymptotic curves belong to the same universality class and exhibit an asymptotic $t^{1/2}$ behaviour with different pre-factors.

In figure 6 we show similar data for $\{D > 1, r < 1\}$ and the three possibilities for $r^2 D$. The specific parameters are $k = 0.002$, diffusion constants $D_a = 0.4$ and $D_b = 0.1$ ($D = 2$), initial concentrations $a_0 = 0.5$ and various $b_0 = 0.24, 0.25$ and 0.26 ($r = 0.69, 0.707$ and 0.721), so that $r^2 D = 0.96, 1$ and 1.04 respectively. The directions of motion are $A \rightarrow B$ ($D > 1$), $B \rightarrow A$ ($r < 1$) and then according to the
It can be seen that at the earliest times the three curves for the various values of $r$ are indistinguishable, which confirms that in this region the behaviour depends on $D$ only. As is evident from the figures, the starting of the asymptotic region occurs at a time which is about an order of magnitude larger than the first switch of direction. The latter occurs at a time of order $k^{-1}$, which is the typical time for the beginning of the asymptotic region in systems with a monotonic motion of the front.

The significance of these results from the experimental point of view is that they can be used to control the motion of the front. Generally one cannot do much to change the values of the diffusion coefficients of the reactants which are determined by the type of solution in which the reaction takes place (Koo and Kopelman 1991). However, the initial densities can be controlled more easily, allowing one to obtain some pre-set values for $r$ and particularly $r^2 D$, in order, for example, to stabilize the front motion, or to have it moving in any preferred direction. In the experiment described by Taitelbaum et al. (1992), $D = 1.14$, $r = 0.26$ and $r^2 D = 0.08$, and indeed
only one switch of direction has been observed, in agreement with the above con-
cclusions. It remains an experimental challenge to obtain the second switch or
the stationary state as well.

4.3. On the parameter dependence of the front motion

The results in the last section imply that a sufficient condition for the non-
monotonic motion of the front is \( \{ D > 1, r < 1 \} \) or vice versa. However, the
perturbation analysis results as appear in table 2 state that there is an upper bound in \( D \)
which is \( D < 3.73 \), or a lower bound for the other case. Malyutin et al. (1997) have
similarly obtained that \( \{ 3.03 > D > 1, r < 1 \} \) or \( \{ 0.33 < D < 1, r > 1 \} \) is a sufficient
condition for the front to change its direction of motion. So the question is whether
there is a contradiction between the unbounded and the bounded conditions? What
does the upper (or lower) limit mean?

We propose that the two sets of conditions simply refer to different time regimes.
While the general condition \( \{ D > 1, r < 1 \} \) means that the change in direction

![Figure 6. The reaction front centre \( x_f \) as a function of time for fixed diffusion constants \( (D > 1) \), and various values of \( r \) \( (r < 1) \) and \( r^2D \). Parameter values are \( k = 0.002 \),
diffusion constants \( D_a = 0.4 \) and \( D_b = 0.1(D = 2) \) and initial densities \( b_0 = 0.5 \) and \( a_0 \) as is indicated in the figure \( (r < 1) \). The initial motion from right (A) to left (B) is
reflected in an initial decrease in \( x_f(t) \). (From Koza and Taitelbaum (1996).)
should occur sometime, the condition in table 2 \( \{3.73 > D > 1, r < 1\} \) refers to the short-time limit only, where the perturbation theory applies. We claim that, when \( 3.73 > D > 1 \), the direction change takes place in the short-time region and, when \( D > 3.73 \), it also happens, but in the long-time limit. In figure 7 we show numerical results that support this claim. In each plot we show both the global reaction rate \( R(t) \) and the reaction front centre \( x_f(t) \) as functions of time. The cross-over in time of \( R(t) \) from a \( t^{1/2} \) increase to a \( t^{-1/2} \) decrease is the boundary between the short-time and the long-time limit. The parameters in figure 7 (a) are \( D = 1.5 \) and \( r = 1/(12)^{1/2} \approx 0.29 < 1 \), namely \( \{3.73 > D > 1, r < 1\} \) and, indeed, for these parameters the direction change occurs before the cross-over in \( R(t) \), that is within the short-time limit. In figure 7 (b), obtained with the same value of \( r \) but with \( D = 10 \), we confirm that, when \( D > 3.73 \), the direction change occurs after the cross-over in \( R(t) \), that is, in the long-time limit. The conclusion is then that the condition \( \{3.73 > D > 1, r < 1\} \) does not preclude that the non-monotonic behaviour can occur at later times, consistent with the general condition \( \{D > 1, r < 1\} \).

In figure 8 we plot the extremum time \( t_e \), defined as the time of the change in direction of the front, as a function of \( D \), for the case \( \{D > 1, r < 1\} \). We also plot the cross-over time \( t_c \) between the short and long time. The two functions cross each other at \( D \approx 3 \). This confirms that, for values of \( D \) less than this value, \( t_e \) is in the short-time region and, for larger \( D \), it is in the long-time limit. Moreover, this plot

Figure 7. The reaction front centre \( x_f(t) \) and the global production rate \( R(t) \) as functions of time. Parameter values are \( k = 0.0002 \), initial densities \( a_0 = 0.0166 \) and \( b_0 = 0.2(r = 1/(12)^{1/2} \approx 0.29 < 1) \), and diffusion constants \( D_a = 0.25 \) and two different values of \( D_b \). (a) \( D = 1.5 \); (b) \( D = 10 \).
also confirms the validity of the conditions for two switches in the direction of motion of the front. We see that for $D > 12$, that is for $r^2 D > 1$, there are two values of $t_c$ for a given $D$, which indicates that a second switch of direction takes place.

It is interesting to note that, when $D$ is extremely large (in this case $D \approx 13$ for fixed $r = 1/(12)^{1/2} \approx 0.29 < 1$), the non-monotonic behaviour breaks down and monotonic motion shows up, as can be seen in figure 8.

Another comment is that the dependence on $r$ of the non-monotonic motion is different. For a fixed value of $D$ and varying $r$, the non-monotonic motion occurs either in the short-time limit or in the long-time limit, depending on the specific fixed value of $D$, but not in both, as is the case as a function of $D$. This means that the behaviour of the reaction front is more sensitive to the value of $D$ than to that of $r$.

§ 5. SUMMARY

We have presented various characteristics of the $A + B \rightarrow C$ reaction–diffusion system with initially separated components, which exhibits a series of cross-overs from an initial to an asymptotic time behaviour. Then we have focused on the kinetics of the reaction front centre and showed that its motion is non-universal. In particular, we have shown that the front can exhibit a non-monotonic motion along the separation axis. We have shown that there are three different parameters, each determines the direction of motion of the front in a different time region. We have predicted the surprising possibility of two switches in the direction of motion of the front, as well as a situation of a stationary front after a single change in direction. We have examined the parameter dependence of the front motion and showed that
the system parameters determine whether the system exhibits its motion anomalies in the short-time or in the long-time limit.

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