Time-dependent reactivity for diffusion-controlled annihilation and coagulation in two dimensions

P.A. Alemany, D.H. Zanette, and H.S. Wio
Centro Atómico Bariloche, Comisión Nacional de Energía Atómica and Instituto Balseiro, Universidad Nacional de Cuyo, 8400 Bariloche, Río Negro, Argentina
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We present a method to obtain the concentration decay for coagulation, $A + A \to A$ $(\epsilon = 1)$, and annihilation, $A + A \to 0$ $(\epsilon = 2)$, of diffusing particles, on two-dimensional lattices. By mapping these reactions into processes that preserve the particle number, we find an approximate solution, which, as compared with numerical simulations for the square lattice, turns out to be exact for short and long times. The particle number along the whole course of the reaction is obtained in a closed form, and can be written as a function of only the mean number of distinct sites visited by a single particle. For a homogeneous initial particle distribution, the particle number behaves at long times as $N(t) \sim \epsilon N(0)(8aDt)^{-1}\ln(8bDt)$, where D is the diffusivity and a and b depend on the lattice type. On the other hand, for a strongly inhomogeneous (fractal) initial distribution, the particle number decays at long times as $N(t) \sim \epsilon N(0)(8aDt)^{-\gamma/2}\ln(8bDt)$, where γ is the fractal dimension of the initial particle distribution $(0 < \gamma < 2)$.

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I. INTRODUCTION

A topic of considerable interest in the study of diffusion limited reaction systems corresponds to one species coagulation $(A + A \to A)$ and annihilation $(A + A \to 0)$ (hereafter labeled by $\epsilon = 1$ and $\epsilon = 2$, respectively) in a discrete space. The advantage of working on a lattice is that it is not necessary to assign a finite volume to the particles, making such models very suitable for numerical simulations [1–4].

It has been established that both annihilation and coagulation processes belong to the same universality class [5], so that both reactions should show the same concentration decay law. For $d > 2$ the mean field result, $C(t) \sim 1/t$, holds, but the kinetics is strongly affected by diffusion for $d < 2$, where $C(t) \sim t^{-d/2}$. It is interesting to note that, in spite of the analytical—in principle, exact—approaches used to deal with this problem [5–7], the exact solution for all times is only known for the one-dimensional case [8–12].

In this work we concentrate on the critical dimension $d = 2$, where the effect of the discretization of the space is not yet well understood. Some analytical methods [5–7] give, for the asymptotic particle concentration decay,

$$C(t) \sim \frac{\ln t}{t}, \tag{1}$$

whereas from other approaches on the lattice [13–15], one obtains

$$C(t) \sim t^{-1}. \tag{2}$$

Results from numerical simulations [1–3] seem to agree with Eq. (1). In other works [4], authors fitted Monte Carlo results with a general power law of the form $C(t) \sim t^{-\alpha}$, and found that, as time increases, α seems to approach an asymptotic value $\alpha_\infty \leq 1$.

Let us recall that the asymptotic behavior given by Eq. (1) can be straightforwardly obtained from the mean number of different sites visited by a random walker, $S(t)$. In fact, in the spirit of the Smoluchowsky approach [16], by considering the survival of independent random walkers in the presence of a single trap, one can assert that [1,17–20]

$$C(t) \sim 1/S(t) \tag{3}$$

should approximately hold for any spatial dimension. Numerical results [20] support this conjecture, but no analytical proof is available. Note that $S(t)$ contains information on the dynamics of only one *single* particle, whereas from the exact solution for $d = 1$ one has learned that the information relevant to the reaction kinetics is involved in the relative motion of *two* particles. In fact, for the one-dimensional problem, it was established that the concentration decay along the whole reaction can be computed from the survival probability of a single *pair* of particles.

In this work we derive relation (3) from an approach that takes into account the interaction of each particle with all the others. For the reactions under study, this yields the following approximated solution, in terms of $S(t)$:

$$\frac{N(t)}{N(0)} = \frac{1}{1 - \frac{\epsilon}{2}C_0 + \frac{\epsilon}{2}C_0 S(2t)}, \tag{4}$$

where $N(t)$ is the number of particles at time t and C_0 is the initial particle concentration. As compared with Monte Carlo simulations on a square lattice, this expres-

sion turns out to be exact for short and long times, and its maximum error reaches about 20% (near $t \approx 1/8D$). The factor 2 in the argument of S reveals the two-particle character of this many particle problem.

II. THE METHOD

We consider a system of purely diffusive particles, so that the mean square displacement of a single particle at all times is exactly given by

$$\langle \mathbf{r}^2(t) \rangle = 2dDt, \tag{5}$$

where D is the diffusion coefficient. We assume that the particles perform a continuous time random walk (CTRW) on a two-dimensional lattice of spacing ℓ, with equal jump probability to any of the nearest neighbor sites. It is known that, in the frame of the CTRW theory, pure diffusion is obtained by assuming that the jumps of a single particle follow a Poissonian statistics, i.e., that the jump waiting time density (WTD) is exponential,

$$\psi(t) = \lambda e^{-\lambda t} = \mathcal{L}^{-1}\{\psi(u)\}, \tag{6}$$

with $\psi(u) = 1/(1 + u/\lambda)$, such that the mean waiting time is $\langle t \rangle = \int_0^\infty t\psi(t)\, dt = 1/\lambda$. Here $\mathcal{L}$ ($\mathcal{L}^{-1}$) stands for (inverse) Laplace transform. For this process, the mean square displacement of one particle is given by Eq. (5), with $D = \ell^2\lambda/2d$. Hereafter, we take $\ell = 1$.

In the coagulation model, the reaction mechanism is such that when a particle arrives at an occupied site, both particles transform into a new single particle and a new waiting time starts. In the annihilation model, instead, both particles are removed.

We shall map this problem into another one, in which the total number of particles $N(0)$ remains constant, while the *identity* of the particles changes when they meet, following the rules [11]

$$A + A \rightarrow \begin{cases} G + A & \text{for coagulation,} \\ G + G & \text{for annihilation,} \end{cases} \tag{7}$$

$$G + A \rightarrow G + A, \tag{8}$$

$$G + G \rightarrow G + G. \tag{9}$$

Thus, after an encounter, both particles become "ghosts," (G), or one of them becomes a "ghost," and the other preserves its identity, A, respectively. In this scheme, each particle behaves as if it were alone in the lattice: its motion is not affected by the other particles. At each encounter of two A particles, the interaction is reduced to an irreversible change of identity, as indicated in Eqs. (7)–(9).

Let us concentrate on a given particle pair (i, j), initially situated at $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively ($\mathbf{r}_i \neq \mathbf{r}_j$). The probability that they meet for the first time within the time interval $(t, t + dt)$ is given by $F_2(\mathbf{r}_j - \mathbf{r}_i, t)dt$, where $F_2(\mathbf{r}, t)$ is given by the first passage time probability density on site $\mathbf{r}$ for a random walker initially situated at the origin, whose evolution reproduces the relative motion of particles (i, j). If the WTD of each particle is given by Eq. (6), this new CTRW has also an exponential WTD, with twice the jump rate:

$$\psi_2(t) = 2\lambda e^{-2\lambda t} = \mathcal{L}^{-1}\{\psi(u/2)\}. \tag{10}$$

We stress that, in general, the relative motion of two random walkers corresponds to a CTRW for which there is not a well defined WTD $\psi_2(t)$, as it is based on the pooling of two renewal processes. This pooling results in a renewal process in turn only for the exponential single particle WTD given in Eq. (6); therefore in principle this method is only valid for an exponential $\psi(t)$.

For the many particle system we must consider the relative motion of each particle i with respect to all the other particles j. The probability that any two particles of the whole system meet for the first time in $(t, t + dt)$ is

$$\mathcal{F}(t)\, dt = \frac{1}{2}\sum_i \sum_{j \neq i} F_2(\mathbf{r}_j - \mathbf{r}_i, t)dt, \tag{11}$$

where $\mathbf{r}_k$ is the position of particle k at $t = 0$. When a pair meets for the first time, the number of particles changes if the encounter corresponds to Eq. (7). The probability for such an encounter to occur is a complicated function of the time, say $\Lambda(t)$, which we shall compute in an approximated form later. In terms of these functions, we are able to write the following evolution equation for the particle number:

$$N(t) - N(t + dt) = \epsilon\Lambda(t)\, \mathcal{F}(t)\, dt, \tag{12}$$

where $N(t)$ is the number of particles A at time t. From here, we obtain

$$\frac{d}{dt}C(t) = -\Lambda(t)\kappa(t), \tag{13}$$

where we have defined the concentration at time t normalized by the initial concentration C_0 as $C(t) = N(t)/N(0)$, and

$$\kappa(t) \equiv \epsilon\frac{1}{N(0)}\mathcal{F}(t) = \frac{\epsilon}{2N(0)}\sum_i \sum_{j \neq i} F_2(\mathbf{r}_j - \mathbf{r}_i, t) \tag{14}$$

is the first encounter rate per particle.

The probability $\Lambda(t)$ cannot be exactly obtained. An approximated form could be written in terms of space correlation functions. If particles are placed at random with occupancy probability C_0, it is known that the particle number decay of this single species reaction-diffusion model is not very affected by the concentration fluctuations [21]. Then for the one species reaction model that we are considering, a first approximation for $\Lambda(t)$ corresponds to taking

$$\Lambda(t) \approx \left[\frac{N(t)}{N(0)}\right]^2 = C^2(t). \tag{15}$$

Within this assumption, the concentration equation becomes

$$\frac{d}{dt}C(t) = -\kappa(t)C^2(t), \tag{16}$$

whose solution reads

$$C(t) = \frac{1}{1+\rho(t)}, \tag{17}$$

with

$$\rho(t) \equiv \int_0^t \kappa(t')\, dt'. \tag{18}$$

According to the above discussion, $\kappa(t)$ has to be computed from the relative motion of two particles, averaged over the initial distances of all the particle pairs. Instead of summing over particles, we can sum over all the lattice sites, $\mathbf{r} = (r_1, r_2)$, by introducing an indicator function,

$$p(\mathbf{r}) = \begin{cases} 1 & \text{if there is a particle on } \mathbf{r} \text{ at } t = 0 \\ 0 & \text{if there is no particle on } \mathbf{r} \text{ at } t = 0. \end{cases} \tag{19}$$

Note that $\sum_{\mathbf{r}} p(\mathbf{r}) = N(0)$, and $\langle p(\mathbf{r}) \rangle = C_0$. In this way, the overall encounter rate becomes

$$\mathcal{F}(t) = \frac{1}{2}\sum_{\mathbf{r}} p(\mathbf{r}) \sum_{\mathbf{r}' \neq \mathbf{r}} p(\mathbf{r}') F_2(\mathbf{r} - \mathbf{r}', t), \tag{20}$$

where now the sums run over all the lattice sites. Thus

$$\kappa(t) = \frac{\epsilon}{2}\sum_{\mathbf{r}\neq\mathbf{0}} p(\mathbf{r}) F_2(\mathbf{r}, t) = \frac{\epsilon}{2} C_0 \sum_{\mathbf{r}\neq\mathbf{0}} F_2(\mathbf{r}, t). \tag{21}$$

In this way we are justifying the introduction of a time-dependent reaction rate in the mean field chemical-kinetic equation, as proposed by Argyrakis and Kopelman in Ref. [22].

III. ANALYTICAL SOLUTION

Let $R(\mathbf{r}, t)dt$ be the probability for a given *single* particle initially situated at the origin, to reach the site $\mathbf{r} = (r_1, r_2)$—not necessarily for the first time—within the time interval $(t, t + dt)$. In the Laplace representation, for a nonbiased random walk on a two-dimensional lattice, we have [23]

$$\begin{aligned} R(\mathbf{r}, u) &= \int_0^\infty dt\; e^{-ut} R(\mathbf{r}, t) \\ &= \frac{1}{\pi^2}\int_0^\pi dk_1 \int_0^\pi dk_2 \frac{\cos(r_1 k_1)\cos(r_2 k_2)}{1 - \psi(u)\omega(k_1, k_2)}, \end{aligned} \tag{22}$$

where $\omega(k_1, k_2) \equiv \omega(\mathbf{k})$ is the structure function of the lattice. Some instances are

$$\omega(\mathbf{k}) = \begin{cases} \frac{1}{2}[\cos k_1 + \cos k_2] & \text{for a square lattice} \\ \frac{1}{3}[\cos k_1 + \cos k_2 + \cos(k_2 + k_3)] & \text{for a triangular lattice} \\ \frac{1}{3}[e^{ik_1} + 2\cos k_2] & \text{for a hexagonal lattice.} \end{cases} \tag{23}$$

Let $F(\mathbf{r}, u)$ be the probability density for the time in which the site $\mathbf{r}$ is reached *for the first time.* In the Laplace representation it can be obtained as [24]

$$F(\mathbf{r}, u) = \frac{R(\mathbf{r}, u)}{R(\mathbf{0}, u)}, \quad \mathbf{r} \neq \mathbf{0}. \tag{24}$$

Considering now the relative motion of two particles, the probability density $F_2(\mathbf{r}, t)$ for the time of their first encounter is given by Eqs. (24) and (22), by replacing $\psi(t)$ by $\psi_2(t)$. In the Laplace representation this corresponds to replacing u by $u/2$, i.e., $F_2(\mathbf{r}, u) = F(\mathbf{r}, u/2)$. Bringing this into Eq. (21) we obtain

$$\kappa(u) = \frac{\epsilon C_0}{2}\left\{ \frac{1}{\pi^2 R(\mathbf{0}, u/2)} \int_0^\pi dk_1 \int_0^\pi dk_2 \frac{\sum_{r_1=-\infty}^{\infty} \cos(r_1 k_1) \sum_{r_2=-\infty}^{\infty} \cos(r_2 k_2)}{1 - \psi(u/2)\omega(k_1, k_2)} - 1 \right\}.$$

Using the Poisson summation formula in the form $\sum_{r=-\infty}^{\infty} \cos(rk) = \sum_{m=-\infty}^{\infty} \delta(k/2\pi - m)$ and the fact that $\omega(0, 0) = 1$, this expression reduces to

$$\kappa(u) = \frac{\epsilon C_0}{2}\left[\frac{1}{[1 - \psi(u/2)]R(\mathbf{0}, u/2)} - 1\right]. \tag{25}$$

Next, we shall recast this expression in terms of the mean number of distinct sites visited by a particle $S(t)$. Let S_n be the mean number of distinct sites visited by a particle as a function of the time step number n, and $P_n(\mathbf{r})$ the probability of finding the random walker—initially situated at the origin—in site $\mathbf{r}$ at step n. It is well known that the generating functions $S(z) = \sum_0^\infty z^n S_n$ and $P(\mathbf{r}, z) = \sum_0^\infty z^n P_n(\mathbf{r})$ are related by [25]

$$S(z) = \frac{1}{(1-z)^2 P(\mathbf{0}, z)}. \tag{26}$$

In continuous time Laplace representation, this corresponds to

$$S(u) = \frac{1-\psi(u)}{u} S(z=\psi(u)) = \frac{1}{u}\frac{1}{[1-\psi(u)]P(\mathbf{0}, z=\psi(u))}. \quad (27)$$

Taking into account that $R(\mathbf{r},u) = P(\mathbf{r}, z=\psi(u))$, we obtain

$$R(\mathbf{0},u) = \frac{1}{u}\frac{1}{[1-\psi(u)]S(u)}.$$

Replacing this into Eq. (25), and from Eq. (17), we finally get

$$C(t) = \frac{1}{1+\mathcal{L}^{-1}\{\kappa(u)/u\}} = \frac{1}{1-\frac{\epsilon}{2}C_0+\frac{\epsilon}{2}C_0 S(2t)}. \quad (28)$$

We stress that the factor 2 in the argument of S makes it evident that, as in one dimension [11–13], this solution involves information on the survival probability of a single *pair* of particles. The calculation of $C(t)$ on a square lattice is explicitly worked out in Appendix A.

The function $S(t)$ deserved the study of many authors [26–28]. In particular, using the results of Henyey and Seshadri [27] we verified the following behavior for long times:

$$S(2t) \approx h(b\tau)\frac{\ln(b\tau)}{a\tau}\left[1+\mathcal{O}\left(\tau^{-1}\right)\right], \quad (29)$$

with $\tau = 8Dt = 2\lambda t = 2t/\langle t\rangle$, where $\langle t\rangle = 1/\lambda$ is the mean waiting time between consecutive steps of a single particle, $(a,b) = (\pi,8), (\frac{2\pi}{\sqrt{3}},12)$, and $(\frac{4\pi}{3\sqrt{3}},12)$ for square, triangular, and hexagonal lattices, respectively, and

$$h(b\tau) = \sum_{j=0}^{\infty}\left(-\frac{1}{\ln(b\tau)}\right)^j \frac{\partial^j}{\partial\beta^j}\frac{1}{\Gamma(\beta)}\bigg|_{\beta=1} \quad (30)$$

is a function such that $h(b\tau\to\infty)=1$. However, this asymptotic value is attained very slowly. For example, for $t = 10^5\langle t\rangle$ it represents a 3% correction, whereas at $t = 10^{16}\langle t\rangle$ it still differs from unity by 1%.

IV. THE REACTION RATE

Before presenting simulation results, it is convenient to analyze the kind of function that this approach yields for the reaction rate $\kappa(t)$. As an example, we shall consider hereafter a square infinite lattice, for which Eq. (25) yields (see Appendix A)

$$\kappa(u) = \frac{\epsilon}{2}C_0\left[\frac{2\lambda+u}{u}\frac{1}{\frac{2}{\pi}K(\frac{2\lambda}{2\lambda+u})}-1\right], \quad (31)$$

where $K(z)$ is the complete elliptic integral of the first kind [29]. It is not possible to obtain the exact inverse Laplace transform of $\kappa(u)$. However, from Tauberian theorems [30], we can infer the long and short time behavior of its integral, Eq. (18),

$$\rho(t) \approx \frac{\epsilon}{2}C_0\left[\frac{(1+2\lambda t)}{\frac{2}{\pi}K(\frac{2\lambda t}{1+2\lambda t})}-1\right] \quad \text{for } t\to\infty \text{ or } t\to 0. \quad (32)$$

Remarkably, this expression agrees with the numerical inverse Laplace transform of $\kappa(u)/u$ in the whole time domain, with a maximum error lower than 6% near $t\sim\langle t\rangle$. Furthermore, from the definition of $\kappa(t)$, Eq. (14) or Eq. (21), it is easy to see that $\kappa(t\to 0) = \epsilon\lambda C_0$. For other times, we have verified that taking the derivative of the expression for $\rho(t)$ in Eq. (32) is a good aproximation, which for long times agrees with Tauberian theorems (Karamata's version [31]),

$$\kappa(t) \approx \frac{\epsilon C_0}{2}\frac{1}{\frac{2}{\pi}K(p)}\left\{2\lambda + 1/t[1-E(p)/(1-p^2)]\right\} \quad \text{for } t\to\infty \text{ or } t\to 0, \quad (33)$$

where $p = (2\lambda t)/(1+2\lambda t)$, and $E(p)$ is the complete elliptic integral of the second kind. Near $z=1$, the function $K(z)$ can be approximated as $K(z) \approx \ln(4/\sqrt{1-z^2})$, showing that Eq. (33) tends slowly to the form

$$\kappa(t) \approx \epsilon\pi C_0\frac{\lambda}{\ln[8(2\lambda t)]} = \epsilon C_0\frac{4\pi D}{\ln(64Dt)} \quad (34)$$

(see Fig. 1).

Coming back to Eq. (17), the approximated form for $\rho(t)$ in Eq. (32) yields

$$C(t) \approx \left[1-\frac{\epsilon}{2}C_0+\frac{\epsilon}{2}C_0\frac{(1+2\lambda t)}{\frac{2}{\pi}K(\frac{2\lambda t}{1+2\lambda t})}\right]^{-1} \quad \text{for } t\to\infty \text{ or } t\to 0, \quad (35)$$

for the concentration decay. In particular, for long times, we have

$$C(t) \approx \left[1-\frac{\epsilon}{2}C_0+\frac{\epsilon}{2}C_0\frac{1+\tau}{\frac{2}{\pi}\ln[4(1+\tau)/\sqrt{1+2\tau}]}\right]^{-1} \approx \frac{2}{\pi\epsilon C_0}\frac{\ln(8\tau)}{\tau}, \quad \tau = 1+2\lambda t = 1+8Dt, \quad (36)$$

in agreement with Eqs. (28) and (29). We stress that a detailed comparison between Eq. (36) and simulation results requires the factors of the time variable to be explicitly considered. In fact, the logarithmic function $\ln(ct) = \ln c + \ln t$ makes the values of c and t equally relevant, although they can differ in some orders of magnitude.

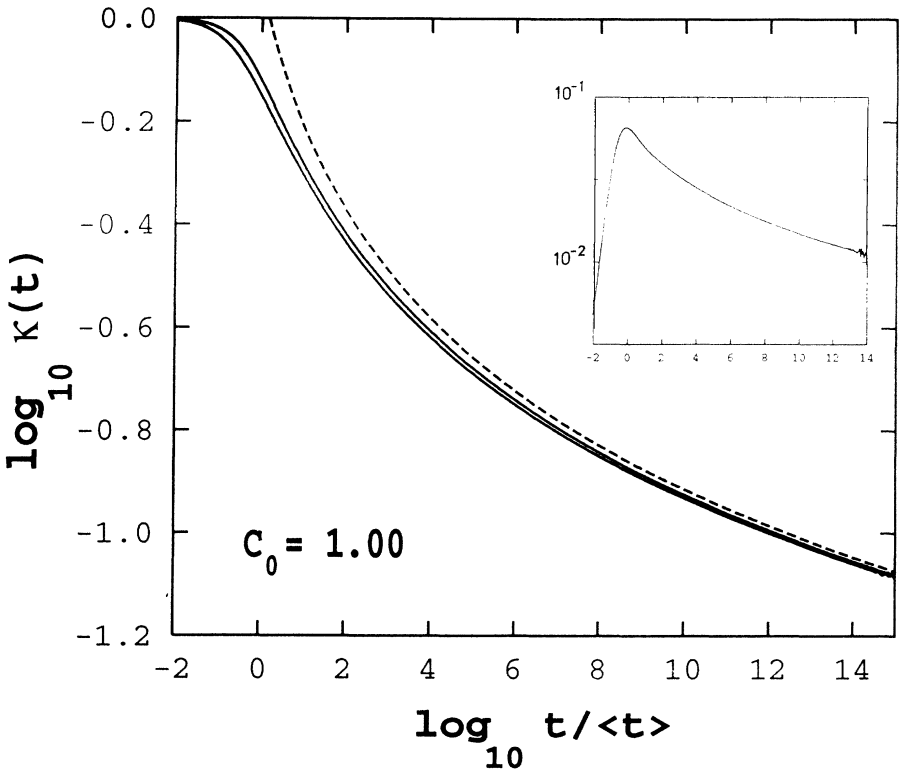

FIG. 1. Logarithmic plot of the rate $\kappa(t)$, for coagulation on the square lattice. The upper full line is the numerical inverse Laplace transform of Eq. (31), whereas the lower full line is the approximated form given by Eq. (33). The dashed line shows the asymptotic form of Eq. (34). Inset: relative difference between full lines, in logarithmic plot, showing that both expressions coincide asymptotically.

V. SIMULATION RESULTS

We have performed numerical simulations of the reaction $A + A \rightarrow A$ on square lattices of unitary lattice spacing. The simulation starts by generating the waiting times for the first step of each particle, from the exponential WTD $\psi(t) = \lambda \exp(-\lambda t)$. Then we pick up the minimum of these $N(0)$ times, say t, and move the corresponding particle to one of their four nearest neighbor sites with equal probability. If the new position had a particle, the incoming particle is rejected, the particle number $N(0)$ is decreased to $N(t) = N(0) - 1$, and the

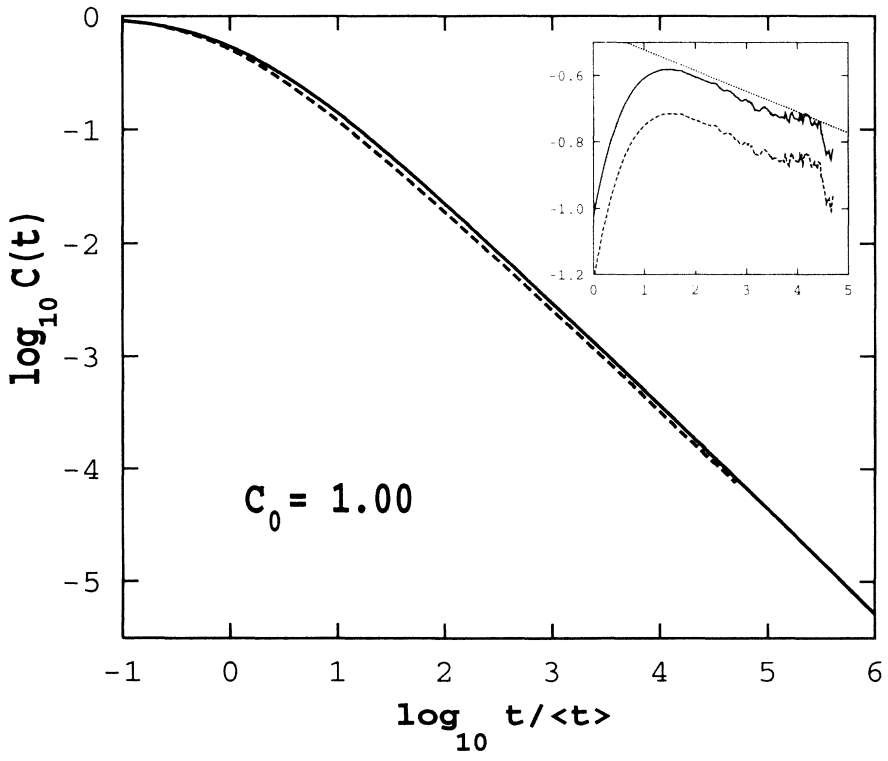

FIG. 2. Decay of the relative concentration $C(t) = N(t)/N(0)$ for coagulation with an initial distribution of one particle per site. The full line is our analytical result. For $t < 10^4\langle t\rangle$ it is calculated as the numerical inverse Laplace transform of Eq. (A3), whereas for $t > 10^4\langle t\rangle$ it is computed from Eqs. (28) and (29). The dashed line represents Monte Carlo simulations on a square 300×300 lattice. Inset: the relative difference between theory and simulations. The full line corresponds to the approximated form Eq. (35), whereas the dashed line corresponds to the numerical inverse Laplace transform, from Eq. (A3). The straight dotted line has slope -0.059.

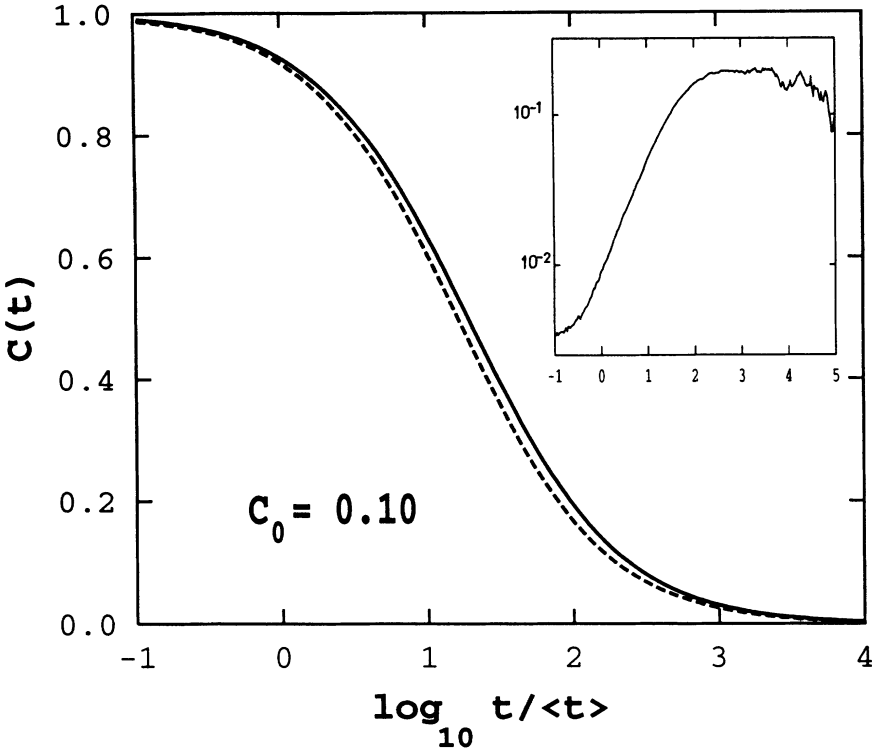

FIG. 3. As in Fig. 2, for an initial concentration $C_0 = 0.1$ on a lattice of 792 × 792 sites.

process is repeated by searching the minimum of the $N(t)$ remaining waiting times. If no particle was in the new position, a new waiting time is generated for the jumping particle, with the same exponential distribution, and the process is repeated.

In Fig. 2 we show the Monte Carlo simulation results over 114 realizations for an initial distribution with one particle per site ($C_0 = 1$), on a 300 × 300 lattice. Here, $\lambda = 0.9$, corresponding to $D = 0.225$. In Figs. 3 and 4 we show simulation results for a random distribution with initial concentration $C_0 = 0.1$ and 0.05, respectively. In Fig. 5 we bring all these curves together, in a log-log plot. In all cases the dashed line corresponds to the simulation result and the full line stands for our

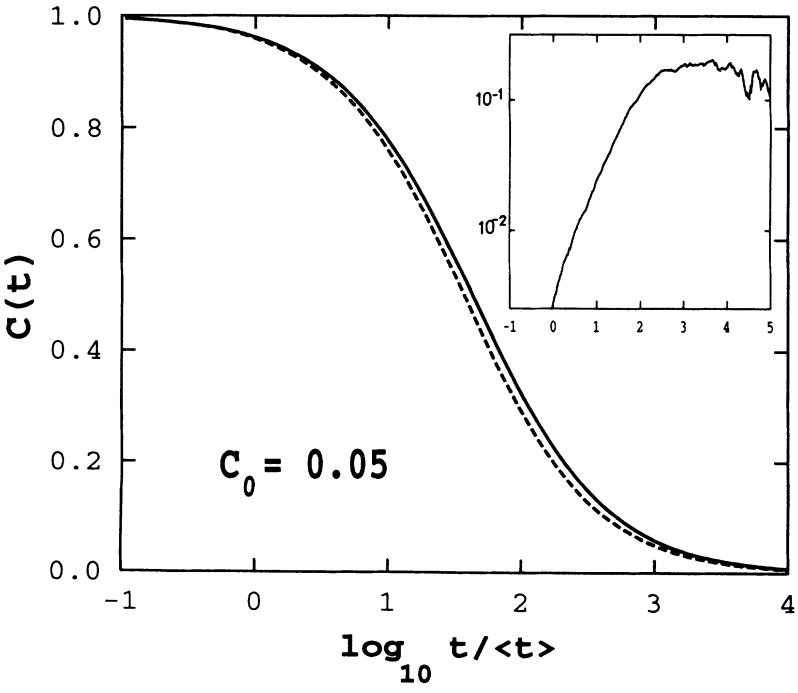

FIG. 4. As in Fig. 2, for an initial concentration $C_0 = 0.05$ on a 1120 × 1120 site lattice.

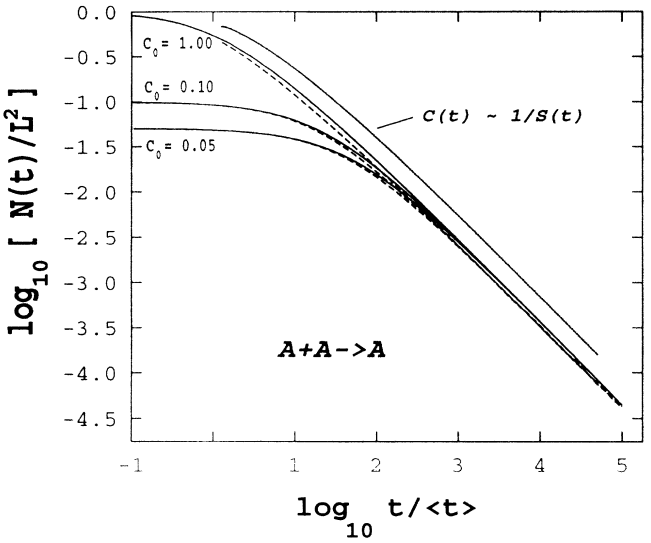

FIG. 5. The same curves as in Figs. 2–4, in a log-log plot. For comparison, the upper line shows the function $C(t) = 1/[1 + C_0 S(t)]$.

analytical prediction, Eq. (35). The inset of each figure shows also, as a log-log plot, the relative difference between simulations, $C^{\mathrm{MC}}(t)$, and theory, Eq. (35), given as $|C(t) - C^{\mathrm{MC}}(t)|/C^{\mathrm{MC}}(t)$. They show that the predicted decay is approached very slowly; for instance, in Fig. 2 it can be seen that this difference decays as slowly as $\sim t^{-0.059}$ (straight line in the inset).

We see that the theory approaches better the simulation results for diluted systems ($C_0 \ll 1$), whereas in all cases it becomes exact for $t \to 0$ and has a systematic excess error during the transient. For $t \to \infty$ it is expected to become also exact. However, this trend is so slow that it is far away from the simulation range, and possibly, from most of the experimental ranges of interest [32].

VI. THE EFFECT OF THE INITIAL PARTICLE DISTRIBUTION

Until now, all the approaches to reaction-diffusion models considered a well defined (nonvanishing) initial particle concentration C_0. What happens, however, if the initial particle distribution on the lattice has a fractal dimension $0 < \gamma < d$? This situation is of interest in the study of formation of domains in the Ising model [33] and for particles in percolating clusters. In this case

$$N(0) \sim L^{\gamma}, \tag{37}$$

where L is the typical size of the system. This means that $C_0 = N(0)/L^d$ would vanish if the lattice were infinitely large. But for all practical cases, one deals with finite size systems, for which the problem is well posed by considering that C_0 depends parametrically on L, with $L < \infty$.

For $d = 1$, it is possible to obtain exactly the particle number decay at all times [34]. The solution shows that the fractal distribution is preserved along the reaction, giving rise to a new asymptotic behavior, $N(t) \sim t^{-\gamma/2}$. For higher-dimensional lattices, scaling arguments [35] provide the general form $N(t) \sim [S(t)]^{-\gamma/2}$. For $d = 2$, this gives $N(t) \sim (t/\ln t)^{-\gamma/2}$, with $0 < \gamma < 2$, whereas for $d = 3$, $N(t) \sim t^{-\gamma/3}$, with $0 < \gamma < 3$.

We can use the present approach in order to test this particle number decay for $d = 2$. We consider first the simple case of particles initially placed on a line, which corresponds to a well defined exponent $\gamma = 1$. Proceeding as in Appendix A for the square lattice, we place the particles along the line $r_1 = 0$. Using the relation

$$\int_0^{\infty} dx\, e^{-x} I_0(xz) \sum_{r \neq 0} I_r(xz) = [1 - 2z]^{-1/2} - 2/\pi K(z)\ ,$$

with $z = \psi(u/2)/2 = \lambda/(2\lambda + u)$, we readily obtain the exact form

$$\kappa(u) = \frac{\epsilon}{2} \sum_{\mathbf{r} \neq \mathbf{0}} F_2(\mathbf{r}, u) = \frac{\epsilon}{2} \left[\frac{\sqrt{2\lambda + u}}{\frac{2}{\pi} u^{1/2} K(\frac{2\lambda}{2\lambda + u})} - 1 \right]. \tag{38}$$

Here, the hypotheses of the suitable Tauberian theorem are satisfied for long times, yielding

$$\rho(t) \approx \frac{\epsilon}{2} \left[\frac{\sqrt{\pi(1 + 2\lambda t)}}{K(\frac{2\lambda t}{1 + 2\lambda t})} - 1 \right] \qquad \text{for } t \to \infty. \tag{39}$$

The relative particle concentration, $C(t) = N(t)/N(0)$, follows from Eq. (17) as

$$\frac{N(t)}{N(0)} = \frac{2}{2 - \epsilon + \epsilon \sqrt{\pi(1 + 2\lambda t)}/K(\frac{2\lambda t}{1 + 2\lambda t})} \approx \frac{\ln(b\tau)}{\epsilon \sqrt{a\tau}}, \tag{40}$$

with $\tau = 1 + 8Dt$, and $(a, b) = (\pi, 8)$. Note that this modifies the above mentioned scaling results, showing that the logarithmic term is not affected by the fractal dimension. This is a peculiar property of the two-dimensional lattice. In Appendix B we prove that this is also the case for $0 < \gamma < 2$,

$$\frac{N(t)}{N(0)} \approx \frac{2^{\gamma/2}\gamma}{\epsilon \Gamma(\gamma/2)} \frac{\ln(b\tau)}{a\tau^{\gamma/2}}, \tag{41}$$

whereas the time-dependent reactivity slows down as [compare with Eq. (34)]

$$\kappa(t) \approx \epsilon \Gamma(\gamma/2) \frac{4\pi D}{(4Dt)^{1-\gamma/2} \ln(64Dt)} \qquad \text{for } t \to \infty. \tag{42}$$

In Fig. 6 we show the simulation for $\gamma = 1$. We started with $N(0) = 5000$ particles on a line of a 5000×5000 lattice, with periodic boundary conditions. The full line corresponds to Eq. (17), after numerical inverse Laplace transform for $\rho(t) = \mathcal{L}^{-1}\{\kappa(u)/u\}$, using Eq. (38). The upper dotted line shows, for comparison, the scaling form $N \sim [\ln(bt)/(at)]^{1/2}$, which is clearly not correct.

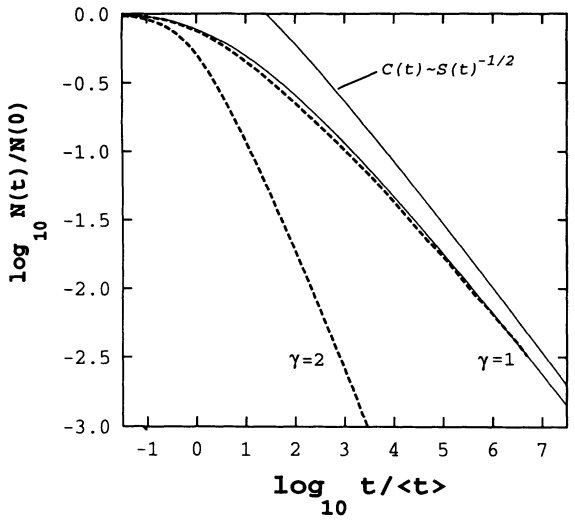

FIG. 6. Particle number decay for $A + A \rightarrow A$ with the particles initially situated on a line. Here, $N(0) = 5000$ and the lattice size is 5000×5000 with periodic boundary conditions. The dotted lines show simulation results. The lower one, shown for comparison, corresponds to a homogeneous initial distribution and coincides with the curve of Fig. 2. The lower full line corresponds to our theory, Eq. (42), whereas the upper full line shows the scaling result $N \sim [S(t)]^{-1/2}$, which is clearly incorrect in this case.

VII. DISCUSSION

In this work we have investigated the particle concentration decay for one species coagulation and annihilation reaction-diffusion models in a two-dimensional lattice. Our approach is essentially based on a scheme in which the initial particle number is preserved, by identifying reaction process as an irreversible particle identity change.

This picture leads to a differential equation, Eq. (13), in which the main ingredients are the overall reaction rate $\kappa(t)$ and the probability of an encounter of two A particles, $\Lambda(t)$. This scheme provides a way to exactly obtain $\kappa(t)$ from CTRW results for the first passage time density of the relative motion of a pair of particles. On the other hand, the probability $\Lambda(t)$ cannot be exactly obtained. Here we approximated it by the square value of the current concentration of A particles, Eq. (15).

This yields a mean field equation, Eq. (16), with a well specified time-dependent reaction rate coefficient $\kappa(t)$, which can be obtained exactly in the Laplace representation, for all integer dimensions. We translated this result in terms of the mean number of distinct sites visited by a single random walker, $S(t)$, obtaining Eq. (28). This equation has the known scaling form, Eq. (3).

Finally, we would emphasize the following remarks on the method introduced here.

(1) It offers an explicit closed expression for the particle number decay along the whole course of the reaction on any two-dimensional lattice. This is exact at short and long times, and the difference with simulation results is mainly due to the approximation in calculating the probability $\Lambda(t)$ and to the fact that the analytical results refer to an infinite lattice, whereas the simulations consider a finite square lattice with periodic boundary conditions. The method is able to distinguish between the very similar decays found in the literature, Eq. (1) and Eq. (2), favoring the first one.

(2) It makes explicit the role of the initial conditions. In particular, for strongly inhomogeneous distributions such as random fractals, the asymptotic behavior becomes, according to Eq. (41),

$$\frac{N(t)}{N(0)} \sim \frac{\ln t}{t^{\gamma/2}},$$

where γ is the fractal dimension.

(3) It offers an alternative path towards a demonstration of the relevance of the mean number of distinct sites visited by a random walk to bimolecular reaction kinetics, in two or more dimensions, as long as the initial particle distribution is homogeneous.

(4) It explicitly shows that, in these reactions, the relevant particle dynamics to be considered is the relative motion of a pair of particles. According to simulations (see Fig. 5), this fact—which was already well established for the one-dimensional case—is essential in the correct description of the concentration decay.

(5) It gives an explicit form for the reaction rate along the whole course of the reaction, Eq. (33) (see Fig. 1), which at long times decays as slowly as $1/\ln(bt)$, confirming in this way the Smoluchowsky ansatz in two dimensions [36]. Moreover, it extends this result for the case of an initial fractal distribution of reactants, for which the reactivity is given by Eq. (42).

(6) These results point out that, in two dimensions, the decay involves logarithmic functions. These cause the asymptotic values to be approached so slowly that one must be able to observe the evolution—experimentally or numerically—over several time decades, in order to verify the analytical predictions.

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APPENDIX A: CONCENTRATION DECAY ON A SQUARE LATTICE

In this Appendix we shall obtain the explicit form of the particle concentration decay for a square lattice. Instead of using the well studied form of $S(t)$, we shall proceed by recasting the expression (22) in the form

$$R(\mathbf{r},u)=\frac{1}{\pi^2}\int_0^\infty dx\; e^{-x}\int_0^\pi dk_1\int_0^\pi dk_2\cos(r_1k_1)\cos(r_2k_2)\exp[x\psi(u)\omega(k_1,k_2)].$$

In particular, for the square lattice, we have

$$\begin{aligned}R(\mathbf{r},u)=&\frac{1}{\pi^2}\int_0^\infty dx\; e^{-x}\int_0^\pi dk_1\cos(r_1k_1)\\&\times\exp\left[\frac{x}{2}\psi(u/2)\cos k_1\right]\\&\times\int_0^\pi dk_2\cos(r_2k_2)\\&\times\exp\left[\frac{x}{2}\psi(u/2)\cos k_2\right],\end{aligned}$$

which can be written in terms of the hyperbolic Bessel functions as

$$R(\mathbf{r},u)=\int_0^\infty dx\; e^{-x}I_{r_1}\left(\frac{x}{2}\psi(u/2)\right)I_{r_2}\left(\frac{x}{2}\psi(u/2)\right).$$

Taking into account Eq. (24), this renders for F_2,

$$F_2(\mathbf{r},u)=\frac{\int_0^\infty dx\; e^{-x}I_{r_1}(x\psi(u/2)/2)I_{r_2}(x\psi(u/2)/2)}{\int_0^\infty dx\; e^{-x}I_0^2(x\psi(u/2)/2)}.\tag{A1}$$

With the identity $\sum_{(r_1,r_2)\neq(0,0)}I_{r_1}(y)I_{r_2}(y)=e^{2y}-I_0^2(y)$, Eq. (21) yields

$$\kappa(u)=\frac{\epsilon}{2}C_0\left\{\frac{1}{[1-\psi(u/2)]\frac{2}{\pi}K(\psi(u/2))}-1\right\},\tag{A2}$$

where $K(z)$ is the complete elliptic integral of the first kind [29] and C_0 is the initial concentration. Finally, from Eq. (17) we get

$$\begin{aligned}C(t)=&\frac{N(t)}{N(0)}\\=&\left[1-\frac{\epsilon}{2}C_0+\frac{\epsilon}{2}C_0\mathcal{L}^{-1}\left\{\frac{1}{u^2}\frac{2\lambda+u}{(2/\pi)K(\frac{2\lambda}{2\lambda+u})}\right\}\right]^{-1}.\end{aligned}\tag{A3}$$

APPENDIX B: CONCENTRATION DECAY FOR A FRACTAL INITIAL DISTRIBUTION

In order to derive Eq. (41) for $0<\gamma<2$ on a square lattice, we first recast $F_2(\mathbf{r},u)$ as

$$\begin{aligned}F_2(\mathbf{r},u)=&F(\mathbf{r},u/2)\\=&\frac{(u+2\lambda)}{\frac{2}{\pi}K(2\lambda/(2\lambda+u))}\\&\times\int_0^\infty dt\; e^{-(u+2\lambda)t}\left[I_{r_1}(\lambda t)I_{r_2}(\lambda t)\right],\end{aligned}\tag{B1}$$

where $\mathbf{r}=(r_1,r_2)\neq(0,0)$. The overall reaction rate is

$$\kappa(t)=\frac{\epsilon}{2}\sum_{\mathbf{r}\neq\mathbf{0}}F_2(\mathbf{r},t),\tag{B2}$$

where the sum runs over all the initially occupied sites. For a fractal initial particle distribution, the number of initially occupied sites within a sphere of radius $r=\sqrt{r_1^2+r_2^2}$ centered on a typical particle grows as $r^{\gamma-1}$ [cf. Eq. (37)]. In polar coordinates, this sum can be calculated as

$$\begin{aligned}&\sum_{r>0}r^{\gamma-1}I_{r_1}(\lambda t)I_{r_2}(\lambda t)\\&=\int_0^{2\pi}d\theta\int_0^\infty dr r^{\gamma-1}I_{r\cos\theta}(\lambda t)I_{r\sin\theta}(\lambda t).\end{aligned}\tag{B3}$$

The hyperbolic Bessel functions admit the following approximation for large argument [29]:

$$I_\nu(x)\cong\frac{e^x}{\sqrt{2\pi x}}\left(1-\frac{1}{x}\right)^{\nu^2-\frac{1}{8}},\tag{B4}$$

which yields

$$\begin{aligned}\sum_{r>0}r^{\gamma-1}I_{r_1}(\lambda t)I_{r_2}(\lambda t)&=\frac{e^{2\lambda t}}{\lambda t}[1-1/(\lambda t)]^{-1/4}\int_0^\infty dr\; r^{\gamma-1}\left(1-\frac{1}{\lambda t}\right)^{r^2/2}\\&=\Gamma(\gamma/2)\frac{e^{\lambda t}}{2^{1-\gamma/2}\lambda t}[1-1/(\lambda t)]^{-1/4}\left\{\ln\left[\frac{1}{1-1/(\lambda t)}\right]\right\}^{-\gamma/2}\approx\Gamma(\gamma/2)e^{2\lambda t}(2\lambda t)^{-1+\gamma/2}.\end{aligned}$$

In this way we find

$$\begin{aligned}\kappa(u\sim0)=&\frac{\epsilon}{2}\Gamma(\gamma/2)\frac{(u+2\lambda)}{\frac{2}{\pi}K(2\lambda/(2\lambda+u))}\\&\times\int_0^\infty dt\; e^{-ut}(2\lambda t)^{\gamma/2-1}.\end{aligned}$$

We must keep in mind that this holds for large t, as it gives information only for small u. The leading term is

$$\kappa(u)\approx\frac{\epsilon}{2}\Gamma^2(\gamma/2)\frac{\pi(u/\lambda)^{-\gamma/2}}{2^{1-\gamma/2}K\left(\frac{2\lambda}{2\lambda+u}\right)},\tag{B5}$$

implying that, for long times,

$$\rho(t)=\frac{\epsilon}{2}\frac{\Gamma(\gamma/2)}{\gamma}\frac{\pi(2\lambda t)^{\gamma/2}}{K(\frac{2\lambda t}{2\lambda t+1})}\approx\frac{\epsilon}{2}\frac{\Gamma(\gamma/2)}{(\gamma/2)}\frac{\pi\tau^{\gamma/2}}{\ln(8\tau)},\tag{B6}$$

with $\tau=2\lambda t=8Dt$. Note that this coincides exactly with Eq. (32) when $\gamma\to2$, corresponding in this limit to a homogeneous (two-dimensional) initial distribution with concentration $C_0=1$.

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