

## The diffusion-limited reaction $A + A \rightarrow 0$ in the steady state: influence of correlations in the source

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We study theoretically the kinetics of the diffusion-limited reaction  $A + A \rightarrow 0$  in the steady state. We consider the effect of an external source which adds correlated pairs of particles. We show that in dimensions below 2 and in the low-density limit spatial self-organization of reactants occurs and is controlled by the correlation in the source term. At higher densities there is a cross-over to a regime similar to the random landing case, exhibiting a non-classical order of reaction.

In recent years, there has been a great deal of work showing the anomalous behavior of diffusion-limited reaction kinetics in confined media and/or in fractal structures [1,2]. In the steady state it was shown that for a medium with a spectral dimension  $d_s \leq 2$  (including fractal sets as well as Euclidean spaces), a mesoscopic scale of self-organization is generated and leads to anomalous rate laws. This self-organization is directly linked to topological properties of the random walk in these media. In particular, theoretical treatments [3,5], computer simulations [6,7] and experiments [8,9] have shown non-classical kinetics for the one-species,  $A + A \rightarrow 0$  and  $A + A \rightarrow A$ , diffusion-limited annihilation and fusion in the steady state. For a medium of spectral dimension  $d_s < 2$ , the effective order of the reaction is found to be  $X = 1 + 2/d_s$  instead of the classical result  $X = 2$  for a bimolecular reaction. However, most of the investigations on binary diffusion-limited reactions assume that particles land randomly on a lattice, which may not be correct in some real chemical systems. For example, two atoms may land at adjacent sites as a result of a dissociative adsorption of diatomic molecules, and solitons and antisolitons may be created in pairs on a polymer (e.g. trans-polyacetylene) [10].

Some theoretical approaches have considered correlations in the external particle source. Rácz [3] derived the rate law of  $A + A \rightarrow 0$  steady state reactions in one-dimensional systems for the case in which particles are produced in “geminate” pairs at the nearest-neighbor lattice sites. The reaction order is found to be 2. Li and Kopelman [11] have studied the self-organization aspect of this problem in 1D for arbitrary correlation lengths using computer simulations. A good deal of work has been done on source correlation for the  $A + A \rightarrow 0$ ,  $A + A \rightarrow A$  [9,12–16],  $A + B \rightarrow 0$  [14,18] *batch* reactions, as well as  $A + B \rightarrow 0$  *steady state* reactions [17,19,20,22]. In particular, in the case of  $A + B \rightarrow 0$ , the importance of the source term structure and the influence of correlation between the landing species was carefully studied [20–22]. Here we follow the same theoretical scheme we developed in a previous work [4]. We give a general treatment of the influence of correlations in the source term for the  $A + A$  case in the steady state limit. We also compare results with recent simulations [11].

We consider an external source creating particles in pairs which land on the substrate separated by a fixed distance  $\lambda$  and with a rate of arrival  $R/2$ . Of course, in a real situation, the actual number of particles landing on the substrate and the distribution of distances  $\lambda$  would depend on the detailed interactions between the pairs, the substrate and the other particles. To treat all possible differences in the details of the sources (vertical anni-

hilation, random sequential adsorption, etc.), we would have to consider a wide variety of different correlation rules for the source term. However, we are here interested in the low-density limit; thus we can avoid problems of jamming and higher correlation effects due to random sequential adsorption which may indeed take place at higher densities [4]. In this limit, the detailed structure of the source term does not play a fundamental role as long as a typical correlation length is present. In fact, for all the specific sources we considered we are led to the same rate equation, and all the differences are absorbed into an *effective* rate of arrival  $Q$  (which is equal, in the steady state, to the bimolecular reaction rate). This simplification was also emphasized in ref. [4] for random landing of particles. Note that the  $A + A \rightarrow 0$  case is different from the  $A + B \rightarrow 0$  case where the exact definition of the source is crucial even in the low-density limit.

Our theoretical approach and notations follow ref. [4]. We note that all the contributions to the kinetics should be identical to the random landing case except, of course, for the source term. If  $\rho$  is the average density and  $f(r)$  is the two-particle density correlation function, we have the Smoluchowski boundary condition [23],

$$Q = 2D\Sigma_a \left. \frac{\partial f(r)}{\partial r} \right|_{a^+}. \quad (1)$$

$D$  is the diffusion constant,  $\Sigma_a$  and  $a$  are respectively the reaction surface and the radius of a particle A. Neglecting higher order correlations in the source, we have an effective source term  $Q = R(1 - v\rho)^2$ , where  $v$  is an excluded volume of the order of  $a^d$ . If we apply dimensional analysis we find  $\delta f(r)/\delta r|_{r=a^+} = \rho^2/\Lambda$ , where  $\Lambda$  is a typical length scale picturing the microscopic organization of reactants. Note that mean-field classical kinetic approach always takes  $\Lambda$  to be of the order of a microscopic size  $a$ . Thus eq. (1) can be put into the form

$$Q = 2\Sigma_a D \frac{\rho^2}{\Lambda}. \quad (2)$$

The contribution to the equation of motion of the correlation function,  $f(r)$ , of two sites separated by a distance  $r$  can be split into two terms. First, suppose that a particle occupies one of the sites and a member of the pair lands on the other (empty) one. Thus, we have a contribution  $S_1$  to the equation of motion which is on the average

$$S_1 = 2R[\rho - v f(r)]. \quad (3a)$$

The second source term  $S_2$  takes into account the case where a pair lands on two unoccupied sites. In the continuum limit we obtain

$$S_2 = R[1 - 2v\rho - v^2 f(r)] \frac{\delta_{r-\lambda}}{\Sigma_\lambda}, \quad (3b)$$

where  $\delta_x$  is the delta function and  $\Sigma_\lambda$  is the surface of the sphere of radius  $\lambda$ . For the other terms, namely, diffusion and two- and three-particle correlation contributions, we use the forms already derived in ref. [4]. Let us recall that we take into account higher moments of multi-particle correlations coming from the BBKY expansion [24] by replacing the exact contribution of the three-particle correlation function by an effective term which is taken to be  $-2\alpha f(r)$ . It implies an effective constant  $\alpha$  that is calculated using a consistency condition  $(1/V) \int dr f(r) = \rho^2$  and the boundary condition (2). In this approximation, we have an easy interpretation for  $\alpha$ , i.e.  $\alpha^{-1} = \rho/R$ , corresponding to an average life-time for a particle in the field of the others. Finally, we obtain in steady state the equation

$$2D\nabla^2 f(r) - \frac{2R}{\rho} f(r) + 2R\rho - \frac{Q}{\Sigma_a} \delta_{r-a} + \frac{Q}{\Sigma_\lambda} \delta_{r-\lambda} = 0. \quad (4)$$

This is the same equation as found in ref. [4] for a random source, except for the delta function located at  $r = \lambda$ . It is a continuum approximation not suited to deal with exact geminate landing, i.e. with  $\lambda = a$ , as is done in

computer simulations and in lattice calculations. In this case, our theory leads to a divergent reaction rate. Using the transformation  $f(r) = \rho^2 [1 - g(r)]$  and the length scale

$$\xi = \sqrt{\frac{\rho D}{R}}, \quad (5)$$

we obtain the differential equation

$$\nabla^2 g(r) - \frac{g(r)}{\xi^2} = \frac{Q}{2D\rho^2} \left( -\frac{\delta_{r-a}}{\Sigma_a} + \frac{\delta_{r-\lambda}}{\Sigma_\lambda} \right). \quad (6)$$

A Fourier transform of eq. (6) gives

$$\tilde{g}_q = \frac{Q}{2D\rho^2} \frac{\Phi(aq)/\Sigma_a - \Phi(\lambda q)/\Sigma_\lambda}{q^2 + \xi^{-2}}, \quad (7)$$

where  $\Phi(xq)$  is the Fourier transform of  $\delta_{r-x}$ . Now, we now derive the rate equations in Euclidean dimensions  $d=1, 2$  and  $3$ .

In  $d=1$  we have  $\Sigma_a=2$  and  $\Phi(xq)/\Sigma_x = \cos qx$ , then

$$g(r) = \frac{Q}{2D\rho^2} \frac{1}{2\pi} \int_{-\infty}^{\infty} dr \frac{\cos aq - \cos \lambda q}{q^2 + \xi^{-2}} e^{-iqr}. \quad (8)$$

We obtain, after integration,

$$g(r) = \frac{Q\xi}{8D\rho^2} \{ \exp[(a-r)/\xi] + \exp[-(a+r)/\xi] - \exp[-|\lambda-r|/\xi] + \exp[-(\lambda+r)/\xi] \}. \quad (9)$$

In the limit  $a \ll \xi$ , we expand eq. (9) and use the boundary condition  $g(a) = 1$ . We obtain a reaction law which is consistent with eq. (1). We find

$$Q = \frac{4D\rho^2}{\xi[1 - \exp(-\lambda/\xi)]}. \quad (10)$$

Thus we obtain a scale of organization  $A$  which corresponds to an average depletion size around each particle:

$$A = \xi[1 - \exp(-\lambda/\xi)]. \quad (11)$$

The correlation function  $g(r)$  is

$$g(r) = \frac{1 - \cosh(r/\xi) \exp[-(\lambda-r)/\xi]}{1 - \exp(-\lambda/\xi)} \exp(-r/\xi), \quad \text{for } a < r < \lambda,$$

$$g(r) = \frac{1 - \cosh(\lambda/\xi)}{1 - \exp(-\lambda/\xi)} \exp(-r/\xi), \quad \text{for } r \geq \lambda. \quad (12)$$

For  $\lambda \ll \xi$ , we have the depletion scale  $A = \lambda$  and we obtain a classical reaction rate with an order of reaction  $X=2$ . Eq. (5) shows that this situation is likely to happen at lower densities. For geminate landing, corresponding to  $\lambda = a$ , we do not any longer have a divergence of the reaction rate, and we obtain the result of Rácz [3] for the rate law up to a constant factor. For  $\lambda \gg \xi$ , we have the depletion scale  $A = \xi$  and we obtain a reaction rate with the order of reaction  $X=3$ , the same as found in the theory of the random landing case [4]. Note that this constant is different from the result of the exact calculation by Rácz [3].

Our theoretical result compares well with the outcome of computer simulations on a line [11] for different values of  $\lambda$ . The validity of eq. (11) was especially checked by Li and Kopelman [11] and this equation could fit the computed values up to a rescaling of  $A$  by a factor 1.2.

In  $d=2$  we have  $\Sigma_a = 2\pi a$  and  $\Phi(xq)/\Sigma_x = J_0(xq)$  where  $J_0(z)$  is a Bessel function,

$$g(r) = \frac{Q}{4\pi D\rho^2} \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} q \, dq \frac{J_0(aq) - J_0(\lambda q)}{q^2 + \xi^{-2}} \int_0^{2\pi} d\theta \exp(-iqr \cos \theta), \quad (13)$$

we obtain after evaluation of this double integral:

$$g(r) = \frac{Q\xi}{4\pi D\rho^2} [I_0(a/\xi)K_0(r/\xi) - I_0(r/\xi)K_0(\lambda/\xi)], \quad \text{for } a < r < \lambda,$$

$$g(r) = \frac{Q\xi}{4\pi D\rho^2} [I_0(a/\xi)K_0(r/\xi) - I_0(\lambda/\xi)K_0(r/\xi)], \quad \text{for } r \geq \lambda, \quad (14)$$

where  $I_0(z)$  and  $K_0(z)$  are Bessel functions. From the condition  $g(a) = 1$  and in the limit  $a/\xi \ll 1$ , we extract a rate law compatible with eq. (1):

$$Q = \frac{4\pi D\rho^2}{C_0 + \ln(2\xi/a) - K_0(\delta/\xi)}, \quad (15)$$

where  $C_0 = \Psi(1) = 0.557\dots$ . The correlation function  $g(r)$  is then

$$g(r) = \frac{K_0(r/\xi) - I_0(r/\xi)K_0(\lambda/\xi)}{C_0 + \ln(2\xi/a) - K_0(\lambda/\xi)}, \quad \text{for } a \leq r < \lambda,$$

$$g(r) = \frac{1 - I_0(\lambda/\xi)}{C_0 + \ln(2\xi/a) - K_0(\lambda/\xi)} K_0(r/\xi), \quad \text{for } r \geq \lambda. \quad (16)$$

For  $a \ll \lambda \ll \xi$ , we have  $A = \ln(\lambda/a)$  and we obtain a classical reaction rate with an order of reaction  $X=2$ . For  $\lambda \gg \xi$ , we obtain the depletion scale  $A = C_0 + \ln(\xi/a)$ , which is the result of the random landing case, and there is no simple power reaction law. As in  $d=1$  we have, at a fixed  $\lambda$ , a cross-over between the low density limit, where we observe a self-organization at a scale  $\lambda$ , and the higher density limit, where we recover the result of random landing. This cross-over is observable when  $\lambda$  is larger than the macroscopic size  $a$ .

In  $d=3$  we have  $\Sigma_a = 4\pi a^2$ ,  $\Phi(qx) = 4\pi \sin(qx)/qx$  and

$$g(r) = \frac{Q}{2D\rho^2} \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} q^2 \, dq \frac{\sin(aq)/aq - \sin(\lambda q)/\lambda q}{q^2 + \xi^{-2}} \int_{-\pi}^{\pi} d\varphi \exp(-iqr \cos \varphi). \quad (17)$$

Then we obtain

$$g(r) = \frac{Q}{16\pi D\rho^2} \frac{\xi}{r} \{ \exp[-(r-a)/\xi] - \exp[-(r+a)/\xi] - (a/\lambda) \{ \exp(-|r-\lambda|/\xi) - \exp[-(r+\lambda)/\xi] \} \}. \quad (18)$$

Using the boundary condition  $g(a) = 1$  and in the limit  $\xi \gg a$  we obtain

$$Q = \frac{8\pi Da}{1 - (a/\lambda) \exp(-\lambda/\xi)} \rho^2. \quad (19)$$

Thus the organization length  $A$  is microscopic, i.e. of the order of  $a$ . Explicitly, we get

$$A = a[1 - (a/\lambda) \exp(-\lambda/\xi)]. \quad (20)$$

In the low-density limit case, we have a classical rate law with a slight deviation from the classical length scale:  $A = a(1 - a/\lambda)$ . In fact it is a reaction enhancement due to the presence of reactive pairs in a close proximity.

In summary, we have shown in a simple theoretical calculation, that in a dimension lower than two and in the very-low-density limit, a spatial self-organization of reactants is present and is controlled by the correlation in

the source term. At higher densities there is a cross-over to a regime similar to a random landing exhibiting a non-classical order of reaction. This cross-over is determined by comparing the correlation scale  $\lambda$  with the mean diffusion length of a particle in the medium before elimination by reaction.

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