

Fluctuation statistics in the diffusion-limited $A + B \rightarrow 0$ reaction

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We study the diffusion-limited reaction $A + B \rightarrow 0$ analytically by means of fluctuation statistics. Here we consider both the case of equal ($A_0 = B_0$) and that of unequal ($A_0 < B_0$) numbers of reacting particles. We show that the obtained analytical results are in good agreement with computer simulations, in which we focus on reactions in one and two dimensions. Furthermore, as expected from our analytical development, the simulations for different initial concentrations coincide when properly rescaled.

During the past several years the diffusion-limited $A + B \rightarrow 0$ reaction, where particles move diffusively and react on contact, has encountered much interest. Thus, in solid-state physics it models the recombination of electrons and holes or the annihilation of (radiation-induced) defects. Let $\rho_A(t)$ denote the time-dependent concentration of the A particles [and correspondingly $\rho_B(t)$ for the B particles]. For an initially equal number of A and of B particles, which are randomly situated in space, one has asymptotically¹⁻⁵

$$\rho_A(t) \sim t^{-d/4} \quad (d < 4) \quad (1)$$

where d denotes the spatial dimension. Note that the classical kinetic scheme⁵ predicts only the time dependence $\rho_A(t) \sim t^{-1}$. The behavior of Eq. (1) is due to the fact that in the course of the reaction, local fluctuations in the initial distribution of reactants lead to the formation of clusters of like particles. As only particles at the border of such clusters are prone to react, the overall reaction rate is slowed down.

What happens, however, if one species, say A , is in the minority? For this Kang and Redner³ advanced the asymptotic form

$$\rho_A(t) \sim \exp\{-\text{const} \times [\sqrt{\rho_B(0)} - \sqrt{\rho_A(0)}] t^{d/4}\}, \quad (2)$$

based on the following argument: In the $\rho_A(0) = \rho_B(0)$ case, Eq. (1) may be derived from the formal kinetic equation

$$\frac{d}{dt} \rho_A(t) = -k(t) \rho_A(t) \rho_B(t), \quad (3)$$

when one sets $k(t) \sim t^{d/4-1}$. With this reaction rate the solution of Eq. (3) in the case where $\rho_A(0) < \rho_B(0)$ is Eq. (2). Furthermore, the analysis by Kang and Redner showed that Eq. (2) agrees quite well with computer simulations in one and two dimensions.

On the other hand, however, as also discussed in Ref. 3, the use of Eq. (2) becomes problematic in dimensions higher than two. Thus Eq. (2) predicts a decay which is faster than that found for trapping, i.e., for the $A + B \rightarrow B$ reaction, where the A particles are mobile

and the B particles immobile. Asymptotically the decay due to trapping follows the law^{6,7}

$$\rho_A(t) \sim \exp(-\text{const} \times t^{d/(d+2)}). \quad (4)$$

Thus, in the $A + B \rightarrow 0$ reaction with immobile B particles, the concentration of A particles should not decay faster than Eq. (4). In a recent paper, Bramson and Lebowitz⁸ argued that in the case where $\rho_A(0) < \rho_B(0)$, Eq. (4) should also hold for the $A + B \rightarrow 0$ reaction, if the B particles are fixed. In the other case (B mobile), they derived an asymptotic form similar to that of the target problem, i.e., the $A + B \rightarrow B$ reaction with fixed A particles. In this case one has

$$\rho_A(t) \sim \begin{cases} \exp(-\text{const} \times \sqrt{t}) & (d=1) \\ \exp(-\text{const} \times t / \ln t) & (d=2) \\ \exp(-\text{const} \times t) & (d \geq 3). \end{cases} \quad (5)$$

This point makes it clear that the determination of the correct asymptotic decay for the diffusion-limited $A + B \rightarrow 0$ reaction for an unequal number of A and B particles is still an open question.

In this paper we will demonstrate that the behavior of the $A + B \rightarrow 0$ reaction is amenable to a statistical approach both for $\rho_A(0) = \rho_B(0)$ and for $\rho_A(0) < \rho_B(0)$. Our analysis predicts forms which for $\rho_A(0) < \rho_B(0)$ differ from Eqs. (2) and (5), but which (surprisingly at first sight) also show very good agreement with the computer simulations over several orders of magnitude in decay. It is certainly astonishing to find that the same set of data can be fitted to different decay forms, facts which show that one must be very careful when drawing conclusions about asymptotical decay forms from computer simulations.

We start by discussing the basic ideas, which enter in the heuristic argument leading to Eq. (1) (Refs. 1 and 2). One envisages that during time t a diffusing particle moves in a volume V which is of the order of l_D^d , where $l_D = (Dt)^{1/2}$ is the diffusion length and D is the diffusion coefficient. One then computes the number of surviving particles at time t as being the difference in the number of

particles of opposite kind in volumes of size $V \sim (Dt)^{d/2}$. Evidently, the underlying idea is that during time t in each volume V a complete, pairwise annihilation of particles takes place. As we will show (and was already pointed out in Refs. 1 and 2), for an equal number of A and B particles in the total reaction volume Ω , this procedure yields Eq. (1); this result is due mainly to fluctuations in the actual number of particles in the subregions V of Ω .¹⁻³ In this paper we expand this argument based on fluctuation statistics and analyze also the case of unequal total numbers of A and of B particles.

We thus consider a volume V consisting of N sites on which we distribute the A and B particles randomly and independently, according to their respective probabilities p_A and p_B ($p_A \neq 0 \neq p_B$ and $p_A \neq 1 \neq p_B$). For large N the probability $P_\alpha(n)$ for finding n particles of type α ($\alpha = A$ or B) in V is well approximated by a Gaussian:

$$P_\alpha(n) = \frac{1}{\sqrt{2\pi}\sigma_\alpha} \exp\left[-\frac{(n-p_\alpha N)^2}{2\sigma_\alpha^2}\right] \quad (\alpha = A, B) \quad (6)$$

where the variance σ_α^2 is given by $\sigma_\alpha^2 = p_\alpha N$.

Let m denote the difference in the number of particles: $m = n_A - n_B$. Then the probability $P(m)$ that the particle difference equals m is given by

$$P(m) = \sum_i \sum_j P_A(i) P_B(j) \delta_{i-j, m}, \quad (7)$$

where $\delta_{i,j}$ is the Kronecker δ . In a continuum version Eq. (7) reads as follows:

$$P(m) = \int_{-\infty}^{+\infty} P_A(x+m) P_B(x) dx. \quad (8)$$

Inserting Eq. (6) into Eq. (8), one obtains for the particle difference m again a Gaussian:

$$P(m) = \frac{1}{\sqrt{2\pi}\sigma_m} \exp\left[-\frac{(m-\bar{m})^2}{2\sigma_m^2}\right]. \quad (9)$$

$P(m)$ is centered at $\bar{m} = (p_A - p_B)N$ and has the variance $\sigma_m^2 = \sigma_A^2 + \sigma_B^2 = wN$, where $w = p_A + p_B$.

In a slightly different model (which closely corresponds to our computer simulations to be presented later), double occupancy of sites is forbidden. Hence each site is either empty or occupied by only one A or one B particle. The corresponding probabilities p_A and p_B obey now $p_A + p_B \leq 1$. Here the correct probability distribution $\mathcal{P}(n_A, n_B)$ for finding initially n_A A particles and n_B B particles on the N lattice sites is the trinomial distribution⁹

$$\mathcal{P}(n_A, n_B) = \frac{N!}{n_A! n_B! (N - n_A - n_B)!} \times p_A^{n_A} p_B^{n_B} (1 - p_A - p_B)^{N - n_A - n_B}. \quad (10)$$

As found for the binomial distribution, also the trinomial one may in general be approximated by a Gaussian distribution in two variables when N is large.⁹ Then the probability distribution $P(m)$ of the difference $m = n_A - n_B$,

$$P(m) = \sum_i \sum_j \mathcal{P}(i, j) \delta_{i-j, m}, \quad (11)$$

is again a Gaussian with mean $\bar{m} = (p_A - p_B)N$ and variance $\sigma_m^2 = (p_A + p_B - \Delta^2)N$. One recovers the form of Eq. (9), now with $w = p_A + p_B - \Delta^2$, where $\Delta = p_B - p_A$. Note that w reduces to $p_A + p_B$ for $\Delta^2 \ll p_A + p_B$.

Under reaction conditions the A and B particles will annihilate each other, so that in the long run only particles of the majority species survive. In light of the model outlined above, it is now straightforward to determine $M(N)$, the average number of A particles surviving the annihilation process in the volume V . One has

$$M(N) = \sum_{m>0} m P(m) \approx \int_0^\infty m P(m) dm. \quad (12)$$

For a Gaussian distribution $P(m)$ like that of Eq. (9) the average $M(N)$ is

$$\begin{aligned} M(N) &= \frac{\sigma_m}{\sqrt{2\pi}} \exp\left[-\frac{\bar{m}^2}{2\sigma_m^2}\right] + \frac{\bar{m}}{2} \operatorname{erfc}\left[-\frac{\bar{m}}{\sqrt{2}\sigma_m}\right] \\ &= \frac{\sigma_m}{\sqrt{2\pi}} e^{-z^2} [1 - \sqrt{\pi} z e^{z^2} \operatorname{erfc}(z)], \end{aligned} \quad (13)$$

where we set $z = -\bar{m}/(\sqrt{2}\sigma_m) = \Delta(N/2w)^{1/2}$, and $\operatorname{erfc}(z)$ is the complementary error function, Eq. (7.1.2) of Ref. 10.

Finally, the average concentration $\rho_A(N)$ of surviving A particles is

$$\rho_A(N) = \frac{M(N)}{N} = \frac{\sigma_m}{\sqrt{2\pi}N} e^{-z^2} [1 - \sqrt{\pi} z e^{z^2} \operatorname{erfc}(z)]. \quad (14)$$

For $p_A \neq p_B$ we now divide both sides of Eq. (14) by $\Delta = p_B - p_A$ and obtain

$$\frac{\rho_A(N)}{\Delta} \equiv F(z) = \frac{1}{2\sqrt{\pi}z} e^{-z^2} [1 - \sqrt{\pi} z e^{z^2} \operatorname{erfc}(z)], \quad (15)$$

where $\bar{m} = (p_A - p_B)N$.

This result is very interesting, since it states that for $\Delta \neq 0$ the average concentration of A particles surviving the annihilation reaction $A + B \rightarrow 0$ on N sites is only a function of Δ and z . This means that plotting $\rho_A(N)/\Delta$ versus z should yield the same curve for all initial concentrations. We will later demonstrate through simulation calculations that this scaling relation indeed holds.

Now let us consider some special cases of Eqs. (14) and (15). In the case of equal initial concentrations, $p_A = p_B = p$, one has $\Delta = 0$ and hence also $z = 0$. With $\sigma_m = wN$ one obtains from Eq. (14)

$$\rho_A(N) = \sqrt{w/2\pi N}. \quad (16)$$

As stated above, for diffusing particles $N \sim (Dt)^{d/2}$. Equation (16) then leads to the well-known decay law $\rho_A(t) \sim t^{-d/4}$ (with $d < 4$), Eq. (1).

In the case of $p_A < p_B$, one has $z > 0$. Consider now the two limiting cases $z \ll 1$ and $z \gg 1$ (which means $N \ll N_0$ or $N \gg N_0$, respectively, with $N_0 = 2w/\Delta^2$).

For $z \ll 1$ we get from Eq. (14)

$$F(z) \sim \frac{1}{2\sqrt{\pi}z}, \quad (17)$$

from which we recover for $\rho_A(N)$ the asymptotic form given in Eq. (16).

For $z \gg 1$ we make use of the asymptotic series, Eq. (7.1.23) of Ref. 10:

$$\sqrt{\pi}ze^{z^2}\operatorname{erfc}(z) \sim 1 - \frac{1}{2z^2} + \dots \quad (18)$$

Thus we obtain

$$F(z) \sim \frac{1}{4\sqrt{\pi}z^3} e^{-z^2}, \quad (19)$$

which means

$$\rho_A(N) \sim \frac{\Delta}{4\sqrt{\pi}} \left[\frac{\Delta^2}{2w} N \right]^{-3/2} \exp \left[-\frac{\Delta^2}{2w} N \right]. \quad (20)$$

Therefore we expect a crossover from an algebraic decay for $z \ll 1$ ($N \ll N_0$) to an exponential form for $z \gg 1$ ($N \gg N_0$). The dependence of ρ_A on time will be given later, when the simulation results are discussed.

In the case $p_A > p_B$ one has $z < 0$ and for $z \ll -1$ ($N \gg N_0$) one obtains from Eq. (15) $F(z) \approx -1$, which implies that

$$\rho_A(N) \approx p_A - p_B, \quad (21)$$

i.e., the number of A particles is constant at long times.

We now turn our attention to computer simulations and present results for the diffusion-limited $A + B \rightarrow 0$ reaction, where the B particles are kept fixed and only the A (minority) particles move (for the situation when the B particles are mobile *vide infra*). In our simulations each site is initially occupied by an A particle (probability p_A) or by a B particle (probability p_B), with $p_A + p_B \leq 1$ (trinomial distribution). The underlying lattices are either linear chains, consisting of 10^5 – 10^6 sites, or two-dimensional 1000×1000 square lattices. In both cases periodic boundary conditions are implemented. At each step of the process an A particle is chosen at random and is moved to one of its neighboring lattice sites. Whenever an A and a B particle meet, they annihilate at once. The time increment for each step is equal to the reciprocal of the actual number of A particles. Thus during a time unit each A particle performs on the average one step.

In order to compare the simulation outcomes to the analytical expressions given in terms of the volume V , we have to relate V to the time t . As already mentioned, a heuristic argument relates V to $l_D^d = (Dt)^{d/2}$, with a proportionality constant to be determined. In our simulations the A particles perform a symmetric random walk. Therefore we can use some results from the theory of random walks.¹¹ Thus, in one dimension (1D) the volume V visited by a random walker is equal to the span of the random walk, which in 1D coincides with the number of distinct sites visited by the walker. The average of the last quantity is denoted by S_n , where n is the number of steps. In one dimension one has exactly^{11,12}

$$S_n = \sqrt{(8/\pi)n}. \quad (22)$$

Since in the simulations each A particle performs on the average one step per time unit, one finds for the average

volume V visited during time t the expression $V = N = (8t/\pi)^{1/2}$ in 1D. With this substitution Eq. (20) now becomes

$$\rho_A(t) \sim \frac{\Delta}{4\sqrt{\pi}} \left[\frac{\Delta^2}{2w} \right]^{-3/2} \left[\frac{8t}{\pi} \right]^{-3/4} \times \exp \left[-\frac{\Delta^2}{2w} \left[\frac{8t}{\pi} \right]^{1/2} \right]. \quad (23)$$

Apart from a somewhat different prefactor, this decay form corresponds to that of Bramson and Lebowitz,⁸ Eq. (5), in one dimension.

In a similar fashion we assume that for a two-dimensional random walk V is proportional to $l_D^2 = Dt$, with a proportionality constant to be determined. From our simulations we found that a very good fit to the data is provided by the simple form $N = t$ in 2D. Thus, in this case the asymptotic decay form, as given in Eq. (20), differs from that of Bramson and Lebowitz, Eq. (5), for $d = 2$.

We have performed simulations for various initial concentrations. In Fig. 1 we compare the outcomes of some of these simulations in $d = 1$ (solid lines) to the corresponding results of the fluctuation statistics (crosses), obtained from Eqs. (14) and (15) by taking, according to Eq. (22), $N = V = (8t/\pi)^{1/2}$. Firstly, for equal initial concentrations ($p_A = p_B = 0.4$, curve *a*) we recover the well-known $t^{-1/4}$ law, a fact in perfect agreement with Eq. (16). Furthermore, also for the case $p_A < p_B$ (curves *b*–*d*) our theory based on fluctuation statistics agrees very well with the simulation results. Thus, just by using the correct initial concentrations (and without any parameters) the agreement between simulations and analytical results, Eq. (14), is very good. The slight deviations in

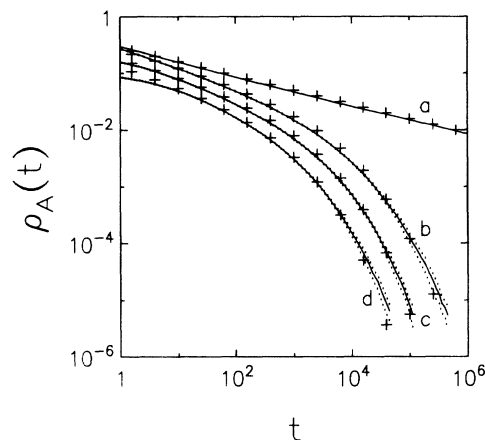


FIG. 1. Results of simulations in 1D (solid lines) and the corresponding analytical curves (crosses), stemming from Eq. (14) with $N = (8t/\pi)^{1/2}$ and $w = p_A + p_B - \Delta^2$. The initial concentrations are *a*, $p_A = p_B = 0.4$; *b*, $p_A = 0.4$ and $p_B = 0.5$; *c*, $p_A = 0.2$ and $p_B = 0.3$; and *d*, $p_A = 0.1$ and $p_B = 0.2$, respectively. The linear chain consisted of 10^5 sites for curve *a* and 10^6 sites for curves *b*–*d*. Each of the curves *b*–*d* was averaged over ten realizations of the reaction. The dotted lines indicate the standard deviation of the simulation results.

the small- t regime are due to the discreteness of the lattice and to the fact that the Gaussian approximation for $P(m)$ is valid only for large N .

A further stringent test of our analytical approach is provided by the scaling law, Eq. (15). In Fig. 2 we therefore rescaled the simulation results, curves $b-d$ of Fig. 1, and plotted $\rho_A(t)/\Delta$ versus $z = \Delta(8t/\pi)^{1/4}/(2w)^{1/2}$. The result is that (after an initial regime) all curves fall together, a fact which demonstrates the scaling behavior. Moreover, Fig. 2 shows that our analytical expression, the function $F(z)$, describes very well the simulated decay over 4 orders of magnitude. In Fig. 2 we have indicated the function $F(z)$ by a dashed line. The dotted line is the asymptotic form of $F(z)$ for $z \gg 1$ [Eq. (19)]. Note that only for $F(z) < 10^{-3}$ does Eq. (19) approximate $F(z)$ reasonably well.

The same is true for simulations in 2D, which are displayed in Fig. 3. As already mentioned, here $N=V=t$ provides a very good fit. Curve a of Fig. 3 indicates the results for equal initial concentrations, $p_A=p_B=0.5$, whereas curve b corresponds to $p_A=0.4$ and $p_B=0.6$. The agreement between the theory based on fluctuation statistics and simulation is again very good.

So we see that our theoretical approach based on fluctuation statistics describes very well the simulated kinetics of the $A+B \rightarrow 0$ reaction both in 1D and 2D over 4 orders of magnitude in concentration decay.

Surprisingly, the simulations for $p_A < p_B$ presented in Figs. 1 and 3 also fit quite well the behavior by Kang and Redner [see Eq. (2)]. This fact shows that one must proceed very carefully when trying to determine asymptotic dependencies from computer-simulation data.

We are aware of the fact that, when the B particles are immobile, our theory based on fluctuation statistics does not hold asymptotically. This can be seen by noticing that with $N \sim t^{d/2}$ the theory predicts an asymptotic decay which is faster than that of the $A+B \rightarrow B$ trapping reaction. [A similar problem arises with Eq. (2) in dimensions $d > 2$, as mentioned above.³] So we must conclude that, although Eq. (14) provides a reasonable approxima-

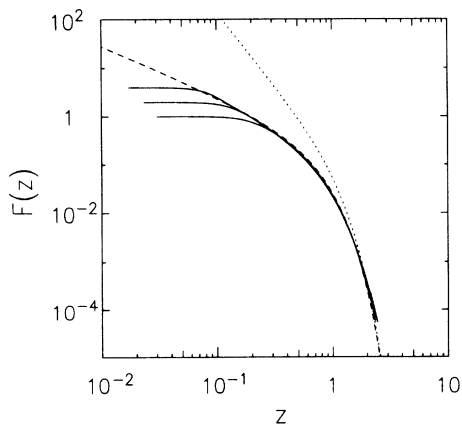


FIG. 2. Curves $b-d$ of Fig. 1 (solid lines), rescaled with respect to $z = \Delta(8t/\pi)^{1/4}/(2w)^{1/2}$ (see text). The dashed line indicates $F(z)$, Eq. (15), and the dotted line is the asymptotic form of $F(z)$ for $z \gg 1$, Eq. (19).

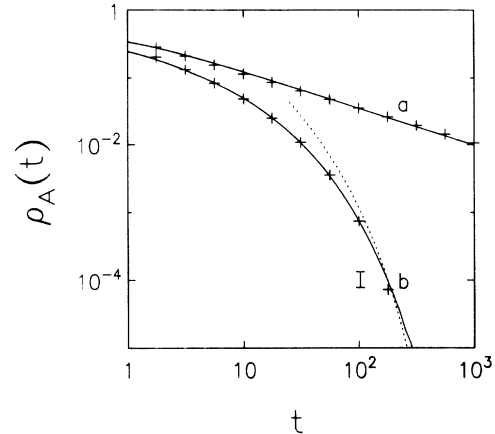


FIG. 3. Concentration decay according to computer simulations in 2D (solid curves) and the corresponding analytical expressions, Eq. (14) with $N=t$, denoted by crosses. The initial conditions are a , $p_A=p_B=0.5$ and b , $p_A=0.4$ and $p_B=0.6$. The dotted line indicates the asymptotic form, Eq. (20), corresponding to curve b . The error bars indicate the standard deviation of the simulation curve b . In order to render them well visible (since the deviations are very small) we shifted the error bars horizontally.

tion over the experimentally relevant part of the decay process, it may not always lead to a correct asymptotic form.

In the long-time regime the picture of fluctuation kinetics may be complemented by features which follow some ideas of Ref. 13. For B immobile and $p_A < p_B$ at very large times one finds only single A particles (or small clusters of A particles) in large holes among the fixed B particles, holes which have been created during the earlier stages of the reaction. At this point in time the A clusters are well separated from each other, and the situation is similar to that encountered for the $A+B \rightarrow B$ trapping reaction, but with a different distribution of hole sizes.

Let us consider this extension of the model for the 1D case. We have already calculated the average number $M(N)$ of A particles surviving the annihilation reaction on N sites. As shown, for the description of the decay over 4 orders of magnitude, identifying N with the average span of the random walkers works very well. At very late stages of the reaction, however, when the A particles move in large holes between the immobile B particles, the distribution of holes (or, for that matter, the span of each walker) is important. Fortunately, in 1D the distribution $P_n(s)$ of the span s (which in 1D is identical to the number of visited sites) of a n -step random walk is known. For $n \gg 1$ one has asymptotically¹¹

$$P_n(s) = \frac{8n}{s^3} \sum_{k=0}^{\infty} \left[\frac{n\pi^2(2k+1)^2}{s^2} - 1 \right] \times \exp \left[-\frac{n\pi^2(2k+1)^2}{2s^2} \right]. \quad (24)$$

Instead of dividing the whole reaction volume Ω into

smaller equally sized volumes V , we now divide Ω into parts of different sizes s which are distributed according to Eq. (24). For each of these volumes of size s , Eq. (14) holds with $N=s$. For s continuous, the average concentration $\bar{\rho}_A(n)$ is given by

$$\bar{\rho}_A(n) = \int_0^\infty \rho_A(s) P_n(s) ds. \quad (25)$$

As $\rho_A(N)$ decays exponentially for large N , the main contribution to the integral in Eq. (25) comes from the small- s region, where the sum in Eq. (24) can be approximated by its first term ($k=0$).¹³ Saddle-point integration of Eq. (25) then yields the asymptotic result

$$\bar{\rho}_A(n) = \sqrt{8/3} \frac{\Delta}{\pi^2} \exp \left[-\frac{3}{2} \left(\frac{\Delta^4 \pi^2}{4w^2} n \right)^{1/3} \right]. \quad (26)$$

Thus for large times we expect the simulations to follow Eq. (26), which has the structure of Eq. (4), rather than Eq. (14), with $N=S_n$. In general, we expect Eq. (4) to provide the correct asymptotic decay form for the diffusion-limited $A+B \rightarrow 0$ reaction in d dimensions for fixed B particles; we hasten to note that (as usual for the trapping problem, see Ref. 5) this asymptotic regime may be well outside the range of experimental interest.

In Fig. 4 we present the results of an extensive simulation (solid curve), where we started with 10^7 A and 2×10^7 B particles on a linear chain with 10^8 sites and averaged over four realizations of the reaction. Thus we are able to observe about six decades in the concentration decay. The dashed line is the analytical curve corresponding to the decay based on fluctuation statistics, Eq. (14) with $N=(8t/\pi)^{1/2}$, whereas the dotted line results from eq. (26). This figure shows that during the early stages of the reaction the simulations are well described by simple fluctuation statistics, whereas at later times the simulation curve approaches more and more the behavior of Eq. (26).

Here we note that when both types of particles move the decay follows an asymptotic behavior which differs from the results presented so far. This feature is reminiscent of the $A+B \rightarrow B$ reaction, where one encounters different kinetics for the trapping problem, in which only the A particles move, and for the target problem, where only the B particles move.⁵ Thus, when in the $A+B \rightarrow 0$ reaction the B particles also move, the concentration decay proceeds faster, and its asymptotic form differs from

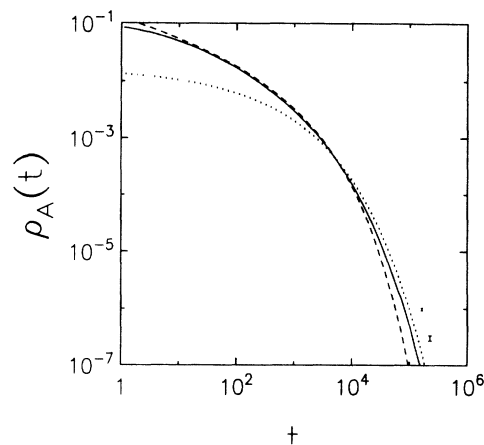


FIG. 4. Results of the simulation of the $A+B \rightarrow 0$ reaction (solid curve) on a linear chain with 10^8 sites, averaged over four realizations with initial concentrations $p_A=0.1$ and $p_B=0.2$. The error bars again indicate the standard deviation of the simulations and are shifted horizontally. The dashed line represents Eq. (14), whereas the dotted line results from Eq. (26).

that found for immobile B particles. Moreover, for mobile B the asymptotic forms seem to be the same, regardless of whether the minority species (A) moves or is kept fixed; only the time scale changes. These features, however, will be discussed in detail elsewhere.

Summarizing, the concentration decay for the diffusion-limited $A+B \rightarrow 0$ reaction, where the majority particles (B) are at rest, is (at early stages of the reaction) well described by a theory based on simple fluctuation statistics, whereas for longer times a crossover to the asymptotic form $\rho_A(t) \propto \exp(-\text{const} \times t^{d/(d+2)})$ is to be expected; here we have demonstrated that this form is indeed well obeyed in one dimension.

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