One-species bimolecular reaction kinetics enhanced by anomalous diffusion

P. Oliva and D. H. Zanette
Centro Atómico Bariloche and Instituto Balseiro, 8400 Bariloche, Río Negro, Argentina
(Received 13 December 1995)

We show that Lévy-walk hyperdiffusion, in which diffusing particles run over all the points of their trajectories, can enhance the kinetics of one-species bimolecular annihilation ($A+A\rightarrow 0$) and coagulation ($A+A\rightarrow A$). Simple probabilistic arguments indicate that the asymptotic particle number decay goes as $N(t)\propto t^{-1/\gamma}$, with γ the Lévy exponent ($0<\gamma<2$). Therefore, for $\gamma<1$ those reactions proceed faster than in the usual chemical-kinetics approximation, which predicts $N(t)\propto t^{-1}$. Our results are validated by numerical simulations. [S1063-651X(96)01707-2]

PACS number(s): 05.40.+j, 82.20.−w

It is by now well known that reaction and transport processes interact in a nontrivial way, affecting the evolution properties of each other [1]. This interplay is relevant in many actual problems of physics, chemistry [2], and biology [3]. Besides, as a paradigm of complex behavior, it also plays a fundamental role in our basic understanding on complex systems.

The mutual effect of reaction and transport is particularly well understood when the underlying transport mechanism is given by ordinary diffusion. This process is characterized by a mean square displacement which is proportional to the time $\langle x^2\rangle\propto Dt$ with D the diffusivity. In particular, for one-species annihilation ($A+A\rightarrow 0$) and coagulation ($A+A\rightarrow A$), it is known that ordinary diffusion affects the long-time decay of the particle number $N(t)$ [4]

$$N(t)\propto\begin{cases}(Dt)^{-d/2} & \text{for } d<2\\ (Dt)^{-1} & \text{for } d>2,\end{cases} \tag{1}$$

with d the dimension of the reaction substrate. For $d<2$, the particle number decay is slower than the decay predicted by the corresponding equation of chemical kinetics $\dot{N}\propto -N^2$. This equation assumes that all the particle pairs have the same reaction probability—a situation which only occurs in a well stirred system— and implies $N(t)\propto t^{-1}$. For $d<2$, ordinary diffusion is not an efficient transport (stirring) mechanism and, therefore, it limits the reaction rate.

In the last few years, transport processes other than ordinary diffusion have attracted great attention. In particular, anomalous diffusion has been shown to act as the basic transport mechanism in a wide class of physical systems, ranging from kinetics in porous media [5] to turbulent flows [6], to chaotic phase-space motion [7]. Anomalous diffusion is characterized by a mean square displacement proportional to a positive power of the time, $\langle x^2\rangle\propto t^{\beta}$ with $\beta\neq 1$. Subdiffusion ($\beta<1$) occurs, for instance, in transport processes on highly heterogeneous substrates [8], whereas hyperdiffusion ($\beta>1$) characterizes transport in turbulent fluids and chaotic systems.

A useful mathematical tool for modeling hyperdiffusion consists in a generalization of random walks, in which the jump-length probability $p(r)$ decays, for large r, as

$$p(r)\propto r^{-d-\gamma}, \tag{2}$$

with $\gamma<2$. These probability distributions have infinite second- (and higher-) order moments and belong to the class of stable or Lévy distributions [9]. Their power-law dependence on the jump length imply that no characteristic length scale can be associated with their large-r behavior, a property which is related to self-similarity (fractal) features in the evolution of the random walk [9,10].

In connection with the kinetics of the one-species bimolecular reactions quoted above, the limitation implied by hyperdiffusion in the decay of the particle number is expected to be less severe than in the case of ordinary diffusion. In fact, as a transport process, hyperdiffusion is more efficient than ordinary diffusion and, therefore, should improve the stirring of the reacting particles. In the frame of Lévy random walks, this is indeed suggested by some simple scaling arguments [11,12], and can be confirmed by a more rigorous analysis based on the continuous-time random-walk (CTRW) theory [13]. This analysis has shown that, for a system of coagulating or annihilating particles which perform a random walk with a jump probability of the form of Eq. (2), the long-time decay of the particle number behaves as

$$N(t)\propto\begin{cases}t^{-d/\gamma} & \text{for } d<\gamma\\ t^{-1} & \text{for } d>\gamma.\end{cases} \tag{3}$$

Note that this result reduces to Eq. (1) in the limit $\gamma\rightarrow 2$, where ordinary diffusion is recovered from Lévy random walks.

In Fig. 1, empty dots stand for the numerical measurement of the exponent α in the asymptotic particle number decay $N(t)\propto t^{\alpha}$ as a function of the Lévy exponent γ, in a series of simulations on a one-dimensional lattice. The curves correspond to the analytical prediction; for $\gamma>2$, the result for ordinary diffusion $\alpha=-1/2$ holds.

Actually, however, the realization of a Lévy random walk admits to be performed in two different ways. In the first one, the jumping particle abandons its site, ''flies'' over the substrate, and finally ''lands'' on the arrival point. This realization of the random walk is more properly called a Lévy flight. In the second form of realization, instead, the particle performs the whole path towards its destination on the substrate, running over all the intermediate points. Such a realization of the transport process is called a Lévy walk. Note

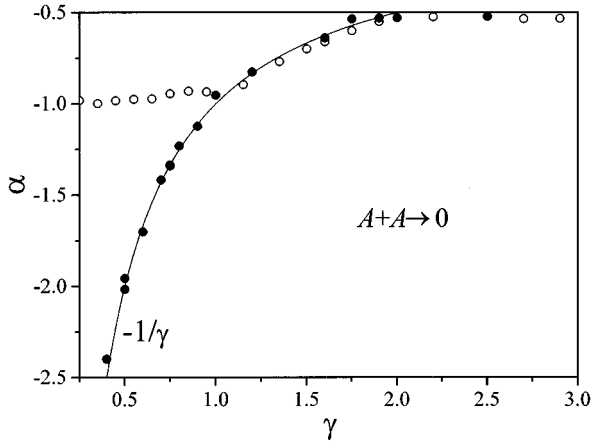

FIG. 1. Numerical measurement of the exponent α in the particle number decay $N(t)\propto t^{\alpha}$ in one-species binary annihilation $(A+A\rightarrow 0)$, versus the Lévy exponent γ. Empty and filled dots correspond to Lévy flights and Lévy walks, respectively. The curve stand for the analytical prediction for α as a function of γ, $\alpha=-1/\gamma$.

that these two instances of realization of a random walk occurs not only for Lévy distributions: they always appear when the length of the jumps is not fixed and admits a certain distribution. The applicability of each type of realization to the description of an actual system depends on the underlying physical processes. For instance, Lévy walks should apply to turbulent flows, whereas phase-space transport in chaotic mappings should be described by Lévy flights.

If the mean time associated with each jump is kept constant [14], the difference between Lévy flights and Lévy walks is irrelevant to the transport properties of the system. On the contrary, this difference could have an important effect on the reaction kinetics. In fact, in Lévy flights a jumping particle can react only if its arrival site is occupied by another particle. In Lévy walks, instead, any particle situated on the path of the moving particle can act as its partner in a reaction event. With respect to reactions, Lévy walks should therefore be a more efficient transport mechanism than Lévy flights.

The analytical tool based on the CTRW theory—which by now provides the most rigorous mean to study the interplay of reactions and anomalous diffusion, producing the results quoted in Eq. (3)—applies only to the case of Lévy flights [15]. A formalism able to take into account the reactions that can occur along the path of a moving particle in a Lévy walk has not been found yet. However, the following simple arguments make it possible to evaluate the asymptotic particle number decay, at least on one-dimensional substrates.

Consider a system of annihilating or coagulating particles which perform a one-dimensional Lévy walk, with a jump probability $p(r)\propto r^{-1-\gamma}$ for large r. At long times, when the particle density is low, the reaction kinetics is dominated by this asymptotic behavior of the jump probability. In fact, only long jumps are relevant to the evolution of the particle number. Suppose that, at a given time, the particle number is $N(t)$. The mean distance between nearest neighbor particles is then $x\propto 1/N$. The reaction rate per particle can therefore be evaluated as the probability that a particle perform a jump greater than x. This probability is proportional to the integral

$$\int_{x}^{\infty} r^{-1-\gamma}dr\propto N^{\gamma}. \tag{4}$$

If, as stated before, the mean time associated with jumps is a constant [14], Eq. (4) implies that the particle number should obey $\dot{N}/N\propto -N^{\gamma}$, which gives

$$N(t)\propto t^{-1/\gamma}. \tag{5}$$

For $1<\gamma<2$, this result coincides with the decay predicted by the CTRW formulation, Eq. (3) with $d=1$, for Lévy flights. For $\gamma<1$, instead—while the CTRW prediction coincides with the result of the chemical kinetics equation $N(t)\propto t^{-1}$—our arguments suggest that the particle number decays *faster* than t^{-1}. This remarkable conclusion indicates that, in the form of Lévy walks, hyperdiffusion is able to *enhance* the kinetics of reactions with respect to the prediction of the chemical kinetics equation. This is in contrast with the limitation imposed by other transport mechanisms (subdiffusion, ordinary diffusion, and Lévy-flight hyperdiffusion), which always retard—or, at most, do not affect—the evolution of the reacting system.

In view of the fact that the enhancement of reaction processes by Lévy-walk hyperdiffusion has been derived from somewhat informal arguments, it is worthwhile to compare this result with numerical simulations. Filled dots in Fig. 1 correspond to the numerical measurement of the exponent α in the asymptotic particle number decay $N(t)\propto t^{\alpha}$ for Lévy walks. For $1<\gamma<2$, α exhibits the same behavior as for Lévy flights, whereas for $\gamma<1$ it still closely follows the curve $\alpha=-1/\gamma$. This confirms our prediction Eq. (5) for $0<\gamma<2$.

We have reported here a completely unforeseen aspect of the interplay of reaction and transport processes. Our results, which are based on some simple probabilistic arguments and have been confirmed by numerical simulations, indicate that Lévy-walk hyperdiffusion in one dimension is able to enhance the kinetics of one-species bimolecular reactions $(A+A\rightarrow 0$ and $A+A\rightarrow A)$. Under this transport mechanism, the particle number decay is faster than the decay predicted by the equations of chemical kinetics. For $\gamma<1$—when even the first moment of the jump probability diverges—Lévy-walk hyperdiffusion is such an efficient transport mechanism that the annihilation of particles in not able to substantially decrease the reaction probability per particle. In fact, this effect could be heuristically incorporated to the equation of chemical kinetics $\dot{N}=-\kappa N^{2}$ by admiting a reaction rate which *increases* with time $\kappa(t)\propto t^{-1+1/\gamma}$. The explanation of this remarkable effect deserves the formulation of more rigorous analytical arguments, in order to study its extension to many-dimensional systems and to other reaction models.

This work has been partially supported by Consejo Nacional de Investigaciones Cientí ficas y Técnicas, Argentina. Financial support from Fundación Antorchas, Argentina, is gratefully acknowledged.

[1] P.C. Fife, *Mathematical Aspects of Reacting and Diffusing Systems*, Lecture Notes in Biomathematics 28, edited by S. Levin (Springer, Berlin, 1979); L. Schimansky-Geier and H. Malchow, *Noise and Diffusion in Bistable Non Equilibrium Systems* (Teubner, Berlin, 1985); J. Smoller, *Shock Waves and Reaction-Diffusion Equations* (Springer, Berlin, 1994).

[2] A.S. Mikhailov, *Foundations of Synergetics I* (Springer, Berlin, 1990).

[3] J.D. Murray, *Mathematical Biology* (Springer, Berlin, 1989).

[4] K. Kuzokov and P. Kotomin, Rep. Prog. Phys. **51**, 1479 (1988).

[5] J.P. Bouchaud and A. Georges, Phys. Rep. **195**, 127 (1991).

[6] M.F. Shlesinger, J. Klafter, and B.J. West, Physica A **140**, 212 (1986); M.F. Shlesinger, B.J. West, and J. Klafter, Phys. Rev. Lett. **58**, 1100 (1987).

[7] M.F. Shlesinger, G.M. Zaslavsky, and J. Klafter, Nature **363**, 31 (1993); J. Klafter, G. Zumofen, and A. Blumen, Chem. Phys. **177**, 821 (1993).

[8] E. Guyon and J.P. Bouchaud, in *Instabilities and Nonequilibrium Structures IV*, edited by E. Tirapegui and W. Zeller (Kluwer, Dordrecht, 1993).

[9] P. Lévy, *Théorie de l'Addition des Variables Aléatoires* (Gauthier-Villiers, Paris, 1937); B.D. Hughes, M.F. Shlesinger, and E.W. Montroll, Proc. Natl. Acad. Sci. USA **78**, 3287 (1981).

[10] P.A. Alemany and D.H. Zanette, Phys. Rev. E **49**, R956 (1994).

[11] G. Zumofen and J. Klafter, Phys. Rev. E **50**, 5119 (1994).

[12] P.P. Oliva and D.H. Zanette, Phys. Rev. E **51**, 6258 (1995).

[13] P.P. Oliva, D.H. Zanette, and P.A. Alemany, Phys. Rev. E **53**, 228 (1996); P.A. Alemany, D.H. Zanette, and H.S. Wio, Phys. Rev. E **50**, 3646 (1994).

[14] This constraint has been relaxed in Refs. [6] and [7], by introducing stable distributions in the time associated with each jump. Although it could be readily incorporated to our arguments, we do not consider such a generalization here.

[15] E.W. Montroll and M.F. Shlesinger, in *Nonequilibrium Phenomena 11. From Stochastics to Hydrodynamics*, edited by J.L. Lebowitz and E.W. Montroll (North-Holland, Amsterdam, 1984).