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LETTER TO THE EDITOR

# Effects of probability of reaction on annihilation reactions in one dimension

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**Abstract.** We report Monte Carlo simulations of annihilation reactions $A+A\rightarrow 0$ in a one-dimensional lattice for hard-core particles. In the model, the particles perform a random walk and can react (occupy the same site and annihilate) with a probability of reaction $p\leqslant 1$. When $p\ll 1$, the density of $A$ particles decays at intermediate times approximately as $\rho(t)\sim t^{-\gamma}$, after an initial plateau at short times. The exponent $\gamma$ is non-universal and depends only on $p$, $\frac{1}{2}<\gamma<1$. Both the diffusion-controlled and the reaction-controlled reactions limits are recovered when $p=1$ and $p\rightarrow 0$, respectively. These results should be relevant for annihilation reactions taking place on effectively low-dimensional substrates of spectral dimension $d_s<2$ such as rough surfaces, porous media and ramified structures.

Diffusion-controlled reactions have attracted much attention in recent years [1–6]. Their understanding constitutes a basic problem in science with applications in a variety of physical and chemical processes [7].

In models describing diffusion-controlled reactions the reacting particles are allowed to perform jumps at random between nearest-neighbour sites of a lattice. When a particle jumps to a site occupied by another particle, they annihilate with each other and are removed from the system. In this case, the reaction rate is entirely determined by the diffusion process [2]. In many physical and chemical processes, however, the reaction does not take place when two particles collide for the first time, but several collisions can occur before they react. This can be modelled by assigning a probability of reaction $p<1$ that two particles annihilate when they attempt to occupy the same site. Physically, such a probability of reaction may be the result of an effective energy barrier that the particles must overcome in order to get close enough to react. After a collision has taken place, the particles may be either reflected back to their previous positions, or react and escape out of the system (annihilation) as, for instance, in a catalytic reaction.

So far, most of the interest in the $A+A\rightarrow 0$ reaction has been focused on the asymptotic behaviour of the particle density $\rho(t)$ [1–5], for interpenetrating particles

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where the excluded volume interaction is absent. In the case of diffusion-controlled reactions ($p = 1$), it is well known that for long times (see e.g. [3])

$$\rho(t) \sim t^{-1/2} \tag{1}$$

in one dimension, while $\rho(t) \sim t^{-1}$ in systems of dimension $d \geqslant 2$. These limiting behaviours correspond in general to the low-density regime. The situation can change considerably when the reaction probability becomes small, $p \ll 1$, in particular in one-dimensional systems. The corresponding effects on $\rho(t)$ are expected to be important in effectively low dimensional disordered systems with spectral dimension $d_s < 2$ such as fractals and ramified structures possessing a high degree of geometrical constraints, and also heterogeneous surfaces where surface diffusion of adsorbed molecules can be described by percolation concepts [8]. In these systems, $\rho(t) \sim t^{-d_s/2}$ [9, 10] where $d_s = 2d_f/d_w$, $d_f$ is the fractal dimension and $d_w > 2$ is the anomalous diffusion exponent characterizing the time behaviour of the mean-square displacement of the random walk. These disordered systems play a role in industrial surface-catalysis, electrode and membrane reactions, excitation trapping in molecular aggregates and composite materials [7, 11].

In order to understand the essential features of the annihilation reaction for hard-core particles in these low dimensional systems when the probability of reaction $p$ is small we consider the simplest case of a one-dimensional lattice. In one dimension, departures from the asymptotic law (1) may be expected at intermediate times. This corresponds to the high-density regime, which in experimental set-ups is more interesting than the low density one. When the reaction probability $p$ is sufficiently small, the transient regime may be long enough to become relevant in the experiments. In addition, the interesting phenomenon of anomalous diffusion characteristic of hard-core particles ($d_w = 4$ [3]) may be observed at short times (before the particles can react) when $p \ll 1$ and the initial density is sufficiently large.

Let us consider first the case that $p$ is smaller but close to one, $p \leqslant 1$. In this case the repulsive barrier between two particles can be overcome after few collisions, the hard-core effect will be negligible at long times and the density will obey (1) asymptotically. If $p$ is decreased, the crossover to (1) will be reached at later times. We may denote as $t_1$ the crossover time to the regime (1). If $p$ is decreased further, the time $t_1$ may eventually occur at times well beyond the experimentally accessible time. For this model, we thus expect that the asymptotic behaviour of $\rho(t)$ will not depend on $p$ [2, 5], i.e. $\rho(t) \sim t^{-1/2}$ when $t \to \infty$, equation (1), as for interpenetrating particles. In this work we are interested in the *intermediate* regime, i.e. for times $t \ll t_1$, when $p \ll 1$. In this intermediate regime, the precise behaviour of $\rho(t)$ has not, to our knowledge, been studied so far.

Let us start with the description of the model. At $t = 0$, each site of a one-dimensional lattice is occupied by identical particles with probability $\rho_0$, which is the initial particle density. The particles perform a random walk between nearest-neighbour sites of the lattice and periodic boundary conditions are employed. Because of annihilation the total number of particles $N(t)$ decreases with time $t$. In the simulations, one of the $N(t)$ particles is picked up at random at time $t$ and attempts to jump to any of the two nearest-neighbour sites with equal probability ($\frac{1}{2}$ in this case). Three possibilities can occur: (i) if the chosen site is empty the particle jumps. (ii) If the chosen site is occupied, the reaction takes place with probability $p$. If successful, both particles are removed from the lattice and the number of particles $N$ is reduced to $N - 2$. Otherwise, (iii) the jump is not performed and the particle remains at its position.

This process is repeated until the number of selected particles (i.e. the number of jumping attempts) reaches the actual number of particles present in the system. Then the time $t$ is increased by one unit and the process is repeated for many unit time steps.

Let us discuss our results. In figure 1, values of the density $\rho(t)$ obtained when $p = 0.01$, for different values of $\rho_0$, are shown as a function of $t$. After an initial regime at short times where the density remains almost constant, an *approximate* power-law behaviour is observed at intermediate times

$$\rho(t) \sim t^{-\gamma} \tag{2}$$

where $\gamma \simeq 0.86$, independently of $\rho_0$ indicating some degree of universality. To see how sensitive our result (2) is, we considered also ordered starting configurations, e.g.: (*a*) $N$ equidistant particles disposed every $l = \rho_0^{-1}$ lattice sites such that $Nl = L$ ($L$ being the lattice length), and (*b*) $N$ particles occupying the first $N$ consecutive lattice sites. In both cases we obtained the same value of $\gamma$.

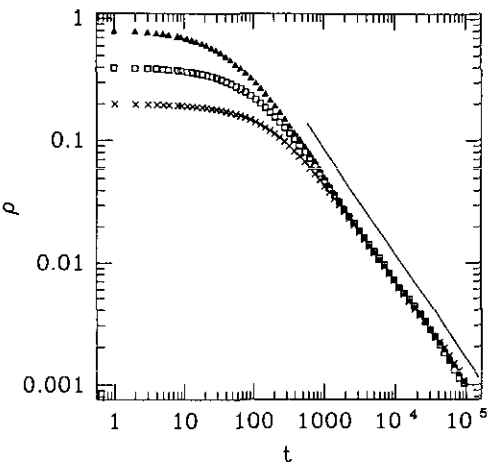


**Figure 1.** Density $\rho$ versus time $t$ for annihilation reactions in one dimension and reaction probability $p = 0.01$. The different symbols correspond to different initial densities $\rho_0 = 0.2$ (crosses), 0.4 (squares) and 0.8 (filled triangles). The straight line is drawn as a guide and has slope $-0.86$. Averages over 20 to 100 initial configurations for each value of $\rho_0$ were performed on systems of $L = 10\,000$ sites.

The power-law dependence (2) is just one possible representation of the numerical data and is adopted here because of its simplicity. It may be viewed as a quantitative interpolation scheme between the plateau at short times and the asymptotic power-law (1). A full theoretical description of the exact time-dependence of $\rho$ is still lacking. In any case, it is interesting to observe that (2) occurs on about two decades in the time scale. The fact that $\gamma \neq \frac{1}{2}$ and $\gamma \neq 1$ is an indication that a non-trivial interplay between interaction and geometry determines the intermediate time behaviour of the density. It should be emphasized that non-universal power laws constitute also a useful representation of experimental data in more complex interacting systems, such as those describing for instance the intermediate frequency regime of the ionic conductivity in many disordered ionic conductors [12].

The asymptotic regime (1) was not reached within our available computer time. For other values of $p$, similar qualitative behaviour was found. However, the corresponding values of $\gamma$ were different but depending only on $p$; the smaller the value of

$p$ the larger is $\gamma$ (see table 1). These results suggest that $\gamma \to 1$ when $p \to 0$, which corresponds to the case of reaction-controlled reactions where diffusion effects are neglected and the mean field approximation $-\mathrm{d}\rho/\mathrm{d}t \sim \rho^2$ holds, $\rho(t) \sim t^{-1}$.

It is apparent from figure 1 that the crossover time $t_0$ between the plateau at short times and the power-law (2) depends on $\rho_0$ for initially disordered configurations. In order to determine the crossover time $t_0$ for fixed $p$ within our approximate scheme, we make the following scaling ansatz for the density

$$\rho(t) = \rho_0 f(t/t_0) \tag{3}$$

which should hold for times $t \ll t_1$. In our case, the scaling function $f(x)$ is expected to behave as $f(x) \sim$ constant for $x \ll 1$ and $f(x) \sim x^{-\gamma}$ for $x \gg 1$ ($t \ll t_1$). Using (2), we find according to (3) that $\rho(t) \sim \rho_0 (t/t_0)^{-\gamma}$ when $t > t_0$. Using the fact that $\rho(t)$ is independent of $\rho_0$ when $t > t_0$, we obtain

$$t_0 \sim \rho_0^{-1/\gamma}. \tag{4}$$

To see how well these predictions actually work, we have plotted in figure 2 values of $\rho/\rho_0$ as a function of $t\rho_0^{1/\gamma}$, for different values of $\rho_0$ and fixed $p$ using the values of $\gamma$ displayed in table 1. The data collapse observed in figure 2 supports our ansatz (3) and the scaling result (4), thus indicating *a posteriori* the plausibility of our choice (2). It should be noted that for initially ordered particle configurations in which the $N$ starting particles occupy $N$ consecutive lattice sites (case ($b$) discussed above), our numerical simulations suggest that the density obeys the scaling form $\rho(t) = \rho_0 g(t/t_0)$

**Table 1.** Exponents $\gamma$ for different values of $p$. The error bars are of about 0.02 for $p \leq 0.03$ and 0.04 for $p = 0.1$.

| $p$ | 0.1 | 0.03 | 0.01 | 0.003 | 0.001 |
|---|---|---|---|---|---|
| $\gamma$ | 0.75 | 0.82 | 0.86 | 0.92 | 0.95 |

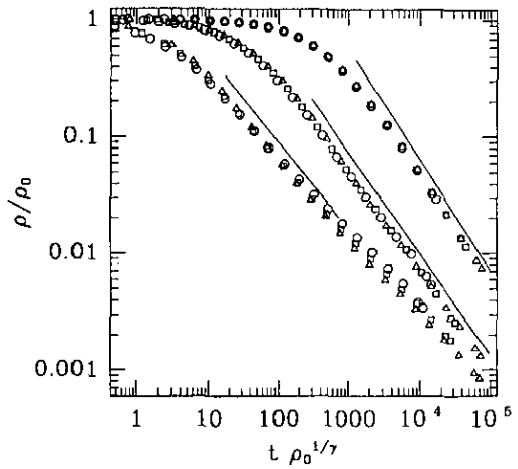


**Figure 2.** Density $\rho/\rho_0$ versus time $t\rho_0^{1/\gamma}$ for different reaction probabilities (from top to bottom) $p = 10^{-3}$ ($\gamma = 0.95$), $10^{-2}$ ($\gamma = 0.86$) and $10^{-1}$ ($\gamma = 0.75$). The different symbols correspond to different values of $\rho_0 = 0.2$ (*circles*), 0.4 (*squares*) and 0.8 (*triangles*). The data collapse strongly supports the scaling ansatz (3). The straight lines have slopes $-\gamma$ and are drawn as a guide.

with $t_0$ *independent* of $\rho_0$ but depending only on $p$, and $g(x) \simeq$ constant for $x \ll 1$ and $g(x) \simeq x^{-\gamma}$ for $x \gg 1$. The independence of $t_0$ on $\rho_0$ for these particular configurations can be expected since these configurations differ only in their initial number of particles $N$ but not in their relative particle distances.

Note that the time interval in which the power-law (2) holds increases when $p$ decreases (figure 2). For larger times, the reaction will be controlled by diffusion and the regime (1) will be reached when $t \gg t_1$. As a result, a breakdown of the scaling behaviour (3) can be expected at larger times. This is indeed observed in figure 2 in the case $p = 0.1$. The regime (1) was found for larger values of $p$. The precise dependence of $t_1$ on $p$ and $\rho_0$ remains to be studied.

When $p \to 1$, the intermediate time regime vanishes, i.e. $t_1 \to t_0$ and $\gamma \to \frac{1}{2}$. Thus $t_0$ becomes the only characteristic time. In this limit, (4) yields the known result $t_0 \simeq \rho_0^{-2}$ [2–5]. In general, both times $t_0$ and $t_1$ need to be taken into account for a complete description of the full time-dependence of $\rho$. Our ansatz (3) describes the scaling behaviour of $\rho(t)$ in the neighbourhood of $t_0$ only. It is interesting that such scaling behaviour actually works in the intermediate time regime.

In summary, we have studied the annihilation reaction $A + A \to 0$ in one dimension for hard-core particles. The $A$ particles diffuse in the system and when two particles collide both disappear (annihilate) with probability $p$, otherwise they are reflected back to their previous positions. For $p = 1$, the reaction is controlled by diffusion and the density $\rho(t)$ of the particles decay, after an initial plateau at short times, as $\rho(t) \sim t^{-\gamma}$ with $\gamma = \frac{1}{2}$. When $p \ll 1$, an intermediate time regime develops which is characterized by an approximate power-law with a non-universal exponent $\frac{1}{2} < \gamma < 1$ (see figure 1 and table 1). The exponent $\gamma$ depends only on $p$ and is independent of both $\rho_0$ and the initial distribution of particles. In addition, the density $\rho(t)$ obeys a scaling relation (3) (for initially disordered particle configurations) from which we obtain the characteristic time $t_0 \sim \rho_0^{-1/\gamma}$ determining the set-in of the intermediate time regime. When $p \to 0$, $\gamma \to 1$ and we recover the limit of reaction-controlled reactions governed by the known mean-field equation $-\mathrm{d}\rho/\mathrm{d}t \sim \rho^2$, $\rho(t) \sim t^{-1}$, i.e. $\gamma = 1$. In all cases $p > 0$, we expect that $\rho(t) \sim t^{-1/2}$ asymptotically. For fractal substrates, similar effects can be expected for sufficiently small $p$ such that $\gamma$ becomes larger than $d_s/2 < 1$. Similar numerical studies of annihilation processes in these disordered systems are in progress.

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