

Fluctuation-Dominated Kinetics in the $A + B \rightarrow 0$ Reaction Between Immobile Particles

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We consider the accumulation of immobile particles landing on a one-dimensional lattice and annihilating via the $A + B \rightarrow 0$ bimolecular reaction. Here we focus on short-range interactions with cutoff. We investigate through computer simulations both the kinetics of the particles' accumulation and also their spatial distribution. The relation between the exponents describing the growth of the particles' concentration and the correlation length of their distribution shows that the kinetics of accumulation is fluctuation-dominated.

KEY WORDS: $A + B \rightarrow 0$; fluctuation-dominated kinetics; immobile particles; black-sphere model; interactions with cutoff.

1. INTRODUCTION

The reaction $A + B \rightarrow 0$ has been investigated extensively in recent years following pioneering work^(1,2) which showed that in the diffusion-controlled regime the behavior of this reaction does not obey the classical kinetic scheme. This very basic bimolecular reaction has been analyzed under several aspects, i.e., for stoichiometric and unstoichiometric initial conditions, for equal and for unequal diffusion coefficients, for correlated and for uncorrelated initial distributions of reactants, under the influence of external stirring, etc.⁽³⁻²³⁾ It turns out that the reaction's kinetics often depends on such effects and that overall time development is in many cases fluctuation-dominated.

In the last few years situations under a steady inflow of reactants have attracted much interest. The salient feature here is that under certain condi-

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tions the reaction never reaches a steady state, in contrast to the classical kinetics predictions, so that an ongoing, steady accumulation of particles takes place.^(9,10,14-16)

In the case of a steady inflow of particles, only the diffusion-controlled reaction was explicitly studied. Paralleling our investigations in refs. 24-26, we shall deal here with reactions between immobile particles. Our previous investigations were carried out for reaction probabilities which depend exponentially on the mutual distance between the reactants.⁽²⁴⁻²⁶⁾ Here we let the particles react via short-range interactions with cutoff. We consider a situation in which the immobile A and B particles are deposited continuously and independently on a discrete lattice of side length unity. The model corresponds to a variant of the so-called "black-sphere" model⁽²⁷⁻³²⁾ in which A and B particles whose mutual distance is smaller than r_0 (the so-called reaction radius) react instantaneously and disappear from the system. As an example, nearest-neighbor interactions are given by having $1 < r_0 < 2$. The black-sphere model is adequate for the description of the recombination of Frenkel pairs in a cascade, induced, say, by a proton in a crystal.

Here we shall be interested in the time dependence of the particles' densities and in the behavior of the two-particle correlation functions. As we shall show, the analysis of the relations between these two quantities allows one to determine whether the reaction considered is fluctuation-dominated. We study both the time dependence of the reactants' concentrations and also the correlation functions via direct computer simulations. Since the effects of clustering and statistical fluctuations are most important in one dimension, we will concentrate on this case only. We deposit A and B particles with the rate η per lattice site and per unit time; the deposition sites are uncorrelated, but we take care that each A deposition is followed by a B deposition and vice versa, so that the overall concentrations are always equal: $n_A = n_B$. We start here by surveying the $A + B \rightarrow 0$ reactions in systems with particle inflow in two special cases, in order to clarify the main features of fluctuation-dominated kinetics.

2. FLUCTUATION-DOMINATED REACTIONS IN ONE DIMENSION

Let us consider the two simplest cases of fluctuation-dominated reactions under a steady influx of particles, namely the case of extremely short-range interactions (the so-called "vertical annihilation") and also diffusion-controlled reactions. For simplicity we restrict ourselves (in the spirit of this paper) to the one-dimensional discrete lattice.

In the case of extremely short-range interactions (vertical annihilation)

the particles are immobile and annihilate only if a particle of type A lands on a site occupied by particles of type B and vice versa. In the black-sphere model this corresponds to having $r_0 < 1$. Hence, in this case reactions occurring on different sites are independent, and the problem has a very simple analytical solution. Since the deposition rate η (per site and unit time) is equal for both types of particles and the A and B particles land independently at each site, the mean number of A (or B) particles deposited at site i is $\langle N_A(t) \rangle = \langle N_B(t) \rangle = N(t) = \eta t$. Note that under the conditions considered here, the deposition process obeys Poisson statistics; therefore at large times (following the central limit theorem) the distribution $p(N)$ of both N_A and N_B is Gaussian, with the dispersion σ being given by

$$\sigma^2 = \langle N_A^2(t) \rangle - \langle N_A(t) \rangle^2 = \langle N_B^2(t) \rangle - \langle N_B(t) \rangle^2 = N(t)$$

As one does not allow the A and B particles to coexist simultaneously at one site, the total number N_0 of particles at a site equals $|A|$, where $A = N_A(t) - N_B(t)$ is the difference of the numbers of A and B particles deposited at the site. The overall concentration of particles of the same kind $n(t)$ equals $\frac{1}{2} \langle |A| \rangle$. Hence

$$n(t) = \sigma / \pi^{1/2} = (\eta t / \pi)^{1/2} \tag{1}$$

which grows algebraically according to $n(t) \sim t^\alpha$, with $\alpha = 1/2$.

Now let us turn to the second limiting case, namely to diffusion-controlled reactions, and continue to focus on particles deposited in a spatially uncorrelated manner. In this case, according to scaling arguments similar to those presented in ref. 3, one may take that all particles inside intervals of the order of the correlation length \mathcal{L} can react with each other. Evidently, here the correlation length is simply the diffusion length, $\mathcal{L} \sim (Dt)^{1/2}$, D being the diffusion constant. This means that due to diffusion and reaction, clusters of A and B particles form, the mean cluster size being of the order of the diffusion length. The total number of particles in such a cluster is equal to the mean number of excess A or B particles landing within a distance \mathcal{L} of each other during the time t . The last quantity, again according to the Gaussian distribution, is proportional to the square root of the total number N_t of particles deposited inside \mathcal{L} : $M = \langle |A| \rangle \sim (N_t)^{1/2} = (\mathcal{L} \eta t)^{1/2}$. The overall concentration is therefore

$$n(t) \sim M / \mathcal{L} \sim t^{1/2} \mathcal{L}^{-1/2}(t) \tag{2}$$

This leads to the time dependence $n(t) \sim t^{1/4}$, a result which is also very well supported by more detailed theoretical considerations.^(7,9,14,15)

Furthermore, note that if the deposition occurs in a different manner, say by allowing the A and B particles to land pairwise, with mean mutual distance l , the particle number fluctuations will vanish in domains of the order of \mathcal{L} at long times, where $\mathcal{L}(t) \gg l$, so that no accumulation will take place.

The preceding arguments may be generalized to the case of uncorrelated deposition when the correlation length has the form $\mathcal{L}(t) \sim t^\beta$. Then the particle concentration grows according to $n(t) \sim t^\alpha$, where α and β obey the relation

$$\alpha = \frac{1 - \beta}{2} \quad (3)$$

as may be readily verified by substituting $\mathcal{L}(t)$ into Eq. (2). Evidently, the diffusion-controlled regime is a special case of Eq. (3) for $\beta = 1/2$. Furthermore, the vertical annihilation is also covered by Eq. (3): it corresponds to $\mathcal{L} = \text{const} \sim t^0$, and for it we have indeed $\alpha = 1/2$. Moreover, the fact that in a particular instance Eq. (3) is found to hold is a strong indication for the reaction being fluctuation-dominated.

We now turn to the more complex case given by the black-sphere model. This model looks very similar to the vertical annihilation. As we proceed to show, for it Eq. (3) also holds, but with β being in general different from either $\beta = 1/2$ or $\beta = 0$. This means that black-sphere models with immobile particles belong in general to universality classes different both from the vertical annihilation and also from the diffusion-controlled regimes. In the following sections we consider first the results of the numerical simulations; then we analyze the fluctuation-dominated aspects of the reaction.

3. NUMERICAL SIMULATIONS

The simulations are carried out on a one-dimensional lattice of size L with periodic boundary conditions. Because of the discreteness of the lattice, only the integer part of r_0 , $\text{entier}(r_0)$, is relevant, and we will denote in the following this integer by r_0 . A particle landing at a site i can interact then with particles on $v_0 = 2r_0 + 1$ sites, including i .

For our simulations two algorithms were used: The first one is more general and allows one to specify r_0 arbitrarily; for this it is more time-consuming, its computing time growing as $n(t) \cdot L^2$. The second one is restricted to nearest-neighbor interactions ($r_0 = 1$), but is much faster for large times and for densities $n(t) > 1$. At each step of the program we let an A and a B particle land on two randomly chosen sites of the chain. Then

we check each landing site for particles of the opposite type at the v_0 relevant neighboring sites. This search procedure determines the computation time, and here the differences between the algorithms become evident: The first algorithm is very general, being suited to calculate reactions in arbitrary dimensions and for all given distance-dependent interactions. The procedure used here computes the distance from the newly landed particle to all particles of the opposite kind; all such particles at a distance less than or equal to r_0 are marked. If any are found, one of them is chosen at random and reacts with the newly landed particle. This algorithm is very convenient at low particle coverage and in high dimensions. The second algorithm only checks the neighboring sites of the newly landed particle and picks one (if any) of the particles of opposite kind found there for reaction.

The results of our simulations are given in Figs. 1–4. Figure 1 shows the particle density as a function of time. The obvious feature of the results is the steady increase of the particle density with time, i.e., the lack of a steady-state situation. Shown are the (renormalized) particle densities for $r_0 = 1, 5, 10,$ and 20 , each calculated from five realizations of the process. In fact the particle density $n(t)$ obeys a simple scaling relation as a function of η and r_0 . Namely, the quantity $N = v_0 n$ (the mean number of the particles in v_0) scales as a function of $T = v_0 \eta t$ (the total number of particles created in v_0 during time t). From Fig. 1 it is evident that the curves scale within the standard deviation of the simulations. Due to this

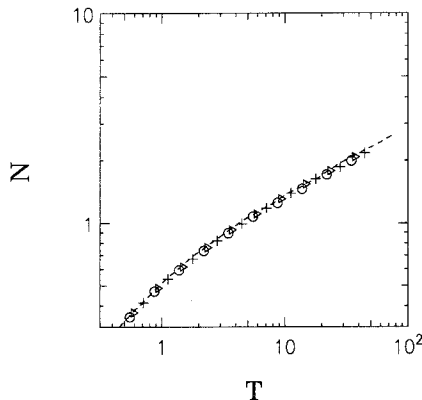


Fig. 1. The particle densities as a function of time for $r_0 = 1$ (dashed line), 5 (triangles), 10 (crosses), and 20 (circles). Each result is the average of five realizations of the process on the linear chains of 1.6×10^4 (for $r_0 = 1$) to 6.5×10^4 (for $r_0 = 20$) sites. To highlight the scaling behavior, we plot N vs. T , where $N = v_0 n$ and $T = v_0 \eta t$; see text for details.

fact we carry out the further simulations for $r_0 = 1$ only: this allows us to use the second (faster) algorithm for the annihilation procedure and therefore to extend our simulations over five orders of magnitude in time, as displayed in Fig. 2. Presented is $N(T)$ as well as its standard deviation, obtained from ten realizations of the process on a chain consisting of 20,000 sites. By inspection it follows that for long enough times (corresponding to $T > 1$) $N(T)$ obeys the power-law form

$$N(T) \sim T^\alpha \quad (4)$$

A least-squares fit leads for α to the value of $\alpha \approx 0.3$. Note that this value is intermediate between $\alpha = 1/2$, as found for extremely short-range interactions, and $\alpha = 1/4$, as displayed by diffusion-controlled reactions.

In order to further investigate the mechanism underlying these findings, we now turn to the correlation functions for particles of different kinds, $Y(r, t)$, and of the same kind, $X(r, t)$. These correlation functions describe the normalized probabilities of finding at time t a corresponding particle at a distance r given that the particle is present at the origin; see ref. 24 for details. In Fig. 3 these functions are given at times $t = 10, 100, 1000$, and $10,000$. The behavior of the curves displays clearly the tendency of particles of the same type to form clusters and to segregate from the particles of opposite type. We may furthermore introduce a correlation length \mathcal{L} defined, say, as being the distance \mathcal{L} , where $X(\mathcal{L}, t) = 2$ or where

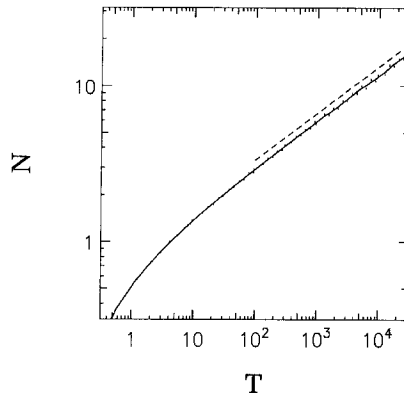


Fig. 2. The normalized particle density N as a function of T for $r_0 = 1$ and $\eta = 1$. The full line gives the result of ten realizations of the simulation on a chain with 20,000 lattice sites. The dots indicate the standard deviation of the mean value. The dashed line has a slope $\alpha = 0.3$, i.e., indicates an $N \sim T^{-\alpha}$ (i.e., $n \sim t^\alpha$) behavior with $\alpha = 0.3$.

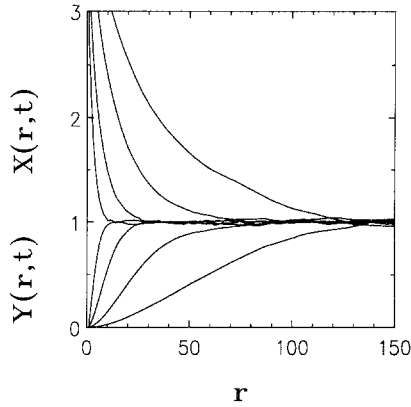


Fig. 3. Displayed are the correlation functions for like particles, $X(r, t)$ (upper part of the figure), and for unlike particles, $Y(r, t)$ (lower part of the figure), for the times $t = 10, 10^2, 10^3,$ and 10^4 (from left to right); see text for details.

$Y(\mathcal{L}, t) = 1/2$. A detailed analysis shows that this correlation length also grows algebraically with time, following

$$\mathcal{L}(t) \sim t^\beta \tag{5}$$

Furthermore, we find $\beta \approx 0.4$, which agrees with the previously found $\alpha = 0.3$ and with Eq. (3). We can also display graphically this finding by plotting the correlation functions in rescaled variables. Namely, the functions $X(r, t)$ and $Y(r, t)$ scale when drawn as functions of the variable $rt^{-\beta}$. Figure 4 presents the results for X and Y from Fig. 3, now as

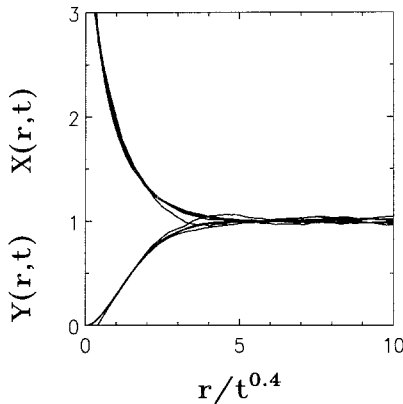


Fig. 4. The correlation functions of Fig. 3, replotted as functions of r/t^β with $\beta = 0.4$.

functions of $rt^{-0.4}$. As is evident, within the accuracy of our numerical modeling the agreement between the different curves is very good. That such scaling is found supports both our conjecture on the correlation length behavior and also, because Eq. (3) holds, our conclusion that the reaction kinetics in the black-space model is fluctuation-dominated.

4. CONCLUSIONS

We have investigated numerically the $A + B \rightarrow 0$ reaction between immobile particles deposited on a linear chain and annihilating via short-range interactions. The kinetics of particle accumulation is governed by a power law $n(t) \sim t^\alpha$ with $\alpha \approx 0.30$, which differs both from the case of diffusion-controlled reactions and also from the case of extremely short-range (vertical) annihilation. The study of the behavior of the correlation functions shows that in the course of the reaction clusters are formed. The correlation length \mathcal{L} of such clusters grows according to $\mathcal{L}(t) \sim t^\beta$ with $\beta \approx 0.4$. The relation $\alpha = (1 - \beta)/2$ holds very accurately also in this case, underlying the fact that the reactions considered here are fluctuation-dominated.

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REFERENCES

1. A. A. Ovchinnikov and Ya. B. Zeldovich, *Chem. Phys.* **28**:215 (1978).
2. D. Toussaint and F. Wilczek, *J. Chem. Phys.* **78**:2642 (1983).
3. K. Kang and S. Redner, *Phys. Rev. Lett.* **52**:955 (1984); *Phys. Rev. A* **32**:435 (1985).
4. G. Zumofen, A. Blumen, and J. Klafter, *J. Chem. Phys.* **82**:3198 (1985); A. Blumen, J. Klafter, and G. Zumofen, in *Optical Spectroscopy of Glasses*, I. Zschokke, ed. (Reidel, Dordrecht, 1986), pp. 199-265.
5. G. H. Weiss, *J. Stat. Phys.* **42**:3 (1986); H. Taitelbaum, S. Havlin, J. E. Kiefer, B. Trus, and G. H. Weiss, to be published.
6. I. M. Sokolov, *Zh. Eksp. Teor. Fiz. Pis'ma* **44**:53 (1986) [*Sov. Phys. JETP Lett.* **44**:67 (1986)].
7. S. F. Burlatskii, A. A. Ovchinnikov, and K. A. Pronin, *Zh. Eksp. Teor. Phys.* **92**:625 (1986) [*Sov. Phys. JETP* **65**:353 (1987)].
8. A. G. Vitukhnovskii, B. L. Pyttel, and I. M. Sokolov, *Phys. Lett. A* **128**:161 (1988).
9. I. M. Sokolov, *Zh. Eksp. Teor. Fiz.* **94**:199 (1988) [*Sov. Phys. JETP* **67**:1846 (1988)].
10. K. Lindenberg, B. J. West, and R. Kopelman, *Phys. Rev. Lett.* **60**:1777 (1988).

11. M. Bramson and J. L. Lebowitz, *Phys. Rev. Lett.* **61**:2397 (1988).
12. V. Kuzovkov and E. Kotomin, *Rep. Prog. Phys.* **51**:1479 (1988).
13. A. Szabo, R. Zwanzig, and N. Agmon, *Phys. Rev. Lett.* **61**:2496 (1988).
14. D. Ben-Avraham and C. R. Doering, *Phys. Rev. A* **37**:5007 (1988).
15. E. Clément, L. M. Sander, and R. Kopelman, *Phys. Rev. A* **39**:6455, 6466 (1989).
16. G. S. Oshanin, S. F. Burlatskii, and A. A. Ovchinnikov, *Phys. Lett. A* **139**:245 (1989).
17. B. J. West, R. Kopelman, and K. Lindenberg, *J. Stat. Phys.* **54**:1429 (1989).
18. P. Argyrakis and R. Kopelman, *J. Phys. Chem.* **91**:2699 (1987); **93**:225 (1989).
19. K. Lindenberg, B. J. West, and R. Kopelman, *Phys. Rev. A* **42**:890 (1990).
20. W.-S. Sheu, K. Lindenberg, and R. Kopelman, *Phys. Rev. A* **42**:2279 (1990).
21. H. Schnörer, I. M. Sokolov, and A. Blumen, *Phys. Rev. A* **42**:7075 (1990).
22. I. M. Sokolov and A. Blumen, *Phys. Rev. A* **43**:2714 (1991).
23. I. M. Sokolov and A. Blumen, *Phys. Rev. Lett.* **66**:1942 (1991).
24. H. Schnörer, V. Kuzovkov, and A. Blumen, *Phys. Rev. Lett.* **63**:805 (1989).
25. H. Schnörer, V. Kuzovkov, and A. Blumen, *J. Chem. Phys.* **92**:2310 (1990).
26. H. Schnörer, S. Luding, and A. Blumen, in *Fractals in the Fundamental and Applied Sciences*, J. Henriques, ed. (Fundacao Calouste Gulbenkian, Lisbon, 1990).
27. E. Kotomin, I. Täle, V. Täle, and P. Kūlis, *J. Phys.: Condensed Matter* **1**:6777 (1989).
28. S. F. Burlatsky and A. I. Chernoutsan, *Phys. Lett. A* **145**:56 (1990).
29. K. Dettmann, *Phys. Stat. Sol.* **10**:269 (1965).
30. V. N. Kuzovkov and E. A. Kotomin, *J. Phys. C: Solid State Phys.* **17**:2283 (1984).
31. V. V. Antonov-Romanovskii, *Phys. Stat. Sol. (b)* **121**:133 (1984).
32. V. V. Antonov-Romanovskii, *Fiz. Tverd. Tela* **27**:1116 (1985) [*Sov. Phys.-Solid State* **27**:674 (1985)].