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Diffusion-controlled reaction, $A + B \rightarrow C$, with initially separated reactants

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We review recent developments in the study of diffusion–reaction systems of the type $A + B \rightarrow C$ in which the reactants are initially separated. We consider two initial boundary conditions: (i) the A and B particles are initially placed uniformly in Euclidean space at $x > 0$ and $x < 0$ respectively, and (ii) the A particles are diffusing and inserted at a given site and the B particles are static and distributed uniformly in space. We present analytical and numerical results for both systems. We consider $d = 1$, 2, 3 dimensional systems as well as fractal lattices.

1. Introduction

The dynamics of diffusion-controlled reactions of the type $A + B \rightarrow C$ has been studied extensively since the pioneering work of Smoluchowski [1,2]. Most studies have focused on homogeneous systems, i.e., when both reactants are initially uniformly mixed in a d-dimensional space, and interesting theoretical results have been obtained. When the concentrations of the A and B reactants are initially equal, i.e., $c_A(0) = c_B(0) = c(0)$, the concentration of both species is found to decay with time as $c(t) \sim t^{-d/4}$ for Euclidean systems with $d \leqslant 4$ [3–10] and as $c(t) \sim t^{-d_s/4}$ for fractals [5,6] with fracton dimension $d_s \leqslant 2$. Also, self-segregated regions of A and B in low dimensions ($d \leqslant 3$) [4] and in fractals [9] have been found. Quantities such as the distributions of domain sizes of segregated regions and interparticle distances between species of the same type and different types have been calculated [11–13]. These systems were also studied theoretically and numerically under steady state conditions and interesting predictions have been obtained [14–17]. However, the above numerical and theoretical predictions have not been observed in experiments, in part because of difficulties encountered when implementing the initially uniformly mixed distributions of reactants.

In recent years it was realized that diffusion reaction systems in which the

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reactants are initially separated [18], can be studied experimentally [19,20] and that the dynamics of such a system have many surprising features [20–26]. These systems are characterized by the presence of a dynamical interface or a front where the reaction takes place. Such a reaction front appears in many biological, chemical and physical processes [27–33].

Gàlfi and Ràcz [18] were the first to study diffusion-controlled reactions with initially separated reactants. They studied the kinetics of the reaction diffusion process by a set of mean-field (MF) type equations,

$$\frac{\partial c_A}{\partial t} = D_A \frac{\partial^2 c_A}{\partial x^2} - kc_A c_B \,, \tag{1a}$$

$$\frac{\partial c_B}{\partial t} = D_B \frac{\partial^2 c_B}{\partial x^2} - kc_A c_B \,, \tag{1b}$$

where $c_A \equiv c_A(x, t)$ and $c_B \equiv c_B(x, t)$ are the concentrations of A and B particles at position x at time t, respectively, D_i are the diffusion constants and k is the reaction constant. The rate of production of the C particles at site x and time t, which we call the reaction-front profile, is given by $R(x, t) \equiv kc_A c_B$. The initial conditions are that the A species are uniformly distributed on the right-hand side of $x = 0$ and the B species are uniformly distributed on the left-hand side.

Using scaling arguments Gàlfi and Ràcz [18] find that the width w of the reaction front $R(x, t)$ scales with time as $w \sim t^\alpha$ with $\alpha = 1/6$, and the reaction rate at the center of the front, called the reaction height, scales as $h \sim t^{-\beta}$ with $\beta = 2/3$.

Experiments [19] and simulations [19, 21–24] for $d \geq 2$ systems in which both reactants diffuse, support the above predicted values for α and β. Indeed, Cornell et al. [23] argue that the upper critical dimension is $d = 2$ and the MF approach should therefore be valid for $d \geq 2$. Indeed, numerical simulations of 1D systems show that the width exponent appears to be $\alpha \simeq 0.3$ and the height exponent $\beta \simeq 0.8$ [23,24]. The origin of the difference between the exponents of 1D systems and those of higher-dimensional systems is due to fluctuations in the location of the front which are important in low dimensions and are neglected in the MF approach.

Taitelbaum et al. [20,22] studied analytically eqs. (1) and presented experiments for the limit of small reaction constant or short time. Their main results are that several measurable quantities undergo interesting crossovers. For example, the global reaction rate changes from $t^{1/2}$ in the short time limit to $t^{-1/2}$ at the asymptotic time regime. The center of the front can change its direction of motion as observed in experiments [20]. Ben-Naim and Redner [25] studied the solution of (1) under steady-state conditions.

2. The form of the reaction-front profile, $R(x, t)$, in the mean-field approach

In a recent work [26] we consider the symmetric case in which both diffusion constants and initial concentrations are equal, i.e., $D_A = D_B \equiv D$ and $c_A(x, 0) = c_B(x, 0) = c_0$. If we define $F(x, t) \equiv c_A(x, t) - c_B(x, t)$, then from eq. (1) follows

$$\frac{\partial F}{\partial t} = D \frac{\partial^2 F}{\partial x^2} , \tag{2}$$

subject to the conditions that initially the A particles are uniformly distributed to the right of the origin while the B particles are uniformly distributed to the left of the origin. Eq. (2) has the solution $F(x, t) = c_0 \operatorname{erf}(x/\sqrt{4Dt})$.

We rewrite the concentrations of A and B particles as (see fig. 1)

$$c_A(x, t) = G_1(x, t) + \delta c_1(x, t) , \qquad c_B(x, t) = G_2(x, t) + \delta c_2(x, t) , \tag{3}$$

where

$$G_1(x, t) = \begin{cases} F(x, t) & (x > 0) , \\ 0 & (x < 0) , \end{cases} \tag{4}$$

and $G_2(x, t) = G_1(-x, t)$. Under the above conditions, $\delta c_1(x, t) = \delta c_2(x, t) \equiv \delta c(x, t)$. Substituting eqs. (3) into eqs. (1) yields

$$\frac{\partial(\delta c)}{\partial t} = D \frac{\partial^2(\delta c)}{\partial x^2} - k \left[c_0 \operatorname{erf}\left(\frac{x}{\sqrt{4Dt}} \right) + \delta c \right] \delta c . \tag{5}$$

The asymptotic solution for this equation that vanishes as $x \to \infty$, is (neglecting the $(\delta C)^2$ term)

$$\delta c(x, t) \sim t^{-1/3} \left(\frac{x}{t^{1/6}} \right)^{-1/4} \exp\left[-\frac{2}{3} \left(\frac{\lambda x}{t^{1/6}} \right)^{3/2} \right] , \qquad t^{1/6}/\lambda \ll x \ll t^{1/2}/a , \tag{6}$$

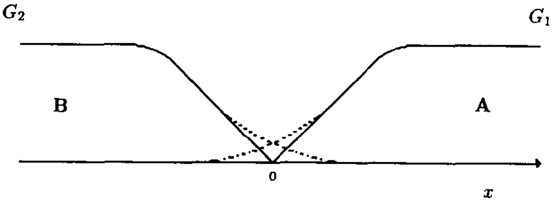

Fig. 1. Schematic picture of the reactant concentration profiles near the origin. The solid lines represent the $G_{1,2}(x, t)$ part of the profile, the dashed lines represent the complete form $G_{1,2}(x, t) \pm \delta c(x, t)$. Note that the profile of species A is given solely by $\delta c(x, t)$ on the left of the origin. (From ref. [26].)

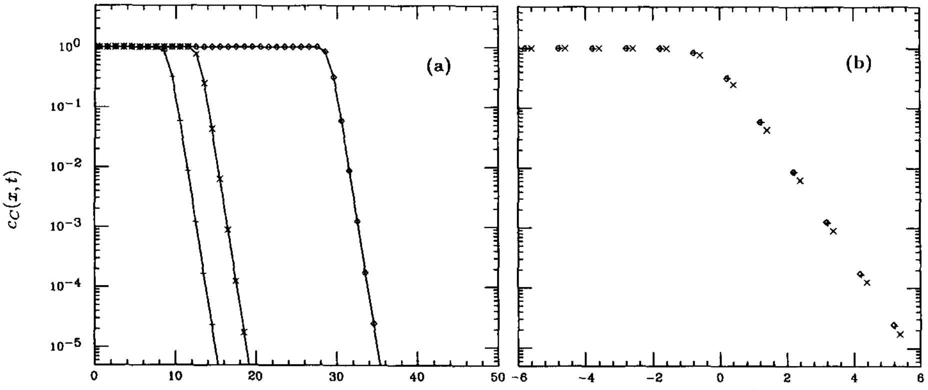

Fig. 2. Numerical solution of eq. (1) for the case $D_B = 0$, $D_A \neq 0$: (a) plot of $c(x, t)$ as a function of x for $t = 500$, 1000 and 5000 (from left to right); (b) the good scaling plot of $c(x, t)$ as a function of $(x - \langle x \rangle) \equiv x - \gamma t^{1/2}$ indicates that $\alpha = 0$ and $\beta = 1/2$.

where $\lambda = (ka/D)^{1/3}$, $a \equiv (c_0/\pi D)^{1/2}$. As may be confirmed by direct substitution, this expression is a solution of eq. (5) up to terms of order $(\delta c)/t$, which can be neglected for large t.

Using eq. (6) we can write an expression for the reaction-front profile $R(x, t)$ defined in (1) as

$$R(x,t) = \frac{kax}{t^{1/2}} (\delta c) \sim t^{-2/3} \left(\frac{x}{t^{1/6}}\right)^{3/4} \exp\left[-\frac{2}{3}\left(\frac{\lambda x}{t^{1/6}}\right)^{3/2}\right]. \qquad (7)$$

It is seen that the width of the reaction front grows as $t^{1/6}$, whereas the height can be identified with the prefactor $t^{-2/3}$ in eq. (7), consistent with the exponents found by Gàlfi and Ràcz [18]. Eq. (7) provides a more quantitative solution of eqs. (1) than the previous scaling arguments [18], as well as information on the dependence of the form of the reaction front on the parameters c_0, k and D, for the symmetric case.

For the case in which one reactant is static no analytical solution (of eqs. (1)) exists for the form of the reaction front profile. However, numerical solutions of eqs. (1) with $D_B = 0$, shown in fig. 2, suggest that $R(x', t) \sim t^{-\beta} g(x'/t^{\alpha}) \exp(-|x'|/t^{\alpha})$, where $x' \equiv x - \gamma t^{1/2}$. The excellent scaling in fig. 2b suggests that the width does not increase with time, i.e., $w \sim t^{\alpha}$ with $\alpha = 0$ and $h \sim t^{-\beta}$ with $\beta = 1/2$, consistent with the scaling arguments in ref. [21].

3. The front, $R(x, t)$, in $d = 1$

The reaction front profile in $d = 1$ systems, $R(x, t)$, when both reactants are diffusing with the same diffusion constant, $D_A = D_B \neq 0$, has been calculated

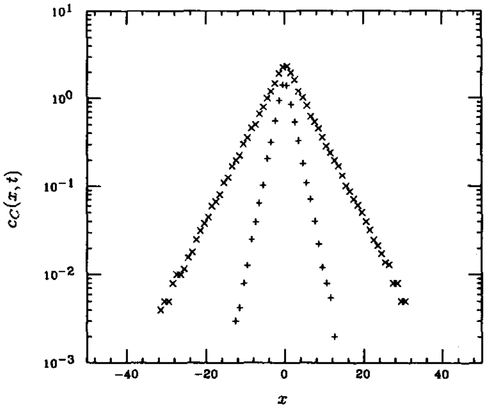

Fig. 3. Plot of $c_C(x, t)$ defined in eq. (8) for a $d = 1$ system with system size $L = 1000$ and $t = 100$ (+) and 1000 (×).

numerically [24]. The data shown in fig. 3 suggest that

$$c_C(x, t) \equiv \int_0^t R(x, t')\, dt' \sim t^{1-\beta} \exp(-a|x|/t^{\alpha}) , \tag{8}$$

with $\alpha = 0.30 \pm 0.02$ and $\beta = 0.80 \pm 0.02$. These values are in agreement with numerical simulations obtained using a cellular automata algorithm [23].

For the case $D_A \neq 0$, $D_B = 0$, analytical and numerical studies [34] yield for the reaction front profile

$$R(x, t) = \frac{1}{4t^{3/4}} \left(\frac{2\gamma^2}{\mu\pi}\right)^{1/2} \exp\left(-\frac{(x-\gamma t^{1/2})^2}{2\mu t^{1/2}}\right) \left(1 + \frac{x - \gamma t^{1/2}}{2\gamma t^{1/2}}\right) , \tag{9}$$

where γ and μ are constants. From eq. (9) follows that $\alpha = 1/4$ and $\beta = 3/4$. It is interesting to note that the time integral of $R(x, t)$, which is the total production of the C particles at x up to time t, is given by

$$c_C(x, t) = \int_0^t R(x, \tau)\, d\tau = \frac{1}{2} \operatorname{erfc}\left(\frac{x - \gamma t^{1/2}}{\sqrt{2\mu t^{1/2}}}\right) . \tag{10}$$

To summarize the case of $A + B \to C$ with initially separated reactants, we list in table I the four sets of exponents discussed above. Since there exists no theory for the $d = 1$ case when both species are moving, it is interesting to examine two main directions which yield a comprehensive explanation for the four sets of exponents. Both directions are based on assumptions about the form of the reaction term in eqs. (1).

One interesting proposition is based on assuming that the reaction term in

Table I
The values of the exponents α and β ($w \sim t^{\alpha}$, $h \sim t^{-\beta}$).

	$d = 1$	MF
Both moving	$\alpha \cong 0.3$ $\beta \cong 0.8$	$\alpha = 1/6$ $\beta = 2/3$
One static	$\alpha = 1/4$ $\beta = 3/4$	$\alpha = 0$ $\beta = 1/2$

eqs. (1) can be written as $kc_A^m c_B^n$. Using scaling arguments similar to Gàlfi and Ràcz [18], one obtains the set of two relations $\alpha - \beta = -1/2$ and $(m + n)(\alpha - 1/2) = -\beta$. Next assume that for mean field, $m = n = 1$ (both moving) and $m = 0$, $n = 1$ (A static), and for $d = 1$, $m = n = 2$ (both moving) and $m = 1$, $n = 2$ (A static). Substituting these values for m and n into the above relations, one obtains the four sets of exponents given in table I. Note that for the mean field case the values of m and n can be justified by simple decoupling of the reaction term in eqs. (1), i.e. neglecting correlations; however, we have no justification for the values of m and n chosen for the $d = 1$ case.

A second possible direction [35] based on the Smoluchowski approach [1] was suggested for $d = 1$ systems. In this approach, the reaction constant k in eqs. (1) should be time dependent as $k = k(t) \sim t^{-1/2}$ [36]. Using this result, the scaling relations for $d = 1$ become $\alpha - \beta = -1/2$, $2\alpha - 3/2 = -\beta$ when both reactants are moving, and $\alpha - \beta = -1/2$, $\alpha - 1 = -\beta$ when one reactant is static. These equations yield $\alpha = 1/3$, $\beta = 5/6$ for both reactants moving and $\alpha = 1/4$ and $\beta = 3/4$ for one reactant static. These results are closer to the numerical values of the exponents in $d = 1$ than the mean field results. In particular, it gives the exact exponents when one reactant is static. Note that for the short time regime α and β have different values from those given in table I [22] and, as was shown by Taitelbaum et al. [20], this short time regime can be observed in experiments.

The case of $A + B \to C$ initially separated on fractal systems was studied on $d = 2$ percolation clusters at criticality [22]. Numerical data support the scaling argument for the reaction rate,

$$c(t) \equiv \int_{-\infty}^{\infty} R(x, t)\, \mathrm{d}x \sim t^{-(1-1/d_w)} . \tag{11}$$

Here, d_w is the anomalous diffusion exponent, defined by the scaling of the mean square displacement of a random walk on the fractal, $\langle r^2 \rangle \sim t^{2/d_w}$ [40]. For the width, $w \sim t^{\alpha}$, and the height, $h \sim t^{-\beta}$, the numerical results in ref. [22] suggest $\alpha \cong 1/d_w$ and $\beta \cong 1$, but more extensive simulations are needed.

4. The reaction $\mathrm{A} + \mathrm{B}_{\mathrm{static}} \to \mathrm{C}_{\mathrm{inert}}$: localized source of A

Another system in which the reactants are initially separated and which is amenable to experiment, is the reaction $\mathrm{A} + \mathrm{B}_{\mathrm{static}} \to \mathrm{C}_{\mathrm{inert}}$ with a localized source of A species. There exist many systems in nature in which a reactant A is "injected" into a d-dimensional substrate B whereupon it reacts to form an inert product C. Recently such an experiment has been performed [37] by injecting iodine at a point of a large silver plate and measuring quantities of the reaction $\mathrm{I}_{2\,\mathrm{gas}} + 2\mathrm{Ag}_{\mathrm{solid}} \to 2\mathrm{AgI}_{\mathrm{solid}}$.

First we consider N particles of type A that are initially at the origin of a lattice. The B particles are static and distributed uniformly on the lattice sites. Using an approximate quasistatic [38] analytical approach for trapping in a moving boundary we derived expressions for $C(t)$, the time-dependent growth size of the C-region, and for $S(t)$ the number of surviving A particles at time t. For extremely short time $t < t_\times \sim \ln N$ we find $C(t) \sim t^d$. For $t > t_\times$ we find [39]

$$C(t) \sim Nf\left(\frac{t}{N^{2/d}}\right) \quad \text{and} \quad S(t) = N - C(t)\,. \tag{12a}$$

The scaling function $f(u)$ is the solution to the differential equation

$$\frac{\mathrm{d}f}{\mathrm{d}\tau} \sim k_d f^{-2/d}(1-f)\,, \tag{12b}$$

and k_d is a constant, depending only on dimension. Fig. 4 shows simulation data supporting (12a).

Next consider the case in which λ particles of type A are injected per unit time at the origin of the lattice. For this case we find [37]

$$C(t) \sim \begin{cases} \sqrt{8Dt\ln(\lambda^2 t/2D)}\,, & d = 1\,, \\ \pi\alpha t\,, & d = 2\,, \\ \lambda t\,, & d = 3\,, \end{cases} \tag{13}$$

and

$$S(t) \sim \begin{cases} \lambda t\,, & d = 1\,, \\ (\lambda - \pi\alpha)t\,, & d = 2\,, \\ C_3(\lambda)\, t^{2/3}\,, & d = 3\,. \end{cases} \tag{14}$$

In (13) and (14), α is the solution of $\alpha\pi = \lambda\exp(-\alpha/4D)$ and $C_3(\lambda) = (\lambda/4D)(3\lambda/4\pi)^{2/3}$. Moreover, we find that for one- and three-dimensional systems $C(t)$ satisfies the scaling relation

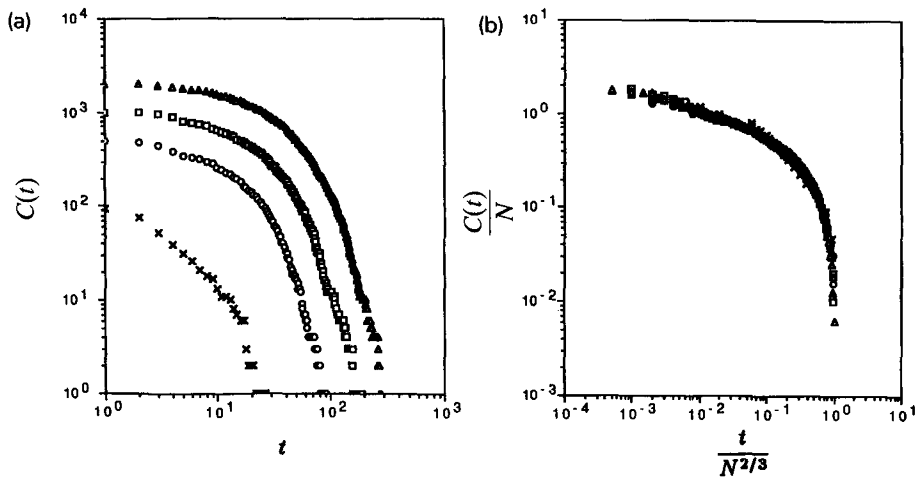

Fig. 4. Numerical simulations of $A + B \to C$ where N diffusing particles of type A are initially at the center of a lattice and particles of type B are static and located at each site of the $d = 3$ lattice: (a) plot of $C(t)$ for $N = 100$ (×), 500 (○), 1000 (□) and 2000 (△) particles; (b) plot of $C(t)$ in the scaling form eq. (12a). Note that the results are of a *single* Monte Carlo run and not averaged – showing that fluctuations are negligible in this process.

$$C(t) \sim \lambda^{d/(d-2)} g\left(\frac{t}{\lambda^{2/(d-2)}}\right). \tag{15}$$

Eqs. (13)–(15) have been supported by numerical simulations [37]. (See also fig. 5.)

Eqs. (12) can be generalized for fractals,

$$C(t) \sim N f\left(\frac{t}{N^{2/d_s}}\right), \tag{16a}$$

where $f(u)$ is the solution of the differential equation

$$\frac{\mathrm{d}f}{\mathrm{d}u} \sim k_{d_s} f^{-2/d_s}(1-f). \tag{16b}$$

Here d_s is the fracton dimension [40] defined by $d_s = 2d_f/d_w$, in which d_f is the fractal dimension and d_w the diffusion exponent [41]. For the case of constant injection rate on a fractal we do not have an analytical derivation. However, we recently calculated [42] the number of distinct sites visited on a fractal by N random walkers starting from the origin, $S_N(t) \sim (\ln N)^{d_f/\delta} t^{d_s/2}$ with $\delta = d_w/(d_w - 1)$. This result can be shown to be valid also for the number of distinct sites visited by random walkers injected at the origin with a constant rate of λ when replacing $N = \lambda t$. Thus we obtain that $[\ln(\lambda t)]^{d_f/\delta} t^{d_s/2}$ is an upper bound for $C(t)$.

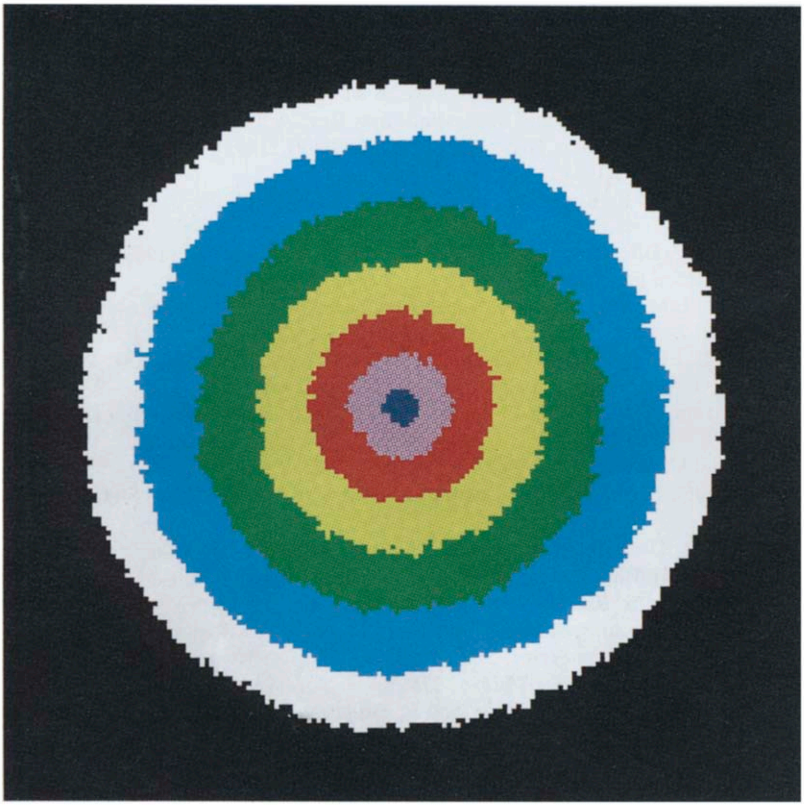

Fig. 5. Numerical simulations of $\mathrm{A} + \mathrm{B}_{\mathrm{static}} \rightarrow \mathrm{C}_{\mathrm{inert}}$ where A particles are injected at rate $\lambda = 5$ at the center of the lattice and particles of type B are static and are located at each site of a $d = 2$ lattice. Plot of the reactant area after $t = 20$, 160, 540, 1280, 2500, 4320 and 6860.

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