Reaction kinetics of annihilating particles with anomalous diffusion

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We present numerical simulations of the effect of anomalous diffusion on the binary annihilation reaction model $A + A \to \emptyset$. Anomalous diffusion is simulated by discrete-time Lévy flights, which facilitate the numerical treatment of that transport mechanism and makes it possible to cover a wide range of Lévy exponents. Results are compared with those of continuous-time approaches, both theoretical and numerical.

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Anomalous diffusion plays a fundamental role as a transport model in a wide class of physical systems [1]. Diffusion in turbulent flows [2], phase-space motion in chaotic dynamics [3], and transport in highly hetereogeneous media, such as porous materials or gels [1,4], are the main instances of those systems.

Ordinary diffusion is characterized by a mean square displacement proportional to the time, $\langle r^2 \rangle \propto t$. On the contrary, depending on the physical system under study, anomalous diffusion can exhibit a variety of alternative behaviors, ranging from generalized diffusion laws, $\langle r^2 \rangle \propto t^\beta$ ($\beta \neq 1$), to situations in which $\langle r^2 \rangle$ is not a well defined quantity. In these cases, the transport mechanism has to be characterized in terms of other statistical properties. These anomalies are related with unusual topological features in the transport process, such as fractal structure [2,5].

In the framework of random walks, two possible approaches can be used to reproduce anomalous diffusion. One of them considers long-tailed waiting-time distributions in the continuous-time formulation [4,6,7]. The other one, which can be incorporated to discrete-time models, takes long-tailed distributions for the jump-length probability [8]. Both approaches can be combined to account for complex scaling laws, as in turbulence problems [2]. Among the discrete-time random walks with long-tailed jump distributions, Lévy flights [9,1–6] are paradigmatic. In Lévy flights, the jump probability distributions $p(x)$ behave as

$$p(x) \sim |x|^{-1-\gamma} \qquad (\gamma > 0), \tag{1}$$

for large x. For $\gamma < 2$ the mean square displacement $\langle x^2 \rangle$ diverges, and the resulting diffusion process is anomalous. In particular, if γ is lower than the Euclidean dimension of the domain where the random walk takes place, the set of points visited by the walker is a fractal of dimension γ [3,5]. In this case, the elapsed time—which is proportional to the number of steps—scales with the total displacement r as $t \sim r^\gamma$.

The interplay of transport and reaction processes has attracted great attention in recent years [10]. Besides its obvious interest in practical applications, the combined effect of reactions and ordinary diffusion has been studied as a model of complex behavior not only in physical and chemical systems but also in biology [11] and other fields of science. In particular, it is known [12] that ordinary diffusion is able to affect in a nontrivial manner the kinetics of some simple reactions such as, for instance, one-species binary annihilation, $A+A \to \emptyset$, and coagulation $A+A \to A$. In these cases, the asymptotic long-time decay of the particle number in the presence of diffusion is

$$n(t) \sim \begin{cases} t^{-d/2}, & d < 2 \\ t^{-1}, & d > 2 \end{cases} \tag{2}$$

on a d-dimensional space.

In view of the relevant role of anomalous diffusion as a transport mechanism in several physical systems, it is natural to investigate its effects on reaction processes. This has been partially solved in the frame of continuous-time random walks ("Lévy walks") in Ref. [7]. In this paper we present some preliminary numerical results on the effect of anomalous diffusion in the reaction $A+A \to \emptyset$—considered only marginally in [7]—in a discrete- time scheme. At the computational level, discrete-time random walks are much easier to manipulate than their continuous-time version. Therefore, they provide a more convenient tool for large-range simulation of anomalous diffusion. In particular, whereas in Ref. [7] the Lévy exponent γ it is restricted to the interval $1 < \gamma < 2$, we consider here that in our Lévy flights it can vary in some orders of magnitude.

We consider a system of particles undergoing the reaction $A + A \to \emptyset$. The particles perform a Lévy-type random walk on a one-dimensional lattice with periodic boundary conditions. At each time step, one particle is chosen at random. It jumps to the right or to the left with equal probability. The jump-length probability $P(n)$ satisfies Eq. (1):

$$P(n) = N(n_0 + n)^{-1-\gamma} \qquad (n = 0, 1, 2, \ldots), \tag{3}$$

where N is a normalization constant. Here, n_0 is a typical length which, in the case of a fractal random walk, stands for the lowest scale at which self similarity manifests. In our numerical simulations we take $n_0 = 1$. The particle then jumps n sites to the right or to the left; if the arrival site was occupied, both particles are removed.

For small values of γ, $1 \gtrsim \gamma$, we expect that the particle number decay as predicted by the "mean field" chemical-kinetics theory, $n(t) \sim t^{-1}$, which does not take into

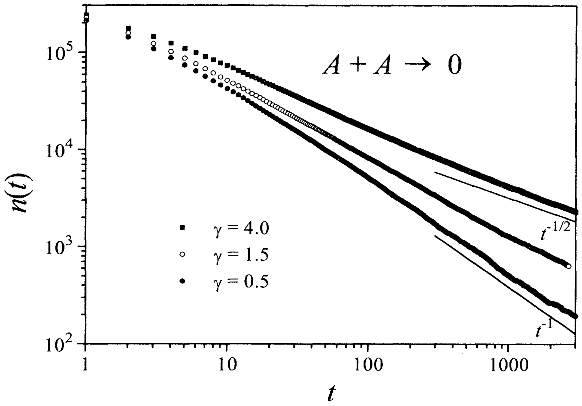

FIG. 1. The number of particles as a function of time for single realizations of the binary annihilation $A + A \to \emptyset$ over a 4.8×10^5-site lattice, for three values of the exponent γ. Straight lines stand for the power-law decays corresponding to ordinary diffusion ($t^{-1/2}$) and to the "mean field" theory (t^{-1}).

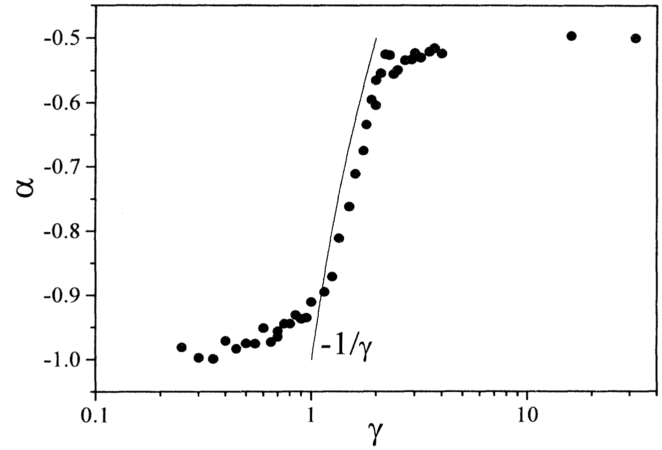

FIG. 2. The power-law "slope" α as a function of the exponent γ. Note the logarithmic scale in the horizontal axis.

account fluctuations in the particle distribution due to diffusion. In fact, for sufficiently small γ, the Lévy flight is a highly efficient transport mechanism with divergent mean jump length. In these conditions, the reacting particles are subject to a strong stirring process and the spatially homogeneous chemical-kinetics result should hold. On the other hand, for $\gamma > 2$, the second moment of the jump distribution in Eq. (3) does exist, the mean square jump length is therefore well defined, and the reaction kinetics observed with ordinary diffusion, $n(t) \sim t^{-1/2}$, should be recovered.

For intermediate values of the exponent γ, we assume that the long-time decay of the particle number will be given by $n(t) \sim t^{\alpha}$, with $-1 < \alpha < -1/2$ [7]. This hypothesis must be confirmed by numerical simulations, which will be also used to determine the dependence of the exponent α on γ. In Fig. 1, we show the result of simulations on a 4.8×10^5-site lattice, with one particle per site at $t = 0$. Each set of points corresponds to one realization for a given value of γ. For $\gamma = 0.5$, the asymptotic slope in this log-log plot is clearly close to $\alpha = -1$. Meanwhile, for $\gamma = 4.0$, $n(t)$ seems to decay a little faster than the expected $t^{-1/2}$ law of ordinary diffusion. For the intermediate value $\gamma = 1.5$ it is apparent that the slope α results as well defined as for the other cases. A least-square fitting for $t > 1000$ produces $\alpha \approx -0.70$.

Simulations show that other values of γ give also place to reaction kinetics with well defined power-law decays for the particle number. Figure 2 displays the slope α versus the exponent γ, as obtained from the numerical evaluation of $n(t)$. As predicted before, for $\gamma < 1$ the slope is close to $\alpha = -1$. We recall that these values of γ produce a fractal random walk, with divergent mean displacement. The "mean field" result is essentially valid, although a deviation is neatly seen near $\gamma = 1$, where $\alpha \approx -0.9$.

The strongest variation of α as a function of γ occurs for $1 < \gamma < 2$. In this interval, the random walk passes from having an infinite mean jump length to having a well defined mean square displacement, which should produce ordinary diffusion. Accordingly, within this range the slope α practically varies from one of its extreme values to the other. For $\gamma = 2$, we find $\alpha \approx -0.6$.

We observe that, although for $\gamma > 2$ the mean square jump length $\langle n^2 \rangle$ of our Lévy flight is finite, higher order moments can diverge. In fact, $\langle n^{\Gamma} \rangle$ is infinite for $\Gamma > \gamma$. According to our results, these anomalies in the high-order moments of the jump distribution seem to affect the reaction kinetics. In fact, α reaches the value which corresponds to ordinary diffusion only for large γ, $\gamma \gtrsim 10$. Just above $\gamma = 2$ the evolution of the particle number differs slightly from the expected $t^{-1/2}$ law.

The solid line in Fig. 2 stands for an approximated result for $1 < \gamma < 2$ based in the analysis of interparticle distances [7], which gives $\alpha = -1/\gamma$. From our simulations we see that this is a reasonable approximation, although a systematic difference is observed.

In summary, discrete-time anomalous diffusion seems to affect simple reaction models in the same way as continuous-time Lévy walks, i.e., by modifying the power-law decay of the particle number. Some slight anomalies are found with respect to the expected theoretical results, in particular, in the limit of ordinary diffusion. A formal treatment of the interplay of anomalous diffusion and reactions could be carried out within the formalism presented in Ref. [13]. In fact, it has been proved to efficiently deal with the anomalies which typically arise in this class of problems. Such a treatment is the subject of work in progress.

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