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# Analytical approach to coagulation and annihilation of particles with anomalous diffusion

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We study the decay of the particle number in the one-species reactions $A+A \to 0$ and $A+A \to A$, when the particles undergo anomalous diffusion. This transport mechanism is modeled by means of Lévy flights in the frame of an analytical formulation, which provides an explicit expression of a time-dependent reaction rate, to be incorporated into the chemical-kinetics equation. We find that Lévy flights modify the power-law decay that is observed for ordinary diffusion. Under appropriate circumstances, this form of anomalous enhanced diffusion is unable to control reactions, and the particle system behaves as described by ordinary chemical kinetics. Detailed comparisons with numerical simulations make apparent the usefulness of our analytical treatment.

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## I. INTRODUCTION

The interplay of reaction and transport processes in natural systems is presently attracting much attention [1]. This is due to a twofold reason. On one side, many systems of practical interest are driven by the combined effect of those processes [2]. On the other, such interplay is a paradigm of complex behavior, related, for instance, to self-organization and anomalous chemical kinetics. This phenomenon has become essential in our comprehension of macroscopic systems in physics and chemistry, as well as in biology [3] and social sciences [4].

Previous work on the interplay of reaction and transport processes has been practically restricted to the consideration of diffusive transport. Reaction-diffusion models have been extensively used to study pattern formation [5]. It has also been shown that diffusion is able to modify in a nontrivial manner the kinetics of some elementary reaction processes. For instance, in one-species binary annihilation ($A + A \to 0$) and coagulation ($A + A \to A$) on a $d$-dimensional substrate, the asymptotic long-time decay of the particle number in the presence of diffusion is [6]

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

For $d \leq 2$ this contrasts with the ordinary chemical-kinetics result, $N(t) \sim t^{-1}$.

Although diffusion plays a fundamental role as a transport mechanism in a vast class of natural processes, many real systems are driven by other forms of transport. Therefore, one is naturally led to consider, for instance, convection [7] or anomalous diffusion. In connection with its interplay with reaction events, this latter mechanism has received attention only recently [8,9].

As a transport process, anomalous diffusion underlies many important physical systems [10]. Diffusion in turbulent flows [11], phase-space motion in chaotic dynamics [12], and transport in highly hetereogeneous media, such as porous materials or gels [10,13], are the main instances of those systems. In contrast to ordinary diffusion, where the mean square displacement is proportional to the time $\langle r^2 \rangle \propto t$, anomalous diffusion can be characterized by a wide class of alternative behaviors. They range from generalized diffusion laws, $\langle r^2 \rangle \propto t^{\beta}$ ($\beta \neq 1$), to situations in which $\langle r^2 \rangle$ is not defined. These anomalies produce unusual topological features in the transport mechanism, such as fractal structure [11,14].

The effect of anomalous diffusion in the kinetics of the one-species reactions $A + A \to 0$ and $A + A \to A$ and on two-species annihilation $A+B \to 0$ has recently been considered in the frame of Lévy flight models [8,9]. In these models, anomalous diffusion is represented by a random walk with a long-tailed jump probability, $p(r) \sim r^{-1-\gamma}$ [15]. Numerically, it has been found that the particle number in a one-dimensional system undergoing the one-species reactions decays for long times as $N(t) \sim t^{-1/\gamma}$ for $1 < \gamma < 2$ [cf. Eq. (1)]. This result can be justified in a semiquantitative manner by studying the distribution of interparticle distances [8] or by means of scaling analyses.

In this paper, we aim at presenting a more consistent approach for describing the reaction kinetics of one-species annihilation and coagulation under anomalous diffusion. As advanced in [9], we exploit here an approximated analytical formulation that has successfully explained the anomalies of those reactions between particles that perform ordinary diffusion in the critical dimension $d = 2$ [16]. In the next section, for the readers' reference, we outline the main steps of the analytical treatment. In Sect. III, the formulation is applied to our problem and some asymptotic results are explicitly obtained. Section IV is devoted to a comparison of the analytical results with numerical simulations.

## II. ANALYTICAL APPROACH

Our method [16] applies in the frame of the continuous-time random-walk theory on the lattice. In this theory, a random walk is characterized by a waiting-time density $\psi(t)$ and a jump probability $p(\mathbf{r})$. The waiting-time density stands for the probability distribution of the time that the walker stays at a lattice site before hopping to another site. Meanwhile, $p(\mathbf{r})$ is the probability that the walker jumps a directed distance $\mathbf{r}$. Successive jumps are supposed to be independent, whereas $\psi(t)$ and $p(\mathbf{r})$ are uncorrelated. Particularly relevant to our formulation are the Laplace transform of the waiting-time density, $\psi(u)$, and the Fourier transform of the jump probability, $\omega(\mathbf{k})$, namely, the structure function of the random walk.

As suggested in Ref. [17], the annihilation ($A+A \rightarrow 0$, $\epsilon = 2$) and the coagulation ($A + A \rightarrow A$, $\epsilon = 1$) problems can be mapped into another one in which the particle number is preserved. The particles that, due to reactions, disappear in the original problems are replaced by "ghost" particles. Reactions are then identified with identity changes from $A$ to "ghost" particles. The evolution of the number of $A$ particles $N(t)$ can then be factored as

$$\frac{dN}{dt} = -\epsilon F(t)\Lambda(t) \ , \tag{2}$$

where $F(t)$ is the probability that any two particles in the system meet for the first time, and $\Lambda(t)$ is the probability that such an encounter occurs between particles of (the "nonghost") species $A$.

In terms of the first-encounter probability of the $i$th and the $j$th particles, $F_2(\mathbf{r}_i - \mathbf{r}_j, t)$, $F(t)$ reads

$$F(t) = \frac{1}{2}\sum_i \sum_{j \neq i} F_2(\mathbf{r}_i - \mathbf{r}_j, t), \tag{3}$$

where $\mathbf{r}_k$ is the initial position of particle $k$. Meanwhile, an approximated expression for $\Lambda(t)$ is given by

$$\Lambda(t) = \left[\frac{N(t)}{N(0)}\right]^2 , \tag{4}$$

which corresponds to neglecting concentration fluctuations. Since these fluctuations do play a role in the kinetics of the reaction, their effect should then be described by $F(t)$. Calling $n(t) = N(t)/N(0)$, Eq. (2) can be recast as

$$\frac{dn}{dt} = -\kappa(t)n^2, \tag{5}$$

with $\kappa(t) = \epsilon F(t)/N(0)$. Note that this equation has the form of an ordinary chemical-kinetics rate equation with a time-dependent reaction rate $\kappa(t)$, to be calculated from the first-encounter probability $F_2$.

When the waiting-time density is exponential with mean waiting time $\langle t \rangle = 1/\lambda$,

$$\psi(t) = \lambda \exp(-\lambda t), \tag{6}$$

the relative motion of two particles is identical to a single random walk with the same waiting-time distribution, except that the mean waiting time is halved, $\lambda \rightarrow 2\lambda$. In the Laplace-transformed distribution this corresponds to change $u \rightarrow u/2$. Therefore, $F_2(\mathbf{r}, t)$ can be calculated from the probability that a single particle starting its random walk at the origin reaches site $\mathbf{r}$ at time $t$. This latter quantity can in turn be evaluated from $R(\mathbf{r}, t)$, the probability that the same particle reaches $\mathbf{r}$ not necessarily for the first time [18]. In the Laplace representation, we have

$$F_2(\mathbf{r}, u) = \frac{R(\mathbf{r}, u/2)}{R(\mathbf{0}, u/2)}, \tag{7}$$

for $\mathbf{r} \neq \mathbf{0}$. On a $d$-dimensional lattice, $R(\mathbf{r}, u)$ is given by

$$R(\mathbf{r}, u) = \frac{1}{\pi^d}\int_0^\pi dk_1 \cdots \int_0^\pi dk_d \, \frac{\prod_{m=1}^d \cos(r_m k_m)}{1 - \psi(u)\omega(\mathbf{k})}, \tag{8}$$

with $\mathbf{r} = (r_1, ..., r_d)$, $\mathbf{k} = (k_1, ..., k_d)$ and, according to Eq. (6), $\psi(u) = (1 + u/\lambda)^{-1}$.

Introducing $C_0$, the initial concentration of $A$ particles, makes it possible to extend the summations in Eq. (3) over the whole lattice. Note that this requires one to suppose the initial particle distribution to be homogeneous, so that $C_0$ is a well defined quantity. Taking into account Eq. (7), we can calculate the Laplace transform of the time-dependent reaction rate as

$$\kappa(u) = \frac{\epsilon C_0}{2}\left[\frac{1}{[1 - \psi(u/2)]R(\mathbf{0}, u/2)} - 1\right]. \tag{9}$$

In general, the Laplace antitransformation of this equation cannot be explicitly performed, and it will be necessary to resort to approximation techniques or to numerical algorithms. In any case, once $\kappa(t)$ has been found, the reduced particle number $n(t)$, solution to Eq. (5), can be calculated from

$$n(t) = \left[1 + \int_0^t dt'\kappa(t')\right]^{-1} = \left\{1 + \mathcal{L}^{-1}[\kappa(u)/u]\right\}^{-1}, \tag{10}$$

where $\mathcal{L}^{-1}[\,]$ indicates Laplace antitransform.

In order to evaluate the reaction rate $\kappa$, our analytical approach reduces to the calculation of $R(\mathbf{0}, u/2)$, which according to Eqs. (8) and (6) reads

$$R(\mathbf{0}, u/2) = \frac{1}{\pi^d}\int_0^\pi dk_1 \cdots \int_0^\pi dk_d \times \left[1 - (1 + u/2\lambda)^{-1}\omega(\mathbf{k})\right]^{-1}. \tag{11}$$

The possibility of performing these integrals depends strongly on the function $\omega(\mathbf{k})$. We recall that this is the structure function of the random walk, and therefore defines the geometrical properties of this transport mechanism. In the following sections we apply this analytical apparatus to the case of a random walk representing anomalous diffusion.

## III. ANOMALOUS DIFFUSION IN ONE DIMENSION

In the framework of random walks, anomalous diffusion can be described by means of a jump probability given by a Lévy distribution [13–15]. Lévy distributions are defined through their Fourier transform as

$$\omega(\mathbf{k}) = \exp(-bk^{\gamma}), \tag{12}$$

where $b$ is a positive constant and $k = |\mathbf{k}|$. The Lévy exponent $\gamma$ satisfies $0 < \gamma < 2$; in the limit $\gamma = 2$ a Gaussian distribution is recovered. The anomalous properties of the Lévy distribution are due to its singular behavior near $k = 0$, $\omega(\mathbf{k}) \approx 1 - bk^{\gamma}$. Although Eq. (12) cannot be Fourier antitransformed to obtain an explicit expression for $p(\mathbf{r})$, it is possible to find simpler forms of the jump probability whose structure function has the same properties as Lévy's. In one dimension, it is sufficient to take $p(r) \sim r^{-1-\gamma}$ for $r \to \infty$.

Note that $p(r) \sim r^{-1-\gamma}$ with $0 < \gamma < 2$ implies a divergent mean square displacement, $\langle r^2 \rangle \to \infty$, which characterizes one type of anomalous diffusion. In the frame of generalized statistics [19,14], this divergence can be "renormalized" to produce other forms of anomalous diffusion, as described in the Introduction.

In order to explicitly calculate the one-dimensional form of $R(\mathbf{0}, u)$ we replace the structure function in the one-dimensional version of Eq. (11) by $\omega(k) = 1 - bk^{\gamma}$. This corresponds to neglecting higher-order terms in $k$ and is therefore implying a condition on the constant $b$. In fact, the inequality $b\pi^{\gamma} \ll 1$ should be fulfilled. We remark that, as it results from Eq. (12), the quantity $b^{1/\gamma}$ is a length scale characteristic of the jump probability $p(r)$. Within this approximation, $R(0, u)$ has a relatively simple expression, which can be exactly evaluated in terms of a hypergeometric function [20]:

$$\begin{aligned} R(0,u) &= \frac{\lambda + u}{u} \int_0^{\pi} \frac{dk}{\lambda b k^{\gamma} + u} \\ &= \frac{\lambda + u}{u}\, {}_2F_1(1/\gamma, 1; 1 + 1/\gamma; -b\lambda\pi^{\gamma}/u). \end{aligned} \tag{13}$$

According to Eq. (9) and using linear transformations of the hypergeometric function, the Laplace-transformed reaction rate can be written as

$$\kappa(u) = \frac{\epsilon C_0}{2} \left[ \frac{u^{1/\gamma}}{A_1} + \frac{u}{B_1}\, {}_2F_1(1, 1 - 1/\gamma, 1; 2 - 1/\gamma; -u/2b\lambda\pi^{\gamma}) \right]^{-1}, \tag{14}$$

with $A_1 = \gamma(2b\lambda)^{1/\gamma} \sin(\pi/\gamma)$ and $B_1 = 2b\lambda\pi^{\gamma}(1 - \gamma)$. This expression is valid except in the marginal cases when $1/\gamma$ is an integer number.

Equation (14) cannot be explicitly antitransformed and, therefore, we are restricted to an approximated analysis of that result. We focus our attention on the long-time limit of our problem, which corresponds to $u \to 0$ in the Laplace representation. In this limit, the hypergeometric function can be approximated by the first terms of its ordinary power series expansion. In order to analyze the resulting asymptotic form of the reaction rate we must consider two cases separately.

### A. The case $\gamma > 1$

For $1 < \gamma < 2$, the first terms of the expansion in powers of $u$ of the Laplace-transformed reaction rate are

$$\frac{2\kappa(u)}{\epsilon C_0} = A_1 u^{-1/\gamma} - \frac{A_1^2}{B_1} u^{1-2/\gamma} + \frac{A_1^3}{B_1^2} u^{2-3/\gamma} + \mathcal{O}[u^{2-2/\gamma}], \tag{15}$$

which in the temporal variable correspond to

$$\begin{aligned} \frac{2\kappa(t)}{\epsilon C_0} &= A_1 \frac{t^{1/\gamma - 1}}{\Gamma(1/\gamma)} - \frac{A_1^2}{B_1} \frac{t^{2/\gamma - 2}}{\Gamma(2/\gamma - 1)} \\ &\quad + \frac{A_1^3}{B_1^2} \frac{t^{3/\gamma - 3}}{\Gamma(3/\gamma - 2)} + \mathcal{O}[t^{2/\gamma - 3}]. \end{aligned} \tag{16}$$

Within this approximation, the reduced concentration $n(t)$ results, according to Eq.(10),

$$\begin{aligned} n(t) = \Bigg[ 1 + \frac{\epsilon C_0}{2} A_1 \Bigg( & \frac{t^{1/\gamma}}{\Gamma(1/\gamma + 1)} - \frac{A_1}{B_1} \frac{t^{2/\gamma - 1}}{\Gamma(2/\gamma)} \\ & + \frac{A_1^2}{B_1^2} \frac{t^{3/\gamma - 2}}{\Gamma(3/\gamma - 1)} + \mathcal{O}[t^{2/\gamma - 2}] \Bigg) \Bigg]^{-1}. \end{aligned} \tag{17}$$

The leading term in the asymptotic decay of the reduced density can be written as

$$n(t) \approx \frac{2}{\epsilon C_0} \frac{\Gamma(1 + 1/\gamma)}{\gamma(2b\lambda)^{1/\gamma} \sin(\pi/\gamma)}\, t^{-1/\gamma}. \tag{18}$$

This anomalous power-law behavior, $n(t) \sim t^{-1/\gamma}$, coincides with the result suggested by numerical simulations and semiquantitative analyses [8,9]. Our approach provides also the analytical form of the prefactor multiplying the time power, which depends rather strongly on the Lévy exponent $\gamma$. A detailed comparison of this result with numerical simulations is presented in Sec. IV.

Note that in the limit $\gamma = 2$, when the Lévy distribution reduces to a regular Gaussian, the ordinary-diffusion result, $n(t) \sim t^{-1/2}$ [cf. Eq. (1)], is recovered. In the opposite limit, $\gamma \to 1$, the density decays as $n(t) \sim t^{-1}$, coinciding with the prediction of the chemical-kinetics rate equation (with constant reaction rate). As we show in the following, this result matches with the case $\gamma < 1$.

### B. The case $\gamma < 1$

Formally, the treatment of this case is identical to that of the previous one. However, the leading terms in the expansion of $\kappa(u)$ in powers of $u$ in the two cases are different. For $0 < \gamma < 1$, the Laplace-transformed reaction rate is, to the first orders in $u$,

$$\frac{2\kappa(u)}{\epsilon C_0} = B_1 u^{-1} - \frac{B_1^2}{A_1} u^{1/\gamma-2} + \frac{B_1^3}{A_1^2} u^{2/\gamma-3} + \mathcal{O}[u^{3/\gamma-4}]. \tag{19}$$

Antitransforming this expression, we obtain

$$\frac{2\kappa(t)}{\epsilon C_0} = B_1 - \frac{B_1^2}{A_1} \frac{t^{1-1/\gamma}}{\Gamma(2-1/\gamma)} + \frac{B_1^3}{A_1^2} \frac{t^{2-2/\gamma}}{\Gamma(3-2/\gamma)} + \mathcal{O}[t^{3-3/\gamma}]. \tag{20}$$

The approximated reduced concentration is then

$$n(t) = \left[1 + \frac{\epsilon C_0}{2} B_1 \left(t - \frac{B_1}{A_1} \frac{t^{2-1/\gamma}}{\Gamma(3-1/\gamma)} + \frac{B_1^2}{A_1^2} \frac{t^{3-2/\gamma}}{\Gamma(4-2/\gamma)} + \mathcal{O}[t^{4-3/\gamma}]\right)\right]^{-1}. \tag{21}$$

Now, the asymptotic evolution of $n(t)$ is dominated by the term

$$n(t) \approx \frac{1}{\epsilon C_0} \frac{1}{b\lambda\pi^\gamma(1-\gamma)} t^{-1}. \tag{22}$$

The power of time in the decay of the density results in being independent of $\gamma$ and, as said before, coincides with the power predicted by the ordinary chemical-kinetics rate equation corresponding to our bimolecular reactions, $\dot{n} \propto -n^2$. This equation is derived from the assumption that any pair of particles in the system is able to react at any time, which is equivalent to supposing that the particles are subject to a very efficient transport mechanism. In other words, ordinary rate equations describe well stirred systems. Equation (22) indicates then that this limit is in fact attained by Lévy random walks for $\gamma < 1$. In these conditions, anomalous diffusion is, as a transport process, strong enough to cease being a limiting factor to the kinetics of the reaction. Note, however, that a dependence on the Lévy exponent remains in the prefactor of $t^{-1}$.

## IV. COMPARISON WITH SIMULATIONS AND SHORT-TIME EVOLUTION

In this section we first compare the long-time asymptotic analytical results obtained above with numerical simulation of the binary annihilation reaction $A+A \to 0$. Then, we study the behavior of the particle number in the numerical system for short times. With these two limits, we propose an interpolation for describing the evolution of $n(t)$ in the whole temporal range.

Our numerical simulations of the reaction $A + A \to 0$ are carried out along the lines already described in Ref. [9]. The particles perform a Lévy-type random walk on a one-dimensional lattice with periodic boundary conditions. At each time step $\Delta t$, whose duration depends on the particle number $\Delta t = 1/N(t)$, one particle is chosen at random. It jumps to the right or to the left with equal probability, and if the arrival site was occupied, both particles are removed. The jump-length probability $p(r)$ is given by

$$p(r) = N_0 (r_0 + r)^{-1-\gamma}, \tag{23}$$

where $N_0$ is a normalization constant. This form of $p(r)$ satisfies the required asymptotic behavior for large $r$. The constant $r_0$ is a typical length related to the coefficient $b$ in Eq. (12) [18]. In order to compare our analytical and numerical results, $r_0$ has to be chosen in such a way that, as stated before, $b\pi^\gamma \ll 1$.

Figures 1 to 3 show the results of simulations for three values of $\gamma$, over a $1.896 \times 10^6$-site lattice, with initial concentration $C_0 = 1$, i.e., with one particle per site. In order to make the plotted curves visible, we only display some logarithmically spaced points representing the reduced particle number $n(t)$, obtained from simulations as a function of time. Full lines in each plot stand for the long-time approximation derived in the preceding section. They represent the contribution of the two leading terms in Eqs. (16) and (20). We can see that these approximations are acceptably good for times $t > 10^4$. Furthermore, they seem to improve for decreasing $\gamma$.

A comparison of numerical and analytical results for short times is more difficult. Indeed, our numerical scheme, defined through the jump probability given in Eq. (23), does not correspond neither to the Lévy structure function (12) nor to its approximated form $\omega(\mathbf{k}) = 1 - bk^\gamma$. Although they coincide in the limit of large $r$, severe differences are found for short jumps. In the temporal evolution, these differences imply that the numerical and the analytical descriptions can be compared

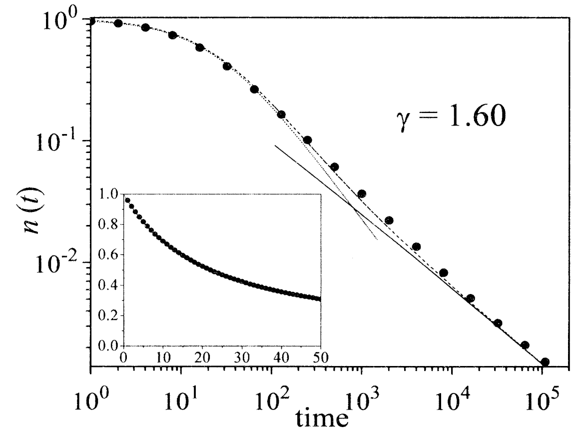

FIG. 1. Evolution of the reduced number of particles undergoing the annihilation reaction $A + A \to 0$ over a $1.896 \times 10^6$-site lattice, with one particle per site at $t = 0$. The Lévy exponent is $\gamma = 1.60$. Dots indicate the result of numerical simulations. The full line corresponds to the analytical result for long times, calculated from the two leading terms. The dotted line stands for the short-time approximation, and the dashed line is an interpolation of the two approximations, defined in the text.

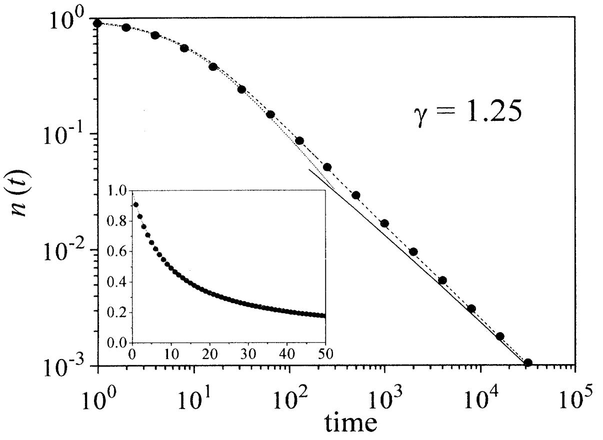

FIG. 2. Same as Fig. 1, for $\gamma = 1.25$.

only when each particle has performed a substantial number of long jumps, so that the length of its trajectory is essentially dominated by them.

On the other hand, the short-time evolution of numerical simulations can be analytically explained from an exact probabilistic description of the very initial stage, achieving acceptable agreement, even for unexpectedly large times. This approach is based on the computation of the mean particle number that is expected after the first temporal step, i.e., for $t = 1/N(0) \equiv \Delta t_0$. In fact, $N(\Delta t_0)$ can equal either $N(0)$, if the chosen particle hops to an empty site, or $N(0) - \epsilon$, in the opposite case. The probability of occurrence of each case can be easily computed by combining the jump probabilities with the occupancy probability. For a homogeneous particle distribution, this latter probability is simply given by the particle concentration. In the discrete lattice, the probability that the particle number equals $N(0) - \epsilon$ after the first jump is

$$P_R = C_0 \sum_{r \neq 0} p(r) = C_0[1 - p(0)], \tag{24}$$

where $p(0)$ is the probability that the chosen particle remains in its site, $C_0$ is the initial concentration measured in particles per node, and the sum runs over all the lattice sites, with the exception of the initial site of the jumping particle. Clearly, $P_R$ depends on the Lévy exponent. The mean particle number after the first jump is then

$$\begin{aligned} \langle N(\Delta t_0) \rangle &= (1 - P_R) N(0) + P_R[N(0) - \epsilon] \\ &= N(0) - \epsilon P_R. \end{aligned} \tag{25}$$

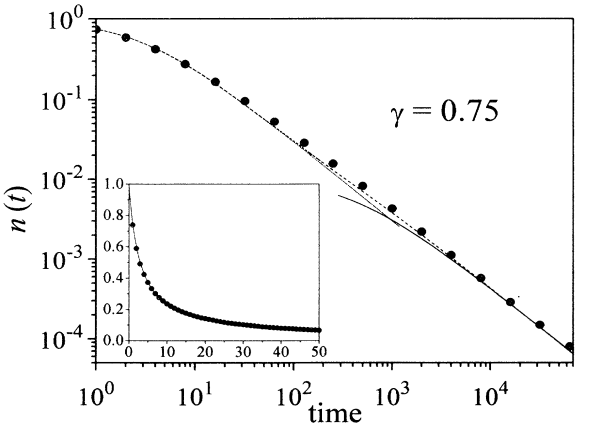

FIG. 3. Same as Fig. 1, for $\gamma = 0.75$.

Now, according to Eq. (10) a heuristic short-time dependence for the reduced particle number of the form

$$n(t) \approx (1 + \kappa_0 t)^{-1} \tag{26}$$

can be reasonably proposed. The constant $\kappa_0$ is chosen in order that this approximated expression of $n(t)$ satisfy $n(\Delta t_0) = \langle N(\Delta t_0) \rangle / N(0) = 1 - \epsilon P_R / N(0)$. We obtain

$$\kappa_0 = \Delta t_0^{-1} \left[ \frac{1}{1 - \epsilon P_R / N(0)} - 1 \right]. \tag{27}$$

In view of the arguments used to propose this short-time approximated density, Eqs. (26) and (27), it could be expected that such an expression be valid only at the very initial stages of the evolution, for times of the order of $\Delta t_0 = 1/N(0)$. It is therefore rather astonishing to verify that, according to our simulations, the approximation is acceptable for times as long as $t = 100$, which is several orders of magnitude larger than $\Delta t_0 \approx 5 \times 10^{-7}$. In the plots inserted in Figs. 1 to 3 we show the results of numerical simulations for times $t \leq 50$. The dotted lines, which have also been plotted in the main plots, stand for the short-time approximation. In the graphics with linear scales this approximation cannot be distinguished from the numerical results. This remarkable agreement seems to indicate that the density fluctuations, which are known to dominate the evolution for long times, begin to act only after a relatively long time interval. During such a period, the evolution would be essentially driven by the uncorrelated events considered to exactly calculate the mean particle number after the first step, Eq. (25).

The good agreement of our analytical approximations with the numerical results for both long and short times, naturally leads us to propose an interpolation to be used as a heuristic description of the evolution in the whole temporal domain. After some trials, we have found that a square average of those approximations reasonably fits with the simulations for all times. Calling $n_S(t)$ and $n_L(t)$ the short- and long-time approximations, respectively, the quantity

$$n_A(t) = \sqrt{n_S^2(t) + n_L^2(t)} \tag{28}$$

defines such an average. It has been plotted in Figs. 1 to 3 as a dotted line. Its usefulness in describing the whole evolution is apparent.

## V. MANY-DIMENSIONAL SYSTEMS

Although the analytical calculation of the evolution of the particle number for a system in a many-dimensional domain requires some further assumptions and approximations, it is a rather straightforward extension of the calculation in the one-dimensional case. Therefore, we here restrict ourselves to outline the calculation of the leading term in the long-time asymptotic evolution, which results in a simple generalization of the one-dimensional situation.

According to Eqs. (8) and (12), $R(\mathbf{0},u)$ can be calculated as an integral on a $d$-dimensional hypercube centered at the origin,

$$R(\mathbf{0},u) = \frac{\lambda+u}{(2\pi)^2}\int_{-\pi}^{\pi} dk_1 \cdots \int_{-\pi}^{\pi} dk_d \, \frac{1}{u+b\lambda k^\gamma}, \tag{29}$$

with $k^2 = k_1^2 + \cdots + k_d^2$, and where we have used the same approximation as in the one-dimensional case, $\omega(\mathbf{k}) = 1 - bk^\gamma$. This many-dimensional integral cannot be explicitly calculated, but can be evaluated in an approximated way at an appropriate limit. In fact, if the integrand is much smaller in the boundaries of the hypercube than in the origin, i.e., if $b\lambda\pi^\gamma \gg u$, it is possible to replace the integration domain by a hypersphere of radius $\alpha\pi$, with $\alpha$ of the order of unity. Note that this small-$u$ approximation stands for the long-time limit. We can roughly say that it is valid for $t \gg 1/b\lambda\pi^\gamma$. Within this approximation, we have

$$\begin{aligned} R(\mathbf{0},u) &= \frac{\lambda+u}{(2\pi)^2}\Omega_d \int_0^{\alpha\pi} \frac{k^{d-1}dk}{u+b\lambda k^\gamma} \\ &= \frac{\lambda+u}{\gamma u}\frac{\alpha^d\Omega_d}{2^d d}\, {}_2F_1(d/\gamma,1;1+d/\gamma;-b\lambda(\alpha\pi)^\gamma/u), \end{aligned} \tag{30}$$

where $\Omega_d$ is the total solid angle in $d$ dimensions.

The Laplace-transformed reaction rate $\kappa(u)$ can now be calculated from Eq. (9). In order to analyze the long-time ($u \to 0$) limit, as in the one-dimensional situation, two cases have to be considered separately. If $d < \gamma$, the antitransformed asymptotic reaction rate results,

$$\kappa(t) \approx \frac{\epsilon C_0}{2}\frac{(2\pi)^d\gamma}{\pi\Omega_d}\frac{\sin(\pi d/\gamma)}{\Gamma(d/\gamma)}(2b\lambda)^{d/\gamma}t^{d/\gamma-1}, \tag{31}$$

and the corresponding leading term in the reduced particle number is

$$n(t) \approx \frac{2}{\epsilon C_0}\frac{\pi\Omega_d}{(2\pi)^2\gamma(2b\lambda)^{d/\gamma}}\frac{\Gamma(1+d/\gamma)}{\sin(\pi d/\gamma)}\, t^{-d/\gamma}. \tag{32}$$

Note that this expression reduces to Eq. (18) as $d \to 1$. Moreover, it does not depend on the parameter $\alpha$ of Eq. (30) and, therefore, the change of the integration domain in (29) has been irrelevant.

As for one-dimensional systems, the decay of the particle number in the case $d < \gamma$ is anomalous, with a power depending on both the dimension and the Lévy exponent. We stress, however, that this situation is relatively marginal. In fact, the structure function given in Eq. (12) does represent anomalous diffusion only for $\gamma < 2$. Therefore, our result (32) applies for $d < 2$ and, having been obtained from an analytical treatment on the lattice, it should hold for $d = 1$ only. In spite of this constraint, we are tempted to conjecture that the decay of the particle number in a system evolving on a fractal substrate of dimension $0 < d < 2$ will follow the anomalous law $n(t) \sim t^{-d/\gamma}$.

In the more relevant case when $d > \gamma$ the long-time asymptotic reaction rate is constant,

$$\kappa(t) \approx \epsilon C_0 \frac{2^d\pi^\gamma}{\Omega_d}\frac{d-\gamma}{\alpha^{d-\gamma}}\, b\lambda, \tag{33}$$

and the reduced particle number behaves as

$$n(t) \approx \frac{1}{\epsilon C_0}\frac{\Omega_d}{2^d b\lambda\pi^\gamma}\frac{\alpha^{d-\gamma}}{d-\gamma}\, t^{-1}, \tag{34}$$

cf. Eq. (22). Unfortunately, these results now depend on the undetermined parameter $\alpha$. But, since we expect that $\alpha \sim 1$, its effect should not be very important. A determination of $\alpha$ could, however, become necessary in a detailed comparison with numerical simulations. In any case, here we are mainly interesed in pointing out the asymptotic temporal dependence of $n(t)$, which indicates that, in this situation, anomalous diffusion acts as a strong transport process and the system is well stirred. This transport mechanism is again unable to control reactions and the particle number decays, as predicted by ordinary chemical-kinetics rate equations. Some preliminary numerical simulations on two-dimensional square lattices, to be presented in a more detailed analysis of many-dimensional systems, have shown that this is indeed the case.

## VI. DISCUSSION AND CONCLUSION

We have studied the effect of anomalous diffusion as a transport process on the chemical kinetics of a system of reacting particles, undergoing the reactions $A+A \to 0$ or $A+A \to A$. Our analysis has been carried out following the lines of a continuous-time random-walk theoretical approach on the lattice [16], able to be compared with numerical simulations. The main goal of this approach is to provide an explicit form for a time-dependent reaction rate, to then be used in the chemical-kinetics equation that governs the evolution of the particle number.

Anomalous diffusion has been represented by means of Lévy flights, a class of random walks characterized by a structure function $\omega(\mathbf{k})$, which, for small $|\mathbf{k}|$, behaves as $\omega \approx 1 - b|\mathbf{k}|^\gamma$ $(0 < \gamma < 2)$. This corresponds to a jump probability with an asymptotic power-law behavior, $p(r) \sim r^{-1-\gamma}$, whose second moment therefore diverges. Lévy flights have been already extensively used as a model for anomalous diffusion in a variety of related problems, such as porous media, turbulent flows, and chaotic dynamics [10–13].

Our main results on $d$-dimensional systems can be summarized as follows. For $d < \gamma$, the particle number decays as $N(t) \sim t^{-d/\gamma}$ for long times. This asymptotic result, which had been advanced in Refs. [8] and [9], is relevant for $d < 2$, as the Lévy exponent is restricted to the interval $0 < \gamma < 2$. Hence, according to our formulation, which is valid for integer dimension, it only applies in the one-dimensional case. One can, however, conjecture that it is also valid on fractal domains with $d < 2$. Besides the asymptotic power-law behavior of the particle number, our results provide also other lower-order terms and the corresponding constant factors, making possible a detailed comparison with numerical simulations.

For $d > \gamma$, the leading order in the asymptotic decay of the particle number behaves as in ordinary chemical kinetics, $N(t) \sim t^{-1}$, which corresponds to a constant reaction rate. In this situation, anomalous diffusion is a sufficiently strong transport mechanism, and as a result is unable to control the kinetics of the reactions. However, it has to be stressed that a dependence on the Lévy exponent $\gamma$ remains in the coefficient of the leading time power, as well as in lower-order terms.

Comparison with numerical simulations has been restricted to one-dimensional systems. We have found an excellent agreement between numerical results and the long-time asymptotic decay of the particle number predicted by the analytical approach. To describe simulations at short times, we introduced a simple probabilistic argument, based on the change of the particle number at the very first stage of the evolution. This result, combined with an *ad hoc* formula suggested by the analytical formulation, has provided a short-time approximation whose validity extends through an unexpectedly long period. Finally, an interpolation of the long- and short-time approximations has provided a heuristic expression to accurately describe the evolution along the whole temporal domain.

We have to point out that, probably, the Lévy flights considered in our formulation are not the most proper model for anomalous diffusion. In fact, in a Lévy flight, a particle jumps from its site, "flies" over the lattice, and "lands" on the arrival point. In a more realistic representation, which cannot be treated within the usual random-walk theory, the particles should perform a "Lévy walk," running over all the intermediate points of their trajectories. We have carried out some simulations in which particles perform these "Lévy walks" on a one-dimensional lattice. The results show that, for $\gamma > 1$, the particle number decays as $N(t) \sim t^{-1/\gamma}$, coinciding with our previous results. But we observed that the same decay occurs also for $\gamma < 1$. In this situation, the particle number decreases faster than $t^{-1}$, the ordinary chemical-kinetics decay. Notably enough, this result can be understood as follows, in terms of very simple arguments. The probability that a particle finds a reaction partner in its "Lévy walk" is roughly proportional to the probability of a jump longer than the mean distance between particles, $x(t) \sim 1/N(t)$. This can be calculated as $\int_x^\infty r^{-1-\gamma} dr \sim x^{-\gamma}$. Then, $\dot{N}/N \sim x^{-\gamma} \sim N^{\gamma}$, which immediately produces $N(t) \sim t^{-1/\gamma}$. Indeed, this very unusual result, which can be readily confirmed by simulations, deserves further consideration.

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