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LETTER TO THE EDITOR

Kinetics of the 'scavenger' reaction

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Abstract. We study the kinetics of a diffusion-controlled reaction in which perfect traps (scavengers) diffuse and consume randomly distributed particles. We find that the number of particles remaining after time t decays as $\exp(-\alpha c t^{d/2})$, for spatial dimensions $d<2$, and as $\exp(-\alpha c t)$ for $d \geq 2$, where α is a constant, and c is the trap concentration. These predictions are supported by Monte Carlo data in $d=1$ and $d=2$. We also discuss the differences between the scavenger reaction and the reaction of particles diffusing and being consumed by randomly distributed static traps. Finally, we treat the situation where both the particles and the traps diffuse.

Very recently, there has been considerable resurgence in studying a variety of diffusion-controlled reactions. One important example is the 'trapping' reaction where particles diffuse in the presence of static, randomly distributed perfect traps. Although this problem has been studied for some time, it has only recently been recognised that the particle density $\rho(t)$ follows an anomalous long-time decay proportional to

$$\rho(t) \sim \exp(-\alpha c^{2/d+2} t^{d/d+2}) \tag{1}$$

where d is the spatial dimension, c is the trap concentration, and α is a constant (Balagurov and Vaks 1974, Donsker and Varadhan 1975, Tanaka 1978, Grassberger and Procaccia 1982, Movoghar *et al* 1982, Zumofen and Blumen 1982, Redner and Kang 1983, Havlin *et al* 1984). This unusual decay law stems from the presence of large (but very rare) trap-free regions. In such a region, the particle lifetime is anomalously long, and the contribution of these long lifetimes leads to the decay of equation (1). If such large fluctuations in the spatial distribution of the traps did not occur, the decay law would be exponential; this can be thought of as the mean-field limit of the decay law.

While there is now a reasonable understanding of the trapping reaction, it appears that the general case where both the particles *and* the traps diffuse has not been considered in detail. Such a situtation may be useful to describe physical processes such as fluorescence quenching and catalysis (see e.g. Calef and Deutch (1983) for a review and extensive references). In this letter, we derive an approximate bound for the decay law of this general situation. In the extreme case of diffusing traps and stationary particles, which we term the 'scavenger' reaction, we argue that the decay law will be proportional to $\exp(-\alpha c t^{d/2})$ for $d<2$ and proportional to $\exp(-\alpha c t)$ for $d \geq 2$, where α is a constant. These predictions are supported by computer simulations in $d=1$ and 2, where we also compare the decay laws of the scavenger and trapping

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reactions. Finally we consider the general situation of both particle types diffusing and we argue that the long-time decay follows that of the scavenger problem.

We begin by discussing the decay law of the scavenger and trapping reactions for short times. For the former reaction, the number of particles that are trapped after time t is proportional to the density of traps c and to the number of particles on the path of the moving trap. Hence

$$\rho(0)-\rho(t)\sim c\rho(0)\langle S(t)\rangle \tag{2}$$

where $\langle S(t)\rangle$ is the mean number of sites visited by the scavenger after time t. For small times, we can rewrite this as

$$\rho(t)\sim\rho(0)(1-c\langle S(t)\rangle)\sim\rho(0)\exp(-c\langle S(t)\rangle). \tag{3}$$

On the other hand, for the trapping reaction, the exact expression for the average survival probability is $\langle(1-c)^{S(t)}\rangle$ (see e.g. Zumofen and Blumen 1982, Redner and Kang 1983). For short times, this average may be approximated by $(1-c)^{\langle S(t)\rangle}$, and by writing $1-c\cong\exp(-c)$, one sees that the decay laws of the two reactions coincide. This should hold until, in the scavenger reaction, the traps diffuse a distance of the order of their initial separation. This crossover time is given by $c^{-2/d}D_{\mathrm{T}}^{-1}$, where D_{T} is the diffusion coefficient of the traps. For longer times, a particle can now be consumed by a trap which was initially very distant from the particle, and the decay in the scavenger reaction should be faster than that in the trapping reaction. Notice that the crossover time can also be obtained by equating the asymptotic decay laws of (1) and (3), and solving for the time.

Now consider the long-time decay of the scavenger reaction. We first discuss the one-dimensional case and then generalise to higher dimensions. As in the trapping reaction, we focus on the rare events where a particle lies in a long trap-free region (Grassberger and Procaccia 1982). A particle is located at the origin, while the traps on one side of the particle are located at l_1, l_2, l_3, ... (figure 1). The probability for the

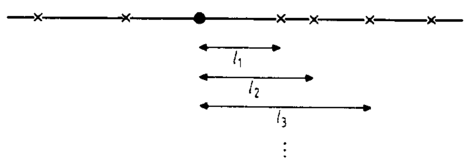

Figure 1. Configuration of one particle (●) surrounded by traps (×) in one dimension. The distances between the particle and the various traps are indicated.

existence of the trap-free region from 0 to l_1 is simply $\exp(-cl_1)$. In order that the particle lives until time t, we require that none of the traps can diffuse to the particle. For the ith trap to avoid the particle until time t, the trap must always remain to the right of the particle. This avoidance probability can therefore be bounded from below by the probability that the trap remain confined to an interval of length $2l_i$ centred about its starting point. This latter probability is (see e.g. Balagurov and Vaks 1974, Grassberger and Procaccia 1982)

$$\exp(-D_{\mathrm{T}}t/4l_i^2). \tag{4}$$

The survival probability of the central particle, $f(t)$, may then be bounded from below by the probability that the initial trap-free region occurs times the probability that all the traps avoid the particle. Hence

$$f(t) \geqslant \exp(-cl_1) \prod_i^{\infty} \exp -(D_T t/4l_i^2)$$

$$\sim \exp(-cl_1) \exp\left(-D_T tc \int_{l_1}^{\infty} \mathrm{d}l/4l^2\right)$$

$$\sim \exp[-c(l_1 + D_T t/4l_1)]. \tag{5}$$

To average this expression over all l_1 as $t \to \infty$, we need only maximise the value of the exponent. Taking this maximising value, and squaring to account for the traps lying to the left of the particle, we obtain

$$\langle f(t) \rangle \geqslant \exp[-c(D_T t)^{1/2}]. \tag{6}$$

To generalise this decay law for any $d < 2$, it is now necessary to multiply the avoidance probability of (4) over all traps lying within a shell of thickness $\mathrm{d}l_i$ and distance l_i from the central particle, and then multiply over all shells. This yields after a number of simple steps

$$f(t) \geqslant \exp(-cl_1^d - D_T tcl_1^{d-2}) \tag{7}$$

and upon averaging over all trap-free regions, we obtain

$$\langle f(t) \rangle \geqslant \exp[-c(D_T t)^{d/2}], \qquad d < 2. \tag{8}$$

Even though this argument provides only a lower bound for $\langle f(t) \rangle$, we may expect the asymptotic dependence in the exponential to be exact in analogy with the situation of the trapping reaction.

For $d \geqslant 2$, the derivation given above is no longer valid because a trap explores a non-compact spatial region (de Gennes 1983, Klafter *et al* 1983), and the expression (4) for the avoidance probability is not correct. To find the correct expression for this probability, let us reconsider the situation of $d < 2$. In this case, the trap explores a compact volume, and once a trap moves a distance of the order of the initial separation from the central particle, trapping is likely to occur. Thus the avoidance probability should be dependent on the initial particle–trap separation as is expressed in (4). For $d \geqslant 2$, however, after time t, the density of points visited by a trap within a sphere of radius $\langle R(t)^2 \rangle^{1/2}$ varies as $\langle S(t) \rangle / t^{d/2} \sim t^{1-d/2}$, and this vanishes as $t \to \infty$. Hence if a trap moves a distance of the order of the initial separation from the particle, trapping is still unlikely to occur, and the avoidance probability should not depend on the initial separation. In the limit that $D_T t$ is much greater than the initial separation between the trap and the particle, the avoidance probability is simply

$$1 - \langle S(t) \rangle / t^{d/2} \sim \exp(-\langle S(t) \rangle / t^{d/2}), \qquad d \geqslant 2. \tag{9}$$

Since this expression does not depend on the initial separation, it is a simple matter to multiply this probability over all traps initially within a spherical shell of inner radius l_1 and outer radius $D_T t$, and then average over all trap-free regions. This gives

$$\langle f(t) \rangle \geqslant \exp(-cD_T t), \qquad d > 2. \tag{10}$$

The reason that an exponential decay holds is that the main contribution to the survival probability for $d > 2$ comes from small trap-free regions.

Notice also that the decay laws of (8) and (10) can be written generally as

$$\langle f(t)\rangle \sim \exp[-c\langle S(t)\rangle]. \tag{11}$$

This is what was already obtained by the naive argument that led to (3).

Evidently in the scavenger reaction, fluctuations play a relatively less important role than in the trapping reaction. In the latter case, for a particle initially in a trap-free region of radius l the average lifetime varies as l^2, and this ultimately led to the anomalous decay of (1). However, for the scavenger reaction, the average lifetime in a trap-free region of radius l is considerably shorter, and averaging over all trap-free regions does not modify the leading $\exp[-c\langle S(t)\rangle]$ behaviour.

The arguments given above can be straightforwardly generalised to the situation of diffusing particles and traps. For $d<2$, an additional factor must be included in (7) to account for the probability of the moving particle to avoid the traps. This gives

$$f(t) \geqslant \exp(-cl_1^d - D_\mathrm{T}tcl_1^{d-2} - D_\mathrm{P}t/l_1^2), \qquad d<2, \tag{12}$$

where D_P denotes the diffusion constant of the particle, and the third factor accounts for the probability for the particle to avoid the traps. Upon averaging this expression over all l_1 we find that the third term is negligible compared with the first two terms at the optimal value of $l_1 \sim (D_\mathrm{T}t)^{1/2}$. The effect of this third term is to modify the amplitude of the decay given in (8). Thus we find

$$\langle f(t)\rangle \geqslant \exp(-D_\mathrm{P}/D_\mathrm{T})\exp[-c(D_\mathrm{T}t)^{d/2}], \qquad d<2. \tag{13}$$

For $d \geqslant 2$, we use the mean-field expression for the avoidance probability, and we thus find that the optimal value of l_1 varies as $(D_\mathrm{P}t/c)^{1/(d+2)}$ just as in the static trapping case. This gives

$$\langle f(t)\rangle \geqslant \exp(-cD_\mathrm{T}t)\exp(-c^{2/(d+2)}t^{d/(d+2)}), \qquad d \geqslant 2, \tag{14}$$

i.e. exponential decay multiplied by the more slowly decaying factor of the static trap reaction.

To test the predicted decay law of the scavenger problem, we have performed computer simulations in one and two dimensions and compared our results with the decay of the trapping reaction (figure 2). For short times the decay laws of the two

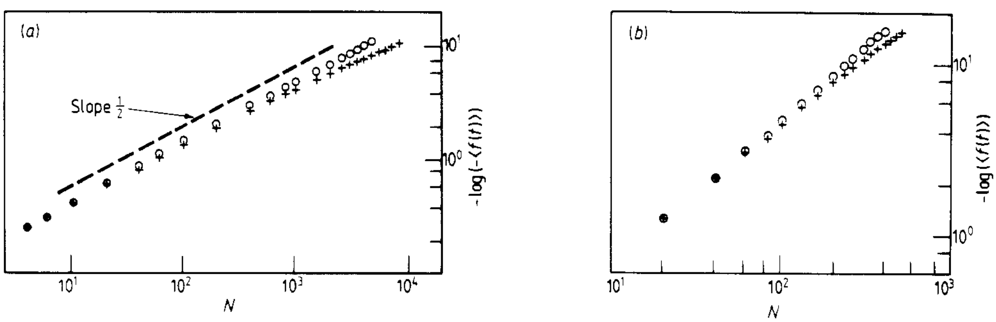

Figure 2. Results of a computer simulation for the scavenger reaction (○), and for the trapping reaction (+) in one dimension (*a*), and in two dimensions (*b*). Plotted is the negative of the logarithm of the survival probability against the number of steps N. For both cases the initial density of particles and traps was chosen to be 0.1. The simulations were performed on a chain of 2.5×10^6 sites in one dimension, and on a 1590×1590 square in two dimensions.

models are identical and in good agreement with the prediction of (8). However, after a time of the order of $c^{-2/d}$, the decays deviate with the trapping reaction proceeding more slowly.

In summary, we have studied the decay laws of a general reaction in which perfect traps and particles can both undergo diffusive motion. For any non-zero value of the trap diffusion coefficient, the decay is asymptotically the same as that of the scavenger reaction, $\exp(-c\langle S(t)\rangle)$. Only for the case of static traps does the decay follow the long-time behaviour of $\exp(-c^{2/d+2}t^{d/d+2})$. These predictions are in good agreement with our computer simulations.

We are grateful to P Grassberger for stimulating correspondence in which he independently derived the decay of the scavenger reaction.

Note added in proof. After this work was completed, we learned of work by M F Shlesinger and E W Montroll (1984 *Proc. Natl Acad. Sci.*, Feb issue) in which some results, similar to those presented here, are given. We are grateful to Dr M Shlesinger for sending a copy of their paper prior to publication.

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