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LETTER TO THE EDITOR

Study of the steady state of a two-species annihilation process with separated reactants

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Abstract. The steady-state behaviour of the irreversible reaction $A + B \rightarrow C$ with separated reactants in one dimension is studied, when currents J of A and B particles are directed towards each other by means of an analytical approach. The interparticle distance distribution in the reaction front is derived. Fixing the reaction constant, and for large J , the process is limited by reaction and the average interparticle distance at the reaction front (l_{AB}) behaves as $l_{AB} \sim J^{-1}$. In the limit $J \rightarrow 0$ the process is limited by diffusion and the behaviour $l_{AB} \sim J^{-1/2}$ holds. The crossover between both regimes is well described analytically and the crossover current is found to be $J_c = \frac{k^2}{\pi D}$. These results are in excellent agreement with Monte Carlo simulation results.

Reaction–diffusion processes play an important role in many areas of science, such as, for example, chemistry, heterogeneous catalysis, biology, astrophysics, solid state physics, etc. These processes have an impact in both fundamental and applied research. Furthermore, they give rise to very rich and complex phenomena which are in most cases difficult to describe and analyse. This is in part due to their nonlinear nature as well as because they take in far from equilibrium situations. In most cases a numerical approach is the only possible way to investigate these processes. In fact, writing the corresponding set of partial differential equations that need to be solved is frequently rather difficult. Also, intrinsic fluctuations are known to play a relevant role in many cases [1–3]. The simplest example is the anomalous kinetics observed in the $A + B \rightarrow C$ reaction–diffusion process. A considerable theoretical effort has been devoted to the study of simple monomer–monomer diffusion-limited reaction processes where the reactants are initially distributed at random (random mixing) [1, 2, 4–6]. In contrast with the numerous theoretical studies which are available in this field, very few experimental results have already been reported [6].

Recently, it has been realized that diffusion–reaction systems in which the reactants are initially separated, are more suitable for experimental studies [7–9] than reactions starting with randomly distributed particles. This is mainly because of the difficulties of implementing initially uniformly mixed distributions of the reactants. Consequently, theoretical interest in these systems has increased because now it is possible to test numerical and analytical predictions.

In the present work we have studied the irreversible reaction $A + B \rightarrow C$ with separated reactants in one dimension. We have adopted the following approaches:

(i) instead of studying the kinetics of the process [10, 11] our attention is focused on the stationary behaviour which arises when opposite currents of A and B particles are present;

(ii) since in many physical and chemical systems the rate of reaction is not only simply limited by diffusion but also by reaction, we have introduced the probability of reaction between species which accounts for the actual energy barrier that particles must overcome in order to get close enough to react; and

(iii) we have undertaken the problem using both numerical simulations and an analytical approach. The steady state of the reaction has been studied previously by Ben-Naim *et al* [12] using a mean-field description which is expected to hold above the critical dimension $d = 2$. Also the scaling behaviour of the steady state formed by opposing currents of A and B species has been analysed by Lee *et al* [13] using renormalization-group techniques.

We will now provide a brief description and some numerical results. The model used for the $A + B \rightarrow C$ reaction is one of particles undergoing discrete-time random walks on a discrete one-dimensional lattice of length L . We have considered the steady state reached when equal currents J of A and B particles are directed towards each other.

Let us describe the model and introduce some parameter definitions [14, 15]. At each time step any of the L sites of the lattice is randomly chosen. The following situations may appear:

(i) if the site is occupied, the particle tries to jump to any of both nearest-neighbour sites with equal probability $\lambda \Delta t$, where λ is the jumping rate and Δt is the size of the time step. The jumping rate is related to the diffusion coefficient D and the lattice spacing Δx by $\lambda = D/\Delta x^2$. If the nearest-neighbour site is occupied by a second particle, the jump is not performed; and

(ii) if the chosen site is one of the extremes of the lattice (site numbers $-L/2$ or $L/2$), and if the site is not occupied, a particle (A or B , respectively), is introduced into the lattice with probability j , this probability is related to the current J . The average number of particles that get into the lattice in a time step is $J \Delta t$. In the same time step we also consider the reaction process. If we have a pair of A and B particles in the reaction front at nearest neighbour they react with probability $p = \beta \Delta t$, where β is the reaction rate. The reaction constant k is defined as $k = \beta \Delta x$. After each time step, time is increased by $t \rightarrow t + \Delta t$. Multiple occupancy of lattice sites is forbidden, regardless of particle type.

Figure 1 shows plots of the concentration profiles $\rho(x)$ versus the distance, obtained through Monte Carlo simulations and for two values of k . Two regions can clearly be observed; on the one hand, close to the particle source, $\rho(x)$ decreases linearly. This region is characterized by the absence of reaction events and the particle current is simply given by

$$J = D \frac{\partial \rho(x)}{\partial x}. \quad (1)$$

On the other hand, the second region, close to the centre of the sample, is dominated by reaction, it is very narrow for $k = 1$ and becomes wider when k decreases.

We now consider an analytic approach. It is known that the reaction front in one dimension is described by several characteristic length scales [11], such as, for example, the width w of the reaction front and the position of the midpoint x_M between the rightmost A particle (RMA) and the leftmost B particle (LMB). Another length scale relevant for the description of the reaction front is the average distance l_{AB} between the RMA and the LMB. So, in this section we develop an analytic approach in order to evaluate the distribution of interparticle distances.

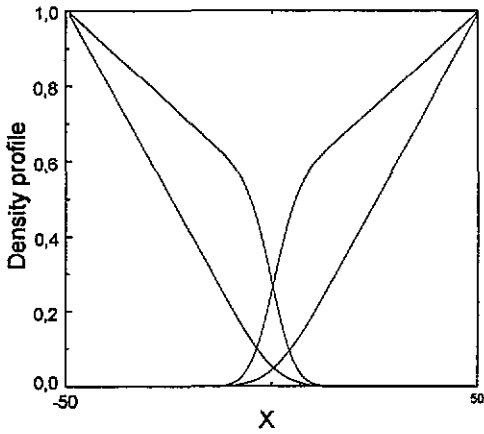


Figure 1. Plot of the density profiles of reacting particles, A (B) at the right (left) of the lattice, for the stationary regime. Results obtained from numerical simulations with lattices of length $L = 100$ and $D = \frac{1}{2}$. Lower curve $J = \frac{1}{100}$ and $k = 1$; upper curve $J = \frac{1}{200}$ and $k = \frac{1}{100}$. The slopes close to the sources are $\frac{1}{50}$ and $\frac{1}{100}$, respectively, in agreement with (1). The units used in the simulations are $\Delta x = 1$ and $\Delta t = 1/L$.

Let us define a discrete stochastic variable $P_i(t)$ which assumes two values: it is 1 if, at time t , RMA and LMB particles are placed at a distance i , and is 0 otherwise. In the continuous limit one has $x = i\Delta x$ and $\langle P_i(t) \rangle = P(x, t)\Delta x$, where the average $\langle \rangle$ is taken over configurations and $P(x, t)$ is the distribution of distances between the RMA and the LMB.

The method that we will use for deriving a differential equation for $P(x, t)$ is very similar to the one used in [14] for coagulation reactions. This case with imperfect reaction is analysed in [16].

The stochastic variable $P_i(t)$ will change due to both diffusion and reaction events. Both cases are treated separately as follows.

Changes due to diffusion. Let $P_i(t + \Delta t)_{dif}$ be the new value of $P_i(t)$ when the time has increased by Δt and due to all possible diffusion events, that is

$$P_i(t + \Delta t)_{dif} = P_{i+1}(t)2\lambda\Delta t + P_{i-1}(t)2\lambda\Delta t\{1 - Q_i(t)\} + P_i(t)\{1 - 4\lambda\Delta t + 2\lambda\Delta t Q_{i+1}(t)\} \tag{2}$$

where the first term accounts for a unitary decrease of the distance due to the jumps of either A or B particles in opposite directions, respectively. The second term corresponds to a unitary increase of the distance due to particle jumps, but here one has to take into account that the jump of a particle may be blocked by another particle placed behind, so we define the variable Q_i which takes the value 1 if site $i - 1$ is occupied by the first particle and site i if it is occupied by the second particle, and is 0 otherwise. The third term corresponds to all cases such that the distance remains unchanged.

In the continuous limit one has $\langle Q_i(t) \rangle = Q(x, t)\Delta x$ and $\langle P_i(t) Q_{i+1}(t) \rangle = \langle P_i(t) \rangle \langle Q_{i+1}(t) \rangle = P(x, t) Q(x + \Delta x, t) \Delta x^2$. The decorrelation of the product of P_i and Q_{i+1} is not an approximation, it is exact due to the way we defined Q_i . Taking a first-order approach to $Q(x + \Delta x, t) = Q(x, t) + \frac{\partial Q(x, t)}{\partial x} \Delta x$ and using the definition of λ it follows that for the continuous limit

$$\left\{ \frac{\partial P(x, t)}{\partial t} \right\}_{dif} = 2D \frac{\partial^2 P(x, t)}{\partial x^2} + 2D Q(x, t) \frac{\partial P(x, t)}{\partial x} + 2D P(x, t) \frac{\partial Q(x, t)}{\partial x} \tag{3}$$

This equation is exact, but, as we will see later, to solve it in the steady state we have to make an approximation for $Q(x)$.

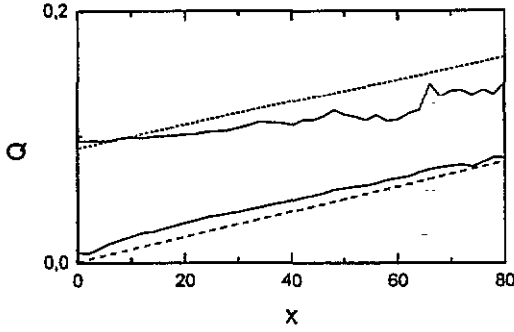


Figure 2. Plots of $Q(x)$ versus x . Simulation results for $L = 1000$ and $D = \frac{1}{2}$. Upper curve $J = \frac{1}{1100}$ and $k = \frac{1}{100}$; lower curve $J = \frac{1}{1000}$ and $k = 1$. The broken lines correspond to the approximation given by (8).

Changes due to reaction. Let $P_i(t + \Delta t)_{\text{reac}}$ be the new value of $P_i(t)$ when the time has increased by Δt and due to all possible reaction events, that is

$$P_i(t + \Delta t)_{\text{reac}} = P_i(t)\{1 - \delta_{i0}\} + P_0(t)\beta \Delta t T_i(t) + P_0(t)\{1 - \beta \Delta t\}\delta_{i0} \quad (4)$$

where δ_{i0} is the Kronecker delta and the variable $T_i(t)$ is defined as follows: it takes the value 1 if site 0 is occupied by the first particle and site i if it is occupied by the second particle, otherwise it takes the value 0. The first term in (4) shows that $P_i(t)$ does not change if $i \neq 0$ because the reaction is not possible, the second term corresponds to a successful reaction and the last term is due to a failed reaction. Then one obtains

$$\{P_i(t + \Delta t)\}_{\text{reac}} = P_i(t) + P_0(t)k \Delta t \frac{T_i(t)}{\Delta x} - P_0(t)k \Delta t \frac{\delta_{i0}}{\Delta x}. \quad (5)$$

In the continuous limit one has $\langle P_0(t) T_i(t) \rangle = \langle P_0(t) \rangle \langle T_i(t) \rangle = P(0, t) T(x, t) \Delta x^2$, as before, the decorrelation of the product is not an approximation. Equations (4) and (5) are exact, but, to get a solvable equation we approximate $T(x, t) = P(x, t)$. Finally

$$\left\{ \frac{\partial P(x, t)}{\partial t} \right\}_{\text{reac}} = kP(0, t)P(x, t) - kP(0, t)\delta(x). \quad (6)$$

The stationary regime. Adding the changes in the distribution due to both diffusion (equation (3)) and reaction (equation (6)), one obtains

$$\frac{\partial P(x, t)}{\partial t} = 2D \frac{\partial^2 P(x, t)}{\partial x^2} + 2D \left[Q(x, t) \frac{\partial P(x, t)}{\partial x} + P(x, t) \frac{\partial Q(x, t)}{\partial x} \right] + kP(0, t)P(x, t) - P(0, t)\delta(x). \quad (7)$$

In the steady state one has $\frac{\partial P(x, t)}{\partial t} = 0$. Furthermore, the number of reactions per unit time is given by $R(t) = kP(0, t)$. We call $R(t)$ the system reaction rate; not to be confused with the reaction rate β , which is a constant. Due to particle conservation the stationary current (or particle flux) J equals R , i.e. $kP(0) = J$. In order to solve equation (7) a reliable approach to $Q(x)$ has to be made for the steady state. We have used the approximation given by

$$Q(x) = P(0) + \frac{J}{D} \frac{x}{2}. \quad (8)$$

Numerical Monte Carlo results show that this approach holds very well close to the reaction front as, for example, it is shown in figure 2.

Finally, for the steady-state regime and $x > 0$, we obtain

$$2D \frac{d^2 P(x)}{dx^2} + J(x + 2D/k) \frac{dP(x)}{dx} + 2JP(x) = 0. \quad (9)$$

Using the normalization condition $\int_0^\infty P(x) dx = 1$ and the boundary condition $kP(0) = J$, equation (9) can be solved exactly giving

$$P(x) = \frac{J}{2D}(x + 2D/k)e^{-Jx(x+4D/k)/4D} \quad (10)$$

From equation (10) it is possible to evaluate the first moment of the distribution which gives the average interparticle distance at the reaction front, that is

$$\langle x \rangle = e^{DJ/k^2} \left(\frac{\pi D}{J} \right)^{1/2} \operatorname{erfc} \left(\frac{\sqrt{DJ}}{k} \right) \quad (11)$$

Equation (10) nicely describes the crossover between the two limiting regimes of the process, i.e. the case $J \rightarrow 0$ (or $k \rightarrow \infty$) which corresponds to the diffusion controlled reaction and the case $J \rightarrow \infty$ (or $k \rightarrow 0$) which corresponds to a reaction limited process. The distribution of distances between particles at the reaction front obtained by means of the analytical calculation is compared with Monte Carlo numerical simulations in figure 3. The excellent agreement found strongly supports the validity of the approaches used in the analytical treatment.

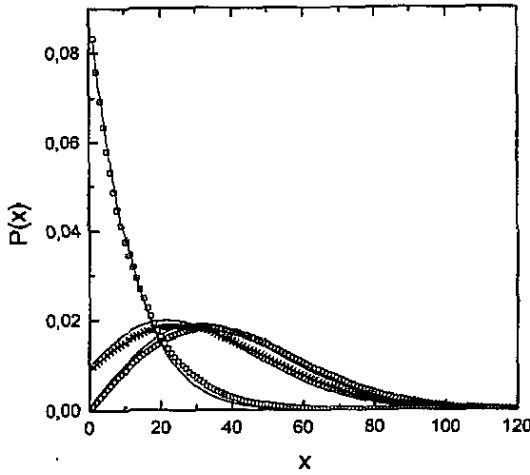


Figure 3. Distribution of interparticle distances at the reaction front obtained using (10) (full curves) and numerical Monte Carlo simulations (points). Results shown for $D = \frac{1}{2}$, $L = 1000$, and different values of k and J : squares: $k = \frac{1}{100}$ and $J = \frac{1}{1100}$, (crosses) $k = \frac{1}{10}$ and $J = \frac{1}{1010}$; and (diamond) $k = 1$ and $J = \frac{1}{1001}$.

For the diffusion-controlled regime the distribution $P(x)$ is very broad (see figure 3), so the typical spatial distance x becomes large and the approach $x \gg \frac{2D}{k}$ holds in (10), which gives

$$P(x) \cong \frac{J}{2D} x e^{-Jx^2/4D} \quad (12)$$

Within this regime the moments of the distribution are given by

$$\langle x^m \rangle = \frac{\Gamma(1 + m/2)}{(J/4D)^{m/2}} \sim J^{-m/2} \quad (13)$$

where Γ is the standard gamma function. For the first moment the known result $l_{AB} = \langle x \rangle \sim J^{-1/2}$ is recovered [13].

Within the reaction-controlled regime the typical length described by $P(x)$ is very narrow (see figure 3) and consequently the approach $x \ll \frac{2D}{k}$ holds in (10), which now gives

$$P(x) \cong \frac{J}{k} e^{-Jx/k} \quad (14)$$

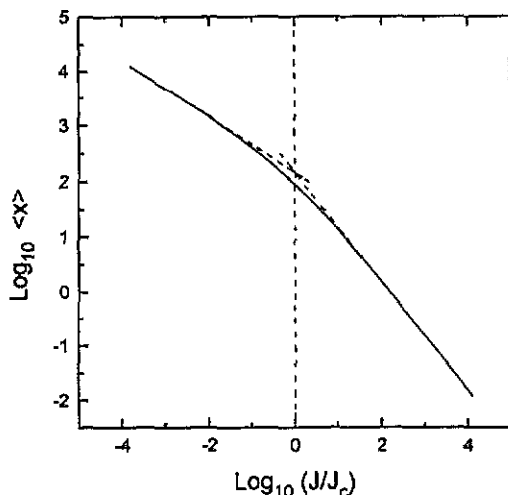


Figure 4. Log-log plot of the average interparticle distance at the reaction front $\langle x \rangle$ versus the particle current J evaluated for $D = \frac{1}{2}$ and $k = 0.01$. We can see the asymptotic behaviours of slopes $-\frac{1}{2}$ and -1 .

Within this regime the moments of the distribution are given by

$$\langle x^m \rangle = \frac{m!}{(J/k)^m} \sim J^{-m}. \quad (15)$$

So, for the reaction-controlled regime the first moment now behaves proportionally to J^{-1} in contrast to the behaviour $J^{-1/2}$ characteristic of the diffusion-controlled regime. Figure 4 shows a log-log plot of $\langle x \rangle$ versus the particle current J/J_c . The crossover between the already discussed regimes can be clearly observed. The crossover current (J_c) defined as the intersection between the straight lines defining the asymptotic behaviour of both regimes is given by $J_c = k^2/\pi D$.

In conclusion, the steady-state behaviour of the irreversible reaction $A + B \rightarrow C$ with separated reactants crosses over from a diffusion-limited regime, when the current of particles $J \rightarrow 0$, to a reaction-limited regime when $J \rightarrow \infty$ for a fixed value of the reaction constant k . An analytical approach which allows us to evaluate the distribution of interparticle distances at the reaction front is developed. The first moment of the distribution, i.e. the average interparticle distance (l_{AB}), behaves as $l_{AB} \sim J^{-n}$, with $n = 1$ ($n = \frac{1}{2}$) for the reaction-controlled (diffusion-controlled) regime, respectively. The crossover current is found to be $J_c = \frac{k^2}{\pi D}$. Analytical results are in good agreement with numerical Monte Carlo simulations.

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