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Bimolecular Annihilation Reactions: Immobile Reactants and Multipolar Interactions

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We study the A + B → 0 annihilation reaction via multipolar interactions $w \sim r^{-s}$ (r distance) in one and two dimensions. For equal numbers of immobile A and B particles we present computer simulations and numerical calculations of the decay. We find at large times that in d dimensions the particle concentration follows $n \sim t^{-d/(2s-d)}$.

KEY WORDS: A + B → 0; reaction kinetics; multipolar interactions; power-law decay; immobile particles.

During the last few years bimolecular reactions between like (A + A → products) and unlike particles (A + B → products) have been thoroughly investigated.(1-16) In addition to works which center on diffusion-limited reactions,(1,2,4-7,9,10,12,13) in several instances also reaction mechanisms for *immobile* reactants(3,8,14-16) were analyzed.

As microscopic interaction models one has:

(i) The so-called black-sphere model,(8) where particles which come closer than a given distance r_0 react instantaneously.

(ii) Recombination through tunneling; here the reaction probability w_{ij} for two particles A_i and B_j depends on their mutual distance $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, following an exponential law(8,11,14-16):

$$w_{ij} = w(r_{ij}) = w_0 \exp(-r_{ij}/r_0) \tag{1}$$

This work is dedicated to Prof. George H. Weiss.

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(iii) Multipolar interactions, where the reaction probability follows a power law,(16)

$$w_{ij} = w(r_{ij}) = w_0 r_{ij}^{-s} \tag{2}$$

The difference between these cases is the range of the interaction, which is extremely short for the black-sphere model and is (on a microscopic scale) longest for dipolar interactions, where $s = 6$.

In this article we consider $A + B \to 0$ reactions with *immobile* reactants A and B, which annihilate via multipolar interactions, following Eq. (2). We are interested in the temporal evolution of the density $n(t)$ of the particles and also in the spatial correlations between particles, characterized by their correlation length $\xi(t)$.

In former articles(11,14,15) we investigated the $A + B \to 0$ reaction mediated by *exchange*, Eq. (1). For one,(11) two,(14) and also for noninteger dimensions (see ref. 15 for the case of a Sierpinski gasket whose fractal dimension is $d = 1.585$) we found that in the long-time domain n and ξ are related through

$$n(t) \sim \xi(t)^{-d/2} \tag{3}$$

where ξ is expressed by

$$\xi(t) = r_0 \ln(w_0 t) \tag{4}$$

which is the solution of the corresponding, implicit relation:

$$w(\xi) t = 1 \tag{5}$$

Hence we get for exchange

$$n(t) \sim [\ln(w_0 t)]^{-d/2} \tag{6}$$

Let us now focus on the case of *multipolar* interactions. A naive extrapolation of Eqs. (3)–(5) in this case would suggest that

$$\xi(t) = (w_0 t)^{1/s} \tag{7}$$

and furthermore, for the long-time domain,

$$n(t) \sim t^{-d/(2s)} \tag{8}$$

However, as we proceed to show, the decay law does not follow Eq. (8) for multipolar interactions: The time decay is indeed algebraic, but, as analytically established in ref. 16, the exponent in Eq. (8) is $-d/(2s-d)$ rather than $-d/(2s)$, i.e.,

$$n(t) \sim t^{-d/(2s-d)} \tag{9}$$

The analysis of ref. 16 focuses on the "optimized cell" method; here one looks for upper and lower bounds for $n(t)$ as a function of the cell size R and then one optimizes the bounds with respect to the parameter R. As shown in ref. 16, the lower bound $n^L(R, t)$ to $n(t)$ has the structure [Eq. (13) of ref. 16]

$$n^L(R, t) = c_1 R^{-d/2} \exp\left[-c_2 R^{-d/2} t \int_{r>R} w(r)\, dV\right] \tag{10}$$

where c_1 and c_2 are constants, and the integration in the exponent extends from the lower cutoff at $r = R$ to infinity. Maximizing Eq. (10) with respect to R leads for exchange to the well-established result, Eq. (6). On the other hand, for the multipolar interactions one obtains Eq. (9) instead of Eq. (8). Furthermore, the analysis of the upper bound $n^U(R, t)$ for $n(t)$ results in [Eq. (17) of ref. 16]

$$n^U(R, t) = \frac{n_0^{3/2} R^{-d/2}}{n_0 - (n_0 - n_0^{1/2} R^{-d/2}) \exp[-t w(R)\, n_0^{1/2} R^{d/2}]} \tag{11}$$

where n_0 is the particle density $n(t=0)$. Now maximizing $n^U(R, t)$ with respect to R, one recovers again for exchange Eq. (6) and for multipolar interactions Eq. (9) as results. Since in both cases the lower and upper bounds to $n(t)$ follow the same decay form, one infers that $n(t)$ itself obeys Eq. (6) for exchange and Eq. (9) for multipolar interactions.

Since the analysis of ref. 16 is quite subtle, and in order to be able to see the crossover behavior and to determine where the asymptotic forms set in, we decided to perform simulation calculations.

In one dimension we used a chain of 10^6 lattice sites and in two dimensions we used a square lattice of 1000×1000 sites, both with periodic boundary conditions. At start, the A and B particles were distributed randomly with initial concentrations $n_0 = 0.01$ each. At each reaction step the mutual annihilation was simulated as follows: First all reaction rates w_{ij} for all AB pairs present in the sample were determined. The time increment τ for this particular step was taken to be the inverse of the sum $R = \sum_i \sum_j w_{ij}$ of the rates of all AB pairs still present: $\tau = 1/R$. Then from all these pairs, one pair was selected randomly, according to its reaction rate, and the corresponding A and B particles were irreversibly removed.

The results for the one- and two-dimensional cases are presented in Figs. 1 and 2, respectively. In each case ten simulations with different initial realizations were performed. In both cases we analyzed both dipolar and also quadrupolar interactions, and thus set the parameter s of Eq. (2) to $s = 6$ and also to $s = 10$. The full curves in Figs. 1 and 2 show the particle densities. The data are presented in a log-log plot, so that a power-law time

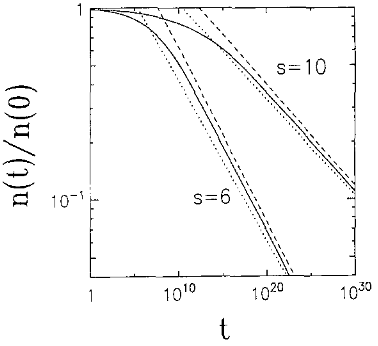

Fig. 1. Decay of the reactant concentration $n(t)$ in one dimension obtained from numerical simulations. Ten realizations of the process were considered with initially 10^4 particles of each kind, distributed on a chain of 10^6 lattice sites and periodic boundary conditions. The full curves give the simulation data for $s=6$ and $s=10$, as indicated; the dashed line gives the slope $-d/(2s-d)$, and the dotted line gives the slope $-d/(2s)$, to be compared to Eqs. (9) and (8).

dependence of the particle density $n(t) \sim t^{\alpha}$ is visible as a straight line with slope α. The slope for the asymptotic behavior of the particle density, $n(t) \sim t^{-d/(2s-d)}$, Eq. (9), is indicated through a dashed line, while the slope resulting from Eq. (8), $n(t) \sim t^{-d/(2s)}$, is given by a dotted line.

The results of Figs. 1 and 2 now show the behavior of the particle densities $n(t)$ over many orders of magnitude (10–30), from very short times to very long ones. Also, the crossover regime is quite evident. Furthermore, at long times we confirm the algebraic decay form. This form is indeed correct over many orders of magnitude in time.

Comparing the slopes given by the approximate forms, it is clear in one and even more so in two dimensions that Eq. (9), given by the dashed lines, describes correctly the long-time regime of the particle density $n(t)$.

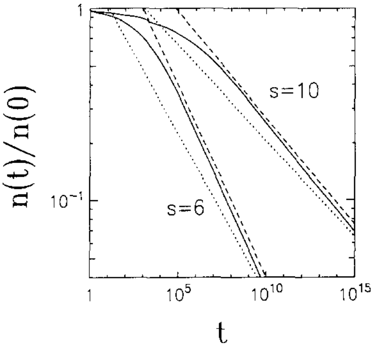

Fig. 2. Same as Fig. 1, for $d=2$ and a square lattice with 1000×1000 sites and periodic boundary conditions.

Especially in two dimensions the failure of Eq. (8) is quite obvious; this failure is also conspicuous in one dimension, when one analyzes the numerical (and not only the graphically displayed) data. Thus, we fully confirm the findings of ref. 16.

Finally we discuss an analytical method which allows us not only to determine the long-time behavior of $n(t)$, but also to obtain numerically the decay in the whole time range. We extend here the method developed and tested for exchange interactions.(8, 11, 14, 15)

The starting point is provided by the following equations.(14) For the density $n(t)$ one has

$$\frac{\partial n(t)}{\partial t} = -n^2(t)\,\gamma_d w_0 \int_0^\infty Y(r, t)\, r^{-m} r^{d-1}\, dr \tag{12}$$

where $d^d r = \gamma_d r^{d-1}\, dr$ denotes an infinitesimal volume element in d dimensions, and where γ_d is the surface of a unit sphere in d dimensions ($\gamma_1 = 2$, $\gamma_2 = 2\pi$, $\gamma_3 = 4\pi$). Here $Y(r, t)$ denotes the A–B correlation function and $X(r, t)$ the A–A (or B–B) correlation functions.

They obey

$$\frac{\partial Y(r, t)}{\partial t} = -w(r)\, Y(r, t) - 2Y(r, t)\, n(t)\, J[X] \tag{13}$$

and

$$\frac{\partial X(r, t)}{\partial t} = -2X(r, t)\, n(t)\, J[Y] \tag{14}$$

In Eqs. (13) and (14) $J[H]$ is a functional of H:

$$J[H] = \int w(r')\, Y(r', t)[H(r^*, t) - 1]\, d^d r' \tag{15}$$

with

$$r^* := |\mathbf{r}^*| = |\mathbf{r} - \mathbf{r}'| = (r^2 + r'^2 - 2rr' \cos\theta)^{1/2} \tag{16}$$

and θ is the angle between $\mathbf{r}$ and $\mathbf{r}'$.

For the details and the approximations involved in deriving Eqs. (12)–(15) see ref. 14.

The numerical solution of the equation system (12)–(14) is found by integration, beginning with the initial conditions $n(0) = n_0$, $X(r, 0) = 1$, and $Y(r, 0) = 1$ and then iterating. The procedure is similar to the one discussed in refs. 11, 14, and 15. This allows one to obtain the particle density $n(t)$ and the correlation functions $X(r, t)$ and $Y(r, t)$ in the whole time domain.

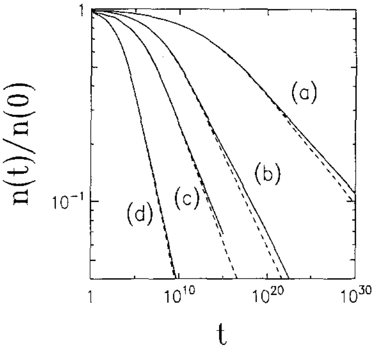

Fig. 3. Decay of the reactant concentration $n(t)$ (full lines) in one and two dimensions obtained from simulations; the results are compared to the numerical calculations (dashed lines). (a) $d=1$ and $s=10$, (b) $d=1$ and $s=6$, (c) $d=2$ and $s=10$, (d) $d=2$ and $s=6$.

To exemplify the findings, we have plotted in Fig. 3 the particle densities which result from this method as dashed curves. The results are given for two sets of parameters ($s=6$ and $s=10$) for the dimensions $d=1$ and $d=2$. For comparison we also display the simulation results, depicted as full curves. One can see that both methods agree very well for the major part of the decay range.

Note that the equation system (12)–(14) cannot be easily simplified. As an example, setting $X(r, t)=1$ leads to

$$n(t) \sim \xi^{-d} \tag{17}$$

and

$$\xi(t) \sim t^{1/s} \tag{18}$$

i.e., it leads to the wrong results.

In summary, we presented for the $A+B \rightarrow 0$ reaction with immobile particles annihilating via multipolar interactions both computer simulations and numerical evaluations of an analytical approach for the decay law. Here we succeeded in obtaining the decay of the particle density in a time regime spanning some 10–30 orders of magnitude.

The results of the simulations and of the numerical evaluations are in very good agreement. In the long-time regime they lead to the behavior $n(t) \sim t^{-d/(2s-d)}$, as predicted analytically by Burlatsky and Chernoutsan.(16)

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REFERENCES

1. A. Blumen, J. Klafter, and G. Zumofen, in *Optical Spectroscopy of Glasses*, I. Zschokke, ed. (Reidel, Dordrecht, 1986), p. 199.
2. L. W. Anacker and R. Kopelman, *Phys. Rev. Lett.* **58**:289 (1987).
3. S. F. Burlatsky and A. A. Ovchinnikov, *Sov. Phys. JETP* **65**:908 (1987).
4. D. ben-Avraham, *J. Chem. Phys.* **88**(2):941 (1988).
5. K. Lindenberg, B. J. West, and R. Kopelman, *Phys. Rev. Lett.* **60**:1777 (1988).
6. D. ben-Avraham and C. R. Doering, *Phys. Rev. A* **37**:5007 (1988).
7. C. R. Doering and D. ben-Avraham, *Phys. Rev. A* **38**:3035 (1988).
8. V. Kuzovkov and E. Kotomin, *Rep. Prog. Phys.* **51**:1479 (1988).
9. E. Clement, L. M. Sander, and R. Kopelman, *Phys. Rev. A* **39**:6455 (1989).
10. E. Clement, L. M. Sander, and R. Kopelman, *Phys. Rev. A* **39**:6466 (1989).
11. H. Schnörer, V. Kuzovkov, and A. Blumen, *Phys. Rev. Lett.* **63**:805 (1989).
12. I. M. Sokolov, *Phys. Lett. A* **139**:403 (1989).
13. J. Klafter, A. Blumen, and J. M. Drake, in *Molecular Dynamics in Restricted Geometries*, J. Klafter and J. M. Drake, eds. (Wiley, New York, 1989).
14. H. Schnörer, V. Kuzovkov, and A. Blumen, *J. Chem. Phys.* **92**:2310 (1990).
15. H. Schnörer, S. Luding, and A. Blumen, in *Fractals in the Fundamental and Applied Sciences*, J. Henriques, ed. (Fundacao Calouste Gulbenkian, Lisbon, 1990).
16. S. F. Burlatsky and A. I. Chernoutsan, *Phys. Lett. A* **145**:56 (1990).