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Bimolecular reaction $A+B\to 0$ at steady state on fractals: anomalous rate law and reactant self-organization

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This paper is a theoretical investigation of the diffusion limited reaction $A+B\to 0$ at steady state and on fractal structures. We propose an extension of a scheme previously applied to Euclidean spaces, using the so-called fractal diffusion operator defined by O'Shaughnessy and Procaccia. We show that for a particular type of source, we obtain distributions of reactants and macroscopic reaction laws that interpolate the results previously found in Euclidean dimensions. More specifically, we show that the relevant dimension of the problem is the spectral dimension d_s and for $d_s<2$ we have a mesoscopic segregation in the medium that may imply anomalous orders of reaction. Some of the predictions are tested via Monte Carlo simulations. More generally, we find that these results can be viewed as examples of a more general property common to other elementary diffusion limited bimolecular reactions.

The bimolecular reaction $A+B\to 0$ is an example of a system with surprising properties. When the rate of reaction is limited by the diffusion of reactant and for a Euclidean dimension $d<4$, the system evolves towards a segregated distribution [1,2] (for an initial random and even distribution in As and Bs). The segregation is responsible for an anomalous decay exponent $\alpha=-d/4$ [1,3], instead of $\alpha=-1$ predicted by the classical theory, where α is given by $\rho\sim t^{-\alpha}$ at $t\to\infty$ and ρ is the density.

Fractal structures exhibit the same segregation properties and the exponent is $\alpha=-d_s/4$ where d_s is the spectral dimension [4,5]. Anomalous relaxation properties due to self-ordering of reactants in lower dimensions are also found for bimolecular reactions of the type $A+A\to 0$ and $A+T\to T$ (see for example the review [6]) (T is a fixed trap). Kang and Redner [4] connected the A+B problem to the A+A problem through an analysis based on reactant fluctuations in a polymolecular reaction. They obtained predictions on the critical dimensions and the decay exponents. But so far, for the decay problem, no general framework common to diffusion limited bimolecular reactions was given in terms of single particle diffusion properties. To illustrate this point, the reason for having different critical dimensions, $d_c=2$ for $A+A\to 0$ and $d_c=4$ for $A+B\to 0$, remains unclear.

When a source of particles is added to the A+B reaction, Lindenberg et al. [7] and ben-Avraham et al. [8] showed that for particles with no excluded volume, segregation is likely to occur for $d\leqslant 2$. Furthermore, it was shown [7–10] that the specific nature of the source has to be considered. For particles with finite excluded volume, we investigated the effect of various sources and, separated them into two main categories, namely the strictly conservative and the statistically conservative cases [9,10]. For strictly conservative sources, we keep the same number of As and Bs on the system at any time. For statistically conservative sources the symmetry between A and B is broken for one realization of the system, but remains true in an ensemble average sense. Interestingly, the case of statistical conservation without other decay mechanisms, exhibits a particular feature called

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saturation where one species becomes predominant, and the reaction stops after a finite time. In refs. [9,10] a theoretical procedure is developed to solve the problem in Euclidean dimensions. We find that $d=2$ is the critical dimension of the problem for particles with a finite size. This paper shows how the procedure may be extended to fractal structures, in the case of statistical conservation.

We recall briefly the main theoretical steps and the results of refs. [9,10]. In a first step, we solve the equation of motion for the correlation function $m(\boldsymbol{r})=\langle\gamma(\boldsymbol{x})\gamma(\boldsymbol{x}+\boldsymbol{r})\rangle$ where $\gamma(\boldsymbol{x})$ is the local difference density, i.e. $\gamma(\boldsymbol{x})=\rho_A(\boldsymbol{x})-\rho_B(\boldsymbol{x})$ were $\rho_A(\boldsymbol{x})$ and $\rho_B(\boldsymbol{x})$ are respectively the local densities in A and in B. Then, using a set of Langevin equations that describe the motion of the first moments $\gamma(\boldsymbol{x},t)$ and $\rho(\boldsymbol{x},t)=\rho_A(\boldsymbol{x},t)+\rho_B(\boldsymbol{x},t)$, we find a necessary condition for the existence of a steady state solution. This condition is the macroscopic reaction law

$$Q=\Sigma D\frac{\rho^2}{2a+\Sigma Dm(a)/Q}, \tag{1}$$

where Q is the reaction rate (or the effective source term), Σ is the reaction surface of a particle, D the diffusion constant, ρ the overall density and a the particle size. From the Smoluchowski boundary condition, generally valid for diffusion limited bimolecular reactions [9,10], we derive a scale Λ which is a typical distance between A and B particles. We write the reaction law in the form

$$Q=\Sigma D\rho^2/\Lambda, \tag{2}$$

where Λ is called the segregation length and we have

$$\Lambda/a=2+\Sigma Dm(a)/Qa. \tag{3}$$

The critical dimension of the problem is $d_c=2$. For $d\leqslant 2$, we find a mesoscopic or a macroscopic segregation. Also, we show the existence of a characteristic time τ which is source dependent and we have for τ large and for $d<2$

$$\Lambda/a\approx\tau^{1-d/2}. \tag{4}$$

For $d=2$, we have logarithmic corrections to (4). For a source that is both strictly conservative and with a random separation between A–B landing pairs, we find

$$\tau\approx L^2, \tag{5a}$$

where L is the size of the system. For a conservative source with A–B landing pairs separated by a fixed distance δ, we have

$$\tau\approx\delta^2. \tag{5b}$$

For statistically conservative sources, in order to have a reactive steady state we have to include an extra decay mechanism such as a vertical annihilation source of intensity R and in this case

$$\tau\approx R^{-1}. \tag{5c}$$

Vertical annihilation designates a source of particles that annihilate their counterparts upon landing (on top of them).

Alternatively, an internal first-order decay process (A→0 and B→0) may be considered with the same decay rate constant Γ for A and B, and then we have

$$\tau\approx\Gamma^{-1}. \tag{5d}$$

Now we seek to extend this procedure to fractals embedded in a Euclidean space of dimension d with a fractal dimension d_f and a spectral dimension d_s. We make a cut-off of the fractal structure at the scale a (the particle size). Then, densities can legitimately be defined. To find the equation of motion for $m(\boldsymbol{r})$ we use the concept of generalized diffusion operator on fractals introduced by O'Shaugnessy and Procaccia [11]. This operator was first used by Vitukhnovski et al. [12] and applied to the study of the A+A→0 reaction decay. This scheme was also used by Clément et al. [13] to study the steady state properties of A+A→0. Before applying this method we need to make a remark. The generalized operator of O'Shaugnessy and Procaccia accounts for diffusion in an isotropic effective medium embedded in a Euclidean space and because of its lack of information about the angular dependence, it can only solve situations with spherical symmetry. Therefore, this method cannot be generalized to systems with diverging correlation lengths because it would necessitate a more complete operator (with explicit angular dependence) in order to account precisely for boundary conditions. Thus, we need to restrict our investigation to systems with a finite correlation length. This is the case of sources with a statistical conservation property, when a first-order decay mechanism is implemented. For example, we have sources with vertical annihilation or systems with symmetric desorption (i.e. internal decay A→0 and B→0 with the same reaction rate Γ).

For Euclidean spaces we established, in ref. [10], that at steady state, the equation of motion for $m(\boldsymbol{r})$ in the statistical conservation case, implies for $r \geqslant a$

$$D\nabla^2 m(\boldsymbol{r}) - \Gamma m(\boldsymbol{r}) = -\frac{Q}{\Sigma}\delta_{r-a}\,, \tag{6}$$

where D is the diffusion constant, Γ a first-order reaction rate, Q the reaction rate or effective source term and Σ the reaction surface. For $r < a$, we have

$$m(r) = m(a)\,.$$

To extend eq. (6) to fractal structures we redefine $m(\boldsymbol{r})$ to be the analytic envelope of $m(\boldsymbol{r})$, and we replace the diffusion part of the equation by the generalized diffusion operator. Then we have

$$K\frac{1}{r^{d_f-1}}\frac{\partial}{\partial r}\left(r^{d_f-1-\theta}\frac{\partial m(r)}{\partial r}\right) - \Gamma m(r) = -\frac{Q}{\Sigma}\delta_{r-a}\,, \tag{7}$$

where K is the generalized Fick coefficient and θ the anomalous diffusion exponent. We define the microscopic diffusion constant to be

$$D = Ka^{-\theta}\,.$$

Eq. (7) is now

$$\frac{1}{r^{d_f-1}}\frac{\partial}{\partial r}\left(r^{d_f-1-\theta}\frac{\partial m(r)}{\partial r}\right) - \frac{a^{-\theta}}{\xi^2}m(r) = \frac{Qa^{-\theta}}{\Sigma D}\delta_{r-a}\,, \tag{8}$$

where ξ is a characteristic length defined by the relation

$$\xi = \sqrt{D/\Gamma}\,. \tag{9}$$

To this characteristic length ξ we associate a characteristic time τ defined as

$$\tau \equiv \xi^2/D = \Gamma^{-1}\,. \tag{9'}$$

In the vertical annihilation case we have

$$\Gamma = Rv\,, \tag{10}$$

where v is a volume of the order of a^{d_f} related to the vertical annihilation cross section (Γ is the probability/time for a particle to be annihilated by a landing particle of the opposite species), and R is the external source rate. We seek to solve eq. (8) with a boundary condition $m(r) \to 0$ when $r \to \infty$. This equation is formally identical to the differential equation solved in ref. [13] for the two-particle correlation function. Therefore, for $r > a$, the solution is of the type

$$m(r) = A\left(\frac{r}{a}\right)^{\beta\nu}\frac{K_\nu((a/\beta\xi)(r/a)^\beta)}{K_\nu(a/\beta\xi)}\,,$$

where $K_\nu(z)$ is a modified Bessel function, and where we have

$$\beta = 1 + \theta/2 = d_f/d_s\,,$$

$$\nu = 1 - d_s/2\,.$$

A is a constant to be determined by inspection of the situation at $r = a$. At this point the function $m(r)$ is continuous but has a kink. Its derivative goes from a value 0 for $r = a^-$, to a finite value for $r = a^+$. Examining eq. (8) we see that the magnitude of this jump has to be equal to the prefactor of the delta function. After calculation of the derivative of $m(r)$ in $r = a$ and identification with the prefactor of the delta function, we determine the coefficient A. The result is

$$A = m(a) = \frac{Q\xi}{D\Sigma_{d_f}}\frac{K_\nu(a/\beta\xi)}{K_{1-\nu}(a/\beta\xi)}\,. \tag{11}$$

Therefore the correlation function $m(r)$ is

$$m(r) = \frac{Q\xi}{D\Sigma_{d_f}}\left(\frac{r}{a}\right)^{\beta\nu}\frac{K_\nu((a/\beta\xi)(r/a)^\beta)}{K_{1-\nu}(a/\beta\xi)}\,.$$

Putting together eqs. (11) and (3) we obtain a segregation length

$$\Lambda = a\left(2 + \frac{\xi K_\nu(a/\beta\xi)}{aK_{1-\nu}(a/\beta\xi)}\right)\,. \tag{12}$$

This equation associated with eq. (2) defines a rate law for spectral dimensions $1 \leqslant d_s \leqslant 2$. We notice that this result interpolates the Euclidean cases $d = 1$ and $d = 2$. Like in the case A + A→0 [13] we have two different regions:

(i) For $\xi/\mathrm{a} \gg \exp[1/(2-d_s)]$, following the result of an expansion already performed in ref. [13], we have the low density limiting behavior,

$$\Lambda = a\left[2 + \frac{\Gamma(1-d_s/2)}{\Gamma(d_s/2)}\left(\frac{d_s}{2d_f}\right)^{d_s-1}\left(\frac{\xi}{a}\right)^{2-d_s}\right]\,. \tag{13}$$

Here $\Gamma(z)$ is the gamma function. For the vertical annihilation case we inject into (13) the value of ξ given by eqs. (9) and (10), then using (2), we obtain a limiting scaling behavior for the reaction law at low densities,

$$Q\approx\rho^{4/d_s}\,. \qquad (14)$$

Therefore, we find an anomalous order of reaction $X=4/d_s$ that generalizes the one found for $d=1$ ($X=4$) [9]. For the symmetric desorption case, injecting the values of ξ from eq. (9′), we obtained a Γ-dependent segregation length,

$$\Lambda\approx\Gamma^{d_s/2-1}\,,$$

but the reaction order remains classical ($X=2$).

(ii) For $1\ll\xi/a\ll\exp[1/(2-d_s)]$ logarithmic corrections to the segregation length are found and prevent us from obtaining, in the vertical annihilation case, a simple scaling expression for the rate law as in eq. (14). It is important to notice that, for symmetric desorption, though a mesoscopic segregation is present a classical rate law is still observed as far as the exponent $X=2$ is concerned.

In fig. 1, we have plotted the reaction laws for dimensions $d=1$, 2, 3 and for a percolation cluster in the vertical annihilation case. The value of the generalized Fick coefficient K used in the fractal case, is determined *independently* by Monte Carlo simulations of the mean square displacement of a random walker. For a "myopic ant" algorithm we have $K=0.377\pm0.004$. The reaction surface Σ is the average number of sites-nearest-neighbors. For the percolation cluster we calculated numerically $\Sigma=2.52\pm0.02$. Therefore, the theoretical reaction laws presented here have *no* adjustable parameters. From fig. 1 we observe that at a given reaction rate, the steady state density increases with the spectral dimension. In fig. 2 we show the results of computer simulations on the largest percolation cluster of a 100×100 square lattice at criticality ($p=0.59$) and on a loop of size $L=500$. In both cases, we represented the theoretical expectation (curve (a)) and the scaling limiting law from eqs. (2) and (13) (curve (b)). The agreement between theory and simulations is good for the percolation cluster for densities smaller than $\rho=2\times10^{-2}$. For the line, one may observe a slight discrepancy for lower densities. We ar-

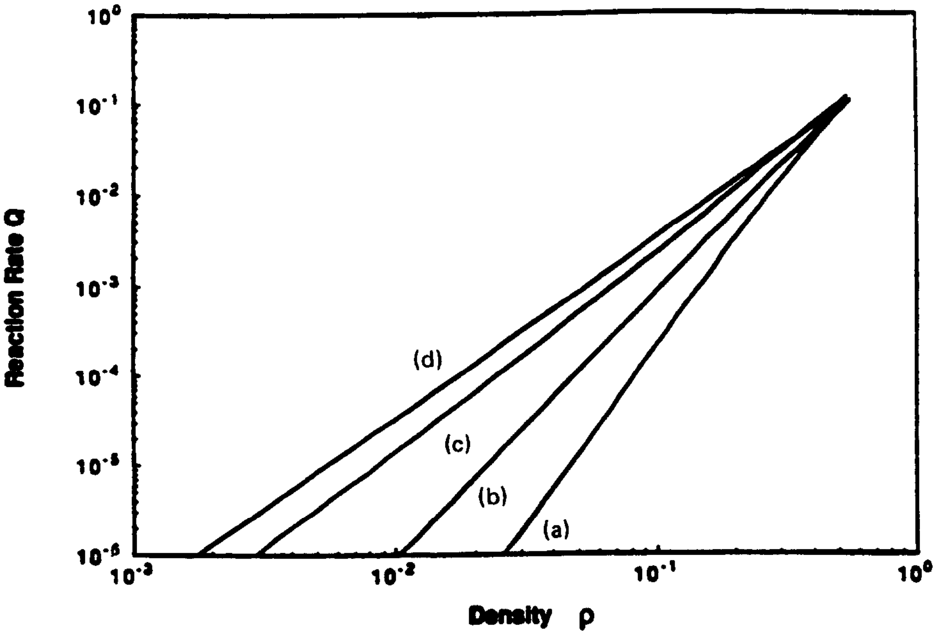

Fig. 1. Theoretical rate laws (log–log scale) with vertical annihilation source. Q is the reaction rate (or the effective source rate) and ρ is the total density of reactants. Curve (a) is for $d=1$, curve (b) is for a percolation cluster, curve (c) is for $d=2$ and curve (d) is for $d=3$.

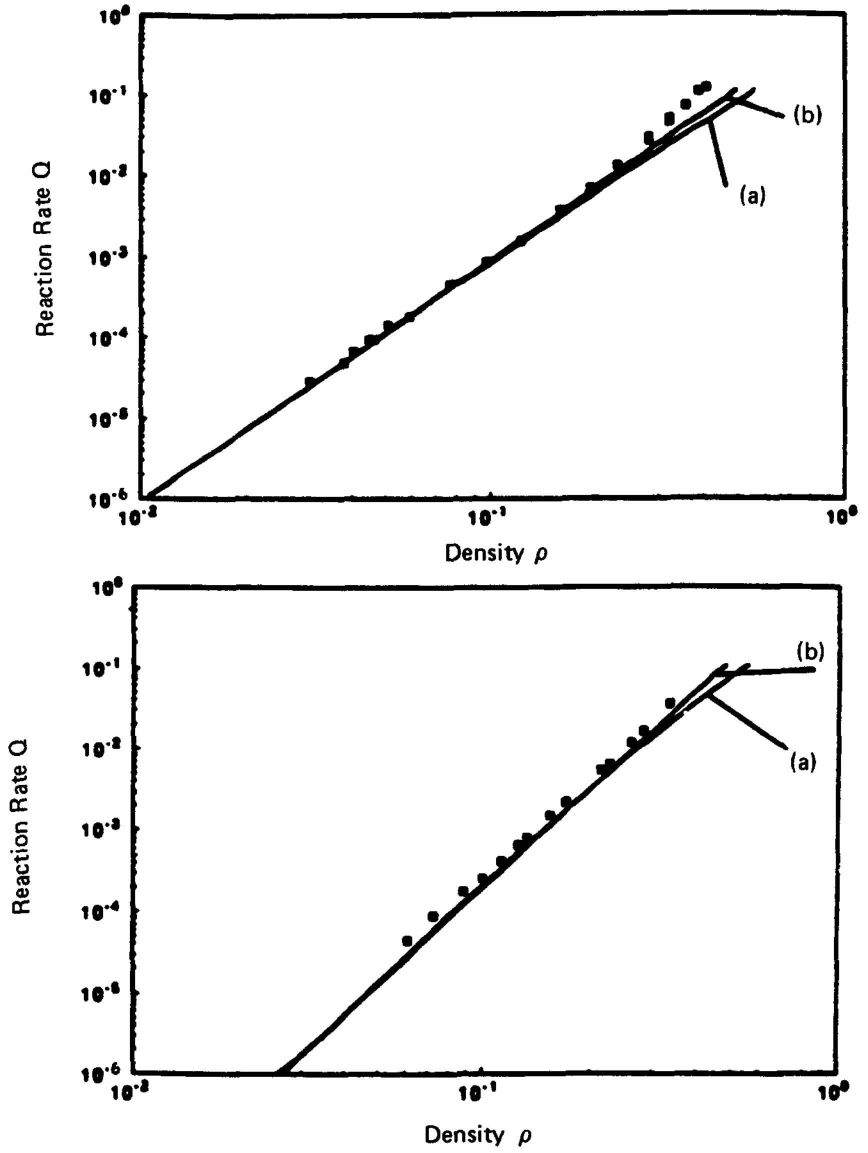

Fig. 2. Computer simulations compared to theoretical expectations on a percolation cluster and on a loop. Curve (a) is the theoretical expectation and curve (b) is the low density asymptotic behavior of (a), showing an effective order of reaction $X = 4/d_s$. Top: results for a two-dimensional percolation cluster on a 100×100 lattice at criticality ($p = 0.59$). Bottom: results for a loop of size 500 sites.

gue that this discrepancy is mainly due to finite size effects on the line which are important in $d = 1$ (we have $L = 500$). In ref. [9] finite size corrections to the rate law in $d = 1$ are calculated theoretically. We define the coefficient α to be

$$\alpha = \frac{Q_{\text{sim}}}{Q_{\text{th}}(\rho_{\text{sim}})},$$

where Q_{sim} is the reaction rate obtained from simulations and $Q_{\text{th}}(\rho_{\text{sim}})$ is the theoretical prediction given the density ρ_{sim} found from simulations. The coefficient α is a much finer test for the goodness of the theory than the log–log plot of fig. 2. In fig. 3 we plot the coefficient α as a function of the external rate for a percolation cluster and a loop (accounting for

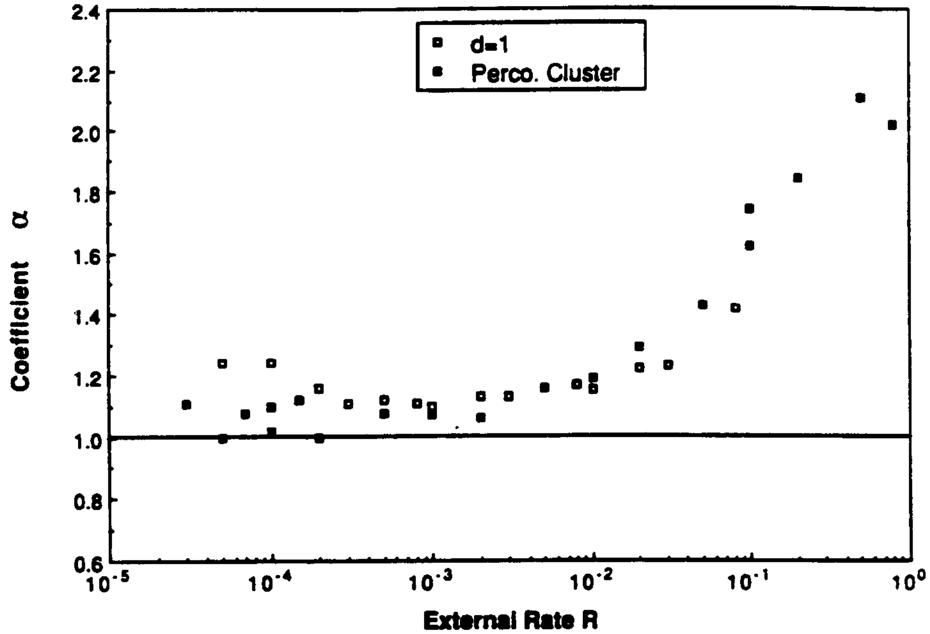

Fig. 3. Coefficient α as a function of the external rate R for a $2-d$ percolation cluster and a loop ($L=500$). For the loop, we accounted for finite size corrections. The line $\alpha=1$ corresponds to a perfect agreement between theory and simulations.

finite size corrections). We obtain a good agreement for $3\times10^{-5}\leqslant R\leqslant10^{-2}$. For the percolation cluster we obtain $\alpha=1.05\pm0.05$ and for the line $\alpha=1.2\pm0.05$. In fig. 4 we show "snap-shots" of two distributions of particles at steady state, on a percolation cluster and on a loop. The circle and the arrow, at the right side of the pictures, have the size Λ calculated from relation (12).

At first sight the A+B→0 problem offers a surprising diversity of results as far as the rate law, the segregation and the overall phenomenology are concerned. The most unexpected result is the extreme sensitivity of the problem with respect to the exact definition of the source. Also, it seems that we have very little in common with other bimolecular reactions. Nevertheless, from the details of this analysis, and other investigations on the A+A→0 [13] problem and the trapping problem A+T→T [14], common features appear. From a general point of view, for bimolecular reactions (when a reactive steady state is obtained), we *claim* in any case, the existence of a characteristic length ξ or a characteristic time $\tau\approx\xi^2$, such that the steady state rate law can be cast

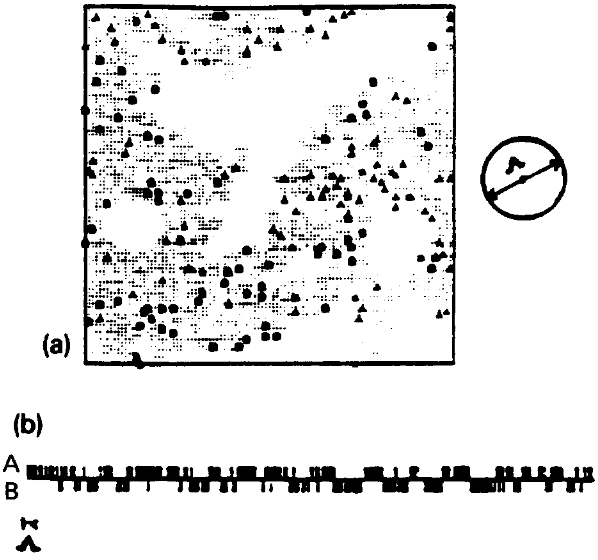

Fig. 4. Snapshots of the distribution of reactants at steady state, on a percolation cluster (a) and on a loop (b), for a vertical annihilation source. The diameter of the circle in (a) and the length of the segment in (b) have the size of the theoretical segregation length Λ.

in the general form

$$Q\approx D\Sigma p^2/\Lambda \tag{15}$$

with Λ having the universal scaling behavior when $\tau\to\infty$,

$$\begin{aligned}&\Lambda\approx\tau^{1-d_s/2}\,, && 1\leqslant d_s\leqslant 2\,,\\ &\Lambda\approx\ln\tau\,, && d_s=2\,,\\ &\Lambda\simeq a\,, && d_s>2\,.\end{aligned} \tag{16}$$

As noted in ref. [13], relations (16) can be cast under a much more compact form,

$$\Lambda/a\approx V_\tau/S_\tau\,,$$

where V_τ is the *total* (cumulative) volume swept out by a random walker during τ and S_τ is the *effective* volume explored (number of distinct sites visited) during τ. This point is related to the notion of compact/noncompact random walk introduced by de Gennes [15] in an early analysis of the bimolecular reaction problem in low dimensions. It is the insertion of the specific value of τ(e.g. eqs. (5a), (5b), (5c) or (5d) in the A+B case) in eq. (16), and then in eq. (15), that may give anomalous rate laws. Also, the interpretation of the self-organization scale Λ differs for each situation. For the A+B case, we call it the segregation length, while for the A+A and trapping problem, we call it a depletion length. For the A+B→0 problem, we have shown that this former point of view is correct for a nonconservative source term provided that a first-order decay is introduced (coming from a vertical annihilation or a first-order decay mechanism). In conservative source cases, the result (16) has been obtained in Euclidean dimensions (see eq. (4)) but was not yet been generalized to fractal sets. Nevertheless, a reasonable guess is that the scaling property (16) is applicable with τ taking the values of eqs. (5a) and (5b). The extension would give

$$\Lambda\approx L^{2-d_s}\,. \tag{17}$$

It is worth noticing that a large scale segregation was observed qualitatively at steady state by simulations on a Sierpinski gasket and a carpet for a conservative algorithm [16]. Also, we need to compare the prediction of equation (17) with the result of Sokolov [17], namely:

$$\Lambda\approx L^{d_f(2/d_s-1)}\,.$$

This prediction is based on the ad hoc assumption that the scale of segregation reaches the extent of the system. Therefore, simulations on fractal structures or deeper theoretical investigations would be needed to confront both approaches.

In conclusion, this paper shows how the bimolecular reaction A+B→0 at steady state can be understood in terms of general properties, common to other bimolecular reactions like A+A→0 and A+T→T (trapping). We found that for a spectral dimension smaller than 2, a self-organization called segregation occurs in the medium. The extension of the segregation is connected to single random walker properties specifically to the number of distinct sites visited. The macroscopic rate laws are explicitly derived for the cases of vertical annihilation and symmetric desorption. The case of vertical annihilation exhibits an anomalous exponent for the order of reaction, due to a source dependent scale of segregation.

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