Stochastic and deterministic analysis of reactions: The fractal case

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The transient diffusion-limited $A+B\rightarrow 0$, $A_0=B_0$ annihilation on fractals is studied both via deterministic reaction-diffusion equations and via simulations of the stochastic many-particle problem. We show that the two approaches are not equivalent, yet the deterministic expressions capture the correct asymptotic behavior. For Sierpinski gaskets our analysis focuses on the overall decay law: $t^{-\alpha}$ with $\alpha=\min(\tilde{d}/4,1)$ and on the superimposed hierarchical oscillations.

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There has been a continuous interest in the diffusion-limited bimolecular reactions $A+B\rightarrow$ inert, where on regular and fractal structures the time evolution of the particle densities, of the segregation phenomena, and the dependence on spatial dimension have been studied [1-9]. In former works we analyzed the problem through stochastic simulations [5,6]. On the other hand, closed-form analytical descriptions for Euclidean spaces usually start from [1,2,10–14]

$$\begin{aligned}\dot{A}(\mathbf{x},t)&=D\nabla^2 A(\mathbf{x},t)-\kappa A(\mathbf{x},t)B(\mathbf{x},t)\ ,\\ \dot{B}(\mathbf{x},t)&=D\nabla^2 B(\mathbf{x},t)-\kappa A(\mathbf{x},t)B(\mathbf{x},t)\ ,\end{aligned}\tag{1}$$

where $A(\mathbf{x},t)$ and $B(\mathbf{x},t)$ are the particle densities, D is the diffusion coefficient, and κ denotes the bimolecular reaction rate. Equations (1) are restricted to first-order density functions due to the truncation of a hierarchy of coupled equations, thus the reaction term $\kappa A(\mathbf{x},t)B(\mathbf{x},t)$ is approximate [11]. In this paper we consider an equal initial number of A and B particles: $A_0=B_0$, which implies $A(t)=B(t)$ at all times. The analysis of Eq. (1) is simplified by setting $q(\mathbf{x},t)=A(\mathbf{x},t)-B(\mathbf{x},t)$ and $s(\mathbf{x},t)=A(\mathbf{x},t)+B(\mathbf{x},t)$, which leads to

$$\dot{q}(\mathbf{x},t)=D\nabla^2 q(\mathbf{x},t)\ ,\tag{2}$$

$$\dot{s}(\mathbf{x},t)=D\nabla^2 s(\mathbf{x},t)-(\kappa/2)[s^2(\mathbf{x},t)-q^2(\mathbf{x},t)]\ .\tag{3}$$

We point out that Eq. (2) holds irrespective of the approximation introduced in Eqs. (1) for the description of the reaction term [11]. The time evolution of the densities is obtained from the spatial or ensemble average: $A(t)=\langle A(\mathbf{x},t)\rangle_{\mathbf{x}}=\frac{1}{2}\langle s(\mathbf{x},t)\rangle_{\mathbf{x}}$. We will first generalize the deterministic approach, Eqs. (1)–(3), by using a discrete formulation which applies also for fractals. We will then contrast the solutions of the discrete equations with the results obtained from simulation calculations of the stochastic problem. We will show that the overall decay is well represented by $t^{-\alpha}$ where $\alpha=\min(\tilde{d}/4,1)$; here $\tilde{d}$ is the spectral dimension for fractals and d for regular lattices. The application of the decay laws for fractals has been recently a matter of debate [4,5,9,15,16].

For discrete lattices, Eqs. (2) and (3) are given without loss of generality by

$$\dot{q}(\mathbf{x}_j,t)=\Gamma\sum_{i\in\sigma_j}[q(\mathbf{x}_i,t)-q(\mathbf{x}_j,t)]\ ,\tag{4}$$

$$\dot{s}(\mathbf{x}_j,t)=\Gamma\sum_{i\in\sigma_j}[s(\mathbf{x}_i,t)-s(\mathbf{x}_j,t)]-(\kappa/2)[s^2(\mathbf{x}_j,t)-q^2(\mathbf{x}_j,t)]\ ,\tag{5}$$

where $\mathbf{x}_j$ are the sites, σ_j denotes the nearest neighbors of site j, and Γ is the hopping rate between nearest-neighbor sites. Equations (4) and (5) hold for fractals as well as for Euclidean lattices. The solution of Eq. (4) can be written in terms of the Green's function $P(\mathbf{x}_j,t;\mathbf{x}_0,0)$, the conditional probability to be at $\mathbf{x}_j$ at time t having started at $\mathbf{x}_0$ at time zero. One has

$$q(\mathbf{x}_j,t)=\sum_i P(\mathbf{x}_j,t;\mathbf{x}_i,0)q(\mathbf{x}_i,0)\ ,\tag{6}$$

where $q(\mathbf{x},0)$ denotes the initial random configuration. $\langle q(\mathbf{x},t)\rangle_{\mathbf{x}}$ is zero at all times and the second moment averaged over space and over initial configurations is

$$\langle q^2(t)\rangle=\langle q^2(\mathbf{x},t)\rangle_{\mathbf{x}}=N^{-1}\sum_j\left\langle\left[\sum_i P(\mathbf{x}_j,t;\mathbf{x}_i,0)q(\mathbf{x}_i,0)\right]^2\right\rangle_{\text{init.config.}}\ .\tag{7}$$

Here N denotes the number of lattice sites considered in the model. As initial distributions we take ($q_0/2$ being the initial occupation probability for A or B particles)

$$q(\mathbf{x}_j,0)=\begin{cases}+1 & \text{with probability } q_0/2\\ -1 & \text{with probability } q_0/2\\ 0 & \text{with probability } 1-q_0\,.\end{cases} \tag{8}$$

Inserting Eq. (8) into Eq. (7) the configurational average is straightforward, since the $P(\mathbf{x}_j,t;\mathbf{x}_i,0)$ are independent of the initial configuration:

$$\begin{aligned}\langle q^2(t)\rangle &= N^{-1}\sum_{j,i,k} P(\mathbf{x}_j,t;\mathbf{x}_i,0)P(\mathbf{x}_j,t;\mathbf{x}_k,0)\\ &\quad\times\langle q(\mathbf{x}_i,0)q(\mathbf{x}_k,0)\rangle_{\text{init.config.}}\\ &= q_0N^{-1}\sum_{j,i,k} P(\mathbf{x}_j,t;\mathbf{x}_i,0)P(\mathbf{x}_j,t;\mathbf{x}_k,0)\delta_{ik}\\ &= q_0N^{-1}\sum_{j,i} P^2(\mathbf{x}_j,t;\mathbf{x}_i,0)\,.\end{aligned} \tag{9}$$

To proceed we consider the Chapman-Kolmogorov equation:

$$P(\mathbf{x}_j,t;\mathbf{x}_i,0)=\sum_m P(\mathbf{x}_j,t;\mathbf{x}_m,t')P(\mathbf{x}_m,t';\mathbf{x}_i,0)\,,\qquad 0\le t'\le t \tag{10}$$

which applies for all Markovian processes. Inserting Eq. (10) into Eq. (9) and considering the symmetry of the propagator $P(\mathbf{x}_j,t;\mathbf{x}_i,0)=P(\mathbf{x}_i,t;\mathbf{x}_j,0)$, we find [18] that

$$\begin{aligned}\langle q^2(t)\rangle &= q_0N^{-1}\sum_j P(\mathbf{x}_j,2t;\mathbf{x}_j,0)\\ &= q_0P(0,2t)\,,\end{aligned} \tag{11}$$

where $P(0,t)$ is the probability to be at the origin after time t, averaged over all starting sites. Equation (11) relates $\langle q^2(t)\rangle$ to the well-understood autocorrelation function $P(0,t)$, whose leading behavior follows asymptotically [7] the power law $P(0,t)\sim a_{\tilde d}\,t^{-\tilde d/2}$. The prefactor $a_{\tilde d}$ depends on the details of the lattice.

From Eq. (6) one can view q at long times as a large sum of terms ± 1 or 0, weighted with the corresponding P factors; thus, for large t the central-limit theorem applies so that $q(\mathbf{x},t)$ becomes Gaussian distributed [2,13]. Therefore $q(t)\equiv\langle|q(\mathbf{x},t)|\rangle_{\mathbf{x}}=[(2/\pi)\langle q^2(t)\rangle]^{1/2}$ holds in general. If one can now approximate $s(t)=\langle s(\mathbf{x},t)\rangle_{\mathbf{x}}$ through $q(t)$, then by using Eq. (11) it follows that

$$\begin{aligned}A(t)=\langle A(\mathbf{x},t)\rangle_{\mathbf{x}}=\tfrac{1}{2}s(t)&\gtrsim\tfrac{1}{2}q(t)\\ &=[q_0P(0,2t)/2\pi]^{1/2}\,,\end{aligned} \tag{12}$$

which, considering the power-law description for $P(0,t)$, leads to

$$A(t)\gtrsim C_{\tilde d}\,A_0^{1/2}t^{-\tilde d/4}\,, \tag{13}$$

with the constant being $C_d=\pi^{-1/2}(d\tau/4\pi)^{d/4}$ for Euclidean lattices and $C_{\tilde d}=(a_{\tilde d}/\pi)^{1/2}(\tau/2)^{\tilde d/4}$ for fractals. Here, τ is the hopping time, which is related to the jumping rate Γ through $\tau^{-1}=z\Gamma$, where z is the coordination number. For hypercubic lattices, setting $D=(2d\tau)^{-1}$, C_d is identical to the results of Ref. [2]. Thus expressions (12) and (13) derived for the general case including fractals reproduce exactly the results of Euclidean lattices [2].

We now concentrate on setting $s(t)\simeq q(t)$ in Eq. (12) and analyze Eq. (5) by taking the average over all lattice sites which leads to

$$\langle\dot s(t)\rangle=-(\kappa/2)[\langle s^2(t)\rangle-\langle q^2(t)\rangle]\,. \tag{14}$$

Here, it is of interest, if and how fast the ratio $\langle s^2(t)\rangle/\langle q^2(t)\rangle$ tends towards the value of 1. Furthermore, we check to which extent $s(\mathbf{x},t)$ and $q(\mathbf{x},t)$ are approximately Gaussian distributed. A measure for this is how fast the ratios $\langle q^2(t)\rangle^{1/2}/\langle|q(t)|\rangle$ and $\langle s^2(t)\rangle^{1/2}/\langle s(t)\rangle$ reach the asymptotic value $(\pi/2)^{1/2}$.

For $\tilde d>4$ Eq. (12) would lead to a decay $t^{-\tilde d/4}$ which is faster than t^{-1}. In this case we argue that $\langle q^2(t)\rangle$ can be neglected in Eq. (14) as compared to $\langle s^2(t)\rangle$; thus assuming that $\langle s^2(t)\rangle^{1/2}\sim\langle s(t)\rangle$, it follows that $\langle s(t)\rangle$ obeys classical kinetics, i.e., $\langle s(t)\rangle\sim t^{-1}$. This imposes an upper marginal dimension of $d=4$ and the corresponding limitation for the validity range of Eqs. (12) and (13). Furthermore, the ratio $\langle s^2(t)\rangle/\langle q^2(t)\rangle$ should diverge for $d>4$ [7,12].

We studied these points by solving numerically Eqs. (4) and (5). For the numerical treatment the ratio κ/τ^{-1} has to be fixed; for comparison to former approaches [11] we took κ as being equal to $2/\tau$.

In Fig. 1 various quantities are shown for $d=1$. To clearly demonstrate the region of long-time behavior, the

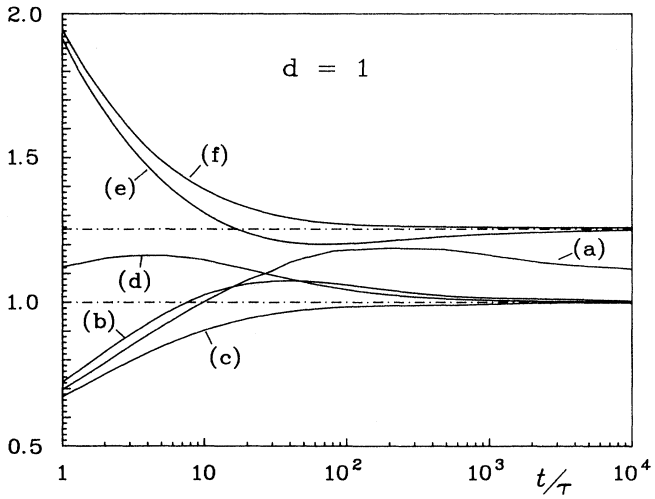

FIG. 1. Results from Monte Carlo (MC) simulations and from the deterministic approach for $d=1$. Curve (a), MC result: $A_{\text{MC}}(t)t^{1/4}/C_1$. Deterministic result of the reaction-diffusion equations: Curve (b), $\langle s(t)\rangle t^{1/4}/(2C_1)$, curve ($c$), $\langle|q(t)|\rangle t^{1/4}/(2C_1)$, curve ($d$), $\langle s^2(t)\rangle/\langle q^2(t)\rangle$, curve ($e$), $\langle s(t)\rangle/\langle s^2(t)\rangle^{1/2}$, curve ($f$), $\langle|q(t)|\rangle/\langle q^2(t)\rangle^{1/2}$. The dash-dotted lines indicate the values 1 and $(\pi/2)^{1/2}$. The initial concentration is $A_0=B_0=0.05$.

quantities were multiplied by their expected asymptotic forms, such that the asymptotic patterns appear as horizontal lines. A lattice of 4×10^5 sites was used. Plotted are $\langle|q(t)|\rangle t^{1/4}/(2C_1)$ and $\langle s(t)\rangle t^{1/4}/(2C_1)$. The displayed curves demonstrate that $\langle|q(t)|\rangle$ reaches quickly the asymptotic regime, whereas $\langle s(t)\rangle$ relaxes considerably more slowly. In the region of moderate times $\langle|q(t)|\rangle$ and $\langle s(t)\rangle$ differ significantly, and $\langle s(t)\rangle$, as presented in Fig. 1, shows a characteristic hump.

These patterns are compared with results taken from Monte Carlo (MC) calculations which were performed on Euclidean lattices and Sierpinski gaskets. Typically 10^6–10^7 particles were used. The simulation results plotted as $A_{\rm MC}(t)t^{1/4}/C_1$ curve (*a*) in Fig. 1, show the same characteristic behavior as $\langle s(t)\rangle$, curve (*b*), however, $A_{\rm MC}(t)$ relaxes significantly more slowly to its asymptotic value than $\langle s(t)\rangle$. We view these differences between MC and deterministic data as resulting from the approximations introduced in the the diffusion-reaction Eqs. (1)–(3) which are thus limited in their ability to describe processes as complicated as particle annihilation. To complete the analysis we display in Fig. 1 also the ratio $\langle s^2(t)\rangle/\langle q^2(t)\rangle$, curve (*d*), which shows a slow convergence to the value 1. Finally, plotted are the two ratios $\langle q^2(t)\rangle^{1/2}/\langle|q(t)|\rangle$ and $\langle s^2(t)\rangle^{1/2}/\langle s(t)\rangle$. Both ratios converge to the asymptotic value of $(\pi/2)^{1/2}$ which is consistent with q and s as being Gaussian distributed at long times. Again the sum variable relaxes more slowly than the difference variable to its limiting value.

In Fig. 2 we compare the results obtained in one dimension (1D) with those obtained for a 2D Sierpinski gasket. Equations (4) and (5) were solved on a gasket at the 11th iteration stage. The MC simulation was performed on a gasket at the 14th iteration stage. We remark the resemblance in the behavior of all quantities considered on the 2D Sierpinski gasket with those reported for the 1D lattice. Both the MC and the numerical method behave in similar fashion on regular lattices and on fractals; we conclude that the same limitations of the diffusion-equation method also apply to fractals.

To emphasize this analysis further we focus now on details typical for hierarchically built structures. For these the autocorrelation function $P(0,t)$ shows an oscillatory behavior which is superimposed on the asymptotic power-law decay [17,18]. The periods of these oscillations are related to the typical residence time of diffusing particles on hierarchial substructures and the oscillations' amplitudes are larger for higher dimensions d. From Eq. (11) it is clear that $\langle q^2(t)\rangle$ should also follow the oscillatory behavior. Furthermore, the oscillations should also be visible in $A(t)$. This is in fact the case and is demonstrated in Fig. 3, where the decay is displayed for Sierpinski gaskets embedded in Euclidean lattices of dimensions $d=2$, 6, and 13. In order to highlight the oscillatory behavior the simulation results are plotted as $A_{\rm MC}(t)t^{\bar d/4}$. They are compared with Eq. (12), $[A_0P(0,2t)/\pi]^{1/2}t^{\bar d/4}$, where $P(0,t)$ was obtained from independent numerical calculations [18].

For a Sierpinski gasket in $d=2$ the oscillations are hardly detectable and the MC calculation tends smoothly to the $P(0,t)$-type expression, however, the relaxation to the asymptotic behavior occurs at times $t/\tau\gtrsim10^4$. For Sierpinski gaskets in $d=6$ and 13 dimensional spaces the oscillations are clearly visible: also the periods and the

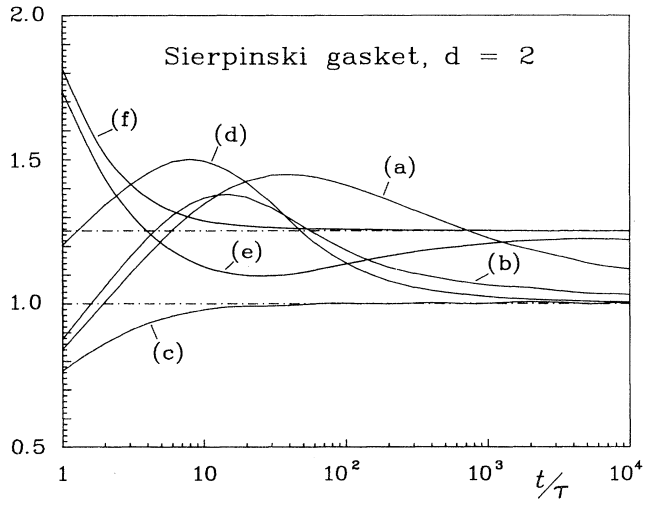

FIG. 2. As in Fig. 1 but for a 2D Sierpinski gasket. From MC calculations: curve (*a*), $A_{\rm MC}(t)t^{\bar d/4}/C_{\bar d}$; and from the solution of the reaction-diffusion equations: curve (*b*), $\langle s(t)\rangle t^{\bar d/4}/(2C_{\bar d})$, curve (*c*), $\langle|q(t)|\rangle t^{\bar d/4}/(2C_{\bar d})$, curve (*d*), $\langle s^2(t)\rangle/\langle q^2(t)\rangle$, curve (*e*), $\langle s(t)\rangle/\langle s^2(t)\rangle^{1/2}$, curve (*f*), $\langle|q(t)|\rangle/\langle q^2(t)\rangle^{1/2}$. The dash-dotted lines indicate the values 1 and $(\pi/2)^{1/2}$. The initial concentration is $A_0=B_0=0.05$.

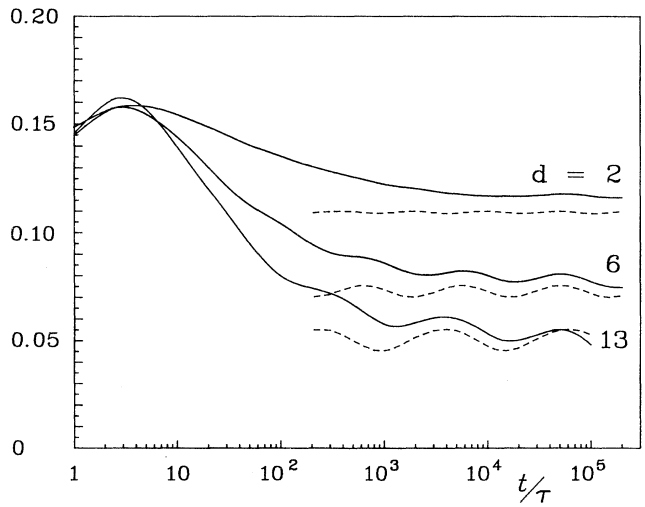

FIG. 3. Time evolution of the particle densities on Sierpinski gaskets. The MC simulations are displayed as $A(t)t^{\bar d/4}$ and are given as solid lines. The theoretical predictions $[A_0P(0,2t)/\pi]^{1/2}t^{\bar d/4}$ are given by dashed lines. The embedding Euclidean dimension d is as indicated and the initial concentration was in all cases $A_0=B_0=0.2$.

phases are in qualitative agreement with the $P(0,t)$-type forms. For $d=6$, the deviations between simulation and $P(0,t)$ evaluation are of the order of 10% at long times. For $d=13$ the oscillatory behavior is again very well reproduced; on the other hand, care has to be used for t values larger than $t/\tau > 10^4$, where finite-size effects begin to be felt.

Finally, we calculated numerically $\langle s^2(t)\rangle/\langle q^2(t)\rangle$ for regular lattices of the dimensions $d=1-5$. We found that this ratio relaxes towards the value 1 for $d \leq 3$, reaches a plateau for $d=4$, and increases steadily for $d=5$. These findings are in accordance with the marginal dimension $d=4$.

Concluding, our analysis has shown that the deterministic approach based on reaction-diffusion equations can provide an asymptotic description of the reaction process and that Eq. (12) represents a lower bound for the density decay. Furthermore, both the deterministic and the stochastic approach support the exponent $\alpha=\min(\tilde{d}/4,1)$ for the $A(t)\sim t^{-\alpha}$ decay.

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[1] A. A. Ovchinnikov and Y. B. Zeldovich, Chem. Phys. **28**, 215 (1978).
[2] D. Toussaint and F. Wilczek, J. Chem. Phys. **78**, 2642 (1983).
[3] P. Meakin and H. E. Stanley, J. Phys. A **17**, L173 (1984).
[4] K. Kang and S. Redner, Phys. Rev. Lett. **52**, 955 (1984).
[5] G. Zumofen, A. Blumen, and J. Klafter, J. Chem. Phys. **82**, 3198 (1985).
[6] A. Blumen, J. Klafter, and G. Zumofen, in *Optical Spectroscopy of Glasses,* edited by I. Zschokke (Reidel, Dordrecht, 1986), p. 199.
[7] S. Havlin and D. Ben-Avraham, Adv. Phys. **36**, 695 (1987).
[8] M. Bramson and J. L. Lebowitz, Phys. Rev. Lett. **61**, 2397 (1988); **62**, 694 (1989).
[9] Wen-Shyan Sheu, K. Lindenberg, and R. Kopelman, Phys. Rev. A **42**, 2279 (1990).
[10] H. Schnörer, V. Kuzovkov, and A. Blumen, Phys. Rev. Lett. **63**, 805 (1989).
[11] E. Clément, L. M. Sander, and R. Kopelman, Phys. Rev. A **39**, 6455 (1989).
[12] B. J. West, R. Kopelman, and K. Lindenberg, J. Stat. Phys. **54**, 1429 (1989).
[13] I. M. Sokolov and A. Blumen, Phys. Rev. A **43**, 2714 (1991).
[14] Zhang Yi-Cheng, Phys. Rev. Lett. **59**, 1726 (1987).
[15] G. Zumofen, J. Klafter, and A. Blumen, Phys. Rev. A **43**, 7068 (1991).
[16] K. Lindenberg, Wen-Shyan Sheu, and R. Kopelman, Phys. Rev. A **43**, 7070 (1991).
[17] B. O'Shaughnessy and I. Procaccia, Phys. Rev. A **32**, 3073 (1985).
[18] J. Klafter, G. Zumofen, and A. Blumen, J. Phys. A (to be published).