Bimolecular annihilation reactions with immobile reactants

H. Schnörer, V. Kuzovkov,[a] and A. Blumen
Physical Institute and BIMF, University of Bayreuth, D-8580 Bayreuth, West Germany

We study the bimolecular annihilation reaction $A + B \to 0$ with immobile reactants in arbitrary dimension. For this we derive a closed set of integrodifferential equations by using Kirkwood's superposition approximation to decouple the infinite hierarchy of equations for the many-center correlation functions. We find that for exchange-type interactions and equal numbers of A and B species the reactant concentration n decays as $n \sim \xi^{-d/2}$, where ξ is time-dependent, $\xi = \ln t$, and may be interpreted to be an effective reaction radius. A comparison to numerical simulations shows very good agreement to the theoretical expressions, both for the temporal evolution of particle concentrations and also for the pair-correlation functions; this confirms the validity of the superposition approximation.

I. INTRODUCTION

Bimolecular reactions between like $(A + A \to$ products$)$ and unlike particles $(A + B \to$ products$)$ have been investigated extensively during the last few years.[1-29] Most of the work centered on diffusion-limited reactions, where particles react on contact after undergoing diffusive motion. It took a long time to realize that the usual kinetic reaction schemes are only approximate, in that they do not accurately reflect the spatial aspects.[2,5,7] Thus, theories which treat only the global particle densities cannot properly describe the problem, since spatial correlations between the reactants have to be taken into account. Although several attempts have been made to find an analytical approach to the problem, up to now only a few exact solutions are known, and this only for one-dimensional systems.[4,16,25,27]

The models currently investigated are of two kinds: In models of the first kind one starts with a random distribution of reactants and monitors the decay of particle concentration during the reaction.[1-12] In models of the second kind particles are continuously inserted into the system and one observes whether a steady state occurs.[13,17,18,24,27,29]

In this article we consider the $A + B \to 0$ reaction model of the first kind and focus on immobile A and B molecules, interacting via exchange. We are interested in the occurrence of spatial correlations and these appear most vividly when the particles are immobile, since diffusion works against cluster formation.

An analytical approach to bimolecular reactions, which takes into account spatial correlations through many-center densities has recently been developed by Kuzovkov and Kotomin.[23] They used the Kirkwood superposition approximation[30,31] to decouple the three-center correlation functions and thus reduced the infinite set of equations to a finite set of coupled integrodifferential equations. These equations can be solved numerically, but, as there does not exist any analytical estimation for the validity of the Kirkwood approximation[30] (which is also extensively used in the theory of fluids), the results have to be compared to computer simulations of the full problem.[32-34]

In this article we perform this comparison for the reac-

tion $A + B \to 0$ with immobile reactants and we show that the Kirkwood approximation works extremely well even in this extreme case; we find a very good agreement both for the global reactant concentrations and for the AB correlations. In a previous letter[32] we have discussed the situation in one dimension. Here we extend the analysis to two and three dimensions. For this we derive in Sec. II the system of equations for the $A + B \to 0$ reaction in the absence of diffusion. In Sec. III we solve these equations numerically and study the asymptotic time dependence of the particle concentrations. In Sec. IV we present the results of computer simulations of the full problem and compare them with the results of our analytical approach. We summarize our findings in Sec. V.

II. THE ANALYTICAL APPROACH

In the following we consider the strictly bimolecular reaction $A + B \to 0$. The simplest kinetic approach to this reaction, expressed by the differential equation[11]

$$\frac{dA(t)}{dt} = -kA(t)B(t), \tag{2.1}$$

has for initially equal particle numbers $A_0 = B_0$ the solution

$$A(t) = \frac{A_0}{1 + A_0 kt} \sim 1/kt, \tag{2.2}$$

whereas for $A_0 < B_0$ one obtains

$$A(t) = \frac{A_0 C}{B_0 e^{Ckt} - A_0} \sim e^{-Ckt}, \tag{2.3}$$

where the constant k is the reaction rate and $C = B_0 - A_0$. The basic assumption underlying this reaction scheme is a totally homogeneous spatial distribution of particles during the whole course of the reaction.

As already pointed out in the introduction, spatial inhomogeneities (such as the formation of clusters of like particles) can drastically alter the decay behavior. Thus, for equal numbers of A and B particles, in the *diffusion-limited* $A + B \to 0$ reaction the particle concentration decays as $t^{-d/4}$ (for $d < 4$) instead of t^{-1}.[2,5] Here the formation of clusters slows down the reaction, because only particles near the border of such clusters are likely to react, whereas particles inside the cluster have to diffuse to the border before

[a] Permanent address: Latvian State University, Rainis Boulevard 19, Riga 226098, USSR.

they can annihilate with a particle of opposite type. With increasing dimensionality d, however, diffusion wipes out more and more the tendency to form clusters, and for $d \geqslant 4$ the kinetic result [Eq. (2.2)] is recovered.

In order to avoid this stirring effect of diffusion, we consider in the following a system of *immobile A* and *B* particles, distributed randomly in d-dimensional space and annihilating mutually via exchange interactions. In this case $w(r) = w_0 \exp(-r/r_0)$ is the probability rate that A and B situated at distance r react (r_0 determines the interaction range). We will show in the following that (due to the absence of diffusion) the results are influenced by the explicit form of $w(r)$. The exponential form is typical for exchange dominated reactions in solids, like scavenging or recombination of electrons and holes via tunneling.[9,11] Here we concentrate on the case of equal numbers of A and B particles ($A_0 = B_0$) in order to make the formalism more transparent and to show parallels to diffusion-limited reactions.

Let $n_{A(B)}(r,t)$ be the microscopic particle concentrations in such an annihilation process; here and in the following all symbols $r_{(i)}^{(\prime)}$ denoting particle coordinates are understood to be vectors (except when appearing in functional expressions, such as e^{-r}). Considering a situation where m A particles are situated at $r_1,...,r_m$ and m' B particles sit at $r_1',...,r_{m'}'$, one defines the many-center densities $\rho_{m,m'}$ as an ensemble averaged product of reactant concentrations:

$$\rho_{m,m'} = \left\langle \prod_{i=1}^{m} n_A(r_i,t) \prod_{j=1}^{m'} n_B(r_j',t) \right\rangle. \qquad (2.4)$$

Thus one has for the single- and for the two-center densities

$$\rho_{1,0} = \langle n_A(r,t) \rangle \equiv n_A(t)$$
$$\rho_{0,1} = \langle n_B(r,t) \rangle \equiv n_B(t) \qquad (2.5)$$

and

$$\rho_{2,0} = \langle n_A(r_1,t) n_A(r_2,t) \rangle \equiv n_A^2(t) X_A(r_1 - r_2,t)$$
$$\rho_{0,2} = \langle n_B(r_1',t) n_B(r_2',t) \rangle \equiv n_B^2(t) X_B(r_1' - r_2',t) \qquad (2.6)$$
$$\rho_{1,1} = \langle n_A(r_1,t) n_B(r_1',t) \rangle \equiv n_A(t) n_B(t) Y(r_1 - r_1',t),$$

where we have introduced the global particle concentrations $n_{A(B)}(t)$ and the pair correlation functions $X_{A(B)}(r,t)$ and $Y(r,t)$. As we consider only situations with equal numbers of A and B particles, we have $n_A(t) = n_B(t) \equiv n(t)$ and $X_A(r,t) = X_B(r,t) \equiv X(r,t)$.

Now, the following infinite system of coupled differential equations for the many-center densities $\rho_{m,m'}$ holds[23]

$$\frac{\partial}{\partial t}\rho_{m,m'} = -\sum_{i=1}^{m}\sum_{j=1}^{m'} w(r_i - r_j')\rho_{m,m'}$$
$$- \sum_{i=1}^{m}\int w(r_i - r_{m'+1}')\rho_{m,m'+1} \, d^d r_{m'+1}'$$
$$- \sum_{j=1}^{m'}\int w(r_j' - r_{m+1})\rho_{m+1,m'} \, d^d r_{m+1}.$$
$$(2.7)$$

The contributions to the decay of $\rho_{m,m'}$ may be readily understood as follows: The first term accounts for reactions between any pair of A and B particles from the (m,m') set, whereas the second and third term involve reactions of one of the particles of the original (m,m') set with a particle of opposite type from outside the (m,m') set.

Use of Eqs. (2.5) to (2.7) leads to the following exact expression for $n(t) = \rho_{1,0} = \rho_{0,1}$:

$$\frac{\partial n(t)}{\partial t} = -n^2(t)\int w(r') Y(r',t) d^d r', \qquad (2.8)$$

by observing that for $(m,m') = (1,0)$ or $(0,1)$ on the right-hand side of Eq. (2.7) only the term containing $\rho_{1,1}$ contributes.

In order to get a closed set of equations for higher (m,m') values we make now use of the superposition approximation[30] to decouple all three-center correlation functions. This approximation was pioneered by Kirkwood[31] and consists in expressing the three-center correlation functions in terms of two-center correlation functions in the following way:

$$\langle n(r_1)n(r_2)n(r_3) \rangle$$
$$\simeq \frac{\langle n(r_1)n(r_2)\rangle\langle n(r_2)(n(r_3)\rangle\langle n(r_3)n(r_1)\rangle}{\langle n(r_1)\rangle\langle n(r_2)\rangle\langle n(r_3)\rangle}. \qquad (2.9)$$

As pointed out in the theory of fluids by Balescu[30] in his discussion of Eq. (2.9): "it is still not possible to justify it or assess its domain of validity. The only tests are either comparisons of its predictions with experimental (or simulational) data or tests of internal consistency."

Equation (2.9) leads in our case to

$$\rho_{2,1} = \langle n_A(r_1,t)n_A(r_2,t)n_B(r_1',t)\rangle$$
$$\simeq n^3(t)X(r_1 - r_2,t)Y(r_1 - r_1',t)Y(r_2 - r_1',t). \qquad (2.10)$$

Using this approximation to decouple the infinite hierarchy of Eq. (2.7), one has with Eqs. (2.5) and (2.6)

$$\frac{\partial}{\partial t}\rho_{1,1} = -w(r_1 - r_1')\rho_{1,1} - \int w(r_1 - r_2')\rho_{1,2} \, d^d r_2' - \int w(r_1' - r_2)\rho_{2,1} \, d^d r_2$$

$$\simeq -w(r)n^2(t)Y(r,t) - n^3(t)\int w(r_1 - r_2')X(r_1' - r_2',t)Y(r_1 - r_1',t)Y(r_1 - r_2',t)d^d r_2'$$

$$- n^3(t)\int w(r_1' - r_2)X(r_1 - r_2)Y(r_1 - r_1',t)Y(r_2 - r_1',t)d^d r_2$$

$$= -w(r)n^2(t)Y(r,t) - 2n^3(t)Y(r,t)\int w(r')X(r' - r,t)Y(r',t)d^d r', \qquad (2.11)$$

where we have set $r_1 - r_1' \equiv r$ and $r_1 - r_2' \equiv r'$ or $r_1' - r_2 \equiv r'$, respectively.

On the other hand, from Eqs. (2.6) and (2.8) it follows:

$$\frac{\partial}{\partial t}\rho_{1,1} = n^2(t)\frac{\partial}{\partial t}Y(r,t) + 2n(t)Y(r,t)\frac{\partial}{\partial t}n(t)$$

$$= n^2(t)\frac{\partial}{\partial t}Y(r,t) - 2n^3(t)Y(r,t)$$

$$\times \int w(r')Y(r',t)d^d r'. \qquad (2.12)$$

From Eqs. (2.11) and (2.12) one obtains after division through $n^2(t)Y(r,t)$,

$$\frac{\partial \ln Y(r,t)}{\partial t} = -w(r) - 2n(t)\int w(r')Y(r',t)$$

$$\times [X(r-r',t) - 1]d^d r'. \qquad (2.13)$$

In a similar way one gets the differential equation for $X(r,t)$,

$$\frac{\partial \ln X(r,t)}{\partial t} = -2n(t)\int w(r')Y(r',t)$$

$$\times [Y(r-r',t) - 1]d^d r'. \qquad (2.14)$$

Equations (2.8), (2.13), and (2.14) are the basis for our further analysis. In general, these equations cannot be solved analytically but have to be evaluated numerically. We have performed this task for several sets of parameters and present the results in the next section.

III. NUMERICAL EVALUATION

In our numerical evaluations we used dimensionless variables by measuring distances in units of r_0, concentration in units of r_0^{-d} and time in units of w_0^{-1}. Thus the reaction rate is now of the form $w(r) = e^{-r}$. Besides the spatial dimension d, the only necessary input is then the initial concentration of reactants, $n(0)$ (in units of r_0^{-d}).

As the concentration $n(t)$ and the correlation functions $X(r,t)$ and $Y(r,t)$ vary on a logarithmic time scale [a consequence of the exponential form of $w(r)$], we introduce a new variable $\xi \equiv \ln t$ to accelerate the numerical procedure. ξ may be interpreted as a reaction radius, as it fulfills $w(\xi)t = 1$. Later we will see that ξ determines the typical size of clusters of like particles. Introducing this new variable into Eqs. (2.8), (2.13) and (2.14), we get

$$\frac{\partial}{\partial \xi}\left(\frac{1}{n(\xi)}\right) = e^\xi \int w(r')Y(r',\xi)d^d r', \qquad (3.1)$$

$$\frac{\partial}{\partial \xi}\ln Y(r,\xi) = -e^\xi w(r) - 2n(\xi)e^\xi \int w(r')Y(r',\xi)$$

$$\times [X(r'-r,\xi) - 1]d^d r', \qquad (3.2)$$

$$\frac{\partial}{\partial \xi}\ln X(r,\xi) = -2n(\xi)e^\xi \int w(r')Y(r',\xi)$$

$$\times [Y(r'-r,\xi) - 1]d^d r'. \qquad (3.3)$$

Thus we have to solve equations of the form

$$\frac{\partial}{\partial \xi}f(\xi) = F[n,X,Y;\xi], \qquad (3.4)$$

where f stands for $1/n$, $\ln X$ or $\ln Y$ and F represents the

corresponding functionals of n, X and Y as given by the right-hand sides of Eqs. (3.1)–(3.3).

For the discretization of Eq. (3.4) we used the symmetric scheme

$$\frac{f(\xi + \Delta) - f(\xi)}{\Delta} = \frac{1}{2}\{F[n,X,Y;\xi] + F[n,X,Y;\xi + \Delta]\},$$

$$(3.5)$$

where Δ is the ξ increment for each step. As this formula does not only involve $F(\xi)$ but also $F(\xi + \Delta)$, which is yet unknown, an additional iteration scheme is used for each ξ increment: Starting with $f^\circ(\xi + \Delta) = f(\xi)$, i.e., $n^\circ(\xi + \Delta) = n(\xi)$, $X^\circ(r,\xi + \Delta) = X(r,\xi)$, and $Y^\circ(r,\xi + \Delta) = Y(r,\xi)$, one iteratively calculates $f^{i+1}(\xi + \Delta)$ by solving the equation

$$\frac{f^{i+1}(\xi + \Delta) - f(\xi)}{\Delta}$$

$$= \frac{1}{2}\{F[n,X,Y;\xi] + F[n^i,X^i,Y^i;\xi + \Delta]\}, \qquad (3.6)$$

until a predefined accuracy $|f^{i+1} - f^i| \leqslant \varepsilon$ is reached. Then one sets $f(\xi + \Delta) \equiv f^{i+1}(\xi + \Delta)$ and continues with the next ξ increment.

The order of convergence of this procedure is 2, i.e., the accuracy is proportional to Δ^2. For the evaluation of the space integrals in Eqs. (3.1)–(3.3) we made use of their symmetry with respect to inversion and evaluated them numerically for discrete values of r, i.e., $r_i = h \cdot i$. In our calculations we used $h = \Delta = 0.1$ and $\varepsilon = 0.001$.

We solved the set of equations numerically for one, two and three dimensions. Figure 1 shows the decay of concentration after starting with $n(0) = 1$ in all dimensions, whereas in Fig. 2 the solutions for three different initial concentrations (1, 0.1 and 0.01) in two-dimensional space are displayed.

Figure 1 shows that the reaction proceeds faster for higher dimensions. This is understandable, since in higher dimensions there are more possibilities for finding reactant pairs nearby. The curves in Fig. 1 all obey an asymptotic time form which depends on the dimension as $(\ln t)^{-d/2}$.
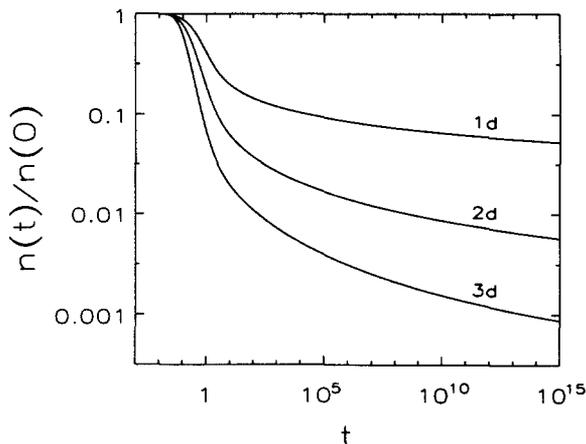

FIG. 1. Decay of the reactant concentration $n(t)$ in one, two, and three dimensions, obtained by numerical evaluation of Eqs. (3.1)–(3.3). The initial condition is $n(0) = 1$ (in units of r_0^{-d}) for each curve.
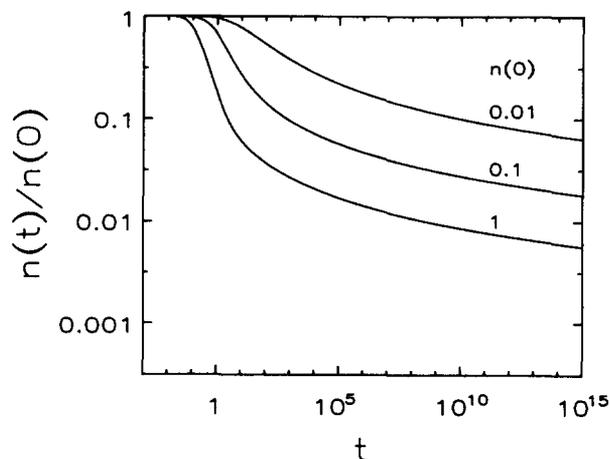
FIG. 2. Decay of the reactant concentration $n(t)$ in two dimensions for the initial concentrations $n(0) = 0.01, 0.1$ and 1 (in units of r_0^{-2}), obtained by numerical evaluation of Eqs. (3.1)–(3.3).

The same behavior is evident in Fig. 2, where the curves follow $(\ln t)^{-1}$. This was verified by us by assuming the form $n(t) \sim (\ln t)^{-\alpha(t)}$ and plotting in Fig. 3 the exponent $\alpha(t)$ for three numerically determined curves in one, two, and three dimensions. Apart from the lowest curve in Fig. 3, the exponents $\alpha(t)$ come quite close to the value $d/2$ in the considered time range.

If we rewrite this result in terms of the reaction radius $\xi = \ln t$ we get the asymptotic dependence[35]

$$n \sim (\ln t)^{-d/2} \sim \xi^{-d/2}. \tag{3.7}$$

The occurrence of the exponent $-d/2$ is remarkable, since a lower level approximation, which neglects correlations between like particles, i.e., $X(r,t) \equiv 1$, predicts $n \sim \xi^{-d}$.

This may be easily verified from Eqs. (3.1) and (3.2) as follows: For $X(r,t) \equiv 1$ Eq. (3.2) reduces to

$$\frac{\partial}{\partial \xi} \ln Y(r,\xi) = -e^\xi w(r), \tag{3.8}$$

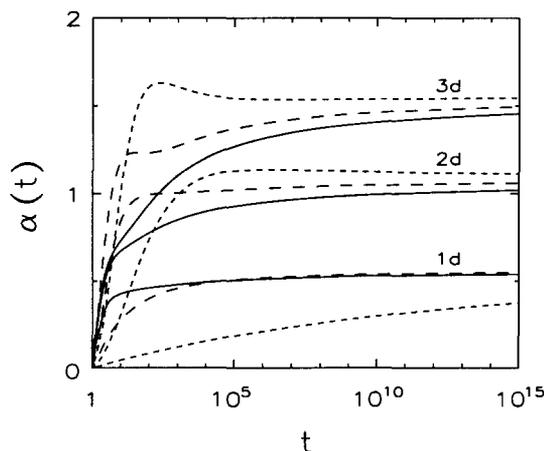
FIG. 3. Exponent $\alpha(t)$ (defined by $n(t) \sim (\ln t)^{-\alpha(t)}$) for three different initial concentrations $n(0)$ in each dimension [— $n(0) = 1$, – – $n(0) = 0.1$, --- $n(0) = 0.01$].

which has the solution

$$Y(r,\xi) = e^{-w(r)e^\xi}. \tag{3.9}$$

Introducing this result and $w(r) = e^{-r}$ into Eq. (3.1), one has

$$\frac{\partial}{\partial \xi}\left(\frac{1}{n(\xi)}\right) = \int e^{\xi - r} e^{-e^{\xi - r}} d^d r$$

$$= c_d \int_0^\infty e^{\xi - r} e^{-e^{\xi - r}} r^{d-1} dr, \tag{3.10}$$

where c_d is the surface of the unit sphere in d dimensions. With the substitution $u = e^{\xi - r}$ one gets

$$\frac{\partial}{\partial \xi}\left(\frac{1}{n(\xi)}\right) = c_d \int_0^{e^\xi} e^{-u}(\xi - \ln u)^{d-1} du$$

$$\simeq c_d \int_0^\infty e^{-u}(\xi - \ln u)^{d-1} du. \tag{3.11}$$

In the last expression we used $\xi \gg 1$. Then one also has by integration

$$\frac{1}{n(\xi)} = \frac{1}{d} c_d \int_0^\infty e^{-u}(\xi - \ln u)^d du + \text{const.} \tag{3.12}$$

Applying the binomial theorem to $(\xi - \ln u)^d$ one finally arrives at

$$\frac{1}{n(\xi)} \sim \frac{1}{d} c_d \xi^d + O(\xi^{d-1}), \tag{3.13}$$

which results in $n \sim \xi^{-d} \sim (\ln t)^{-d}$. Comparison of this result to Eq. (3.7) shows that the neglect of correlations between like particles, i.e., setting $X(r,t) \equiv 1$, leads to a change of the time decay exponent by a factor of 2. Such a change in the time decay exponent is also observed when comparing the results for the diffusion-limited $A + A \to 0$ and the $A + B \to 0$ reaction. In the first case the formation of clusters of A particles is unlikely, as A particles annihilate mutually, a fact which works against clustering. The $A + A$ decay is found to follow $n(t) \sim t^{-d/2}$ $(d < 2)$.[11] Taking into account a second species B, however, and forbidding reactions between like particles, clustering of like particles is encouraged (as we will show in the next section), leading to $n(t) \sim t^{-d/4}$ $(d < 4)$ for the $A + B \to 0$ reaction. Thus in both cases (diffusing and immobile reactants) taking into account the formation of clusters leads to a change by a factor of 2 in the time decay exponents.

Rewriting the results for the diffusion-limited reactions in terms of the diffusion length $l_D = \sqrt{Dt}$,[5] with D being the diffusion coefficient for both A and B, one has $n \sim l_D^{-d}$ for the $A + A \to 0$ reaction (cluster formation unlikely) and $n \sim l_D^{-d/2}$ for the $A + B \to 0$ reaction. Thus in diffusion-limited reactions the diffusion length l_D plays a similar role as the reaction radius ξ in a system with immobile reactants. In contrast to the diffusion-limited case, however, in the absence of diffusion there does *not* exist an upper critical dimension (such as $d_c = 2$ for $A + A \to 0$ and $d_c = 4$ for $A + B \to 0$ for diffusion-limited reactions), above which the effect of clustering can be neglected. As an example, we find for the exchange interaction that in all dimensions $n \sim \xi^{-d/2} \sim (\ln t)^{-d/2}$, a form which does not turn into t^{-1} for any d. We illustrate the formation of clusters in the

next section, where we discuss the direct simulation of the annihilation process.

IV. SIMULATION CALCULATIONS AND RESULTS

Since some simulation results for annihilation reactions in one dimension were already presented by us in Ref. 32 we exemplify our findings by concentrating on the two-dimensional case.

Starting point for the simulations are random distributions of A and B particles ($N_0 = 10^4$ each) on a square lattice of 1000×1000 sites with periodic boundary conditions. The random mutual annihilation of unlike particles was simulated through a minimal process method[33]: From all AB pairs at each reaction step one pair was selected randomly, according to its reaction rate; the time increment τ for this step was computed as $\tau = - (\ln T)/R$, with R being the sum of the rates of all AB pairs present and T being a random number from the homogeneous distribution in the unit interval. The time was measured in units of w_0^{-1} and we stopped the procedure after a maximal time of 10^{15}. The interaction parameter r_0 was set to $r_0 = 5$ (in units of the lattice spacing), which corresponds to typical exchange interactions in organic molecular crystals.

In Fig. 4 we present the distributions of A and B particles at different times during such a reaction process. Whereas at $t = 10$ the distribution of particles still looks quite random, the evolution of clusters of like particles is clearly visible at $t = 10^5$ and proceeds up to $t = 10^{15}$. We have taken care to include only such times in our simulations, for which the typical cluster sizes are well below the size of the whole lattice. The findings in Fig. 4 parallel the results for the one-dimensional case, where (with $r_0 = 5$) cluster formation also became visible from $t = 10^5$ on. By comparison to diffusion-limited reactions,[5] for immobile reactants we find that the clusters are more pronounced by being well separated
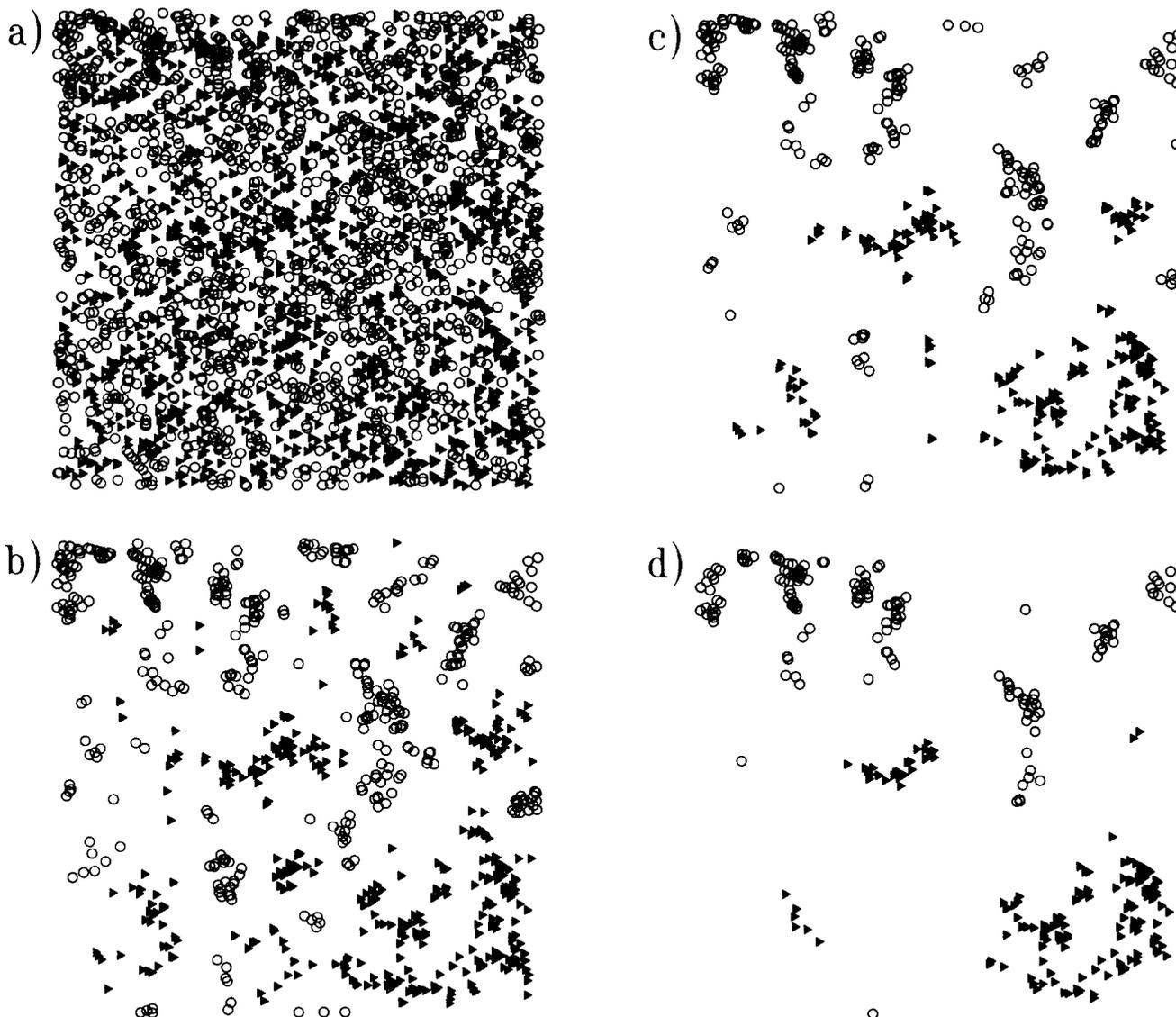

FIG. 4. Spatial distribution of A and B particles during a reaction process with $r_0 = 5$ on a 1000×1000 square lattice (with periodic boundary conditions) after starting with 10^4 particles of each kind. The distributions are shown for (a) $t = 10$, (b) $t = 10^5$, (c) $t = 10^{10}$, and (d) $t = 10^{15}$.
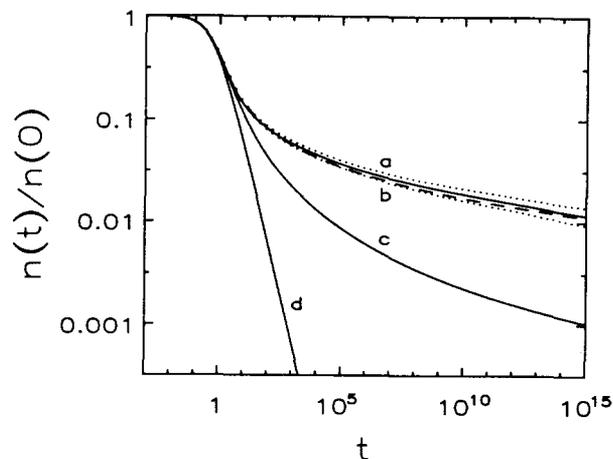
FIG. 5. Decay of the reactant concentration obtained from (a) averaging over 20 numerical simulations with initially 10^4 particles of each kind on a 1000×1000 square lattice and with interaction range $r_0 = 5$ (the dotted lines indicate the standard deviation of the data); (b) numerical evaluation of Eqs. (3.1)–(3.3) for $d = 2$ and $n(0) = 0.25$ (dashed line); (c) a raw approximation [Eq. (3.10)] which neglects correlations between like particles [$X(r,t) \equiv 1$]; (d) the solution of the simple kinetic scheme [Eq. (4.1)].

FIG. 6. Correlation functions for like (X) and unlike(Y) particles, calculated numerically from Eqs. (3.1)–(3.3) with $d = 2$ and $n(0) = 0.25$ (solid lines). The symbols mark the results from numerical simulations: each value is an average over 20 realizations of the process, smoothed out over an interval of $6r_0$. The annihilation process was performed on a 1000×1000 square lattice, having initially 10^4 particles of each kind, which react via exchange ($r_0 = 5$).

from each other. This can be well understood by noting that diffusion stirs the system and works against the tendency to form well-separated clusters.

Figure 5 displays the decay of the number of A (or B) particles (curve a), which was obtained by averaging over 20 different initial configurations. The dotted lines indicate $\langle n(t) \rangle \pm s(t)$, where $s(t)$ is the standard deviation of the 20 individual curves, i.e., $s^2(t) = [\langle n^2(t) \rangle - \langle n(t) \rangle^2]/20$. Curve b (dashed line) in Fig. 5 is the result of the numerical evaluation of Eqs. (3.1)–(3.3) with the appropriate parameters [$n(0) = 0.25$, $d = 2$]. The two curves a and b agree exceedingly well within the statistical errors of the simulation. This agreement is even better than in the already very satisfactory one-dimensional case.[32]

Figure 5 also demonstrates that the neglect of correlations between like particles, as already discussed in the previous section, does not yield the proper asymptotic behavior. Curve c was calculated from Eq. (3.10), which resulted from $X(r,t) \equiv 1$. This curve agrees with the simulation only up to $t \simeq 10$, whereas at longer times the formation of clusters causes the simulation curve a to decay more slowly than curve c. In this figure we also plotted the solution of the simple kinetic approach (curve d), which results from Eq. (2.8) by setting $Y(r,t)$, i.e., by neglecting *all* spatial inhomogeneities. In this case the solution of Eq. (2.8) is

$$n(t) = \frac{n(0)}{1 + 2\pi r_0^2 n(0) w_0 t}. \tag{4.1}$$

This approximation is only valid up to $t \simeq 1$, as shown in Fig. 5. Then the assumption of spatial homogeneity breaks down.

We conclude that the superposition approximation leads to a strikingly good description of complex reaction kinetics even in the very long-time regime.

A further test of the superposition approximation is provided by comparing the correlation functions $X(r,t)$ and $Y(r,t)$ to the simulation data. Here we calculated these func-
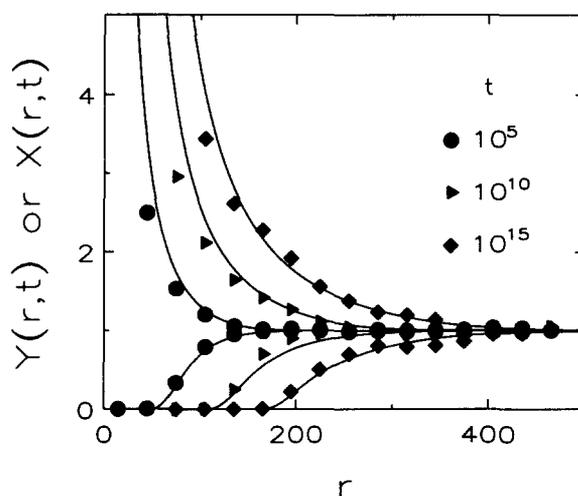
tions from Eqs. (3.2) and (3.3) for the considered set of parameters [$n(0) = 0.25$, $d = 2$]. In Fig. 6 we compare $X(r,t)$ and $Y(r,t)$ to the simulation results, obtained, as before, by averaging over 20 realizations of the annihilation process. The scatter of the simulated data was reduced by averaging over radius intervals of length $6r_0$ (30 lattice constants). Thus the statistical error of the data is comparable to (or less than) the height of the symbols and decreases with increasing distance r [since the number of lattice sites with distance in the interval $(r, r + dr)$ is proportional to $r^{d-1} \, dr$].

Again, simulation data and calculated correlation functions agree well in the major part of the r range. Slight deviations occur only in the small-r regime, where the simulation data for the correlations between like particles lie somewhat below the $X(r,t)$ curves. On the other hand, the $Y(r,t)$ curves, which determine the decay of concentration via Eq. (2.8), fit well in the whole r regime. Taking the value of r, where $Y(r,t)$ begins to deviate from zero, as the typical cluster size, Fig. 6 also reflects the logarithmic time dependence of this quantity, which turns out to mirror rather closely the previously defined reaction radius ξ.

V. CONCLUSIONS

In this article we have studied the strictly bimolecular reaction $A + B \rightarrow 0$, where the particles are immobile and annihilate via exchange interaction. An approximate analytical treatment, based on Kirkwood's superposition approximation, predicts the particle concentration to decay as $n(t) \sim (\ln t)^{-d/2} \sim \xi^{-d/2}$, where $\xi = \ln t$ is the reaction radius. This result was confirmed by comparing the outcome of the analytical expressions to results from direct simulations of the $A + B \rightarrow 0$ annihilation process on a two-dimensional lattice. We found very good agreement between the

simulation data and the evaluation of the analytically derived equations; this both for the particle density $n(t)$ and also for the correlation functions between like $[X(r,t)]$ and unlike particles $[Y(r,t)]$. These findings complement our one-dimensional results (presented in an earlier letter[32]), and indicate that the superposition approximation, which consists in expressing three-center correlation functions by means of two-center correlations and neglecting all higher correlations, leads to a correct picture of the reactant concentration for the whole time regime. The fact that the superposition approximation works so well even in a system with immobile reactants, where correlation effects (like clustering of particles) are much more pronounced than in reaction–diffusion systems, suggests that this approach could turn out to be a method of choice in exploring diffusion-limited reactions in an analytically minded manner.

An analogy can be drawn to the diffusion-limited $A + B \rightarrow 0$ reaction, where the concentration decay can be written in terms of the diffusion length l_D as $n(t) \sim l_D^{-d/2}$. This suggests that in diffusion-controlled reactions l_D plays a role similar to the reaction radius ξ in a system with immobile particles: both parameters determine the typical size of clusters of like particles.

In order to show the effect of such clusters on the time decay exponent we also studied analytically the case where correlations between like particles are neglected $[X(r,t) \equiv 1]$. This led to an asymptotic time decay of the form $n(t) \sim (\ln t)^{-d}$, i.e., the time decay exponent is changed by a factor of 2. A similar change in the time decay exponents appears in diffusion-limited reactions, when one compares the results for the $A + B \rightarrow 0$ reaction $[n(t) \sim t^{-d/4}]$ and for the $A + A \rightarrow 0$ reaction $[n(t) \sim t^{-d/2}]$. This change is also due to the fact that in the $A + A \rightarrow 0$ process clustering is less important.

The results presented in this paper were obtained by concentrating on the case of equal numbers of A and B particles $A_0 = B_0$ and hence $A(t) = B(t)$. Preliminary investigations[34] indicate that the superposition approximation also holds, when one particle species is in excess, say $B_0 > A_0$ and hence $B(t) > A(t)$ at all times. In the later case a quite different temporal behavior of the system obtains,[2,6,11] as is also evident from the discussion of Eq. (2.1).

Summarizing, we have shown that the superposition approximation works very well even in the extreme case of immobile reactants. As already pointed out, this approach could also properly describe diffusion-limited reactions and thus open the way for purely analytical approaches.

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